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BE THE SOLUTION TO SOIL POLLUTION

GLOBAL SYMPOSIUM
ON SOIL POLLUTION PROCEEDINGS



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BE THE SOLUTION TO SOIL POLLUTION

PROCEEDINGS OF THE
GLOBAL SYMPOSIUM ON SOIL POLLUTION

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Regional Soil Partnerships reports on soil pollution

Regional status of soil pollution: Nigeria, West Africa

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Abstract

Soil and environmental protection and sustainability are important aspects of natural resource management that have been neglected for too long. The effect of oil pollution on our soil has been a major concern in the crude oil rich Niger-delta area of Nigeria. . This write up is a review of previous studies on oil pollution and the effects of oil spillage on physical and chemical properties of the soils. The effectiveness of various results obtained depends on the nature of oil, relative properties of the soil and soil environment. Two oil-spill affected areas (Ogali and Agbonchia) were identified as the study areas while a geographically similar but unaffected area (Aleto) served as control. Sampling site was delimited at each area by the grid technique and soil samples were collected at top surface 0-15 cm and sub-surface 130 cm depth. Some physiochemical properties that reflect soil nutrient content and fertility status (K, Ca, Mg, C, P, pH, Cation Exchange Capacity (CEC) and structure) were determined using standard methods and results from the three areas were compared. There was a significant decrease in the Ca K, P (CEC), as well as a significant increase in the sand fraction and Na content of the oil-spill affected soils of (Ogali and Agbonichia) when compared with the non-affected soil of (Aleto). The acidic nature of the soils could not be attributed entirely to the oil spill since the control soil of Aleto was equally acidic. The results indicate that oil-spill has adversely affected the nutrient level and fertility status of Eleme soil, necessitating the inclusion of Eleme in the ongoing remediation technique for soil cleaning in Rivers State of Nigeria. In broad terms, the negative impact of these oil activities includes destruction of wild life, loss of fertile soil, pollution of air and water and damage to the ecosystem of the host communities. The ecological problems observed as a result of oil spill include brownish vegetation and soil erosion, diminishing resources of the natural ecosystem, fertile land turned barren and adverse effect on the life, health and economy of the people.

Keywords: Soil pollution, Oil spillage, Soil properties, Environment, Soil fertility.

Introduction, scope and main objectives

The Niger Delta region of Nigeria is one of the world's largest wetlands and includes by far the largest mangrove forest in Africa. Its biological diversity is of global significance. Within the extremely valuable ecosystem, oil activities are widespread (Niger Delta Development Commission, 2006). Particularly, the community which is Eleme is a community in Rivers State and it's one of the oil producing and agro-ecological areas in the Niger-Delta region of Nigeria, a region with abundant natural resources including good weather and fertile land for agriculture. Although the level of agricultural production in that region is very low given the abundant resource endowment, it is the largest oil producing zone in the country. It is the base of Nigerian oil and gas industry, generating over 90% of the nation `s economy (Odjuvwuederhie *et al.*, 2006). Oil exploration and activities have been concentrated in this Niger-Delta region which has over 1000 production oil-wells and over 47,000 km of oil and gas flow lines (Ngobiri *et al.*, 2007). These negative impacts of this oil activities includes destruction of wild life, loss of fertile soil,

pollution of air and water and damage to the ecosystem of the host communities (Aghalino, 2000). The ecological problems observed as a result of oil spill include a brownish vegetation and soil erosion, diminishing resources of the natural ecosystem, fertile land turned barren and adverse effect on the life, health and economy of the people (Roberts, 1997).

Pollution of the soil is one of the major effects of human technological advancement. It results when a change in the environment harmfully affects the quality of human life including effects on animals, microorganisms and plants. Therefore, Pepper *et al.*, 1996, defined soil pollution as the appearance in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health. The contamination of the environment (mainly terrestrial and aquatic) by crude oil is referred to as crude oil pollution and it is estimated that 80% of crude oil pollution is as a result of spillage (Odu, 1997). Currently, about 80% of land are polluted by products of petroleum origin (hydrocarbons, solvent, etc.) used as an energy source in the oil industry, as well as chemicals (Marinescu *et al.*, 2001). There are a variety of pollutants affecting topsoil and subsoil, such as fuel and oil products, hydrocarbon residues, crude oil, other products resulting from the operation (saturated and unsaturated aliphatic hydrocarbons, and the monocyclic and polycyclic aromatic) (Engelking, 2000). In Nigeria, the major cause of soil pollution is oil spillage and the main sources of the pollution are lack of regular maintenance of the pipelines and storage tanks. Most pipelines from the flow stations are absolute being more than 20 years old making them subject to corrosion and leakage. Some of these pipes are laid above ground level without adequate surveillance, exposing them to wear and tear and other dangers (Oyem, 2001). Another major cause of soil pollution here is sabotage which involves bunkering by some unpatriotic Nigerians. They damage pipelines in the attempt to steal oil from them. Also, as a result of crude oil pollution, soil physical properties such as pore spaces might be clogged which reduces soil aeration, infiltration of water into the soil, increased bulk density of the soil which may affect plant growth. Crude oil which is denser than water may reduce and restrict permeability. Some of the effects of crude oil may have adverse effects on soil physical properties include decreased pore spaces, saturated hydraulic conductivity and increased bulk density. All these possibilities deserve empirical studies to establish their reality or otherwise.

The growth of oil industry combined with population explosion and a lack of environmental regulation have caused substantial damage to the environment of the Niger-Delta. After several years of ignoring or giving little or no attention to the adverse effect of oil spill, the Nigerian government has begun to take steps to mitigate the damage. The role of the environmental agency in checking and documenting oil-spills is getting stronger as the new wave of combating oil spill through phytoremediation is dramatically unfolding in the remediation industry for effective soil productivity in the area.

Nigeria still depends largely on crude oil for income earnings. Crude oil which is abundantly located in the Niger Delta region of Nigeria is spilled on soil due to pipeline destruction (Nwilo and Badejo, 2005). Previous studies on crude oil pollution in soil had revealed its adverse effects on soil productivity (Udo and Fayemi, 1975; Okpowasili and Odokuma, 1990). The present study compares the physicochemical parameters of the oil spill affected soil of Eleme community in Niger-delta of Nigeria with those of the unaffected soil with its main objective to examine the status of soil pollution. The result gives insight to the level of damage that oil spill has done to the fertility and nutrient status of the community farm land. There is therefore a need for continuous research on the problems associated with pollution resulting from spillage and the effects on the soil environment which has a negative impact on crops grown on it.

Results and discussion

The results and discussion are made under five sub headings according to the objectives of the study: number or extension of polluted sites, main sources of pollution, petroleum related laws and regulations, legislation or regulating instruments to address soil pollution, risk posed to both human health and the environment and the soil analysis of the physicochemical properties of soil of Eleme.

Number/extension of polluted sites

Three oil spills have been reported in the press in August and September 2016. All of these spills have had a devastating impact on the agriculture, environments and general well-being of the local communities.

Firstly, in Delta State, Ten Ijaw communities along the Escravos River in Warri South West Local Government Area of Delta State have been affected by a crude oil spill from a Nigerian National Petroleum Corporation (NNPC) facility. The spill occurred on August 17th 2016, and journalists in the area were told that it was traced to a crude oil trunk line from the Pipelines and Products Marketing Company (PPMC), the products marketing and distribution subsidiary of the NNPC. The communities that were affected were the Tebujur/Okpele-Ama, Ikpokpo, Okerenkoko-Gbene, Opuedebubor, Opuede, Opuendezion, Atanba, Oto-Gbene, Meke-Ama Communities in Gbaramatu Kingdom, along the Escravos river in Warri South West Local Government Area of the state.

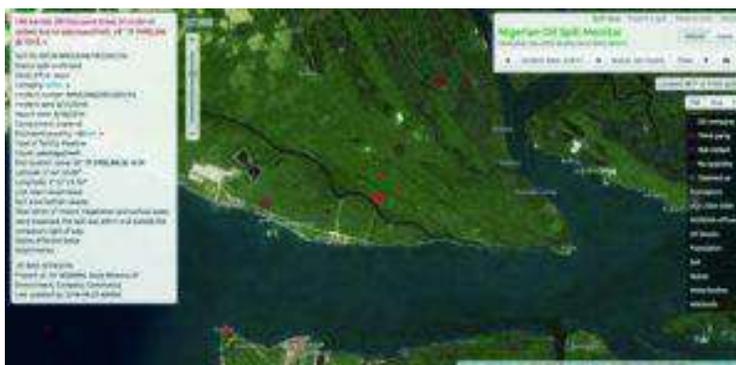


Figure 1. The oil spill

These communities have accused the PPMC of not carrying out a proper joint investigation of the incident by a properly constituted team comprising representatives of the community, NNPC, Department of Petroleum Resources and the National Oil Spill Detection and Response Agency, NOSDRA. According to the communities, the PPMC brought in military men to chase away villagers.



Figure 2. A zoomed out to show the wider area.

According to the Oil Spill Monitor it appears that a JIV was carried out on 19th August, and NOSDRA, State Ministry of Environment, and reps from the company and community. That is clearly a different account of the oil spill and follow up report to journalists by the local communities in Warri.

Secondly, in Bayelsa state, according to local residents, primarily the Kalaba community which has been recently plagued by gas leaks, a spill was discovered in August, which is continues to spill crude oil into the forests and swamps, threatening local ecosystems and agriculture capacity. The oil field from which the reported spill has come from is operated by Nigerian Agip Oil Company. Representatives from the area are appealing to the Federal Government to prevail on Agip to make necessary clean up and remediation.



Figure 3. The area from which the spill has been reported, which is north of Yenagoa and South of the Bayelsa Forest

Unfortunately, according to the Oil Spill Monitor in the area, this incident has yet to have been monitored, officially reported, or have been dealt with by a Joint Investigation Visit. Thus, the matter needs to be researched more thoroughly and be documented on the OSM by NOSDRA.

Thirdly, in reference to a third oil spill in Ahoada East, Rivers State in August, indigenes of Odiemerenyi community reported a clash between military officers attached to the management staff of Total and local community youths. The former had previously been denied access to the spill site whilst attempting to carry out an inspection tour, and reportedly returned with reinforcements and shot at the youths in order to gain access, and burned six houses to the ground. A reconciliation meeting between community representatives and Total held last week, and Total asked the community representatives to retract a press statement they had issued before negotiations could continue. This spill has damaged farmland, drinking water and fisheries.



Figure 4. The visit and spill which is yet to be reported on NOSDRA's oil spill monitor

It is of note that of these three oil spills that have occurred in the past month, only one has been documented on the Oil Spill Monitor, and two out of three have involved violence between officers and the local community. This suggests a causal link between environmental and wider socioeconomic frustrations within the local communities, and escalation of tensions to violence.

Main sources of pollution

Oil spills may occur for numerous reasons such as equipment failure, disasters, deliberate acts, or human error (Anderson and LaBelle, 2000). Figure 1 shows the percentage each subcategory has contributed to the total number of oil spills in Nigeria in the past five years (Shekwolo, 2005). Crude oils are exclusively natural products, most of which are produced from artificial wells. Natural seepage of crude oils occurs in various parts of the world, not only on land, but also on the seabed. Seeps emerge through fractures in the crests of folds in rock formations beneath the sea floor that contain oil and gas deposits. Oil and gas tend to rise and become trapped in anticlinal folds in subsea rock strata. Seepage occurs through fracture zones where the folds are truncated at the sea floor. Seeps may emanate from a single point or as many as 3×10^4 individual seepage signals may be merged onto a high resolution profile record (Clark *et al.*, 2000).

Table 1. Potential sources of pollution

Source of pollution	Representativeness
Sabotage/Bunkering	36%
Engineering	0.50%
Human Error	2%
Corrosion	36%
Equipment Failure	6%
Others	2.50%

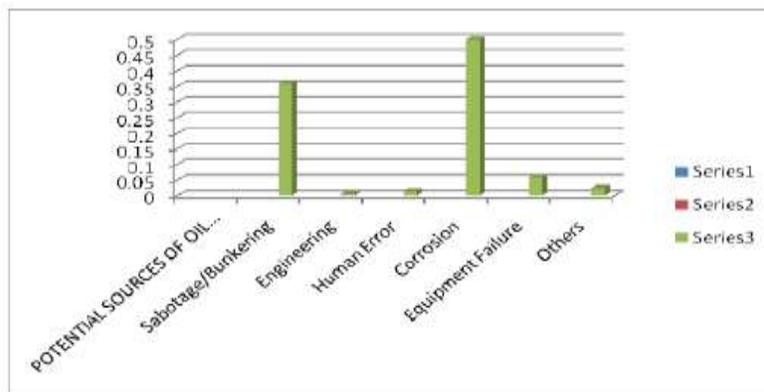


Figure 5. Graphical representation of potential sources of pollution

Petroleum related laws and regulations

Part of the means of managing the environment is to have in place the necessary laws, regulations and guidelines. According to the Federal Environmental Protection Agency, Lagos Nigeria, the following relevant national laws and international agreements are in effect:

- Endangered Species Decree Cap 108 LFN 1990.
- Federal Environmental protection Agency Act Cap 131 LFN 1990.
- Harmful Waste Cap 165 LFN 1990.
- Petroleum (Drilling and Production) Regulations, 1969.
- Mineral Oil (Safety) Regulations, 1963.
- International Convention on the Establishment of an International Fund for Compensation for Oil Pollution Damage, 1971.
- Convention on the Prevention of Marine pollution Damage, 1972
- African Convention on the Conservation of Nature and Natural Resources, 1968.
- International Convention on the Establishment of an International Fund for the Compensation for Oil Pollution Damage, 1971.

Legislation or regulating instruments of controlling soil pollution

The Federal Government, oil companies and non-governmental agencies have made several efforts to manage oil spill disaster along our coastline. These efforts are discussed in the following sections:

Nigerian Government Action

To reduce the rate of oil incidents along the Nigerian Coast particularly as a result of vandalism, the Federal Government through an act of the National Assembly created the Niger Delta Development Commission (NDDC). Part of the responsibilities of the Commission is to develop a master plan for the development of the Niger Delta, provide infrastructure and create an enabling environment for industrialization and employment. There are also several other laws dealing with issues related to oil pollution in the environment. Furthermore, standards for the development of the environmental sensitivity index maps for the coast of Nigeria have been developed by the Environmental Systems Research Institute (ESRI). These standards are to be used by all the oil companies to prepare ESI maps for their areas of operations in Nigeria. A number of Federal and state agencies deal with the problems of oil spill in Nigeria. The agencies include: the Department of Petroleum Resources (DPR), the Federal Ministry of Environment,

the State Ministries of Environment and the National Maritime Authority. A National Oil Spill Detection and Response Agency (NOSDRA) has been formed and approved by the Federal Executive Council of Nigeria. The Ministry of environment, which initiated the Agency, has also forwarded to the federal executive council for approval, the reviewed draft National Oil Spill Contingency Plan (NOSCP) which the Agency would manage (Alexandra Gas and Oil Connections, 2006). The establishment of the contingency plan and the agency was in compliance with the International Convention on Oil Pollution Preparedness, Response and Cooperation (OPRC90) to which Nigeria is a signatory. According to the ministry's sources, the draft bill on the NOSDRA was being put together and would be forwarded to the National Assembly to be enacted into law (Alexandra Gas and Oil Connections, 2006). Apart from intensifying efforts towards compliance monitoring and enforcement of oil and gas regulations and standards, the ministry is also mounting pressure on the oil and gas operators for a gas flare-out. Effort is also being made, according to the sources; to ensure the use of environmental-friendly drilling fluid and mud systems (Alexandra Gas and Oil Connections, 2006). There is a need to create serious awareness among the populace on the implications of oil spill incidents on the environment. Governments must assist the rural communities in claiming their rights on oil spills and ensure that digital ESI maps are readily available for managing oil spill maps. Government should have strict rules for local oil tankers that would ply our coastal and inland waters as a result of the new cabotage law that is just being passed into law in the country (Nwilo & Badejo, 2005).

Efforts of the oil companies and non-governmental agencies

Due to increasing awareness in preventing and controlling spills in Nigeria, the Clean Nigeria Associates (C.N.A.) was formed in November 1981. The C.N.A. is a consortium of eleven oil companies operating in Nigeria, including N.N.P.C. The primary purpose of establishing the C.N.A is to maintain a capability to combat spills of liquid hydrocarbons or pollutants in general (Nwilo & Badejo, 2005). Oil spillage can also be treated or removed by natural means, mechanical systems, absorbents, burning, gelling, sinking and dispersion. Oil spillage can be removed by natural means through the process of evaporation, photochemical oxidation and dispersions (Wardley-Smith, 1977). Bioremediation can also be used for managing oil spill problems (Hoff, 1993; Prince, 1993; Atlas, 1995). In addition, apart from the mechanical and chemical oil spill cleaning methods that have been used in managing oil spill problems, oil spill models have on several occasions being used to manage oil spills on the Nigerian Coast (Nwilo & Badejo, 2005).

Nigerian Sat 1

The Nigerian Sat 1 Satellite has joined the Disaster Monitoring Constellation, an international early-warning satellite network transmitting real-time information about droughts, earthquakes, deforestation and man-made disasters observable from space. The Nigeria Sat-1, an Orbit Satellite for geographical mapping, would also help to check the perennial problem of oil pipeline vandalism, and assist in combating and managing oil spill incidents. The Nigeria Sat-1 would help in monitoring oil spill by providing the spill position which would serve as input data into the oil spill model. It would also give the extent of coastal water and coastal areas polluted. These information are vital for quick cleanup of oil impacted areas.

International co-operation

Cracking down on smugglers has proved difficult. To shore up the fight against oil smugglers in Nigeria, the US has donated three 56 meter (180ft) refitted World War two-era patrol boats to the navy. United Nations has also said that United States would donate additional four vessels. The Pentagon is funding each boat's refurbishment to the tune of USD 3.5m. The efforts of the Federal

Government with the assistance of the US are already yielding fruits. The Nigerian Navy has intercepted several tankers.

Geographic information system for managing oil spill incidents

A successful combating operation to a marine oil spill is dependent on a rapid response from the time the oil spill is reported until it has been fully combated. In order to reduce the response time and qualify the decision-making process, application of Geographic Information Systems (GIS) as an operational tool has been suggested. Information on the exact position and size of the oil spill can be plotted on maps in GIS and a priority of the combat efforts and means according to the identified coastal sensitive areas can be carried out. GIS offers opportunities for integration of oil drift forecast models (prediction of wind and current influence on the oil spill) in the computer program framework (Milaka, 1995). Required information for oil spill sensitivity mapping can be depicted on a set of thematic maps using GIS even though they can in theory be depicted onto a single sheet. With the use of a GIS, however, all the relevant information or themes can be stored in the system and produced onto maps in a format that befits the needs of the day. Alternatively, modeling exercises using the GIS can be conducted to assess the adequacy of any given oil spill contingency plan (Parthiphon, 1994). The creation of regional spill response centres along coastlines will help in managing oil spill problems (Smith and Loza, 1994). The centres will use oil spill models for combating oil spill problems. Using data collected with an airborne system to input one or several new starting point(s) into the model, will improve the accuracy of the further predictions (Sandberg, 1996).

New oil spill model (NOSM)

NOSM simulates the shoreline deposition through an exponential decay function. The movement of oil slick in the model actually represents the movement of the centroid of the slick. The new oil spill trajectory mathematical model capable of simulating oil transport along our coastal waters came to limelight. In developing this new mathematical model, the major factors responsible for transporting and advecting oil on water was considered. The assumption made in the work was that oil will not mix with water, and that the density of oil spill is less than that of water, thus the oil spill will move on water and not sink. The work is also limited to oil spill on open coastal water or deep sea. No attempt to model the movement of oil spill on land or on swamps.

Advection

This is the main mechanism that governs the transportation of suspended and surface oil slick. The combined effects of the following factors advect oil on water:

1. Wind drift current
2. Waves
3. Tides
4. Ocean Current
5. Long shore Current

Biological remediation

The use of biological remediation has also been implemented in areas of the delta to detoxify and restore ecosystems damaged by oil spills. Bioremediation involves biological components in the remediation or cleanup of a specific site. A study conducted in Ogbogu located in one of the largest oil producing regions of Nigeria has utilized two plant species to clean up spills. The first stage of cleanup involves *Hibiscus cannabinus*, a plant species indigenous to West Africa. *H. cannabinus* an annual herbaceous plant originally used for pulp production. This species has high rates of absorbency and can be laid down on top of the water to absorb oil. The oil saturated plant material is then removed and sent to a safe location where the hydrocarbons can be broken down and detoxified by microorganisms. The second stage of bioremediation involves a plant known as *Vetiveria zizanioides*, a perennial grass species. *V. zizanioides* has a deep fibrous root network that can both tolerate chemicals in the soil and can also detoxify soils through time requiring little maintenance. The people of Ogbogu hope to use these methods of bioremediation to improve the quality of drinking water, soil conditions, and the health of their surrounding environment. Within the Imo State of Nigeria, a study was conducted in the city of Egbema to determine the microflora communities present at the site of an oil spill. These microorganisms have the ability to break down the oil, decreasing the toxic conditions. This is recognized as another method of bioremediation and scientists are trying to determine whether the properties these microorganisms possess can be utilized for the cleanup of future spills. However bleak this situation may seem for the Niger Delta region there are clearly alternatives that can be implemented to save it from future contamination. Satellite imagery combined with the use of Geographical Information Systems (GIS) can be put to work to quickly identify and track spilled oil. To hasten the cleanup of spills, regional cleanup sites along the problem areas could help contain spills more quickly. To make these tasks feasible more funding must be provided by the stakeholders of the oil industry. Nongovernmental organizations will keep fighting the damaging effects of oil, but will not win the battle alone.

Risk posed to both human health and the environment

Although there is considerable public concern about the environmental impacts of oil pollution in the Niger Delta of Nigeria, actual evidence on the pathological and psychological effects in the health of local communities is minimally known. We sought to associate the perspective measures of exposure to oil pollution with health outcomes (inventory of health symptoms and functional capacity limitations) and determine how emotional reactions to environmental risks moderate these health outcomes. Most of the participants lived in areas with visible oil pollution and/or near gas flaring facilities and regularly suffered direct exposure to oil in their environment. High level of emotional distress was a part of everyone's life for the study population. Risk perception in the study area was mediated, to a large extent, by dreaded hazards (catastrophic fears of pipeline explosions and oil spill fire), visual cues (gas flares and smoke stacks) and chemosensory cues (off-flavor in drinking water). The exposure metrics were found to be significant predictors of the health effects and influencing factors (emotional reactions). Multi-levels models suggest that at the individual level, the demographic variables and direct contact with oil pollution were important mediators of functional capacity limitation. At the community level, emotional distress from fear of the sources of exposure was an important mediator of the health symptoms. Emotional distress can induce dysregulation of multiple interrelated physiological systems including the cardiovascular, endocrinological and immunological systems and hence are risk factors for a wide range of pathological diseases (Peek *et al.*, 2009 and Brosschot *et al.*, 2006); the high burden of disease symptoms found in this study is noteworthy. As example, people with type II diabetes mellitus, a rapidly rising condition in Nigeria, are twice as likely to suffer from depression compared to the general population, which in turn can lead to greater difficulty with self-care (Cosgrove *et al.*, 2008). People with emotional distress are more likely to smoke cigarettes as other people (Lasser *et al.*, 2000 and Felker *et al.*, 2010); we show that 17% of the

participants smoked regularly and this rate may be rising. Patients who are depressed have higher the risk of having a heart attack compared to the general population (Rugulies, 2002). Of particular significance in Nigeria is that fact that annoyance and intolerance are among the instantiations considered to be risk factors for aggression through loss of self-control (Denson, 2012). People who show heightened aggressive cognition, physiological arousal, and anger tend to make hostile attributions about others' behavior (polluters in the Niger Delta for instance), which heightens the tendency towards aggression (Denson *et al.*, 2011). The cause-effect relationship between exposure to oil pollution and high level of violence in the Niger Delta as well as the hostility towards the oil producing companies is an intriguing question for further research. The results of this study make a strong case for national attention to be paid to what our study has shown to be a silent epidemic of psychological problems in communities of the Niger Delta area

Conclusions

This result has accentuated the negative and statistically significant impact of oil-spill on the soil of Eleme which accounts for the rapid destruction of vegetation and farmland. The fertility status of the soils is reduced as the oil makes most of the essential nutrient unavailable for plant and crop utilization Eleme should therefore be included in the remediation technique going on in the Niger Delta region for cleaning up affected soils. The problems of oil-spills can be minimized if the oil companies should be more environment conscious and follow strictly the provisions of the law and standards set by regulatory bodies or agencies. They should also have regular monitoring of oil production activities and facilities and pay adequate compensation to the host affected communities.

This study also documents high levels of disease symptoms and environmental distress (worry, annoyance and intolerance) associated with oil pollution in the Niger Delta areas of Nigeria. It highlights the need for some intervention to ameliorate the psychological distress associated with living under such environmental adversity.

Soil pollution by oil spillage is caused by human errors and carelessness, but sometimes by natural disasters such as hurricanes or earthquakes. Deliberate acts by terrorists, countries at war, sabotage and bunkering, or illegal dumpers however, prove that oil spills are not always accidents. Some oil from any spill is degraded into simpler substances naturally by microorganisms. Use of biosurfactants have been shown to be of desirable characteristics, therefore it is one of the best approaches suitable for emulsification of crude oil spills for biodegradation. The biodegradation process is relatively slow, and when an oil spill occurs, workers must act fast to protect the environment. Most crude oils are inherently biodegradable, but they contain essentially no nitrogen, phosphorous or other trace elements that are necessary to stimulate the microbes that degrade the oil.

In the same vein, the Nigeria Sat-1, would help in monitoring oil spill by providing the spill position which would serve as input data into the oil spill model. It would also give the extent of coastal water and coastal areas polluted. These information are vital for quick cleanup of oil impacted areas. In order to reduce the response time and qualify the decision-making process, application of Geographic

Information Systems (GIS) as an operational tool has been suggested. Information on the exact position and size of the oil spill can be plotted on maps in GIS and a priority of the combat efforts and means according to the identified coastal sensitive areas can be carried out. The creation of regional spill response centres along coastlines would help in managing oil spill problems (Smith and Loza, 1994). The centres will use oil spill models for combating oil spill problems. Using data

collected with an airborne system to input one or several new starting point(s) into the model, will improve the accuracy of the further predictions.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Regional status of soil pollution: Central America, Mexico and the Caribbean

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Abstract

Prevention of soil contamination remains the best way to maintain healthy soils and food safety. Unfortunately, the well-founded information in the literature about soil contamination in the 15 countries belonging to the Regional Soil Partnership for Central America, Mexico and The Caribbean, is scarce and consequently also the information of the population. Different human activities may result in the pollution of soils and adjoining water bodies caused by fertilizers and agrochemicals used in high-input agriculture, and from mining and oil spills. It is required to develop and establish a harmonized methodology that will allow the regular monitoring of the content of heavy metals and other pollutants in the Region and to establish National Legal Regulations about the subject.

Keywords: fertilizers contamination, pesticides contamination, mining contamination, soil legislations

Introduction, scope and main objectives

Soil may filter, fix and neutralize, but also release pollutants when conditions change. Therefore, prevention of soil contamination remains the best way to maintain healthy soils and food safety in accordance to the Sustainable Development Goals.

Contaminants can enter soils from a variety of sources including agricultural inputs, land application of by-products, atmospheric deposition, flood and irrigation water, accidental spills, inappropriate urban waste and wastewater management, and other means (FAO, 2017).

Despite the lack of information for the Region of Central America, Mexico and the Caribbean, it is considered that the main causes of soil pollution are different human activities that result in the pollution of soils and adjoining water bodies caused by fertilizers and agrochemicals used in high-input agriculture and from mining and oil spills. In relation with this situation is that in general terms, many of the countries in the Region have not enough regulating instruments to address soil pollution (FAO and ITPS, 2015).

The following paper constitutes an approximation of soil pollution status on the Region of Central America, Mexico and the Caribbean.

Results and discussion

One of the most common problems in relation to soil pollution have to do with human activities. Soils suffer the constant discharge of all types of waste, since they can retain and accumulate pollutants for years, the most common being heavy metals, hydrocarbons, mineral oils, fertilizers and pesticides. Unfortunately, the well-founded information in the literature about soil contamination in the 15 countries belonging to the Regional Soil Partnership for Central America, Mexico and The Caribbean, is scarce and consequently, the population is usually not well informed about the situation and the risks for human health.

In the Region, Mexico is the nation most affected by the high levels of PM₁₀ (particulate matter from the gases emitted by vehicles and factories), Ozone (exceeds by 15% the figures allowed by the WHO) and Carbon Dioxide, (DF and Guadalajara stand out negatively due to their high concentration).

Different human activities may result in the pollution of soils and adjoining water bodies caused by fertilizers and agrochemicals used in high-input agriculture, and from mining and oil spills. Phosphoric fertilizers are the reason of non-permissible amounts of cadmium (Cd) on some soils and agricultural products. Residues of herbicides such as glyphosate have been observed in soils and groundwater in fields devoted to no-till farming.

Mining is a highly polluting industry, directly affects water, soil and air, which translates over time into effects on people, animals, plants, etc. that is, they affect ecosystems, but it is an important economic activity in the Region. According to Nolasco (2011), the percentage area with mining concessions in El Salvador, Nicaragua, Honduras and Guatemala reaches an average of 14% of the area of these countries and of them, Honduras the highest with 31%. Costa Rica was not included in the report because of the lack of sufficient information. Besides, Costa Rica and El Salvador have only projects in the exploration stages, none in operation. In general terms, gold (Au), silver (Ag), Pb, Zn and others were the metals extracted and Fe, Pb, Hg, Cd, As and cyanide, the main contaminants detected. The use of mercury (Hg) and arsenic (As) compounds in mining activities and the use of huge amounts of water for shale oil exploitation are causing downstream pollution in soils and waters (FAO and ITPS, 2015). The bauxite mining industry in Jamaica is having a devastating impact on the environment and surrounding ecosystems. It is also posing serious health problems for local communities. The sun baked sludge contains heavy metals and other pollutants.

The increasing use of organic manures and compost as nutrients in agricultural productions without previously considering its origin, is cause of the increasing presence of heavy metals like Pb and Cd in non-permissible amounts in soils and agricultural products. Also, agricultural by-products and sludge increase N concentrations in groundwater and cause eutrophication.

In our Region also must be mentioned, the natural high content of metals as Ni and Cr in some soils due to the parental material. It is the case of soils developed from serpentinite with very high nickel (Ni) (2 000 mg.kg⁻¹), Chromium (Cr) and cobalt (Co) contents, fortunately most of them in forms not available to plants, Muñiz *et al.*, 2015).

Special attention must be given to the need of regular monitoring of the content of heavy metals and other pollutants in soils of the Region. This is known, but no even one country do it as a regular service to areas where are known or suspected. Even more, it is necessary the harmonization of the methodologies for soil analysis and in particular the criterion for soil content evaluation.

In relation to the existence of National Regulations about soil contamination. In general terms, the topic of soil contamination and its monitoring is not specifically included in the legislation of the 15 countries belonging to our Regional Sol Partnership. Anyway, the protection of natural resources is mentioned in a general manner on the main National Legislations. Only in the case of Cuba, soil conservation is mentioned explicitly. Another 6 countries use in their Regulatory Framework the use of incentives aimed at forestry mainly: Costa Rica, Cuba, Honduras, Guatemala, Mexico and Nicaragua.

All current Mining Laws mention or refer to the prohibition to cause environmental damage, but very little is said or specified what will be the control mechanisms to avoid this type of damage. It is also required official plans for the reclamation of the affected areas.

An example is Cuba's National Environmental Strategy of 2011/2015, which characterizes soil degradation as one of the fundamental environmental challenges in the country and had implemented action plans and programs for soil conservation, including mining areas (CITMA, 2011). Countries like Mexico and Costa Rica, they have also.

Conclusions

1. The main human activities that lead to the contamination of soils and adjoining water bodies in the Region are caused by fertilizers and agrochemicals used in high-input agriculture and from mining and oil spills.
2. It is required to develop and establish a harmonized methodology that will allow the regular monitoring of the content of heavy metals and other pollutants in the Region.
3. There are few National Legal Regulations about soil contamination and corresponding soil reclamation in the Region

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Regional status of soil pollution: Eurasia

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Abstract

This report provides an overview on soil pollution in Eurasian countries in support of the initial global assessment on the state of soil pollution that promoted by of FAO Global Soil Partnership in context of achieving common GSP Goals/Outputs and soil health commitments. Eurasian Soil Partnership includes mainly post-Soviet countries, which have similar history of soil inventory and monitoring. However, during the last 25 years after the fall of the Soviet Union the systems of soil monitoring significantly transformed depending on the priorities in each country. Punctual sources of pollution such as industrial contaminants and mining tails are widespread in all the countries, but their number decreased due to the general economic decline, especially in the 1990s. Radionuclide's pollution is still a challenge in Ukraine, Belarus, Russia and northern Kazakhstan. In some countries local contamination is monitored, but the number of sites is insufficient for reliable risk assessment. Diffuse soil contamination induces by overuse of agrochemicals is one of the priorities in Eurasia irrespective of current low fertilizers doses compared to that in European Union. In most countries pesticides content in agricultural soils is monitored. The actual extent of diffuse pollution is still mostly unknown across the region, and a trans-regional study is required to provide a holistic and up-to-date picture of the state and risks of soil contamination in Eurasia. The main obstacle for adequate assessment of contamination is the lack of coordination among the ministries and agencies responsible for soil monitoring or the absence of political will and resources for the establishment of an effective monitoring system.

Keywords: radionuclide, industrial contamination, pesticides, post-Soviet countries

Introduction, scope and main objectives

The review tries to provide a general view on soil pollution in the countries – members of the sub regional Eurasian Soil Partnership (EASP). The EASP includes the countries that constituted the Soviet Union before 1991 with the exception of the Baltic States, which are members of the European Union. Turkey is also a member of EASP because of its historical cultural ties with South Caucasus and Central Asian countries. In the majority of the ex-Soviet EASP countries the situation with soil pollution is complex due to the past extensive development of industry and agriculture in the Soviet Union. In most cases quick increase in the industrial and agricultural production had priority over the safety for the environment and human health. Even after drastic decline in the industrial development and a decrease in the doses of agricultural chemicals vast areas of arable lands, pastures and natural ecosystems remain heavily polluted. This paper discusses three major sources of contamination: radionuclide pollution due to civil and military USSR nuclear programs, local contamination from industrial and mining sources, and pesticides use leading to local and diffuse

contamination. These issues are addressed to different extent in different countries, and there is no joint approach to legislation in the area of soil pollution for the region. It causes certain obstacles to the monitoring and control of soil contamination, especially in the case of cross-boundary pollution.

Results

Radionuclide contamination

Extensive areas in Eurasia were affected by radionuclide contamination. The most infamous area of this type of contamination is Chernobyl (Ukraine), where a nuclear power plant exploded in April 1986 that has been considered the worst incident in civil nuclear programs ever recorded. More than 37 million people were affected by the fallout, and actually extensive areas remain polluted with radionuclides: in Ukraine the area is estimated as 8.40 million ha, in Belarus around 0.25 million ha, and Russian Federation up to 5.51 million ha. The main contaminating agent is cesium-137. In Russia, there also other sites with residual radioactivity related to nuclear accidents in 1949, 1957 and 1967 in Urals and West Siberia. The other important source of contamination is the zone of Soviet nuclear tests at the Semey, “Kapustin Yar” and “Lira” test grounds in Kazakhstan. At the former Semipalatinsk (Semey) nuclear test ground, about 2.00 million ha of agricultural lands have been subjected to radioactive contamination (Saparov 2014). The radionuclides include isotopes of thorium, barium, and radium. Other local sources of radioactive substances are related to uranium mines in Kazakhstan, Uzbekistan and Kyrgyzstan. Though these are punctual sources, they might have an important negative impact on agricultural lands in the vicinity, especially if the winds are blowing the contaminated sediments. The situation is especially dangerous in Kyrgyzstan, where the uranium mines are located mainly on steep slopes, and radionuclides might easily migrate to the valleys used for agriculture.

Local industrial, urban and mining contamination

Though the entire sub region has numerous industrial and mining sites potentially dangerous for the environment, the exact number of contaminated sites is unknown. In Turkey the number of contaminated sites is expected to be in the range of 1000-1500, of which 5-10 % are believed to be sites requiring remediation, but in reality, only few of these sites were really treated (Burcu Ozkaraova Gungor 2008). In Russian Federation only 35-40 sites are studied annually, with some overlapping from year to year for monitoring dynamics at the most contaminated sites. Obviously, the number of potentially contaminated localities is much higher. In Belarus, 44 cities have been studied within five-year inventory to provide an assessment of petroleum products, heavy metals, and sulphates and nitrites. Also soils around the main 10 machine-building, petrochemical and construction plants in Belarus are continuously monitored. The monitoring showed that though in some places the concentration of pollutants was high, the environmental effect was local due to the insignificant contaminated area. The total area of contamination due to technogenic emissions may be estimated roughly in some countries, while the others do not make any inventories.

In Azerbaijan, the area of contaminated soils is estimated to be 33,300 ha, including 11,143 ha contaminated with petrochemistry products, around 11,000 ha under mining products, and 5,000 ha under construction waste. In general, untreated and even illegal waste disposal is an important challenge for soil contamination in the country. In Ukraine, the area of agricultural lands contaminated with heavy metals equals to 1.61million ha. In Kazakhstan, lands contaminated with heavy metals and radioactive substances occupy about 21.50 million ha (Saparov 2014). In Belarus most of the contaminated soils are found in urban environments (78 thousand ha) and around the highways (119 thousand ha), while only 10 thousand ha of agricultural soils are

contaminated. In Russian Federation, the area of soils contaminated with heavy metals is around 730 thousand ha, and with petroleum and by-products exceeds 100 thousand ha. Total area of contaminated soils in Russia is estimated on the level of 3.60 million ha, including 1.4 million ha of agricultural lands.

Local contaminating industrial plants may also cause cross-boundary contamination. For example, Tursunzade aluminum plant in Tajikistan, being one of the biggest smelters in the region, continuously causes contamination on the territory of bordering Uzbekistan. Recently, a synthesis report «Waste and Chemical in Central Asia: A Visual Synthesis» has been published under support of the Swiss Federal Office for the Environment (FOEN) (Zoi Environment Network 2013). This report is to catalyze remedial action on environmental legacies and responsible approaches to waste and chemicals management by sharing information and improving public awareness of situations and trends, and main areas of concern and notable responses.

In such countries as Azerbaijan, Turkmenistan, Kazakhstan, and Russian Federation petroleum industry is one of the main sources of pollution. In Russia, around 30 thousand ha of reindeer pastures were lost due to oil spills. In the oil regions of Western Kazakhstan and the Torgay plain, on an area of more than 500 thousand ha, there are large sections of soil contaminated with oil and radioactive materials, high levels of salinity with industrial wastewater and technological transformation of the soil landscape, leading to the accumulation of toxic heavy metals such as lead, cobalt, nickel, vanadium etc. (Saparov 2014). The main hot spots of contamination in Central Asia are presented in Table 1. The table was modified, because initially it included also the sites with water contamination. As parties to international conventions related to chemicals and waste, the countries of the region are making these a political priority. Together with new standards for industrial production and new technology, this political attention is fueling progress. Increasingly, municipal waste is an issue in the Central Asian capitals and other major cities as they strive to maintain an image of cleanliness. Most of the hazardous waste in the region is located in desert areas with low populations, but some industrial towns also have their share. In the mountainous countries - where all the waste is upstream from the lowland countries - even small amounts of waste carry significant risks.

Table 1. List of Waste and Chemical Hotspots for selection polluted sites in the Central Asia counties, modified after (Zoi Environment Network, 2013)

#	Hotpot	Waste and chemical issue
1.	Kyrgyzstan	
1.1.	Waste and Chemical Issues in Issyk Kul lake region	Issyk Kul region qualifies as a priority site for three reasons - its biodiversity, its importance as a tourist destination and its complicated waste and chemical issues. Kadji-Say tailings contaminated with radioactive materials are close to the lake. An echo of a Soviet era spill of tailings material at Aktuz and the current appalling conditions of tailings at Aktuz and Orlovka are additional concerns. Since independence, the application of fewer chemicals has resulted in less pollution.
1.2.	Mayli-Suu uranium tailings	Located on the edge of the Ferghana Valley in Kyrgyzstan, the Mayli-Suu mine started uranium production in the World War II years. The area, which is near the borders with other states, is prone to natural disasters - torrential rains, flash floods and earthquakes that trigger landslides and the destruction of tailings dams. The total volume of waste in Mayli-Suu tailings is estimated at 2 million cubic meters. The health impacts of Mayli-Suu waste are evident in the high rate of cancers and abnormal births.
1.3.	Min-Kush uranium tailings	This uranium mine and processing facility, located in the center of Kyrgyzstan, has four radioactive waste sites recognized by risk assessments as needing priority attention. The tailings, which are near the headwaters of the river, are in appalling condition and represent a significant risk to

		downstream areas. Landslides could affect both a former uranium processing facility on the edge of town and one of the tailing sites. A lack of knowledge - and an absence of Geiger counters - has led to a situation where many people are now affected. Remediation necessarily means phasing out the use of contaminated buildings, and may entail the relocation of people.
1.4.	Khaidarkan mercury mining and waste	Opened during World War II, the Khaidarkan mine first produced mercury for use by the military. Eventually, Khaidarkan grew to encompass the mines at Chauvay and Ulug-too, and is still an active mercury mine. The mine operators made no provision for backfilling the waste either into the open pits or into the underground spaces and as a result, the amount of industrial hazardous waste (more than 20 million tonnes of slag) was the highest in Kyrgyzstan. Part of the Khaidarkan area is contaminated with mercury sludge at much higher concentrations than background levels. The environment and health risks have been initially assessed, and important next steps include a more detailed investigation of the contaminated hotspots, addressing those risks through monitoring, land use revision and remediation.
1.5.	Suzak obsolete pesticides dump	The Suzak pesticide dump is located about 10 kilometers from the city of Jalalabad in the western part of Kyrgyzstan. The largest pesticide waste site in Kyrgyzstan, the Suzak dump has approximately 1 500 tonnes of chemicals on hand. As at the Vakhsh and Kanibadam dumps, the local population excavates obsolete pesticides, and cattle graze the area. Direct exposures and the consumption of contaminated meat from agricultural animals that grazed here led to cases of toxic poisoning in 2004, with some cases resulting in death.
2.	Tajikistan	
2.1.	Taboshar uranium tailings and other waste Tajikistan	Uranium production at the Taboshar open pit mine in Tajikistan started in 1942 and continued to the 1970s, and later converted to underground in-situ leaching. Taboshar has 7 million cubic meters of tailings spread over 65 ha (an area equivalent to 100 football fields) and over 34 million cubic meters of waste rock. Because of its large amount of waste, its proximity to a populated area and the potential for natural disasters, the site has been selected as a hotspot with high priority for remediation.
2.2.	Chkalovsk, Gafurov and Degnay uranium tailings	Chkalovsk is Tajikistan's former hub for uranium ore processing. Larger in scale than Mayli-Suu and Taboshar and with more sophisticated and more highly enriched uranium products, Chkalovsk took ore from throughout Central Asia. One result of this is the largest amount of waste (55 million tonnes in 10 tailings) in Tajikistan. Processing began right after World War II and continued until 1998. In the early years the rush to produce enriched uranium led to the storage of uranium waste in the middle of the city of Gafurov near Chkalovsk. The area is now covered, fenced and monitored, but is still radioactive, and in need of improved containment. A larger, more permanent Degmai tailing site was later established 5-7 kilometers outside the city, and the waste material was covered with water. After independence, production stopped, and the uranium tailings dried out, creating substantial risk.
2.3.	Vakhsh obsolete pesticides dump	During the Soviet era, the agrochemical dumps at Vakhsh and Kanibadam in Tajikistan received waste from local agriculture and from Kyrgyzstan and Uzbekistan, and are now two of the largest obsolete pesticide waste sites in Central Asia. Vakhsh, located in southern Tajikistan, has some 7 000 tonnes of waste, while Kanibadam, in the northern part of the country, has 3 000 tonnes, including more than 500 tonnes of dichlorodiphenyltrichloroethane (DDT). Located within five kilometers of settlements, both dumps were poorly planned. The original simple fences are long gone, and the sites are now accessible to people and animals. The degraded conditions of the dumps and the illegal trade have increased the spread of pollution.

3. Kazakhstan		
3.1.	North Caspian oil reserves in Kazakhstan	By international standards, the North Caspian oil reserves are very large. The Tengiz oil field, discovered in 1979 on the Kazakhstan shore of the Caspian Sea, has been in operation since 1993. The even larger offshore Kashagan field, also in Kazakhstan, was discovered in 2000, and is scheduled to start operations in 2013. At 14 per cent, the sulfur content of the oil is high. The separation of the sulfur from the oil has produced large sulfur stockpiles. As an offshore facility, Kashagan is subject to storms and ice events. The environmental conditions in the area are compromised by abandoned and flooded oil fields.
3.2	Eastern Caspian region: Aktau nuclear complex in Kazakhstan	For years, mining and industrial operations near the city of Aktau, Kazakhstan, used Koshkar-Ata - a natural depression - as a waste storage facility. With some 120 million tonnes of tailings and wastewater, Koshkar-Ata is now the largest tailings site in Central Asia. The waste had been stored under water to prevent the release of radiation and to inhibit wind erosion and dust formation, but when the industries stopped producing, the site was left to dry out, and radioactive releases occurred. When initial remediation of high priority sites began in 2008-2010, some waste material was relocated and covered with plastic, clay, cement or soil.
3.3.	Shymkent and Taraz phosphorous plants	Former phosphorous plants in two cities - Taraz and Shymkent - in the southern part of Kazakhstan produced significant amounts of waste with high phosphorous content. Now abandoned, these waste and tailings sites represent serious fire and toxic hazards. Located on the edges of the cities, these sites each hold about 500 000 tonnes of waste, and threaten a combined urban population of almost 1 million people. Phosphorous waste is prone to self-ignition, and produces a toxic cloud when it burns. One fire has already broken out, but the local fire brigade quickly extinguished it. The high inflammability of the waste, combined with the absence of safety measures, makes for a significant threat.
3.4.	Balkshash and Ust-Kamenogorsk	The Darial-U station near Lake Balkshash in Kazakhstan was a restricted military site in the Soviet period, and abandoned after independence. A recent inventory found 15 000 capacitors leaking PCBs. Hundreds of tonnes of PCB waste were released into industry waste ponds over this period and levels of contamination are high. Altogether the PCB contamination in Kazakhstan - an estimated 2 million tonnes of soil and 250 000 tonnes of PCB-containing waste - is probably the highest in Central Asia.
4. Turkmenistan		
4.1.	Eastern Caspian region: Khazar and Balkanabat on the Chek-elen Peninsula in Turkmenistan	Industrial facilities in the towns of Khazar and Balkanabat on the Chek-elen Peninsula in Turkmenistan have produced bromine and iodine since the 1940s. With a production capacity of 250 tonnes per year, the industrial operations, which involve activated carbon, have generated a significant amount of radioactive waste - in excess of 21 000 tonnes. An oil refinery in Saymonov bay at Turkmenbashy (formerly Krasnovodsk) started operation in the late 1940s, and discharged wastewater with little or no treatment for decades.
5. Uzbekistan		
5.1.	Industrial waste in Navoi province	Located in the center of Uzbekistan, Navoi Province is home to most of the country's gold and uranium mines and to most of the waste from mining and processing - 30-35 million tonnes of hazardous waste annually, approximately 90 per cent of the total hazardous waste produced in the country. The Uchquduq uranium mine, located in the middle of the Kyzylkum desert, has several tailings, leaching ponds and numerous waste-rock dumps. This bulk waste represents less of a problem, but large stocks of waste from open pit mining are still present. Fortunately, most of the waste is in desert areas far from population centers, and is therefore a low priority for remediation.

		Most of the waste in Navoiy Province is concentrated in three areas - in tailings from a metallurgical processing plant in Navoiy city (60 million tonnes of waste), at the Muruntau gold mine nearby Zarafshan city (90 million tonnes of waste) and at the Uchquduq uranium mine (1 500 ha of open-air uranium leaching ponds and polluted soils). Some areas with high radioactivity have already been remediated, and the work is continuing.
6	Cross-border risks reduction	
6.1.	Cross-border risks posed by waste and chemical pollution in the Ferghana Valley area	With the highest population density in Central Asia outside the cities, the Ferghana Valley is also home to the highest concentration of industrial sites. Industrial development of mineral resources in the mountains around the Ferghana Valley during the twentieth century generated around 100 million tonnes of waste rock and a nearly equal amount of tailings from uranium mining; at least 20 million tonnes of waste from mercury mining and smelting; and a significant amount of industrial waste from antimony, copper, gold and iron smelting and processing. Poorly maintained agricultural chemicals waste sites at Suzak, Kyrgyzstan and Kanibadam in Tajikistan present additional health and environment risks. Industrial waste sites that require priority attention and cross-border cooperation include those at Mayli-Suu, Shekaftar, Khaidarkan, Kadamjay and Chauvay in Kyrgyzstan, Taboshar and Chkalovsk in Tajikistan and Charkesar in Uzbekistan. In the event of a major release, the countries need an early warning system to alert each other and minimize or prevent cross-border contamination.

Diffuse contamination

Agriculture is the main pollutant of soil, water and land resources. According to estimating data more than 60% of total volume of contamination of watersheds causes diffusive sources of contamination (agrochemical, phenol, petrochemicals and the others.), coming in from irrigated areas, livestock farms, F&L depositories, aerodromes and rural settlements. There is close relationship between water quality, health and poverty. Almost quarter of the country population of Uzbekistan (more than 6 million people) feels negative influence of contaminated water (ADB 2007). Environmental contamination with industrial, mining, and petroleum extraction products is also a significant pressure. Diffuse pollution reduces the ability of soil to work as buffer and filter for pollutants, their role in hydrological and nitric cycles, and their ability to ensure habitat and sustain biodiversity.

Diffuse contamination is commonly associated with the excessive use of fertilizers and plant protection products. Blaming USSR for abuse of agricultural chemicals is common in ecological literature, but in fact the use of fertilizers was continuously decreasing from 1980s, and dramatically fell down in the 1990s practically in all the ex-Soviet countries. For example, in Kazakhstan the total amount of mineral fertilizers was more than 1000 kilotons in 1986 and only 31 kiloton in 2008; the doses per ha of arable land decreased from 29 kg NPK to 1.5 kg. Thus, on the major part of the territory of post-Soviet countries mineral fertilizers are not applied in excessive quantities, in contrast, one can expect nutrient mining from soil. However, pesticides use still constitutes a problem.

There are two aspects of pesticides contamination in Eurasia. On the one hand, in places these products are used excessively. On the other hand, there are storehouses of obsolete pesticides that act as potential sources of contamination. On the territory of Ukraine there are about 3000 such storehouses, not taking into account almost 2000 so-called "hot spots" - polluted sites of ruined storehouses (Moklyachuk *et al.* 2014). In Russia such storehouses are continuously monitored, and in most cases the prognosis for their safety is optimistic (SPO "Taifun" 2017).

The area polluted with pesticides is dynamic and depends not only on the year, but also on the season. Modern pesticides are not very stable in soils, and their content directly depends on the doses of their application in the year of the study and on the weather conditions. In Russia

The GLADIS reference base (FAO 2008) confirms that the drylands of the Eurasian region are most prone to suffer soil pollution and land degradation. The total area affected by water erosion is over 30 million hectares, and by wind erosion – about 67 million hectares (CACILM 2006). Between 40-60 percent of irrigated croplands in CA are salt-affected and/or waterlogged (Qadir *et al.* 2008). The data indicate that total area of highly saline soils in the Aral Sea Basin increased by 30% in the 10-year period from 1990 to 1999 (GEF WEMP 2001). About 54% of surveyed soil in Uzbekistan is polluted by pesticides. The special concern is the local pollution of soil near to former agricultural airfields, warehouses for storage of pesticides, organic and mineral fertilizers.

Legislation

The legal status of soil contamination monitoring, penalties for soil contamination and measures for soil remediation are mainly regulated by national laws and other regulating documents. However, international agreements may also act as effective instruments for managing soil pollution.

In the context of the global environment all countries of EASP are Parties to three Rio Conventions: the Convention on Climate Change (UNFCCC 1999) “Convention on Biological Diversity (UNCBD 1995) and Convention to Combat Desertification (UNCCD 1994)” together with a number of other international Agreements and Protocols in the areas of environmental conservation and sustainable development, including:

- The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1989);
- The Vienna Convention for the protection of the Ozone Layer (1988)
- The Montreal Protocol on Substances that Deplete the Ozone Layer (1989);
- The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (1998);
- The Stockholm Convention on Persistent Organic Pollutants (2001);
- The Strategic Approach to International Chemicals Management (SAICM, 2006).

The Strategic Approach to International Chemicals Management (SAICM) principles that was developed by the ICCM-2006 in Dubai, United Arab Emirates, is a policy framework to help achieve the goal agreed in the 2002 Johannesburg World Summit on Sustainable Development of ensuring that, by the year 2020, chemicals are produced and used in ways that minimize significant adverse impacts on the environment and human health.

The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) is an internationally agreed tool for chemical hazard communication, incorporating harmonized chemical hazard classification criteria and provisions for standardized labels and safety data sheets. It was developed in follow-up to the 1992 Rio Summit and was adopted in 2002 by the United Nations Economic and Social Council (ECOSOC) Subcommittee of Experts on the GHS (SCEGHS). The World Summit on Sustainable Development (WSSD) endorsed a global GHS

implementation target of 2008. The United Nations Institute for Training and Research (UNITAR) and the International Labor Organization (ILO) were nominated as focal points for assisting countries in building their capacity to implement the GHS. It is an important new tool that countries can use as a basis for establishing comprehensive national chemical safety programs.

National legislation in all the EASP countries, except of Turkey, has roots in Soviet regulations for the quality of environment. These regulations were based on maximum permissible concentrations (MPC) for contaminated substances in air and water. The MPC levels were very strict, and in most cases in the industrial areas temporary, much higher limits were used. In post-Soviet epoch new environmental legislation has been developed in all the countries taking European environmental regulations as a basis. The public management of natural resources and environmental protection in the EASP countries is based on the system of laws and other sub-laws and regulations, i.e. there is no unique law on soil pollution, monitoring and reclamation. As an example, currently, there are more than 120 laws and regulations existing in Uzbekistan aimed at managing the environment and natural resources. The most important of these are as follows:

- "On Environmental Protection" (1992), creating legal, economic and institutional framework for environmental protection, ensuring sustainable development;

- "On Water and Water Use" (1993) providing for rational water management, protection of water resources, prevention and mitigation of negative impacts, and compliance with the national legislation;

- "Land Code" (1998) providing for the basic rules and regulations for land use and stipulating land use rights;

- "On National Security Concept" (1997) containing the main frameworks for attaining the national environmental security;

- "On Protection of Population and Territories from Natural and Man-made Emergencies"

- "On Safety of Hydraulic Structures" (1999);

- "On Environmental Impact Assessment" (2001) requiring a mandatory expert impact assessment on environmental and human health, etc.

Relevant nature protection normative documents issued by government include:

- "On approval of the State Environmental Appraisal" (No. 491, 31.12.2001);

- "On approval of the State Environmental Monitoring" (No. 49, 3.04.2002);

- "On granting the status of Specially Protected Natural Areas of national importance to fresh groundwater formation zones" (No. 302, 26.08.2002);

- "On approval of the Procedure on Cadastral Division of the Territory of the Republic of Uzbekistan and Cadastral Numbers of Land Plots, Buildings and Structures" (No. 492, 31.12.2001);

- "On measures on radical improvement of land reclamation system" (No UP-3932 29.10.2007);

- “Provision on reservoir water protection zones and other water storages, rivers and main canals and collectors, and also sources of potable and domestic water supply, medical and cultural-health improving purpose in the Republic of Uzbekistan”(No 174. 07.04.1992);

- “On approval of order for issue permits for special water use or water consumption” (No 171. 14.06. 2013);

- “On approval of provision on the order for issue of permits for drilling wells for water” (No 214. 04.08.2014) and other.

Similar example may be presented for the Republic of Belarus, which also has multiple laws and regulations for the environmental protection.

- The Law of the Republic of Belarus of 26.11.1992 No.1982-XII "On Environmental Protection" as amended by the Law of 17.07.2002 No. 126-3;

- The Law of the Republic of Belarus "On the Protection of Atmospheric Air" of December 16, 2008 No. 2-3;

- The Law of the Republic of Belarus "On Waste Management" dated July 20, 2007 No. 271-3;

- Water Code of the Republic of Belarus of July 15, 1998 No. 191-3;

- The Land Code of the Republic of Belarus of July 23, 2008 No. 425-3;

- Resolution of the Council of Ministers of the Republic of Belarus No. 247 of 20.04.1993 "On the Establishment of a National Environmental Monitoring System in the Republic of Belarus (NNME)";

- Resolution of the Council of Ministers of the Republic of Belarus of 14.07.2003 No. 949 "On the National System for Monitoring the Environment in the Republic of Belarus";

- Resolution of the Council of Ministers of the Republic of Belarus No. 021 of 08.02.1999 "On local monitoring of the environment in the Republic of Belarus";

- Regulations on the procedure for the local monitoring of the environment and the use of its data as part of the National Environmental Monitoring System in the Republic of Belarus (Resolution of the Council of Ministers of the Republic of Belarus No. 482 of April 28, 2004);

- Instruction on the procedure for conducting local environmental monitoring by legal entities carrying out the operation of sources of harmful impact on the environment ", approved by the Decree of the Ministry of Natural Resources of the Republic of Belarus from 01.02.2007, No. 9 with subsequent amendments and additions;

- "List of enterprises defined by the regional and Minsk city committees of natural resources and environmental protection in the first, second and subsequent lines of local environmental monitoring", approved by the Order of the Ministry of Natural Resources and Environmental Protection of the Republic of Belarus of 12.05. 2001 No. 41;

- "List of legal entities carrying out local environmental monitoring as part of the National Environmental Monitoring System in the Republic of Belarus", approved by the Resolution of the

Ministry of Natural Resources and Environmental Protection of the Republic of Belarus dated 21.05.2007 No. 67 with subsequent amendments and additions.

In Azerbaijan the basic documents used for regulating soil monitoring and protection are:

- The Law on Environmental Protection (1999);
- The Law on Industrial and Household Waste (1998);
- The Land Code (1999);
- The Law " State Land Cadastre, Land Monitoring and Land Management ";
- The Law on the Earth's interior (1998);
- The Law on Mandatory Environmental Insurance (2002);
- International Convention on the Protection of Nature and the Environment, which participate in the Republic of Azerbaijan;
- "Strategic road map for the prospects of the national economy of the Republic of Azerbaijan";
- "National Strategy for the Protection and Sustainable Use of Biodiversity in the Republic of Azerbaijan for 2017-2020";
- "Azerbaijan 2020: a look into the future. Concept of development";
- "State Program of Social and Economic Development of the Regions of the Republic of Azerbaijan for 2014-2018".

In Ukraine the basic documents regulating soil quality, soil monitoring including contamination, are:

- The Land Code of Ukraine No. 2768-III, 25.10.2001;
- The Law of Ukraine "On Environmental Protection" No. 1264-XII, 25.06.1991;
- The Law of Ukraine "On Land Fee" of 19.09.1996;
- The Law of Ukraine "On Pesticides and Agrochemicals" No. 86/95, 2.03.1995;
- The Law of Ukraine "On the quality and safety of food products and food raw materials" No. 77, 123.12.1997;
- The Law of Ukraine "On State Technological Center for Soil Fertility Protection" No. 1218, 4.08.2000;
- The Law of Ukraine "On Land Reclamation" No. 1389-XIV, 14.01.2000;
- The Law of Ukraine "On Improvement of the State Control System in the Field of Soil Fertility Control" No. 243, 14.08.2001;

- The Law of Ukraine "On State Control over the Use and Protection of Land" No. 963, 19.06.2003;

- The Law of Ukraine "On the Protection of Land" No. 962-IV, 19.06.2003;

- The Law of Ukraine "On the Basic Principles of the State Agrarian Policy for the Period until 2015", No. 2982-IV, 18.10.2005;

- The Law of Ukraine "On Land Assessment" No. 1378-GU, 11.12.2003;

- The Law of Ukraine "On State Land Cadastre" No. 3613-VI, 07.07.2011;

- The Law of Ukraine "On the Basic Principles (Strategy) of the State Environmental Policy of Ukraine for the Period until 2020" of 21.12.2010, No. 2818-VI;

- The Law of Ukraine "On Approval of the National Program for the Development of the Mineral Resources of Ukraine until 2030 No. 4731-VI (4731-17), 17.05.2012;

- The Law of Ukraine "On the Production and Circulation of Organic Agricultural Products and Raw Materials"; 2014, No. 20-21;

- Draft National Program for Land Use and Protection (2004);

- Strategy for balanced use, reproduction and management of Ukrainian soil resources (2012);

- National Program of Ukraine for Soil Conservation (2015).

In Russia the main documents regulating soil quality, including contamination, are:

- The Land Code of the Russian Federation No. 136-FZ of October 25, 2001;

- Federal Law of 10.01.2002 No. 7-FZ "On Environmental Protection";

- Federal Law of June 18, 2001 No. 78-FZ "On Land Management";

- Federal Law of 16.07.1998 No. 101-FZ "On State Regulation of Providing Fertility of Agricultural Land".

For a long time, soil experts try to lobby the adoption of a special law on soil protection that should include also the details on soil pollution, penalties for soil degradation and necessary measures for soil restoration and remediation. However, a common opinion of legislators is that "soil" need not be mentioned in laws, and all the issues related to soils may be successfully regulated under land legislation. The difference between the concepts of land (territory or landscape) and soil (fertile substrate) is completely ignored. However, on the local level, e.g., in Moscow region, there are regional regulations that distinguish soil as an object of law.

Some countries, like Kyrgyzstan, have a unique document that regulates soil-related issues in the country, in this case Regulation on monitoring of agricultural land of the Kyrgyz Republic from 01.03.1999, No. 115. Responsible body for monitoring is the State Ecological Inspectorate and the Ministry of Emergency Situations under the Government of the Kyrgyz Republic. Other countries have multiple regulations, including specific regulations for focal territories, such as The Law of Ukraine "On the legal regime of the territory radioactively contaminated due to the Chernobyl

disaster" of 27.02.1991 No. 791a - HP. Assessment of the risk of radiation contamination is carried out by the Ministry of Health.

Turkey actually has, maybe, the most developed legislation mechanisms for controlling soil pollution. The general framework is formed by the Environmental Law adopted in 1983, and amended in 2006. The adoption of the law was followed by important regulations, such as the Solid Waste Control Regulation (1991), the Environmental Impact Assessment Regulation (1993), and especially the Hazardous Waste Control Regulation (1995) that provided the necessary measures to inhibit soil pollution. Finally, in 2001 the Soil Pollution Control Regulation, which is currently the major regulation related to soil pollution, was enforced (Burcu Ozkaraova Gungor 2008).

Discussion

All the countries of the Eurasian sub-region are subjected to soil pollution both due to the historical contamination and to the present technogenic fallings and overuse of chemicals. Though the challenge is high in all the countries, the most extensive and severe pollution can be observed in Ukraine, Russia, Kazakhstan, and Kyrgyzstan. The major contaminants are heavy metals, petrochemical products, and plant protection products.

The national priorities and target tasks to ensure environmental protection, natural resource use and implementation of the international agreements are integrated into the strategies, regional and national programs and regional initiatives of the EASP country-partners.

In national initiatives, the Central Asian countries have developed strategies to respond to the global conventions and initiatives on waste and chemicals. All the countries have recently developed waste and chemicals management programs, and in the countries with sufficient financing, many actions are already underway. The countries are developing national chemical profiles to identify producers, users and regulators, and to identify any gaps that may exist. They also participate in SAICM.

All the countries have legislation on soil contamination, but almost all of them are still lacking specific laws and regulations on soil pollution. The latter is treated under the regulations on environment, waste treatment, land use etc. A good example of a country with specific legislation on soil pollution is Turkey. The other challenge is that in some countries soil pollution is controlled by several ministries and offices, which in places cannot effectively coordinate their activities. For example, in Russia agricultural lands are monitored by the Ministry of Agriculture, while urban areas, forested lands and contaminated industrial sites are monitored by the Hydro meteorological Service under the Ministry of Natural Resources. Similar situation exists in some other countries.

Besides the lack of effective legislation, the lack of financial resources impedes soil pollution monitoring and especially soil remediation. In many cases the lack of finance for remediation means just the lack of political will, because even prosperous countries do not invest in the conservation of contaminated sites.

Conclusions

The soils of the major part of the Eurasian sub-region may be regarded as strongly polluted. It is related with unwise intensive industrial development of the Soviet Union, excessive militarization of some areas, and imbalanced use of agrochemicals. Currently soil pollution continues in spite of decreased industrial activity and limited use of fertilizers in most places. The main sources of soil

pollution are heavy metals, crude oil and petrochemical products. For agricultural fields pesticides are the main sources of contamination. Strong political will is needed for addressing the challenge of contamination in the region. Improved legislation and significant investment are the requisites for successful soil restoration.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Regional status of soil pollution: Europe

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Abstract

This report is an attempt to provide an overview of soil contamination in Europe as a contribution to an initial global assessment on the state of soil pollution, conducted by the FAO Global Soil Partnership.

This report is based on a range of soil assessments for Europe which have been carried out during the past 15 years. No attempt has been made to derive firm conclusions given the very limited time given to compile the information. A more comprehensive assessment on the issue is foreseen, for example in the context of the State and Outlook of the Environment Report (SOER 2020).

The overview of soil contamination assessments is supplemented with a heterogeneous, non-exhaustive and non-prioritised list of relevant knowledge and data sources that were readily available at the time of writing.

The terms pollution and contamination are used synonymously in this report.

Keywords: soil contamination, soil pollution, contaminated sites, contaminated land, health

Introduction

‘Contamination’ reflects the presence of an unwanted substance or impurity in a material, which leads to a reduction in quality. Contaminants can be biological, chemical, physical or radiological substances. While contamination is often referred to human health or environmental degradation, there are also non-toxic conditions (e.g. impurity of wine or fuel by water). Contamination receives attention if the presence of a substance harms humans and other living organisms. This holds especially to low-level (or chronic) constant exposure of humans, especially infants, to pollutants, which implies increasing risks in a highly industrialized environment. Pollution thus receives a negative connotation as it reflects the introduction or presence of contaminants into the natural environment which has harmful or poisonous effects¹. In some languages, ‘contamination’ and ‘pollution’ are used synonymously. The following text reflects this situation.

Soil pollution is predominantly caused by the presence of anthropogenic matter in soil that eventually may impact soil-based ecosystem services. Pollutants are introduced to soil primarily through industrial activity, certain land management practices, or the inappropriate disposal of waste, but also through indirect sources such as road traffic and domestic heating. Common types of pollutants found in soil are petroleum hydrocarbons, poly-nuclear aromatic hydrocarbons,

¹ Oxford English Dictionary

solvents, plant protection products, and metals. The presence of these substances is closely linked to industrial development and the intensity of chemical usage. Pollution can also be a natural process reflecting the presence or accumulation of toxic condition due to environmental processes (e.g. salinity, lead in parent material).

Pollution is often characterised as being a point source or diffuse. The former reflects a single identifiable source of pollution that is predominantly related to specific industrial activities (e.g. chemical refinery, mines and ore treatment plants, landfill sites, constrained agricultural activities, etc.). Point source pollution usually affects a specific location with rather restricted geographic extent. Non-point or diffuse pollution results from non-specified sources causing indirect transport to larger areas, such as from agricultural applications. Soil pollution can be an ongoing process or reflect historical activities that have now ceased but the effects of their operations are still apparent. Both, local and diffuse contamination are serious threats to the environment in Europe.

The concern about the effects of soil pollution arises from potential health risks either due to direct contact with the contaminated soil or from secondary contamination of water supplies, inhalation of particles or uptake by plants.

The main sources of soil pollution in Europe are the result of industrial emissions and accidental spills including radionuclides, waste disposal (e.g. landfill, illegal dumping, biosolids), mis- or overuse of agrochemicals, contaminated surface water (e.g. floods, irrigation) and ammunition residues in areas of conflict or military training areas. Concerning local soil pollution, municipal and industrial wastes are the main sources of soil contamination (38%) in the European Union, followed by the industrial and commercial sector (34%). Mineral oil and metals are the main contaminants, contributing around 60% of the overall soil contamination (JRC 2014).

An overview of soil contamination assessments

Many existing reports touch upon the issue of soil contamination in the European Union (EU) and Europe in a broader sense that provide an insight on its status.

Legislation

In **2006**, The **EU Thematic Strategy for Soil Protection** (EC 2006) was adopted and consisted of a Communication ([COM\(2006\) 231](#)) from the European Commission to the other European Institutions, a proposal for a framework Directive (a European law), and an Impact Assessment. The strategy identifies soil contamination as one of the key soil threats in the EU. Prior to the proposal for a Directive, extensive preparatory work was carried out involving EU Member States, (then) Candidate Countries, European Institutions, Networks of Regional and Local Authorities and a broad community of European-wide stakeholder organisations (e.g. civil society, NGOs, researchers, industry, international and professional organisations). Working Groups were set up which produced a number of in-depth technical reports, one of which addressed "Contamination and land management" (Van Camp *et al.* 2004). The study provided an in-depth assessment of all aspects of soil pollution, considering local sources, diffuse input and contaminated land management. It evaluated existing law (not specific for soil) that touches the realm of soil contamination, and provided a series of recommendations for policy, for the establishment of soil contamination monitoring (including lists of parameters to be monitored) and for future research needed on the topic. It elaborated on cross cutting issues (climate change, health, biodiversity, role of agriculture and forestry) and described in detail the status of soil contamination in Europe in 2004. According to this report, there was no widespread **diffuse pollution** of European soils, except for acidification and eutrophication. Diffuse pollution is

rather concentrated to specific areas or hot spots, mainly urban areas in the vicinity of industrial facilities, where it may add to pollution coming from local sources. As diffuse input were considered: deposition of acidifying and eutrophying substances, inputs from agriculture (fertilisers, pesticides, sewage sludge) including over applications of nitrogen (N) and phosphorous (P), and emissions and concentrations of selected persistent pollutants (metals, persistent organic pollutants). **Contaminated land management** refers mainly to the management of contaminated sites, and in particular, the study refers to the development of an indicator that shows how remediation progress is achieved at national scales.

The **Impact Assessment** (EU [SEC \(2006\) 1165](#) and EU [SEC\(2006\) 620](#)) which accompanied the EU Thematic Strategy contained an analysis of the economic, social and environmental impacts of various options that were considered in the preparatory phase of the strategy and of the measures finally retained by the Commission. It includes statements such as "...the completion of the inventory of contaminated sites would cost up to €240 million yearly for the EU25 over 25 years" and "... An independent study estimated that the costs of soil contamination could amount annually to up to €208 billion. Nevertheless this estimate had a high degree of uncertainty, therefore the intermediate value of €17.3 billion per year was retained ..." Of interest is the attempt to quantify both on-site and off-site costs associated with soil pollution where the latter are borne by public administrations, the private sectors, tax payers and society as a whole. The assessment concludes that it is difficult it is to quantify the costs due to soil contamination due to a lack of quantified data on off-site costs, in particular, for healthcare of neighbouring populations.

The **2006 proposal for a Soil Framework Directive** (EU SFD 2006) aimed to ensure a sustainable use of soils and protect their function in a comprehensive manner in a context of increasing pressure and degradation of soils across the EU. This proposal included measures to limit the introduction of dangerous substances into the soil (to avoid accumulation in soil that would hamper soil functions and create a risk to human health and the environment); and the setting up an inventory of contaminated sites, a mechanism for funding the remediation of orphan sites, a soil status report, and establishing a national strategy for remediation of the contaminated sites identified. The 2006 proposal was not unanimously adopted by Member States and in May 2014 the Commission withdrew it, however explicitly remaining committed to the objective of soil protection through the [Seventh Environment Action Programme \(2014-2020\)](#) (EU 7EAP 2014-2020) that recognises that soil degradation is a serious challenge, with many references to soil contamination and in particular to the remediation of contaminated sites.

In the meantime, in **2012**, the European Commission published a **policy report on the implementation of the Soil Thematic Strategy** and ongoing activities (EU [COM\(2012\) 46](#)), with many references to soil contamination, for instance in relation to financial instruments for soil remediation; as an example, with reference to the EU Cohesion Policy: "Despite the fact that there is no specific EU legal basis for soil protection, around €3.1 billion have been allocated to the rehabilitation of industrial sites and contaminated land as part of the Cohesion Policy in the period 2007-2013 out of a total of around €49.6 billion of planned EU investments under the Environment theme"

In **2016**, the European Commission performed a wide-ranging study named "[Updated Inventory and Assessment of Soil Protection Policy Instruments in EU Member States](#)" (Frelih-Larsen *et al.* 2016), that aimed to take stock of existing soil protection policies and measures at the EU and Member State levels, and to **identify key gaps in protection** with respect to soil threats and functions identified in the Thematic Strategy for Soil Protection. The study covered explicitly the areas of "Industrial and Point Source Contamination" and "Diffuse Contamination and Water Management"

Concerning "*Industrial and Point Source Contamination*" the following regulatory instruments were considered:

EU policy instruments were examined that are in place to prevent, limit and remediate industrial and point source contamination. The focus is on emissions to land and soils with two types of target for control: activities generating pollution now and potentially in the future, and contamination that persists already on land and in soils.

EU policies were identified linked to industrial and point source soil contamination, entailing different types of policy intervention, focused on regulating high risk activities or contaminants, preventing release, limiting emissions or remediating damage:

- **Environmental Liability Directive (ELD)**: focuses on local emissions of pollutants that change the status of land, water and biodiversity. Hence highly relevant to both increasing caution around questions of emissions to land and also addressing emissions/securing remediation when a change does occur.

- **Industrial Emissions Directive (IED)**: emissions from installations should be managed, with installations operating to Best Available Techniques (BAT).

- **Landfill Directive (LD)**: should ensure containment of pollution and so prevent emissions to local soils.

- **Waste Framework Directive**: waste management measures should take account of soil protection measures

- **Mercury Regulation**: direct control on sites holding, storing and disposing of mercury requiring certain management activities to limit contamination of land/soils.

- **Water Framework Directive (WFD) and daughter Directives**: by controlling inputs to water courses potentially point sources would be addressed, although these are more the focus of other measures.

Concerning *diffuse contamination*, the identified EU policies addressing are:

- **Water Framework Directive (WFD)**: Key instrument to control diffuse pollution in water (including routes to water)

- **Floods Directive (FD)**: some measures may interact with diffuse pollution routes

- **Nitrates Directive (ND)**: key instrument tackling nitrogen pollution from agriculture applied directly to soils

- **Pesticides Framework Directive**: key instrument tackling pesticide pollution from agriculture

- **Sewage sludge Directive**: Key instrument tackling pollution from sludge use in agriculture applied directly to soils

- **Industrial Emissions Directive (IED)**: diffuse pollution from installations should be managed but is more challenging to address

- **Seveso III Directive:** aims to prevent accidents and manage pollution if accidents occur
- **Landfill Directive (LD):** should ensure containment of pollution and so prevent diffuse pollution
- **Waste Framework Directive:** waste management measures should take account of soil protection
- **National Emissions Ceiling Directive (NECD):** a key instrument to tackle diffuse pollution from acidifying substances

All these EU policies have significantly contributed to the protection of soil despite it is not their main purpose. None of these instruments propose mandatory requirements for addressing soil contamination, and the approach depends on Member States' willingness to implement legislation.

As an illustration, Figure 1 shows the main EU Instruments that indirectly contribute to soil protection and the number of times that 'soil contamination' is mentioned in these legal instruments.

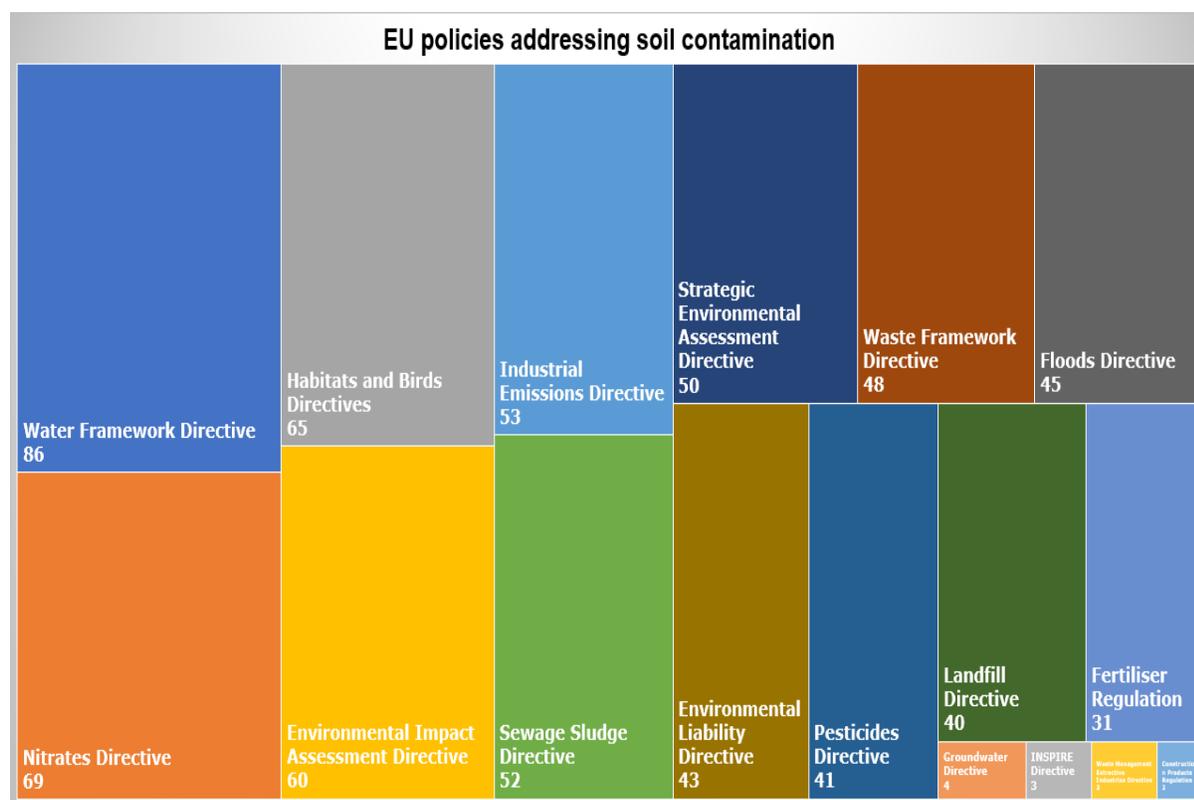


Figure 1. Main EU instruments.

An analysis is then made of the **strengths, weaknesses, opportunities and threats** in relation to soil protection of all these instruments, for both point and diffuse pollution, followed by an integrated assessment in relation to soil functions and other soil threats. Also these European instruments are **compared** to the instruments and measures in place in the EU Member States.

Even though both types of contamination are addressed in various policies, traceable objectives and targets are rather weak. For example, under the Water Framework Directive, pollutants and thresholds for water monitoring are listed; local sources need to be identified if polluting water bodies. The sewage sludge directive contains limits for heavy metals in sludge. Under the NECD, acidification, eutrophication of natural and nature-close ecosystems are to be monitored. The IED requires countries to establish Inventories of industrial operations (emitting SO₂, NO_x, dust), and to monitor them.

As another illustration, Figure 2 shows the number of national and regional legal tools that address soil pollution.

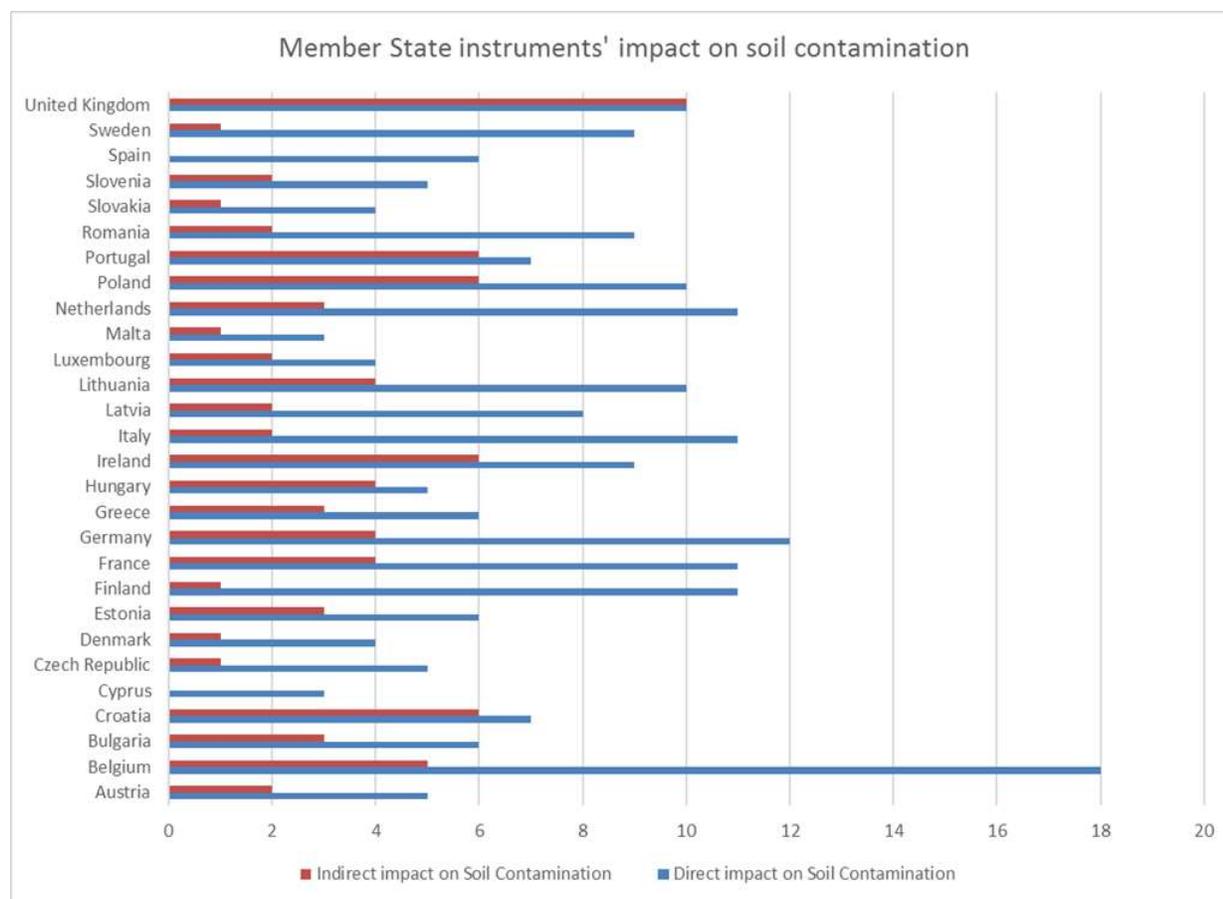


Figure 2. National and regional legal tools that address soil pollution.

Many countries have developed national plans or codes that implement at the same time multiple EU Directives in order to facilitate the applications of these laws. The most relevant examples are the Environmental Code of France, which implements 17 EU instruments, the Swedish Environmental Code that implements twelve EU Directives, or the proposal of a Dutch Environmental and Planning Act, that in case of approval shall adopt twenty EU legal instruments.

In relation to the subject of this in-depth study, it should be noted that also many non-EU European countries have developed national strategies, legislations and monitoring systems to tackle the soil pollution.

Pan-European assessments

The first EEA State of the environment report (the Dobris Assessment - 1995) (EEA Dobris 1995) contains an entire chapter where **soil contamination** issues are addressed in a European context. The causes, magnitude, impacts and possible remedies of soil pollution by metals, acid deposition, pesticides and other organic contaminants, nitrates and phosphorous, and industrially contaminated land, are described, with reference to the European context. Soil contamination with artificial radionuclides is also described.

a) A later reference report 'The State of Soil in Europe' (JRC 2012), produced by the European Commission Joint Research Centre (JRC) and the European Environment Agency (EEA) provided a comprehensive overview of the understanding of soil resources and degradation processes. It was developed and as a follow up to the State of the Environment Report (SOER) 2010.

The chapter on "**State and trends in soil contamination**" distinguishes clearly between local soil contamination (the result of intensive industrial activities or waste disposal) and diffuse soil contamination covering large areas.

State of soil contamination:

It is difficult to quantify the real extent of *local soil contamination* as many European countries lack comprehensive inventories and there is a lack of EU legislation obliging Member States to identify contaminated sites (the Directive on the management of waste from extractive industries is an exception (EC, 2006a)). Estimates show that the number of sites in Europe where potentially polluting activities are occurring, or have taken place in the past, now stands at about 3 million (EEA, 2007). Some locations, depending on their use and the nature of the contaminant, may only require limited measures to stabilise the dispersion of the pollution or to protect vulnerable organisms from pollution. However, it should be noted that around 250 000 sites may need urgent remediation. The main causes of the contamination are past and present industrial or commercial activities and the disposal and treatment of waste (although these categories vary widely across Europe). The most common contaminants are heavy metals and mineral oil.

Data on *diffuse contamination* across Europe is even more limited than that for local contamination as there are no harmonised requirements to collect information. Rodriguez Lado *et al.* (2008) attempted to map the concentrations of eight heavy metals based on samples from the Forum of European Geological Surveys Geochemical database of 26 European countries, but noted mixed accuracies during the validation phase. Bouraoui *et al.* (2009) modelled fertiliser application rates across EU-25 and showed that approximately 15% of the land surface experienced soil nitrogen surpluses in excess of 40 kg N ha⁻¹. Proxy measurements such as the concentration of nitrates and phosphates in water bodies, including groundwater supplies, can be used as an indication of excessive nutrient application to soils.

Trends in soil contamination:

Due to improvements in data collection, the number of recorded polluted sites is expected to grow as investigations continue. If current trends continue and no changes in legislation are made, the numbers reported above are expected to increase by 50% by 2025 (EEA, 2007). There is some evidence of progress in remediation of contaminated sites, although the rate is slow. In recent years, around 80 000 sites have already been treated while many industrial plants have attempted to change their production processes to generate less waste. In addition, most countries now have legislation to control industrial wastes and prevent accidents. In theory, this should limit the

introduction of pollutants into the environment. However, recent events such as the flooding of industrial sites in Germany during extreme weather events leading to the dispersal of organic pollutants and the collapse of a dam at an aluminum plant in Hungary in October 2010 shows that soil contamination can still occur from potentially polluting sites. Trends in the deposition of heavy metals from industrial emissions are discussed in the SOER 2010 Assessment on Air Pollution.

While reports show that fertiliser sales have remained stable or fallen slightly in EU-15 countries, consumption in Europe as a whole has continued to grow steadily during recent years (Eurostat, 2010; FAO, 2008). Although it is too early to detect any impact of the current economic crisis on fertiliser applications, a number of indicators (e.g. IRENA Gross Nitrogen Balance; EEA 2005) and reports (EC, 2010) have noted that nitrate levels in water bodies across Europe have fallen markedly (in 70% of monitored sites between 2004 and 2007). Given that the major source of nitrates in water bodies is runoff from agricultural land, one would expect to observe a similar situation in soil. If biofuel production becomes an important issue in the EU, this could lead to increased fertiliser applications and an increase in areas affected by diffuse contamination.

In EU-27, the total area under organic farming increased by 7.4% between 2007 and 2008 and accounted for 4.1% of the total utilised agricultural area (Eurostat, 2010b). Increased use of organic farming methods throughout Europe should result in an improvement of diffuse soil pollution from agro-chemicals. However, good agricultural practices should be followed to reduce the risk of pollution of water courses from manure applications.

The chapter on Impacts of Soil Degradation in the same report contains many references to soil contamination; a few extracts:

"... **Soil sealing** can lead to the contamination of soil and groundwater sources because of higher volumes of unfiltered runoff water from housing, roads and industrial sites. This is exacerbated during major flood events and was clearly demonstrated by the 2002 floods on the Elbe which deposited levels of dioxins, PCBs and mercury from industrial storage areas to the soils of floodplains, in excess of national health thresholds (Umlauf *et al.*, 2005) ..."

"... **Landslides** can also affect mine waste tips and tailings dams and landfills, causing fatalities and contaminating soils, and surface- and ground water ..."

"... Soil contamination can have lasting environmental and socio-economic consequences and be extremely difficult and costly to remediate. Contamination can seriously affect the ability of soil to perform some of its key ecosystem functions. Thresholds for most pollutants exist in most countries but these can vary and often do not consider the multifunctional use of soil (Huber *et al.*, 2008). In extreme situations where contaminant levels exceed a critical threshold, the soil body may be considered as 'functionally dead'. Pollution by heavy metals and organic contaminants is probably the most serious problem as the contamination is practically irreversible. Contamination can affect human health either through direct contact or by ingestion through the food chain."

"**Diffuse contamination** by excess nutrient applications, fertiliser impurities (e.g. cadmium) and biocides is more concentrated in areas under intensive agricultural production and can have significant impacts on soil biology communities (and thus soil functions), groundwater sources, and crop uptake."

"Industrial emissions of persistent organic compounds such as PCBs and dioxins to agricultural soil and their subsequent introduction into the food chain can lead to the development of tumors in people ..."

b) These findings were subsequently used and slightly expanded to compile the section on Soil Contamination in the FAO and ITPS Report "Status of the World's Soil Resources" (**FAO and ITPS 2015**), in the Chapter on Regional Assessment of soil changes in Europe and Eurasia.

Knowledge and data on soil contamination in Europe

The overview of soil contamination assessments above is supplemented with the following non-exhaustive and non-prioritised list of relevant knowledge and data sources in Europe concerning the topic, which were readily available at the time of writing.

European research funding projects

Under various programmes, the EU has funded, and is still funding, many projects strictly related to soil. An overview of more than 200 such projects from Research Framework Programmes since 2004 in FP7, H2020, LIFE, REGIO-funds, BIODIVERSA-funds and INTERREG) reveals no less than 40 projects deal with soil contamination or pollution, in a direct or indirect way.

One of the objectives of the highly relevant EU-funded **2013-2016** project RECARE (Preventing and Remediating Degradation of Soils in Europe through Land Care) (RECARE 2016) was to assess the state of soil degradation and conservation on the EU territory. In the 2016 RECARE-based JRC technical report "Soil threats in Europe - Status, methods, drivers and effects on ecosystem services" (Stolte *et al.* 2016), includes a chapter on soil pollution, covering both point and diffuse contamination. The point contamination section provides an update based on data collected from EEA EIONET NRC Soil Network to update the 2014 EEA Indicator "Progress in the management of Contaminated Sites": "... According to the received data, the total number of identified contaminated sites caused by point pollution is 2.5 million, the estimated number of potentially contaminated sites is 11.7 million. Municipal and industrial wastes contribute most to soil contamination (37%), followed by the industrial / commercial sector (33%). Mineral oil and heavy metals are the main contaminants contributing around 60% to soil contamination. In terms of budget, the management of contaminated sites is estimated to cost around 6 billion Euros (€) annually ..."

Other sections report on the state of soil pollution with respect to: heavy metals, emerging pollutants from industrial/urban sources and agrochemicals". It elaborates also on drivers and pressures of soil contamination, and includes references to European legislation that are directly or indirectly associated to the phenomenon (see also the list of EU Legislation above), such as:

- **EU Sewage sludge Directive** (Directive on the protection of the environment, and in particular of the soil when sewage sludge is used in agriculture – 86/278/EEC)

- **Environmental Liability Directive** (ELD) (Directive 2004/35/CE) on environmental liability with regard to the prevention and remedying of environmental damage) establishing a framework of environmental liability, based on the "polluter-pays" principle, to prevent and remedy environmental damage, and thus generally applicable to soil.

- **Industrial Emission Directive** (Directive 2010/75/EU) establishing a general framework for the control of the main industrial activities. In order to ensure the prevention and control of

pollution (including the one to soil), each installation should operate only if it holds a permit or is registered.

- **Landfill Directive** (Directive 99/31/EC) has as objective to prevent or reduce negative effects on the environment (thus including soil) from the landfilling of waste, by introducing stringent technical requirements for waste and landfills.

- **Waste Incineration Directive** (2000/76/EC) aims at preventing or reducing negative effects on the environment (including soil) caused by the incineration of waste. It sets emission limit values and monitoring requirements for pollutants to air such as dust, NO_x, SO₂, HCl, HF, heavy metals, dioxins and furans.

The RECARE-study elaborates further on what could be the **key indicators** to assess soil contamination (consistent with the key indicators proposed in 2008 by the ENVASSO project (see below)), and which **methods** could be used to **assess its status**. The chapter concludes with an interesting overview of the **effects of soil contamination on various soil functions**: on biomass production in agriculture and forestry, on storing, filtering and transforming capacities for nutrients, substances and water, on acting as carbon and biodiversity pool, and on being a physical and cultural environment for humans and human activities, with reference to human health.

The latest State of the Environment Report ([SOER 2015](#)) by the EEA (EEA 2015) concludes that environmental pollution has grown into a global transboundary problem that affects air, water, soil and ecosystems. It highlights that pollution of water and soil results from diffuse agricultural or urban/industrial sources. While soil contamination is mentioned in relation to the "storage, filtration and transformation capacity as a supporting service of soil", there is little evidence of the impact of soil pollution on human health and ecosystem services.

The topic was further pursued by the EEA-Eionet European Topic Centre on Urban, Land and Soil Systems (**ETC/ULS**). A model approach was used to estimate and compare balances for Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn) in arable soils, with the aim to study the impact of land use policy changes like the proposed revision of the EU Fertiliser Regulation (EU2003-2003) on soil and crop quality at a regional level across the EU. They found accumulation rates of Cd (+0.7 g ha⁻¹ yr⁻¹), Cu (+54 g ha⁻¹ yr⁻¹) and Zn (+202 g ha⁻¹ yr⁻¹) under current balances, whereas only slight accumulation of Pb (19 g ha⁻¹ yr⁻¹). As to be expected, there are pronounced differences for cropland and grassland but also for different soil and climatic conditions. The proposed changes in the EU fertiliser legislation (EU2003/2003) as well as the End of Waste initiative would have considerable impact on the balance of all metals considered. The results will be presented in the SOER2020.

Soil and Health in Europe

The HERACLES research project (2004-2007) (Carlon 2005, 2007) dealing with human and ecological risk assessment for contaminated land in European Member States promoted the development of common references of risk assessment. The project described the state of the art of screening values derivation methods and their application in Europe, it assessed commonalities and main differences among national methods and identified opportunities for harmonisation. Differences among national procedures (geographical and biological, socio-cultural, regulatory, political or scientific led to differences in derivation methods. For the same contaminant, the difference between the lowest and highest national SVs was often more than one order of magnitude. In general, the differences were larger for organic contaminants than for metals and metalloids. A common regulatory framework in Europe would facilitate the promotion of

information exchange and harmonisation of methodologies in risk assessment and risk management of contaminated sites.

Studies

A very informative **2013** report produced for the European Commission (Soil Contamination: Impacts on Human Health - Science for Environment Policy In-Depth Report (EC 2013)) sketches the general problem of the possible health impacts of soil contamination, both locally and diffuse, and adds a number of case studies on the European territory. It covers health issues in relation to metal levels stating that the understanding of how metals in soils lead to human health risks is limited, compared to knowledge of impacts via air or water. The report focuses specifically on health impacts for the four elements identified in the World Health Organization's 'ten leading chemicals of concern' list, namely arsenic, cadmium, lead and mercury. Also dioxins and dioxin-like chemicals (e.g. PCB) are considered, followed by organic pollutants (including pesticides). It also touches on methodological challenges relating to the study of soil science, human biology, sampling and the interactions between large numbers of influencing factors on soil and health (- absolute certainty of cause and effect in the more common cases of low level, long-term exposure to a cocktail of chemicals from soil, and other sources, may not be achievable) and describes the difficulties in measuring soil contamination in relation to health impacts.

Case studies in soil remediation

Two initiatives by the JRC in close collaboration with the EIONET NRC Soil resulted in two publications that describe the restoration of contaminated sites. Remediated sites and brownfields success stories in Europe (RS 2015) presents good examples of remediation of contaminated soils in various contexts and different European countries. Twenty-nine cases illustrate how soil and brownfields remediation along with sustainable land management have become essential for reversing the trend of soil degradation and for ensuring the provision of ecosystem services by soil.

European achievements in soil remediation and brownfield redevelopment (RS 2017) presents seventeen cases from eight European countries and Regions on how polluted sites and brownfields have been remediated illustrating what national, regional or local governments are doing to improve the quality of the environment and the living conditions of their population.

Progress in the Management of Contaminated Sites in Europe.

Since many years the EEA and the JRC, with inputs from European countries through the EIONET NRC Soil, have worked on the quantification of the progress in the management of contaminated sites in Europe. The data are compiled as an EEA indicator "Progress in the management of contaminated site in Europe". The latest published results are from 2014 (JRC 2014). Since then, the indicator content has been revised by an Eionet Ad-hoc working group and, based on a newly designed questionnaire, data were collected to assess the following policy-relevant questions: What is the estimated extent of soil contamination? How much progress has been achieved in the management and control of local soil contamination? Which sectors contribute most to soil contamination? What are the main contaminants affecting soil and groundwater in and around Contaminated Sites? How much money is spent on cleaning up soil contamination? And how much of that money comes from the public budget?

From the collected data, the following conclusions can be made:

- In the present decade, an overall improvement in the management of contaminated sites in Europe has been observed.

- For the total of the 39 surveyed countries, it was estimated that in 2.5 million sites polluting activities have taken place. More than 650 000 sites are registered in national and regional inventories of replying countries; more than 235 000 sites have been remediated.

- Since many countries already have an accurate inventory of sites, efforts are mainly focused on the further investigation and subsequent remediation of sites where polluting activities took/are taking place. Overall, the production sectors contribute more to local soil pollution than the service sectors (60 % compared to 32 %).

- The most frequent contaminants are mineral oils and heavy metals.

- The most commonly used remediation procedure seems to be the ex-situ technique “dig-and-dump”, which implicates the excavation and off-site disposal of contaminated soil.

- From the available data provided by replying countries, the average (per country) overall expenditure to address soil pollution accounts for €4,3 billion where on average more than 32% of total expenses comes from a country's public budget.

Monitoring and indicators

The FP7 ENVASSO Project (Environmental Assessment of Soil for Monitoring –Huber *et al.*, 2008) aimed to define and document a soil monitoring system for implementation in support of a European Soil Framework Directive and contained a chapter addressing soil contamination. A number of possible indicators of soil pollution were proposed to assess diffuse and point pollution. These included:

- Diffuse contamination by heavy metals and other inorganic contaminants

Heavy metal contents in soils

Critical load exceedance by heavy metals

- Diffuse contamination by nutrients and biocides

Area under organic farming

Gross nutrient balance

- Diffuse contamination by persistent organic pollutants

Concentration of persistent organic pollutants

- Diffuse contamination by soil acidifying substances

Topsoil pH

Critical load exceedance by sulphur and nitrogen

- Local contamination by point sources

Progress in the management of contaminated sites.

New settlement area established on previously developed land.

Status of site identification.

In an implementation setting, it was proposed that a focus should be placed on a) heavy metal contents in soils (related to national thresholds); b) diffuse contamination by soil acidification which was judged to be important; possibly it was more of an issue at the time of the report - improvements to industrial emissions have resulted in a reduction of soil acidification across Europe (EEA) which may mean that diffuse contamination by inorganic or organic contaminants may now be more relevant; c) progress in management of contaminated sites.

The ENVASSO report also considered baseline and threshold values for the above indicators. In this context, attention should be drawn to the JRC publication by Carlon (2007) which reviewed and evaluated national procedures towards the harmonisation of soil screening values (SVs) that are used to regulate contaminated sites. This report notes that methods of SVs have both scientific and political bases, that they differ from country to country, and SVs numerical values vary consequently. In relation to the common environmental policies in Europe, this variability has raised concern among both regulators and risk assessors.

Diffuse pollution and LUCAS soil campaigns

Since 2006, Eurostat carries out a LUCAS survey on the land use/land cover situation and changes in the European Union. The survey is conducted every three years for around 270,000 georeferenced points extracted from a regular 2 × 2 km grid across the EU. In 2009, a soil component was added to evaluate selected physical and chemical parameters of topsoil in the EU. The aim of the **LUCAS Soil** Component was to create a harmonised and comparable dataset on topsoil at the EU level for supporting policymaking. Soil samples were collected from approximately 20,000 locations across EU countries, according to the land use, land cover heterogeneity and topography of each country.

The soil samples are analysed by central laboratories. LUCAS topsoil surveys have happened in 2009 and 2015, and the 2018 survey is in preparation.

Analysis of metals in LUCAS Topsoil Survey

The LUCAS Topsoil Survey (Toth *et al.* 2013; Orgiazzi *et al.* 2018) provides an opportunity to monitor certain metal elements in topsoil across EU, using standard methods of sampling and analysis. In recent years, there has been an increased concern for soil contamination due to human activities such as industry, mining and waste management. Therefore, **analysis of metals was included in the LUCAS 2009** Topsoil Survey. Arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), magnesium (Mg), manganese (Mn), phosphorous (P), lead (Pb), vanadium (V) and zinc (Zn) were analysed in about 22,000 topsoil. The **analysis of heavy metals will be repeated again in the LUCAS 2018** Topsoil Survey. On this occasion, the analysis for metals will be repeated only in topsoil samples collected from locations where the concentration of the metal was above a certain threshold value. Analysis of the metal data from 2009 is still in progress.

Analysis of Plant Protection Products (PPPs) in LUCAS Topsoil Survey

In the LUCAS 2015 Topsoil Survey, various PPPs (see table 1) were analysed in 300 topsoil samples collected from agricultural lands from 10 Member States (UK, DK, IT, EL, ES, HU, PL, NL, FR and DE). The crops with highest use of PPPs were selected for the study: cereals, root crops, non-permanent industrial crops, dry pulses and fodder crops, permanent crops and vegetables.

Table 1. List of PPPs analysed in the LUCAS 2015 Topsoil Survey

Group of substances	Category
Dicarboximide	Fungicides
Phthalimide	
Glyphosate and AMPA	Herbicides
Organochlorines: HCHs, DDTs, other OCPs	Insecticides
Organophosphorus	

The study of PPPs will be extended to more substances in the LUCAS 2018 Topsoil Survey. The selection of PPPs to be analysed will be based on the following criteria: (1) most hazardous active substances in the EU, (2) persistence of the substances in the environment (i.e. soil), (3) toxicity for biodiversity and humans, (4) volume used in the EU. Among the PPPs under consideration are neonicotinoids (insecticides) since the proposal for restrictions in their use is under discussion with EU Member States and they have a perceived impact in pollinators. The study of PPPs will focus on topsoil samples located in managed lands (agricultural lands and grasslands).

"Heavy metals in agricultural soils of the European Union with implications for food safety" based on LUCAS topsoil data

This 2017 [publication](#) by Toth *et al.* 2017 states that soil plays a central role in food safety as it determines the possible composition of food and feed at the root of the food chain. The paper claims that the quality of soil resources as defined by their potential impact on human health by propagation of harmful elements through the food chain has been poorly studied in Europe due to the lack of data of adequate detail and reliability. The 2009 LUCAS soil campaign enables a reliable overview of the concentration of metal(loid)s. This article proposes that in some cases (e.g. Hg and Cd) the high concentrations of metal concentrations in soil attributed to human activity can be detected at a regional level. While the majority of EU agricultural land can be considered adequately safe for food production, **an estimated 6.24% or 137 000 km² needs local assessment and potentially remediation action.**

GEMAS (Geochemical Mapping of agricultural and grazing land soil of Europe)

GEMAS was a cooperation project between the EuroGeoSurveys Geochemistry Expert Group and Eurometaux, that sampled, collected and analysed 2 211 samples of agricultural soil (Ap-horizon, 0-20 cm, regularly ploughed fields), and 2 118 samples from land under permanent grass cover (grazing land soil, 0-10 cm) across Europe. It delivered in 2015 data on metals in the soil of agricultural and grazing land; in addition, soil properties, known to influence the bioavailability and toxicity of metals (and other elements), were determined. An interesting observation from the study is that "the impact of **diffuse contamination** on the quality of European agricultural soil is vastly overestimated at present" and that "Contamination from anthropogenic sources plays an important role at a much more local scale (e.g., the impact of cities like London and Paris on the mercury concentrations in soil), but remains undiscernible at the continental scale. Another observation related to health says that for some trace elements such as the metals cobalt (Co), copper (Cu) and zinc (Zn), for which contamination is a much discussed issue, deficiency of these elements in soil may be a much larger issue warranting attention. Very few soil samples seem to

reach concentrations where toxicity may become a concern, while for more than 10% of the samples, there is such a low concentration that deficiency is an issue for optimum plant and animal health and productivity.

Substances of concern

1. Pesticide risk in Europe

At EU-level, the European Statistical Office (Eurostat) manages an agri-environmental indicator named pesticide risk (EUROSTAT 2017a) which should be based on an index of risk of damage from pesticide toxicity and exposure. The conceptual and modelling framework underpinning this indicator needs still to be developed. It refers to aquatic and **soil ecological risk**, and builds on the concepts developed in the HAIR (2004-2007) and FOOTPRINT (2006-2010) EU-funded projects (HAIR 2007; FOOTPRINT 2010). It aims to provide a synthetic representation of pesticide risk in Europe using the limited information available; it is computed as a weighted sum of exposure-toxicity ratios for all chemical classes used in Europe, under conservative assumptions. The approach can be extended to human health risk as well as other endpoints, in a straightforward way.

The EEA Annual Indicator Report Series (AIRS) studies the impact of pesticide sales. The Seventh Environment Action Programme (7th EAP) sets the objective that by 2020 the use of plant protection products does not have any harmful effects on human health or unacceptable influence on the environment. The AIRS states that the total reported sales of pesticides in the EU stayed constant between 2011 and 2015. However, it can be assumed that substitution by new compounds and the concentration and intensification of cropland management (e.g. no-till), negatively affects the balance of pollutant input from plant protection measures.

2. Pollution by Phosphorous in EU

Since the early 1940s, European agriculture has intensified greatly resulting in large inputs of nitrogen (N) and phosphorus (P) to soil by fertilizers and manure. This has not only led to an increase in crop growth and soil fertility in terms of elevated N and P contents, but also an imbalance in N and P budgets leading to surpluses. Surpluses of fertilizers and manure induced an elevated leaching of N and P, which resulted in eutrophication of freshwater and coastal ecosystems in parts of Europe.

One of Eurostat's agri-environmental indicators is risk of pollution by phosphorous (EUROSTAT 2017b). The indicator provides an indication of the **potential surplus of phosphorus (P) on agricultural land**, with as sub-indicator **Vulnerability to phosphorus leaching/run-off** (still to be developed). The website provides of an overview of recent data, complemented by all information on definitions, measurement methods and context needed to interpret them correctly.

There are a number of **important international conventions** in relation to phosphorus use in agriculture; these include UNEP/MAP (United Nations Environment Programme/Mediterranean Action Plan), CBD (Convention on Biological Diversity) and OSPAR (Oslo & Paris Convention to prevent pollution). Such international treaties often give an impetus to harmonise standards amongst all Member States of the European Union. Despite the significant off-site impact that **diffuse contamination of phosphorus** from agricultural land poses, there is no specific legislation that is directly concerned with the use of phosphorus in agriculture at European level. There is a lack of appropriate institutional arrangements specific to the environmental pollution of phosphorus. Aspects of the phosphorus problem are however

integrated in several policy areas and related legal instruments at European level. Eurostat makes an overview of existing regulations and directives dealing with farm-level nutrients (and phosphorus) use and production at international and European level.

3. EEA: Agriculture nitrogen balance

The 2010 EEA Indicator 'Gross nitrogen balance' estimates the potential surplus of nitrogen on agricultural land. This is done by calculating the balance between nitrogen added to an agricultural system (nitrogen input can be taken as a proxy indicator for the general intensity of agricultural management) and nitrogen removed from the system per hectare of agricultural land. The indicator accounts for all inputs to and outputs from the farm, and therefore includes nitrogen input. A positive balance (or surplus) reflects inputs that are in excess of crop and forage needs. It can result in **diffuse pollution** through the loss of nutrients to water bodies, decreasing water quality while promoting eutrophication. Surplus nitrogen can also be lost to air as ammonia and other greenhouse gases.

The European Topic Center on Urban, Land and Soil Systems (ETC/ULS) has studied critical nitrogen inputs and their exceedances by current inputs in EU. Apart from crop yield increase, increased nitrogen (N) fertilizer and manure inputs have caused various unwanted side-effects including increased ammonia (NH₃) emissions and elevated runoff of N, causing nutrient enrichment of terrestrial and aquatic ecosystems. Calculated current (year 2010) N inputs at EU-27 level exceed critical N inputs in view of either the protection of terrestrial or aquatic ecosystems by approximately 45%. The simultaneous protection of both systems even requires more than 50% reduction in N inputs.

4. Emerging contaminants

With increasing frequency, countries and organisations are faced with chemicals that have not been considered as 'contaminants' before. Some of these chemicals could pose potential risks to humans and the environment. These are referred to as 'emerging contaminants'. Characteristically, little is known about the occurrence of emerging contaminants, the actual hazard that they pose and the approach to formulate appropriate policy and legislation. Examples of emerging contaminants include disinfection by-products, pharmaceutical and personal care products, persistent organic chemicals, and mercury, as well as their degradation products. To properly identify how to deal with emerging contaminants knowledge, more awareness and understanding is necessary.

Commissioned by the Ministry of Infrastructure and Environment (the Netherlands) and the Public Waste Agency of Flanders (Belgium), an **inventory** (EMC 2016) on awareness and policy on emerging contaminants in Europe was developed. This inventory aimed to collect available knowledge and experience related to legislation, governance and policy. The focus is on the presence and the curative policy on emerging contaminants that are already present in the soil, groundwater and sediments. The website <http://www.emergingcontaminants.eu/index.php/> aims to share information about the subject and the inventory. A questionnaire has been circulated among the members of the **Common Forum** as well as related networks such as SedNet and NICOLE.

A very interesting extract from this work: "The group of emerging contaminants (**ec**) is very diverse, for example in terms of toxicity, behaviour and waste water treatment or remediation techniques. During the past decade, more than **2 100 scientific studies** have shown that this group of substances poses a potential risk to humans, plants and/or animals. There is, however, a lack of knowledge about the factual situation and risks in the soil, sediment and groundwater

system. Also, the policy approaches in different countries are not well known. Hence, the scale of the environmental problem caused by these contaminants in soil, groundwater and sediments is unclear. There is a lot of scientific information regarding the chemistry, toxicity and fate of emerging pollutants. Several international scientific networks, for example the NORMAN Network (NORMAN 2018), summarised and interpreted all this information which is shared this on their website. The knowledge from these networks could be used to prioritise data collection and environmental monitoring. The political prioritization of the prioritised substances, based on their toxicity and environmental hazards, is defined in the Stockholm Convention on Persistent Organic Pollutants (POPs). For all other emerging pollutants it applies that the lack of understanding, the effects and the lack of factual data in soil, groundwater and sediment are by far the main obstacle to develop a practical approach. Generally, the soil and groundwater system responds slowly. Therefore the effects of emerging pollutants will be notable in the long run ..."

5. Soil acidification

Soil acidification has been a major soil threat across Europe, as introduced for instance in the first EEA State of the environment report (the Dobbris Assessment - 1995) (EEA Dobbris 1995). This report contains an entire chapter where **soil contamination** issues are addressed in a European context. In addition to **soil acidification**, the causes, magnitude, impacts and possible remedies of soil pollution by metals, pesticides and other organic contaminants, nitrates and phosphorous, and (industrially) contaminated land (including contaminated sites), are described, with reference to the European context. Soil contamination with artificial radionuclides is also described.

As a contribution to the quantification of the risk of soil acidification across Europe, the JRC created, through Digital Soil Mapping techniques, a map of estimated soil pH values across Europe (Soil pH in Europe)(Reuter et al. 2008) from a compilation of 12,333 soil pH measurements from 11 different sources, and using a geo-statistical framework based on Regression-Kriging. The result might serve as a proxy to the sensitivity of soils to the process of acidification. Any further assessment of sensitivity of soils to acidification should take into account not only the pH but also the soil organic matter content, soil texture, Al and Fe contents as well as the sulphate sorption capacity of soils.

Atmospheric emissions of acidifying substances such as sulphur dioxide (SO₂) and nitrogen oxides (NO_x), mainly from the burning of fossil fuels, can be transported over thousands of kilometers, when they undergo chemical conversion into acids (sulphuric and nitric). The primary pollutants sulphur dioxide, nitrogen dioxide and ammonia (NH₃), together with their reaction products, lead after their deposition to changes in the chemical composition of the soil. This process interferes with ecosystems, leading to what is termed 'acidification'. The decline of forests in Central and Eastern Europe and the many 'dead' lakes in Scandinavia are examples of damage which are, in part, due to acidification. Modern forestry and agriculture contribute to but can also be affected by acidification. By the end of the 1970s, acidification was widely recognised as a major threat to the environment. Due to international agreements with explicit objectives for reducing emissions of pollutants leading to acidification, emissions of the acidifying pollutants, nitrogen oxides (NO_x), sulphur oxides (SO_x) and ammonia (NH₃), have decreased significantly in most of the individual EEA member countries between 1990 and 2011². Emissions of SO_x have decreased by 74%, NO_x by 44% and NH₃ by 25% since 1990 within the EEA-33. See maps at

² <https://www.eea.europa.eu/data-and-maps/indicators/emissions-of-acidifying-substances-version-2/assessment-4>

http://eusoils.jrc.ec.europa.eu/SOER2010/images/Map2-7_SO111_CSI005_Acid1980-2010.png

Acidification has also intensively investigated in European forest monitoring (ICP Forests Level I and the BioSoil demonstration project as one of the studies supporting Article 6 of Regulation (EC) No. 2152/2003 (Forest Focus). Investigating more than 5,000 plots across Europe, on average there is a mean pH decrease of 0.03 pH units over a monitoring period of 10 to 15 years. The pH in extremely acid forest soils (pH < 4.0) 'recovered' (and base saturation increased) but further decreased when pH > 4.0 (base saturation decreased in forest soils with BS > 20%).

6. Degradation of soils by pesticide pollution

Pesticide use and processes

Agro industrial production systems have globally strongly increased food production in the last decades. Pesticide use simultaneously strongly increased worldwide with strong differences of average application rates per country (Plumer 2013).

Actually, more than 488 active substances for pest and weed control are present in more than 2000 pesticides on the European market and 37 active substances pending (Reg.(EC) No 1107/2009), worldwide the number is much higher as many substances, forbidden in Europe are still on the international market available such as the herbicides Paraquat, Deiquat, Atrazin, Simazin etc. .

Pesticides enter into the soil as a result of plant protection measures (weed control and pest control). Although the persistence of pesticides in the last decades strongly decreased, a number of studies describe the occurrence of mixtures of (persistent) pesticides in soils as a result of long-term annual applications (e.g., Organochlorines like DDT and its metabolites, forbidden in 1973 in Europe, in the 1990 in most other countries) (Oldal *et al.*, 2006; Ferencz and Balog, 2010) or Glyphosate and its metabolite AMPA (Guo *et al.*, 2014). The persistence, distribution and transport of pesticides in soil are governed by physico-chemical and biological processes. The degradation of pesticides in soil can be partial (resulting in metabolite accumulation) or total (total mineralization of pesticides). Sorption of pesticides to soil particles (organic matter, clay, Fe-oxides) reduces pesticide mobility and the risk of water pollution. Nevertheless, by reducing pesticides bioavailability, the microbial degradation of adsorbed pesticides is slower.

Status on degradation of soils by pesticide pollution

Several studies on food safety reported mixtures of pesticide residues in food and even in mother milk. The site effects of intensive pesticide application on water quality is well studied, and international monitoring programs of water quality show that pesticide and antibiotics are present in surface and groundwater bodies with changing concentrations over the years.

However, soil pollution with pesticides is a not well studied phenomenon worldwide and so far only few (inter)national monitoring programs exist with respect to pollutants in agricultural soils (Drevno *et al.*, 2016; Stolte *et al.*, 2016, Silva *et al.* 2017).

For Europe maps are available for many soil threats (Panos *et al.* 2012), and a first assessment was made for Glyphosate residues in soils (Silva *et al.* 2017). There is some knowledge in single publications that indicate soil pollution with pesticides even decades after they are forbidden.

Trying to assess the severity of pesticide presence in agricultural soils on a global scale, a recent study was conducted on pesticide residues in agricultural soils from 11 selected European countries (Portugal, Spain, France, Germany, United Kingdom, Italy, Netherlands, Denmark, Hungary, Poland and Greece), based on LUCAS 2015 soil samples. These data will be published in short term (Silva *et al.* in prep.). It is already possible to conclude that:

More than 80% of the 317 European soils tested, all from agricultural areas, present one or multiple pesticide residues; soils from cereals cultivations and from permanent crops are the most contaminated while soils from vegetable productions are the less. Multiple residues are present in 58% of the samples. Regarding the results per country, Denmark has the highest percentage of contaminated soil samples (the majority from areas of cereals production) while the less polluted soils seem to be in Italy.

The world most used herbicide Glyphosate and its main metabolite AMPA are the most common compounds in the tested soils, AMPA present in 42%, Glyphosate in 21%, partly in high concentrations (>1 mg kg⁻¹). In Southern Europe, glyphosate is the predominant form in soils while in NW Europe, AMPA has higher concentrations (Silva *et al.* 2017).

Effects of pesticides on soil biota

Pesticide residues in soils affect soil fauna and flora at different scales (as individuals, population and community) in short and long term, therefore affecting the soil services that soil biota provides i.e. decay of pesticides, decomposition, infiltration, organic matter decomposition (Pélosi, 2014). Herbicides generally have less negative effects on soil organisms than insecticides and fungicides, but they significantly reduce the plant biodiversity. Insecticides have a greater direct effect on soil organisms, and also reduce springtail density and earthworm reproduction. Carbamate insecticides significantly reduce enzyme activity in earthworms. Persistent compounds like DDT and lindane cause long-term reduced microbial activity. Fungicides have even greater effects on soil organisms than herbicides or insecticides, especially copper based fungicides, which cause long-term reductions of earthworm populations and microbial activity since copper accumulates in the soils. Little is known about the effects of pesticide formulations on soil biodiversity, however some adjuvants seem to increase the toxic effect of the active ingredient (Bünemann *et al.* 2006). Synergistic effects between mixtures of pesticides are rarely studied.

Actually, no maximum tolerable values in soils exist in legislations for approved pesticides in Europe. Only a few threshold values are included in some national legislation with respect to forbidden persistent pesticides such as DDTs, Carbuforan etc.

Transport of pesticides to the environment

It is known that pesticides present in the soil can be transported with soil erosion into the water bodies and affect there aquatic life, and can also be transported by wind erosion and so directly affect human health by inhalation. Actually, transport of pesticides by leaching to the groundwater (FOCUS), by drift (FOCUS) and by runoff to surface water bodies is considered in European models applied for environmental risk assessment (FOCUS). While groundwater and surface water quality is continuously monitored (e.g. Water Framework Directive), particulate transport of pesticides adsorbed to the soil particles and transported with the eroded soil to the surface water bodies are only roughly estimated in the FOCUS models. For regions prone to soil erosion pesticide content in the upper layer of the soil is relevant and the particulate transport can then be predicted by new developed models such as Lisem-PestPost or should be monitored in the field.

Silva *et al.* (2017) made a first approach to estimate glyphosate and AMPA export by soil erosion on European scale.

Pesticide export by wind erosion is neither monitored nor predicted in Europe. Only very scattered information is available indicating that Glyphosate can be concentrated in dust particles < 10 µm (Bento *et al.* 2017) and can reach nearly 10 mg kg⁻¹ for instance in a field study in the Netherlands. The direct human health risk by inhalation is unknown.

Contaminated Land/Soil networks

1. Common Forum

The Common Forum on Contaminated Land (CF 2018), initiated in 1994, is a network of policy makers, regulators and technical advisors from Environment Authorities in the EU Member States and European Free Trade Association countries dealing with the topic of **contaminated land**. It aims to be a platform for the exchange of knowledge and experience, for initiating and following-up of international projects among members. It is also a discussion platform on policy, research, technical and managerial concepts of contaminated land, and it offers an **exchange of expertise** to the other stakeholders, in particular via collaboration with existing European and international networks.

2. NICOLE

NICOLE (Network for Industrially Co-ordinated Sustainable Land Management in Europe) (NICOLE 2018) is a forum promoting co-operation between industry, academia and service providers on the development and application of sustainable technologies for the remediation of contaminated soils. Its overall objective is to proactively enable **European industry** to identify, assess and manage industrially contaminated land efficiently, cost-effectively, and within a framework of sustainability. It focuses its activities in three main areas: the provision of a European forum for the dissemination and exchange of good practice, practical and scientific knowledge and ideas to manage contaminated land in a sustainable way; the stimulation of coordinated, interdisciplinary projects on collaborative, problem oriented research and knowledge transfer to address identified needs; and the development of new relationships and strengthening of existing relationships with other networks.

Common Forum initiative: Survey for the collection information on diffuse pollution

At the moment of writing, a survey (through a questionnaire among the Common Forum members) is taking place that calls for information regarding diffuse soil pollution **to compare national and regional concepts as well as practical approaches on a European level**. A draft report of the results of the exercise will be presented in the autumn of 2018.

The aim of the report is to provide an overview on how diffuse soil pollution is managed in practice in different countries. “Management” includes tasks such as setting up an inventory, investigations, risk assessments and remediation and the establishment of recommendations on land-use (restrictions). Questions that will need to be answered include:

Is diffuse soil pollution/contamination managed differently from punctual pollution/contamination? Are different approaches applied? How is the boundary defined? Do limit values/thresholds exist to evaluate soil diffuse pollution/contamination? If yes: for which pollutants, for what type of soil use, what are the necessary measures in case values/thresholds are exceeded; on what is the establishment of such values based? What knowledge regarding soil

diffuse pollution/contamination do you have? Do you distinguish between geogenic pollution and background pollution?

Conclusions and way forward

This report is an attempt to provide an initial overview of soil contamination in Europe.

There is an extensive body of knowledge in Europe on the potential impacts of polluting substances within soil on human health and the provision of ecosystem services.

Many countries have accurate inventories of polluted sites and efforts are mainly focused on further investigation and subsequent remediation of locations where polluting activities took or are taking place. Overall, the production sectors contribute more to local soil pollution than the service sectors (60% compared to 32%). The most frequent contaminants are mineral oils and metals.

Data from a broad grouping of European countries indicates that there has been an overall improvement in the management of contaminated sites. More than 650 000 sites are registered in national and regional inventories of replying countries while more than 235 000 sites have been remediated. The most commonly used remediation procedure seems to be the off-site disposal of contaminated soil.

From the available data provided by replying countries, the average (per country) overall expenditure to address soil pollution accounts for €4,3 billion where generally more than 32% of total expenses comes from a country's public budget.

There is a well-developed approach to assess progress in the remediation of contaminated sites although there is no European consensus on common definitions for 'contaminated site' and 'potentially contaminated site' which leads to uncertainties in assessing the overall situation. Some countries may only report major industrial facilities while others may regard landfill sites and underground fuel storage facilities contaminated sites. The development of common terminology would be a great asset in this respect.

Data on diffuse pollution across Europe is more heterogeneous and generally lacking due to a lack of harmonised assessments across countries. For forests, the distribution and change of heavy metals in soils has been well-investigated based on the ICP Forests and Biosoil inventories. For cropland and grassland, the broad spatial distribution of microelements has been mapped via in two geochemical inventories, however, trends cannot be derived there, and the spatial resolution is low. The most important current tool for investigating state and trend of soil pollutants is the LUCAS Soil Survey; the 2018 sampling campaign will aim to produce a first baseline assessment of 'substances of concern' for the EU.

A fuller assessment involving stakeholders such as the ESP national focal points and partners, together with members of the EIONET NRC Soil network (EEA-39) and other networks, will supplement and extend the findings at European level with national or other level information.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Regional status of soil pollution: Colombia

Gobierno de la República de Colombia¹

¹ Ana Maria Rivero Santos, Ministerio de Relaciones Exteriores, Punto Focal Político ante la Alianza Mundial por el Suelo

Resumen

La Política para la Gestión Sostenible del Suelo (PGSS) expedida por el Ministerio de Ambiente y Desarrollo Sostenible en el año 2017 es el instrumento de política pública de Colombia que aborda la contaminación de suelos como una problemática de interés para el país, más allá de los temas estrictamente ambientales. Esta identificó, entre otros elementos, la necesidad de avanzar en la formulación y puesta en marcha de una estrategia de generación y gestión de la información sobre la calidad del suelo y de avanzar en investigación de suelos en temas relacionados con la evaluación de su contaminación, las estrategias de recuperación y rehabilitación, la evaluación de los impactos de su degradación sobre los ecosistemas y la calidad de vida de las comunidades, entre otros aspectos.

Palabras clave: Política para la Gestión del Suelo, calidad de suelo, evaluación de la contaminación, efectos en los ecosistemas, monitoreo de degradación.

Introducción, alcance y objetivos

El objetivo de la Política para la gestión sostenible del suelo es promover el manejo sostenible del suelo en Colombia, en un contexto en el que confluyan la conservación de la biodiversidad, el agua y el aire, el ordenamiento del territorio y la gestión de riesgo, contribuyendo al desarrollo sostenible y al bienestar de los colombianos.

Los objetivos específicos de la política son:

- Generar acciones de preservación, restauración y uso sostenible del suelo, con el fin de mantener en el tiempo sus funciones y la capacidad de sustento de los ecosistemas.
- Fortalecer la institucionalidad y la articulación interinstitucional e intersectorial para la toma de decisiones relacionadas con la gestión sostenible del suelo.
- Fortalecer los instrumentos de planificación ambiental y sectorial para la gestión sostenible del suelo.
- Promover la investigación, innovación y transferencia de tecnología para el conocimiento de los suelos, su preservación, restauración, uso y manejo sostenible.
- Fortalecer políticas, normas e instrumentos relacionados con la gestión sostenible del suelo.
- Impulsar procesos de educación, capacitación y divulgación que fortalezcan la participación social y la gestión ambiental para la conservación y uso sostenible del suelo.
- Adelantar procesos de monitoreo y seguimiento a la calidad de los suelos que faciliten la toma de decisiones para su gestión sostenible.

La PGSS identifica a la contaminación como uno de los procesos de degradación más relevantes en Colombia, junto a la erosión, el sellamiento de suelos, la pérdida de la materia orgánica, la salinización, la compactación y la desertificación.

Asimismo, la PGSS identifica como uno de los servicios ecosistémicos asociados al suelo la depuración de la contaminación, junto a la producción de alimentos; el filtrado e intercambio de gases; la regulación climática e hídrica; el reciclaje de nutrientes; el filtrado de agua; el soporte para industria, infraestructura y turismo; entre otros (Blum, 2005; Bone et ál., 2010; Millennium Ecosystem Assessment, 2005).

La PGSS reconoce que la contaminación, entre otros elementos como la pérdida de nutrientes, su desbalance en el suelo y los cambios indeseables en el pH, está asociada a la degradación química del suelo. De la misma manera, afirma que los cambios indeseables en el pH del suelo reducen la capacidad de éste para soportar la vegetación y tienen efectos negativos para la biota edáfica; en el caso de la acidificación (reducción del pH) elementos como el aluminio (Al) pueden llegar a niveles tóxicos; por su parte, la acumulación de metales pesados y el aumento del pH por sales, debido al uso excesivo de fertilizantes, al riego inadecuado y al mal drenaje, conllevan a la afectación de la biodiversidad del suelo. Por otra parte, el inadecuado manejo de residuos orgánicos provenientes de la producción animal (ganadería, porcicultura, avicultura, entre otros) o de rellenos sanitarios, puede generar problemas de contaminación de suelos y provocar emisiones de gas metano o CO₂ (FAO, 2007), incrementando el efecto invernadero.

Sobre el particular, la PGSS afirma que la contaminación de los suelos se produce por el desarrollo de actividades industriales, mineras y urbanas insostenibles, que generan residuos sólidos, líquidos o gaseosos destacándose particularmente los residuos o desechos peligrosos que afectan la biota del suelo, las aguas subterráneas, la inocuidad de los alimentos y por ende la salud humana. Otras actividades que pueden generar contaminación de suelos son: la disposición de residuos sólidos en rellenos sanitarios y escombreras, la construcción de bóvedas en cementerios y el vertimiento de residuos líquidos.

De acuerdo a lo anterior, la PGSS pretende abordar la reducción de riesgo de contaminación de suelos y de aguas superficiales y subterráneas, que ocurre por derrames de petróleo o debido al uso de sustancias contaminantes en las explotaciones mineras. Igualmente, se busca reducir los impactos ambientales indeseables que se generan en la construcción de hidroeléctricas, puesto que al desviar cauces se afecta negativamente la biodiversidad y se incrementa el riesgo de erosión y sequía en diferentes zonas.

La PGSS de igual manera identifica el uso inadecuado e intensivo de plaguicidas y otros agroquímicos, como desencadenante contaminación de suelos agrícolas aportando metales pesados (p. ej.: fertilizantes fosforados o ciertos plaguicidas) (Universidad Nacional, 2009) y generando desbalance de nutrientes en el suelo.

Adicionalmente, la PGSS tiene en cuenta la contaminación biológica de suelos por microorganismos, nematodos y otras especies, que pueden afectar las plantas cultivadas y el ecosistema, reduciendo la capacidad de uso del suelo, su productividad y valor económico.

La contaminación del suelo por actividades industriales, agropecuarias, mineras y de extracción de hidrocarburos, de acuerdo a la PGSS, afecta las propiedades químicas, físicas y biológicas del mismo y genera acumulación de sustancias químicas y microorganismos que pueden migrar a las fuentes de agua y a los cultivos y afectar la salud de las personas y animales por consumo de agua y alimentos con altos contenidos de metales pesados, plaguicidas, microorganismos patógenos, entre otros.

Otras actividades identificadas por la PGSS como generadoras de contaminación de suelos son: las actividades turísticas, que desarrolladas de forma insostenible ocasionan problemas de contaminación y el sellamiento de los suelos, por vertimientos y residuos, pérdida de la cobertura vegetal, conflictos de uso del suelo, deterioro de ecosistemas, entre otros aspectos; las actividades portuarias, que pueden conllevar impactos en el suelo como la pérdida de la capa vegetal, erosión y compactación, cambios en los patrones de drenaje y contaminación por inadecuados manejo y disposición de combustibles y residuos sólidos; la expansión urbana, entre otras.

La Política además identificó uno de los factores limitantes para la aplicación de cualquier método de monitoreo y seguimiento a la calidad del suelo y su afectación por la contaminación, que es la disponibilidad y calidad de los datos existentes, por lo cual, y en consonancia con el objetivo específico N° 7, se requiere una estrategia de generación de información básica. La PGSS aborda estas dificultades a través de dos estrategias: Monitoreo y seguimiento a la calidad del suelo e Investigación e Innovación y Transferencia de tecnología, las cuales proponen la formulación y puesta en marcha de un programa de monitoreo y seguimiento que involucre la generación de acuerdos o espacios interinstitucionales y el fortalecimiento de la capacidad institucional.

La PGSS reconoce que la contaminación originada por el uso inadecuado de agroquímicos y otras sustancias provenientes de la industria o minería, está relacionada con la situación social y política de Colombia durante los últimos años, la inequidad, la pobreza, los enfrentamientos armados, el narcotráfico y la explotación ilícita de minerales, así como las debilidades en los sistemas de educación, de investigación y desarrollo tecnológico, que han dificultado extraordinariamente el manejo adecuado de los suelos.

Finalmente, la PGSS asume la importancia de la intersectorialidad en la identificación e implementación de soluciones para el abordaje de los problemas asociados con la contaminación de los suelos, con el acompañamiento y apoyo de actores internacionales como PNUMA, FAO y la Convención de Naciones Unidas de Lucha Contra la Desertificación. Es de resaltar que uno de los temas centrales en la agenda del PNUMA para el posconflicto en Colombia consiste en un proyecto de soluciones ambientales para la construcción de la paz y la resiliencia, que incluye acciones dirigidas a remediar la contaminación por metales pesados, particularmente mercurio, en zonas afectadas por el conflicto armado en el país.

Lo anterior permite evidenciar la importancia del tema de Contaminación de Suelos en Colombia en la actualidad y de cara al posconflicto, y el avance que representa la elaboración y puesta en práctica de la Política para la Gestión Sostenible del Suelo en el país. Colombia se encuentra en la búsqueda de alianzas estratégicas que permitan al país avanzar en el desarrollo de sus objetivos y estrategias, con el fin de fortalecer y avanzar en el conocimiento del estado del suelo lo cual soportará la toma de decisiones acertadas que conlleven a una gestión sostenible de este recurso.

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Regional status of soil pollution: Islands of the Pacific

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Introduction, scope and main objectives

The islands of the Pacific are a living, breathing and embodiment of paradise on earth and attracted people from all walks of life to visit our shores. This promotional image is hiding the vulnerability of the Pacific Island countries to climate change and the extent of environmental pollution these islands are facing. *Fiji Times News Paper reported in 2016 that our land is a living nightmare and is being polluted and abused constantly and we are unable to calculate the damage incurred. Such activities are conducted citing development, and the same affects the land drastically.* The history of ecological change in the Pacific Islands is one of continued environmental degradation.

The Pacific Region consists of Australia, New Zealand and 22 Pacific Islands. These islands can be classified into 4 geological categories: (i) continental islands such as Papua New Guinea, New Caledonia, and Solomon Islands are made from rocks similar to nearby continents. These islands can have large areas of natural resources such as minerals and forests; (ii) volcanic islands such as East New Britain in Papua New Guinea and Fiji are made from volcanic materials forced up through weaknesses in the ocean floor. These islands are generally large and covered with tropical forests; (iii) uplifted coral atolls such as Tonga, Niue and some of the islands of Cook Islands showered with volcanic materials; and (iv) low-lying coral atolls such as Tuvalu and Kiribati formed by coral growing on the remnants of volcanic islands. Due to their low elevations, these types of islands are among the most vulnerable on the earth to impacts of climate change.

Studies and reviews of the region have identified domestic sewage-discharges, solid waste from domestic, industrial, and construction activities, fertilizer use, sediments, and increasingly toxic wastes from industrial, agricultural, and domestic sources as the significant land-based sources of pollution. Domestic wastes dominate the waste stream from land-based sources. Nevertheless, the relatively small quantities of hazardous and toxic materials (e.g. persistent organic pollutants [POPs] and heavy metals) are of critical concern based on known and potential effects on the marine environment.

This paper tries to paint the picture of soil pollution in the islands of the Pacific from the limited information available in literature and personal discussions with regional experts in soil science.

Keywords: [Pacific Islands, Soil Pollution, Contaminated sites]

Soils of the Pacific Islands

As reported by Morrison, Gangaiya and Koshy (1996), a review of the information available on the South Pacific island soils (Morrison, 1982; Leslie, 1984) shows that Inceptisols (Soil Survey Staff, 1975; 1994) are the most abundant, with significant areas of Mollisols, Alfisols, Ultisols, Oxisols, Andisols and Entisols. In the low atolls, Entisols are dominant where they rest on coral sand, rubble or reef limestone. Andosols, formed from young volcanic ash, have been identified in northern Vanuatu, in Santa Cruz in the Solomon Islands, in Taveuni, Koro and Rotuma in the Fiji group, and in Upolu and Savai'i in Western Samoa (Morrison *et al.*, 1989). Mollisols of Tonga if reclassified will become Andosols. These soils are important agricultural soils in the region and have very high

P-fixation capacity. Vertisols and Histosols are found in limited areas, determined by parent material, geomorphology and climate, the latter particularly have considerable agricultural significance. Spodosols are rare with, to date, only one Spodosol series being confirmed in Fiji and one in New Caledonia. No Aridisols have been identified in this region.

The region is generally wet, with most soils having udic soil moisture regimes (Soil Survey Staff, 1975). On the windward coasts of the larger islands the soil moisture regimes may even be perudic, with ustic soils usually occurring only in the rain shadow areas. In much of the region, significant leaching occurs, with the result that any contaminants added to the soil surface are subject to potential movement by water. Soil temperature regimes are generally isohyperthermic (average temperature $\geq 22^{\circ}\text{C}$) or isothermic (average temperature $15\text{-}22^{\circ}\text{C}$), which means that solubilities and reaction rates are among the highest found in soils.

The most common minerals found in South Pacific soils are kaolinites, iron and aluminium oxyhydroxides, smectites, and carbonates; although on some of the smallest islands such as Niue and Nauru the soils may be dominated by phosphate minerals. The Andosols are dominated by allophane, imogolite and ferrihydrite. Mineralogy and clay content are useful indicators of the behaviour of contaminants in soils. In the larger islands many of the soils on the older rolling landscapes have significant ($>35\%$) clay contents with high surface areas and contaminant adsorption capacities.

Most of the soils of the South Pacific island countries can be termed low in fertility (Asghar *et al.*, 1988; Craswell, 1989). As most parent materials in the region are deficient in P and potassium, the soils developed from these also show similar deficiencies. The organic matter levels of most soils tend to be relatively high but this often rapidly declines with cultivation. The coralline soils of the atoll islands are extremely poor in most plant nutrients and as a result, the local flora is limited.

Contaminated soils

Soil contamination in the Pacific Islands is an important problem mainly in relation to impurities in agricultural chemicals (fertilizer and pesticides), mining, waste disposal, and nuclear testing. Reviews

of the history of soil contamination in the region are provided by Naidu *et al.* (1996), Singh, Levett and Kumar, (1996) and Morrison, Gangaiya and Koshy, (1996). Burns *et al.* (2000) in their survey of waste and obsolete chemicals and contaminated sites in 14 Pacific Islands reported surveying about 100 contaminated sites. These studies and a survey by UNEP and SPREP of pollutant sources and activities affecting the marine, coastal, and freshwater environment in the Pacific Region probably started the movement to manage waste in the Pacific Islands.

Agrochemicals

Fertilizers

The use of fertilizers has become necessary to sustain food production for export and for food security in the Pacific Islands. The increase in exports in the countries is matched by an abrupt increase in the import and usage of agricultural chemicals. Fig 1 below shows that some countries the fertilizer use is above world average.

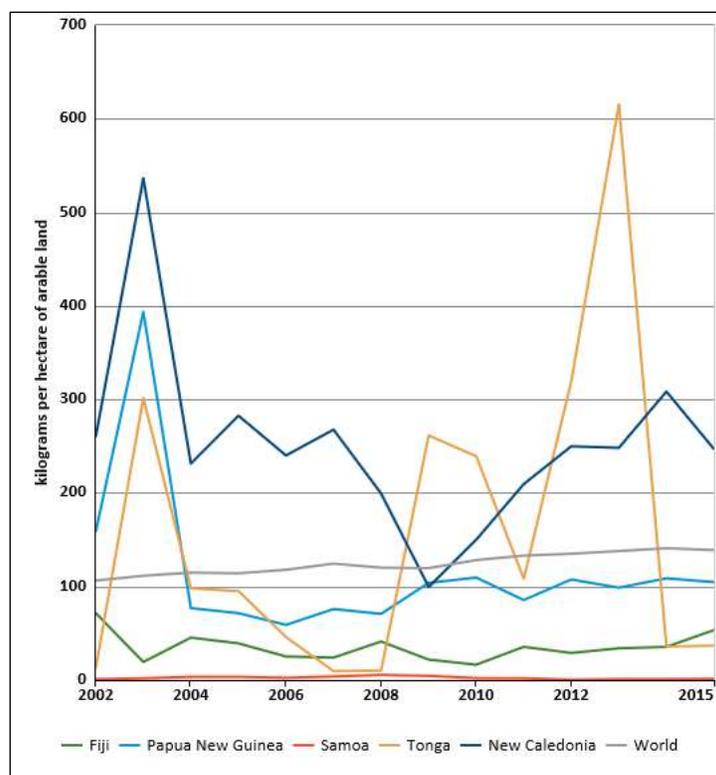


Figure 1. Fertilizer use some of the Pacific Island countries. (Data from Knoema World Development Indicators)

The real concerns are some of this fertilizer getting to our ground waters and contaminating them, getting to surface water and causing algal bloom, and some impurities in fertilizers and soil amendments such as lime and gypsum can include cadmium, fluorine, lead and mercury and contaminate the soils. In some of the Pacific Islands local seismic and volcanic history has resulted in presence of high concentrations of some metals (Morrison *et al.*, 1996). They include Cu and Zn in Fiji (Leggo, 1977; Rugless, 1983) where Cu concentration in the soil is over 3000mg/kg. On Nauru the total Cd averaged 80 – 120 mg/kg which is well over global average. This Cd content led to production of high Cd phosphate fertilizers with Cd contents averaging 243mg/kg P₂O₅. This was later found responsible for the high levels of Cd in soils where they were used in Australia and New Zealand.

Concentrations of nitrates in the drainage water leaving the root zone of the squash measured by Van der Velde *et al.* (2004) in squash production in Tonga at 50ppm approximately five times the WHO limit for drinking water quality of 11.5 ppm N-NO₃.

Pesticides

Many of the more harmful pesticides and herbicides are now banned or their use tightly controlled in the islands but still some of the banned ones get to the farmers and are being use. In a survey of 14 countries not including PNG by Burns *et al.* (2000) they found 46 tons of waste pesticides and an additional 7 tons of contaminated packaging. They included some chemicals known to be persistent in the soil and have toxic breakdown products. Notable of these chemicals DDT, Lindane, Heptachlor, Aldrin, Endosulphan, Aldicarb and 2,4,5-T.

It is also important to show in this discussion how some of the chemicals biomagnify as they pass through the food chain. Table below showed analysis of chemicals as they pass through the food chain particularly DDT. These were data from Tonga in 1980s.

Table 1. Pesticides found at different stages of the food chain in Tonga (modified from Chesher, 1984)

Sample	T Lindane	Heptachlor	T Aldrin	Endosulfan	T DDT
Cabbage	0.08	0.01			
Banana	0.05		0.09		0.02
Cucumber	0.02		0.03		
Tomato	0.01				
Water (n=9)	0.18	0.11	0.09	0.06	0.04
Milk	0.02 – 0.1	0.03 – 0.05	0.01 – 0.07		0.09 – 0.43
Human Fat					1.4 - 42

Vegetables, milk, human tissues – mg/kg; water – mg/litre.

The question from this set of data is – are the residues showing us that the pesticide degradation is almost complete or has just started. If it has just started then where DDT was used in Tonga, it can still be a real problem.

Mining

Mining operations and their mining waste disposal methods are considered one of the main sources of environmental degradation in the region. Social awareness of this problem is of a global nature and government actions to stem the damage to the natural environment have led to numerous international agreements and laws directed toward the prevention of activities and events that may adversely affect the environment.

In Papua New Guinea and New Caledonia toxic waste from the mines has polluted many areas of the two countries. After most of the targeted metals have been removed mine tailings are often toxic, and if not contained, are harmful to the environment and are being dumped on land or in the sea or rivers. Tailings from gold mining operations contain high levels of many types of heavy metals such as arsenic, cadmium, mercury and lead (Pearce 2000). And if cyanide leaching is also used to extract metals like gold then the tailings can be high in cyanide. Millions of tons of waste rocks from mining are also dumped in rivers. In Nauru, the mining processing is mainly crushing and drying of the phosphate rock mined there for use in superphosphate manufacture. The high Cd concentration of Nauru soils posed pollution problems in these soils and side effects of mining.

Waste Disposal

Pacific Islands have designated places for dumping household rubbish and other municipal wastes. Solid waste generation in the South Pacific Region is increasing at a rapid rate (Table 2). As urbanization, increases and the local economies are transformed from the traditional subsistence economies to cash economies there is an increased use of non-biodegradable materials and products. Domestic and industrial solid wastes are usually co-disposed in the Pacific region. Industrial and commercial solid wastes often include process waste, solvents, cleaners, construction debris, metals, acids, petroleum products, etc. Household waste may also contain hazardous wastes from cleaners, pesticides, used oils, and infectious wastes. Leachate generated from solid waste landfills may contain a number of toxic chemicals and infectious

agents. The leachate can adversely upset the ecosystems and may be injurious or fatal to a number of aquatic species.

Table 2. Estimated waste generation for 2016 – estimated with per capita generation rate of 0.36/person/day.

Country	Population 2016	Estimated annual waste production for 2016
Federated States of Micronesia	104,600	38,179
Fiji	880,400	321,345
Kiribati	115,300	42,084
Papua New Guinea	8,151,300	2,975,224
Samoa	194,000	70,810
Solomon Islands	651,700	237,869
Tonga	100,651	36,737
Tuvalu	11,534	4,210
Vanuatu	272,459	99,447

Table 2 also shows how some countries like the atolls of Kiribati will have problem to manage that enormous amount of weight generation and as resulted in old rubbish dumps being allocated for residences posing these households with potential problems of toxic wastes.

The legacy of nuclear testing

Morrison, Gangaiya and Koshy (1996) reviewed the legacy of nuclear testing in the Pacific. Nuclear testing in the Marshall Islands throughout 1940s to 1950s resulted in serious contamination and impacts on resident populations. Sites in the Marshall Islands were monitored for over 40 years and the detailed investigations include impacts on soils. Some areas were deemed contaminated forever. In undisturbed areas, most of the radioactivity (>80 percent) is in the upper 0.15m of the soil profile. The terrestrial food chain is still the most significant potential exposure pathway, but in some locations there may also be health problems from the intake of resuspended radioactive soil particles. Access to several islands is still restricted because of contamination.

Robison and Hamilton (2010) have since shown that there is an environmental loss of (¹³⁷) Cs from soil to groundwater that results in a more rapid loss of (¹³⁷) Cs from the atoll ecosystem. The mean effective half-life of (¹³⁷) Cs at the atolls is 8.5 y. Moreover, treatment of coconut trees with potassium (K) reduces (¹³⁷) Cs concentration in drinking coconut meat at Bikini Atoll to about 5% of pre-treatment concentrations. The magnitude of reduction is dependent on the concentration of (¹³⁷) Cs in soil, and thereby in food crops, and is less for Enjebi and Rongelap Islands than for Bikini Island. Treatment of food crops and fruit trees with K and removal of the top 15 cm of soil around houses and community buildings prior to construction to reduce external exposure where people spend most of their time has been presented to the communities as a "Combined Option" remediation strategy. Doses presented here are calculated using the Combined Option, effective half-life of (¹³⁷) Cs at the atolls, and a diet of both imported and local foods. The average natural background dose in the Marshall Islands, plus the anthropogenic nuclear test-related dose at Bikini, Enjebi, and Rongelap Islands, is less for each of the islands than the average background dose in the U.S. and Europe.

France nuclear testing in French Polynesia started in 1966 until 1996. The International Atomic Energy Agency (IAEA, 2007) was asked to conduct a study evaluating the effects of nuclear testing on the Mururoa and Fangataufa Atolls and surrounding areas (de Vathaire *et al.*). The research team that conducted the study was comprised of scientists and experts from all over the world.

The study took two years to complete and engaged about one hundred people in all. The purpose of the study was to assess the radiological safety of the atolls and the possible hazards to people. The researchers concluded that radiation was not a threat to the people or other flora and fauna in the surrounding area (IAEA). The IAEA did not recommend any further environmental monitoring at Mururoa and Fangataufa Atolls, but the agency did recommend the monitoring of radiation concentrations in the rock and test cavities, because the emission of radiation from the rock and cavities may be of particular interest to science in general. This was because the two atolls where tests were conducted were closed and nearest inhabited island was 120km away. The reluctance of the French authorities to allow full investigation of the test sites has fueled comments that contamination is occurring, even though the evidence to support these comments is limited. Morrison, Gangaiya and Koshy (1996) conclude that the impact on surrounding islands which are occupied by Polynesians living a traditional lifestyle is expected to be small, but in the absence of detailed investigations, this cannot be confirmed.

Nuclear testing were conducted by UK and US in the 1950s and 1960s in Kiritimati (Christmas Island). Radioactivity concentrations in soil are consistent with global fall-out levels for a low rainfall equatorial area, and no site on the island presents a risk to the health of the local population or requires any restriction on land use. The fact that as late as 2004, a cleanup was conducted and radioactive waste was shipped to the UK suggest that problems from these tests may still be there.

Conclusion

This paper presented a review of available data on soil contamination in the Pacific Islands. There is generally a lack of information and research being undertaken by regional national institutions dealing with contaminants and soil quality in the countries. There is plenty of works on impacts of different sources of inputs on productivity and food production but their potential impacts on the environment is much less studied. Even economic development is being developed many times compromising the environment and the health of the people. Many of our so-called good big brothers are knowingly promoting knowledge and development with good knowledge of the side effects and negative effects on the environment and health of our Pacific Nations. Soil pollution is everyone's – globally the international organizations and developed countries must understand that we in the Pacific are divinely given some of the harshes environment on this earth so help us to address our inherent problems including soil contamination. Our regional institutions and universities must relook their approaches and their priorities to include areas related to soil pollution. National governments must develop results based policies and must use hard data on soil pollution to support sustainable soil management policies. In addition, stakeholders of the soil must be made to understand and practice sustainable management of their soil resources to avoid soil pollution.

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Sub-theme 1.1: Drivers of soil pollution in agricultural fields

1.1.1. Drivers of soil pollution in agricultural fields

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Abstract

There are multiple sources of pollutants in soil, and it is important to note that for some pollutants geogenic sources can be as important as anthropogenic sources in terms of risks to human health and soil function. Pollutants may be added to soil directly and deliberately (through disposal of wastes to land) or indirectly and inadvertently (through accession by soil of atmospheric emissions or addition of fertilizers and soil amendments). The most widely studied soil pollutants are metals and metalloids, which also occur naturally in all soils to varying degrees. The area of soil contaminated by arsenic (As) and cadmium (Cd) globally is large, and these elements pose the greatest risk to human health. Adverse effects on human health of soil pollution by As and Cd have been clearly demonstrated, especially for As in South-East Asia. Other metals, metalloids and halogens in soil pose lower hazards to human health, but may be phytotoxic, toxic to grazing animals, or a threat to soil function. Widespread pollution of soils by radionuclides has also occurred as a result of incidents at nuclear energy power plants. Compared to metals/metalloids and radionuclides, contamination of soils by organic chemicals is generally much more limited in areal extent and localised around urban or industrial centres. Control of soil pollution is essentially effected through a control of direct inputs to soil, be these agricultural inputs or inputs through the land application of waste streams from urban or industrial sources, as well as controls on indirect accession of pollutants from atmospheric sources by emission controls. Contrasting philosophies are used by different countries to control soil pollution – some jurisdictions allow soil contamination up to a threshold concentration designed to prevent adverse effects, while others control pollutant inputs to a level that prevents net accumulation in soil.

Keywords: metals, metalloids, halogens, persistent organic pollutants, pesticides

Introduction

Agricultural activities significantly alter soils from their natural state, and the addition of fertilizers, crop protection products, crop growth enhancers, waste streams from agricultural, urban, mining or industrial activities may inadvertently lead to soil contamination (defined here as elevation of concentrations of chemical elements and compounds above those expected at ambient or background concentrations). If contamination proceeds unchecked, pollution of soil may occur (defined here as accumulation of contaminants to levels that affect soil function in the widest sense) so that remediation activities or land use change may be required to avoid the expression of the resultant adverse effect/s. Probably less well recognised is that the function of agricultural soils may also be impaired due to changes in soil or irrigation water physico-chemical conditions that lead to enhanced bioavailability of elements from geogenic sources e.g. acidification due to agricultural activities releasing nickel (Ni) from ultramafic minerals (Anderson *et al.* 1979) or cadmium (Cd) from naturally Cd-rich parent materials (Mellum *et al.* 1998) or addition of geogenic arsenic (As) or fluorine (F) to soils in irrigation waters (Meharg 2004) or volcanic dust (Cronin *et al.* 2003), respectively.

This paper overviews the sources of contaminants in agricultural soils, describes the main types of pollutants present, and controls required to protect the soils, especially vulnerable soils, from irreversible degradation due to soil pollution.

Sources of pollutants in agricultural soils

Geogenic sources

Some might argue that elements cannot be contaminants if they are derived from the underlying parent rock materials – this may be true in most cases but there are notable exceptions. For example, fluoride ion (F⁻) is present in many soil parent materials as a constituent of many minerals, but if deeply buried sources of F are deposited on the soil surface, for example through volcanic eruptions (Cronin *et al.* 2003), significant risks to grazing livestock may be manifest. Similarly, if previously buried and insoluble sources of arsenic (As) are mobilized and brought to the surface due to changes in the chemistry of groundwater used for irrigation, significant risks to humans may be manifest due to As contamination of water supplies and the food chain (Meharg 2004).

Anthropogenic sources

Contaminants introduced into soil by man can be either directly added to soil e.g. agricultural chemicals, sewage wastewaters and biosolids, urban liquid and solid wastes, etc., or can be indirectly and inadvertently added to soil through addition in fertilizers and soil amendments, or by atmospheric deposition from anthropogenic sources e.g. emissions from smelting, waste incineration, transport, energy production (oil, coal and nuclear), dust deposition and runoff from impacted areas. A wide range of contaminants derive from human activity on the globe, which can either mobilize metals, metalloids or halogens from the geosphere into the biosphere, or create and disperse organic contaminants through the synthesis of new compounds not present naturally in the biosphere or geosphere.

Types of pollutants in agricultural soils

Pollutants in agricultural soils are either inorganic elements, synthetic organic chemicals or radionuclides and each group differs in their properties and in the severity and global extent of soil pollution.

Inorganic elements

Perhaps the most widely studied inorganic pollutants globally are the potentially toxic metals cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) and the metalloid arsenic (As). Inorganic elements are present naturally in soils at concentrations that vary according to the soil parent material (McLaughlin 2002), and risks to both humans and biota can be expressed at high “background” concentrations (Reimann and Garrett 2005) where the source is solely geogenic (Anderson *et al.* 1979, Yang *et al.* 1983). However, high concentrations of potentially toxic metals and metalloids in soil are more commonly a result of disposal of urban or industrial wastes (Chaney 1973), from use of fertilizers and soil amendments (McLaughlin *et al.* 1996, Menzel 1968), from use of contaminated irrigation water (Rahman and Hasegawa 2011) and/or from soil accession of atmospheric emissions from urban, mining or industrial sources (Cartwright *et al.* 1976, Freedman and Hutchinson 1980, Kelly *et al.* 1996). In terms of hazards to human health, As and Cd are probably the most important elements, with the adverse effects due to geogenic As exposure in South-East Asia affecting more people than any other element (Meharg 2004). Adverse effects on human health due to Cd exposure were manifest in the 1960s and 1970s (Nogawa *et al.* 1975) but are rare now given maximum Cd limits in foods, soils and agricultural inputs imposed by many

countries in response to the World Health Organization's Provisional Tolerable Weekly Intake (PTWI) for Cd set in 1989, revised to a Provisional Tolerable Monthly Intake in 2011 (WHO 2011). Contamination of soils by lead (Pb) is more localized to urban and industrial centres and, due to the insolubility of Pb in soils, the major risk pathway is soil ingestion by animals and humans in contaminated areas. Copper, Ni and Zn pose a greater risk to plants and soil organisms than to human health (Chaney 1980), while Hg pollution of soils is less common and hazards to humans are through the aquatic/marine food chain (Nelson *et al.* 1971). Of the halogens, chloride ion (Cl⁻) is probably the most ubiquitous in soils (usually co-existing with sodium) and excessive concentrations in soil from either geogenic sources (saline irrigation water or groundwater) or anthropogenic sources (e.g. urban or industrial wastewaters) often lead to expressions of phytotoxicity (USDA 1954) – despite this, Cl⁻ is rarely recognised as a soil pollutant. Fluorine present as the fluoride ion (F⁻) has also been identified as of concern where natural or industrial irrigation waters rich in F⁻ are used (Scholz *et al.* 2015) or as an impurity in phosphatic fertilizers (McLaughlin *et al.* 2001), the risk being principally to grazing livestock ingesting contaminated soil and forage (Cronin *et al.* 2000).

Synthetic organic chemicals

Compared to metals, metalloids and radionuclides, the global footprint of soil highly contaminated by organic contaminants is much smaller, with contamination of the food chain being localised around industrial or urban centres, through waste re-use on land and the legacy of use or disposal of persistent and bioaccumulative organic chemicals (principally organochlorines (OCs), polychlorinated dibenzo-p-dioxin (PCDD), polychlorinated dibenzofurans (PCDF) and poly- and perfluoroalkyl substances (PFAS)). Levels of soil contamination are usually lower than for metals/metalloids/halogens – generally sub mg/kg concentrations in soil, especially for dioxins, furans and PFAS compounds. Due to the strong binding of many persistent organic compounds in soil, risks to plant growth and soil function are usually low, with the primary concern being soil ingestion by humans or animals, or contamination of the food chain. The pathway of uptake into the food chain depends on the properties of the organic contaminant – principally the volatility (Henry's Law constant), the hydrophobicity (octanol/water partition coefficient) and the solubility in water. Hydrophilic organic contaminants with low volatility (e.g. PFAS) will principally enter the food chain through root uptake and translocation to food parts (Navarro *et al.* 2017), while volatile hydrophobic contaminants (e.g. dioxins, furans and polychlorinated biphenyls (PCBs)) will tend to accumulate in the food chain through an atmospheric uptake pathway (Figure 1) as they are generally strongly sorbed in soil (Collins *et al.* 2006). However, unlike metals and metalloids, the incidence and severity of adverse effects on human or soil health caused by soil contamination by organic chemicals is much less well documented or demonstrated, likely because smaller areas of land are affected and contamination levels are generally lower.

Radionuclides

Radionuclides may also present a potential threat to food quality, through atmospheric deposition of radionuclides on soil from nuclear energy accidents, or the addition of radionuclides to soil in fertilizers or nuclear industry wastes and by-products (Mortvedt 1994). The potential for transfer of radionuclides from soil to plants and the food chain was first identified in the 1950's in restricted areas where nuclear weapons testing had taken place, but the Chernobyl nuclear accident in 1986 was the first documented widespread pollution of soils by radionuclides (principally iodine-131, cesium-134 and cesium 137) (Bell *et al.* 1988). Uptake from soil into forages was followed by contamination of grazing animals, and led to restrictions being placed on the sale and slaughter of sheep from affected areas in the UK (Smith *et al.* 2000). Widespread contamination of the food chain by the same radionuclides also resulted after the Fukushima nuclear accident in Japan (Berends and Kobayashi 2012).

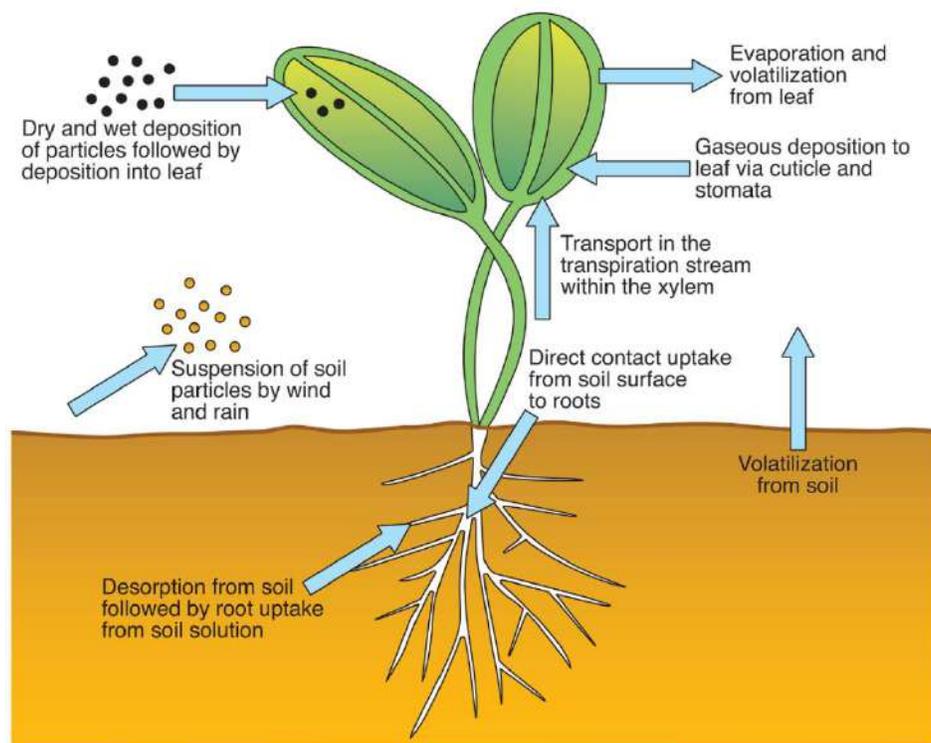


Figure 1. Principle uptake pathways for the uptake of soil contaminants by plants (adapted from Collins *et al.*, 2006).

Controlling pollution of agricultural soils

Given the sources of pollutants discussed above, controls on pollution of agricultural soils will involve not only restrictions on additions of pollutants in agricultural inputs (fertilizers, chemicals, soil amendments, etc.) but also restrictions need to be considered for more diffuse sources of pollutants reaching soils, such as anthropogenic atmospheric emissions from urban and industrial sources (smelters, incineration, etc.). While adverse effects of pollutants on food quality or soil function may not be manifest until a critical concentration is reached in soil, the critical concentrations will be different for different environmental receptors and/or land uses, and dependent on soil physico-chemical properties (Smolders *et al.* 2009). Many countries use maximum concentration limits in soil (Carlon 2007) to control accumulation of pollutants below critical thresholds for effects (e.g. biosolid reuse guidelines/regulations or soil quality standards) while for some countries input controls are based on a philosophy of no net accumulation of contaminants (Witter 1995). To retain multifunctionality of land use in perpetuity, the goal of no net accumulation of contaminants in soil should be strived for into the future, but may not be achievable in the short term. Use of soils for disposal of wastes (solid or liquid) needs to be carefully controlled to maximize recycling of beneficial nutrients and organic matter, while minimizing accumulation of potentially toxic constituents (Cameron *et al.* 1997).

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1.1.2. Heavy metals assessment in Cuban soils

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Abstract

Food Security is of highest priority for the Ministry of Agriculture (MINAG) of Cuba and special attention must be paid to the safety and quality certification of products of agricultural origin, thus avoiding the risk to human health that cause the toxic contaminants, including Heavy Metals (HM). In this sense and considering that all agricultural production is supported by the soil, it is also required to ensure Soil Quality on time. During the last 20 years, Soil Institute (MINAG) and the Centre of Technological Applications and Nuclear Development, CEADEN (CITMA) maintain a very fruitful collaboration about potential HM contamination on soils, organic manures and crops cultivated mainly in areas of intensive agriculture and Urban Agriculture. The objective of this study was to establish preliminary quality reference values for Cd, Pb, Zn, Cu, Ni, Cr, in soils of Cuba. It was employed the Brazilian methodology CONAMA and the analytical technique USEPA 3051a and ICP. Three values were determined for each element: Reference Value (RF), Prevention Value (PV) and Investigation Value (IV). Results showed that some Cuban soils are characterized by high natural levels of these elements, even in places without human influence, due to the parental material. That is the case of Ni and Cr due to the presence of serpentinite in the parent material, fortunately they have low bioavailability. This was also ratified by soil HM sequential studies and others about the dynamic of HM uptake by some of the main crops. In addition, the analysis of hundreds of soil samples in areas of intensive agriculture along the country, allows to state that, in general way, HM soil content is not a risk for human health in Cuban soils and agriculture. Anyway, deepen studies are required.

Keywords: soil contamination, soil quality, Heavy Metals permissible limits

Introduction, scope and main objectives

Food Security is of highest priority for the Ministry of Agriculture (MINAG) of Cuba and special attention must be paid to the safety and quality certification of products of agricultural origin, thus avoiding the risk to human health that cause the toxic contaminants, including Heavy Metals (HM). In this sense and considering that all agricultural production is supported by the soil, it is also required to ensure Soil Quality. This concern has given rise to specific laws of national or regional scope, which provide tools for monitoring soil quality.

During the last 20 years, Cuban institutions, Soil Institute (MINAG) and the Centre of Technological Applications and Nuclear Development, CEADEN (CITMA) maintain a very fruitful collaboration about potential HM contamination on soils, organic manures and crops cultivated mainly in areas of intensive agriculture and Urban Agriculture.

The objective of this study was to establish Cuban preliminary quality soil values for Cadmium (Cd), Lead (Pb), Nickel (Ni), Chromium (Cr), Zinc (Zn) and Copper (Cu).

Methodology

The Brazilian methodology CONAMA was used, in which three values are determined: Reference Value (RV), value without anthropic influence, only due to the parental material; Intervention Value (IV), value over which exist a risk for human health and life (not allowed for agriculture); and Prevention Value (PV), intermediate value (can be used, but it must be monitored).

For obtaining Reference Value (RV), the procedure was based on a sampling of soils throughout the country, which was carried out in the contours of 35 soil profiles selected from the reference profiles of the National Soil Map of Cuba at a scale of 1: 25,000, in areas with minimal anthropic action. The samples were taken at a depth of 0-20, 20-40, 40-60, 60-80 and 80-100 cm depending on the actual depth of each type of soil, as described in ISO-11464. (1999). The USEPA 3051A analytical technique was used to extract the contents of the MPs, and microwave oven for the digestion of samples. Analytical quality control was determined using the international reference standard SRM 2709 (NIST 2002).

The Intervention Value (IV) were derived from the risk value obtained using the mathematical model of Risk Analysis proposed by the Ministry of Health of the Netherlands, Csoil version 1.0 (Brand *et al.*, 2007; Swartjes *et al.*, 2012)

The sequential extraction of Ni and Cr by Shuman (1979) was also carried out to determine the fractions of these elements found in the soil to know their availability to the plants.

For the metal determination ICP-OES and AAS were employed.

Besides dynamics of HM uptake of crops like beans and tomato cultivated in Nitisols was evaluated by plants organs using as a criterion of toxicity for fruits, the Codex Stan 193-1995 (2016).

Results and discussion

The RV of quality for each metal was calculated based on the 75th percentile of samples, with the anomalies being previously withdrawn through a boxplot. Average, minimum and maximum values, as well as the standard deviations for all elements analyzed, were also calculated (Table 1). These results are mainly a reflection of the source materials and pedogenic processes, together with the geomorphological and climatic conditions that make the metal levels in each soil specific. The

very high Standard Deviation values for Ni and Cr is due to the existence of Cuban soils with unusual high total content of both elements (ultramafic soils) and that it is recommended to analyze those soils separately.

Table 1. Benchmarks of quality (RV), average, minimum and maximum values and standard deviation for Heavy Metals in soils of Cuba

Metal (mg kg ⁻¹)	n (1)	n (2)	Percentile (75 %)	Average	Minimum	Maximum	Standard Deviation
Cd	32	3	0,64	1,15	0,10	6,05	1,54
Pb	34	1	50,03	35,51	5,20	113,56	23,19
Zn	31	4	86,09	90,45	26,10	260,10	52,64
Cu	30	5	82,66	83,63	9,50	269,85	52,88
Ni	29	6	169,84	475,05	9,80	3488,20	926,77
Cr	28	7	153,08	580,21	9,90	4418,25	1062,66

n (1). Total samples used.

n (2). total anomalous (retired) samples from the boxplot

Therefore, to extrapolate soil values obtained in other countries is a misguided strategy. This statement is evident when observing the high metal levels found in Cuban soils, which are generally higher than those found in soils of other countries and Brazilian states. The average concentration of some metals in Cuban soils exceed the average concentration range for unpolluted soils (Kabata-Pendias and Pendias, 2000), and even PV for Cu and IV for Ni, Cr, and Sb, according to the Brazilian legislation (CONAMA 2009). This is due to the existence of soils developed on ultramafic rocks, as well as the fact that soils originated from sedimentary limestone (70 % of Cuban soils) received the influence of arc-shaped ultramafic rocks from the north of the island, with high Ni and Cr contents (Camacho and Paulín, 1983; Ruiz and Pérez Jiménez, 1984).

The separation into fractions relating to lability is a way of inferring the mobility and/or availability of these elements in the soil. Most of these elements are not available to the plants but are found linked to crystalline iron oxide (Table 2). Thus, the contamination risk for the food chain and, consequently, humans is low. Ni had the highest concentrations in the analyzed soils. It is noteworthy that Ni is not very toxic when absorbed orally, which is the main route of exposure for humans. Ni can cause lung and nasal tumors, but exposure to the element via inhalation is usually limited. The Netherlands, for instance, established intervention values based on human health as high as 1470 mg kg⁻¹ (Swartjes *et al.*, 2007). Although the metal ingestion via contaminated food is the primary route of exposure for humans, further studies considering all forms of contact, including direct ingestion of soil, must be carried out.

Table 2. Average content (mg kg⁻¹) of Ni and Cr fractions in soil samples from Cuba

Element	Soil	Fractions				Total
		Available	Organic	Amorphous	Crystalline	
Ni	Nitisols	0.22	< 0.002	0.78	68.21	180.96
	Ferralsols	11.92	< 0.002	1.48	153.29	3430.50
Cr	Nitisols	0.32	< 0.002	1.89	41.44	177.98
	Ferralsols	10.18	14.39	29.05	318.78	2952.00

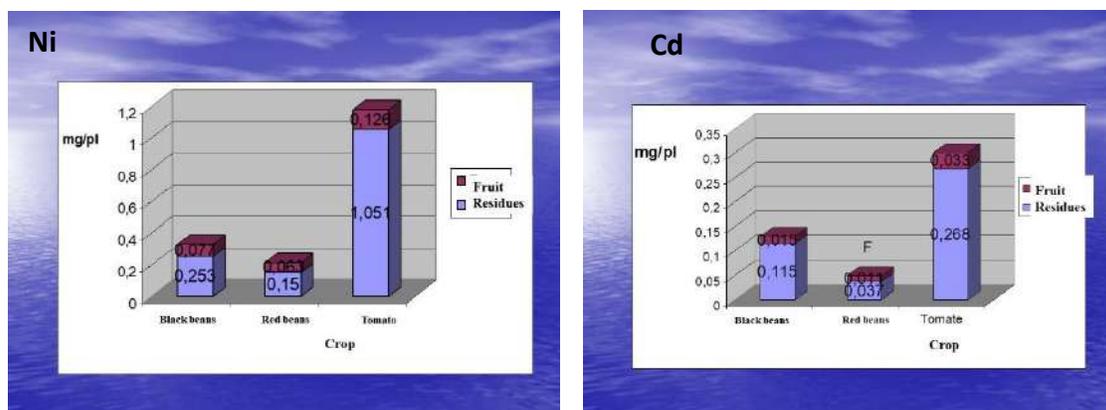


Figure 1. Uptake of Ni and Cd by different crops cultivated in a Nitisols from district Quivicán, Cuba.

Fig. 1 shows the Ni and Cd uptake by *Phaseolus* beans and tomato by organs of the plant (fruit and residues). It is evident that most part of the corresponding HM remains in the crop residue and in all cases the content in tomato fruit and beans grain were below than the permissible contents established by Kabata-Pendias and Pendias (2000) and Codex Stand (2016)

Finally, the Investigation Values (IV) were determined by means of Risk Analysis using C soil software and the Prevention Values (PV) were, as was said previously, intermediate values between RV and IV.

Table 3. Preliminary criterion for the evaluation of HM content in Cuban soils

Element	RV	PV	IV
	mg kg ⁻¹		
Cd	0,6	2	3
Pb	50	72	180
Zn	86	300	450
Cu	83	150	200
Ni	170	300	400
Cr	150	300	400

Table 3 presents the proposed preliminary criterion for the evaluation of HM content in Cuban soils. In the case of Ni and, Cr the results must be reanalyzed without considering the ultramafic soils. But anyway, the final decision on the establishment of permissible HM contents for Cuban soils is dependent on political, economic, and social matters and in-depth risk analyses considering all routes of exposure to these elements (Rodríguez *et al.* (2015).

Conclusions

The reference and intervention values of soil quality or permissible limits based on natural or reference values and risk analysis were obtained for the first time for Cuba.

The HM contamination risk for the Cuban population is, in general, terms low.

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1.1.3. 60 years of pesticide application – pitfalls and prospects

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Abstract

Since 60 years, pesticides are worldwide intensively applied. Use in agriculture for achieving food security was the main driver, however, unfortunately it created downside effects also.

At present, ca. 2000 pesticides, containing 500 active ingredients (a.i.), are approved for different uses within the EU. A.i. are evaluated according to their environmental impact before approval. Recent field assessments urges the need to critically reflect on current practices and pave the way for required innovations.

First, within the evaluation process of an a.i. to be used in a pesticide product, only a few indicators and criteria are used which are not necessarily complete, or resembling actual field conditions. Mismatches and inconsistencies in this process will be highlighted, including ways for improvement.

Second, the wide spread use of pesticides urges to monitor the actual content of mixtures of a.i. in soils, currently not a common practice or obligation within countries or the EU. Recent evidence of alarming occurrence of glyphosate residues in EU agricultural top soils underpins this statement, and maximal tolerable pesticide residue contents in soils are urgently needed.

Third, soils are exposed to a range of a.i. requiring to investigate effects of pesticide mixtures on soil quality and soil life. So far, this aspect is not considered and explicitly accounted for in the evaluation process of a.i. before approval, neither their possible related long-term effects.

Fourth, a.i. can be bound to soil particles, designed so by purpose to minimize potential leaching risks towards underlying groundwater reservoirs. However, the result is that pesticide residue levels are generally the highest in the surface layers of soils, being a source for transport by water and wind erosion, having the potential to transport these pesticide residues to the atmosphere and the surrounding aquatic environment, and at the end to humans also.

To conclude, many pitfalls exist with regard to pesticide approval and use, and a clear need exists to improve related legislation, field monitoring of cumulative residue levels, and safe-guarding the environment to protect our fragile soil resources and the life therein.

Keywords: Pesticides, risk assessment, soil biota, water erosion, wind erosion

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

1.1.4. The contamination state in Pampas soils. An overview.

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Abstract

The soils in each specific area of the world are subject to accumulation of contaminants from different anthropogenic sources. Due to the pedogenetic characteristics of the Pampas Region soils and their demographic and productive features, fertilizers, pesticides and irrigation water could be its main sources of pollutants. The region is the main agricultural area in Argentina, showing a surplus of food production, which is exported to other countries. The region shows a dual panorama about agricultural inputs: an historical deficit in fertilizer use and, conversely, a large utilization of agrochemicals. The objective of this communication is to provide an overview of the current status of the pollution of agricultural and urban and suburban soil of the Pampas region, focusing on heavy metals, herbicides and geogenic toxic elements.

The agricultural soils of the Pampas contain low concentrations of heavy metals. Conversely, the presence of pesticides, especially herbicides, in soils, water and air was registered, rising the concern of some people. The incorporation of arsenic, other elements and soluble salts due to irrigation is a new risk in some agricultural areas. In contrast, in urban areas, the soils show significant accumulation of heavy metals, geogenic elements and other contaminants. In those areas there are several activities causing pollutant rich emissions or residues. No effects of local contamination were registered on crops yield or quality with the exception, although in a limited extent, in suburban areas.

Keywords: Pampas region, soil pollution, heavy metals, pesticides, toxic elements

Introduction, scope and main objectives

Soils accumulate contaminants from anthropogenic sources, like manufacturing industry, mining and smelting, oil extraction and their processing, urban life (vehicles, calefaction, wastes, and sewage sludge) and agriculture, animal husbandry and forestry. The status of the soils in each specific area of the world shows a unique balance, resulting from the main factors affecting them. Present communication focuses the main agricultural area in Argentina, the Pampas Region. This is a large agricultural area located in the southern cone of South America (33-35° S, 62-64° W). This plain of fertile lands is suitable for growing temperate field crops. The soils, mostly Mollisols, were mainly developed from eolian loess-like sediments. Based in this area, the country has a surplus of food production and is able to supply grains, oil and meat, fruits and so on, to other countries. Crop production in the Pampas increased during the last 50 years. The cropped area increased by 190% but yields increased by 420%. There was a clear global productivity increases with a significant change in the proportion between cereals and oil crops. At present oil crops, soybean and in lesser extent sunflower, means 60% of crops production. This change was caused by the adoption of a technological package including direct drilling and genetically modified seeds, resistant to herbicides, and the prices of grains in the international market. In the Pampas region, the population is scarce and concentrate in cities, manufacturing industry is localized in them, mining and oil extraction are almost inexistent, wastes and sewage sludge are virtually not recycled in croplands. Inputs used in agriculture with contamination potential are phosphate fertilizers, in lesser extent lime and gypsum and manure (used mainly in intensive crops) carrying

heavy metals (HM), and pesticides. In some limited locations other source of contamination is irrigation water, carrying some toxic elements (TE) (Lavado 2016; Lavado and Taboada 2009).

The region shows a dual panorama about agricultural inputs: an historical deficit in fertilizer use and, conversely, a large utilization of agrochemicals. In contrast with the high technological level of the agriculture, the crop nutrient supply in the Pampas is still based on the soil reserves and there is a negative balance of nutrients. Fertilizer use increased from the 1990-decade and today nearly 100% of the wheat and around 83% of the maize is fertilized but the rates of fertilizers application are still low and the nutrients exported by the Pampas crop harvest exceed fertilization inputs. Fertilization restored only 31, 39, 31 and 3% of nitrogen, phosphorus, sulphur and potassium, respectively, removed globally by the main crops of the region (soybean, wheat, maize, sunflower, barley). The mineralization of soil organic matter supplies most nutrients required by crops (Lavado and Taboada 2009). In contrast, Argentina is second among main agricultural countries for the large use of herbicides per hectare, exceeding the rates used in countries like Australia, Brazil, Canada and USA. Herbicides mean 87% of the total pesticides consumption in Argentina, being glyphosate 65 % of the total. The other herbicides are 2,4D, atrazine, diclosulam and chletodim. This is somewhat related to tillage system used (direct drilling) (Lavado and Aparicio 2018).

Other source of problems in agricultural soils is the supplementary irrigation applied in some areas. This technology supplies water to crops during periods of water deficiency in any area prone to periodical droughts. In the region, there is a great variation in total rainfall, across and within years. Water stress, the main individual factor causing yield reductions, is frequent and could occur any time. Supplementary irrigation technology is slowly but steadily adopted. The main source of water, the groundwater, could carry arsenic, fluoride, vanadium or boron. Irrigation could be a way those elements enter in soils and crops, which was documented also in several countries (Bustingorri and Lavado 2015). Soluble salts cause other type of soil contamination, causing varying degrees of soil salinization and/or alkalization. The groundwater available for irrigation parameters are: Electrical Conductivity 0.5 - 2.0 dSm⁻¹, Sodium Adsorption Ratio 1 - 20 and pH 7.5 - 8.5), contains predominantly bicarbonates (Ghiberto *et al.* 2007). The urban and suburban soils differ, sometimes very markedly, as compared with agricultural or pasture soils in their degree of pollution. This is due to intensive agriculture, manufacturing plants, traffic and other nearby sources of contamination (Lavado and Aparicio 2018).

The objective of this communication is to review the pollution of agricultural, urban, and suburban soil of the Pampas region, from the point of view of heavy metals (HM), pesticides and geogenic toxic elements (TE), like arsenic.

Methodology

The pollution of soils with HM was studied in several surveys, long-term experiments of fertilizer application, experiments in controlled conditions, and so on. Pesticides dynamics and accumulation in soils were evaluated in several surveys, run off parcels, aeolian erosion plots, column experiments, etc. Geogenic TE were assessed among other methodologies by means of field irrigation experiments, pot test, some modelization and laboratory test.

The determinations of HM and other TE were carried out using ICP-AES previous acid digestion. The determinations of pesticides and other organic substances were made with liquid chromatography techniques (HPLC or UPLC). General determinations included standard laboratory techniques. Details of methodologies are given in the references.

Results

The HM present in the phosphoric rocks remains in the phosphoric fertilizers and could be a source of their accumulation in soils. The results from local long-term fertilization experiments, ranged from no significant accumulations of HM in soils to a very slight increase in the content of cobalt (i.e. 0.16 mgkg⁻¹ to 0.20 mgkg⁻¹ total Co), copper, lead and nickel. In accordance, predominant soils of the Pampas, as well as paleosoils and the loess material, show low concentration of HM (i.e. 0.05 mgkg⁻¹ total Hg; 12 mgkg⁻¹ total Cr or 15.7 mgkg⁻¹ total Pb) (Lavado *et al.* 2004).

Glyphosate plus AMPA (amino metil phosphonic acid - its intermediate product of degradation) was found in agricultural soils in concentrations ranging from 0.5 to 3600 µg kg⁻¹. Also glyphosate and AMPA was detected in watercourses. The detection percentages decreased in the water from the day of application but were higher in the particulate material carried in the water (percentage detection 4 month after application of glyphosate: water 7%; particulate material 87%; river bed 6%). Glyphosate and AMPA were detected in some places where soils never received the herbicide. This phenomenon was credited to aeolian erosion and indicates migration from the application zones by movement of particles from the soil suspended in the air (concentration range of glyphosate and AMPA in particles suspended in air: 17 to 115 µg kg⁻¹). Concentrations of glyphosate were high on top soils (0-10 cm depth) but the herbicide concentration decreased dramatically toward depth (Okada *et al.* 2016). Glyphosate adsorption was positively related with the clay content and the soil exchangeable capacity, and negatively related to pH and phosphorus content. Agricultural practices also affect those processes (Primost *et al.* 2017).

Soils of some punctual sites of the Pampas receive a load of arsenic and fluoride, because the use of geogenic contaminated groundwater. In pot experiments, the arsenic concentration in the edible parts of studied crops (soybean, sunflower and others) was far lower as compared to roots and shoots (Bustingorri and Lavado 2015). On the other hand, slight salt buildup, not enough to limit crop production, was found. Sodicity, conversely, generally significantly increases in the irrigated soils, accompanied by pH increases. Accordingly, physical properties (water infiltration, aggregates stability and so on) of those soils usually showed sign of degradation (Ghiberto *et al.* 2007).

Soils of the large city of Buenos Aires showed high concentrations of cadmium, copper, lead and zinc (128 mgkg⁻¹ total Zn) but around 50 km from downtown the soils shows no signs of contamination (i.e. 55 mgkg⁻¹ total Zn). Inside the city soils of industrial areas show higher concentration of some HM when compared with soils taken in residential areas (Lavado *et al.* 1998). Soils located near highways around cities, are enriched in lead, zinc and other elements compared to soils far from those roads. The highest HM accumulation in suburban areas was found in horticulture belts around cities (i.e. 125 mgkg⁻¹ total Pb) (Giuffré *et al.* 2005).

Discussion

The information, indicate that globally, the buildup of HM by the application of P fertilizers is still not a local problem (Lavado *et al.* 1999; Zubillaga and Lavado 2002). This could be accredited to the short term and the low doses this input is applied to soils. Present concentration and dispersion values of them in soils are similar to that observed in other non-contaminated soils of the world, mostly in the lower range. Elements showing high environmental risk were found in concentrations lower than limits established by the UE and the US-EPA regulations. The distribution of HM in the soil profiles is mainly related to parent material and pedogenetic process, being an indication for the lack of anthropic contamination (Lavado *et al.* 2004). Other

confirmation that the agricultural soils are not contaminated is that HM are found mainly in more insoluble fractions (Orroño and Lavado 2009).

Glyphosate and AMPA are present in soil and the herbicide reaches watercourses by runoff (Aparicio *et al.* 2013). Glyphosate is a strong chelate agent and the adsorption process causes higher herbicide persistence in solid matrix. Later, because desorption processes, it is released again in the soil or the water, where finally is degraded. To deal with this accumulation of the herbicide, and pesticides in general, in soils the establishment of threshold concentrations would be important. However, different to drinking water, no limits concentrations were established for pesticides in soils, in the country and elsewhere. Several studies in that direction were performed in the country but still are far from present applicable results. There is not a unique vision about the impact of those pesticides application on soil microorganisms and mesofauna. Results reported from null, minimum and/or transient effects on composition and functioning of communities to negative effects on specific groups and on their impact on other organisms from the ecosystem (Lavado and Aparicio 2018).

When sprinkler irrigation was applied, part of the water spread over plants fell and reach the soil that retained most arsenic and fluoride added. The accumulation of them in the soil is related to their concentration in the irrigation water. Arsenic and fluoride applied through the irrigation water tends to be adsorbed to soil components like a range of aluminum, iron and manganese oxides, clays, carbonates and organic matter. It was hypothesized that crops seldom accumulate arsenic at concentrations hazardous to human and animal health because phytotoxicity usually occurs, and plants died before such concentrations are reached. In the case of fluoride, it is difficult to speculate whether its concentrations may result hazardous to human health (Bustingorri and Lavado 2015). Irrigation supplies between 10 to 30% of the water required by crops and even with this low irrigation water/rainfall water ratio there are some long-term negative impacts on soil properties. No negative effect on crops and pastures were registered: yields increased and were more stable across years.

Soils in large cities exceed the HM standard limits of the World Health Organization and other organizations. The atmospheric deposition from the urban and industrial activity is recognized as the cause of HM concentration at some distance from the contamination sources. In those cases, soils growing pastures show the highest concentrations of those elements. The lack of tillage, which dilutes HM in the tilled layer, was recognized as the main cause of the increases registered in those areas (Lavado 2006). The high HM accumulation in horticulture belts around cities are due the intensive use of agrochemicals, fertilizers and manure, and irrigation water plus local atmospheric deposition. Suburban areas around industrialized cities also receive several organic contaminants, coming from petroleum spills and effluents from petrochemical plants (Arias *et al.* 2013). Finally, in non-agricultural areas of the periphery of the Pampas region, some local lead contamination caused by hunting of pigeon or ducks was found (Ferreira *et al.* 2016).

Conclusions

The agricultural soils of the Pampas contain low concentrations of heavy metals. Due to the demographic and productive features of the area, their soils did not suffer significant HM incorporation. Other results indicate the occurrence of pesticides, especially herbicides, in soils and water of the studied area, which rise concern of some people. Conversely, on cities and their periphery, the soils show significant accumulation of HM, TE and other contaminants. In those areas large population lives and there are several activities causing pollutant rich emissions or residues. The incorporation of arsenic, fluoride and sodium soluble salts due to irrigation is a new risk in agricultural areas of the country. The effect of the different sources of local soil

contamination on crops yield or quality did not show negative effects, except, still in a limited extent, in suburban areas.

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1.1.5. Status of heavy metals in agricultural soils and the need for adapted soil thresholds, case study from Lebanon

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Abstract

Soil contamination by HM is one of the direct health and environmental hazards. Assessing the natural occurrence and accumulation of heavy metals (HMs) in agricultural soils are starting points for soil contamination assessment and land use control. The available Lebanese data points to the absence of local criteria and norms related to the thresholds of soil pollution with HMs. National soil information provides soil data for land capability and suitability assessment based on soil physical and physico-chemical characteristics. Land quality and notably soil pollution is still excluded from any evaluation. With increasing human pressure, the status of HMs in the soils constitutes the basis to evaluate the impact of land use on soil pollution and to assess the applicability of the European standards to local soil conditions. The European standards (Eikman and Kloke) are listed in function of content of HM in the soil as threshold of soil contamination and suitable land use. The level of HM for the multifunctional land use and other uses must be based not only on given element concentration in the soil matrix but also on soil attitude and properties. Determining the

trigger values and intervention levels is very important for the decision makers and farmers to define appropriate agricultural and non-agricultural land use with minimum public health and environmental threats. This work focused on two pilot areas, the first study area is located in the Central Bekaa plain, totaling about 12753 ha. The second study area is about 60000 ha and located in North Lebanon. The Bekaa plain consists of fan deposits and a mixture of colluvial and alluvial material representing mainly deep, non-calcareous Fluvisols and Cambisols with some inclusions of Vertisols and Regosols. Beside these soil types, North Lebanon has a dominance of basalt and derived Andosols. Agriculture in the both areas is practiced mainly with field crops, fruit trees and vegetables. Spatial analysis and HM mapping were done using the universal kriging method with a matrix table of 5 m x 5 m resolution. Results showed a relative accumulation of Cr and Ni in some soils of the Bekaa plain approaching the soil contamination value II (100 mg kg⁻¹) with a steady increase of HM from the plain towards the summit of surrounding hills. Some areas of the Bekaa plain showed an increase of HMs content on the soil surface by more than 50% for Co, Cr, Ni, Cu, Zn and by more than 100% for Pb. Other locations showed the increase of HM content in the subsoil (160-180 cm), implying that contamination was probably not due to surface accumulation and migration. The soils of the North Lebanon showed the levels of some HM exceeding the contamination level III (200 mg kg⁻¹). The soil groups derived from volcanic rocks and soft limestone showed the highest background level of Ni found in the soil surface horizon with average of 190 ppm and highest values reaching 280 ppm (exceeding level III). Human activities are the main factors contributing to additional soil contamination and probable pollutants transfer to the aquifer and other ecosystems. Linking the soil quality with the soil physic-chemical properties suggests the creation of adapted soil thresholds for arid and semiarid zones for national and local decision makers for suitable land use to reduce public health and environmental risks.

Keywords: Chemical pollution, sources of HMs, agriculture, soil quality, food quality, food safety

Introduction

Soil contamination by heavy metal is one of the direct health and environmental hazards. Assessing the natural occurrence and accumulation of heavy metals in agricultural soils are starting points for soil contamination assessment and land use control. The available Lebanese soil data points to the absence of local criteria and norms related to the soil pollution with heavy metals. Despite the recent efforts to complement national soil information in the country (Darwish *et al.* 2006), the use of produced soil georeferenced database does not exceed soil mapping for land capability and suitability assessment based on soil physical and physic-chemical characteristics. With increasing human pressure, the status of heavy metals in the soils constitute the base serving to evaluate the impact of land use on soil pollution and to assess the applicability of the European standards to local soil conditions. While the European thresholds are listed in function of content of hazardous elements in the soil (Eikmann and Kloke, 2000), building the criteria of soil contamination, i.e., level of trace elements for suitable land uses must be based not only on trace element concentration in the soil matrix, but also on soil attitude and properties as well as heavy metals bioavailability. Determining the trigger values and intervention levels in the soils of arid and semi-arid regions is very important for the decision makers and land users to decide on appropriate agricultural and non-agricultural land uses with minimum public health and environmental threats.

Heavy metals in the soil have a geogenic and human origin caused by the lithology and land use history. Many industrial processes involve solubilization or leaching of heavy metal ions to aqueous solutions which then are released into the environment via waste water (Nestle 2002). Upstream and downstream mismanagement of water and fertilizer inputs are impacting the limited natural resources (Muller and Darwish 2004). This is particularly observed in pollution problems due to excessive use of fertilizers and pesticides, dumping of industrial and domestic wastes and discharge of untreated wastewater into rivers, dry wadi beds, sand pits and quarries

(Darwish *et al.* 2011). Farmers, therefore, both in the coastal areas and inland, irrigate with water of low quality. This, besides the low nutrient use efficiency of fertilizers, and in the absence of adequate extension services, has caused nutrient build up in the soils and soil salinization in open field especially in semi-arid Lebanese areas (Darwish *et al.* 2005). Byproducts in fertilizers, emissions from industry and energy sectors contaminated the soil and groundwater with heavy metals (Kassir *et al.* 2012). Because the public health and agro biodiversity are affected, monitoring the origin, state and development of soil and groundwater pollution with heavy metals are of extreme importance. Until now, 6% of the Lebanese lands were tested for heavy metal pollution, thus the need for national assessment of soil quality to adapt local soil thresholds and on time implement policy for proper land protection and sustainable use.

Materials and Methods

Two study areas were chosen: the first is located in the Central Bekaa plain, totaling about 12,753 ha. It extends from Mount Lebanon westward through Litani River towards the eastern mountain chain. The second study area is about 60,000 ha and located in North Lebanon. The climatic conditions of the areas are characterized by 600-700 mm of precipitation and a mean annual temperature of 15 degrees C. The mean PET reaches about 1500 mm/year, while the seasonal ET is 1200-1400 mm/year (Nimah, 1992). The Bekaa plain consists of fan deposits and a mixture of colluvial and alluvial material representing mainly deep, non-calcareous Fluvisols and Cambisols with some inclusions of Vertisols and Regosols (Darwish *et al.* 2006). Beside these soil types, North Lebanon has a dominance of basalt and derived Andosols. Agriculture in both areas is practiced mainly with field crops, fruit trees and vegetables.

Soil profiles were excavated in a grid system and described and sampled horizon wise up to the depth of 200 cm or to the water table depth whenever its level was shallower. The samples were collected starting from the bottom of the pit upwards, in order to avoid cross contamination. The soil samples were cleaned from roots and gravels, air dried, ground and sieved through 2 mm sieve. The soil physical and chemical characteristics were analyzed by methods adopted for the Middle East region (Ryan *et al.* 2001). Aqua Regia was used for the digestion of the soil samples for the determination of the heavy metal content in the soil of Bekaa Plain. Analyzes were carried out in the BGR-soil-laboratory, Hannover, Germany. The soil samples from North Lebanon were analyzed by particle induced X-ray emission (PIXE) in the laboratories of the Lebanese Atomic Energy Commission (LAEC). Both procedures were done after relevant ISO and IEAE methodologies and quality control. The level of soil pollution by heavy metals was evaluated using the criteria of Eikman and Kloke (2000). This concept considers three levels of soil contamination with HM: I. Non polluted soils with multifunctional land use, II. Slightly contaminated soils with restriction to use under leaf vegetables and, with increasing HM content, controlled suitability for technical crops, fruit trees and agroforestry, III (Table 1). Contaminated soils that need restoration. Spatial analysis and HM mapping were done using the universal kriging method with a matrix table of 5 m x 5 m resolution.

Table 1. Use- and “Site and Protection Group specific Land Use Options” oriented values for hazardous elements in soils in mg/kg

Land Use Group	BW*	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Multifunctional land use	BW I	20	1	50	50	0.5	40	100	150
Children’s Playground	BW II	20	2	50	50	0.5	40	200	300
	BW III	50	10	250	250	10	200	1000	2000
House and small gardens	BW II	40	2	100	50	2	80	300	300
	BW III	80	5	350	200	20	200	1000	600
Sports and Playgrounds	BW II	35	2	150	100	0.5	100	200	300
	BW III	90	5	350	300	10	250	1000	2000
Park and Recreation Area	BW II	40	4	150	200	5	100	500	1000
	BW III	80	15	600	600	15	250	2000	3000
Industrial and Business area	BW II	50	10	200	500	10	200	1000	1000
	BW III	200	20	800	2000	50	500	2000	3000
Agricultural Crops- Fruits and Vegetables	BW II	40	2	200	50	10	100	500	300
	BW III	50	5	500	200	50	200	1000	600
Non Agrarian Ecosystems	BW II	40	5	200	50	10	100	1000	300
	BW III	60	10	500	200	50	200	2000	600

BW* = Soil Value

Results and discussion

Results showed a relative accumulation of Cr and Ni in some areas of the Bekaa plain approaching the soil contamination value II. It is considered that the geology of the study area does not have lithologies that host mineralization that could have supplied those heavy metals (Khawlie, 1983). Thus, we can speculate that the main sources of pollution with heavy metals in Bekaa Plain could be manmade. But, we undertook soil sampling in altitudinal sequence within a distance of 7.5 km, starting from the Litani River banks (elevation of 750m) up to the summit of nesting hills (elevation of 1050m). Results showed a steady increase of HM from the plain towards the summit with significant difference between the slopes and foot slopes and plain (Figure 1). If we exclude the recent erosion-deposition process from the hills, such spatial distribution of HM in the agricultural plain might be due to human activities including fertilization, irrigation with contaminated waters and Pb emission from heavy traffic before the introduction of unleaded oil.

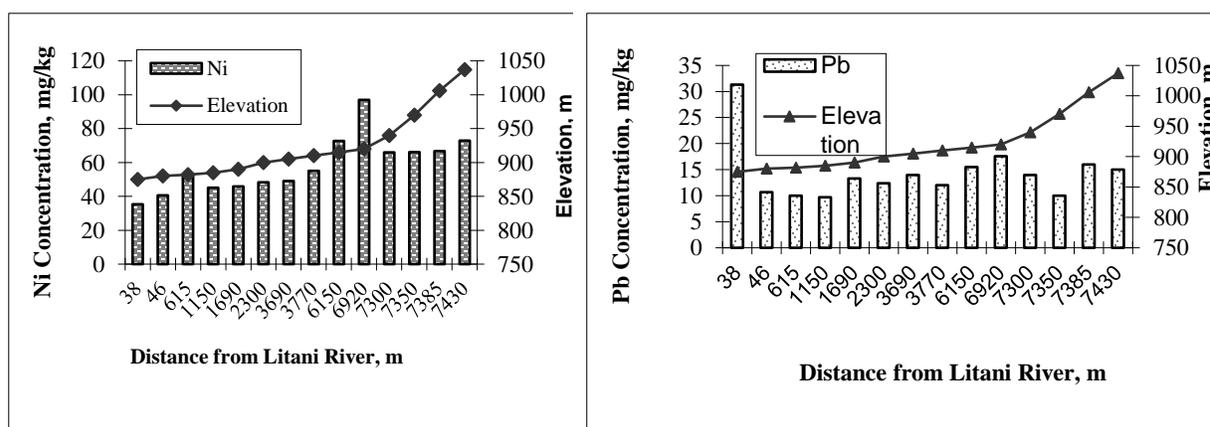


Figure 1. Spatial Distribution of Ni in the soils of Central Bekaa, Lebanon

Some areas of Bekaa plain showed an increase of HMs content on the soil surface by more than 50% for Co, Cr, Ni, Cu, Zn, and by more than 100% for Pb (Table 2). Other locations showed

increase of HM content in the subsoil (160-180 cm), implying that contamination was probably not due to migration. In this area, water table level was observed at 180 cm with sign of mottling throughout, implying higher mobility of hydrated forms of HM during the winter season.

The seasonal fluctuation of water table can bring these metals to subsoil, but need to monitor human activities, land use change and check whether there is a time-dependent variation in agricultural practices. Moreover, the issue should be related to the soil properties and soil-heavy metal-plant interaction.

Table 2. Distribution of heavy metals in the soils of Bekaa Plain, Lebanon

Area	Soil Depth	Zn	Pb	Cd	Ni	Cr	Cu	Water Table Depth
	cm	mg kg ⁻¹						cm
Saadnaeal	0-3*	147.0	21	0.28	29.7	40.0	30.7	180
	0-40	62.0	10.0	<0.2	33.7	43.3	17.0	
	40-85	62.3	9.7	<0.2	31.7	41.7	16.3	
	120-160	51.0	7.3	<0.2	34.7	43.0	15.0	
	160-180	84.0	14.0	<0.2	53.0	79.1	26.0	
Taalabaya	0-10	77.3	14.7	0.41	59.7	70.3	35.3	800
	10-70	79.7	16.7	0.41	60.7	71.3	35.7	
	70-92	63.3	8.3	0.48	46.3	57.7	24.3	
	92-150	51.3	7.0	0.39	39.7	48.3	20.3	
	150-200	41.0	5.3	0.32	30.7	35.7	15.3	

* Superficial sediment on soil surface after irrigation with non-treated sewage water

The pH of the soils is neutral and the temporary anaerobic conditions can affect HM mobility. The concentration of As, Cd, Hg, Pb and Zn in the surface horizons was explained by the rotation of vegetation, atmospheric deposition and their adsorption by the soil organic matter (Duchaufour, 1977). Elements found concentrated in the lower horizons of the soil profile, under positive water balance and downward percolation regime, tend to be associated with accumulations of the leached clays and hydrous oxides. Some soil units of the Bekaa Plain show uneven distribution of HMs with depth, probably due to the origin of the alluvial-colluvial material forming some Fluvisols and Regosols. The relative increase of Cr and Ni, detected by Oulabi *et al.* (1999) in some Lebanese springs and sediments could support the natural enrichment of rocks with these HMs.

The soils of the North Lebanon showed a prevalence of the levels of some HM exceeding the contamination level III. The soil groups derived from volcanic rocks and soft limestone showed the highest background level of Ni found in topsoil (Figure 2). An average of 190 ppm with highest values reaching 280 ppm (more than contamination level III) is recorded which is in agreement with the high average value of Ni in basaltic igneous rocks. Soils derived from quaternary deposits are enriched with nickel showing the highest values reaching 321mg.kg⁻¹.

The absence of systematic difference in the distribution of zinc background and highest values suggest a possible dependence on application of fertilizers and pesticides as well as possible use of sewage sludge on arable lands. Indication on higher Zn and Cu accumulation in arable lands was associated with the application of animal manure, fungicides and fertilizers (Kabata-Pendias and Adriano 1995). Both Quaternary arable lands and soils developed from hard limestone in North Lebanon showed no lead in many samples. This supports the anthropogenic emissions as the primary source of lead. Similarly, the absence of arsenic and its main occurrence as scattered

point source of contamination supports the hypothesis of the application of poultry manures as As is added as chicken growth promoter.

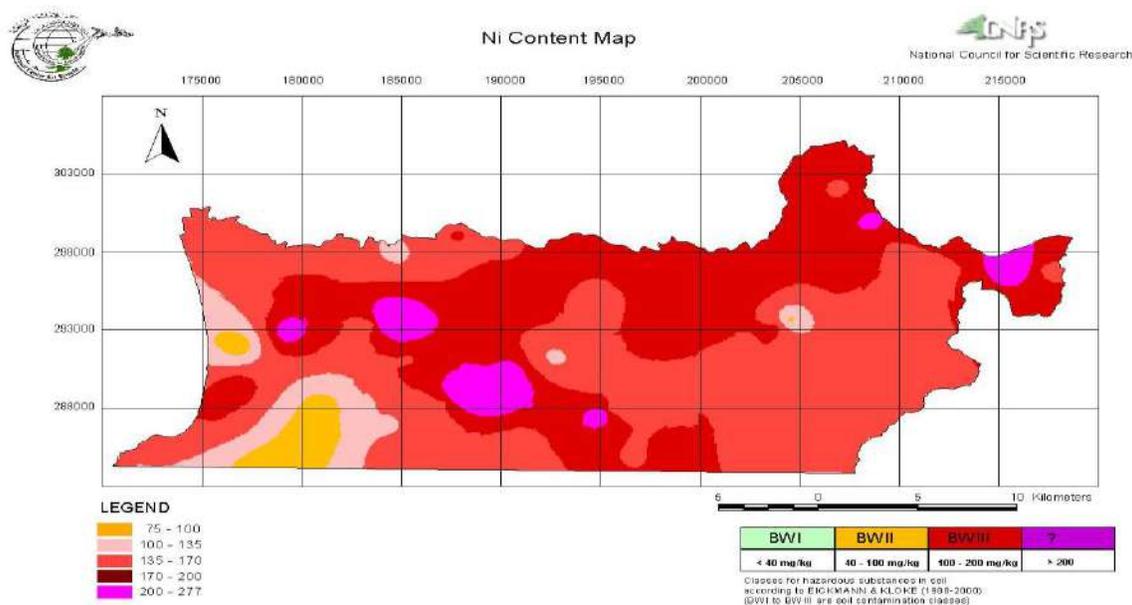


Figure 2. Nickel content (mg kg^{-1}) in the topsoil of North Lebanon

Conclusion

The occurrence of heavy metals in cultivated soils are derived from different sources through rock weathering and their accumulation can be caused by pedogenic processes as well as intensive fertilizer application and use of non-treated sewage water, containing industrial waste, in agriculture. These factors are determining the background value and threshold values detected in Lebanese soils. Human activities are the main factors contributing to additional soil contamination and probable pollutants transfer to ecosystems. Linking soil quality with soil physic-chemical properties suggests the creation of adapted soil thresholds for heavy metal pollution in arid and semiarid zones. Such approach can provide relevant information for decision makers and landowners for suitable land use to reduce and omit public health and environmental risks.

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1.1.6. Geochemical and anthropogenic factors of variability of heavy metals content in the soil of Ukraine at the example of copper

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Abstract

It was established that the spatial distribution of the content of the available forms of copper in the upper layer of soils in Ukraine varies greatly and almost does not depend on the type of parent rock and type of soil formation, but is determined mainly by geochemical and anthropogenic factors. The activities of powerful industrial enterprises, such as the coke industry, lead to excessive accumulation of heavy metals, in particular copper, in soils and increase their absorption by plants.

Keywords: soils, heavy metals, copper, available forms, spatial distribution, technogenic contamination

Introduction, scope and main objectives

Under natural conditions, the content of available forms of heavy metals (HM) in the soil varies considerably and is determined mainly by the peculiarities of the geological structure of the territories and soil properties - their granulometric composition, pH value, the content and qualitative composition of the organic matter, the oxidation-reducing potential, and others. Today, for industrially developed areas, man-made sources of HM inflow to soil are much more dominant than their natural sources (Liang J. *et al.* 2017, Sahraoui H. *et al.* 2016). Waste disposal and industrial activities are the most important sources of soil contamination overall in Europe. The most frequent contaminants are heavy metals and mineral oils (FAO 2015). The main drivers of man-made masses of the HM for the environment are also interconnected energy, chemical and metallurgical industries (FAO, 2014, Rodríguez-Bocanegra *et al.*, 2017, He *et al.*, 2015). The result of such plants is the inflow into the atmosphere of a large number of gaseous pollutant emissions, based on sulfuric anhydride and oxides of HM. An example of the risk areas in Ukraine is Donbass and Central Podneprovye (Fatjejev and Pashchenko, 2003). Soil is the main receiver and accumulator of these substances, and anthropogenic pollution of the environment by HM mainly manifests itself in excess of the natural content of elements in soil and plants, violation of the patterns of their circulation, etc. (Kabata-Pendias, 2010).

Main objective is to assess the variability of the HM content in soils at the regional and local levels, due to various factors - natural and man-made origin, at the example of copper. Anthropogenic way of HM inflow into the soil is the territory that is exposed to atmospheric emissions from the Avdii'vka Coke Chemical Plant (ACCP), which is the largest enterprise in this direction in Europe.

Methodology

The research was carried out on the basis of the nationwide GIS "Microelements in soils of Ukraine", which was developed in the Soil Conservation Department of the NSC ISSAR. Soil samples were selected by an irregular grid with a georeferencing using a GPS navigator, taking

into account soil and lithological heterogeneity in different soil-climatic conditions. In total, samples of more than 3000 soil kinds of all administrative regions of Ukraine were surveyed and analyzed. Investigation of the spatial distribution of the content of available copper forms in soils in the zone of influence of ACCP atmospheric emissions (20-kilometer zone near the city of Avdii'vka, Donec'k region) was carried out according to the rhumbs taking into account the *wind rose* with a georeferencing using a GPS navigator. There were taken the samples of test plants into a phase of full ripeness of crops simultaneously with the soil sampling.

Determination of the content of available copper compounds in soils was carried out by extraction with ammonia-acetate buffer solution at pH 4.8 for one hour on a rotator with a ratio soil: extractant - 1: 5. Determination of the copper content in plants was performed by dry ashing at 550 ° C for 5 hours and subsequent dissolution of ash in 10% HCl. The instrumental completion in both cases is atomic absorption with flame atomization of a mixture of acetylene/air. Statistical processing of the results was performed using the programs Statistica 10 and MapInfo 11.0.

To determine the status of territories by the content of available forms of Cu in soils, appropriate gradations were used: less than 0,5 mg/kg - low content, which is unfavorable for the growth and development of agricultural crops; 0,5 – 3,0 mg/kg of soil - the normal content of this element, more than 3.0 mg/kg - exceeds the maximum permissible concentration (MPC) and causes the risk of excessive accumulation of copper in plants. The hygienic suitability of crop production was also determined by the MPC, which is 10,0 mg/kg of absolutely dry matter.

The geostatistical method of research - kriging (statistical version of interpolation) was used for constructing of maps. The soil maps of Ukraine with different scale - from 1: 2 500 000 to 1: 200 000 and 1:10 000 - were used as a cartographic basis. The classification of spatial data was carried out by grouping the numerical values of one attribute (Cu content).

Results and discussion

The differentiation of the soil cover of Ukraine with the content of the available forms of copper is uneven. Its high content is observed in Gray forest soils and Podzolized soils of the Western and Left-Bank Forest-Steppe - up to 2,0 and 1,8 mg/kg of soil (Fig. 1). Areas with high levels of copper are also allocated on Haplic Chernozems - up to 1,87 mg/kg, Sodpodzolic soils of Western Polissya (average 1,84 mg/kg), soils of the Carpathian region (0,40 – 2,52 mg/kg).

Areas of optimal content of available forms of copper are also present in the southern part of Ukraine, where Calcic Chernozems (up to 1,77 mg/kg) and Dark chestnut saline soils (up to 1,42 mg/kg) are common. However, the content of available forms of Cu in the most soils in Ukraine is less than 0,50 mg/kg of soil, which poses a certain risk of deficiency of this element in the crop nutrition and indicates the need to use copper-containing microfertilizers to prevent it.

Copper is an important element in the processes of synthesis of proteins and cereals, as a rule, react positively to its application. However, it should be noted that in Ukraine there are certain biogeochemical provinces with a high natural content of available copper, which exceeds the threshold value and poses the risk of contamination of agricultural products even under background conditions.

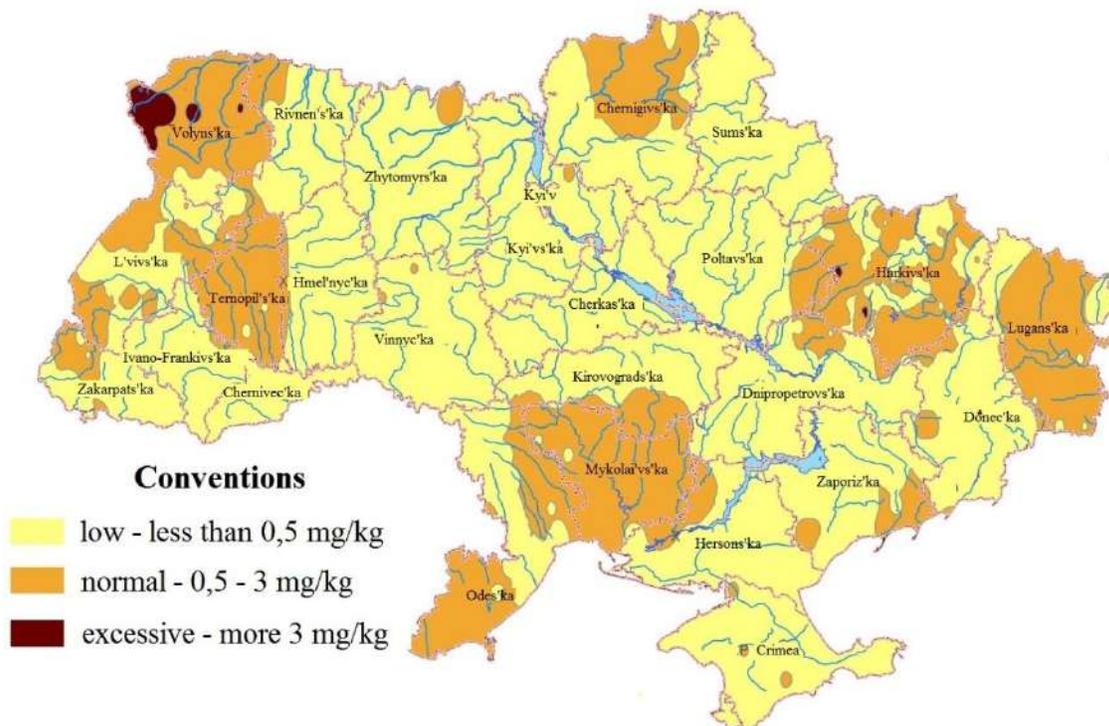


Figure 1. The content of available forms of copper in the soils of Ukraine (0-30cm)

An example of such geochemical anomaly is the western part of the Volyn' region, where the content of available forms of Cu reaches 8,3 mg/kg of soil, although there are no powerful industrial enterprises and widespread soils of light texture formed on ancient alluvial and fluvial-glacial sands.

Small areas of excessive content of available Cu in the soils shown in Figure 1 are primarily due to man-made pollution. It is known that in areas of industrial pollution, the availability of heavy metals and variation of their content in soils are significantly increased. There is also the danger of the HM accumulation by plants directly from atmospheric emissions, while the airborne inflow of harmful substances can substantially exceed their root absorption from the soil.

The activity of the ACCP has led to significant changes in the content of the available forms of copper in the soil, which indicates the significant impact of atmospheric emissions from the chemical industry on agroecosystems and the environment as a whole. The average content of available Cu in soils of the studied area is 1,59 mg/kg and varies widely - from 0,01 to 6,80 mg/kg, with the value of MPC of available forms of 3,0 mg/kg of soil. In more than 25% of soil samples, the content of available copper reached the limit value, or even exceeded it. However, despite the presence of areas of excessive Cu content, soil in about 8% of the investigated area contain not enough of this element (Fig. 2).

Excessive accumulation of heavy metals was characteristic not only for soils but also for crop production, which only emphasizes the need to control the state of the environment in areas where industrial and agricultural activities are closely interleaved. For example, the average amount of Cu accumulation in cereal grains is 6,67 mg/kg, varying from 0,54 to 18,3 mg/kg. Over 30% of plant samples in the studied area have excess copper content.

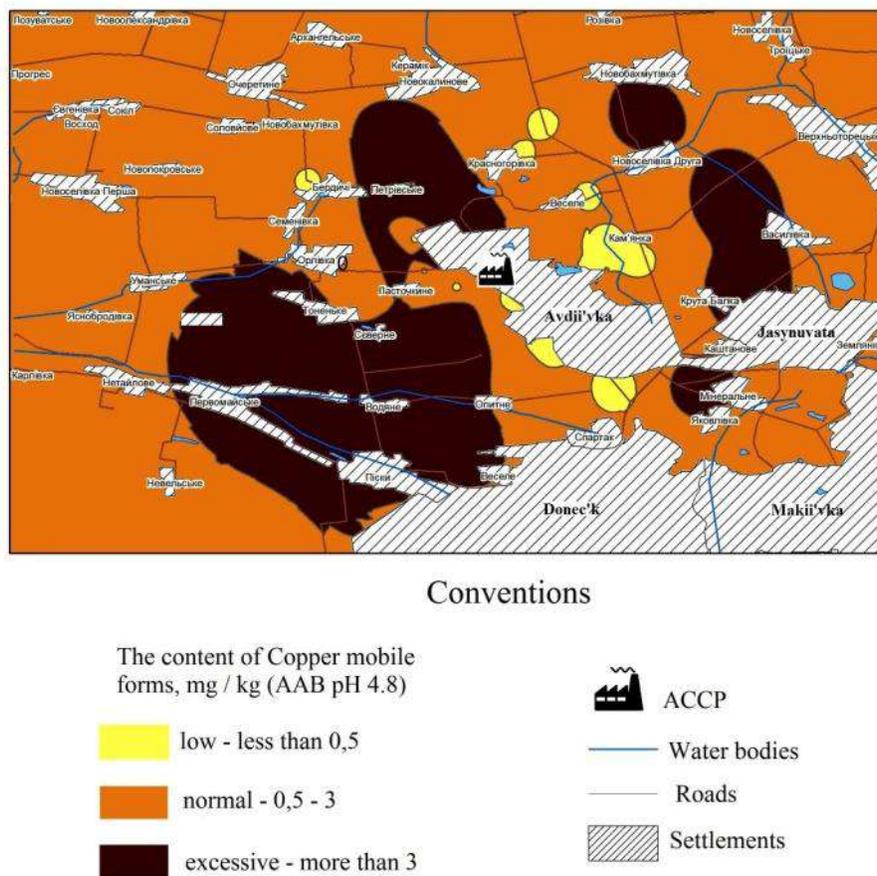


Figure 2. Content of available forms of copper in soils in the zone of ACCP influence (Donec'k region)

It is necessary to note the similarity of the location of areas of excessive Cu content in soils and plants, since it is known that the spread of man-made aerosols and their precipitation on the soil or plants surface depends considerably on the dominant wind directions and features of the terrain (Fig. 3).

However, the areas of agricultural products pollution are considerably inferior to the areas of soil contamination, because of the manifestation of the barrier function of Haplic Chernozems, which have a heavy granulometric composition, high content of humus and soil pH close to the neutral.

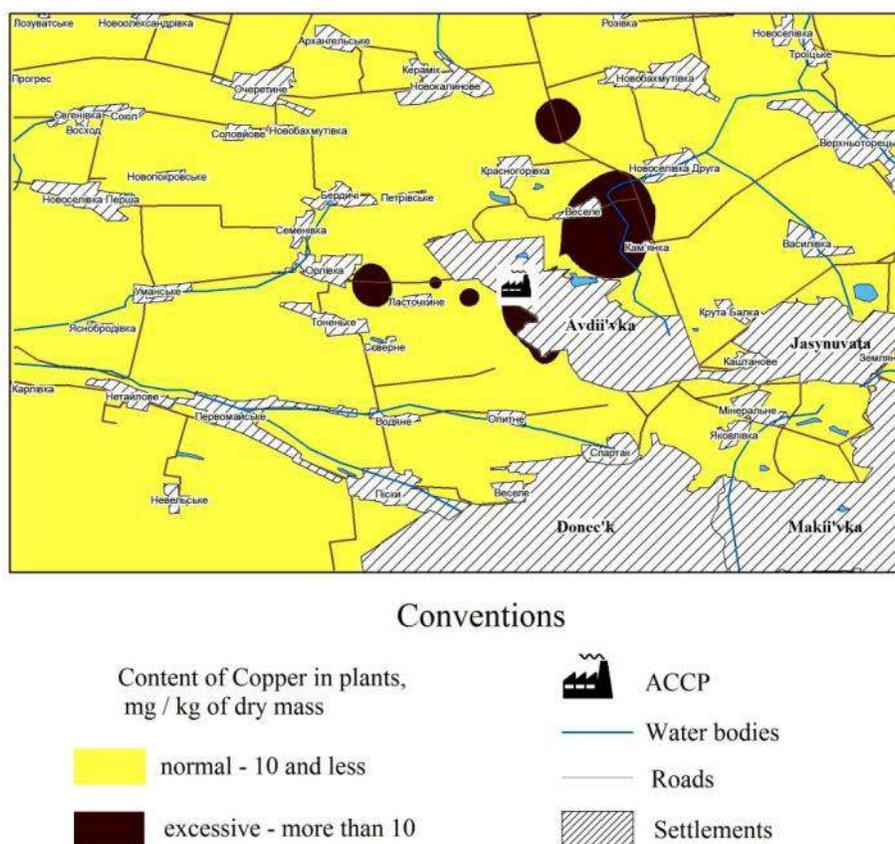


Figure 3. The content of copper in grain of cereal crops in the zone of influence of ACCP atmospheric emissions (Donec'k region)

Conclusions

There is a significant variability for available forms of copper in Ukrainian soils of farmland - their content varies from 0,01 to 8,30 mg/kg of soil. The presence of areas of excessive content of this element may be due to natural (geochemical, lithological) and anthropogenic factors. Areas of excessive accumulation of heavy metals in soils and plants near powerful industrial enterprises have a similar character, indicating a need to control crop production in areas where industrial and agricultural production are closely linked with each other.

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1.1.7. Soil pollution through agricultural, urban and industrial activities and its impacts on food production and safety, the environment and overall human health

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Abstract

Fundamental and field studies conducted have abundantly illustrated that while leaching of nitrate beyond plant rooting zone could be substantial in rice fields fertilized with fertilizer N (FN) in porous soils, integrated nutrient management (INM) could diminish the accumulation of NO₃⁻ in the soil profile and hence minimize potential nitrate leaching as organics act as slow release fertilizers synchronizing N supply with plant need. Long-term applications of fertilizer P (FP) could cause enormous movement of P to deeper layers in a coarse-textured soil having low adsorption and retention capacity for nutrients whereas INM reduces accumulation of labile P in soils as well as downward movement to deeper soil layers.

INM significantly reduced gaseous N losses as compared to the application of FN alone in rice-wheat system. INM through legume green manure (GM), crop residue (CR) and FN in different cropping systems has the long-term benefit of C sequestration and improved soil health resulting in high crop yields, help maintain balanced nutrients supply, check multi-nutrient deficiencies and sustain crop yields at a higher level. These studies demonstrated that adequate, balanced and integrated use of fertilizers and manures could minimize the soil and environmental pollution that influences the plant-animal-human food chain.

Keywords: Integrated nutrient management, legume green manure, organic manures, animal wastes, chemical fertilizers, crop residues, conservation agriculture, Biological Nitrogen fixation, Carbon sequestration in soils

Introduction, scope and main objectives

As in other parts of the world, the success story of green revolution of 1970-90 in India was due to the concerted efforts of agricultural scientists in developing high yielding crop varieties and improving production technology, expansion in irrigation facilities, availability of fertilizers and agrichemicals, provision of remunerative prices through a system of minimum support price and assured procurement by the government. The creative interaction among political leadership, agriculture scientists, and government departments related to the development of agriculture, a well-knit extension system, and the robust and enterprising farming community has played a key role.

However, the quantum-jump in production of various commodities has resulted in soil pollution through fertilizers and manures, urban and industrial activities, which has impacted food production and safety, the environment and overall human well-being in various ways. This paper gives a very brief account of large number of studies conducted in Punjab State of India on the impacts of (a) fertilizers and manures, (b) crop residues' burning in open fields, and (c) urban and industrial activities on soil pollution along with possible remediation options for such deplorable situations.

Environmental impacts of fertilizers and manures

Application of nutrients through fertilizers and manures in excess of crop requirements can increase both the cost of production and the risk of adverse environmental effects leading to human and animal health problems. If NO_3^- -N in the drinking water exceeds the safe limit of 10 mg l^{-1} , ingested nitrate is converted to nitrite that is absorbed in blood, causing methemoglobinemia, commonly known as 'Blue Baby Syndrome', and gastric cancer. In intensively cultivated soils of Punjab, where average fertilizer N consumption increased from 56 to $188 \text{ kg N ha}^{-1} \text{ year}^{-1}$ during 1975 to 1988, NO_3^- -N concentration in the shallow-well waters increased by almost 2 mg l^{-1} (Aulakh and Bijay-Singh 1997). In some central districts of Punjab, fertilizer N levels exceed $300 \text{ kg N ha}^{-1} \text{ year}^{-1}$ and on several farms, fertilizers are poorly managed (Aulakh and Pasricha 1997). In a survey analysis of groundwater samples from 21- 38 m depth, 78 % samples had less than 5 mg NO_3^- -N l^{-1} , and 22 % had 5 - 10 mg NO_3^- -N l^{-1} . Sixty percent of water samples from shallow (9-18 m) depths had 5 - 10 mg NO_3^- -N l^{-1} and 2 % samples had more than 10 mg NO_3^- -N l^{-1} .

Animal wastes appear to be the major contributors to high NO_3^- -N in groundwater under village inhabitations and feedlots. In Punjab, animal wastes are generally dumped near feedlots in the outskirts of villages. The level of NO_3^- -N in the water samples of 367 hand-pumps used in several villages of four districts and in 45 water samples collected beneath feedlots, was several folds higher than in 236 water samples of tubewells of adjoining areas, clearly illustrating that animal wastes and feedlots act as a point source of nitrates (Bajwa *et al.* 1993). The wide variations in NO_3^- -N

concentration in groundwater is attributed to variations in land use and management practices and unscientific disposal of animal dung and urine around dairy sheds.

Integrated and balanced application of N fertilizers could significantly reduce the amount of unutilized nitrates in the root zone and help enhance nutrient-use efficiency of crops. Decreased rate/amount, but increased frequency of irrigation water, in conjunction with a split application of fertilizer N, helps in minimizing the movement of NO_3^- N to deeper soil layers. In the predominant rice-wheat system of Punjab, application of recommended 120 kg fertilizer N ha^{-1} for each crop for 4 years resulted in 35 kg of residual NO_3^- -N ha^{-1} in the 150 cm soil profile over control whereas only 17 kg NO_3^- -N ha^{-1} remained where 120 kg N ha^{-1} was applied through the consecutive use of 20 t legume green manure ha^{-1} and fertilizer N decreasing potential for groundwater nitrate contamination (Table 1). Soil NO_3^- leaching to 60 cm in the rice crop was used by the subsequent wheat crop, which has a deeper and more extensive rooting system.

Table 1. Effect of integrated use of fertilizer N, legume green manure (GM), wheat residue (WR), and rice residue (RR) on yields, nitrate leaching, soil organic C, denitrification losses, and N_2O emissions in rice-wheat system (Aulakh *et al.* 2000, 2001a, 2001b).

Treatment		[†] Rice yield	[†] Wheat yield	[§] Nitrate Leaching	[§] Soil Org. C	Denitri. losses [#]	[#] N_2O emission
Rice	Wheat	(q ha^{-1})	(q ha^{-1})	(kg N ha^{-1})	(g kg^{-1})	(kg N ha^{-1})	(kg N ha^{-1})
Control		34.0	47.3	59	3.74	18	6.9
FN ₁₂₀	FN ₁₂₀	56.2	47.7	94	3.71	58	12.4
[†] GM ₂₀ + FN ₃₂	FN ₁₂₀	58.5	50.1	76	4.05	50	11.8
[†] WR ₆ + GM ₂₀ + FN ₃₂	FN ₁₂₀	59.2	50.1	-	4.92	52	11.8
FN ₁₂₀	[†] RR ₆ + FN ₁₂₀	56.3	50.0	-	4.33		
LSD (0.05)		2.4	2.1	12	0.22	6	3.4

[†]Amount of 120 kg N ha^{-1} applied through 20 t GM and the balance through fertilizer N.

[†]WR and RR applied at 6 t ha^{-1} ;

[†]3-year mean yields.

[§]Measured at the end of 4-year experiment; [#]Cumulative denitrification losses for rice-growing period.

Excessive accumulation of residual P in soil may enhance downward movement of P, which may eventually reach groundwater. Coarse-textured soils have large number of macropores and thus the resultant by-pass flow could lead to greater and deeper leaching of P in such soils. Besides the potential for groundwater contamination, P lost from agricultural soils through leaching may be intercepted by artificial drainage or subsurface flow accelerating the risk of P transport to water bodies with serious implications for water quality including eutrophication. Long-term studies where fertilizer P has been applied in different rates, frequencies and periods have revealed possibility of P leaching especially in coarse textured soils. After 29 years, 45 to 256 kg of residual fertilizer P accumulated as Olsen-P ha^{-1} in 150cm soil profile (43-58 % below 60 cm depth) illustrating enormous movement of fertilizer P to deeper layers in a coarse-textured soil having low absorption and retention capacity for nutrients (Figure 1). Other studies with different cropping systems have further revealed that interplay between the fertilizer P management (alternative vis-à-vis cumulative P application, and optimal vis-à-vis excessive rates of fertilizer P in different crop rotations), amount of labile P accumulated in soil profile, and soil characteristics (silt, clay and Soil organic C) largely control the downward movement and resultant potential for P leaching in subtropical soils (Garg and Aulakh 2010).

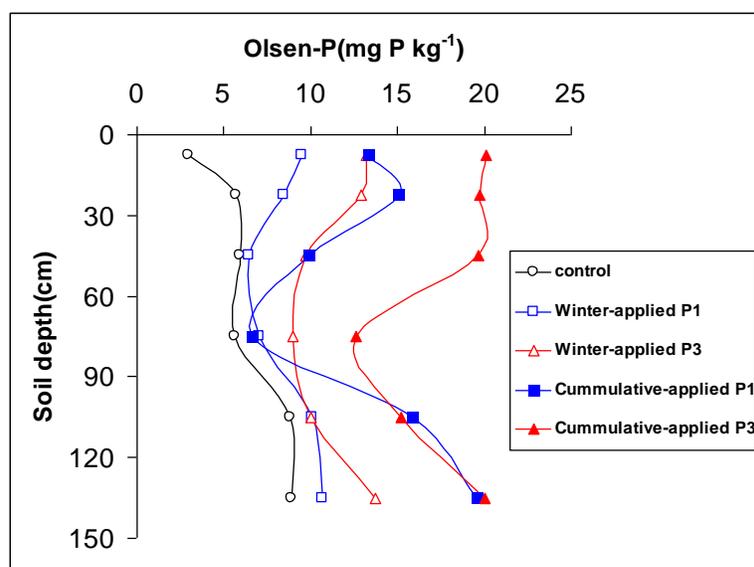


Figure 1. Olsen-P accumulation and leaching in soil profile of no-P control and four P treatments after 29 years of groundnut-based cropping systems. From Aulakh *et al.*, 2007. Fertilizer P was applied at optimal (P1) and super optimal (P3) rates either to winter crop only or to both winter and summer crops (Cummulative) each year.

Emission of greenhouse gases such as N_2O through denitrification and nitrification, CH_4 from submerged and waterlogged soils could be induced/enhanced by management practices (Aulakh and Adhya 2005). These gases are known to cause global warming; and in addition N_2O leads to destruction of stratospheric ozone layer that protects humans and animals from UV rays. In a field study at Ludhiana, denitrification losses during the rice crop were high varying from 23 to 33 % of applied fertilizer N (Aulakh *et al.* 2001b). While incorporation of wheat residue had no effect, green manure resulted in less denitrification (50 kg N ha^{-1}) than when $120 \text{ kg fertilizer N ha}^{-1}$ was used (Table 1). N_2O emissions from soil ranged from 20 to $60 \text{ g N ha}^{-1} \text{ d}^{-1}$ during the pre-rice period, 40 to $3440 \text{ g N ha}^{-1} \text{ d}^{-1}$ during the rice crop, 20 to $43 \text{ g N ha}^{-1} \text{ d}^{-1}$ during post-rice fallow, and 5 to $33 \text{ g N ha}^{-1} \text{ d}^{-1}$ in the wheat season. Rice-wheat system could emit 12 to $15 \text{ kg N}_2\text{O-N ha}^{-1}$ annually. Substantial amounts varying from 0.02 to $9.5 \text{ kg CH}_4 \text{ ha}^{-1} \text{ d}^{-1}$ were emitted from rice fields primarily during first half of the growing season (Aulakh *et al.* 2001c).

Impacts of crop residues' burning in open fields

Despite enormous benefits of the crop residues (CR), most of crop residues are removed and/or burnt in open fields after harvesting crops in India. In Punjab, for instance, about 70% of the total rice straw produced from combine harvest is burnt in the open fields. Similarly, after combine-harvesting wheat, 70% of wheat straw is converted to *bhusa* for animal feed and the remaining is burnt in the field. Unlike wheat straw, rice straw is not used as a cattle-feed because of high silica and oxalate content in it. Besides the loss of organic matter and plant nutrients, burning of crop residues also causes atmospheric pollution due to the emission of toxic gases like CH_4 , CO_2 , CO, and N_2O that poses a grave threat to human and ecosystem health. In the weeks following the rice harvest, flames and dense smog can be seen above the rice fields, which engulf the vast surroundings. However, the common justification advocated by the farmers regarding burning of crop residues are to: (i) ensure a quick seedbed preparation, (ii) get rid of the pest, diseases, mice etc., which harbor the residues and (iii) avoid risk of reduced crop yields associated with the incorporation of wide C:N ratio. Notwithstanding the validity of these contentions, and going by the pros and cons, blanket burning of crop residues can hardly be justified.

Several technologies have become available for managing the crop residues as plant nutrient resources. Mechanical difficulties in tilling residue-laden fields can be managed by using a straw chopper and spreading the residues as evenly as possible.

The benefits of sequestering soil organic carbon (SOC) for sustaining crop productivity with the application of organic amendments, CR and inclusion of legumes in crop rotations have been illustrated by several multiyear field studies. A 4-year study on rice-wheat system (Aulakh *et al.* 2001a), green manuring enhanced SOC concentration when no WR was added (Table 1). Incorporation of WR resulted in more C sequestered into SOM than with RR and GM. This was due to the wider C:N ratio WR (C:N = 94) than RR (C:N = 63), which was found negatively correlated to C mineralization. Depending upon the ease of mineralization as related to C:N ratio of added organics, 6 to 21% of added C was sequestered into the soil. Thus, INM through GM, CR and FN in a rice-wheat system have the long-term benefit of C sequestration resulting in high crop yields.

Appropriate reduced or conservative tillage technology while retaining crop residues on the soil surface has shown encouraging results. In a recent field study with soybean (Aulakh *et al.* 2017), where biological nitrogen fixation (BNF) was estimated using ^{15}N dilution technique and ^{15}N natural abundance methods, the irrigated soybean could biologically fix N_2 ranging from 81-125 kg ha^{-1} (68-85% of total N uptake), depending upon tillage and CR management. Significant increases in BNF by soybean were recorded where CR was retained on soil surface of conservation agriculture, presumably due to better activity of rhizobia because of the relatively cooler rhizosphere environment. Thus, when soil moisture and other nutrients status in soil are favourable for the growth of host plant and *Rhizobium*, the intrinsic N-fixing capacity of legume crops enables them to meet the larger proportion of their N requirement.

Impacts of urban and industrial activities

Application of sewage sludge to agricultural soils, and irrigation of field crops with sewage water and untreated industrial effluents alone, or in combination with ground/canal water, are common practices worldwide and are also used in India, especially in the vicinity of large cities, as these are considered reusable sources of essential plant nutrients and organic C. However, some of the elements present in sewage water and untreated industrial effluents, could be toxic to plants and pose health hazards to animals and humans.

Large variations in the composition of sewage waters of industrial and non-industrial cities of Punjab have been reported. The concentration of potentially toxic elements was higher in sewage water of industrial towns of Ludhiana, Jalandhar and Amritsar, as compared with less or non-industrial towns of Sangrur and Abhoar (Singh and Kansal 1985). Analysis of industrial effluents revealed that, in general, Pb, Cd and Ni were in higher concentration in effluents of industries manufacturing metallic products as compared with textile and woolen industries. The chemical analysis of sewage-water samples collected from different locations of an open drain, commonly known as Budda Nullah, downstream from entry into Ludhiana city, revealed that the concentration of metals in the drain increases many folds as it passes through Ludhiana city. This is because the number of industries pouring their untreated effluents increased as the distance downstream increased. This implies that the open Budda Nullah drain, which is a natural fresh-water stream before its entry into Ludhiana city, turns into a highly polluted sewage channel when it passes through the interior of the city, receiving effluents from various types of industries on its way.

Dheri *et al.* (2007) further showed that the concentrations of Pb, Cd, Ni and Cr were not only significantly higher in water samples of Budda Nullah drain but also in those collected from shallow hand-pumps located within 200m from the drain, as compared with deep-tubewell water. The influence of urban and industrial effluents released into Buddha Nullah sewage drain on groundwater (hand pump and tubewell) pumped out for drinking purposes and irrigation was also observed by Soni *et al.* (2008). The concentrations of Pb, Cr, Cd and Ni in these groundwater samples were higher than the maximum permissible levels of drinking water standards. The water samples of all the hand pumps near *Buddha Nullah* showed the presence of coliform. In a similar study, pathogenic profile of 100 domestic-supply water samples, collected from Municipal Corporations and Councils of Ludhiana, Jalandhar and Patiala districts by Jairath (2005), revealed that the drinking water from tubewells installed in different municipalities contained several pathogenic microorganisms.

Khurana *et al.* (2003) found that mean concentrations of DTPA-extractable Pb, Ni, Cd, Zn, Mn and Fe in surface soils (0-15 cm) surrounding the densely industrialized city of Ludhiana, irrigated largely with sewage effluents, were 4.2, 3.6, 0.30, 11.9, 25.4 and 49.2 mg kg⁻¹ as compared, with 2.8, 0.40, 0.12, 2.1, 8.3, 10.9 mg kg⁻¹, respectively, in the soils around less industrialized city of Sangrur, indicating greater loading of soils of Ludhiana with potentially toxic metals through sewage irrigation. Marin (2011) observed that application of sewage sludge to agricultural soils for two consecutive years enhanced the concentrations of Pb, Ni, Cr and Cd in surface and sub-surface soils at Punjab Agricultural University, Ludhiana. There was movement of Pb, Cd, Cr and Ni from surface to sub-surface soil. Sequential fraction analysis of different heavy metals in sludge applied soils showed that the non-residual fractions dominated over the residual fractions of Cd, Ni and Pb in sludge-amended soils, suggesting that the continuous application of sludge for subsequent years leads to enhancing heavy metal concentrations in bioavailable pool making it hazardous for plants and humans. Thus, by considering both useful effects (nutritive and irrigation potential) and harmful effects, sewage sludge and water should be treated to meet some quality parameters before they are discharged to drains or used for irrigation of the agricultural lands.

Conclusions

Continuously increasing use of fertilizers, pesticides and other agrichemicals due to large-scale adoption of high-yielding fertilizer-responsive crops and varieties in India have led to gradual buildup of nutrients and toxic chemicals in soils and groundwater as well as enhanced the emission of greenhouse gases into the atmosphere. Secondly, untreated sewage of major cities and industrial effluents are disposed of on the agricultural land, which lead to the accumulation of heavy and toxic metals in soil, groundwater and plants. Thirdly, burning of crop residues, especially rice straw in open fields causes atmospheric pollution due to the emission of toxic gases like CH₃, CO₂, CO, and N₂O that poses a grave threat to human and ecosystem health. Thus, at present, the agriculture in India is both source of soil and environmental pollution as well as victim of environmental pollution.

Considering fast contamination of groundwater, soils and water bodies, there is an urgent need to draft and implement a road map for mitigating environmental pollution so that sustainable development is maintained with least disturbance to the ecosystem. As the population grows, stress on natural resources increases, making it difficult to maintain food security. Long-term food security requires a balance between increasing crop production, maintaining soil-animal-human health and environmental sustainability.

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1.1.8. Contamination of agricultural soil by highways in urban and peri-urban zones

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Abstract

Highways are major, open and dynamic sources of contaminants that present a risk to adjacent agricultural soils. Soils in urban and peri-urban zones are particularly at risk because of the greater density of highways and high traffic volumes. In developing economies, these soils support food production but also income generation by the urban poor. In addition, in more developed economies there is growing interest in urban food production. Soil contamination from highways includes metals, toxic organic pollutants and plastics. Transfer of contaminants from vehicle emissions as well as from vehicle and highway, wear is via airborne particulates and dust, splash and spray and runoff. Contamination is greatest within 10m of the highway edge but extends to > 50m. Reported levels of metals in soil adjacent to highways including As, Cd, Cr, Cu, Pb, Ni, Zn sometimes exceed thresholds above which there is a potential risk of harm to food production. Elevated levels of non-threshold carcinogens (e.g. polycyclic aromatic hydrocarbons (PAHs)) are reported for soil adjacent to highways, with significant attribution to highway emissions. Mitigation options include better vehicle design and performance, porous asphalt pavements, physical and vegetative barriers and better drainage. A priority is targeted soil monitoring to identify where highway contamination already presents a significant risk of harm to food production and to identify and assess trends in response to mitigation measures.

Keywords: Urban food, soil, contamination, highway, road

Introduction, scope and main objectives

Urban and peri-urban soils support food production. In developing economies, this production provides food but also valuable income, including importantly for women. The future strategic importance of this production to urban security is debated (Badami & Ramankutty, 2016) but it remains significant, including in the expanding mega cities. In addition, there is an increasing interest in multifunctional use of soil in urban environments of developed economies (Zasada, 2011), including for food production. However, highways pollute soils and this presents a risk to healthy food production, especially in urban and peri-urban areas where the density of road networks and high traffic volumes mean that more of the cultivated area is exposed to contamination. An additional concern is that highway pollution can be captured on leafy vegetables and transferred to the food chain at harvest. However, the focus here is on soil contamination. This review aims to describe this contamination and the risks it may present to soil for food production, highlight the need for targeted measures to mitigate these risks and describe some mitigation options. Firstly, highway contaminants are identified that may harm agricultural soil quality. Secondly, the pathways are described that transfer highway contamination to soil. Thirdly, observed levels of pollution in roadside soils are reviewed with a preliminary assessment of the risk these may present to food production. Fourthly, some risk mitigation options are described.

Methodology

Relevant reviews and reports were identified using Scopus and Google Scholar, focusing on work published since 2007. Key words used were “highway / road + soil + pollution” together with a descriptor e.g. “metals” or “containment”.

Results and discussion

Highway contaminants and their sources

Table 1 summarises highway contaminants and their sources. Many studies have confirmed that levels of metals in roadside soils are elevated and decrease with distance from the highway and soil depth (e.g. Werkenthin *et al.*, 2014). The sources of these metals include vehicle emissions and wear components but also the highway itself, including wear of the highway pavement and road markings and corrosion of signage and other static equipment. Toxic organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs)) are present in vehicle emissions and also arise from the tar and bitumen-based materials used in pavement construction (e.g. Makiewicz *et al.*, 2017). Less data is available on the levels of pesticides introduced to soil by pavement and verge maintenance, although their use is ubiquitous. Highways are sources of plastic and rubber that may carry contaminants. Large quantities of rubber and plastic dust arise from tyre wear (Wik & Dave, 2009) while discarded plastic packaging and objects accumulate on roadside soils. Asbestos is present in some braking systems and may contaminate soil, but this is not confirmed. Runoff from highway pavements may modify adjacent soils and as runoff from highways tends to be alkaline (Kayhanian *et al.*, 2012), this can increase soil pH and lower the availability of some metals for plant uptake.

Highway surfaces also act as collectors for pollution dispersed from local and distant stationary sources. Wet and dry deposition originating from local sources (e.g. from local smelters or domestic heating) accumulates on highway surfaces and is eventually dispersed, including to roadside soils.

In summary, valuable food, production occurs on soils in urban and peri-urban zones. However, these soils are exposed to highway contamination, which is a hazardous and presents risk to soil quality for food production.

Pathways of highway contaminants to soil

Highways are open to the wider environment and highly dynamic. Contamination is dispersed to the surrounding environment via direct and indirect emissions to air and by runoff generated during storm events.

The three main pathways for transfer of contaminants to nearby soils are (Bohemen & Van Den Laak, 2003; Schipper *et al.*, 2007; Werkenthin *et al.*, 2014):

- (1) airborne transmission of particulate and aerosol that may reach soils in a zone reaching several 100m distant from the highway;
- (2) splash generated by traffic during rainfall events affects a zone extending to about 10m from the highway edge;
- (3) runoff - which will be contained within the immediate vicinity of the highway where the highway drainage is effective, but may flow across adjacent land when drainage is either inadequate, poorly maintained or overwhelmed during intense storms.

Splash and runoff offer an efficient pathway for most contaminants to reach agricultural soil, albeit this is mainly restricted to soil < 10m from the highway. Longer range contamination occurs via aerial transfer of fine particulate and dust and via the aerosol generated by traffic when the highway is wet.

Levels of highway contaminants in soil

Table 2 provides some illustrative data for levels of some metal and metalloid contaminants observed in roadside soils. Of course, the total metal content of soil includes a natural background contribution as well as that from highway and other sources of pollution. While most investigations have focused on As, Cd, Cr,

Cu, Pb, Ni, and Zn, other elements emitted by highways that may be hazardous to agricultural soils include Pt, Pd, Sb and V. The levels reported in table 2 fall above and below critical values set by different jurisdictions to indicate potential risk. For example, Finland has set threshold and lower guideline values for soil contamination (MEF, 2007). Exceedance of threshold values indicates a need to investigate potential risk, while exceedance of the lower guideline value indicates a requirement for action to mitigate potential unacceptable risk. The threshold and lower guideline values are as follows (as mg/kg): Cd (1 &10); As (5 &50); Cr (100&200); Cu (100 &150); Pb (60 & 200); Ni (50 &100); Zn (200 &250). Comparison of these values with the metal contents of roadside soils collated in table 2 indicates that the mean values are generally at or below the relevant threshold value. Nonetheless, the range of values for some metals likely exceeds the threshold values and there are some exceedances of the lower guideline value.

Table 1. Types and sources of contaminants from highways

Sources		Contaminants			
		Metals	Organics	Rubber and plastics	Other
Vehicles	Engine exhaust and exhaust system	Cd, Cu, Ni, Pb, Pd, Pt, V, Zn			
	Braking system wear	Cd, Cu, Sb, Zn			
	Tyre wear	Zn, Cd		Plastic (e.g. styrene butadiene styrate); vulcanised rubber	
	Fluid leakage (fuel, oil, hydraulic fluid, etc.)		Hydrocarbons, PAHs		
	Body and component wear	Cd, Cr, Cu, Ni, Sb, Zn		Plastics	
	Cargo spillage	Various			
	Contamination from elsewhere e.g. shedding of previously attached dirt				
Pavement and embankments	Dust from surface abrasion (e.g. bitumen, concrete); erosion of road markings	Cd, Cr, Pb, Zn	Hydrocarbons, PAHs, phenolics		Alkaline dust and leachate
Static equipment	Corrosion of signage, cables, etc.	Cd, Cu, Zn			
Maintenance and operations	Road marking (e.g. with PbCrO ₄ , ZnO and ZnS containing thermoplastics); de-icing; snow clearing; verge maintenance and weed control	Cd, Cr, Pb, Zn	Herbicides		Salt (possible CN ex anti-caking agents)
Litter and illegal waste deposits	Materials abandoned on highway and its verges			Various plastics	Paper, glass

A complex mixture of organic pollutants are present in highway emissions, including PAHs and pesticides (Markiewicz *et al.*, 2017). Data on the levels of pesticides in highway runoff is sparse and even more so for that in roadside soils. Table 3 provides some illustrative data for levels of PAHs observed in roadside soils. Source apportionment based on ratios of individual PAHs indicates that the PAH content of roadside soil is elevated significantly by highway emissions, as well as by background deposition and waste disposal. PAHs levels in road dust are much higher than those on roadside soil and transfer of this dust especially during rainfall events is likely a major candidate for the elevated levels observed in soil adjacent to highways, while aerial deposition of this dust and entrained PAHs will extend much further. The roadside levels presented in table 2 vary from <100 $\mu\text{g kg}^{-1}$ to in excess of 30,000 $\mu\text{g kg}^{-1}$. This compares with background median levels of PAHs in the range 66 to 720 $\mu\text{g kg}^{-1}$ in non-industrial areas in Europe (although individual data points range up to about 11000 $\mu\text{g kg}^{-1}$). Direct uptake of PAHs by plants is negligible, but indirect uptake in to the food chain occurs via transfer of PAHs in soil attached to harvested crops and ingestion by grazing animals. As some PAHs are non-threshold carcinogens, their elevated presence in soil used for food production is concerning.

Many millions of tonnes of natural rubber and synthetic rubber particles from tyre wear are emitted from highways annually (Wik and Dave, 2009). Concentrations of 600–117,000 mg kg^{-1} have been

found in soil immediately adjacent to the highway. Runoff is the main transfer mechanism and soil contamination may extend further from the highway when runoff is not captured successfully in drains. The toxicological risk to soil and plants of tyre wear products including related organic contaminants has not been explored much.

Table 2. Total metal contents of roadside soils

Location	Distance from highway (m)	Total metal content of soil (mg / kg)						
		As	Cd	Cr	Cu	Pb	Ni	Zn
China ^a	Not specified	10.18	0.43	58.87	31.17	37.55	27.53	117.72
Europe ^b	0-5		0.1 - 10.5	0.42 - 240.3	7 - 413	2.7 - 228	5.1 - 1769	25 - 1580
	5-10		0.39	9.98	15.05	40.6	9.9	179.5
	10 - 25		0.2	13.82	15.05	6.93	24.0	57.7
India ^c	5-10		0.5	21.2	20.7	5.9		360.3
Jordan ^d	1		1.0		19.1	177.0		129.0
	10		0.9		14.5	169.4		126.3
	25		0.8		10.1	149.8		122.0
Nigeria ^e	0-10		Not detected - 0.366	10.57-77.10	7.70-80.13	24-157.667	1.83-14.87	30.8-219.23
Russia ^f	6				72.2	120.1		170.7

^a Wei & Yang (2010). Mean values for roadside agricultural soils; ^b Wekenthin *et al.* (2014) - Range reported for 0-5m zone and median values for 5-10m and 10-25m zones; ^c Bhatti *et al.* (2018) - Mean values for roadside agricultural soils; ^d Alsbou & Al-Khashman (2018); ^e Ogundele *et al.* (2015); ^f Nikolaeva *et al.* (2017).

Table 3. Total PAHs contents of roadside soils

Location	No. PAHs	Total PAHs ($\mu\text{g kg}^{-1}$)
^a China (Shanghai)	19	Not detected – 34600 (mean 7770)
^b China (Shanghai)	16	3031 - 21932 (mean 7043.3)
^c China (Beijing)	16	Overall mean 583; branch roads' mean 1136
^d Germany & Poland	16	3047 - 29225
^e Mexico	16	54 - 1863 (mean 308)
^f Russia	13	668 - 1163

^aPan *et al.* (2010); ^bLiang *et al.* (2011); ^cZhai *et al.* (2018); ^dWawer *et al.* (2015); ^eGarcia-Flores *et al.* (2016); ^fNikolaeva *et al.* (2017)

Mitigation options

Soil contamination has been a minor consideration in impact assessments of highways. Attention has focused on economic benefits relative to environmental costs from e.g. noise, air pollution and truck movements. However, appropriate vehicle and highway design has potential for reducing soil contamination and deserves more attention where soil adjacent to the highway is used for food production.

Vehicle emission controls that are aimed at improving air quality will also reduce pollutant loadings e.g. of PAHs. The environmental performance of engines continues to improve and this is set to continue. Steps to remove older more polluting vehicles and ensure vehicles are well-maintained are being taken in many countries to reduce air pollution and this will also help to protect soils. Electric vehicles are less polluting, but continue contamination from vehicle wear, including of tyres. Highly toxic materials e.g. As, Cd, need to be eliminated from vehicle components to protect soil as well as the wider environment and general public health.

Highway design should aim to minimise the transfer of contamination to roadside soils during storm events (Bohemen & Van Den Laak, 2003). Splash and spray is less when the highway pavement is porous asphalt (Ahmad *et al.*, 2017) and not sealed bitumen or concrete, because less water pools on the road surface. Moreover, percolation of water through the asphalt removes contaminants. Efficient drainage ensures that surface water runs off quickly, again reducing splash and spray. And the overall highway drainage system needs to be adequate as well as efficient: uncontrolled runoff to the surrounding land is an important pathway for contaminants to reach adjacent land being used for food production. Especially on branch and more minor roads, drainage systems may be basic and rely on runoff draining to neighbouring land without concern for soil contamination. Designs that incorporate Sustainable Urban Drainage Systems (SUDs) can be effective in containing water and act as sinks for contaminants (Leroy *et al.*, 2016), but consideration should be given to the potential for longer term contamination of soil resources, particularly if these SUDs are poorly maintained.

Ditches, vegetation and fences can provide barriers to transfer of pollutants from highways to adjacent land (Gallagher *et al.*, 2015; Abhijith *et al.*, 2017). And these barriers should be useful to prevent food production close (e.g. < 2m) to the highway because soil contamination reduces with distance from the highway edge. Well maintained ditches will intercept runoff and splash. Physical barriers improve air quality and reduce noise pollution, but will also intercept airborne contaminant transfer to soil. Vegetation can be similarly effective, if planting is of the right type, density and width. Ideally, the highway design will combine ditches, fencing and vegetation to provide an effective pollution barrier.

Maintenance operations such as road sweeping can remove potential contamination, but only if the waste material is removed for off-site treatment and disposal rather than being deposited on the highway verge.

Critically, most highway contaminants are cumulative in soil e.g. metals, non-biodegradable plastics, or they have long half lives in soil e.g. PAHs. Although there are many research studies of soil contamination by highways, there is little systematic and ongoing monitoring of soil in agricultural use close to highways in urban and peri-urban settings. This is an essential requirement to inform measures that may be needed to protect the environment and public health. As a starting point, soil adjacent to highways that is already severely contaminated and for which formal risk assessment shows a significant risk to healthy food production needs to be identified and appropriate actions taken, which in the extreme may include prohibition of food production.

Conclusions

1. Urban and peri-urban food production is affected by highway contamination of soils. This production is significant and the risk to it from highway contamination deserves more attention.
2. Soil contamination by highways is complex and includes As, Cd, Cr, Cu, Pb, Pt, Pd, Ni, Sb, Zn, toxic organic pollutants e.g. PAHs and pesticides, rubber and plastics.
3. The transfer of contamination from highways to adjacent soil occurs mainly via airborne particulate and dust transfer, splash and aerosol drift and runoff, with soil within 10m of the highway edge being highly contaminated although some contamination extends out to > 50m.
4. Levels of contamination in soil adjacent to highways have been measured that exceed thresholds for potential risk to food production.

5. More attention is needed to ensuring highway design, construction, use and maintenance minimises risk to soils used for food production. Porous asphalt surfaces, better drainage and barriers (fences, ditches and vegetation) can reduce contaminant transfer to soil.
6. Future monitoring of contamination in agricultural soils should include sampling of urban and peri-urban soils used for food production close to highways.

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1.1.9. Can microplastics leach to groundwater?

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Abstract

Plastic mulch are widely used in arid areas around world to reduce evaporation, decrease irrigation amounts while maintaining crop yield. Although effective as a water saving strategy an increasing amount of plastic residues are found on farm land. These plastic residues may degrade, and lead to the presence of microplastics (MP) in the soil of mulch covered farmland. The consequences of MP presence in the soil are largely unknown as most studies on MP pollution focus on aqueous systems. Huerta (2017) and Rillig (2017) found that biogenic activities, such as burrow formation by earthworms, affected MP distribution and degradation in soil environment. Earthworm activity promoted MP transport into deep soil layers. Incorporation of MP in deeper soil layers raises the question if MP can potentially pollute groundwater, either aided by biogenic activity, or simply by water transport through the soil. According to this, a laboratory experiment was designed which aims to indicate whether MP (Polyethylene) in soil columns will be transported and leached out with and without earthworms (*Lumbricus terrestris*). The laboratory experiments were designed with four treatments and each treatment had eight replicates: (T1) sandy soil and MP, (T2) sandy soil and MP mixed with dry litter on surface, (T3) sandy soil, dry litter on surface with two adult earthworms in each column, (T4) sandy soil, MPs with litter and two adult earthworms in each column. Preliminary results of these experiments will be presented.

Keywords: Plastic mulch, microplastics, soil, groundwater pollution, biogenic activities.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.1.10. Erosion as a pollution factor of agricultural soils with copper compounds

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Abstract

The results regarding content and forms of copper compounds in Gray forest eroded and diluvial soils of different agricultural uses showed that erosion is an important factor that is enhanced by the influence of anthropogenic influences and affects the distribution and transformation of copper compounds. With increasing of erosion degree, the share of copper mobile forms in soils, and copper compounds with organic matter and primary minerals decreases; the share of acid-soluble compounds of Cu and, Cu forms in the composition of oxides and clay minerals increases. Erosion processes enhance geochemical interface of landscape elements due to intense surface solid and liquid runoff. The average Cu losses constitute in low-eroded soils of 14-29%, in moderately eroded - 27-39%, in heavily eroded soils - 33-50%. Erosion processes are more pronounced in plowland and vineyard slope, less in the grassing field slope. In non-eroded, low-eroded and diluvial soils of the vineyard slope, the organic matter belong to the leading place in Cu bonding; in moderately and strongly eroded soils - clay minerals. Thus, the main amount of imported Cu is bound by humus, which is washed off during erosion.

Keywords: agricultural soils, copper, mobile forms, pollution, soil erosion.

Introduction, scope and main objectives

By its nature, gravity, complexity and implications, soil pollution through erosion has multiple negative consequences on the soil and the environment. The soil contains and receives, due to the agriculture chemicalisation, a large quantities of chemicals that differ in toxicity. The transfer of these substances, due to erosion processes is a serious danger, both in terms of destruction and pollution of the environment, and the degree of damage depends on the extent to which the chemicals are easily driven. Erosion is evident in large areas, and it is very difficult to develop environmentally effective and cost-effective measures to combat it. It follows that the traditional concept of erosion processes as a phenomenon of soil degradation is not sufficient to fully understand the problems.

In the Republic of Moldova, soil erosion is quite pronounced, which is facilitated by the dismemberment of the relief, the stormy nature of precipitation and the improper treatment of soils for many centuries. It manifests itself on 80% of the area (Константинов, 1987). Eroded soils cover most of the slopes. Only moderately and strongly eroded soils occupy about 30% of the territory. By capacity, humus reserves and nutrient elements of plants, productivity of agricultural crops, eroded soils have lost their initial fertility by 40-60% (Крупеников, 2008).

The aim of the research is to study the geochemical properties of soils of transit-accumulative landscapes with eroded soils and different agricultural uses. The main tasks included: - to determine the content of copper and its profile distribution in Gray eroded and diluvial (cumulative) soils, and the transformation of copper forms under the influence of erosion processes; - to establish the levels of chemical pollution and the ecological state of gray eroded and diluvial soils, as well as the degree of soil availability with microelement for plants.

Methodology

Gray forest soils were studied in three erosion-diluvial catena (chain) of different agricultural uses: arable land, vineyard (about 20 years), a 20-year-old grassing soil after a 7-year used under vineyard. All three catena are located on the slope of the south-western exposure, 2-10°, 800-1000 m long, the soil cover of the slope is represented by gray forest soils of all erosion degrees. The compounds of Cu in soils were determined by the atomic absorption method.

Results and discussion

Mineral and organic fertilizers, metal-containing preparations, various pesticides, irrationally used on sloping lands, are the most frequent sources of soil contamination. Soil pollution through erosion is demonstrated by the determination of copper content, forms and compounds in the soil of different agricultural use. Copper in this case is a pollutant of the vineyards soils.

The humus content in the surficial layer (0-7 cm) of Gray forest virgin soils reaches 7.5%, but in the next horizon (A₂) it decreases more than twice (2.8%). The agricultural Gray forest soils differ considerably in humus content from those - the arable layer (0-16 cm) contains up to 2% humus. The humus content in eroded soils is different and quite well correlates with the degree of their erosion.

The average of global forms content of Cu in Gray forest soils (0-40 cm) is Cu-25.5 mg/kg, mobile forms - Cu-0.35 mg/kg (Стрижова, 1967). When comparing the content of available forms of individual trace elements in different soils with their consumption by the main field crops, it is established that the majority of soils fall into the categories of lower and moderate insurance with copper (Leah, 2003).

The initial impact of the pollutant is tested by the surface humus horizon of the soils, which acts as a complex geochemical barrier that retains most of the contaminant. In the humus horizon A_p of the non-eroded soil on the plowland contains up to 26.5 mg/kg of Cu, in highly eroded - up to 17.7 mg/kg, which is below the average content for forest soils of Moldova. In the same horizon of non-eroded soil of the vineyard, the concentration of Cu reaches - 135.1 mg/kg, exceeding the average content by 5 times. The high content of Cu is due to the use of copper-containing preparations (Bordeaux liquid) for spraying the grapevine. With an increase in erosion degree of soils, the amount of Cu decreases, but the degree of contamination remains high - in strongly eroded soil it exceeds the average by 3 times (82.3 mg/kg).

Such concentrations of Cu are toxic not only for plants, but also for microflora: Cu and its compounds are part of the biochemically active pollutants group (Ковда, 1985). In the sod horizon (A_d) of the non-eroded soil of the 20-year grassing soil, the concentration of Cu reaches 78 mg/kg, in the low-eroded - 53 mg/kg, in the moderate-eroded - 47 mg/kg, in the highly eroded - 39 mg/kg. The concentration of total Cu in the lower horizons of eroded soils does not exceed average content for these horizons (Leah, 2014).

The total reserve of Cu in the upper horizons varies from 255 kg/ha in the vineyard to 42 kg/ha on the arable land. According to the degree of erosion, Cu reserves decrease along the slope and accumulated in diluvial soils. In them, the Cu content is almost the same as in the full-profile soils of the watershed. In diluvial soils closer to the bed of the girder, where flushing of the upper horizons is observed in connection with flood waters, the total reserve of Cu is less than in medium- and heavily eroded soils. When eroded, on plowland and vineyard, up to 14-16% of Cu

is washed away from poorly eroded soil, 27-28% with moderately and 33-39% with strongly eroded compared to non-eroded soil.

The amount of mobile Cu can be traced the same distribution character, as for the global content, in descending order: *the vineyard soil - the sod soil - the arable soil*. On arable land, in all eroded soils there is a lack of mobile Cu - 0.5 mg/kg and less, which can adversely affect plants and microorganisms. With a lack of Cu, the resistance of plants to fungal diseases and activity of enzymes oxidases decreases (Маринеску, 1987). The sod horizon of the non-eroded soil contains 4.0 mg/kg of mobile Cu, in the highly eroded - 1.3 mg/kg. In the vineyard the highest content of mobile Cu is noted in the arable layer of non-eroded soil - 22.0 mg/kg, and the lowest in highly eroded soil - up to 16.2 mg/kg.

When predicting the contamination of soils with copper because of its excess or deficiency, it is necessary to take into account the composition of pollutants, as well as the forms in which biologically active elements and their compounds are present in the soils. Accumulation in the upper horizons is a common feature of the distribution of Cu in the soil profile. This phenomenon is the result of various factors, but above all, the concentration of Cu in the upper soil layer reflects its bioaccumulation, as well as the current anthropogenic influence. The observed contamination of soils by Cu can lead to an extremely high accumulation of it in the upper layer of soils of vineyards and orchards (Grigeli *et al.* 1998).

The distribution of copper in soils, which is natural in a wide range, shows that in its initial state they are controlled by two main factors - the parent rocks and the soil-forming processes. The predominantly mobile form of Cu in surface media is a cation with a valence of +2, but other ionic forms may be present in soils (Кабата-Пендиас & Пендиас, 1989). Copper ions can be strongly retained in exchange positions on both inorganic and organic substances. All clay minerals of soils are capable of adsorbing copper ions from the solution (Lăcătușu, 2000). This is most pronounced in the sod and vineyard soils: in the surface layer, the proportion of Cu compounds with clay minerals increases with the growth of erosion (4.5-47.9% and 2.8-38.9% of global content). Non-eroded and slightly eroded arable lands contain 28.3% and 33.0% Cu of total content, medium- and heavily-eroded - 13.0%. In all soils, copper migration is observed with accumulation in illuvial and partly carbonatic horizons of soils.

The largest amounts of adsorbed Cu are always associated with Fe and Mn oxides (Lăcătușu, 2000; Ладонин, 2002). In all the soils of the sod and vineyard catena, erosion has led to a decrease in the Cu-oxide compounds. They range from full-profile to highly eroded soils in the upper horizon of the sod soils - 33.2-19.8%, vineyard soils - 12.6-1.3% of Cu from total content. There is a slight increase in the plowland: from 12.8 to 22.6% of Cu. In all soils in the illuvial and carbonatic horizons, 20-36% Cu with oxides are contained. The Cu fraction, enclosed in various mineral structures, has a high propensity to bind to immobile compounds, which are the most stable form in the soil. The compounds with primary minerals make up on the average about 30-40% of the Cu total content. Concerning this fraction, one must bear in mind that the methodology for its determination is far from being improved, so that the differences in the degrees of soil erosion are not always clearly visible.

The ability of organic constituents of soils to bind Cu is well known (Степанова, 1976). Many organic compounds form soluble or insoluble complexes with Cu, so the ability of soils to bind Cu or to contain it in dissolved form depends strongly on the amount and nature of the organic matter in the soils. In these soils, these compounds correlate well with the total content of humus in them. With an increase in the erosion degree, humus is lost, and with it, and Cu. The grassing of moderately and heavily eroded gray soils promoted the formation of an accumulative horizon with a high content of humus.

In the sod horizon of gray soil, the Cu content associated with organic matter is 4.1 mg/kg (5.3% of total content) in the full-profile soil. In the same soils of the vineyard, 10 times more (40.0 mg/kg or 29.6% of total Cu) are contained, due to the secondary application with copper preparations. The nature of the bond of Cu with organic matter in eroded gray soils depends on the erosion degree and agricultural use.

The organic matter is capable of forming stable complexes with Cu, when it is present in small amounts. Thus, on the non-eroded soil in the sod horizon, this fraction consists 5.3%, in the arable horizon of the plowland - 9.8% and vineyard - 29.6% of the global content. In highly eroded soils, the surface layer contains, respectively: 4.6-11.9-10.3%. A direct relationship between these compounds and the humus content is noted: with decreasing its content down the profile, their quantity decreases.

Although, the copper is one of the least mobile heavy metals in the soil, its content in soil solutions is large enough in all eroded soils, especially in the soils of the vineyard. Water-soluble copper compounds in the surface layer of non-eroded soil of the vineyard constitute 1.54% of the gross content. With the increase in the erosion degree, they decrease, and in highly eroded soil is 0.79%. In the upper horizons of eroded soils, arable land contains 0.3-0.4% (from the watershed to the highly eroded soil), sod soil - 1.12-0.57% of the Cu total amount.

Acid-soluble compounds make up in the upper horizons, from non-eroded to strongly eroded soils: 15-32% in arable land, 47-45% in vineyards land, 44-5% in sod (grassing) land. There is a decrease of acid-soluble Cu forms in the profiles of all soils.

As already noted, soil contamination with Cu compounds is the result of using copper-containing preparations. The study of the behavior of the Cu forms compounds in slope soils under different agricultural uses has shown that when it is introduced an increase in the fraction of readily soluble forms occurs, which is a source of pollution of Cu plants, and in some cases, of groundwater.

The most important in the soils contamination of Cu is the great propensity of the surface humus layer of soils to accumulate it. As a result, the Cu content in the eroded soils of the vineyard has grown to extremely high values, the threshold value of 100 mg/kg has long been exceeded. This applies not only to the soils of vineyards, but also to soils of orchards, etc. (Jigău *et al.* 2004). It should always be borne in mind that copper retained in the surface humus layer of the soil affects its biological activity and can become accessible to plants.

In the diluvial soil of the catena with arable land, the content of global Cu reaches a maximum at a depth of 65-100 cm in the buried humus horizon, which suggests the initial enrichment of this horizon with Cu compounds. It is also possible for it to bioaccumulate in this horizon, which contains up to 23.3 mg/kg, and in the surface layer 20.4 mg/kg. The diluvial soils, formed at the foot of the slopes with a sod (grassing) and a vineyard, copper contain in the surface layers 2 times less than in the same soil from the slope of arable land. The content of global Cu in these layers is 39.0 and 36.8 mg/kg. Beginning with the II layer, its content decreases sharply, even in the buried horizon A - the concentration of Cu is on the average 12-15 mg/kg. It should be noted its accumulation in the transition to carbonatic buried horizons, where up to 20 mg/kg of copper accumulates.

Compared to eroded soils, the diluvial soils are very poor in mobile forms of Cu. Traces of water-soluble forms of compounds in all soils are noted. Exchange and readily soluble forms of Cu were found in the diluvial soils of the slope - the sod and the vineyard, and the arable land - traces. In these soils, they form in the surface layers 1.0-1.5 mg/kg (4-7% of the gross content), and with depth they decrease.

Other compounds forms of Cu are also in smaller quantity than in soils of slopes. Most of all the Cu is in the composition of oxides and content 20-40% in the surface layers of soils, 34-60% in the humus horizon.

Conclusions

Erosion processes are more pronounced in plowland and vineyard, less in the grassing field. With increasing of erosion degree, the share of copper mobile forms, compounds with organic matter and primary minerals decreases in soils; the share of acid-soluble compounds of Cu and its forms in the composition of oxides and clay minerals - increases. The copper compounds entering in the soil undergo partial or complete changes under the influence of erosion. With erosion increase there is a redistribution and a slow process of converting readily available forms of copper into inaccessible or immobile compounds. This process was observed in the soils of all catena, especially in the upper soil horizons. The study of individual forms of compounds of chemical elements has shown that for anthropogenic, such as Cu, organic matter, oxides and clay minerals have a major role in their sorption.

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1.1.11. Irrigation: estimation contamination by heavy metals in "water - soil - plants" system

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Abstract

The accelerated marking of the ecological standards of permissible anthropogenic pressure on the agroecosystems and standards of ecological safety for the state service of monitoring and soil conservation is one of the ways of a solution of an ecological problem in Ukraine. The quality of water in irrigation agriculture requires of the special attention: the direction of soil processes and evolution of soils, rise and progressing of a degradation of processes depends on it. We have extended results of long-term observation by a composition of irrigation waters and direction of soil processes. Analysis of the international standards and regulations, long-term study of conduct of heavy metals in systems “ water - soil - plant ” and “water - soil - groundwater ” have allowed us to elaborate principles of rate setting, system of indexes of quality of irrigation water in order to the warning of its possible negative influencing on components of environment and on health of the population. With technogenic loading, the deterioration of the ecological condition of irrigated agro-landscapes is observed, which to increase the concentration of heavy metals in irrigated water, soils, their migration capacity and accumulation in agricultural products.

There was is created collection of normative documents, adjusting quality of irrigation water on ecological criterion's and allowing estimation contamination of irrigation water, irrigated ground and agricultural plants by heavy metals.

Our studies are not confined only to elaborating of indexes and rate setting of irrigation agrocenosis quality. We elaborated methods of improvement of quality and optimization of irrigation waters composition, that is including the introduction of ameliorants and adsorbents of different nature into the soil; soil flushing using special substances that increase solubility of compounds of heavy metals; phytomelioration; selection of crop resistant plants; bioremediation using microorganisms.

Keywords: heavy metals, irrigation, irrigation water, ecological regulation, soil

Introduction

At state level in many countries worldwide (and Ukraine as well) are coming up to understanding a necessity of undertaking urgent actions to prevent the global environmental crisis resulting from destruction, pollution and degradation of soils (FAO, 2015, National Program...,2015).

Much attention should be paid to monitoring the state of water and soil resources, assessing their quality status, balanced land and water use, environmental security as a result of the growth of the rate, extent and extent of land degradation.

The functioning of all components of the natural environment changes with the beginning of irrigation. We need to assess the quality of irrigation water, soils and plants to predict and prevent negative processes in them. Heavy metals are essential components of the system "water - soil - plant". When the content exceeds allowable, we consider them as hazardous contaminants. In this regard, the work related to the assessment of the water-soil-plant system quality is important.

The purpose of the research is estimation contamination by heavy metals in "water - soil - plants" system in irrigated agro-landscapes with technogenic impact, development of differentiated measures for detoxification of the soil-plant system).

Methodology

The research was conducted in Forest-steppe and Steppe zones of Ukraine, where the 98% irrigated lands are localized. The objects of our research were:

- Irrigation water: for irrigation in Ukraine are used basically water of main river arteries and created on their base water storage's and ponds. In zones Forest-steppe and Steppe - waters of Dnieper's and cascade of Dnieper's water storage's, Dniester's and others;
- Irrigated soils: the total area of irrigated lands in Ukraine is 2.1 million hectares, actually 0.5 - 0.7 million hectares are being watered annually the structure of topsoil irrigated lands is presented basically by chernozems (typical, ordinary, southern and meadow-chernozemic) and dark-chestnut solonetz soils;
- Agricultural plants, grown in conditions of irrigation (grains, vegetables, fodder's and technical cultures).

The main methods there were field, model, analytical and statistical research.

The content of available forms of heavy metals in soil was determined by atomic absorption method with extraction by acetate-ammonia buffer solution with pH-4,8 (DSTU 4770.1: 2007- 4770.9: 2007). The quality of irrigation water according to environmental criteria was assessed according to State Standard of Ukraine 7286-2012.

Results

The quality of irrigation water influences upon directivity of soil processes and evolution of soils, often bringing to development is soil-degradation processes - salinization, appearance solonetz, alkalization, contamination and other of degradation processes.

The main methodical approach to estimation of quality of natural water - experimental-expert estimation in system "water (irrigation) - soil - plant".

We have accumulated extensive material of quality indexes of irrigation water on characteristics of water and contents of materials, which negatively influence upon condition and functioning agroecosystems and components environment. Simultaneously the study of stability of soil systems and qualities of agricultural product was conducted. The complex analysis of data has allowed to proceed to standardization of irrigation water quality on ecological criterion's for the reason warning the possible negative influence upon components of environment and on health of population.

The arrival of heavy metals in soils and plant from atmosphere vastly increase. Irrigation water intensifies the danger of contamination them irrigated soils, grown on irrigated lands of agricultural plants and arrivals them in dangerous concentrations in organism of peoples. In this connection standardization of contents of heavy metals in irrigation water, irrigated ground and plants denominated in irrigated conditions there was exceedingly actual.

The analysis of the international standards and regulations has shown that in different countries of world is designed and act the standards on quality of irrigation water.

The following stage in development of standardization of contents of heavy metals in water for irrigation, soils and plants was concluded in study of behavior of metals in system "water (irrigation) - soil - subsoil water" and "water - soil - plants".

There were determined levels of heavy metals contents to irrigation water, irrigated soil and agricultural plants.

We have established:

- certain increasing of total concentration of heavy metals in irrigation water exists when change the conditions from Forest-steppe to Steepe, increasing an aridization of climate and mineralization of natural water. Such increasing in greater degrees characteristic of for the ponds, lakes, water storage's, to a lesser extent for small and middle rivers and not noted in water of large rivers (Dnieper, Danube). Increases the total concentration of heavy metals in irrigation water also in regions with high geochemical background (Donbas) and beside with large industrial enterprises with high emission of elements;

- contents of heavy metals in irrigated soils occurs according to the general geochemical zonality and is characterized the more high concentrations in soils of south Steppe in comparison with north Steppe and Forest-steppe. Local contamination of irrigated soils exists in industrial developed regions or in regions with high geochemical background. The priority pollutants are such elements: Pb, Cd, Ni, Cr. The irrigation intensifies the processes of migration (the redistributions) of heavy metals in soils and promotes more intensive their leaching from upper layer in lower;

- different levels of contents of heavy metals in irrigation water and soils influence on quality of agricultural product. Same heavy metals, which in the most degrees pollute soils and waters, can be accumulated in plants in concentrations above at most possible.

We can observe dependency in considered system "water - soil - plant" in size level of contamination and on composition of group of metals-pollutants.

Analysis of the international standards and regulations, long-term study of conduct of heavy metals in systems " water - soil - plant " and "water - soil - groundwater " have allowed us to elaborate principles of rate setting, elaborate indexes describing state of natural waters, of soils and vegetative

productions in conditions of irrigation agriculture at affecting of technogenical contamination's by heavy metals and to issue the Department normative document 33-5.5-06-99 "Water, soil and vegetative resources conservation's from contamination's by heavy metals in irrigation conditions".

Under "degradation of soils" we understand the natural and anthropogenic processes of worsening in the natural properties and regimes of the soils, which produce steady negative changes in their functions, decrease stability and fertility.

The estimation of the soil degradation is achieved with the method of comparison of the parameters of the soils, which are fixed in the initial period of observations, or standard soils with the same parameters after the corresponding periods of the soil using. The criteria of evaluation of the development of degradation processes are worked out on the basis of these observations, the levels of their ecological danger and unprofitability are determined, the preventive and straight anti-degradation methods of using the ameliorated soils are proposed.

We determine the degrees of degradation on the level of deviation from the optimum of the basic parameters of the soils, which are determining for the fertility formation:

- the soils without degradation: the soils, the properties and regimes of which are not worsened, which fulfill functions inherent in it, productivity corresponds its natural fertility (deviation from the optimum to 5 %);
- the soils with low degree of degradation: deterioration of properties and regimes, negative changes in the functions, reduction in the productivity do not exceed 20 %;
- the soils with average degree of degradation: the average degree of the manifestation of negative changes in the soil properties and regimes, functions, reduction in the productivity in the range 20- 50 %;
- the soils with strong degree of degradation: the strong degree of the manifestation of unfavorable soil changes in the soil properties and regimes, functions, reduction in the productivity are more than 50 %.

The effective control (monitoring) of the soils degradation include: 1) the systematic observation of state, properties, regimes of soils; 2) the analysis of the stability of soils to the diverse degradation processes; 3) the evaluation of the different types of the human economic activity, its positive and negative influence on the soil cover - impact-analysis; 4) the computer data bases creation and cartography; 5) forecast and prevention of the degradation processes.

In the result of our further work we received possibility to elaborate and to put into operation the National Standard of Ukraine "Quality Of Natural Water For Irrigation. Ecological Criteria" DSTU 7286:2012 (Effective from 01/07/2013). The standardization of heavy metals contents in irrigation water is organized in this document. The standardization quality of irrigation water quality on contents of heavy metals before put into operation National Standard of Ukraine DSTU 7286:2012 was not realized.

On ecological criterion's we distinguish three classes of water: 1 class - «suitable», 2 classes - «bonded suitable», 3 classes - «unsuitable». 1 class of water is applied without limitations. 2 classes of water is applied under condition of conducting control (monitoring) behind their quality and complex of agroamelioration actions under the warning of rise of the negative phenomenon in soils. 3 classes of water is not suitable for irrigation. A complex of agroamelioration actions in this case to apply economically and ecologically is not justified. Depending on the ecological and agro-

amelioration status of irrigated land, areas of further use of land in agricultural production are determined and measures are being developed to detoxify the soil-plant system. If the level of environmental degradation reached a high level, then the agricultural use of such land is inappropriate.

Nowadays, it is stated at the legislative level that degraded, technogenically polluted land whose use is environmentally hazardous, economically ineffective and does not allow ecologically pure products to be extracted from circulation and preservation (Articles 170, 172 of the Land Code of Ukraine, "Land Conservation Procedure", Approved by the orders of the State Committee of Ukraine for Land Resources (No. 175 dd. 17.10.2002) and the Ministry of Agrarian Policy of Ukraine (No. 283 dated April 26, 2013).

However our studies are not confined only to elaborating of indexes and rate setting of irrigation agroecology quality. We elaborated methods of improvement of quality and optimization of irrigation waters composition, that is reached in the process of their acids, calcium amelioration (gypsum, chalk decomposed by sulfuric acid, nitrocalcite etc.); actions on reduction of arrival of heavy metals in plants (heavy metals fixing by means of natural sorbents, mineral fertilizers, organic material; selecting the cultures and sorts and others). On the basis of analysis and generalization of the results of long-term studies, recommendations (Baliuk S.A. *et al.*, 2014) were prepared, in which the main measures (physical, chemical, biological) for reducing the toxic effect of the heavy metals in the "soil-plant system" are described, including the introduction of ameliorants and adsorbents of different nature into the soil; soil flushing using special substances that increase solubility of compounds of heavy metals; phytomelioration; selection of crop resistant plants; bioremediation using microorganisms.

A common chemical method is the use of adsorbents, for example, iron-calcium, calcium ameliorants, the positive effect of which is due to the formation of complex compounds, as well as the saturation of the soil absorb complex with calcium, which improves the physical and chemical properties of the soil. In the micro units, the detoxification of contaminated chernozem with the use of iron-calcium sludge of steel-wire production had a positive effect, which was manifested in reducing the content of available forms of pollutants in the soil, reducing their translocation in plants and increasing the yield of crops by 10-59.

For soils with a low degree of contamination it is expedient to use ecologically safe methods of detoxification of contaminated soils - biological, which are based on the use of the metabolic potential of biological objects, such as plants, microorganisms.

Phytomelioration measures include growing on contaminated soils of plants that can accumulate and carry a large amount of toxic substances with biomass, due to the significant content of specific cells that can bind metals, weakening their toxic effects and retaining the ability to reproduce other plant cells.

The advantages of this method are ecological cleanliness, safety of use, minimal impact on soil properties, low cost of application, but it is a long-term one. For the phytoextraction of heavy metals from the soil, it is possible to use both crops and wild plants.

Conclusions

Analysis of the international standards and regulations, the generalization of results long-term observation by a characteristics and composition of irrigation waters and direction of soil processes and quality of agricultural product have allowed us to elaborate created collection of normative documents, adjusting quality of irrigation water on agronomic and ecological criterion's and

allowing value contamination of irrigation water, irrigated ground and agricultural plants by heavy metals; methods of improvement of quality and optimization of irrigation waters composition, that is reached in the process of their acids, calcium amelioration and actions on reduction of arrival of heavy metals in plants. The designed criterion's and the indexes of quality have refilled normative basis of process ecologization of irrigation agriculture and receiving of non-polluting agricultural commodity in Ukraine. The main conclusions should be summarized here, and can also include recommendations or suggest application of the results beyond the study.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.1.12. Long term organochlorine soil pollution in agriculture: The lessons learnt from the Chlordecone pollution in French West Indies

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Abstract

The French West Indies face nowadays a diffuse and long term environmental pollution related to historical use of organochlorine insecticide in banana fields, Chlordecone (CLD). Due to its stability, it now pollutes soil, waters, agricultural products and leads to a global exposure of people and ecosystems. We wonder how to manage such a complex pollution system involving all environmental compartments, linked each other.

For that, we have been conducting research studies for more than 15 years in the field of agronomy and environment to explore the fate of the molecule in the environment, the impact on food safety, and also the remediation options. Three main points are addressed: i) how to characterize the pollution and to make easier the diagnosis? ii) how to assess the impacts on environmental compartments and agricultural products? iii) How to manage the pollution?

The tools we developed make a diagnosis of such pollution easier at different scales (field, farm, watershed, and territory). We built monitoring support systems for the water quality of rivers with models helping to understand variability of water contamination. We built also decision support systems to farmers to manage their soil pollution and choose the crops that will ensure food security. Now CLD content of local crop products on the market complies with the Maximum Residue Limit. Management is more complex for animal products, and further investigations are needed.

We investigated alternative solution to enhance CLD soil sequestration, using physical properties of French West Indies volcanic soil and organic matter amendment. Increased organic matter content in soil reduced drastically the CLD transfer from soil to water, but this effect was not perennial and amendment had to be regularly applied.

Our results show that an integrative approach is needed to build efficient policies to manage such pollution than to prevent new ones.

Keywords: soil and water pollutions, food safety, population exposure, decision support tools.

Introduction, scope and main objectives

Chlordecone (CLD) is an organochlorine molecule used in agriculture to fight against banana black weevil from the 70's to the beginning of 90's in Guadeloupe and Martinique (French West Indies). It has been applied as a powder around banana tree. Because of its poor solubility, its high affinity to organic matter and its high stability, CLD has been accumulated into soil compartment during around 20 years, inducing a long term and diffuse environmental pollution (Lesueur Jannoyer *et al.*, 2016). Now, it is polluting soil, waters, agricultural products and leads to a global exposure of people and ecosystems. Thus it led to a public health issue (Multigner *et al.*, 2016; ANSES, 2017).

Our team worked for more than 15 years in the field of environment and agronomy, to better understand CLD fate in the environment (diffusion, accumulation) and provide decision and support tools to manage the pollution, and ensure food safety. We worked at the border of various scientific disciplines. Our aim was to elaborate a holistic approach taking into account the different scales relevant for the pollution monitoring and management. Our aim was to answer some basic questions such as where is the pollution, what are the levels of CLD content in the environmental compartments, for how long the pollution will be observed and will impact the environment, and finally how to manage the pollution for soil, water, crops and animals to reduce the global population exposure to the pollutant?

We present here a set of work to illustrate the complexity of processes, levers and constrain to elaborate an efficient management and also the necessity to gather a wide range of disciplines to tackle all the mentioned above issues (Lesueur Jannoyer *et al.*, 2016). The objective here is to demonstrate how all these works contributed to the global management of CLD pollution and how they could be useful in the management of other agricultural pollution or prevent such situation.

Methodology

We developed specific tools according to the scale and the management objectives, with related publications for each of them, aiming to characterize the pollution state of the environmental compartments and the processes determining transfer between them.

To assess the field mean CLD content, we applied specific sampling methods and simulated the optimal sampling grid and number of samples at the field scale (Clostre *et al.*, 2014). We also studied the effect of ploughing on the CLD pollution profile in soils, analyzing the CLD content in the top soil layer (0-30cm) and in the soil horizon B (30-60 cm).

To assess the water CLD content and its spatial and temporal variations, we elaborated a monitoring system at the watershed scale and modelled the CLD transfers (Mottes *et al.*, 2016). Using spatial statistics, we simulated the spatial contribution of polluted fields to the river pollution and put forward the river pollution profile (Della Rossa *et al.*, 2016). This kind of work was useful to identify where the pollution was coming from and where to take priority management measures.

To assess the crop contamination, we analyzed the relationship between soil and plant CLD content as well as the contamination of different organs (root, stem, leaf, fruit) for different type of crops (root and tubers, cucurbits, salads, fruits, vegetable) (Clostre *et al.*, 2017). We also measured the capacity of absorption and the time exposure and contamination relationship for animals, especially poultry (Jondreville *et al.*, 2013).

As biological (Chaussonnerie *et al.*, 2016) and chemical (Legeay *et al.*, 2017) degradation was not efficient enough in our field conditions (anoxic conditions *vs* soil for agriculture), we thought about an alternative to enhance CLD soil sequestration. We tested the trapping effect of volcanic soil clays, allophane and halloysite, with the addition of 10% organic matter in soil and analyzing the CLD content in the soil water solution (Woignier *et al.*, 2013).

Results

To assess the mean CLD content in the soil of a plot, we proposed a systematic sampling grid, with at least 20 samples a plot (Clostre *et al.*, 2014) and 2 depths (0-30 cm and 30-60 cm). Soil pollution depends on the frequency and the depth of ploughing. Field with no tillage led to high superficial soil pollution, while deeply and frequently ploughed field led to the pollution of deep soil layers, with reduced/diluted CLD content. Modelling demonstrated that only slow transfer from soil to water was naturally occurring (Cabidoche, pers com) and more than one to five hundred years were needed, according to the soil type, to achieve depollution this way.

To assess and simulate the CLD content in the water of a river along time and according field location and practices, we used the WATPPASS model (Mottes *et al.*, 2015) at the watershed scale. We demonstrated that the CLD content in river was quite constant around year with a slight increase during dry period (Crabit *et al.*, 2016). This reflects that the main pathway for CLD transfer from soil to river was underground flow rather than surface transport (Charlier *et al.*, 2009; Mottes *et al.*, 2017). At the watershed scale, we also showed that whatever the plot location, the plot was contributing to the river pollution, and thus all polluted fields have to be considered to manage river pollution. CLD content in river varies also along the flow, with increasing values when crossing soil polluted area i.e. historical fields of banana. In the case of the Galion basin with polluted area mid-stream, this leads the CLD river profile to increase from upstream to mid-stream and to decrease from midstream to downstream (Della Rossa *et al.*, 2016).

To assess the crop contamination, we surveyed crops according to the soil CLD content, the field soil type and the type of crop. We identified three types of behavior for crops: roots and tubers that are very sensitive to contamination; cucurbits, sugar cane and salads that can transfer CLD to stem, leaves and fruits from a certain level of CLD soil pollution; and non-sensitive crops such as banana, fruit trees, pineapple and Solanaceae that are free of CLD whatever the soil pollution. We also elaborate a conceptual model of CLD transfer from soil to plant. A passive transfer and

decreasing gradient was observed from soil solution, root, stem, leave and fruit. For root and tuber, direct contact of the pollutant on the peel was also accounting for the CLD contamination, with a higher CLD content in the peel (Clostre *et al.*, 2015). We built a support system for farmers to help them choosing their crops according to the soil CLD content of their field and ensuring to fit with the regulation with crop CLD content under the Maximum Residue Limit (20µg/kg Fresh Matter) (Clostre *et al.*, 2017).

The management of animal contamination is more complex because first animals, as well as people, concentrate the CLD molecule in their body and second the farm practices led them to move from a field to another. Their CLD exposure comes mainly from the consumption of polluted soil and water. For example, poultry has a very efficient capacity to extract CLD from soil when they eat soil particle (Jondreville *et al.*, 2013). Thus even when the soil is slightly polluted, hens and eggs are highly contaminated. Animals have also the capacity to excrete CLD, but decontamination time is not realistic for poultry and livestock raising/animal husbandry constrains.

We also thought about depollution but, since nowadays biological and chemical solutions are not operational, we tested alternative option such as sequestration. Tropical volcanic soils have physical properties that allow sequestering high amount of Carbon and pollutant. We thus combined the CLD chemical affinity for organic matter and the structure and property of allophane clays to trap the pollutant (Woignier *et al.*, 2013). The addition of organic matter in soil reduce CLD leaching and increase the trapping effect, but the process is not a long term one and organic matter has to be re-added on the field (Woignier *et al.*, 2016).

Discussion

The different tools, soil sampling grid and depth of soil sampling, support decision for crop choice, are now used by framers, government services and authorities. Many of the management and sanitary recommendations are based upon our results: sampling, peeling generously the root and tuber, avoiding polluted soil contact for household poultry ... For more than 8 years, the majority of crops comply with the regulation with no marketed crop product over the MRL. But household products still expose people to CLD (ANSES, 2017), and deeper analysis is needed to adapt recommendations.

If now the situation of CLD pollution is quite well characterized, management is still an issue as pollution will persist and cross disciplines approaches are needed in the field of environment, agriculture and public health.

Conclusions

Our work tackled a complex and long term environmental pollution due to agricultural use of pesticides years ago. Thanks to focused efforts and interdisciplinary approach, we built numerous tools and supports systems to assess, monitor and manage CLD pollution. However, further studies are still needed to deepen the comprehension of transfer and degradation processes to improve remediation and depollution. Specific efforts are to be made to coordinate actions and elaborate a consistent management plan.

We built an expertise on this kind of diffuse and long term pollution. We applied our tools to simulate the fate and pressure of other pesticides used nowadays in agriculture. We wish this kind of approach and support systems could be useful to prevent such environmental pollution.

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1.1.13. Nutrient risk management using organic manures in radish production at Chitwan, Nepal

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Abstract

Nitrate leaching is a problem in medium textured Inceptisols of Chitwan district, Nepal. A field experiment was conducted in sandy loam soil of Agriculture and Forestry University, Rampur, Chitwan, Nepal from October 2016 to January 2017 to evaluate effect of different sources of organic manure in nutrient risk management. The experiment was carried out in a Randomized Complete Block Design with six treatments (Poultry manure, goat manure, FYM, biogas byproduct, recommended dose of fertilizer and control) replicated four times. Pyuthane Red variety of radish was used as a test crop. After analysis of primary nutrients of the organic manures, rate of manure was fixed on the basis of nitrogen content. The highest (49.41 Mg/ha) root yield was obtained from poultry manure application which was similar with recommend rate of fertilizer. The highest soil pH (4.722), moisture content (15.82), CEC (10.41meq/100g soil) and soil porosity (48.9%) and the lowest bulk density (1.191g/cm³) was obtained from poultry manure application. The highest organic matter content (1.01%) was observed from biogas byproduct application which was similar with FYM and poultry manure application. The highest infiltration rate (0.522 mm/sec) was obtained from FYM whereas the lowest was obtained from control plot. In 30 cm soil depth, the residual NO₃-N was highest (0.075%) from goat manure which was similar with poultry manure application where as in 60 cm soil depth highest (0.046%) NO₃-N was recorded from RDF which was similar with biogas byproduct and goat manure application whereas lowest (0.46%) was recorded from control which was similar with FYM and poultry manure application. The most of the soil properties were enhanced by application poultry manure and FYM. Furthermore, poultry manure played an important role in increasing nitrate nitrogen availability in upper depth and reduces the potentiality of nitrate nitrogen leaching to the lower depth. In addition, this study indicates the possibility of poultry manure application to enhance the physio-chemical properties of sandy loam soil of Chitwan.

Keywords: Leaching, nutrient risk, organic manure, radish

Introduction, scope and main objectives

Continuous and indiscriminate use of chemical fertilizer cause many soil problems which are loss of soil organic matter, degradation of soil structure, decreased surface infiltration of water, high runoff, leaching of nutrients and decreased soil micro-organism population (Jordhal & Karlen, 1993; Logsdon *et al.*, 1993) Agricultural lands are being degraded through depletion of soil organic matter, nutrient loss and imbalance, accelerated soil erosion, water logging and salinity in irrigated areas, degradation of soil structure leading to crusting and compaction of the surface soils, and decline in soil water and nutrient retention capacities (Lal, 2009). The control of soil erosion and loss of organic matter has been proposed as critical to nutrient risk management (Liu *et al.*, 2010). Sustainable nutrient risk management aims at maintaining or enhancing soil nutrients and crop production, reducing the level of nutrient risk, protecting the potential of natural resources and preventing the degradation of soil and water quality, while being

economically viable, socially acceptable and environmentally friendly (FAO, 1993; Schjonning *et al.*, 2004).

Most of the soil of Chitwan is sandy loam due to which nutrient depletion and drought related problems are the major risk factor. Sandy loam soils have low nutrient content, water holding capacity, cation exchange capacity, buffering capacity, soil aggregate formation and high infiltrability and hydraulic conductivity. Most of the rainfall occurs in rainy (>80% in June – Aug.) season and farmers face many drought related problems in other season due to low water holding capacity of sandy soil which becomes a great risk of nutrient leaching. Limited studies on the effect of organic manure on nutrient risk management on radish grown in sandy soil, as well as yield and productivity are reported for Nepalese conditions. Likewise, due to lack of sufficient knowledge and appropriate technology, Nepalese farmers are growing radish without the knowledge of optimum quantity of nutrient requirement by this crop. Therefore, the main objective of this study were to make safe soil environment via viable nutrient risk management option by determining the effect of different sources of organic manure on soil properties, nitrate retention capacity in correlation with radish yield.

Methodology

The field experiment was conducted at the horticulture farm of the Agriculture and Forestry University (AFU), Rampur, Chitwan, Nepal. The experimental site was located at 27° 37' North Latitude and 84° 25' East Longitude (Thapa and Dongol, 1988) at an altitude of about 228 masl. The experiment was set in a randomized complete block design with six treatments (Table 1) and four replications. The area of each plot was 8 m² (4 m x 2 m). As a test crop Pyuthane Rato variety of radish was planted in geometry PP x RR 30 x 20 cm. Recommended dose of chemical fertilizer 100:60:40 kg NPK/ha was incorporated in soil at the time of sowing. A full dose of P and K and half dose of N were applied as basal dose. The remaining 1/2 N was applied at 35 DAS during intercultural operation.

Table 1. Treatment description of the experiment

SN	Treatments	Rate of N applied through organic manure (kg/ha)	Amount of manure equivalent to N (kg/plot)
T1	Poultry manure	100	5.71
T2	Goat manure		21.32
T3	FYM		33.68
T4	Biogas byproduct		57
T5	Recommended fertilizer		173.91gm
T6	Control	0	0

The quantities of organic manures for the experiment were calculated on the basis of their respective nitrogen content (Table 2). Two fold increase in manure quantity for each plot as only 50% of nutrients was released from organic manure in first season of application (Brady and Weil, 2005). The required amount of organic manures were well incorporated in soil one month before seed sowing.

Table 2. Nutrient status of various organic manures.

Organic manures	pH	N (%)
Poultry manure	7.8	3.5
Goat manure	8	1.25
FYM	7.4	0.95
Biogas by-product	7.2	0.70

Note: Nutrients content in the organic manure was calculated on dry weight basis.

Biomass and root yield was calculated from 1 m² plot which is then converted into Mg/ha. Soil sample from field before sowing and after harvesting of radish was taken from two depth 0-30cm and 30-60 cm. Before research one composite sample from each block was taken. After the harvesting, soil samples were taken from individual plots and analyzed with standard methods (Table 3).

Table 3. Analysis methods for various soil parameters.

S.N	Parameters	Analysis methods
1	Soil pH	Digital pH meter
2	Soil moisture	Gravimetric method
3	Soil texture	Hydrometer method
4	Soil organic matter	Photo colorimeter method
5	Dry bulk density	Core ring method
6	Total nitrogen	Kjeldhal distillation
7	Nitrate nitrogen	Vernier probe
8	Available phosphorous	Spectrophotometer
9	Available potassium	Flame photometer
10	Cation exchange capacity (CEC)	

All data were subjected for normality test and found the data followed normality trend. F-test of the normal data carried out with the help of Genstat version 4. Duncan's multiple range test was carried out to separate means with 5% level of significance.

Results

Effect of organic manures on root diameter, root length and yield of radish

The highest biomass yield (75.16 Mg/ha) was obtained from poultry manure application which was significantly higher than other treatment but at par with RDF. Lowest biomass yield (26.91Mg/ha) was obtained from control plot. Highest root yield was obtained from poultry manure (49.41 Mg/ha) which is similar to RDF and significantly different from Biogas byproduct and control (Table 4).

Table 4. Effect of organic manure on root diameter, root length and yield of radish

Treatments	Yield (Mg/ha)	
	Biomass	Root
Poultry manure	75.16 ^a	49.41 ^a
Goat manure	63.20 ^{bc}	39.82 ^{ab}
Farm Yard Manure (FYM)	60.98 ^{bc}	40.64 ^{ab}
Biogas by product	55.97 ^c	34.75 ^b
Recommended doses of fertilizers (RDF)	70.88 ^{ab}	46.78 ^a
Control	26.91 ^d	15.28 ^c
Grand Mean	58.9	37.8
Sem±	3.86	3.15
LSD (0.05)	11.63	9.49
C.V %	13.1	16.7

Means followed by the same letter (s) in a column are not significantly different at 5% level of significance as determined by DMRT

Effect of organic manures on soil moisture content, soil pH, bulk density, particle density and soil porosity

Soil moisture content, soil pH bulk density, particle density and soil porosity was significantly affected by the application of various treatments (Table 5). At the time of radish harvest, moisture content of the plot treated with poultry manure was significantly higher than other treatments except biogas byproduct and FYM application. Poultry manure was superior to all the manure for holding highest moisture content (15.88%) which was followed FYM and biogas byproduct application. The lowest soil moisture content (15.03) was found in the control treatment. As compared with initial soil pH (4.45), application of organic manure increased soil pH but recommended fertilizer is responsible for decreased soil pH. Poultry manure was superior to all the manure for increasing soil pH (4.7) which was followed by biogas byproduct application (4.5). The lowest soil bulk density (1.191 g/cm³) was obtained from poultry manure application and it was significantly lower than other treatments except FYM. The height particle density (2.3 g/cc) was obtained from poultry manure which was significantly different from others treatments. Similarly, the highest porosity (48.90%) was obtained from poultry manure used which was similar with the FYM and biogas byproduct whereas the lowest (31.56%) porosity was obtained from recommended dose of fertilizer (Table 5).

Table 5. Effect of organic manures on soil moisture content, soil pH, bulk density particle density and soil porosity

Treatment	Soil moisture content (%)	soil pH	Bulk density (g/cc)	Particle density (g/cc)	Porosity (%)
Poultry manure	15.82 ^a	4.720 ^a	1.191 ^a	2.332 ^a	48.90 ^a
Goat manure	15.08 ^{bc}	4.505 ^{ab}	1.264 ^b	2.091 ^{bc}	39.43 ^b
FYM	15.60 ^{ab}	4.475 ^b	1.253 ^{ab}	2.75 ^{ab}	44.90 ^{ab}
Biogas byproduct	15.60 ^{ab}	4.522 ^{ab}	1.259 ^b	2.71 ^{ab}	44.43 ^{ab}
RDF	14.96 ^c	4.405 ^b	1.336 ^c	1.967 ^c	31.56 ^c
Control	14.19 ^d	4.475 ^b	1.396 ^c	2.296 ^{ab}	39.10 ^b
Grand Mean	15.21	4.517	1.2831	2.206	41.39
Sem±	0.2	0.0723	0.02134	0.0662	2.166
LSD (0.05)	0.6028	0.2178	0.06432	0.1997	6.53
C.V %	2.6	3.2	3.3	6	10.5

Means followed by the same letter (s) in a column are not significantly different at 5% level of significance as determined by DMRT

Effect of different sources of organic manure in soil infiltration

Soil infiltrability is not significantly influenced by the sources of organic manures. The highest (0.0448 mm/sec) infiltration rate was found in FYM treated plot. Whereas lowest final infiltration rate (0.0258 mm/sec) was obtained from control plot (Figure 1).

Effect of organic manures on CEC, OM and nitrate nitrogen of soil

Application of organic manure has positive effect on CEC, OM content and residual nitrate nitrogen in soil (Table 6). The highest (10.408 meq/100gm) cation exchange capacity was found in plot with poultry manure application which was similar with goat manure and FYM application.

Whereas lowest (7.950 meq/100g) CEC was recorded in control plot which was similar with RDF. The highest (1.01%) amount of OM content in soil was obtained from biogas byproduct application which was significantly higher than control, RDF and goat manure application but similar with FYM and poultry manure application. The lowest (0.776%) SOM content was obtained from RDF which was similar with control. Residual soil nitrate nitrogen in 30 cm depth was recorded highest (0.075%) in goat manure applied plot which was significantly higher than other treatments but similar with RDF and poultry manure. Similarly in 60 cm soil depth, highest amount (0.087%) of nitrate nitrogen leaching was recorded from RDF which was significantly higher than FYM, poultry manure and control plot but similar with biogas byproduct and goat manure application.

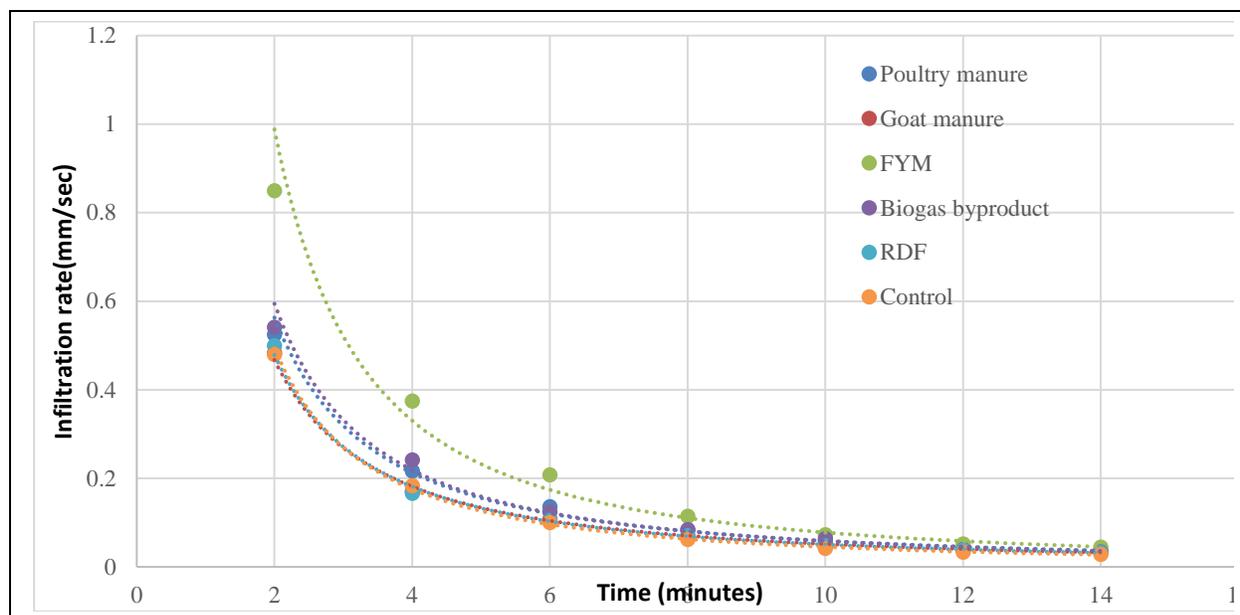


Figure 1. Soil infiltrability as influenced by different sources of organic manures.

Table 6. Effect of organic manures on CEC, OM and nitrate nitrogen of soil

Treatment	CEC (meq/100g)	OM (%)	NO ₃ -N (30cm)	NO ₃ -N (60 cm)
Poultry manure	10.408 ^a	0.9319 ^{ab}	0.061 ^{ab}	0.06 ^{bc}
Goat manure	9.55 ^{ab}	0.8864 ^b	0.075 ^a	0.073 ^{ab}
FYM	9.225 ^{ab}	0.967 ^{ab}	0.045 ^{bc}	0.048 ^c
Biogas byproduct	8.975 ^{bc}	1.01 ^a	0.045 ^{bc}	0.078 ^{ab}
RDF	8.575 ^{bc}	0.776 ^c	0.065 ^{ab}	0.087 ^a
Control	7.950 ^c	0.7761 ^c	0.0348 ^c	0.046 ^c
Grand Mean	9.11	0.891	0.0542	0.0651
Sem±	0.385	0.0343	0.00693	0.00728
LSD (0.05)	1.162	0.1033	0.021	0.0219
C.V %	8.5	7.7	25.6	22.4

Means followed by the same letter (s) in a column are not significantly different at 5% level of significance as determined by DMRT

Discussion

The lower values radish yield and soil physio-chemical properties obtained from control treatment as compared to other treatments could be as a result of initial low soil nutrients status

that often characterizes continuous cultivation of land without fertilizer application. This finding was supported by Mohammed and Solaiman (2012). The highest root diameter, root length and yield of radish from poultry manure treatment could be due to the least value of C/N ratio of poultry manure also encouraged faster decomposition and quick release of nutrients for crop uptake and higher root yield parameters. This observation was supported by Ijoyah and Sophie (2009) who reported that the application of poultry manure increased cabbage yield. Costellanos and Pratt (1981) estimated that 60 per cent of the organic N in poultry manure was available. Due to its rapid mineralization, poultry manure was recognized as a valuable source of plant nutrients for crops. Espitiru *et al.* (1995) reported that the crop yield improvement due to addition of poultry manure was attributed to the presence of both readily available and slow release nitrogen. The application of RDF significantly increased the root diameter and radish yield than that of goat manure and biogas byproduct application and this could be due to the supply of readily available nutrients from the NPK fertilizer to the plant. This observation agreed with that of Makinde (2013) who reported that an increase in the readily available nitrate from the NPK fertilizer unlike the organic manure which must be mineralized before being utilized by crops. The increase in water holding capacity, bulk density and porosity of soil from the application of poultry manure might be due to an increase in C content of the soil increases aggregation, decreases bulk density, increases water holding capacity, and hydraulic conductivity (Biswas and Khosla, 1971; Gupta *et al.*, 1977; Weil and Kroontje, 1979). The increase in soil pH from poultry manure application might be due to higher calcium content which decreased the activity of Aluminium (Hue, 1993; Materechera and Mkhabela, 2002). Decrease in nitrate leaching in lower soil depth from FYM and poultry manure application agreed with that of Yanwang *et al.* (2002). Higher amount of nitrate leaching was obtained from biogas byproduct agreed with that of Schröder *et al.* (2005). Also, Tong *et al.* (1997) reported higher rate of nitrate nitrogen leaching which polluted underground water particularly with the continuous use of chemical fertilizers compared to the organic fertilizers. The findings are further supported by several researcher (Adekiya and Agbede, 2009; Akani and Ojeyniyi, 2007).

Conclusion

Among the various treatment poultry manure was the best source of organic manure resulting higher root yield of radish by improving soil moisture content, soil pH, bulk density, soil porosity, CEC, nitrate nitrogen availability and reducing the leaching of nitrate nitrogen in lower depth. Hence, poultry application was recommended in sandy soil to reduce risk by improving soil properties. This research was conducted in winter season so that further long term research is necessary in other seasons for strong recommendation.

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1.1.14. Assessing agricultural soil pollution risks from organic waste recycling: informing regional participatory waste management

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Abstract

The well-informed recycling of organic waste to agricultural land becomes increasingly desirable in dynamic, developing regions worldwide. Pursuing locally optimal benefit-risk ratios, agro-environmental research in support of OW recycling does not focus on avoiding contamination *per se*, but on the control of dynamics, in soil and other environmental compartments, in order not to exceed risk thresholds. We present a series of empirical research efforts that inform decision-making in regions under OW pressure on OW-contained trace contaminant fate under local conditions. Their results illustrate that the present understanding of trace elements fate allows for the ex-ante assessment of fate under specific use scenarios and local conditions, with a limited set of simplifications. A well-established set of analytical tools provides the information required by such assessments. Understanding of OW-borne organic contaminants is less advanced, but the present capacity to project fate under local conditions does allow for the approximate appreciation of risk levels, the major benefit of which is to focus subsequent research on substances of concern. Ongoing long-term field trials may critically advance our understanding of OW-borne contaminant fate in soil. Developing a reasonable capacity to assess biological contaminant fate is one of its priorities.

Keywords: organic waste, recycling, industrial symbiosis, trace elements, organic contaminants, fate modelling, decision support

Introduction: costs and benefits of recycling organic waste in agriculture

Recycling organic waste (OW) to agricultural land is as old as agriculture itself. However, industrialization, agriculture's subsequent green revolution (particularly synthetic fertilizer use) and globalization largely disrupted this habit and therefore local nutrient cycling and soil preservation. While allowing for major increases in agricultural production and expansion of the producing area, the environmental boomerang effect of these profound changes has put the recycling of organic residues progressively back on the political agenda. The current interest in OW recycling relates to its potential contribution to the improvement of eco-efficiency and resilience, i.e. two high priority goals on agricultural research agendas (Deane *et al.* 2010; <http://resilience2011.org>). OW recycling is particularly desirable in strongly developing regions where, on the one side, organic residue concentration induces critical environmental and human health risk levels while, on the other, long-term intensive conventional agriculture provides a significant potential for ecological intensification (Doré *et al.* 2011). Two main types are: (1) isolated territories (e.g. islands) with very limited natural resources, especially arable land, and increasing demographic pressure, and (2) peri-urban areas of fast growing large cities in emerging countries. The latter type of situation is rapidly becoming more frequent. In such strongly developing regions, OW recycling carries the promise (i) to avoid pollution and health risks due to their accumulation and uncontrolled discharge; (ii) to reduce the environmental footprint of cropping; (iii) to reduce

the level of dependence on external inputs of the region's agricultural sector. As such, OW recycling would contribute to SDGs 3, 6, 9 and 11.

However, like all waste flows and in line with the second law of thermodynamics, OW has a high entropy. Besides elements and compounds of potential value to agriculture, depending on the amount applied to soil, others constitute notorious contaminants, even though they mostly originate from marketed products, their use in the manufacturing of which was duly authorized (e.g. pharmaceutical and health care products, hormones, feed additives, but also plasticizers, flame retardants, etc.). Through a range of pathways, many such contaminants have become ubiquitous, while most are mobile to various extents. Molecular compounds can degrade and living pathogens may not survive. Science indeed should monitor and evaluate the consequences of "life in a contaminated world" (Guillette and Iguchi 2012). The focus of agro-environmental research in support of OW recycling though is not on avoiding contamination *per se*, but on the control of dynamics, in soil and other environmental compartments, in order not to exceed pollution thresholds, be they set by regulation, risk assessment or stakeholder concerns. In the following, we provide an outline of our view on the characteristics of such agro-environmental research in support of OW recycling, as well as examples of achievements by our research group.

Methodology: hard science in a constructivist framework

We argue that general guidelines and uniform national policies are imperfect and often insufficient tools for achieving an effective control of soil pollution. First, regulation lags behind the state-of-the-art, even in most stringently regulated countries: due to the sheer number of substances produced by industry, as well as the increasing technical capacity of science to determine their presence in the environment. Some 50,000-100,000 chemicals are currently produced commercially in a range of quantities, with approximately 1000 (mostly organic) chemicals being added each year (Mackay *et al.* 2006). The fact is that we know very little about the vast majority of the chemicals we use. Consequently, many organic compounds of recent concern are not (yet) covered by regulations and norms, while standards for elements tend to correspond to worst-case scenarios and may preclude efficient solutions. Lastly, with contaminant *fate* being the focus, and fate being highly dependent on local condition, science should aim to inform stakeholders directly, through *ex ante*, modelling based fate assessment.

In regions where the accumulation of organic waste induces critical environmental and human health risk levels, industrial symbiosis may provide a systemic solution to a problem induced by the sectoral partitioning of the economy. We developed a facilitated, participatory approach for co-designing agricultural OW recycling solutions, starting from a science-based plausible promise (Wassenaar *et al.* 2014; Wassenaar and Queste 2015). Empirical science informs such initiatives to best of its abilities, both on risks and services of envisaged agricultural recycling solutions, in order to generate information for society in such situations where "facts are uncertain, values in dispute, stakes high and decisions urgent" (Funtowicz and Ravetz 1991).

Results and discussion: examples of research for the ex-ante assessment of contaminant fate

Informing agricultural OW recycling in a specific context: the case of trace elements in Réunion

Réunion is an increasingly densely populated island. It is a large nutrient sink due to net imports, both for agriculture and inhabitants. Soils have developed on mafic lava rock and heavy metal contents are naturally high. National regulations, without considering the origin of metals, prohibit the recycling of certain organic residues on soils with such concentrations. The impact of recycling

organic residues on trace metal mobility (in soil and risks of transfer to groundwater or crops) in Réunion was studied through field experiments over several years with sewage sludge (Doelsch *et al.* 2006b) and pig slurry (Legros *et al.* 2012) applied on crop fields. Laboratory-scale basic research results have shown that the mobility and phytoavailability of trace metals in Réunion soils are very limited. This has been confirmed by field level observations (Collin and Doelsch 2010; Legros *et al.* 2012) and contrasts with our findings in other settings, like the mobility of OW-borne trace metals in the arenosol and fluvisol of the market gardening agrosystem near Dakar, Senegal (Hodomihou *et al.*, 2016). In collaboration with institutional stakeholders, researchers have convinced competent authorities to issue a waiver authorizing the use of sewage sludge in agriculture in Réunion (Collin and Doelsch 2010), as well as the use of green waste, exceeding the regulatory threshold for chrome and nickel, but which proved to originate from soil particles attached to roots.

At the same time though, these results underscore a long-term accumulation risk, hence the relevance of modelling the fate of heavy metals in tropical soils. Available accumulation models are usually parameterised through generic multiples regression equations taken from the dominantly temperate climate based literature. This proves to substantially over-predicted trace metals concentration in the edible organs of plants and in the soil solution and thus overestimated trace metals output from the upper soil layer by plant uptake and leaching. Once adjusted to local data, the model correctly predicted trace metals accumulation in the upper soil layer amended with organic wastes (Oustrière *et al.* 2013). This constitutes a precious decision support tool since it allows relating application frequency and dose to a time lag before reaching e.g. regulatory or eco-toxicity soil concentration thresholds. Its major limitation is that the OW induced evolution of basic soil physical, chemical and biological parameters (pH, CEC, hydraulic conductivity, microbial biomass, etc.) is not taken into account.

Developing knowledge and tools for ex-ante risk assessment in a wide range of settings

Our research also revealed that predicting OW trace metal fate in a wide range of soils requires considering trace metal speciation, in OW (Legros *et al.* 2010), in soils (Doelsch *et al.* 2006a; Levard *et al.* 2007), in soils after residue application (Doelsch *et al.* 2006b) and speciation changes due to mineralization (Doelsch *et al.* 2010). This is a worthwhile aim to pursue. Livestock manure contained zinc and copper for example account for the highest metalloid elements inputs in agricultural soils (Belon *et al.* 2012; Jensen *et al.* 2016). We deploy the full range of analysis techniques available: size fractionation, X-ray diffraction, scanning electron microscopy, coupled with energy dispersive spectrometer, and extended X-ray absorption fine structure, which is one of the most widely known structural techniques for direct determination of speciation of trace elements present in complex solid samples even at very low concentration. Applied to pig slurry-contained zinc, these techniques revealed that 75% of total Zn was bound to particles in the 0.45 to 20 µm size range, thus drawing attention to colloidal transport in soil. They also revealed that 49% Zn was bound to organic matter, 37% amorphous Zn hydroxide, and 14% sphalerite. These three Zn forms seemed to be soluble in neutral or weakly acid soil systems, meaning that the long-term impact of pig slurry spreading could lead to Zn leaching (Legros *et al.* 2010).

A technique for experimentally assessing contaminant phyto-availability completes this set of approaches deployable, at a low cost, to inform stakeholders on risks in their local context. The RHIZOTest (ISO 16198) is a plant-based biotest to account for rhizosphere processes (Bravin *et al.* 2010). Beyond trace elements, the test is currently also used to assess plant transfer risks of OW contained organic contaminants – persistent pollutants as well as pharmaceutical and personal care products – and even the possible transfer of biological contaminants: pathogens as well as antimicrobial resistant genes.

The scope for the ex-ante assessment of OW-borne organic contaminant induced risk

Concerning organic and biological contaminants, the sketchy understanding of OW-borne biological contaminants' fate so far precludes any meaningful ex-ante risk assessment. The uncertainty surrounding the fate of organic contaminants in a particular setting and soil also remain very high. Nevertheless, combining currently available models with general and easily obtainable information on OW and soils allows producing useful fuzzy fate estimates. For particular recycling scenarios of wastewater sludge and pig slurry onto Réunion soils, a soil balance calculation based on first order removal constants allowed to approximate the possibility range for the remaining soil concentration at user-defined time horizons (Wassenaar *et al.* 2015; figure 1). Local soil pH allowed to assess each particular organic contaminant detected in OW as being present in soil either in a dominantly neutral or dominantly ionized form. Removal through volatilization, biodegradation and leaching could then be approached thanks to information on local conditions and their variation like soil mixing depth, bulk density, temperature, carbon content, rainfall and crop yield. The main limitation of such an approach is the impossibility to estimate plant uptake of ionic substances: no model has yet been adapted to them. We anticipate that continued empirical research efforts soon will allow addressing various such limitations. While not restricted to organic contaminants, the by now extensive documentation of the structural presence of trace levels of organic contaminants in many OW sources makes it a pressing issue. Among other initiatives, an increasing collection of long-term field trials like those of the French network of SOERE-PRO observatories (<https://www6.inra.fr/valor-pro/>) exemplifies such efforts.

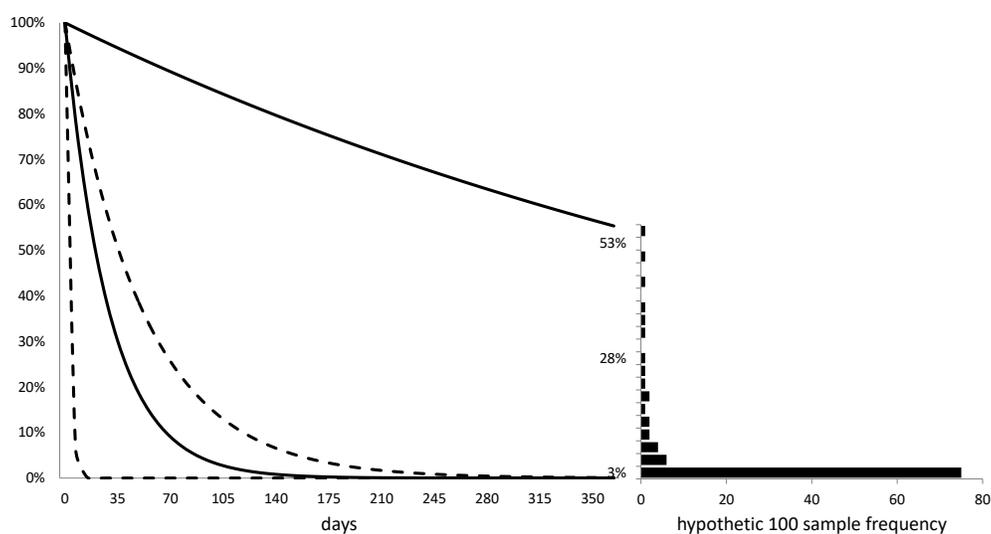


Figure 1. Interpretation of upper and lower bounds based removal dynamics. Solid lines indicate high and low soil removal dynamics of Tris(chloropropyl)phosphate, a sludge-borne flame retardant, recalcitrant when compared, for instance, to nonylphenol (dashed lines). The histogram on the right indicates the frequency distribution that would be obtained between these high and low removal limits from a hundred samples after 1 year if the removal rate distribution would be uniform. From Wassenaar *et al.*, 2015

Conclusions

The above research examples testify of a rapidly increasing understanding of, as well as an increasing capacity to model the fate of contaminants in soil other than the classically considered nutrient loading risks. Clearly, while biophysical research continues to progress, the present state-of-the-art allows to inform local development efforts in order to avoid adverse effects of initiatives. Directly informing stakeholders, through ex-ante, modelling based contaminant fate assessment within the frame of participatory OW management centred industrial symbioses carries the promise to contribute to SDG targets 6.3, 9.4 and 11.3.

Beyond the present capacity to inform, there is an increasingly realistic prospect for a near future capacity to account in a satisfactory manner for the fate of all contaminants in all situations. One example of current developments pointing in that direction is a new clustering methodology called TyPol, which allows classification of organic contaminants and their degradation products, according to both their environmental behavior and molecular properties (Servien *et al.* 2014). Another essential direction we presently explore is the integration of fate models into dynamic system models. Such models allow simulating the functioning of modifications envisaged in complex systems. Dynamically representing contaminant fate in complex human-environment systems will allow to go beyond characterizing selective individual situations, to increase the probability of simulated situations to be realistic, and to assess environmental fate and impact at larger scales.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.1.15. Agricultural soils of the European Union contaminated with pesticide residues

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Abstract

Pesticide use is a major foundation of the agricultural intensification observed over the last decades. The use of pesticides continues to increase worldwide and, due to the high persistence and toxicity of some pesticides, soil contamination with pesticide residues has become a major threat to soil quality and soil functions.

In this study, for the first time at such large scale, the co-occurrence and concentrations of 76 pesticide residues (including active substances and metabolites of both historical and current use pesticides) were evaluated in 317 EU agricultural topsoil samples. The soils, collected in 2015, were originated from 11 European Union Member States and six cropping systems.

Overall, only 13% of the tested agricultural soils were pesticide-free; 25% of the soils had 1 pesticide residue and 58% had multiple pesticide residues. 43 different residues were present in the soils at least once and, 16 of them were (metabolites of) active substances non-longer approved in the EU markets. The most common compounds in soils were glyphosate and its metabolite AMPA; the long term banned DDTs and the broad-spectrum fungicides: boscalid, epoxiconazole, tebuconazole and phthalimide (metabolite of folpet).

Total pesticide contents varied significantly according to the country of origin and land cover, with an average and a maximum concentration of respectively 0.25 and 2.90 mg of (total) pesticide residues per kilogram of soil. The distribution of total pesticide contents in agricultural soils was represented at the NUTS 2 level, identifying some areas of bigger concern.

Such results reinforces the problematic of accumulation of multiple pesticide residues in soils, which might not only affect local food productivity, soil biodiversity and soil functions but also represent a potential risk to other areas via erosion of contaminated soil particles. It is therefore urgent to establish and implement monitoring and surveillance programs of these compounds in soil.

Keywords: Agricultural soils, European Union, mixtures of pesticide residues.

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1.1.16. The retention and release of nutrients from polyhalite into the soil

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Abstract

Future food security will require improvements in nutrient use efficiency from fertilizers to improve yields. Achieving efficiency without adversely affecting soil environments will need fertilizer plans to consider all six macro-nutrients (nitrogen, phosphorus, potassium, calcium, magnesium and sulphur). Recent discoveries of polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$) in the UK offer opportunities to improve yields through efficient fertilizer plans. This work investigated the interaction of polyhalite with the soil environment using conical flask extractions and leaching columns.

Conical flask extractions use two soil types (Camisol and sand) to evaluate polyhalite effects with the soil CEC and clay surfaces. Results showed nutrient in polyhalite did not affect the CEC and were governed by ionic substitution with soil exchange sites. Leaching column studies used different physical forms of polyhalite (powder and granules) to evaluate the movement of potassium, calcium, magnesium and sulphur through the soil profile. After six years of simulated rainfall, the nutrients from polyhalite were found to be available, at 30 cm depth, with calcium showing signs of interacting with the soil to release bound nutrients. Field trials are required to investigate the effect of polyhalite on soil environments over several years.

Keywords: Polyhalite, fertilizer, soil, nutrient movement, agriculture

Introduction, scope and main objectives

The world population is expected to reach 9.8 billion by 2050 requiring farmers increase yields from decreasing farm sizes whilst avoiding soil pollution from fertilizer usage (UN 2017; Lowder *et al.* 2016). Along with nitrogen and phosphorus, potassium, calcium, magnesium and sulphur are other macro-nutrients required for optimal growth for crop production. Supplying all six macro-nutrients can significantly improve nutrient use efficiency by balancing fertilizer plans using multi-nutrient fertilizers (Venterea *et al.* 2011). With the increasing demand for fertilizer, the potash industry undertook global exploration work to identify new potassium-bearing salt deposits (Cocker *et al.* 2016). One possibility is polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$), a potassium bearing mineral that was discovered in North Yorkshire, UK with a deposit consisting of over 2.5 billion tonnes (Kemp *et al.* 2016). Research into polyhalite as a multi-nutrient fertilizer has shown improvements in crop yields (Pavuluri *et al.* 2017; Mello *et al.* 2018a, 2018b). However, the nutrient availability from polyhalite within a soil environment is poorly understood and possible impacts on soil environment are not known. The application of base cations (e.g. calcium) to the soil is well known to affect soil environments both physically and chemically that can help remediate degraded soils or improve nutrient availability. Therefore, this work looked to investigate the impact of polyhalite on soils using conical flask extractions and controlled leaching columns to understand the interactions with soil and the nutrient availability in the soil profile.

Methodology

Conical Flask Extraction

Two soils were selected for this study. Inch is a Brown Forest (Cambisol) under arable production, with a sandy loam texture, and sourced from NE Scotland. The other soil was acid washed fine sand that has no exchange sites. Polyhalite was mixed with each soil at application rates of 0, 356, 756 and 1067 kg ha⁻¹ and left to equilibrate for 24 hours before a 2-gram subsample was taken. This was added to a conical flask with either 50 ml, 100 ml or 500 ml of deionised water, equivalent to 76 mm, 151.5 mm or 757.5 mm of rainfall. All treatments were replicated three times.

Each extraction involved two steps- one that was pH *buffered* and one at native *unbuffered* pH of the soil. The reason for this is that the exchange behaviour of the soil is pH dependant. The procedure requires the use of an ammonium salt to displace cations. The next step is to remove excess ammonium from the soil (as the first step has saturated it and we only wish to focus on the ammonium at the exchange site). Finally, the ammonium is displaced by sodium. This is carried out in a pH buffered and unbuffered system. A summary of the steps involved is provided below.

Buffered

Step 1- 40 ml of 1 M ammonium acetate (pH 7.0) was added to 2 g of soil, agitated in an end-over-end shaker for 30 minutes, stored for 12 hours at 4 °C, for minutes and then centrifuged for 15 minutes at 1250g.

Step 2- Retain supernatant for base cation analysis, wash soil in 50 ml ethanol and centrifuge for 15 minutes at 1250g.

Step 3- 40 ml of 1 M sodium chloride displaces the ammonium, mix and centrifuge. Retain supernatant for ammonium analysis.

Unbuffered

Step 1- 40 ml of 1 M ammonium chloride (this attenuates to the pH value of the soil) was added to 2 g of soil, mixed and centrifuged as described above for buffered.

Step 2- Retain supernatant for base cation analysis, wash soil in ethanol and centrifuge.

Step 3- 40 ml of 1 M sodium chloride displaces the ammonium, mix and centrifuge. Retain supernatant for ammonium analysis.

Extracts were measured for Ca, K, Mg and S using atomic absorption spectrophotometry (AAS). The amount of N-NH₄⁺ was measured with flow injection analysis (FIA).

Leaching Columns

Leaching columns were packed with 770 g Inch soil at a density of 1.2 g cm⁻³, typical of field conditions. Layers of sand were placed above (360 g) and below (125 g) the soil to improve the homogeneity of water flow that was controlled with a peristaltic pump to provide a controlled flow rate of water through the column. Water flows from the top to the bottom of the column, with the outlet leachate water collected in sample tubes for subsequent analysis. There were four soil treatments examined: (1) 0 kg ha⁻¹ polyhalite, (2) 711 kg ha⁻¹ polyhalite powder, (3) 711 kg ha⁻¹ polyhalite granules and (4) 166 kg ha⁻¹ muriate of potash (potassium chloride). These were

mixed homogeneously with the soil. All amended soils received 100 kg K₂O ha⁻¹ with all treatments replicated three times

The columns were initially saturated with deionized water. The flow rate of deionized water through the column was maintained at 100 mm/hour until the equivalent of 4500 mm of water had leached through the sample. This is more rapid than would be expected from natural precipitation but it allows for the equivalent of a several years of rainfall to be investigated over a shorter period. Periodically leachate subsamples were taken to measure pH with an electrode, K, Mg and Ca with an AAS, as described previously and S using a Dionex. Each run took approximately two weeks to complete.

Results

Conical Flask Extractions

The pH value had no effect on the dissolution or retention of polyhalite in the soil matrix- i.e. soil exchange parameters of polyhalite were pH independent. Results for the buffered system showed that quantities of potassium (0.004 -0.008 cmol/kg) and magnesium (0.008 – 0.012 cmol/kg) were increasing in the extracts, with the amount of added water. Calcium showed no consistent pattern with the amount of added water or polyhalite content (0.140 – 0.161 cmol/kg). Extracts from the Inch soil samples were generally higher due to the presence of nutrients in the soil prior to polyhalite amendment. There was little variation in calcium (0.432 -0.449 cmol/kg) and magnesium (0.06 -0.07 cmol/kg) with any amount of water or polyhalite amendment. Potassium showed a greater level of variation (0.079 -0.121 cmol/kg) most noticeably at polyhalite amendments of 1067 kg ha⁻¹ where potassium dropped having been exhausted from the soil.

The addition of polyhalite at a range of concentrations combined with leaching by water had no influence on CEC in either sand (0.25 – 0.35 NH₄-N cmol/kg) or Inch soil (1.34 – 1.41 NH₄-N cmol/kg). This indicates that the direct dissolution of polyhalite is the factor that governs the release of potassium, calcium and magnesium into soil solution resulting in ionic substitution with the soil exchange sites.

Leaching Columns

Polyhalite granules produced a greater amount of potassium compared to the powder form over the duration of the study. After 4500 mm of simulated rainfall the control, powder, granules, and MOP treatments had released 53.9, 81.4, 92.9, 78.7 and 60.6 µg potassium g dry soil⁻¹ respectively. Both polyhalite forms outperformed the control and MOP, that were similar, over the course of the study. All treatments continued to release calcium up to 4500 mm of simulated rainfall where the cumulative release for the powder and granules treatments was 206.4 and 212.3 µg Ca g dry soil⁻¹ compared to 154.8 and 174.5 µg calcium g dry soil⁻¹ for the control and MOP respectively. Polyhalite granules and powder has similar release rates over the duration of the leaching. After 4500 mm of rainfall there was no difference between the polyhalite treatments in release of Mg with powder and granules treatments releasing 39.8 and 40.1 µg g dry soil⁻¹ respectively. Control and MOP had 28.1 and 31.2 µg magnesium g dry soil⁻¹ released, respectively, after 4500 mm of rainfall. Finally, polyhalite amendments had the highest amount of sulfate leached with 349.6 and 358.4 µg SO₄²⁻ g dry soil from powder and granules respectively after 4500mm. By comparison, control and MOP approximately five times lower amounts of sulfate with 67.3 and 65.7 µg SO₄²⁻ g dry soil that was present in the soil.

Discussion

Delivery of nutrients through the soil profile within the rooting zone is an efficient use of fertilizers. Nutrient capture must be considered when devising a fertilizer plan but nutrient movement is not straight forward due to ionic exchanges. Calcium is known to displace other cations into solution that can lead to leaching. A study by Moraes *et al.* (2016) found that increasing gypsum application led to increased potassium, calcium and magnesium in leachate from an Oxisol. Polyhalite also contains calcium and the results from both experiments exhibit similar results found by Moraes *et al.* (2016). The different results between polyhalite forms could be due to particle size. The granules are made using a continuous batch vertical drum granulator from the powder. As a result, the granules have a particle size of 2000 - 4000 μm compared to the powder that has 250 μm . This could mean there were concentrated flow paths that would create hotspots resulting in concentrated flow paths that would decrease interaction with the soil. Differences in nutrients were not significant ($p < 0.05$) except for potassium ($p = 0.049$).

The design of the experiment should be considering when interpreting the findings. Firstly, the simulated rainfall amount used in this study is representative of six years of annual average rainfall for parts of the UK. In addition, the flow rate that achieved an equivalent of 100 mm/hr would not normally occur in the environment. Hence, the accelerated nature of the experiment offers insights under extreme conditions. Secondly, the experiment does not account for agricultural practice by having a single application at the start and no crop. Farmers would apply fertilizer regularly as crops demands nutrients to grow over time. As the crop grows the amount of nutrients removed will increase whilst rainfall will vary resulting in fluctuations of nutrient movement in the soil profile. The next step is to investigate dissolution and leaching of polyhalite over several years in the field.

Conclusions

The use of polyhalite to deliver efficient, nutrient balanced fertilizer plans can be supportive of improving food security and preventing soil pollution. This study has evaluated the interaction of polyhalite with the soil environment and found that polyhalite is an effective fertilizer at supplying potassium, calcium, magnesium and sulphur. Notably, the calcium in polyhalite appears to interact with the soil environment through ionic substitution that release potassium from the soil that would be advantageous to crop production. Importantly, the amount of nutrients being released over time from polyhalite do not suggest adverse effects on the soil environment. Field trials are required to validate the findings of this study. These trials would allow for a greater range of soil types to be tested under real time conditions. In addition, nitrogen and phosphorus could be applied with the polyhalite to grow crops and monitor nutrient movement through the soil profile to better understand the efficient use of fertilizers.

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1.1.17. Risk assessment of glyphosate/AMPA in wind-eroded dust derived from agricultural soil in North-Netherlands

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Abstract

Glyphosate (GLY) and its main metabolite aminomethylphosphonic acid (AMPA), can be transported by wind-eroded sediment and dust, leading to off-site pollution and human exposure nearby or far away from the region of application. However, field observations on wind-erosion related GLY transport have not been elucidated yet. Therefore, we conducted a field study in potato cultivation in N-NL to assess the short (10 m) and longer distance (125 m) transport of GLY and AMPA by wind erosion. In spring 2017, 2.5 L ha⁻¹ Roundup, Ultimate was applied and soil samples (<1 cm depth) were taken at day 3 and day 50 after application when a wind erosion event occurred. Dust was captured from 20 cm to 120 cm height from dust collectors in 10 m and 125 m distance of the treated soils placed in the main wind direction and combined to a mixed sample. The surrounding soil of the longer distance collector was sampled at day 50 as well. GLY and AMPA content in the soil directly after application ranged from 16.6-23.1 µg g⁻¹ of GLY and 1.4-1.8 µg g⁻¹ of AMPA and at day 50 from 0.2-1.3 µg g⁻¹ of GLY and 0.5-1.0 µg g⁻¹ of AMPA in the treated soils. However, the contents were 0.1-1.9 of GLY and 1.01-3.86 of AMPA at day 50 in the untreated soil. GLY and AMPA content in short distance dust ranged from 1.0 to 9.9 µg g⁻¹ and from 0.5 to 0.9 µg g⁻¹ respectively. Longer distance dust contained 2.0-2.1 µg g⁻¹ GLY and 0.9-1.5 µg g⁻¹ AMPA. These indicated that strong accumulation of GLY in the dust fraction with very low dissipation rate during 50 days comparing with the related soil samples in the field. Therefore, high content of GLY transported by dust should be concerned for human exposure. Further study would be considered about wind-eroded soil particles and contaminated dust particle clusters to evaluate exposure risks of air-transported pesticides.

Keywords: Glyphosate, wind erosion, dust contamination, Particle-facilitated transport, Risk assessment

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1.1.18. Is agricultural production of the upper basin of Pergamino stream responsible for soils and water degradation?

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Abstract

The uncertainty associated with soil and water quality in the Humid Pampa region difficult to evaluate the environmental impact of agriculturization on ecosystem services. To address this uncertainty, the aim of the present study was to measure the contribution of different production systems on soil and water quality degradation in the upper basin of the Pergamino stream where such land uses dominate. For this purpose, an annual elements balance (N, P, SO₄, Ca, Na, K), NO₃ concentrations and pesticides presence (glyphosate, atrazine, clorimuron, dimethoate, epoxiconazole, tebuconazole y metconazole) were measured in groundwater and surface water. We found that all elements balances were negative. Cattle production was less extractive than the agricultural system. The NO₃ concentration surpassed the acceptable limit for human consumption only in the water table. However, pesticides were detected in both surface water and groundwater. Atrazine showed the greatest spatial-temporal distribution. The agroecosystem under study was able to produce food and energy but to the detriment of water quality and soil ecosystem services. The principal cause for this could it be the loss of soil organic matter.

Keywords: Basin, Agriculturization, Nutrient balance

Introduction, scope and main objective

The determination of the causal factors of environmental degradation is complex due to the diverse processes that interact in the generation of environmental impact (Laband *et al.* 2012). In Argentinian Rolling Pampa basins, which are mainly under agricultural use, no tillage served to control erosion, but since the 1990s, the trend towards simplified agricultural schemes with high frequency of soybeans has led to an increase in runoff, the tendency to rapid floods, the mineralization of soil organic matter (MOS) and the replenishment of nutrients and the water infiltration capacity have been reduced (Viglizzo *et al.* 2001). In addition, the grazing of riparian strips has increased the discharge of sediments in the streams, reducing the filtering service (Darder *et al.* 2012).

According to CEPAL (2005), with the information currently available for the Humid Pampa region, it is difficult to establish which environmental services are most affected by this change in soil management. In particular, the level of uncertainty regarding the state of the soil and aquifer components makes it difficult to assess the environmental impact of agricultural intensification (CEPAL 2005). In order to reduce it, the objective of this work was to dimension the contribution of the production systems that are practiced in the upper Pergamino stream basin, strictly under agricultural use, to the degradation of soils and water.

Methodology

The study area was the upper basin of the Pergamino stream (966 km²) (Buenos Aires-Argentina). It extends from the Juncal swamps (occupied by saline/sodic soils) to before the mouth of El Botija stream (Fig. 1). The Pergamino stream basin (2092 km²) is located in the basin of the Arrecifes river, which belongs to the Paraná river system. The stream lacks riparian vegetation, receives the

contribution of small temporary and permanent courses and has increased its drainage as a result of a large amount of canalization works (INA 2007). Like the rest of the Pampean streams, it behaves as an effluent, constituting the underground flow its base flow (Galindo *et al.* 2007). The upper basin is strictly under agricultural use (Reynoso and Andriulo 2009), being the first soybean the majority crop (56% of the surface) (Cabrini and Calcaterra 2008). Livestock has been displaced towards the marginal (low) areas of the landscape, with less agricultural aptitude (Darder *et al.* 2012). The climate of the region is humid temperate without dry season and with an average annual rainfall of 990 mm 1910-2016, (agroclimatological network database, Instituto Nacional de Tecnología Agropecuaria, INTA).

The annual balance of N, P, SO₄, Ca, Na and K was made applying the Laband *et al.* (2012) methodology. As input of nutrients were considered: 1) atmospheric deposition (Carnelos *et al.* 2014); 2) fertilizers (Cabrini and Calcaterra 2008); 4) a biological nitrogen fixation in soybean of 50% (Salvagiotti *et al.* 2008); and as exit: 1) exit from the basin (Torti 2014); 2) export in grains and cattle (Cabrini and Calcaterra 2008, Mancassola *et al.* 2015); 3) losses due to leaching (Portela *et al.* 2009) and 4) volatilization from the soil (Taboada 2011).

In a monitoring and gauging station located at the exit of the upper basin (Figure 1), the nutrients load (N, P, SO₄, Ca, Na and K) and the presence of pesticides (glyphosate, atrazine, chlorimuron, dimethoate, epoxiconazole, tebuconazole and metconazole) were measured. Nutrients were assessed during 19 seasonal sampling campaigns from June 2010 to May 2012 (Torti 2014) and pesticides during 4 seasonal samplings between November 2012 and July 2013. On the other hand, there are 24 wells (5 up to the base of the aquifer and 19 to the water table) distributed in 5 sub-basins where NO₃ were determined from January 2010 to October 2013 and also the presence of pesticides during the summer of 2012.

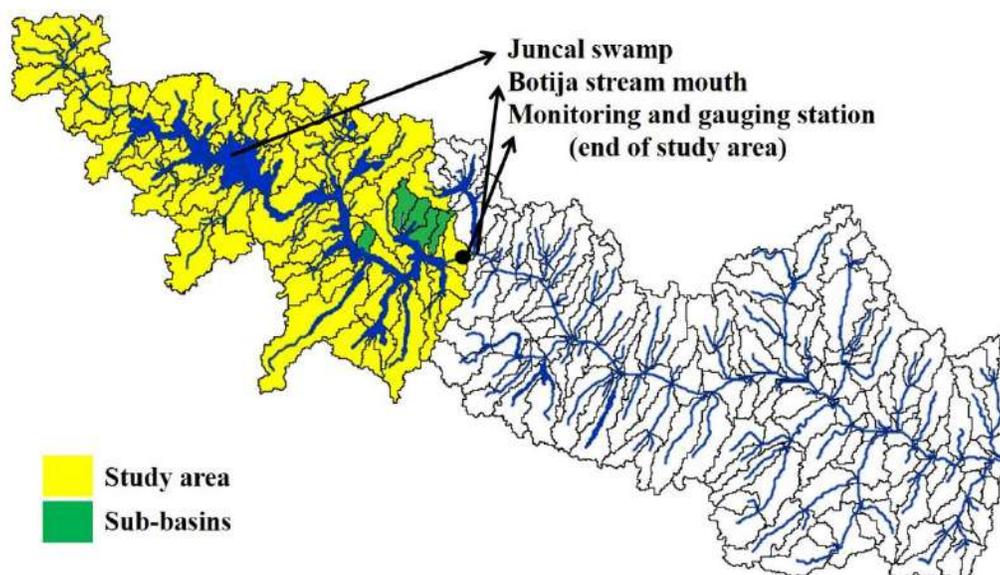


Figure 1. Map of the study area and the Pergamino stream basin.

Nutrients were measured following the APHA methodology (1989). The pesticides were determined in an Ultra Performance Liquid Chromatograph (ACQUITY UPLC® Waters), coupled to a mass/mass spectrometer (Quatro Premier XE). The water velocity of the stream was measured in coincidence with the water samples.

Results

The balances were negative for all the elements (Table 1). The livestock system was less extractive than the agricultural system due to the low animal load (~ 1.5 animals ha^{-1}). Regarding the N, the quantity exported with the harvest grains (mainly soybean) was three times greater than the amount entered. Phosphorous fertilization rates did not compensate for the extraction (grains + livestock).

Table 1. Balance of some elements in the upper basin of the Pergamino stream.

Element	Input		Output					ΔE
	Atmospheric deposition	Fertilization	Basin output	Grains	Cattle	Lixiviation	Volatilization	
	$\text{kg ha}^{-1} \text{ year}^{-1}$							
N	6.1	20.5	5.9	82.0	3.1	5.3	3.0	-72.7
P	na	12.7	1.3	17.7	0.1	0.0	-	-6.4
SO ₄	7.2	21.8	2513.1	26.6	0.8	0.0	-	2511.5
Ca	3.3	2.0	160.6	7.0	0.0	50.4	-	-212.7
Na	12.3	sd	2407.9	sd	sd	322.0	-	2717.6
K	3.1	0.0	128.5	46.0	0.3	32.8	-	204.5

na: does not contribute. sd: no data. ΔE : nutrient balance.

On the other hand, at the exit of the study area, NO₃ was not detected while all pesticides were detected in spring, summer and autumn, except for glyphosate and atrazine, which were also detected in winter.

At the base of the aquifer, NO₃ threshold for human consumption was never exceeded (45 mg l^{-1}) and pesticides were detected in $\sim 50\%$ of the wells, except for atrazine, which was detected in all of them. At the water table level, only 9% of the measurements exceeded the NO₃ threshold, chlorimuron was detected in 26% of the wells, glyphosate, dimethoate, epoxiconazole, tebuconazole and metconazole were detected in 63% while atrazine was detected in all of them.

Discussion

The biological nitrogen fixation (by soybean) did not compensate for this loss, with the SOM mineralization being the main source of N (Portela *et al.* 2006). Torti (2014) found that, at the exit of the basin, the N was found mainly in dissolved organic form, reaffirming its organic origin.

Torti (2014) found, at the exit of this basin, that 27% of the P was under particulate form. In the same area, Darder *et al.* (2012) determined that the riparian strips closest to the stream (0-5 m) could drain up to 3.7 kg P ha^{-1} under simulated high-intensity rain (60 mm h^{-1}). As the soils of the rolling Pampas are genetically very rich in P, it is considered that the superficial flow is the main source to the stream channel (Torti 2014).

The high amount of SO₄, Na, Ca and K transported by the stream was due to two issues: first, that the stream was born in saline/alkaline soils developed on postpampean sediments of high salinity and concentration of sulfate resulting from the oxidation of metallic sulfides that contains (Auge

2004); and second, to the increase in the drainage produced by the construction of artificial canals before the sampling point (INA 2007).

The measurement of water and chemical flows at the landscape and basin scale is the beginning of the generation of possible solutions through temporal and spatial scales. Although the system produces food and energy, it is not efficient since it affected water quality and some ecosystem functions of the soil. The main cause would be associated with the loss of soil organic matter (SOM), since it governs most soil functions (Weil and Magdoff 2004). In the Rolling Pampa, after 120-150 years of continuous agriculture, ~ 40% of the SOM reserves were lost (Milesi Delaye *et al.* 2013). In the same study area of this work, Milesi Delaye *et al.* (2014) estimated, for the period 2010-2080, that if soybean monoculture continues, the loss of SOM will be inevitable while intensification of crop sequences with pastures and/or cover crops would result in mitigate schemes of soil degradation. Restovich *et al.* (2012) found significant reductions in soil NO₃ content when cover crops are included, reducing their leaching risk. In addition, Irizar *et al.* (2015) concluded that the introduction of perennial bioenergy crops that do not require an intensive supply of agrochemicals and fertilizers represent an alternative with high potential to improve the quality of marginal and/or degraded soils. Finally, the fragility of the riparian strips closest to the watercourse show the need to exclude livestock from this area and establish natural vegetation strips (Darder *et al.* 2012). The generalized spatiotemporal distribution of atrazine, when corn occupies 13% of the surface, is worrisome.

Conclusion

The approach used allowed to identify the contribution of the current land uses of the upper basin of the Pergamino stream to the degradation of soil and water. The ecosystem services of filtering, recycling and storage were affected, translating into the detriment of water and soil quality. Agriculture was the source of the greatest impact. There is still uncertainty about the effects of current use on biodiversity. The incorporation of the variables society and economy are still pending.

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1.1.19. Soil pollution in urban agriculture can derive from cultivation

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Abstract

Urban horticulture for self-production is of growing importance in planning and managing towns and cities. Benefits are recognised related to environmental services, the economy and human well-being, especially on the elderly, immigrants, low-income families. Some studies have highlighted the potential risk of contamination by metals of vegetables grown in urban areas and the lack of appropriate site-specific risk assessments. However, unless the cultivated sites are near to a source of pollution, the soil levels of metals are not such to raise a worry. On the other hand, the lack of awareness in many gardeners can lead to overuse phytochemicals, so trace metals can eventually accumulate in soil. We assessed the presence of metals in an area in Pisa (Italy) used for urban horticulture. We analysed the soil for the main chemical and physical characteristics (texture, bulk density, water stability index, pH, cation exchange capacity, organic carbon, total nitrogen, phosphorous) and elements (Pb, Cu, Ni, Cr, Zn, K, Al and Mn). Our results showed that heterogeneity, in soil physical and chemical characteristics, was due to the effects of different cultivation techniques employed. Nitrogen and electrical conductivity varied in the different

allotments. The metal content in general was lower than the threshold limits and the soil conditions (pH=8) greatly reduced metal mobility. Copper concentration in some of the soil samples was higher than the limits, due to the accumulation in time of the treatment residuals, so representing possible stress factor for the soil microbial biodiversity and fauna. Our findings demonstrate that site-specific surveys are necessary before planning urban cultivation areas and educating urban gardeners regarding sustainable cultivation techniques is a priority for food safety and environment. We strengthened our results with focused questions to the allotment holders.

Keywords: urban allotments, heavy metals, soil properties, copper soil enrichment

Introduction, scope and main objectives

The cultivation of food in urban areas can provide solutions to the concern about food security (Lal, 2017) and to the access to nutritious food, which is lacking for poor groups of urban society (Gerster-Bentaya, 2013). On the other side, because of urban pollution, there is a worry about the safety of food. Researches were conducted on the possible transfer of metals from soil to edible parts of the vegetables; they showed that the translocation to the plants is negligible if the soil properties do not enable the mobility of the metals (Sipter *et al.*, 2008; Weeks *et al.*, 2007). However, the contaminants in resident or commercial urban soil are generally either low or immobile, due to the alkaline pH of urban soil. As the major sources of pollution in cities are traffic and industries, contributions to the contamination of the home-grown vegetables come directly from the atmosphere (Amato-Lourenco *et al.*, 2017). Contamination levels and health risks can be reduced by the isolation of the allotment area from traffic and the careful cleaning of the produce (Bretzel and Calderisi, 2011; Samuel *et al.*, 2012). On the other hand, the scarce quality of urban soil makes difficult to grow plants for self-production, which are demanding in terms of soil fertility. Urban gardeners can try to resolve this problem with overusing chemicals, thereby impoverishing the soil biota mass and reducing long-term fertility, along with the risk of self-intoxication and ingestion of the residues through the food (Flemming and Trevors, 1989).

The aim of our study was to assess the soil conditions and the presence of trace metals of an urban area used for self-production of vegetables in relation to the management techniques chosen by the gardeners.

Methodology

The study area is located in Pisa, Italy (90,000 inhabitants). The climate is warm and temperate, the average annual air temperature is 14.3°C and the average annual rainfall is 900 mm. The allotment area is in a very populated district built in the 1960s, in the east of the town near the river Arno. The area, used as municipal vegetable gardens since 1995, is divided into 72 allotments, each of about 90 m² and is located in the floodplain of the river Arno, sloping 1 m in a south-north and east-west direction. The area is far from the main roads, isolated from the effects of traffic by distance and the river embankment. Ten allotments were selected and sampled were chosen to analyse soil characteristics. Soil was air-dried at room temperature. Texture, bulk density (BD), pH (H₂O), cation exchange capacity (CEC), organic carbon (Corg), total nitrogen (N_{tot}) were determined on the 0-2 mm fraction by means of standard methods (ASA-SSSA 1996). The concentrations of Pb, Cu, Ni, Cr, and Zn, K, Al, Mn were determined using ICP-OES spectrometry (Liberty Axial Varian, Turin, Italy) after acid attack (EPA 3051A). To investigate the metal potential mobility and their possible translocation in plant tissues, the soil samples underwent a Sequential Extraction Procedure (SEP) according to Petruzzelli *et al.* (2015): the first step with H₂O, the second step with KNO₃, and the third step with EDTA.

Results

The results of the analysis of the soil properties and metal concentrations at cultivated area are reported in Tables 1 and 2. Allotment area was uniform in terms of texture, which was sandy loam; in the different allotments sand ranged from 70 to 49%, silt from 43 to 20%, clay from 15 to 7%. Soil pH was moderately alkaline, CEC was medium, EC showed the typical values of a sandy loam soil. The C/N ratio was averagely 8 (Table 1).

The values of the metals in soils were generally low for uncontaminated urban soil. However, some allotment showed a higher value of soil total Cu (Table 2). Values of total Cd, and mobility test of Zn and Pb, in water and KNO₃, were below the detectability level (0.05 mg/L). The EDTA mobility test showed very low values for all the metals and did not evidence phenomenon of possible bioavailability. Total Cu was strongly related to EDTA Cu (Fig. 1). The allotment holder answers related to the use of Cu-anticryptogamic products confirmed the trend of Cu in the different allotments.

Table 1. Main soil properties

Allotment	pH H ₂ O	EC mS cm ⁻¹	Corg %	Ntot %	C/N	CEC cmol ⁽⁺⁾ /kg
1	7.9	1.22	2.0	0.22	9.1	18.7
2	8.2	0.88	1.8	0.35	5.1	16.7
3	8.1	1.08	1.1	0.22	5.0	13.7
4	7.7	1.79	1.8	0.15	12	15.0
5	7.9	2.68	1.3	0.24	5.4	16.7
6	7.9	2.24	1.8	0.13	14	18.0
7	7.9	1.45	1.3	0.12	11	16.8
8	7.9	1.45	1.3	0.12	11	16.8
9	8.1	1.63	1.7	0.17	10	17.5
10	7.8	1.31	2.3	0.34	6.8	16.8

(EC=electrical conductivity, CEC=cation exchange capacity)

Table 2. Concentration of metals (Total and EDTA-extracted) in soil allotments (mg kg⁻¹)

Allot - ment	Cr tot	Ni tot	Cu tot	Zn tot	Pb tot	Mn tot	K tot	Al tot	EDT A-Cu	EDTA-Ni	EDTA-Zn	EDTA-Pb
1	33.7	29.4	75.8	69.7	8.2	543	1770	11541	17.5	1.47	9.52	4.45
2	55.0	31.5	158.7	70.6	11.9	599	4242	11745	32.5	1.45	8.67	4.79
3	49.4	30.1	71.3	58.3	9.1	517	3122	9811	17.4	1.32	4.99	3.40
4	36.2	28.6	81.0	52.7	7.2	536	1915	12505	21.0	1.37	6.32	3.42
5	47.8	30.0	55.7	38.4	6.3	494	3428	10307	15.0	1.47	5.85	2.92
6	33.4	29.1	82.3	56.0	6.3	524	1977	12367	19.4	1.55	7.64	3.62
7	37.8	32.3	55.5	52.5	5.8	531	1699	13646	12.6	1.24	4.97	3.32
8	37.8	32.3	55.5	52.5	5.8	531	1699	13646	12.6	1.24	4.97	3.32
9	32.3	27.4	109.7	47.5	6.7	476	2044	10878	22.9	1.25	4.19	3.32
10	54.7	33.6	97.3	56.2	7.2	536	4735	11746	20.9	1.25	4.92	2.47

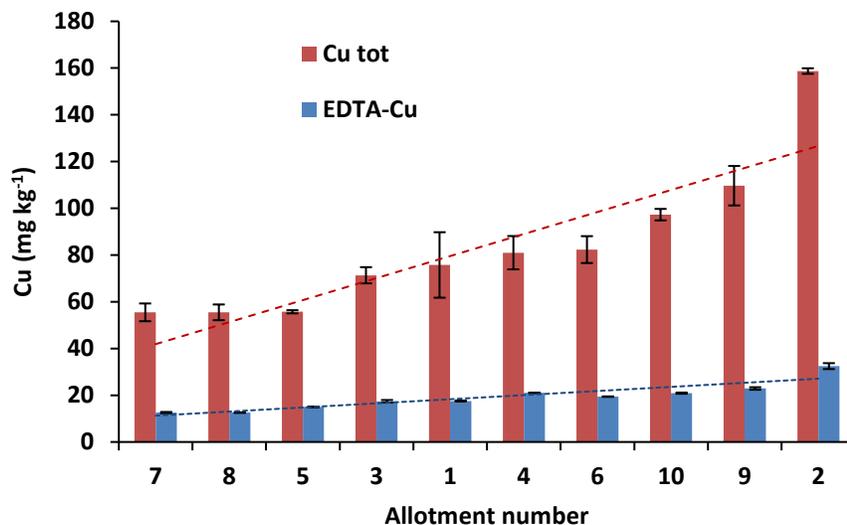


Figure 1. Copper concentration (total and available) in the different soil allotments. Increase of Cu tot reflects the increase of EDTA-Cu



Figure 2. Lettuce production in the urban allotment. Plant size indicates that N fertilisation has been carried out.

Discussion

Our results show that the cultivation led to improve organic carbon and dissolved salts (EC), due to the addition of organic matter (manure) and partially the burying of the cultivation residues. Nevertheless, the C/N ratio in some allotments was low, which could be due partly to N fertilisation carried out by the allotment holders to increase the production (Fig. 2). At the same time, our study evidences a presence of total and bioavailable copper in soil, possibly deriving from the anti-fungal treatments by means of copper-spraying treatments, especially on tomatoes, that in some allotment caused the accumulation in soil of this element. Those findings are confirmed by the garden holders' testimonials. The antifungal treatments are carried out by all of them, in some cases (e.g. allotment 2) with improper tools, which spread the product in excess.

Conclusions

Our study highlighted that the management of urban allotments entails some changes of urban soil properties, and these changes are heterogeneous, in relation to the individual choices of the allotment holders. In particular, organic carbon increased in some cases thanks to the use of manure, and the low C/N revealed that the nitrogen fertilisation was in excess. The Cu-residuals in soil due to antifungal treatments were high in some cases, and the mobile fraction was noticeable and correlated to the total amount. The possible accumulation of copper in urban agricultural soils can constitute a risk for the quality of soil, affecting the biota and the cycle of nutrients.

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1.1.20. Photochemically-Induced Fluorescence (PIF) and UV-Vis absorption determination of diuron, kinetic of photodegradation and rate of leach ability in soils.

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Abstract

Several physicochemical studies were undertaken and evaluated for diuron pesticide. At first time, we have studied in aqueous water the kinetic of photodegradation by UV-visible absorption method for the diuron; second order kinetic with lifetime's values of 0.5 hours is found. This compound exhibited fluorescence emission only under UV irradiation because of their transformation into fluorescent photoproducts. The influence of various physicochemical parameters affecting the sensitivity of the PIF method, such as solvent system, pH, and UV irradiation time was investigated. PIF method was, therefore performed in optimal analytical condition. The limits of detection (LOD) are particularly low, ranging between 8.5 and 96 ng/mL according to the solvent. Finally, a study destined to investigate the rate of leach ability in soils has been conducted in agricultural soil. The obtained rate of infiltration is: 12.7 mm/min. These results show that diuron has high potential of pollution of groundwater.

Keywords: Pesticide, diuron, UV-Visible absorption, photodegradation, photochemically-induced fluorescence, soils leach ability.

Introduction

Anti-parasitic products for farm like pesticides are widely used in Senegal and in the near under-region. Most of these compounds present a great photochemical instability and are rapidly degraded in our country characterized by a very sunny and warm dry summer climate. With the aim of finding analytical methods able to solve problems related to pollution and toxicity, therefore intended to safe the use of pesticides, we have undertaken a study for diuron used in agriculture in Senegal. For this purpose, we used two methods: UV-VIS absorption and photochemically-induced fluorescence (PIF method) in order to evaluate the environmental parameters of the studied compound. Diuron is an herbicide used in a range of crops and gardening and other non-crop areas to control the development of weeds. Herbicide is widely used in Niayes area in agriculture to increase crops yields by killing pests or eliminating diseases. The herbicide diuron is frequently detected both in surface and groundwater (Meffe and Bustamante 2015). The wide spread use of these herbicides has, together with its persistence, resulted in it

becoming common pollutant in both soil and water (Villaverde *et al.* 2017; Quitantes *et al.* 2017; Ali *et al.* 2014). Suitable methods of analysis diuron have been published. Most of them are based on LC or HPLC (Vega *et al.* 2015; Lourencetti *et al.* 2008) and GC-MS (Dagnac *et al.* 2005).

Hence, in this work, we use UV irradiation to degrade diuron and monitored the photoproduct using the absorption and fluorescence spectrometry. Therefore in the present paper, we developed and evaluated several physicochemical studies for selected diuron including, kinetic of photodegradation in aqueous media and the determination of rate of leach ability in soils.

Methodology

Reagents and Sampling

Diuron (97.5 %, m/m) was purchased from Cluzeau Info Labo (Sainte Foy la Grande, France). Hydrochloric acid (36 %, m/m) and sodium hydroxide (97 %, m/m) were obtained from Sigma Aldrich (Taufkirchen, Germany). Spectroscopic-grade solvents including acetonitrile, methanol, dimethyl sulfoxide and cyclohexane were from Merck (Darmstadt, Germany). Dune soils samples were collected from Malika (suburb of de Dakar) in a coastal agricultural area called “Niayes area”. Samples were taken from the 0-10 cm upper layer of the horizon and brought to the laboratory where they were air dried, sieved to pass a 2 mm mesh and stored at room temperature. The chemical structure of diuron is presented in Fig. 1.

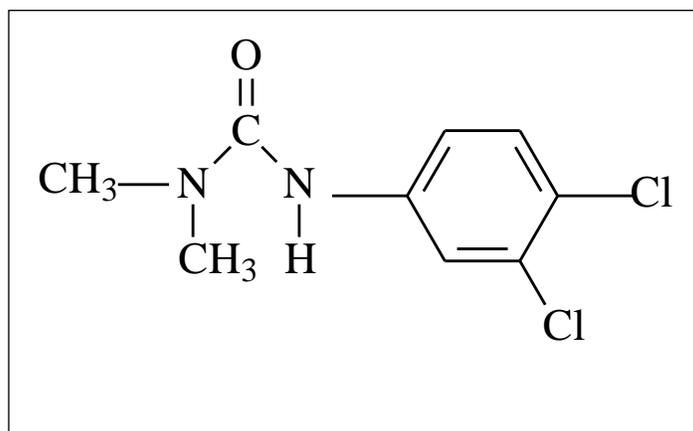


Figure 1. Chemical structure of diuron.

Apparatus

All the UV-Visible absorption measurements were performed with Helios Gama thermospectronic spectrophotometer controlled by software Visiolite. Fluorescence measurements were made with Kontron SFM-25 spectrophotofluorimeter connected to a computer and processed by software LCWIN-25. An unfiltered Osram 200W HBO high pressure mercury lamp with an Oriel Model 8500 power supply was utilized for photolysis reaction. The photochemical set up included a light-box consisting of a fan, the mercury lamp and a quartz lens. Standard Hellma 1-cm path length quartz absorption or fluorescence cuvette was placed on an optical bench at 47 cm from the mercury lamp. During photolysis, the quartz cuvette solution was stirred magnetically. pH measurements were performed with a Consort pH-meter Model P107 and a micropipette (pipetman) of 50 and 1000 μ L were used for dilution. All fluorescence analytical measurements were carried out under the same condition of voltage (high voltage = 500) and sensitivity (factor = 9).

Preparation of solutions

Stock solution of diuron (10^{-3} M) were prepared by dissolving in acetonitrile analytical solvent. Serial dilutions were performed to obtain working solutions. All solutions were protected against light with aluminium foil and stored in a refrigerator. Stock solutions of HCl (2N) and NaOH (2N) were prepared with distilled water and serial dilutions were made from these stock solutions.

Photolysis reactions and analytical measurements

The photolysis reactions were performed by irradiating aliquots of the diluted pesticide solution placed in quartz cuvette with UV light for a fixed time. All photolysis studies were carried out at room temperature. No cooling device was necessary as no significant heat was generated during irradiation. For the absorption spectra experiments, the influence of UV photolysis was monitored by recording the absorption spectra intensity versus UV irradiation time at the maximum absorption wavelength of the diuron (Fig. 2).

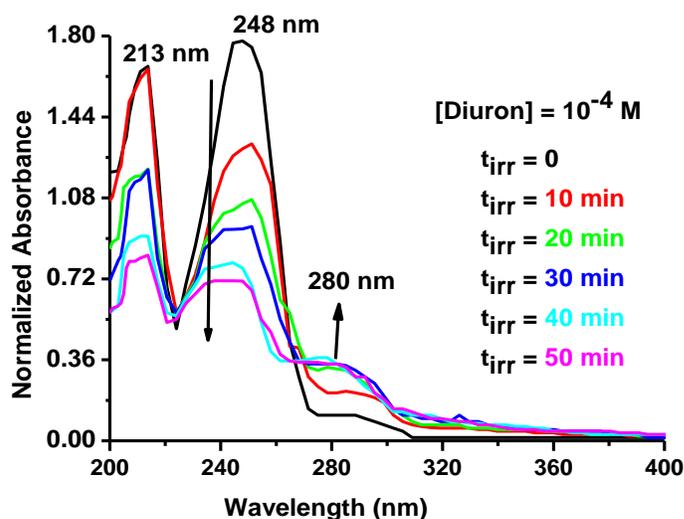


Figure 2. Influence of the UV irradiation time on the normalized absorbance of diuron in water.

For the fluorimetric method, the curves of PIF intensity (I_{PIF}) as a function UV irradiation time (t_{irr}) were constructed at the analytical excitation (λ_{ex}) and emission (λ_{em}) wavelengths of the diuron photoproduct using 2-5 min intervals according to the solvent (Fig. 3). Linear calibration curves were obtained at the same analytical wavelength values by measuring the PIF spectra signal height corresponding to the optimum t_{irr} . All PIF intensity measurements were corrected for the background signal with the appropriate blanks.

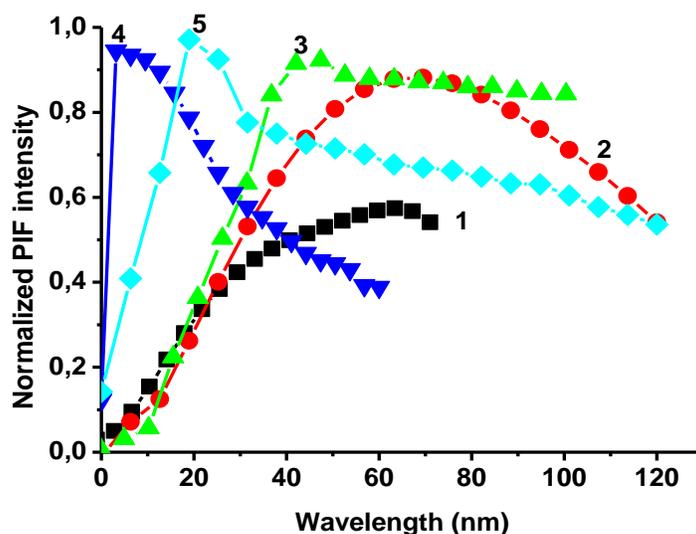


Figure 3. Influence of the UV irradiation time on the normalized PIF intensity of diuron (10^{-5} M) in different solvents:

Water (pH12) (1), acetonitrile (2) methanol (3), cyclohexane (4), DMSO (5).

Soils leaching procedure

Leaching was studied in a PVC laboratory made hand-packed soils column (50 cm long, 12 cm diameter) sealed at the bottom with a fine mesh in order to retain soil and permitting a regular stream of the leachate. Before filling the column soil sample were washed three times with tap water and rinsed with distilled water. The leachate stream were maintained constant at the value of 0.5 mL/min by the mean of a separatory funnel filled with distilled water and fixed above the top of the PVC soil column.

Results

In this study, the measure of the rate of the photodegradation reaction involved were accomplished by the first method while the second is more suitable for quantitative studies and was used for this after transforming the pesticide original molecule into fluorescent photoproduct.

Absorptiometric photodegradation kinetic study

In this paragraph, we studied the kinetic of photodegradation of the diuron in water by UV-Visible absorption spectrophotometer. The electronic absorption spectra recorded for fixed pesticide concentration ($C = 10^{-4}$ M) before and after UV irradiation process are shown in Fig. 2.

Diuron spectra show two peaks (at 213 and 248 nm) which decrease rapidly with increasing irradiation time. A small blue-shift of the peak at 248 nm is observed while a new band appears at higher wavelength in the near 280 nm corresponding to the formation of a photoproduct. Table 1 summarizes the parameters of the photodegradation kinetic for the studied compound in solvents.

Table 1. Kinetic parameters of the diuron photolysis reactions in different media

Solvent	λ_{ab} (nm) ^a	ϵ (mol ⁻¹ .l.cm ⁻¹) ^b	K ^c (min ⁻¹ or M ⁻¹ min ⁻¹)	$t_{\frac{1}{2}}$ (min) ^d	Order ^e	r ² ^f
Acetonitrile	250	1.9 x 10 ⁴	114,5 (± 9.2)	87.5	2	0.989
Water	248	1.8 x 10 ⁴	362 (± 21.7)	27.6	2	0.997
Methanol	248	2.3 x 10 ⁴	1,8 (± 0.05)x 10 ⁻²	37.5	1	0.999

^a λ_{ab} = maximum absorption wavelengths. ^b Molar extinction coefficient values. ^c k = photolysis rate constant (min⁻¹ or M⁻¹ min⁻¹) and absolute error (±). ^d $t_{1/2}$ = photolysis reaction half-life time (min). ^e Order = reaction kinetic order. ^f r² = kinetic equation correlation coefficient.

Photochemically induced fluorescence (PIF) study

PIF characteristics

When a dilute solution of the studied pesticide was submitted to UV radiation, fluorescent photoproducts were generated which PIF properties (Coly and Aaron 2001; Coly and Aaron 2009; Thiaré *et al.* 2015), *i.e.*, optimum irradiation time, λ_{ex} and λ_{em} depended to the solvent nature (Table 2). The observed PIF signal generally increase until the optimum irradiation time (t_{irr}^{opt}) is reached and then decrease further. The values of t_{irr}^{opt} are very short in solvent such as cyclohexane and DMSO. In the others media, t_{irr}^{opt} varied and remain too high since it is superior to 20 min in general.

Table 2. Medium effect on the diuron PIF properties and photolysis reaction kinetics.

Solvent	λ_{ex} (nm)	λ_{em} (nm)	t_{opt} (min)	I _{PIF}
DMSO	342	410	20	1.71
Cyclohexane	348	405	5	1.64
Methanol	320	414	45	1.60
Acetonitrile	333	408	60	1.54
Water (pH =12)	345	433	45	1.00

The PIF signal intensity or stability is generally affected by the pH of the media. In our study, the curve describing the evolution of PIF intensity versus pH of the aqueous solutions is characterised by maximum pH value of 12. This value was adopted for further investigation.

The usefulness of the PIF method for the analysis is based in part to the relative stability of the obtained photoproduct. In our study, we check this feature for a short time *viz.*, 30 min and more such as in a period of a week. The diuron was irradiated in the different solvents and then a 30-min kinetic study was performed. Afterward, the samples were covered with aluminium foil and stored in a refrigerator from which a PIF spectrum was recorded daily during a week. In a period of 30 min observation, photoproducts generated in the different organic solvents are stable. In contrast, after 8 days observation, the PIF signal of most of the photoproducts in the different media changed markedly. Except the case of DMSO and cyclohexane, the PIF signal increase with time and then decrease for the others solvents.

The parameters of the calibration graph for the determination of the pesticide by PIF detection under optimum conditions are presented in Table 3. These statistical parameters obtained from triplicate PIF signal measure were performed for at least six concentrations and yielded satisfactory relative error < 0.8%. Linear log-log calibration plots were established over about two

orders of magnitude with a good accuracy ($r^2 \geq 0.98$). The limits of detection were low, ranging between 8.5 and 96 ng/mL according to the solvent.

Table 3. Analytical figures of merit for the PIF determination of diuron.

Solvent	LD (nm)	LQ (nm)	r^2
Cyclohexane	8.5	28	0.986
DMSO	96	317	0.993

Soil leaching ability study

Before the application of the pesticide, we investigate the column soil permeability to water. The reparatory funnel, above the top of the column, filled with distilled water was used to maintain a constant flow rate of 0.5 mL/min. During eight hours, leachate was collected every 30 min, and when the cumulative amount of water were plotted against duration of the elution, a straight line is obtained. This result concluded in favour of the uniformity of the pore size distribution of the studied soil.

The amount 10^{-2} M of the studied pesticide were dissolved in analytical solvent acetonitrile and sprayed to the top of the column. After the pesticide application, the column was leached with aqueous water and leachate were collected every 30 min interval, submitted to extraction procedure (see experimental section) and PIF analysis. The pesticide concentration detected in leachate were obtained for short times values of 0.5h. Table 4 summarizes the environmental parameters related to the diuron under study. The calculated rate of infiltration is 12.7 mm/min.

Table 4. Infiltration speed of diuron in soil.

Infiltration time (min)	Infiltration speed (mm/min)	$t_{\frac{1}{2}}$ (min)
30	12.7	30

Discussion

Diuron follow a second order kinetic with correlation coefficient of the corresponding straight line larger than 0.98. The calculated molar extinction coefficient values at the different peaks were larger than $16\ 000\ \text{M}^{-1}\ \text{cm}^{-1}$. This information means that it occurs strong $\pi \rightarrow \pi^*$ band absorption for the compound and consequently, accurate absorbance measures can be expected. This study has revealed also that solvent has a noticeable effect on the half-life times of the studied diuron. The data presented in Table 1 shows the result of half-lives for three solvents including water, methanol and acetonitrile. On the other band, the half-life times of second order reaction been inversely proportional to the initial concentration, diuron is very persistent in water under light effect. Hence we have to consider the risks of contamination of surface water by streaming or groundwater through infiltration. In section Soil leaching ability study, we assessed this risk by studying his infiltration rate in soil to better appreciate his power of contamination of surface and under groundwater. On the other hand, the pesticide initial concentration has no significant effect on the values of t_{irr}^{opt} . For example, we found 0.1% as relative error value. About the PIF intensity, it has been noted that aqueous water solutions inhibit the photoproduct fluorescence signal while organic solvents enhance it. For analytical studies, cyclohexane and DMSO media offer better conditions. However, the shape of the excitation and emission spectra of the photoproducts remains unaffected. These results mean that our developed PIF analytical procedure is reproducible in a minimum 30-min interval times.

In contrast, diuron, who's a high rate of leach, are in the position to contaminate groundwater allowing them to escape partially from microbial degradation. From a public health standpoint, it would be very useful to determine the content of the diuron in sols, water flows and under groundwater, at least, in risks zones.

Conclusions

In the present communication, we have developed and evaluated several physicochemical studies for diuron. Some environmental behaviour has been assessed using UV visible absorption and PIF method. Diuron, groundwaters seems to be their final destination after spray. However, in all cases, PIF method could be used to monitor herbicide with satisfactory results.

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1.1.21. Effect of the soil properties in the partitioning of pesticides (glyphosate and paraquat) used in corn and coffee beans Colombian crops

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Abstract

The first environmental soil resource policy was released in Colombia last year and many institutions have begun to study the soil contamination problem from an environmental point of view. Corn and coffee beans are common crops in Colombia, and Glyphosate and Paraquat are the agrochemicals used on these crops. In order to provide environmental evidence of soil contamination, we decided to study the adsorption of these chemicals related to the soil properties and develop a model to predict these concentrations. The study used two soils of corn and coffee crops, and then the adsorption measured as the partition coefficient could then be determined. These coefficients were modelled with the partitioning of the pesticides of the most representative fractions of the soil properties. To do that, we conducted batch experiments near 1:1 soil to solution ratios reflecting field conditions using a Paraquat and Glyphosate agricultural solution concentrations of corn and coffee beans crops. The experiment involved 2 days of adsorption and then the concentrations of chemicals were measured to determine the adsorption of these substances. The project used the multilinear model to predict the adsorption concentration, which uses: organic carbon, clay content and extractable iron soil information. These were all measured and used to verify the application of the model. The most important observation was that for each pesticide, we successfully predicted the partition coefficients, improving them by a factor of 2 in the accuracy compare with the traditional approach using organic carbon only.

Keywords: Glyphosate, Paraquat, Corn, Coffee Beans Crop, Partitioning, Multilinear Model

Introduction, scope and main objectives

In Colombia, glyphosate and paraquat agrochemicals are used to eradicate different types of weeds in annual and perennial crops such as bananas, coffee and corn, among others. The direct application of these chemicals can cause negative effects in living beings (human and animals) due to its toxicity. Glyphosate by National Pesticide Information Center (2017) is an herbicide. It is applied to the leaves of plants to kill both broadleaf plants and grasses. It can persist in the soil for up to 6 months depending on the climate and the type of soil. Paraquat is a synthetic, non-selective contact herbicide that can cause local skin damage. Prolonged contact will produce erythema, blistering, abrasion, ulceration, and fingernail changes (National Pesticide Information Center 2017). Research in this area is costly but it is necessary to determine their concentrations and establish the environmental impact to make political decisions and protect the environment, especially in countries with incipient regulations in this area.

The project has a main objective to determine if the soil properties have an important effect in the partitioning of glyphosate and paraquat used in corn and coffee beans Colombian crops using the Multilinear Model. When modelling in soils, it is well known that the organic matter is generally the most important soil constituent responsible for the sorption of organic compounds. This has led to the use of the organic carbon normalized partition coefficient, K_{oc} ($L\ kg^{-1}$), the octanol-water partition coefficient, K_{ow} ($L_{water}\ L_{octanol}^{-1}$), and fraction of organic carbon in the soil, f_{oc} to describe this phenomenon. These simplifications have been successfully employed to model the partitioning of many hydrophobic organic chemicals like PCBs and PAHs, but their application to pesticides results in order of magnitude errors. For this reason, we use the multilinear model. The Multilinear model was developed by Gonzalez (2014) and demonstrated the importance of including additional properties of the soil in sorption modelling of nitro-compounds as explosives. This finding has also been observed by many authors such as Sheng *et al.* (2001), Van Noort (2010) and Dontsova *et al.* (2009). The model calculates the partition coefficient (nitro-compound concentration into the soil/ nitro-compound concentration into the water) K_p from the sum of three linear terms, one for the organic carbon, the second one for the clay size particle and the third one as the extractable iron content as the fraction of each component times their corresponding sorption coefficients. Equation 1 shows the multilinear model:

$$K_{ps,c} = K_{oc} c(f_{oc})_s + K_{Clay} c(f_{Clay})_s + K_{Fe} c(f_{Fe})_s \quad (1)$$

Where:

K_{oc} = sorption coefficient to organic carbon in the soil;

K_{Clay} = sorption coefficient to the clay in the soil;

K_{Fe} = sorption coefficient to the extractable iron in the soil;

f_{oc} = fraction of the organic carbon in the soil;

f_{Clay} = fraction of the clay in the soil;

f_{Fe} = fraction of the extractable iron in the soil and:

s = soil;

c = nitro-compound;

f_{oc} , f_{clay} and f_{Fe} are properties of a soil and K_{oc} , K_{clay} and K_{Fe} are function of the nitro-compound used.

Methodology

This study employed two soils collected from the Research and Training Center La Isla located in Sasaima, and the Matapantano Farm located in Yopal city belonging to La Salle University with corn and coffee beans crops. To collect the samples, the national authority of soils in Colombia IGAC (Agustin Codazzi Geographic Institute) methodology were used. The Yopal soil for coffee and corn crops had no variations, the soil was not eroded at any point, there was no vegetation that did not belong to the crop and there was no body of water in the area to be studied. In Sasaima, although the farm has some topographical variations (presence of slopes), the coffee and corn crops were in flat terrain. In addition, there was no other vegetation besides corn and coffee and the soil was uniform with no erosion. It was a composite sample taken in Sasaima and Yopal for each crop. According to Tan (1996), a composite sample is necessary instead of a simple sample since it has a greater accuracy. The sampling was done by the zigzag method, which consisted in dividing the land in a zigzag way, taking 25 subsamples. These subsamples were mixed in a bucket until a homogeneous composite was obtained. From this homogeneous mixture, two samples of one kilogram was taken and then they were packed in a plastic bag with airtight seal and labelled. One of the samples was sent to the IGAC to perform the analysis of the fraction of organic carbon, extractable iron and clays. The other sample was transported to the laboratory of La Salle University for the sorption experiment. Table 1 shows the fractions of the chemical characteristics of the soils obtained by calculation from the IGAC analysis.

Table 1. Fractions of the chemical characteristics of the soils used in the study

Soil	Crop	fFe	fckay	foc
Yopal	Coffee Beans	0.0069	0.2430	0.0147
Yopal	Corn	0.0070	0.2040	0.0147
Sasaima	Coffee Beans	0.0025	0.1660	0.0520
Sasaima	Corn	0.0026	0.1650	0.0617

For the sorption experiment, 5 ± 0.0001 grams of soil were added to 12 mL borosilicate centrifuge tubes with phenolic caps and PTFE liners. Batch sorption experiments were conducted at 1:1 (w/v) soil to solution ratio, reflecting near field conditions and at room temperature. Soils were hydrated for 5 days prior to the addition of pesticides in a solution containing 0.01 M calcium chloride (CaCl_2) and 0.01 M sodium azide (NaN_3). CaCl_2 was added to prevent flocculation of soil components and NaN_3 was present as a microbial growth inhibitor. After the 5-day hydration time, 5 mL of pesticide solution were added. The concentration of each pesticide was determined by the typical agricultural application for each crop. This information was obtained by surveys made with the farmers of the places where the samples were taken. Table 2 shown the concentrations of chemicals used.

Table 2. Concentrations of Glyphosate and Paraquat used in the study

Soil	Crop	Glyphosate Conc. (mg/L)	Paraquat Conc. (mg/L)
Yopal	Coffee Beans	250	63
Yopal	Corn	354	89
Sasaima	Coffee Beans	290	70
Sasaima	Corn	365	90

Triplicate samples were vortex mixed for 15 seconds to suspend the soil and next they were shaken at 10 rpm in an end-over-end shaker for 2 days (this methodology was the same as Gonzalez, 2014 applied the multilinear model develop). Subsequently, the tubes were centrifuged for 30 min at

3000 rpm (750 G), the decanted supernatant was filtered and analysed by COD (Chemical Demand Oxygen) as organic matter. A calibration curve relating COD and pesticide concentration was done to determine the pesticide remaining in the solution after the adsorption. After that, calculations were done and soil pesticide concentration and Kp were determined.

Results

The partition coefficient Kp in L Kg⁻¹ was calculated from the data as the relationship between the amount of chemical sorbed per mass of soil and the concentration remaining in the solution after equilibration in the adsorption. The parameters Koc, KClay and KFe were calculated for all the chemicals and soils. They were obtained by fitting the multilinear model by the minimization of the log residuals square between the Kp calculated from the experimental data and the Kp obtained by the model using the Excel solver tool. Table 3 shows the observed data obtained by the sorption experiment and table 4 the multilinear model results.

Table 3. Partition Coefficient (Kp) Observed by the Sorption Experiment

Agrochemical	Value	Kp Observed			
		Coffee Beans / Sasaima	Corn / Sasaima	Coffee Beans / Yopal	Corn / Yopal
Paraquat	Quartile 1	2.8273	2.8528	2.5403	2.3576
	Median	3.1065	3.0962	3.5522	2.6810
	Average	4.1765	3.4681	3.3074	3.1062
	Quartile 3	4.8736	3.7115	2.5403	3.5192
Glyphosate	Quartile 1	1.3451	1.3758	-	3.3914
	Median	1.7368	1.7511	-	4.1636
	Average	1.7368	1.9073	-	5.2141
	Quartile 3	2.0317	2.2248	-	5.9863

- No data.

Table 4. Multilinear Model Results

Agrochemical	Soil	Kp Observed	Kp Model	Koc	Kclay	KFe
Paraquat	Corn / Yopal	4.6889	4.6858	0.1000	0.4558	663.0469
	Coffee Beans / Sasaima	1.7126	1.7991			
	Corn / Sasaima	1.8147	1.7333			
Glyphosate	Coffee Beans / Yopal	2.9850	2.9673	47.2253	0.0000	324.7215
	Corn / Yopal	2.9160	2.9348			
	Coffee Beans / Sasaima	3.7460	3.7581			
	Corn / Sasaima	3.2822	3.2675			

Discussion

The Koc, Kclay, Kfe coefficients indicate the importance of the soil properties (organic carbon, clays and extractable iron) in the adsorption of the agrochemicals. Paraquat depends mainly on extractable iron and clay content with Kfe values of 663.0469 and Kclay of 0.4558 respectively. As the iron value is higher than clay, Paraquat adsorption is driven by this metal. On the other hand, Paraquat was poorly affected by the organic carbon, because Koc was near to zero. Glyphosate does

not depend on the clay content because their partition coefficient was equal to zero, so that its adsorption is given by organic carbon and extractable iron having coefficients of 47.2253 and 324.7215 respectively. As the K_{fe} coefficient is higher than K_{oc}, glyphosate adsorption as paraquat is driving by extractable iron, so this metal influence is mainly in this kind of chemicals.

K_p Observed and K_p determined by the Multilinear Model for Glyphosate and Paraquat of Table 4 show that all K_p are greater than 1, indicating soil retention of these chemicals. In addition, it is observed that the Multilinear Model makes a good simulation of the K_p model since these values are very similar to the K_p Observed in both Glyphosate and Paraquat and the residuals are between -0.002 and 0.002 to Glyphosate and -0.02 and 0.02 to Paraquat.

To analyze the usefulness and corroborate that the Multilinear Model can be used in the estimation of this kind of data, different statistical errors were calculated, the mean square error (RMSE), the concordance index (d), the BIAS (medium bias) and the normalized mean error (NME) to. The errors can be seen in Table 5.

Table 5. Error Prediction of the Multilinear Model

Soil	RSME	d	BIAS	NME
Paraquat	0.6183	0.9520	0.0007	0.0239
Glyphosate	0.5443	0.9930	-0.0004	0.0119

RMSE shows that the dispersion of data in both agrochemicals is low with values of 0.6183 and 0.5443 for the Paraquat and the Glyphosate respectively, indicating that the model made an adequate prediction regarding the observed data. d concordance index is near to 1, which means there was a perfect agreement between the measured and estimated values. This result shows a good accuracy of the data modeled against the experimental ones.

In the BIAS error, the Paraquat has a positive value, which means that there is an overestimation of the model. This indicates that the prediction of the model exceeds the observation. The glyphosate presents a negative value with an underestimation of the model. This indicates that the prediction of the model is below the observation. However, the overestimation of Paraquat and the underestimation of glyphosate is minimum because the values are close to zero with values of 0.0007 and -0.0004 respectively, indicating a high precision of the Multilinear Model. Finally, the normalized absolute mean error (NME) was calculated. With this error, the good precision of the model was confirmed for the calculation of the destination of the glyphosate and the Paraquat with percentages of error below 1% in both cases.

Conclusions

The multilinear model can be used to predict the fate of Glyphosate and Paraquat in the soils of corn and coffee beans because the RMSE obtained to compare the K_p measured and K_p modeled were very low (0.62 and 0.54 respectively).

The parameters of the models K_{oc}, K_{clay} and K_{fe} indicates that Glyphosate has more affinity to iron and organic carbon as soil properties rather than extractable iron. For Paraquat, the extractable iron is the main soil property that controls the adsorption phenomena.

The soil properties have an important effect of the modelling adsorption/partitioning of Paraquat and Glyphosate in corn and coffee beans crops. This study can be used to make decisions in contaminated soils.

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Sub-theme 1.2: Drivers of soil pollution in non-agricultural soils

1.2.1. The legacy of surface mining: remediation, restoration, reclamation, and rehabilitation

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Abstract

Surface mining is a global phenomenon. When dealing with the land disturbances caused by surface mining operations, the terms remediation, reclamation, restoration and rehabilitation (R4) are commonly used interchangeably or otherwise vaguely defined. Expectations associated with these terms may differ significantly from one stakeholder to another, however. Regulators, industry, environmental practitioners, local communities and the general public therefore stand to benefit from a precise terminology based on agreed-upon end-goals. The latter range from the avoidance of exposure to pollutants (remediation) to the full recovery of the original ecosystem (restoration). Although frequently claimed as the end-goal, restoration may often not be feasible, because of altered hydrology, habitat fragmentation, contamination, climate change, prohibitive costs and other environmental and socio-economic boundary conditions. Alternatives are then reclamation, which aims to recover key ecosystem services and biogeochemical functions within a replacement ecosystem, or rehabilitation, which implies a repurposing of the landscape. Here, we illustrate the usefulness of a clear, ecology-based differentiation of R4 terminology in a comparative analysis of the environmental management of the legacies of peat extraction in Ireland, mountaintop coal mining in Appalachia, and surface mining of oil sands in Alberta.

Keywords: Surface mining, remediation, reclamation, restoration, rehabilitation, resource extraction

Introduction, scope and main objectives

In surface mining, soil and rock overlying or hosting a shallow ore deposit is physically removed to access the resource. Surface mining comprises different practices – strip mining, open-pit mining and mountaintop-removal mining – and accounts for more than 80% of ore mined each year (Ramani, 2012). Surface mining disturbs the landscape and impacts habitat integrity, environmental flows and ecosystem functions; it raises concerns about water (Miller and Zégre, 2014), air and soil quality (Mummey *et al.*, 2002), and often also public health. Legacies of surface mining may include loss of soil structure and fertility, altered hydrology, and long-term leaching of contaminants from tailings and end-pit lakes (Isosaari and Sillanpää, 2010; Li, 2006; Ramani, 2012). Very large-scale surface mining activities may cause ecosystem fragmentation and affect regional biodiversity (Rooney *et al.*, 2012).

Long-term legacies whose environmental effects extend far beyond the lifetime of the mining operations represent some of the more difficult issues facing regulators and industry (Bernhardt *et al.*, 2012; Bullock *et al.*, 2012; Rooney *et al.*, 2012). Existing environmental management guidelines and policies invariably refer to the need to remediate, reclaim, rehabilitate, restore, or some combination thereof, of the mining site after closure. Remediation, reclamation, rehabilitation and

restoration (hereafter referred to as R4), however, are used interchangeably in the scientific literature or in government reports and policy documents (Hüttl and Weber, 2001; Li, 2006). For example, one may find reclamation defined as “restoring the top-soil” (Mitchell and Casman, 2011), or directives that aim for the “land to be cleared” and the “soil handled” (Alberta Environment, 2010). Existing policies for coping with surface mining legacies have therefore been criticized for their lack of clarity (Bernhardt *et al.*, 2012) and for setting ill-defined or unrealistic goals (Bullock *et al.*, 2012; Rooney *et al.*, 2012).

The chosen case studies consist of carbon extraction that to different scales, present large-scale surface mining. Throughout the years, Mankind has explored nature for fuel: first trees and peat (in the lack of forestry), then coal and lastly oil. Although there are other examples of surface mining impacts, here we compare three examples of still active exploitation: peat extraction in Ireland, coal mining in Appalachia (United States) and oil sands exploitation in Alberta (Canada). We revisit the R4 terminology in the context of surface mining and propose a decision tree to help identify the appropriate R4 strategy based on the desired end-point for the post-mining site. A discussion will be followed regarding the actions taken at each case study and whether they achieved the envisioned R4 end-point.

R4 terminology revisited

The call for more uniformity and consistency in R4 terminology is not new (Wali, 1996). Clear definitions of the R4 terms may be key to the participatory planning and communication of long-term solutions for surface mining legacies. However, more important than redefining these R4 terms is to clarify the objectives for site end-use and expectations each involved part has regarding post-mining land-use. Considering previous idiosyncratic literature e.g. (Society for Ecological Restoration International Science & Policy Working Group, 2004), definitions have been established vaguely to encompass a wide variety of R4 practices. However, the end-points of R4 programs should be established at the earliest possible time, preferably even before mining operations begin (Figure 1) to avoid post-mining adversities. Figure 1 was developed based on Table S1 definitions and consists of an attempt to simplify R4 definitions. Contamination control, i.e. remediation, needs to occur before re-establishing a land-use. Restoration proposes to bring back the pre-existing ecosystem. If re-establishing the original is not feasible due to temporal considerations, but we would like to recover ecosystem services that the original ecosystem provided, decision makers arrive at reclamation (Foley *et al.*, 2005; Grant *et al.*, 2008; Powter *et al.*, 2012). Rehabilitation is a managerial term that measures costs and benefits of maintaining environmental quality and optimize local land management capacity and includes practices such as agriculture, forestry, urbanization, etc. (Box, 1974; Haigh, 2007; Wali, 1996). Note that due to interchangeability of the terms rehabilitation and reclamations, we use here reclamation as the more ecological terms, see (Lima *et al.*, 2016).

In reality, surface mining operations covering large geographic areas may require a spatial mix of R4 strategies, while land end-uses may have to be revaluated periodically, as a result of, among others, scientific and technological advances, adjustments to cost projections, new legal and spatial planning constraints, and shifts in public perception. Thus, the decision tree presented in Figure 1 should not be viewed as a rigid, one-time process, but rather as an adaptive tool to help maintain consistency during the (re)assessment of environmental site management options under spatially and temporally variable boundary conditions.

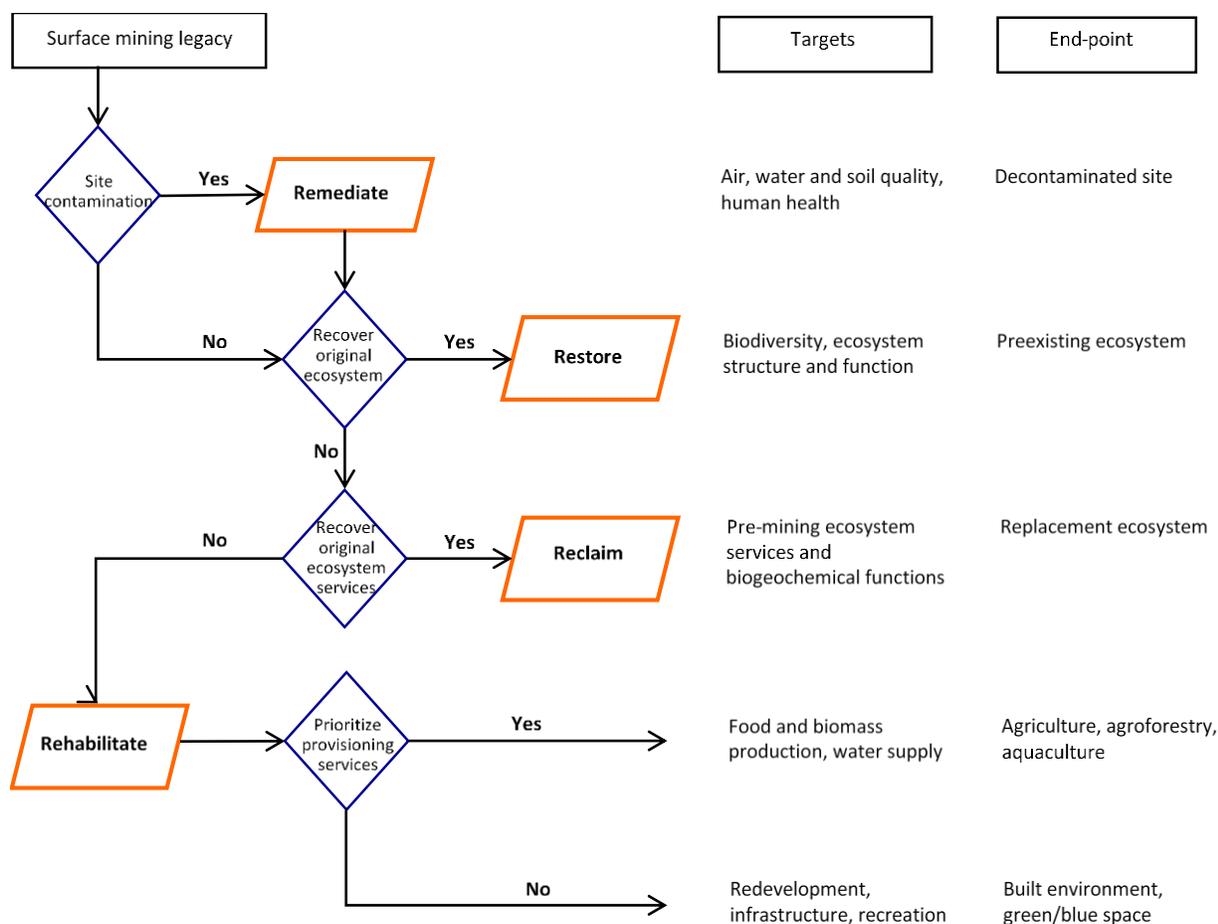


Figure 1. Proposed R4 decision tree based on targets and end-goals for post-mining recovery.

Conclusions

Surface mining worldwide exerts significant pressures on land, water and biological resources, hence, increasing the demand for the sustainable recovery of the impacted landscapes. Present and future endeavors can reap the benefits of past mistakes and land-use exploitations. The planning, implementation and evaluation of appropriate solutions are complex, multi-stakeholder undertakings that require consideration of diverse environmental, economic and social impacts. A meaningful dialogue between the stakeholders benefits from consistent remediation, restoration, reclamation and rehabilitation (R4) terminology to designate the activities to be carried out. In this paper, we propose a simplification of the R4 terminology based on objectives for site recovery that are formulated in terms of environmental quality, human health, land end-use, ecosystem structure and function, and ecosystem services. For any given surface mining operation, the decision support tool of Figure 1, in principle, can be translated into site-specific objectives and indicators that can be measured or valued.

Peat post-mining efforts have been varied, but necessarily the original intention: restoring the previous ecosystem. This goal could be unrealistic, regarding timeframe and costs. Therefore, forestry and agriculture, intertwined with areas of peat restoration may be economically viable. Peat subsidence events still need to be tackled (Dykes and Kirk, 2006). In Appalachia, mountaintop removal and extensive coal extraction and processing has provoked contamination issues downstream. Existing ecosystem restoration (or rehabilitation, reclamation) efforts have failed to

solve these contamination effects. Alberta ongoing oil-sands extraction will rise to 470,000 ha (6 times the size of New York city) (Pembina Institute, 2015). There is still time to clearly define the end-point of post-mining land and prevent previous large-scale mining liabilities.

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1.2.2. Analyses of native vegetation for a detailed characterization of soil contaminated by tannery waste disposal

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Abstract

The risks for human health and ecosystem due to Potential Toxic Elements (PTEs) in a farmland classified as potentially contaminated by Cr and Zn due to illegal dumping of tannery sludge, were investigated by analysing native vegetation and rhizo-soils. From this analysis, rhizo-soils of different plant species were found enriched not only by Cr and Zn but also by Cd As, Pb and Cu, elements neglected by the official environmental characterization. The ecological risk index had a mean value of 510, showing high to very high risk in different habitats. In particular, the rhizo-soils of *Lolium perenne*, *Erigeron sumatrensis*, *Piptatherum thomasi* and *Amaranthus retroflexus* have ERI above the very high-risk threshold. Two of the four plant species (*Erigeron sumatrensis* and *Amaranthus retroflexus*) accumulated Cd in the shoots above the threshold for forage, suggesting that there might be a potential risk of contaminant transfer to the food chain. The element posing the highest risk and most contributing to the Ecological risk index was Cd. *Cynodon dactylon* was the most suitable plant species for phytostabilization and securing of the contaminated site showing the highest bioavailable Cd accumulation in roots, the highest frequency and soil covering capacity during spring-summer when the risk of soil resuspension is generally more intense. The adaptability factor resulted a useful tool, considering the tolerance of plants species to the specific pedo-climatic and PTEs stress.

Keywords: Phytoremediation; Spontaneous flora; Potential toxic elements; Ecological Risk Assessment; Bioaccumulation Coefficient.

Introduction, scope and main objectives

The actual regulations about soil contamination are based on total Potential Toxic Elements (PTEs) content that includes fractions that are not available to plants, microorganisms, or soil biota (Zhang *et al.* 2001). For that reason, the determination of the bioavailable fraction is very important in risk assessment and is often predicted through single chemical extraction (McLaughlin, 2002).

The analysis of PTE uptake by native species of contaminated sites can give synthetic, but realistic information about the bioavailability of PTEs and thus on their hazard for human health and environment (Alloway *et al.*, 1991).

Phytoremediation is the most environmental friendly approach for reclamation of contaminated sites by removing the bioavailable fraction of PTEs from soil and accumulating them in the harvestable parts of the plants (phytoextraction) or by immobilize them in rhizosphere (phytostabilization), thus interrupting the exposure pathways (securing). The establishment of a vegetation cover is a cheap and eco-compatible way to reduce PTEs leaching and prevents the dispersal of contaminants through wind erosion typical of bare soils. Furthermore, contaminated sites have usually soil degraded both from physical and chemical points of view. Therefore, few species can be adapted to these limiting conditions. Consequently, the use of native species in phytoremediation programs is the better solution because such species are already adapted to the specific pedo-climatic conditions (Barrutia *et al.*, 2011).

The bioaccumulation coefficient (BAC) for shoot and roots and translocation factor (TF) are the most utilized indices for phytoremediation plant evaluation and selection (Putwattana *et al.*, 2015), but also a modified bioaccumulation coefficient (mBAC) was calculated for shoots and roots (Barbafieri *et al.*, 2011). However, the phytoremediation ability also depends on the characteristics of the plant species like growth rate, tolerance to the target PTE toxicity, and adaptability to local environmental conditions (Li *et al.*, 2017). For that reason, an adaptability factor was calculated as a screening criterion of the study.

Therefore, this study has been aimed to study the native vegetation of a contaminated site for: (a) investigating the risks for biological communities and ecosystem due to PTEs pollution; (b) identifying the target PTEs for phytoremediation; (c) evaluate the potential for phytoremediation of native plant species growing on the site.

Methodology

Site description

The site (Giugliano – Campania Region, Italy) was a six ha farmland, where in nineties tannery wastes were illegally disposed. According to Italian law (L. D. 152/2006), after Environmental Characterization, the site was classified as potentially contaminated by Cr and Zn because these PTEs in soils were above the Baseline Values of the area and above the Screening Values (SV) for agricultural soils (L.D. 152/2006). A risk analysis was carried out showing that site cannot be considered as contaminated by Cr and Zn and these pollutants do not represent a risk for human health and groundwater quality.

Plant and soil sampling

In July 2015, a floristic survey was carried out in the site. Eleven plots (3 x 3 m) were bordered; within each plot, a variable number of representative plant species (>three when possible) were sampled along with rhizo-soils and identified.

Plant analysis

Plants samples were separated in shoots and roots and then washed with tap water followed by distilled water, oven dried at 60°C until constant weight and finely ground. A composite sample representative of plants of each plot was analysed (acid digestion with *aqua regia* followed by ICP-MS) for PTEs content. Their values were compared to PTEs thresholds in forage, considering the native species as a potential pasture (UE Reg. 1275/2013).

Soil analysis

Rhizo-soil samples were dried at 50°C until constant weight, homogenized and sieved at 2 mm. The fraction < 2 mm was characterized for the PTEs concentrations (acid digestion with *aqua regia* followed by ICP-MS). The bioavailable fraction was estimated by a single extractions: 0.05 mol L⁻¹ DTPA solution (Lindsay e Norwell, 1978). PTE concentration in the solution was determined by inductively coupled plasma-atomic emission spectrometry (Perkin Elmer ICP-AES Optima 7300DV).

Potential ecological risk assessment

The potential ecological risk index (ERI) was used to evaluate the potential risk for biological community and ecosystems from combined pollution of multiple PTEs. The equation used is as follow (Hakanson, 1980):

$$ERI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i = \sum_{i=1}^n \left(T_r^i \times \frac{C_i}{C_n^i} \right)$$

where: E_r^i is the potential ecological risk index of the PTE i ; T_r^i is the toxic response factor for a specific PTE i (e.g. As=10, Cd=30, Cr=2, Cu=5, Pb=5, and Zn=1); C_f^i is the contamination factor of PTE i ; C_i is the content of PTE i in the samples (mg kg^{-1}), and C_n^i is the background value of PTE i in the study area (mg kg^{-1}).

In this study, soil background values (BV) of Campania Region reported by Salminen *et al.* (2005) were used (As: 13.00; Cd: 0.23; Cr: 18; Cu: 14; Pb: 29.0; Zn: 66.0 mg kg^{-1}). The monomial potential ecological risk of each PTE (E_r^i) was classified as low ($E_r^i < 40$), moderate ($40 \leq E_r^i < 80$), considerable ($80 \leq E_r^i < 160$), high ($160 \leq E_r^i < 320$), and very high ($E_r^i \geq 320$). The combined risk represented by ERI was classified as low risk ($ERI < 95$), moderate risk ($95 \leq ERI < 190$), high risk ($190 \leq ERI < 380$), and very high risk ($ERI \geq 380$) (Rehman *et al.*, 2018).

Calculation of PTEs accumulation indices and adaptability factor

The following indices were applied to evaluate the ability of the plants to accumulate PTEs: bioaccumulation factor for shoots (BAC_s), bioaccumulation factor for roots (BAC_R) and translocation factor from roots to shoots (TF).

$$BAC_s = \frac{\text{PTEs concentration in aerial part (mg kg}^{-1}\text{)}}{\text{PTEs concentration in soil (mg kg}^{-1}\text{)}}$$

$$BAC_R = \frac{\text{PTEs concentration in roots (mg kg}^{-1}\text{)}}{\text{PTEs concentration in soil (mg kg}^{-1}\text{)}}$$

$$TF = \frac{\text{PTEs concentration in aerial part (mg kg}^{-1}\text{)}}{\text{PTEs concentration in roots (mg kg}^{-1}\text{)}}$$

To evaluate the capacity of plants to uptake the bioavailable fractions of contaminants, a modified bioaccumulation coefficient (mBAC) was calculated both for shoots and roots (Hamon and McLaughlin, 1999) as follow:

$$mBAC_s = \frac{\text{PTEs concentration in aerial part (mg kg}^{-1}\text{)}}{\text{bioavailable PTEs concentration in soil (mg kg}^{-1}\text{)}}$$

$$mBAC_R = \frac{\text{PTEs concentration in roots (mg kg}^{-1}\text{)}}{\text{bioavailable PTEs concentration in soil (mg kg}^{-1}\text{)}}$$

To evaluate the plants adaptability to soil contamination an adaptability factor was calculated as proposed by li *et al.* (2017), based on their ecological status on the site and the pollution level of their habitats.

The plant ecological status was set as: rare (R, abundance < 50%), common (C, 50% < abundance < 75%), and dominant (D, abundance > 75%).

The habitats pollution levels were set as: moderate risk site (MRS) for plots with ERI under 190, considerable risk site (CRS) for plot with ERI over 190 (Rehman *et al.*, 2018).

Moreover, four categories were set to evaluate the adaptability factor of the plants:

(G1) The species was dominant (D) in CRS sites;

(G2) The species was common (C) in CRS sites;

(G3) The species was dominant (D) in MRS sites;

(G4) Contained the rest of the plants, including the species common (C) in MRS sites and those resulted rare (R).

Results

Plant community characteristics

Table 1 shows an inventory of species identified in the study area. The frequency (the ratio between the number of areas in which a species occurs and the total areas studied) and the abundance (the ratio between the total number of individual of species and the areas where a species occurs) were calculated for each species. Twelve species and seven families were reported for the site. The most frequent families were Poaceae and Asteraceae. The most frequent species with the highest abundance was *Cynodon dactylon*.

Table 1. Botanical characteristics of the species collected from the site, analysis of frequency and abundance

Plant Species	Family	Frequency (%)	Abundance (%)
<i>Amaranthus retroflexus</i>	<i>Amaranthaceae</i>	9.1	20.0
<i>Aster tripolium</i>	<i>Asteraceae</i>	18.1	15.0
<i>Cirsium arvense</i>	<i>Asteraceae</i>	18.1	40.0
<i>Cynodon dactylon</i>	<i>Poaceae</i>	63.6	53.5
<i>Cyperus rotundus</i>	<i>Cyperaceae</i>	18.1	7.5
<i>Echium vulgare</i>	<i>Boraginaceae</i>	18.1	7.0
<i>Erigeron sumatrensis</i>	<i>Asteraceae</i>	54.5	18.3
<i>Hordeum leporinum</i>	<i>Poaceae</i>	9.1	40.0
<i>Lolium perenne</i>	<i>Poaceae</i>	27.2	36.6
<i>Mercurialis annua</i>	<i>Euphorbiaceae</i>	9.1	30.0
<i>Piptatherum thomasi</i>	<i>Poaceae</i>	27.2	8.3
<i>Rumex spp.</i>	<i>Polygonaceae</i>	18.1	10.0

Characterization of rhizospheric soils and PTEs contamination (Tab. 2)

Based on Italian Legislation for agricultural soils (L.D. 152/2006), we found that: Cu concentrations in soils not exceeded Screening values (SV) or Background values (BV) while Cr, Zn, Pb, Cd and As concentration resulted above both SV and BV.

The ecological risk index had a mean value of 510 (Fig. 1), showing high to very high risk in different habitats. In particular, the rhizo soils of *L. p.*, *E. s.*, *P. t.* and *A. r.* have ERI above the very high-risk threshold 380. *C. d.*, *M. a.* and *C. r.* rhizo soil showed high risk, while the other soils showed a moderate risk. The mean monomial potential ecological risk index (E_r^i) of As, Zn, Pb and Cu was classified as low while Cr showed moderate risk. E_r^i of Cd displayed high to very high risk in many of plants habitat. Cd contributed from 42 to 93 % of ERI with a mean value of 390, while Cr contributed from 5 to 30 percent of ERI with a mean value of 53.70.

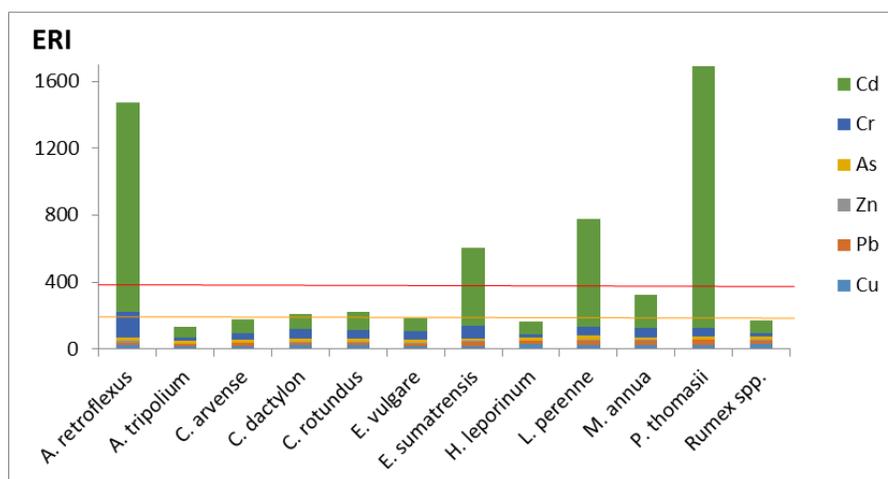


Figure 1. Ecological Risk Index of the habitats of plant species

PTEs concentration in plants (Tab. 2)

No one of the plant species accumulated Pb above the 30 mg kg⁻¹ threshold for forage (Reg. UE 1275/2013) as well as no plant species accumulated As above PTEs threshold of 2.00 mg kg⁻¹ (Reg UE 1275/2013).

Total Cd concentrations in the roots ranged from 0.04 to 0.93 mg kg⁻¹, the maximum value occurring in *C. a.* like for Cu. Shoots concentration values ranged from 0.02 to 2.65 mg kg⁻¹ with maximum concentration in *A. r.* Only *E. s.* and *A. r.* accumulated Cd above threshold of 1.0 mg kg⁻¹ for forage (Reg. UE 1275/2013).

Bioaccumulation and adaptability of native plant species

According to the adaptability factor, *Cynodon dactylon* was in G2 category, while all the other species fall within G4 category. Among the selected 11 plants samples, BAC_S and BAC_R were lower than 1 for Cu, Pb, Zn, Cr and As for all the species except for *C.a.* that showed a BAC_R higher than 1 for Cd. TF was higher than 1 in: *C.a.* for Zn; in *E.s.* for Cu, Zn and Cd; in *A.r.* for Cu, Zn, Pb and Cd; in *M.a.* for Zn; in *C.r.* for Cd; in *H.l.* for As. The modified bioaccumulation coefficient for the shoots (mBAC_S) and the modified bioaccumulation coefficient for the roots (mBAC_R) for each species were also calculated. *C.r.* showed a mBAC_S higher than one for Cd while *C.a.*, *C.d.*, *R.s.*, *P.t.* and *E.v.* reported a mBAC_R higher than 1 for Cd. mBAC_S values were lower than BAC_S values.

Table 2. PTEs concentrations in different plants part and in rhizo-soils of the native plant species

Plant	Status	Habitat		As	Cd	Cr	Cu	Pb	Zn
			mg kg ⁻¹ (d.w.)						
<i>Amaranthus retroflexus</i>	R	CRS	Soils	23.0	9.60	1414.0	65.7	83.8	696.0
			Shoots	0.1	2.65	2.2	5.0	2.2	88.1
			Roots	0.2	0.04	4.2	3.6	0.7	58.7
<i>Aster tripolium</i>	R	MRS	Soils	23.0	0.50	137.0	44.5	81.4	175.0
			Shoots	0.3	0.07	3.2	9.7	0.3	29.9
			Roots	2.0	0.31	48.4	11.1	0.4	36.6
<i>Cirsium arvense</i>	R	MRS	Soils	23.0	0.60	357.0	47.7	106.0	267.0
			Shoots	0.1	0.08	2.4	9.0	0.4	35.1
			Roots	0.4	0.93	5.6	10.4	1.0	29.4
<i>Cynodon dactylon</i>	C	CRS	Soils	22.4	0.68	524.0	66.0	89.4	389.0
			Shoots	0.2	0.05	6.50	7.2	1.1	56.9
			Roots	0.6	0.52	26.2	10.1	2.5	67.1
<i>Cyperus rotundus</i>	R	CRS	Soils	23.0	0.80	504.0	62.2	83.3	366.0
			Shoots	0.1	0.27	25.2	8.8	1.0	96.0
			Roots	6.1	0.13	173.2	11.4	4.1	143.0
<i>Echium vulgare</i>	R	MRS	Soils	14.0	0.60	488.0	44.3	77.2	251.0
			Shoots	0.1	0.02	1.9	10.2	0.3	54.2
			Roots	0.2	0.29	3.9	9.0	1.5	62.8
<i>Erigeron sumatrensis</i>	R	CRS	Soils	17.0	3.57	674.0	55.8	135.0	401.0
			Shoots	0.1	1.33	2.2	12.6	0.4	54.5
			Roots	0.3	0.14	11.1	8.8	1.2	25.2
<i>Hordeum leporinum</i>	R	MRS	Soils	25.0	0.60	142.0	83.5	99.6	206.0
			Shoots	0.4	0.03	3.1	2.0	0.5	43.6
			Roots	0.1	0.10	26.4	9.5	3.7	54.2
<i>Lolium perenne</i>	R	CRS	Soils	32.0	4.90	472.0	59.7	152.0	659.0
			Shoots	0.1	0.08	4.6	5.1	0.8	52.1
			Roots	0.4	0.11	9.6	14.1	5.2	64.6
<i>Mercurialis annua</i>	R	CRS	Soils	23.0	1.50	509.0	64.5	140.0	404.0
			Shoots	0.2	0.03	3.8	4.5	0.6	69.7
			Roots	0.9	0.10	9.8	5.2	2.4	34.5
<i>Piptatherum thomasi</i>	R	CRS	Soils	25.0	12.0	415.0	72.3	156.0	351.0
			Shoots	0.2	0.05	2.6	4.7	0.7	22.2
			Roots	0.5	0.21	6.9	19.2	20.4	145.2
<i>Rumex spp.</i>	R	MRS	Soils	28.0	0.60	158.0	88.9	109.0	217.0
			Shoots	0.2	0.03	2.5	6.2	0.6	19.8
			Roots	0.3	0.20	8.4	10.8	2.6	54.3

Discussion

Twelve species and 7 families were reported for the site. The most frequent families were *Poaceae* and *Asteraceae*. The most frequent species with the highest abundance was *Cynodon dactylon* (*C.d.*).

Even if different rhizo soils of the site showed PTEs concentrations higher than SV, the results of potential ecological risk assessment reported that the target PTE should be considered Cd due to the highest monomial potential ecological risk index (E_r^1). Furthermore, this PTE is considered one of the most dangerous also for human health, indeed the reference dose of oral soil ingestion (RfD in mg d⁻¹ Kg⁻¹ body weight) given by USEPA (1989) are 0.0010 for Cd, 0.0035 for Pb, 0.0400 for Cu, 0.3000 for Zn and 1.5 for CrIII. The RfD of Cd is lower than the other PTEs thus indicating the highest health risk for people, like agricultural workers, exposed to PTEs, while the Chromium that is the PTEs with the highest concentration in this site, has the highest RfD, thus indicating a lower risk for human health.

The adaptability factor showed that the plant species better adapted to site contamination was *Cynodon dactylon* which falls in the G2 category. All the other plant species reported lower adaptability to the site contamination and fall within G4 category.

C.a. was the only species that reported a BAC_R higher than 1 for Cd, so according to Yoon *et al.*, 2006 and Lorestani *et al.*, 2011, *C.a.* has the potential for phytostabilization of Cd. Even if TF was higher than 1 for some species, the concentration in the plants was too lower to consider that plant for phytoremediation purpose.

C.r. showed the ability to transfer the potential bioavailable fraction of Cd to the aerial part. *C.a.*, *C.d.*, *R.s.*, *P.t.* and *E.v.* reported the ability to accumulate Cd in the roots with a $mBAC_R$ higher than 1.

Conclusions

The site of the present study was classified by Italian Environmental Agency as potentially contaminated by Cr and Zn due to illegal dumping of tannery sludge, while the following risk analysis considered the site as not contaminated by Cr and Zn since they don't represent a risk for human health and groundwater quality.

The analysis of native plant species showed a high ecological risk index in the majority of the plant habitats. The calculation of the Ecological Risk Index (ERI) allowed identifying Cd as the more dangerous contaminant since it reported the highest monomial risk and most contributed to ERI, while it was excluded any risk for Zn and Cr also if they showed the highest concentrations in soil. It should also be noted that Cd was neglected by the official characterization. The risk of Cd is mainly linked to the inhalation and ingestion of contaminated dust spread by the wind (direct risk), but some plant species (*Erigeron sumatrensis* and *Amaranthus retroflexus*) accumulated Cd in the aerial part above threshold of 1.0 mg kg^{-1} for forage (Reg. UE 1275/2013), suggesting that there might be a potential risk of contaminant transfer to the food chain. The most frequent species with the highest abundance was *Cynodon dactylon* that was the most adapted to site contamination according to the adaptability factor (G2 category). Considering modified BAC for shoot and roots calculated by using the bioavailable metal concentrations (DTPA) from the rhizo-soils, *Cyperus rotundus* showed the ability to transfer the potential bioavailable fraction of Cd to the aerial part, while *Cirsium arvense*, *Cynodon dactylon*, *Rumex spp.*, *Piptatherum thomasi* and *Echium vulgare* reported the ability to transfer Cd to the roots protecting groundwater by reducing contaminant leaching. According to adaptability factor and $mBAC$, the most suitable plant species for phytostabilization of Cd resulted *Cynodon dactylon*. It is a macrothermal grass species with higher growth during the summer, so its cover also contributes to avoid the soil resuspension generally more intense in dry seasons.

The adaptability factor revealed a useful tool in addition to BAC and TF, considering the abundance of plants and contamination of habitats that indicates the tolerance of plants species to different PTEs stress.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.3. HCH and Lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue

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Abstract

1, 2, 3, 4, 5, 6-Hexachlorocyclohexane (HCH) has been one of the most extensively used pesticide and has been industrially produced mainly after the Second World War. Only the gamma isomer (lindane) has insecticidal properties and the other 85% HCH isomers resulting from production remained as by-products and became finally hazardous waste. For each tonne of lindane 8 - 12 tonnes of waste HCH isomers were produced and production of the approximately 600,000 t of lindane has therefore generated 4.8 to 7.2 million tonnes of HCH/POPs waste. These isomers have ended mostly as hazardous waste often uncontrolled dumped at many sites around the world. The stockpiles and the large contaminated sites can be categorized as “Mega sites”. Countries with HCH legacy problems include Albania, Argentina, Austria, Azerbaijan, Brazil, China, Croatia, Czech Republic, France, Germany, Hungary, India, Italy, Japan, Macedonia, Nigeria, Poland, Romania, Russia, Slovakia, South Africa, Spain, Switzerland, Turkey, The Netherlands, UK, Ukraine and USA.

The problem of stockpiles of HCH generated by the former production of Lindane is now documented and globally known as Lindane and alfa- and beta-HCH have been listed as POPs in the Stockholm Convention since August 2010.

This article describes briefly the legacy of HCH and lindane that has been created. Three of the Mega sites are being briefly discussed and demonstrate the increase in pollution footprint. Recent developments in the EU including the Sabinanigo project in Aragon/Spain and the European Parliament and global level are presented. A short overview is given on lack of activities and on actions of countries within their obligations as Parties of the Stockholm Convention. Furthermore, current country activities supported by the Global Environment Facility (“The GEF”), the financing mechanism of the convention are listed. Finally, conclusions and recommendations have been formulated that contribute to the solution of this problem over the next 25 years.

Keywords: HCH, Lindane, contaminated land, groundwater and soil-pollution

Introduction, scope and main objectives

1, 2, 3, 4, 5, 6-Hexachlorocyclohexane (HCH) has been one of the most extensively used pesticide and has been industrially produced mainly after the Second World War. HCH was available in two formulations: technical HCH and lindane. Generally, technical HCH contains the isomers in the following percentages: α : 55-80%, β : 5-14%, γ : 8-15%, δ : 2-16%, and ϵ : 3-5%. Of these isomers only, the gamma isomer has specific insecticidal properties. Lindane contains more than 90% of γ -HCH. The production and application of lindane and technical HCH during the last 5 decades has resulted in environmental contamination with global dimension (Fernandez *et al.* 2013; Götz *et al.* 2013; Torres *et al.* 2013; Vijgen 2008; Vijgen *et al.* 2011; Wycisk *et al.* 2013).

In the late 1940s and 50s the Technical HCH mixture, was sprayed in Europe (and other countries). However, it was soon discovered that the application of the technical HCH resulted in inedible crops, vegetables and fruits, due to the bad smell and taste of some of the HCH isomers. Therefore, some companies started already in the 1950s with the isolation of the active, and in the applied concentration tasteless, gamma isomer and sold it under the trade name lindane.

The other HCH isomers resulting from production remained as by-products and became finally hazardous waste. For each tonne of lindane 8 - 12 tonnes of other HCH isomers are produced (Vijgen 2006; Vijgen *et al.* 2011). The production of the approximately 600,000 t of lindane has generated 4.8 to 7.2 million tonnes of HCH/POPs waste (Vijgen *et al.* 2013). These isomers have ended mostly as hazardous waste, which were dumped often uncontrolled at many sites around the world.

The problem of stockpiles of HCH generated by the former production of Lindane is well known as Lindane and the alfa- and beta-HCH have been included as POPs since August 2010 and are dealt with within the Stockholm Convention. The following countries have HCH legacy problem: Albania, Argentina, Austria, Azerbaijan, Brazil, China, Croatia, Czech Republic, France, Germany, Hungary, India, Italy, Japan, Macedonia, Nigeria, Poland, Romania, Russia, Slovakia, South Africa, Spain, Switzerland, Turkey, The Netherlands, UK, Ukraine and USA. It is also known that other countries had formulation facilities, but it is not supposed that these ones had large environmental consequences. The stockpiles and the large contaminated sites can be categorized as “Mega sites”.

That fact that many of the original stockpiles, have been widely spread and are present in large quantities in soil and are a merely forgotten contaminated land problem, as only a smaller part of the problem has been dealt with over the years in the EU and globally. Over decades, these Mega-sites have been and are still leaching into the underground and polluting groundwater and partly surface and drinking water.

For getting an insight into the challenges of the legacy of HCH production, some cases are shortly described.

This article describes briefly the legacy the legacy of HCH and lindane that has been created. A number of contaminated Mega-sites from The Netherlands, Basque country and France are being briefly discussed and some conclusions made why the HCH and Lindane issue has increased its seize but also its attention. Recent developments in the EU with focus on the Sabinanigo project in Aragon and the European Parliament and global level are presented. A short overview has been made on the actions the countries have taken within their obligations as parties of the Stockholm Convention, as well as at the actions of “The GEF” (Global Environment Facility), the financing mechanism of the convention, has taken. Finally, conclusions and recommendations have been formulated that contribute to the solution of this problem over the next 25 years.

Results

Examples of clean-up of contaminated HCH-sites

The Legacy of “Technical” HCH production in the eastern part of the Netherlands.

One of the most known Lindane production facilities was in the eastern part of the Netherlands, where more than 5,500 tons of HCH-waste were generated. In 1956, 1,500 tons of HCH isomers were sold by this facility to another producer in the Netherlands for reprocessing. The rest remained stored next to the production site. In the 1950s and 1960s, a portion of the remaining waste isomers were illegally collected and mixed with soil for construction purposes and dumped at numerous locations. Approximately 290 sites have been identified in a predominantly agricultural area in the eastern region of the Netherlands. In 1974 there was a massive fish kill in a canal next to a site where some of the isomers were stored (see photo 1). At this time there was a public outcry concerning the incident and in 1975 the Dutch regional government put pressure on the new owners of the facility to pay for the complete removal of 4,000 tonnes of waste isomers, which were consequently shipped to Germany for disposal.



Photo 1. HCH-stockpiles at the former Lindane production location

At the end of the 1980s, the Dutch government accordingly authorized a large project to deal with this regional contamination issue. In 1988, a temporary storage site was established on top of a former landfill site. Approximately 200,000 tonnes of soil, excavated from the most contaminated areas of the region, were stored at this site (see photo 2). Due to the high concentrations of chlorine, at that time no adequate technology was available to treat the soil. The Dutch government invited companies to develop technologies to treat the soil and investigated their efficacy. By the beginning of 2002, all soils at the temporary storage site had been treated. The site is now capped, secured, and used by the farming community for summer festivals.



Photo 2. Temporary storage of 200,000 tonnes of contaminated soil

Current Status: The Dutch government spent approximately 27 million Euros to clean up soil highly contaminated with waste HCH isomers in the eastern region of the Netherlands. Currently there are additionally 200,000 tons of less contaminated soils remaining that may need remediation in the future (NARAP, 2006, Vijgen, 2006).

The Basque Country in Spain.

For more than forty years, technical HCH was produced by two companies located in the Basque Country in north central Spain. Starting in 1953, lindane was extracted from the technical HCH mixture, leaving behind significant amounts of waste HCH isomers (See Photo 3). The authorities in the Basque Country have calculated that 82,000 tons of waste HCH isomers have been dumped at more than thirty sites in their region. Dumping of waste isomers stopped in 1987 when the Basque authorities banned this practice. Due to the mixing of waste HCH isomers with soils and other wastes, the authorities estimate that there are between 500,000 and 1 million tons of contaminated residues in their region.

In addition to environmental problems and unacceptable risks to inhabitants, this contamination has in the past, hindered important development projects in areas near sites where the isomers were dumped. The authorities developed a strategy to manage the contamination. Over a period of 10 years they conducted inventories and constructed two secure hazardous waste landfills for the contaminated soils, one for 176,000 tonnes and the other for 480,000 tonnes of waste residues and contaminated soils.



Photo 3. Cattle grazing around HCH-wild dumping (Gobierno Vasco, IHOBE, 1998)

In addition, the Base Catalyzed Dechlorination (BCD) process has been tested and adapted in the laboratory and thereafter a full-scale plant has been built. It has treated 3,500 tonnes of HCH waste isomers stored at the production site (see Photo 4).

Current Status: The Basque Country Region of Spain spent over a decade and an estimated 50 million Euros to build two secure landfill sites for wastes and contaminated soils. Of that total amount, 8.4 million Euros were spent on the Base Catalysed Dechlorination process (NARAP, 2006, Vijgen, 2006, Alzola *et al.*, 2015).



Photo 4. Waste HCH isomers being collected inside a former lindane production facility in Basque Country Region of Spain. (©IHOBE, Basque Country)

Remediation Eugene Kuhlmann of former Lindane factory, Huningue, France

Ugine-Kuhlmann started the HCH-production in 1947. It is located on French soil in Huningue at the river Rhine. There, a fence marks the border to Switzerland. Until 1972, large white

mountains of HCH were piled up on the site (see Photo 5). The prevailing northwesterly wind transports dust from the HCH waste to Germany and Switzerland. Therefore, massive contamination of mother's milk and cow milk was found. The authorities recommended the mothers to stop breastfeeding their babies. The cow milk was destroyed. Even until 2007, HCH was still found in breast milk. From the end of World War II and until 1975, Ugine-Kuhlmann has produced around 100.000 tons of HCH-waste. (Forster, 2015).

The Swiss chemical company Sandoz bought the Ugine-Kuhlmann-site at Huningue and established there a waste water treatment plant in 1980. The present owner Novartis closed the waste water treatment plant on the former Ugine-Kuhlmann-site in 2012. In 2013, Novartis started to excavate the HCH-contaminated soils.

It is important to say that Novartis declared that on the site no pure HCH-waste has been present ("Zehnder, personal communication, 12 -02-2018"). From 2013 till present about 200,000 m³ of contaminated soil has been excavated and the soils with concentrations up to 20,000 mg/kg HCH, have been transported and treated in thermal desorption plants and the soils with concentrations of more than 20,000 mg/kg dm. The thermal desorption treatment was made for around 72 %, hazardous waste incineration around 25 %, and the recycling / Chlorine production around 3 %. All treatment has been taken place ex-situ (ARA STEIH, 14.10.2014).

In the beginning of the 1970s, Ugine-Kuhlmann company had to find a 'solution': The so called waterproof concrete (Béton hydrofuge). This concrete was produced in a concrete mixer and comprised an equal quantity of gravel, cement and HCH-waste. For this purpose, Ugine Kuhlmann excavated around 4.000-5.000 m³ of contaminated gravel and sand on its site at Huningue. Over the years this material has been spread over around a dozen small roads in France and has led to numerous contaminations (see Table 1), (Forster, 2015).

Current status: So far, we conclude that the original HCH quantities of 100, 000 tonnes have created, due to illegal dumping at many locations, a huge soil contamination of approx. 200,000 m³ due to leaching and other excavation actions at this site.

Additionally, one can conclude that the original problem of 100,000 tons of pure HCH, being spread and mixed and distributed over numerous locations in France and in Switzerland, is still not been dealt with!

Costs for the remediation of the Huningue site were estimated 140 Million SFR (Swiss Francs) (Basellandschaftliche Zeitung, Okt 2013). However, latest estimates are now doubled to around 200 Million Euro (Basellandschaftliche Zeitung, Nov 2015) and new contaminations have recently been found. Newest information (5 May 2018) states that till present 375,000m³ contaminated soils have been remediated, which is about 675'000 Tonnes and the finalization of the remediation works is expected to be finalized presumably in 2. Quarter of 2021. (Novartis, Media Release, Update zum Sanierungsprojekt ARA STEIH in Huningue, 5 May 2018).



Photo 5. 1972, UGINE Kuhlmann stores on its factory site large mountains of HCH-waste. The wind blows the poisoning dust also to Germany and Switzerland. Photo: Staatsanwaltschaft Basel Stadt, 2.11.1972. (Forster, 2015).

Table 1. Overview of sites in Alsace (France), where definitely and/or probably HCH-waste, -concrete, and with HCH polluted gravel and other excavated material stemming from the former lindane factory UGINE-Kuhlmann, have been dumped and/or has been buried (status 2015) (Forster, 2015).

Where?	Name of the Site	possibly HCH-waste	definitely HCH-waste	works implemented
St-Louis/Bourgfelden	Simon-Grube		demolition material of the factory	none
Gouneans-Haut Saône	-		HCH-waste	groundwater pumping
Hagenthal-le-Bas	fdirt roads		gravel and sand contaminated with HCH from the factory site	investigated
Hagenthal-le-Bas	dirt roads		gravel and sand contaminated with HCH from the factory site	investigated
Hagenthal-le-Bas	dirt road		HCH-concrete	investigated
Allschwil	road		gravel and sand contaminated with HCH from the factory site	investigated, low concentrations; no active treatment needed
Hésingue	dredging pit	HCH-waste		none
Hochfelden			HCH-waste	groundwater pumping
Huningue	former factory site		HCH-waste HCH-concrete	under excavation
Huningue	Nouvelle Sablière de Huningue	HCH-waste		none
Kingersheim	Eselsacker		HCH-waste	groundwater pumping
Magstatt		HCH-waste		none
Village-Neuf	Stade de Huningue		HCH-waste	none
Sierentz	Brunner-Grube		HCH-waste	excavated and stored on site in a clay-bag
Sierentz	Bäumlin-Grube		excavation-material from the factory-site	None
St-Louis	Grande Sablière de St-louis	HCH-waste		None
St-Louis	garden of the building Phoenix		excavation-material from the factory-site	None
Winzenheim	Grube Ritzenthaler		HCH-waste	groundwater pumping

Result of inaction – increase in contamination

The three cases document that in all three cases, the Dutch case with originally relatively small quantities of HCH-waste (estimated more than 4,000 tons), the Basque case with large quantities (estimated 82,000 tons) and the French case with more than 100,000 tons of waste HCH-isomers, which have developed to larger problems due to non-action and due to illegal transport and dumping to 200,000 tons in the Netherlands and between 500,000 and 1 million tonnes of contaminated soils in the Basque country and in France to still unknown total quantities. But at least a quantity of 375,000 m³ being eliminated plus the original quantity of waste of 100,000 tons of HCH that has been spread to numerous locations, but the present total and its conditions have still not been fully investigated, but it is obvious the total problems have grown many times its original extent.

During the years after termination of the production of Lindane, often several decades, the size and environmental damage has heavily increased (factor 50 in the Netherlands, factor 8 in Basque Country and a minimum factor 2 -3 in the France case) due to many years of non-action or lack of enforcement by the concerned authorities which made it possible that these large number of illegal transports and dumping at so many locations have taken place. Also, often long-lasting court cases were hindering progress and frequently it has been impossible applying the “Polluter Pay” principle, when owners were bankrupt or are former governments (such as in Central Europe and the Former Soviet Union).

Discussion and recent national and international developments

National Implementation Plans: What are governments of HCH-owning countries doing?

Many of the National Implementation Plans (NIPs) developed in the framework of the Stockholm Convention of the main producing countries, lack proper inventory data on the concerned sites. Some examples are given in the following section.

For example, the NIP of **Germany** as the largest historic lindane producer states only that “*During production of lindane (γ -HCH), large quantities of α - and β -HCH were created as “by-products”, which used to be stored above ground, including in Germany. With the inclusion of the compounds as POPs, these landfill sites are to be viewed as being POP contaminated sites” (UBA/Friedrich pers. comm. 2011). Vijgen (2006) assumes that 390,000 to 450,000 tonnes of HCH residues exist in Germany” (Germany NIP, pp. 63).*

Details or descriptions of results of inventories and/or eventual remediation actions of the many sites in former East Germany and West Germany are lacking in the NIP. Only recent science papers on the former production in Bitterfeld (Wycisk *et al.* 2013) and Hamburg (Götz *et al.* 2013) show the contemporary relevance.

France as another big producer, writes only under “1) The pesticides, substances Les pesticides, Substances of main concern: DDT, chlordane, hexachlorocyclohexanes (including lindane), pp.20, and further sub-products: the HCHs alpha and bêta have been produced in the have been produced in the past as by-products of lindane manufacture today banned in France.” (France NIP pp. 22). Also, here details or descriptions of results of inventories and/or eventual remediation actions of the many sites in France are lacking.

Romania just mentions that “Alpha and Beta – HCH is likely to be found in the lindane contaminated sites in and around the former chemical platforms that produced Lindane in the past.” (Romania NIP pp. 35)

However detailed information is needed about the production sites of Romanian’s largest producer Oltchim with around 250,000 tonnes of HCH waste in the Olt valley and the Turda site with 44,000 tonnes of HCH waste and related contaminated soils.

The **United Kingdom** NIP states under: Chapter 5.1.2 “Identifying and assessing emissions from potential waste piles from historical lindane production, that: “A review of historical lindane producers will be undertaken to establish the disposal routes for the waste generated by the industry. The information will be used to assess the potential for ongoing emissions from any identified waste sites.” In the Implementation plan, a review of the historical lindane producers to establish the disposal routes for the waste generated by the industry and identify potential sources of emissions was planned by the Environment Agency from 2013 till 2014. (UK NIP, 2013 pp. 40-

41). However, in the latest 2017 NIP, only HCH treated wood was considered and preliminarily assessed. UK, NIP, 2017, pp. 77-78).

We conclude that the UK Environment Agency, apart from the treated wood issues, has not made the necessary historical investigations at the former Lindane producer(s) to identify possible stockpiles and land contaminations. ICI was the first company in the world to produce Lindane and had considerable exports and therefore large waste legacies can be expected (Vijgen *et al.* 2013)!

There are however some countries with activities at production sites:

Czech Republic (Czechia NIP 2006) with detailed description of the “famous” Spolana Neratovice site, **Poland** with the "Rudna Góra" Central Waste Landfill and the "Organika-Azot" S.A. facility (Poland NIP 2013) and **Spain** (Spain, NIP 2013) describing the Aragon site in Sabinanigo, Porriño in Galicia, and Barakaldo in Basque Country) provided detailed information about their problems.

In **Slovakia**, recently positive developments on the solution of the HCH-stockpile from the chemical company Chemické Závody Juraja Dimitrova (CHZJD) are taking place.

The HCH-landfill was built, with permission, in part of a dried-up branch of the Little Danube River in 1966 and closed in 1979. Later, it was covered with an inert material. However, according to the mayor of Bratislava, dangerous chemicals are contaminating underground water and each day are progressing further towards Žitný Ostrov. Žitný Ostrov (Rye Island) is an area of national importance, as it is the biggest reservoir of drinking water in central Europe, with the capacity to supply as many as 15 million people, according to estimates by experts. There are two possible solutions for the waste dump – removal or encapsulation. The Environment Ministry prefers encapsulation. This involves building a wall around the waste dump, which covers about 4.65 hectares and holds about 120,000 cubic meters of HCH POPs waste. The wall would be built to a depth of 20 meters, where there is an impermeable layer of subsoil. The site would also need to be covered to prevent rain water getting into it. The cost of encapsulation is estimated to €20 - 25 million, for which the ministry plans to use EU funds. By comparison, the cost of removing the waste and cleaning up the site would be €120 million (The Slovak Spectator, 2016).

The respective authorities had known about the problems for years, making their first measurements in the 1990s. Already in 2002, they recommended that the inhabitants of Vračuňa do not drink or use water from their wells (The Slovak Spectator, 2017).



Photo 6. Vračuňa's citizens presented apples washed in water with leaked toxins at the protest. (The Slovak Spectator, 2016).

Activities with the support of the European Union

In 2015, the International HCH & Pesticides Association has organized its 13th Int. HCH & Pesticides Forum together with the Government of Aragon and support of the EU Life programme via the project “Life Discovered”. At this forum journalists presented newly documented alarming cases of HCH production Mega-sites in Slovakia (Contaminated Future in Slovakia) and Romania, (Contaminated Future in Romania) at the eastern borders of the European Community and showed the extent and the unacceptable threats to the health of the population (See also www.contaminatedfuture.org). However, such mega-sites are also still present today in the EU member countries like France, Germany, Poland and Spain. As these sites are huge and a remediation costly (e.g. Wycisk *et al.* 2013), mostly no sustainable remediation has been done but only simple containment measures have been taken. Therefore, the legacy a huge threat is increasingly occurring. An impressive price winning movie has document activities and present situation of a Spanish site “Discovering Lindane – The legacy of HCH production” (Vimeo).

On January 17th 2016, IHPA published a **Press release: Mega Pollution on Mega Sites**, calling for actions. Special attention was given to the enormous environmental consequences due to the legacy of the Lindane producer Inquinosa, which has produced between 1974 and 1992 140,000 tons of HCH waste that were buried in several uncontrolled dumps in Sabiñánigo, Spain. Currently the pollution affects more than 40,000 people only in the Gállego River basin. The Gállego River flows into the Ebro River. A river that flows through Zaragoza – inhabited by more than 650,000 people. And several times in 2014, the population living at the border of the Rio Gallego was warned of too high Lindane concentrations in its drinking water – more than 20 years after the Inquinosa Company stopped its activity. (IHPA PR, 2016)

This was followed by a special session In September 2016, a special public session MANAGEMENT OF AGRO-CHEMICALS, ELIMINATION OF ‘BLACK SPOTS’ AND CREATION OF ‘WHITE SPOTS’ was organized by the Greens/EFA led by Members of the EU Parliament Margrete Auken, Benedek Javor and Jordi Sebastià to draw renewed attention on the problems of old pesticides, and where IHPA explained the serious situation of the HCH-Megasites, as specifically within the European Community, where the largest quantities of Lindane have been produced, and requested EU Commission and EU Parliament to take urgent actions and start to make a proper Action Plan in the UI and slow progress on the elimination of the HCH- stockpiles and strongly related with the stockpiles, the large contaminated land areas, which are hesitantly being dealt with globally, but in October 2014, the Committee on Petitions of the EU Parliament received a Spanish request demanding an EU intervention through co-funding a decontamination plan for the Rio Gallego, as well as a sanctioning of the government of Spain for breaking EU Legislation on Water Health and Environment (move later to rear part). Thereafter a study was commissioned by the European Parliament’s Policy Department for Citizens’ Rights and Constitutional Affairs at the request of the Committee on Petitions (PETI). This led at the end of 2016 to the publication of a study report by an international consultant with the title: **Lindane (persistent organic pollutant) in the EU (EU Parl 2016)**. The report states that “Lindane was extensively produced in the EU until the 1990s and used as a broad spectrum insecticide until 2008. The use and production of lindane is now banned in most countries around the world. However, it unfortunately continues to pollute. Its persistence, bioaccumulative and toxic properties, spillages from former production sites and the illegal dumping of HCH-waste, have given rise to serious concerns as understanding grows about the ability of HCH-polluted-spots to widely disperse HCH pollution into surface and groundwater. The report presents an updated mapping of the lindane production plants and HCH-waste dumping sites in the EU. Potential remediation techniques, including laboratory and field experiences, are also provided with a selection of best practices regarding the restoration of contaminated sites and the participation of stakeholders. The information on lindane from official websites is also analysed.

The report was discussed in the EU Parliament and the report have been distributed by the EU Commission to all EU Member states representatives for POPs.

Activities of the Global Environment facility

The first achievements of the GEF, as financial mechanism in the framework of the Stockholm achievements (Turkey-Macedonia and Brazil planning)

Stockholm Achievements (Turkey, Macedonia and Brazil planning)

The GEF is the only existing financial mechanism that is trying and has been trying to start some of the project on HCH-stockpiles.

- A first project that is financed and under implementation by UNDP, is the Turkish HCH-storage site of Koaceli, South of Istanbul. where about 3,000 tonnes have been stored over decades will be destroyed
- A GEF financed UNIDO project is currently assessing potential management options of the HCH waste legacy from the lindane production in Macedonia. The objective is the destruction of around 10, 000 tons of HCH-waste.
- Also, the legacy of HCH production in Brazil (Torres *et al.* 2013) is under preparation with the objective of the destruction of 5000 tonnes of HCH-waste.



Photo 7. HCH-waste in the storage in Kocaeli (Source John Vijgen)

Conclusions and recommendations

What are now the barriers for the solution of the HCH-legacy problems?

First the lack of political commitment at national levels of the member countries (Parties of the Stockholm Convention!). But the convention is also not providing the appropriate tools to stimulate progress. A major issue is the **lack of clear objectives and time plans for elimination of HCH-waste**. A time line has been determined e.g. for PCB wastes where activities are much more

focused to achieve elimination. This is also missing for the other POPs pesticides, but if clear solutions are really wanted then such plans have to be agreed by the Parties to the Convention.

The huge quantities and the related high costs for destruction accumulate to enormous total costs that avoid that countries, especially those with weak economies even start thinking of tackling the problem. But in case the problems are dealt with, then the goal of irreversible destruction is avoided, and the cheapest options of encapsulation are preferred, with often costs of 1 to 10% of the costs for excavation and irreversible destruction. However, encapsulation is mostly transferring the waste and the problem to future generations.

How to tackle the problem?

In order to solve the problems of HCH-waste and large HCH-contaminated sites, it is necessary that all national governments of countries with these problems take steps in making the necessary inventory works, estimate costs of elimination and prioritize their solution and make this information publicly available in the National Implementation Plans for the Stockholm Convention and the EU Member Countries report also, the EU Commission in the framework of the Union's Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants (UIP), which is at present being updated and is highly dependent on the wishes and needs of the EU Member States.

At the same time the UIP should be modified from a pure administrative document to a real implementation plan and include the necessary actions to be taken to eliminate the consequences of HCH waste and HCH contaminated land as well as other POPs waste and contaminated land in the EU within e.g. the next 2 decades.

IHPA urgently calls upon the national governments in the EU, the European Commission and the GEF, the financial mechanism of the Stockholm Convention, and all governments that have ratified the Stockholm Convention to fulfil their obligations: Develop National Implementation Plans, seek co-operation, invest in facilities for elimination of these dangerous chemicals and for the industrial countries to support the countries with developing and transition economies.

IHPA proposes that the EU Commission will establish an EU “HCH-waste and soil” research and applied technology program with the objective to find sustainable solutions (technologies) that are more economically feasible and that also fulfil the conditions of a circular economy considering marketable products that can be generated from HCH as a potential resource (e.g- HCl). It is also recommended that the EU Commission should establish several financial incentives similar the GEF is presently using, where up to 30% of funding is provided based on sufficient national contribution and other private support. For a number of locations that have “potential” investment value, the creation of a co-funding structure with Assistance of DG Enterprise could support with seed-funding and help to engage also more additional private funding. IHPA is ready to discuss these proposals with EU Commission and other interested stakeholders.

What are the lessons learnt?

The problem of the legacy of HCH- waste and contaminated land are only marginally dealt with in the EU and globally even after so many years that the main Lindane production has been terminated. As described before the extent of the problem has strongly increased.

If we (including the global organochlorine industry) are not able or willing to deal with this old legacy after so many years and after inclusion in the Stockholm Convention, we must strongly rethink production and waste strategies. And if we are so slow in solving this issue, what are we

expected to with other contemporary global issue of the legacy of Glyphosate, the most produced pesticides in all times, which will soon be forbidden, a problem with potentially high costs of ground water and other pollution to be dealt with. Who would pay for that when the producers would not be liable? We have to learn from the mistakes of the past and develop frames of strong polluter pays principles and do not repeat decade after decade the same mistakes.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.4. LAND STEWARDSHIP, Investing in the natural, societal and economical capital of industrial land

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Abstract

Land Stewardship a mutual interest of NICOLE and Common Forum

The current way of production, use of resources, land and natural capital is not sustainable. Transitions in energy, mobility, circular economy, food production and city development are needed. We need to transform towards a restorative and circular economy, based on value creation and where public and private stakeholders cooperate to achieve public and private goals. Land restoration, land use and land management (land stewardship) are key in this transform.

The Network for Industrially Co-ordinated Sustainable Land Management in Europe (NICOLE) and the Policy makers of the Common Forum have executed a study on Land Stewardship. Land Stewardship being the recognition of our collective responsibility to retain the quality and abundance of our land, air, water and biodiversity, and to manage this natural capital in a way that conserves all of its values [Ref. 1]. Land Stewardship (LS) has a wider scope than Sustainable Land Management (SLM) or Brownfield (BF) redevelopment. Where SLM focusses on the sustainable use, protection and management of land, LS also looks at the understanding of the natural and social values land represents, both at sites in transition/redevelopment as at sites in continued use.

With a large working group Nicole and Common Forum have drafted a concise report on the definition of Land Stewardship and the components Stakeholder Involvement, Options Appraisal and the most important elements of Natural and Social Capital. It also contains a chapter and example on the Economic and Social value that an industrial site in operation can represent. This way of thinking also represents a paradigm shift from an industrial site being a potential threat to the environment to industrial land contributing to the delivery of welfare and employment to the community. Such an activity can also provide the means to enable investments in the natural, social and economic value of land.

Keywords: Land Stewardship, Natural Capital, Stakeholder involvement, Social Capital, Sustainable Remediation

Introduction, scope and main objectives

The land we work and live on is the best example of a circular, non-renewable resource. Soil is next to water one of the most reused resources on earth. With countless pressures on the land, there is an obvious restriction on the use of green fields, and the availability of “fresh” land is rapidly becoming scarce. The value land represents is therefore irreplaceable. It is a source of geo and ecosystem services contributing to private and public welfare; it supplies various resources, it is the

basis for food production, energy supply, building and construction and production of drinking water, etc. [Ref. 2]

Together with Common Forum, NICOLE set out to draft a framework for their members on Land Stewardship, aiming to move beyond the current policy phase of sustainable land management. Coming from Risk Based Land Management [Ref. 3] and the Sustainable Remediation of contaminated Land [Ref. 4], it is time to step into a new phase where the focus is on circular use and optimizing the value of Land, which is within the context of NICOLE industrial Land. The ultimate aim is to show that when Land Stewardship falls on fertile ground, and industry and society invest in the natural, social and economic capital of land, the community and the environment benefit most. This can only be achieved by broad involvement and participation.

Methodology

The efforts of NICOLE and Common Forum are not the outcome of scientific research based on a scientific methodology but an outcome of a working group with specialists, gathering expertise and practical examples from renowned sources and references, and bundling this to a framework, a guidance on Land Stewardship for Industrial Sites.

Results and discussion

The main result is a concise booklet with examples on Land Stewardship. In this section the different elements of Land Stewardship as described in this booklet are summarized.

Stakeholder involvement

As anticipated in former sections, LS is a concept, which overlaps and extends from Sustainable Land Management, while looking at site life cycle in a broader holistic manner. As such, in addition to defining physical and time boundaries to be considered for site re-evaluation, for successful LS it is critical to identify the key stakeholders, their roles, and opportunities to involve them in the decision making process and option appraisal.

While traditional land management is typically led by decisions primarily driven by the site owner (according to regulation requirements), LS entails collaboration and proactive stakeholder engagement, to be defined by specific planning considering site complexity, and expected community end goals.

Communication from land manager to public is a fundamental initial step [Ref. 5] and should be an open, multi-way conversation. The ability to collect input from stakeholders (in form of surveys, brainstorming meetings, role plays, public debate, voting, etc.) in an efficient and manageable manner, is key to LS success and to promote best possible function of infrastructures and industrial sites.



Figure 1. Stakeholder Involvement

This still requires appreciation and respect of mutual responsibility and accountability (land owner, approval authorities, versus neighbors, general public having an indirect or potential impact from the site conditions and redevelopment) and fostering social engagement experiences and partnership frameworks such as, for example:

- Triple A approach; Ambition, Alliance and Action
- Public-private partnerships
- Long term funding for managing green open spaces

NICOLE, in its sustainable remediation road map [Ref. 6] defines an easy, scalable approach to identify and prioritize environmental, social and economic criteria, and to weigh them qualitatively and quantitatively to support sound and transparent decision-making. This requires a step-wise process that includes:

- engaging stakeholders,
- discussing options and indicators,
- evaluating and recordkeeping.

Natural capital

There is an increasing awareness and understanding among industry that natural capital is a factor that materially affects an organisation's ability to create value.

This has driven the need for governments and businesses to find means of integrating the value of natural capital into decision-making. With increased stakeholder focus on organisations' contributions to the environment and society, there is increasing pressure on the private sector to not only improve the sustainability performance of their facilities and assets, but also to demonstrate and effectively communicate this to their stakeholders. Taking a natural capital approach is an effective means of achieving this.

What is natural capital?

When we talk about natural capital, we mean the elements of nature that directly or indirectly produce value to people, including ecosystems, species, freshwater, land, minerals, the air and oceans, as well as natural processes and functions (figure 2). Natural capital is a broad term that includes many different components of the living and non-living natural environment, as well as the processes and functions that link these components and sustain life.

In describing natural capital, we often talk in terms of assets. Any capital asset has the capacity to produce various goods and services. Natural capital is simply those assets provided by nature with the capacity to generate goods and services. In fact, natural capital can be regarded as the source of all other types of capital: whether manufactured, financial, human or social.

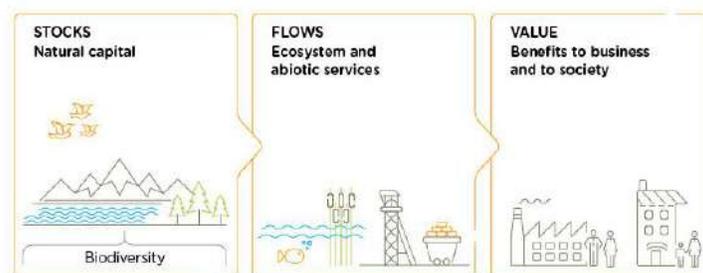


Figure 2. The natural capital

Box 1: Definitions

“Those elements of the natural environment which provide valuable goods and services to people, such as the stock of forests, water, land, minerals and oceans.”

(UK Natural Capital Committee)

“The stock of renewable and non-renewable resources (e.g. plants, animals, air, water, soils, minerals) that combine to yield a flow of benefits to people.”

(Natural Capital Coalition)

The benefits provided by natural capital include clean air, food, water, energy, shelter, medicine, and the raw materials we use in the creation of products. It also provides less obvious benefits such as flood defence, climate regulation, pollination and recreation. Value lies at the heart of the natural capital concept. Accordingly, assessing the value of changes in natural capital and services it provides is fundamental in business decisions to enhance land stewardship. By incorporating natural capital into your decision-making ensures you are future proofing your business for significant risks and opportunities (figure 3).

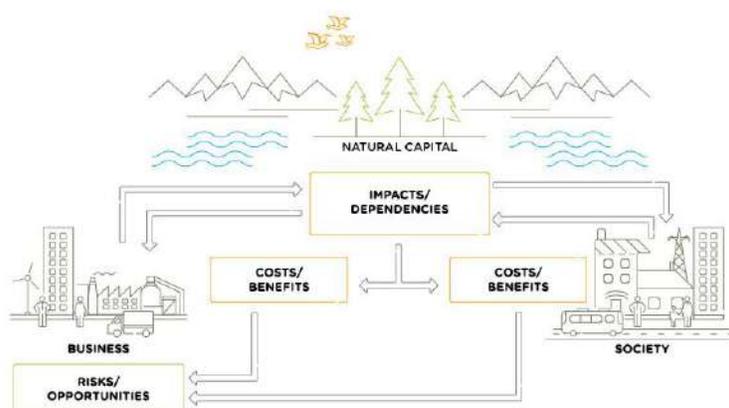


Figure 3. Natural capital and society

Social capital

With increased stakeholder focus on organisations’ contributions to the environment and society, there is increasing pressure on the private sector to not only improve the sustainability performance of their facilities and assets, but also to demonstrate and effectively communicate this to their stakeholders. As part of this shift, there is increasing awareness and understanding that social capital is integral to an organisation’s ability to create value. Integrating social capital into decision-making can embed the sustainability of business operations and improve stakeholder relations over time.

Social capital as a concept has been developing since the 1990s and is defined by the World Business Council for Sustainable Development (WBCSD) as simply the “resources and relationships provided by people and society” [Ref. 7]. Essentially, social capital refers to the value added by the interactions of individuals and groups of people internally and between the organization and the diverse communities in which it operates. For example, the social capital that an industrial facility draws upon includes good relationships with environmental bodies and

government organizations, partnership with local community and education organizations, and employee loyalty and support.

Emerging approaches

Approaches in social measurement and valuation

First strides have been made in the formalization of approaches to social capital. In 2015 the World Business Council for Sustainable Development launched ‘Towards a Social Capital Protocol – A call for collaboration’, an initiative to push for the development of a harmonized approach for businesses to measure and value their contributions to society [Ref. 8].

There are a number of ways to value social capital including market valuation, non-market valuation and secondary data valuation. Capturing the monetary value of social capital is a challenging process as social capital does not have a direct market value, which can result in its benefits being undervalued. By qualitatively and quantitatively capturing social capital in itself, however, sufficient data can be provided to inform and influence corporate decision-making. An example of this is the handbook to measure potential and actual social impacts throughout the product life cycle as a result of the Roundtable for Product Social Metrics [Ref. 9].

Challenges arise in selecting appropriate and comparable values in the absence of direct market valuation. The emergence and development of social capital accounting offers a mechanism for organizations and governments to capture these values and should ultimately enable a better understanding and management of social capital risks and opportunities, facilitating more informed decision-making and a more-resilient business model.

‘Social Capital Accounting’ is the term used to describe the variety of methods used in the marketplace to measure and value organizations’ impacts and dependencies on social capital. Incorporating social impacts for a range of stakeholders into a valuation exercise, more accurately reflects the value that organizations are achieving.

Why measure the social capital of industrial land stewardship initiatives?

By actively measuring and monetizing social capital, land managers can demonstrate a more comprehensive understanding of the total value of their activities in the community. Benefits from enhanced industrial land stewardship potentially provide outcomes and marketable opportunities that have intrinsic value for local communities. There are both direct and indirect benefits that contribute to social capital. Direct benefits are understood to be benefits that are gained by individuals engaged in the land stewardship and appreciation of it themselves, such as enhanced wellbeing through the enjoyment of friendships and positive outdoor activities. Indirect benefits are benefits that accrue to the wider community, such as improved sense of satisfaction living in an area due to an enhanced industrial site. By understanding these benefits better, we can enhance decision making among NICOLE Members for future land stewardship planning and decision-making.

The social and economic value of the industrial use of land

Introduction

Land stewardship focusses on managing and protection of the values of land by sustainable practices. The industrial use of land obviously has economic and social (employment etc.) value but can affect nature and the ability to sustain biodiversity and provide ecosystem services. For

optimal land stewardship therefor land management also needs to focus on sustainable use of natural capital and resources. Our commitment to land stewardship in industrial area's includes managing and monitoring impacted lands and any other environmental matters to ensure lands can be effectively and efficiently used and or returned to another use for the societies long-term planning.

General

Industrial activity responds to a societal need for goods and services. Land planning, i.e. public authority decides where industry can operate. Operation is done under various permits that reflects societal concerns; tolerance of environmental (emissions) and social impacts (worker health protection). The obvious priority of an industrial site is the production in a most effective way under its constraints (permit, market, neighbors...).

Assets in production

The dilemma for industrial sites in operation is to get a proper balance between production and environmental protection (to any emission) but also to support the ecosystem services (availability of organic matter, air, fresh water, etc.) of the land. This being said, there are many examples where environmental impact occurred and corrective actions are taken while maximizing sustainability in production and in remediation (e.g. reuse of process water, reuse of water from a pump & treat as in process, use of natural processes for remediation). Furthermore, idle land in an industrial perimeter could be temporary used for other purposes, e.g. temporary nature, sport field, as long as there is a guarantee that those temporary uses will not impair the primary destination of the land as industrial use when new projects arise.

Surplus assets

Former industrial, mining sites or landfills, often qualifying as "surplus assets" for which there is no industrial future, are another issue. It is neither industry nor society interest to let them lay idle, as they would soon become brownfield. It is important to give those sites a new use. If contaminated, remedial actions should be taken to make the land fit for re-use with no risk for the intended future use. Depending on the legacy, the location can be redeveloped to a higher economical value project (other industrial, commercial, housing, historical) or to lower economical value but higher natural, societal services (park, landscape, nature). Industry bears the cost of dismantling, demolition and remediation either directly by executing the work or indirectly by transferring the assets to a redeveloper where legislation allows. Liability cost are not always offset by the land value, hence this kind of operation is not necessary beneficiary for industry. Nevertheless, from an industrial point of view, it is important to minimize its portfolio of "surplus assets" that represent liabilities that are in the radar of investors and financial institutions.

Industrial land re-use will also decrease the need for new greenfield to be used for industrial purpose. Recycling remediated land is part of the land life cycle. In conclusion, enabling land reuse is often an operation where industry investment is not offset by the value of the remediated land. But on the long term putting industrial "surplus assets" into new use is of interest for industry and for society. This is not necessarily only driven by short-term economic benefit. Other aspects, e.g. image, social, environmental also play a role.

Conclusions

Land Stewardship opens up a world of possibilities. The value land, being a non-renewable resource, represents is irreplaceable. Land managers, who recognise its intrinsic value and manage their land in a way that retains its quality, can create even more value inside and outside their fences by connecting industrial land management to societal, ecological, and economic challenges. Natural capital and social capital are part of this equation and pro-active stakeholder engagement is a must. NICOLE and Common Forum are putting effort in bringing Land Stewardship into wide application.

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1.2.5. Heavy metal mobility and PAHs extractability relationships with soil hydrophobicity in coal ash reclaimed technogenic soils (Technosols)

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Abstract

Soil hydrophobicity (water repellency) has major implications for surface and subsurface water transport and organic and inorganic contaminant mobilization and transport. Polycyclic aromatic hydrocarbons (PAHs) extractability and heavy metal mobility and speciation in solutions from acidic coal ash reclaimed Technosols from a major coal mine region in Eastern Europe were studied with the aim to reveal relationships with soil hydrophobicity and other soil characteristics. The Technosols from the mine area exhibit small-scale spatial variability of water repellency. Non-vegetated and pine-vegetated spoils reclaimed with coal ash were studied. The “water drop penetration time” (WDPT) varied from 14-14440s. Exchangeability and solubility of metals (1M NH₄NO₃, 0.01 M CaCl₂) were closely related with the cation exchange capacity (CEC) and WDPT. Principal Component analysis (PCA) and cluster analysis involving exchangeable and soluble forms of Co, Cu, Fe, Mn, Ni, Zn and Pb and other soil properties and characteristics revealed that soil hydrophobicity and 0.01 M CaCl₂ soluble and exchangeable fractions of most heavy metals had a similar source. Especially strong was the link between WDPT, OC and soluble (0.01 M CaCl₂, H₂O) and exchangeable Fe. All heavy metals (1M NH₄NO₃, 0.01 M CaCl₂), except Pb were positively related with the sand content due to accumulation of coal and ash particulate organic matter in the sand fraction. The majority of heavy metal species were represented by free ions (M²⁺) and sulfate complexes (MSO₄^o). Individual 16 PAHs (except acenaphthylene) were below the maximum permissible loads defined by the Bulgarian national legislation, and were not correlated with WDPT. Results obtained in this study suggest that lignitic coal and ash particles are the main source for soluble and mobile fractions of heavy metals. The high share of free and neutral dissolved species may pose a risk for heavy metal contamination in the hydrophobic Technosols.

Keywords: technogenic soil, hydrophobicity, heavy metal mobility, speciation, PAHs, principal component analysis (PCA), cluster analysis

Introduction

The overburden dumps at Maritsa-Iztok coal mine in South-Eastern Europe are often characterized by elevated bioavailability of metals, lack of enough moisture, increased compaction and relatively low organic matter content. In addition, high acidity due to pyrite and metal sulphides (Kostova, 2006) may generate acid-mine drainage. Pliocene sediments composed of yellowish-green and greyish-green clays located above the coal seems are used as a main substrate for reclamation purposes (Garbuchevev *et al.* 1975). A common practice in land reclamation is the application of surface soil humus layer, which prevents further oxidation of the overburden layers of black clays consisting of sandstone, pyrites and waste coal admixtures (Barnhisel and Hower, 1997). Forestation, also called biological reclamation, is considered a useful practice for initiating soil-forming processes in surface coal mine spoils (Krümmelbein *et al.*, 2012). In spite of the low humus content, the slightly alkaline pH (Zheleva and Tsoleva, 2004) of the overburden clays prevents mobilization of heavy metals. In the beginning of the reclamation period (1970s), however the black

clays situated just above the coal seams have been inadvertently mixed with the yellowish-green and greyish-green clays thus causing serious problems, due to extreme acidity. A useful amendment and ameliorant was considered the addition of coal ash (pH 7-7.3) a waste product from the nearby coal incineration thermal power plant. Schwab *et al.* (1991) and Chadwick *et al.* (1987) found that the elements including As, Cd, Hg, Pb and Zn are mostly concentrated in the organic matrix of the coal, Cr, Cu and Se were present in both the mineral and organic fraction, while ash was enriched with trace elements (Fernandez-Turiel *et al.*, 1994).

High concentrations of Al and Fe are typical for acid sulfate waters (Bigham *et al.* 1996). It has been estimated that in acid sulfate drainage waters from mine waste tailings, sulfate may modify the aqueous geochemistry of Al, Fe and other heavy metals and the solubility of Al/Fe is controlled by Al/Fe oxides, oxyhydroxides and sulfates (Shum, M., & Lavkulich, L. 1999).

Polycyclic aromatic hydrocarbons (PAHs) are common constituents of coal and their contents vary widely, from 1-2500 mg/kg (Achten and Fofmann, 2009). Heavy metals and PAHs are mainly bound to soil organic matter (SOM) and their mobility is caused by distribution between soil mineral and organic phases and dissolved organic carbon (DOC) and mineral complexes, including colloidal species.

To our knowledge few studies have been concerned with contaminants behaviour in water repellent soils possessing coatings of hydrophobic (amphiphilic) compounds (Atanassova and Doerr, 2010). The transport of contaminants in these soils follows heterogeneous preferential flow path patterns of water.

The objective of the present study was to assess mobile (soluble and exchangeable) metals, and labile (organic solvent extractable) PAHs in hydrophobic Technosols reclaimed with coal ash and investigate links with soil hydrophobicity (soil water repellency).

Methodology

Total organic carbon (TOC) in the studied spoils was determined by oxidation with $K_2Cr_2O_7/H_2SO_4$ and fractionated TOC into humic organic carbon (HOC) and fulvic organic carbon (FOC) upon treatment with 0.1 $MNa_4P_2O_7$ and 0.1 M NaOH by the methods of Kononova (1966), cation exchange capacity (CEC) was assessed as sum of titratable acidity (pH 8.2) and extractable Ca, by saturation with K malate at pH 8.2 (Ganev and Arsova, 1980). Electrical conductivity was determined in soil water (1:5) according to ISO 11265:2002. Soil pH/Eh were measured in a soil:water slurry of 1:2.5. Texture was analysed by the method of Kachinski (Kachinski, 1965). Soil water-repellency (soil hydrophobicity) was measured by the water drop penetration time (WDPT) method (Doerr *et al.* 2002). Statistical analysis (principal component PCA and cluster) was performed by SPSS 22 for MS Windows.

The study was carried out on two plots at Obruchishte village, between Troyanovo 1 and Troyanovo 3 mines of Maritsa-Iztok coal mine in Bulgaria. The experimental plots were located on several hectares of large area, afforested with *P. nigra*. These spoils consisted of loam-textured Pliocene overburden sediments from the nearby open-cast lignite mines (N 42.16434, E 25.94285, and N 42.16452, E 25.94318). Lack of plant density and water repellency was observed at areas of ~ 200 m² amongst a uniformly pine vegetated area. At the two sites, grids $\Delta 2$ m, ~ 40 m² were constructed and sampling was at two depths where water repellency was demonstrated on the field 0-5 (10) cm and at 10-20 cm. At the non-vegetated site of Obruchishte, soils were of sandy loam texture mixed with degraded finely dispersed lignitic particles and coal ash, and of sandy clay (0-5 cm) and clay texture (10-20 cm) at the pine vegetated site. Layers of greyish-green and yellow clays intermixed with black clays containing coal and ash were located at surface depths of 0-10 cm.

Soil cores were taken to a depth of 0- 5(10) and 10-20 cm using a 3 cm wide and 25 cm long core sampler. Soil samples at the field were classified as non-repellent (WDPT < 5s), strongly (60 s < WDPT < 600 s) and severely > 600s water repellent according to the scale of De Bano (1981). The soil samples were equilibrated at the ambient air humidity for four days before measuring water drop penetration time (WDPT) in the laboratory at recorded humidity and temperature.

Heavy metals in soils (in three replications) were determined by the following methods: water soluble forms in soil water ratio 1:5, shaking for 1 hour, centrifuging and filtering through 0.45 µm acetate cellulose filter (Katoh *et al.*, 2012); 0.01M CaCl₂ extractable forms in soil:solution ratio (1:5) and shaking for 2 hours (Van Ranst *et al.*, 1999); pseudo-total forms of metals (PT) were analyzed by aqua-regia digestion (ISO 11466:1995). Cationic composition of metals in 1M NH₄NO₃ and aqua regia extracts was determined by AAS (Perkin Elmer). Anions in the soil solution including dissolved organic carbon (DOC) were analysed with Spectroquant tests, Merck Millipore (PHARO 100). Heavy metal speciation was performed by using Visual Minteq V 3.1.

The analytical laboratory investigations of H₂O and 0.01M CaCl₂ extracts were performed with a high resolution radial viewing ICP - OES system - HORIBA JY ULTIMA 2 (Jobin Yvon, Longjumeau, France). Each element was determined by two most prominent lines, free from line interference level from the matrix elements (Al, Ca, Fe, Mg and Ti).

PAHs were analysed according to ISO 18287:2006 using 1:1 v/v acetone:hexane in a microwave extraction system and GC-MS analysis (Thermo Scientific-Trace GC Ultra). The chromatograms are taken in full scan and SIM mode, splitless injection, column TG-5MS, 30 m, 0.25 mm, 0.25 µm film thickness, oven T°: 2 min-80 °C isothermal, 30 °C/min to 120 °C; 0 min isothermal; 5 °C/min to 280 °C, 10 min isothermal; electron ionization 70 eV. External standard calibration curve was used for compound quantification.

Results and discussion

Metal solubility and mobility

General soil properties are presented in Table 1a,b. It is evident that the non-vegetated Technosols have higher contents of sand than the pine-vegetated, respectively lower clay contents, however the CEC values, EC and TOC are higher. This is owing to the accumulation of coal particles in the sand fraction (data on soil aggregate analysis not published, Project DN 06/1 NSF) and the high proportion of humified organic matter in coal (Piccolo *et al.* 1997). Total heavy metal contents did not exceed the national regulation standards for agricultural soils, except for Cu and Pb at pH < 5.

To get more information about the interrelation between the various forms of metals and major soil properties and characteristics we conducted Principal Component Analysis (PCA) and cluster analyses. For the 0.01M CaCl₂-soluble forms three major components with eigenvalues >1 were distinguished containing 80% of the total variance, for the H₂O - soluble forms, four components with eigenvalues >1 containing 86% of the total variance and for the exchangeable 1M NH₄NO₃ forms three components containing 81% of the total variance (Tables 2, 3, 4). Mobility and solubility of metals (1M NH₄NO₃, 0.01 M CaCl₂) were closely related with the cation exchange capacity (CEC) and WDPT. Lead solubility and mobility was less satisfactorily predicted from measured soil characteristics than solubility and mobility of the other heavy metals. Principal Component analysis (PCA) and cluster analysis involving exchangeable and soluble forms of Co, Cu, Fe, Mn, Ni, Zn, Pb and other soil properties and characteristics (CEC, organic carbon (OC) content, % clay, % sand and WDPT) revealed that soil hydrophobicity and soluble and exchangeable forms of most heavy metals had a similar source (Tables 3, 4). All heavy metals (1M NH₄NO₃, 0.01 M CaCl₂), except Pb were positively related with % sand.

Water extracts of Fe (Fe_W) only were significantly correlated with WDPT ($r=0.80$, $p < 0.003$) and Fe_W, WDPT and TOC loaded on one component (Table 1).

Cluster analysis supported the data from the PCA analysis (Figures 1, 2, 3). For the water soluble metals the dendrogram was composed of four main groups, clustering WDPT, Fe_W and TOC into one sub-group. For the metal-0.01M CaCl₂ (M_S) and metal-NH₄NO₃ (M_Ex) fractions the dendrogram was divided into three main groups. Soluble metals, CEC, % sand, WDPT and TOC comprise the 1st main group, silt the 2nd main group and % clay and soluble Mn (Mn_S) the 3rd main group. Similarly, the exchangeable metals M_Ex were linked in one main group with CEC, % sand and organic carbon (TOC), exchangeable Pb is linked with % silt into the 2nd main group and % clay is separately grouped in a 3rd group, implying association of exchangeable metals to particles in the sand fraction.

Table 1a. Main soil properties of the experimental soils (From Atanassova *et al.*, 2018)

Site	Depth cm	WDPT (s)	Sand %		Silt %		Clay %		Hygroscopic moisture %	
		Range median	Mean \pm	SD	Mean \pm	SD	Mean \pm	SD	Mean \pm	SD
Pine vegetation	0-5	14 - 9589 1200	47.5	7.21	22.4	0.07	28.0	7.21	8.2	0.69
	10-20	2 - 128 10	25.5	20.45	22.04	0.03	55.1	21.72	8.4	0.54
non-vegetated	0-10	76-14440 1282	59.0	1.89	21.8	0.08	17.8	3.86	8.2	0.63
	10-20	202-2470 614	62.8	4.84	21.3	0.10	17.0	2.37	7.8	1.9

Table 1b. Main soil properties of the experimental soils (continued) (from Atanassova *et al.*, 2018)

Site	Depth cm	CEC		pH		EC		TOC %	
		Mean \pm	SD						
Pine vegetation	0-5	41.27	3.89	4.58	0.20	0.19	0.14	5.09	0.42
	10-20	44.60	3.52	4.18	0.43	0.63	0.14	3.00	1.67
non-vegetated	0-10	67.77	6.16	3.18	0.11	1.72	0.76	6.43	3.98
	10-20	69.90	8.70	3.13	0.10	1.61	0.69	6.11	0.96

Table 2. Component matrix: WDPT, TOC, clay, sand and silt contents and H₂O-soluble metals.

Rotated Component Matrix^a				
	Component			
	1	2	3	4
WDPT	.118	.910	.132	.178
OC	.033	.889	.201	-.250
CLAY	.214	.495	.728	-.292
CEC	.691	.279	.121	.206
Co_W	.494	.242	-.561	.514
Cu_W	.870	.261	-.035	.034
Fe_W	.297	.847	-.214	.219
Mn_W	.649	.053	-.375	-.042
Zn_W	.358	.061	.068	.898
Ni_W	.932	.052	.021	.252
SAND	-.109	-.263	-.947	.050
SILT	-.074	-.232	.829	.403
Al_W	.893	-.032	.283	.202

Table 3. Component matrix: WDPT, TOC, clay, sand and silt contents and 0.01M-CaCl₂ soluble metals.

Component matrix			
	Component		
	1	2	3
WDPT	.612	.485	.504
TOC	.737	.213	.432
CLAY	-.693	.655	.023
CEC	.911	-.048	-.261
Co_S	.944	.108	-.187
Cu_S	.850	.199	-.126
Fe_S	.788	.413	.277
Mn_S	-.446	.382	-.232
Zn_S	.740	.130	-.223
Ni_S	.871	.021	-.265
SAND	.724	-.570	-.136
SILT	.134	-.626	.619

Table 4. Component matrix: WDPT, TOC, clay, sand and silt contents and 1M NH₄NO₃-metals

Component matrix			
	Component		
	1	2	3
WDPT	.611	-.417	.596
TOC	.667	-.053	.614
CLAY	-.646	-.681	-.049
CEC	.932	.094	-.218
Pb_Ex	-.352	.602	.070
Ni_Ex	.934	.055	-.194
Cr_Ex	.559	-.288	-.600
Co_Ex	.957	.059	-.167
Fe_Ex	.825	-.356	.322
Mn_Ex	.930	-.031	-.005
Zn_Ex	.849	-.079	-.143
Cu_Ex	.931	-.058	-.082
SAND	.680	.597	.011
SILT	.105	.620	.267

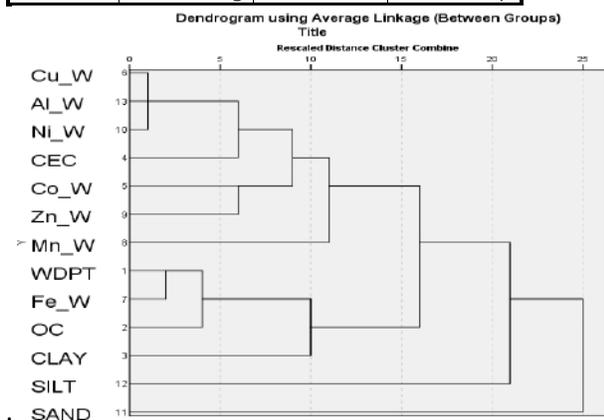


Figure 1. Cluster analysis representing soluble (H₂O) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents.

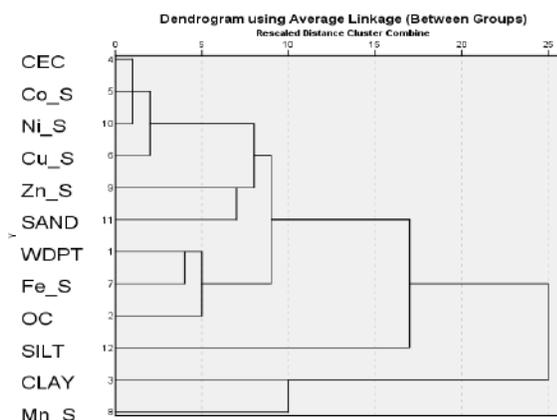


Figure 2. Cluster analysis representing soluble (0.01M CaCl₂) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents.

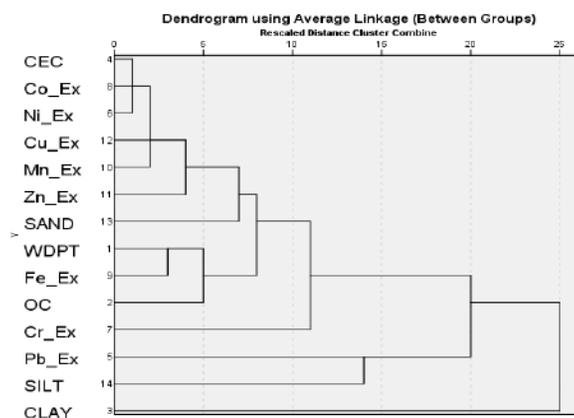


Figure 3. Cluster analysis representing exchangeable (1M NH₄NO₃) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents.

Ion speciation in solution

The majority of heavy metal species in the Technosols were represented by free ions (M^{2+}) and neutral sulfate complexes (MSO_4^0). Generally, solutions were extremely acidic (pH 3-4) and possessed high electrical conductivity at the non-vegetated site (1.61-1.72 mS/cm (Table 1b) with large amounts of weathering products derived from pyrite oxidation (Fe^{2+} , SO_4^{2-} , H^+), as well as Al^{3+} , Ca^{2+} , Mg^{2+} and Mn^{2+} from mineral weathering. The metal speciation (Table 5) showed that: (i) in the more acidic non-vegetated plot (pH \sim 3.0) mono and disulphate complexes were the most dominant species for Al^{3+} , while M^{2+} were the most common for Cu, Fe, Mn, Ni and Zn; (ii) the distribution of Fe species is controlled by the SO_4^{2-} concentration in solution. Generally, in the Obruchishte soil with a pH \sim 3.0, Fe was found as free Fe^{2+} and $FeSO_4^0$ complexes. In addition, the H_2O and 0.01 M- $CaCl_2$ soluble metal concentrations of Fe, Mn, Ni, Cu and Zn, provoked by the extremely acid pH \sim 3 were higher than maximum permissible levels for surface waters (Decree No 12, 2002) and may become a source of contamination.

We speculate that the low share of dissolved organic complexes of heavy metals, although Cu is known to form strong complexes with dissolved organic carbon (DOC), is because, soil organic matter (SOM) in water repellent soils is more chemically inert than SOM in wettable hydrophilic soils. The hydrophobic interactions in the soil organic matrix help decrease the release of organic colloids. In addition, at the acid pH range (3-4) acidic functional groups on organic compounds are protonated, which leads to a weaker dissociation and charge reduction further lowering metal binding through electrostatic interaction.

Table 5. Metal speciation in the water extracts.

Metal ion	pM*	% of total dissolved ions in solution	Species
Al^{+3}	3.95 – 4.65	3.86 - 11.12	Al^{+3}
		0.04 – 0.08	$AlOH^{+2}$
		57.65 - 70.69	$AlSO_4^+$
		17.37 – 27.78	$Al(SO_4)_2^-$
		0.01 – 6.36	$AlHPO_4^+$
		0.17 – 0.26	$/FA-Al+3G(aq)$
		1.49 – 4.70	$/FA_2Al+(aq)$
Co^{+2}	6.12 – 7.10	53.6 – 68.4	Co^{+2}
		28.5 – 41.0	$CoSO_4(aq)$
		1.36 – 2.54	$/FA-Co+2G(aq)$
		0.46 – 0.61	$/FACo+(aq)$
Cu^{+2}	6.04 – 6.90	34.2 – 63.0	Cu^{+2}
		0.01 – 0.06	$CuCl^+$
		19.5 – 43.3	$CuSO_4(aq)$
		0.02 – 0.03	$CuHSO_4^+$
		0.38 – 1.59	$/FA-Cu+2G(aq)$
		0.77 – 8.20	$/FA_2Cu(aq)$
		6.73 – 30.3	$/FACu+(aq)$
Fe^{+2}	4.03 – 5.26	43.2 – 66.6	Fe^{+2}
		0.01 – 0.03	$FeCl^+$
		33.1 – 55.6	$FeSO_4(aq)$
		0.22 – 17.4	$FeH_2PO_4^+$

		0.09 – 2.3	/FA-Fe+2G(aq)
		0.12 – 0.79	/FA-Fe(II)+(aq)
Mn ⁺²	3.96 – 4.46	51.1 – 73.4	Mn +2
		0.01 – 0.03	MnCl+
		26.5 – 47.6	MnSO ₄ (aq)
		0.49 – 1.20	/FA-Mn+2G(aq)
		0.03 – 0.34	/FAMn+(aq)
Ni ⁺²	5.39 – 5.89	47.1 – 69.8	Ni +2
		0.09 – 1.10	/FA-Ni+2G(aq)
		28.2 – 49.3	NiSO ₄ (aq)
		0.01 – 0.02	Ni(SO ₄) ₂ ⁻²
		1.90 – 12.2	/FANi+(aq)
Zn ⁺²	4.95 – 5.78	40.3 – 64.6	Zn+2
		0.36 – 0.94	/FA-Zn+2G(aq)
		0.01 – 0.06	ZnCl+
		29.5 – 46.2	ZnSO ₄ (aq)
		2.71 – 11.3	Zn(SO ₄) ₂ ⁻²
		1.01 – 4.31	/FAZn+(aq)

*Negative log activity of free metal ions.

Polycyclic aromatic hydrocarbons

The contents of 16 EPA PAHs are presented in Table 6 and were close to the background values for normal non-polluted soils and lower than the maximum permissible loads (Regulation 3, 2008, Bulgaria). Correlation and principal component analysis did not reveal links of individual or total PAHs with WDPT or total organic carbon. We speculate that the extremely acidic soil reaction prevents dissolution and mobilization of hydrophobic compounds through sorption to dissolved organic carbon and organic colloids. Therefore, PAHs are probably present in “bound residues” in SOM and are strongly adsorbed by inert and hydrophobic insoluble organic matter and are therefore not released through extraction with organic solvent unable to disrupt ester or ether bonds in SOM. Acenaphthylene is a common ingredient in coal tar and crude oil and is also often produced as an industrial or municipal waste. High contents of acenaphthylene have been detected in fly ash from fluidized bed combustion systems (Liu *et al.* 2000) and we suspect the high contents of acenaphthylene may originate from the fly ash amended waste dumps. The sum of PAHs (due to the high acenaphthylene content) exceeds the maximum permissible levels as stated in Decree No 3 (2008), national legislation of Bulgaria.

Table 6. PAHs contents (means) +/- SD in hydrophobic non-vegetated and pine-vegetated Technosols.

Compound* µg/kg	NAPH	ACY	ACE	FLU	PHE	ANT	FLA	PYR	SUM
mean	3,74	1313,90	3,37	4,97	11,62	2,67	3,94	8,33	
SD	1,92	474,06	1,31	2,60	7,99	1,35	1,72	4,83	
compound ug/kg	BaA	CHR	BbF	BkF	BaP	IND	DbahA	BghiP	
mean	4,88	9,46	5,86	3,63	4,28	3,56	0,90	2,89	1875,8
SD	2,39	5,12	3,59	1,75	1,99	1,95	0,43	0,98	900,9

* NAPH-naphthalene; ACY- acenaphthylene; ACE- acenaphthene; FLU- fluorine; PHE-phenanthrene; ANT- anthracene; FLA- fluoranthene; PYR - pyrene; BaA- benzo(a)anthracene; CHR- chrysene; BbF-benzo(b)fluoranthene; BkF – benzo(k)fluoranthene; BaP- Benzo(a)pyrene; IND – indenopyrene; DbahA- dibenzo(a,h)anthracene; BghiP- benzo(g,h,i)perylene

Conclusions

Our key findings are the following: (1) Mobility, i.e. exchangeability and solubility of metals (1M NH_4NO_3 , 0.01 M CaCl_2) were closely related with CEC and WDPT. (2) Water soluble Fe was significantly correlated with water drop penetration time WDPT and organic carbon; (3) Lead mobility was less satisfactorily predicted from measured soil characteristics than solubility and mobility of the other heavy metals; (4) Principal component and cluster analysis demonstrate that lignitic coal and ash particles are the main sources for soluble (0.01 M CaCl_2) and exchangeable fractions of heavy metals; (5) The high share of free and neutral dissolved species may enhance heavy metal mobility and transport in the reclaimed hydrophobic Technosols; (6) PAHs extractability was not related to organic matter contents or WDPTs. Very low quantities of labile (organic solvent extractable) PAHs were detected in the Technosols amended with coal ash, due to the high sorption affinity to the organic matter.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.6. Technogenically contaminated soils of Ukraine

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Abstract

The modern ecological state of the soil with the influence of the pollution factor was determined by the analysis and generalization of the data of the soil cover survey of Ukraine. It was determined the nature and extent of atmotechnogenic (heavy metals), radioactive (¹³⁷Cs and ⁹⁰Sr), hydrocarbon (petroleum and petroleum products) pollution and soil contamination with pesticide residues (HCH, DDT and 2,4-D).

It was defined the area of the territories corresponding to the dangerous and extremely dangerous level of pollution by heavy metals in zones of influence of atmospheric emissions of enterprises of ferrous and nonferrous metallurgy, coke industry, thermal power stations, dumps of mines and highways. The decay rate of soil cover with radioactive contamination in the post-emergency period of thirty years has been established. The extent of destruction and pollution of soils as a result of oil and gas production, accidents of oil and product pipelines was determined. Positive dynamics of reduction of content of pesticide residues in soils was established.

Keywords: soil, contamination, heavy metals, radioactive elements ¹³⁷Cs and ⁹⁰Sr, hydrocarbon (petroleum and petroleum products), pesticide residues (HCH, DDT and 2,4-D).

Soil Resources of Ukraine

As of 2017, the land area of Ukraine is over 60.4 million hectares; 42.4 million ha - agricultural land (70.5% of the total area) and 34.4 million ha - arable land (57% of the total area of agricultural land). 60% of the soil cover of Ukraine is represented by chernozem soils. According to Article 14 of the Constitution of Ukraine, chernozems are recognized as national treasures that are under special protection of the state and are the basis for solving socio-economic problems and ensuring food independence of the country.

Soil, at the present stage of soil science development, is considered not only as a means of agricultural production but also as a basic component of the environment (the soil is an integral part of biogeocoenoses and agrophytocenoses) and the main ground for the reproduction of life on Earth through the conservation of biological diversity, and therefore the diversity of soils for environmental protection from abnormal anthropogenic influences, various types of degradation; to ensure the environmental safety of the environment.

Properties, processes and soil conditions determine their ecological functions. The specificity of their manifestation is determined by the fact that the soil is a multiphase, multicomponent, heterogeneous bioinert system with the exchange of substances, energy and information. That is why the most important condition for the conservation of the biosphere is the protection and conservation of soils, their structure and properties, environmental and production functions.

In modern conditions of growing anthropogenic loads on soils, it is observed soil pollution with chemical compounds of organic and inorganic nature against the backdrop of deficiencies of plant nutrition elements following the substantial transformation of the biogeochemical cycle of chemical elements, the direction (directions, pace) of their migration in the trophic chains, the volumes of take-over and accumulation; violation of the substance-energy balance, which negatively affects the quality of plant and animal products, the ecological state of soils and leads to their degradation and the destruction of other components of the biosphere with the formation of anthropogenically transformed landscapes.

Under such conditions, damage to agriculture is determined by the direct impact on plants of contaminated air flows and indirectly - through contaminated soils due to the negative changes in their structure, functions and properties. The environmental rehabilitation of the soil-plant system, which requires significant resource costs, is topical.

Methodology

Methods of research: methods of theoretical generalization and comparison, system approach, abstract-logical, expert, calculation and analytical, soil-geochemical, chemical-analytical methods.

Determination of heavy metals (HM) in soils was carried out by atomic absorption method in acetylene flame (device «*Saturn-4*»).

The areas of soils, contaminated by HM, were determined by soil surveys in zones of atmotechnogenic emissions of ferrous and non-ferrous metallurgy, chemical and coke industry, thermal power plants, highways of mines and dumps, big cities.

Taking into account the multicomponent nature of soil contamination by HM in Ukraine, it was used a total pollution indicator for assessing, followed by a ranking of the contents of the HM by categories that correspond to dangerous and extremely hazardous levels of soil contamination.

The content of oil and petroleum products in soils was determined by gas chromatography (gas chromatograph "Agilent").

The content of pesticides in soils was determined by thin layer of chromatography, the content of ^{137}Cs in soils – by the spectrometric method (device *AMA-03F*), the content of ^{90}Sr in soils - on the device *UMF -1500* with low background for measurements of beta activity and the spectrometer of beta-radiation energies of *SEB-01- 70G*.

The areas of soil contaminated with pesticides and radionuclides were determined with agro-chemical certification by the subsidiaries of the State Institution of Soil Protection of the Ministry of Agrarian Policy and Food of Ukraine.

Results

The current state of soils in Ukraine by impact of soil pollution factor

Soil Conservation Department of NSC ISSAR carries out scientific research on the priority areas of monitoring (diagnosis, evaluation, forecasting) of soil contamination; the regulation of the content of pollutants in soils, the ecological rehabilitation of technogenically contaminated soils and the development of effective ways of their use. Background (reference) monitoring of soil contamination in Ukraine is currently under development.

The results of the analysis of information on the ecological status of soils in Ukraine [1-2] indicate an increase in the rate of soil degradation. An important factor in soil degradation is the impact of pollution. According to the expert estimates of the NSC ISSAR it was found that the area of degraded (low-productive and contaminated) soils in the territory of Ukraine reaches almost 15 million hectares.

According to estimates by the Soil Conservation Department of the NSC ISSAR it was found that the total area of contaminated land in Ukraine is about 8.6 million hectares, of which 4.2 million hectares are radiation-polluted land; 1.6 million hectares - land contaminated by HM; 2.8 million hectares - land contaminated with toxicants of organic and inorganic origin. The sources of soil pollution in Ukraine are emissions from industrial enterprises of ferrous (13) and nonferrous (3) metallurgy, thermal power plants (15), enterprises of chemical and coke chemical industry (13), coal mines (173) and motor vehicles; mining, transportation and processing of minerals, utilization of waste water and sediments, industrial and domestic waste for violations of these works; abnormal introduction and storage of agrochemicals and pesticides, soil improvers; the consequences of the Chernobyl disaster and so on.

Due to the excessive concentration of industrial production and high urbanization, zones of the dangerous level of environmental pollution have been created in Ukraine, especially in the Donetsk, Luhansk, Dnipropetrovsk and Zaporizhzhia regions, as well as in the Carpathian regions of Lviv and Ivano-Frankivsk regions.

Thus, the most dangerous groups of technogenic pollution of soils of Ukraine are:

- atmotechnogenic pollution with heavy metals (HM) - Pb, Cd, Cu, Zn, Cr, Ni, Hg and others (significant danger to humans, animals, plants due to high toxicity and accumulation capacity in the trophic chains);

- contamination with radioactive substances (significant danger, primarily because of their chemical properties, they are similar to non-radioactive elements and easily penetrate into all living organisms, because of high mobility fall into the trophic chains very quickly);

- hydrocarbon pollution with oil and petroleum products (creation of a stable hydrophobic membrane on the surface of soil particles, worsening physical properties, water retaining capacity of soil and quality of groundwater with the migration of light petroleum products in the soil);

- pesticide contamination (significant danger, pest control crops and weeds can be found in large amounts in the soil and are highly toxic chemically stable compounds that adversely affect the useful soil microflora).

Technogenic soil contamination may spread to large areas and have fuzzy spatial boundaries with a small concentration of pollutants (total technogenic pollution), but may be concentrated near one or several sources of man-made pollution and have clear spatial limits (local technogenic contamination).

Atmotechnogenic soil contamination

The soils of industrial cities and industrial agglomerations of Donetsk-Pridniprovsky region of Ukraine (Donetsk, Luhansk, Dnipropetrovsk, Zaporizhzhya, Kherson regions) have a different level of pollution by the HM, as well as different contaminated areas.

In the most polluted cities of Ukraine (Kostyantynivka, Mariupol, Alchevsk), the average content of HM in soil exceeds the maximum permissible concentration by 1.5-10 times.

Dangerous and extremely dangerous levels of soil contamination are located within 5-15 km around the centers of man-made emissions (TES, metallurgical and chemical plants, underground mines, mining quarries, transport networks, etc.).

The areas of soil pollution by ferrous and nonferrous metallurgy enterprises amounted to 36.0 thousand hectares, 888.0 thousand hectares of coke plants, and about 306.0 thousand hectares of mine shafts. An important part in the technogenic contamination of soil is transport vehicles.

In Ukraine, the length of highways with an intensity of traffic of 3000-7000 cars per day (international and national roads) is 12883 km. At the same time, the area of road bands, the soils of which have a dangerous category of pollution, reaches 25.8 thousand hectares.

In addition, exhaust gases of engines of internal combustion of cars contain more than 160 harmful derivatives of hydrocarbons; Pb and Ni; tires contain Cd. It was established that for road sections, which are not protected by forest belts, the distribution of atmospheric pollution is observed at a distance of 50-100 m from the roadway.

Accumulation of different HM in soils negatively affects their physical, biological and chemical properties. Contamination of the compounds of the HM changes the soil parameters, in particular, the decrease of pH, increase of mobility of organic matter, calcium and magnesium, decrease of the content of moving forms of phosphorus, potassium, zinc and copper. High absorption energy of HM (Cd > Cu > Pb > Ni > Co > Zn > Ca > Mg) promotes displacement of calcium

and magnesium from the soil absorption complex, which reduces the aggregate stability of the thinly dispersed part of soils [3].

The result of the "unpacking" of soil aggregates in a complex with soil dispersion is the increase in the availability of organic matter and its migration from the boundaries of the arable layer of soil. In soils contaminated with Cd, Pb, Cr, Ni, the content of available phosphorus, potassium, zinc and copper decreases; the negative conditions for soil formation are created, the soil ability to self-purification is reduced and the processes of chemical degradation of soils are intensified.

Soil pollution of agricultural land with HM leads to a decrease in the activity of the microflora of the soil, reduction of yield and increase of the content of HM in plant and animal products. The concentration of HM in the soil persists for decades and even centuries.

At the expense of annual inflow of a considerable quantity of HM with gas-dust emissions, which also contain other pollutants of inorganic (sulfur dioxide and nitrogen, carbon monoxide and nitrogen, hydrogen sulfide) and organic (phenol, benzopyrene, formaldehyde) origin, around large industrial enterprises there is considerable pollution of soils, plants, animals and adjacent environments (surface and subsoil waters, atmospheric air, etc.), which adversely affects people's health.

Radioactive contamination of soils

The result of the Chernobyl disaster was radioactive soil pollution in a large area in 12 regions of Ukraine. 119 thousand hectares of agricultural land were removed from the use, including 65 thousand hectares of arable land. According to the Law of Ukraine dated February 27, 1991, № 791a-XII, contaminated territories were divided into four areas [4]:

1) Exclusion area from which the evacuation of the population was carried out in 1986. The density of pollution by ^{137}Cs isotope - 1 480 kBq / m², economic activity in this zone is not carried out.

2) Area of obligation to resettle the population. The pollution density is ^{137}Cs - 555 kBq / m² and above, or by ^{90}Sr - 111 kBq / m². Soils in agricultural production are not used. Area of the village land – 35.6 thousand hectares.

3) Area of guaranteed voluntary resettlement. The pollution density is ^{137}Cs - 185-555 kBq / m², or by ^{90}Sr - 5.55-111 kBq / m². Agricultural production is under strict control. Agricultural land is 115.8 thousand hectares.

4) Area of enhanced radiological control with a density of ^{137}Cs - 37-185 kBq / m², or ^{90}Sr – 0.74-5.55 kBq / m². Area of the village land – 1012.1 thousand hectares.

According to surveys of the specialists of the State Institution of Soil Protection, contaminated territories of Ukraine, in the Polissya natural and climatic zone of Ukraine concentrate more than 80 % of soils contaminated with ^{137}Cs and ^{90}Sr . In particular, the pollution density ^{137}Cs - 185-555 kBq/m² is 4.8 thousand hectares and 38.3 thousand hectares with a pollution density ^{90}Sr – 5.55-111 kBq / m² or 0.1 % and 0.8% respectively. In the soils of the Polissya zone, the processes of non-radionuclide absorption are weakened; as a result, radionuclides migrate rapidly in adjacent soil environments.

In the Forest-Steppe zone, the area of soils with a density of pollution is much lower, at ^{137}Cs - 185-555 kBq / m² - 200 hectares, and by ^{90}Sr - 5.55-111 kBq / m² - 8.8 thousand hectares, or 0.03% and 1.1 % of the surveyed area.

The generalization of data shows that 25 years after the Chernobyl accident, the area of contaminated ^{137}Cs soils of agricultural lands of Ukraine at 37 kBq / m² is distributed on 462 thousand hectares, of which arable land is 346 thousand hectares.

The area of contaminated ^{90}Sr soils at the level of 0.74 – 5.5 kBq / m² is 4.6 million hectares (52 % of the surveyed area). It was established that in the post-rain period the soil area of contaminated ^{137}Cs and ^{90}Sr decreased more than twice [5] due to radioactive decay, fixation and redistribution in the soil; conducting a set of countermeasures, which also ensured the reduction of radiation contamination of food products.

Hydrocarbon contamination of soils

Soils around the facilities of the oil and gas complex have the high risk of petroleum contamination (gasoline, kerosene, diesel fuel). More than 311 petroleum, gas and gas condensate fields have been opened in Ukraine; there are more than 5 thousand km of main and more than 20 thousand km of industrial oil pipelines covering all natural and climatic and economic regions [3].

Soil contamination is due to emergency situations in the oil and gas industry, the number of which in Ukraine, according to statistics, exceeds 1.5 thousand per year. Extraction of 1 ton of petroleum is accompanied by the destruction or contamination of soil with a volume of 1.0-1.3 m³.

Petroleum products influence the transformation of soil structure with the formation of powder-like structure, it greatly changes the physical and physical-chemical properties of soils, accelerates the migration of hydrocarbons to groundwater.

By contamination of soils with petroleum and petroleum products on the surface of soil particles there are formed resistant hydrophobic membranes and, depending on the chemical and physical properties of the pollutant, granulometric composition of the soil and the level of pollution, the impact of oil and petroleum products on the soil is differed significantly.

The hydrophobic properties of soils contaminated with petroleum and petroleum products to a large extent depend on the concentration of pollutants and their qualitative composition. Light fractions of petroleum affect these soil properties in a short time, the impact of heavy petroleum products is significant and pollution does not disappear for many years [3].



Figure 1. Plots after drilling operations (Kharkiv region, Ukraine)

The main mechanisms of soil degradation by petroleum pollution are inhibition of biological processes, reduction of soil moisture, blockage of nutrients and soil dispersion. Cleaning of soil from light hydrocarbons takes place for six months to three years, from heavy hydrocarbons - ten years and more.

Soil contamination with pesticide residues

Modern technologies of cultivating crops to produce high yields require the use of pesticides. In agrarian production in Ukraine, the area of application of pesticides reached 32.1 million hectares, as a result of their slow expansion in the soil there is a gradual accumulation of them.

There was a problem of storage and disposal of prohibited and unsuitable pesticides. Their unauthorized disposal leads to the creation of extremely dangerous stocks of soil, plant contamination, etc., and their use poses a threat to public health.

The most resistant pesticides to soil decomposition are HCH, DDT and 2.4-D, but eventually they decompose. In particular, according to the State Institution “Institute of Soil Conservation”, in recent years, from surveyed soils in the area of 17 311.5 thousand hectares only in the soil with an area of 2 520 hectares the HCH content exceeded the MPC, the content of DDT from 17 313.1 thousand hectares exceeded the MPC on 6 690 hectares and 2.4-D - 2 500 hectares with 9 144 thousand hectares.

At this time, the area of contaminated soils is 0,014% HCH, 0,038% DDT and 0,027% 2.4-D. According to the results of studies on the dynamics of content in soil DDT found that in 10 years its content in soils decreased by 3 times with the dynamics of decomposition from 5 % to 15 % of this pesticide in one year. Thus, with the prohibition on the use of pesticides and the transition to the use of modern chemical plant protection products, a gradual reduction of the residues of dangerous pesticides in the soil has been defined.

Conclusions

The analysis and generalization of the survey data of the soil cover of Ukraine determined the modern ecological state of the soil for the influence of the pollution factor.

The nature and magnitude of atmospheric (heavy metals), radioactive (^{137}Cs and ^{90}Sr), hydrocarbon (petroleum) pollution and soil contamination with pesticide residues (HCH, DDT and 2,4-D) are defined.

It is determined the area of the territories corresponding to the dangerous and extremely dangerous level of pollution by heavy metals in zones of influence of atmospheric emissions of enterprises of ferrous and nonferrous metallurgy, coke industry, thermal power stations, dumps of mines and highways.

The decay rate of soil cover for radioactive contamination in the post- accident period of thirty years was defined. The zone of radiation contamination of Ukraine reaches 8401.6 thousand hectares. The area with a pollution density of ^{37}Cs – 3.7-37 kBq / m² and ^{90}Sr - up to 0.74 kBq / m² of agricultural land is 7238.1 thousand hectares is allowed to use without special restrictions.

The extent of destruction and pollution of soils as a result of petroleum and gas extraction was determined. Extraction of 1 ton of petroleum is accompanied by destruction or contamination of 1.0-1.3 m³.

Positive dynamics of reduction of content of pesticide residues in soils was established. From the studied soils, the soil area according to the content of DDT, HCH and 2.4-D above the MPC is 0,038 %, respectively; 0.014 % and 0.027 %. For 10 years of observation, the content of DDT in the soil above the MPC has decreased by 3 times, or from 5 to 15 % per one year.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.7. Considerations for a new integrated policy on polluted sites and soils in Switzerland - current implementation problems, prospective analysis and proposals for improvement

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Abstract

For the first time a comparative analysis of the two policies “polluted sites” and “polluted soils” has been carried out since the introduction of the legal bases almost 20 years ago.

The goals of the analysis were set as follows:

- Draw up a comprehensive picture, if possible, of the current implementation problems.
- Understand the implementation and evolution of legislation on polluted sites and soils in Switzerland.
- Analyzing the political-administrative programs of the two public policies in order to highlight convergences, divergences, inconsistencies and gaps.
- Propose recommendations for a future harmonization of the two policies.

This assessment of the situation in Switzerland, from the establishment of the legal basis to the current problems, provides an interesting insight into the key points for optimised management of polluted sites and soils and might provide useful practical information for other countries.

Keywords: soil policy, soil legislation, diffuse pollution, contaminated sites

Introduction, scope and main objectives

As elsewhere in Europe, the soil in Switzerland is subject to many pressures. It disappears to make way for built-up areas or is severely degraded and can no longer fulfil all its functions. It suffers from physical damage (sealing, compaction), biological damage (by pathogenic or non-native organisms) and chemical damage. On the latter aspect, the Federal Office for the Environment (FOEN) considers that there are no more unpolluted soils in Switzerland. Nearly 90% of the unsealed land is slightly polluted, 9% moderately polluted and 1% strongly polluted. Pollution mainly affects urban areas (gardens and parks), land near industrial facilities and soils where special crops are grown (arboriculture, viticulture).

In addition to these pollutions, which can be considered diffuse, there are more than 38 000 sites polluted by waste, including landfills, company sites and accident sites. While the majority of these sites do not pose a threat to man or the environment, a number of them, estimated at 4 000 today, need to be remediated as they directly endanger human health and natural resources.

Despite its importance, the soil is currently rather poorly protected under Swiss law. With regard to chemical soil pollution, one of the major problems is that the legislation deals with soil pollution in two different and independent chapters of the Federal Environmental Protection Act and in two

separate ordinances (on soil damage and on the remediation of polluted sites), depending on whether it is considered diffuse or originating from a point source emission. The measures required in each case and especially their financing are different, which makes implementation difficult, as many current examples confirm.

Even before the two ordinances came into force in 1998, problems of coordination between them were identified and the cantons (swiss sub-states), which are responsible for the implementation of federal environmental legislation, have been calling for a harmonisation of the legal bases on the treatment of chemical soil pollution for several years..

Methodology

A detailed analysis of the national legislation and sectoral policy of polluted sites and polluted soils was carried out in 2016; it was structured by means of the so-called politico-administrative program PPA (programme politico-administratif PPA), a tool developed at IDHEAP (Institut de hautes études en administration publique, Lausanne).

The PPA represents the set of standards and regulatory acts that parliaments, governments and implementing authorities consider necessary to implement public policy. The PPA contains the normative objectives of the solution envisaged to solve the public problem, the means made available for this purpose and the principles of the administrative organisation of implementation.

Results

The analysis of the two sectoral policies (on polluted sites and on soils) using the PPA methodology shows important differences at several levels. The great strength of the polluted sites policy is its functionality and coherency. The evaluative elements (data to be collected in order to determine exactly how well the objectives have been achieved) are highly developed, as are certain intervention instruments such as regulatory arrangements, i.e. prohibitions, obligations and legal entitlements, with the possibility to impose sanctions to directly influence the target groups. Incentive systems, in particular with federal financial compensation, also play a major role. Another positive aspect is the very strong endowment of legal, monetary and cognitive resources. Thanks to the legal implementation of the polluter pays' principle specifically for polluted sites and the possibility of federal compensation, costs are not a major obstacle to the implementation of measures.

On the other hand, the policy for the management of polluted soils is much less well-endowed in terms of evaluation, operational and resource elements.

Conclusions

The analysis shows that it is most probably thanks to the restriction of the topic to sites with a limited extent polluted by waste that the efficient tools in this area have been politically accepted and developed. By isolating these waste-polluted sites from the general problem, the legislator has enabled effective measures to be taken quickly to solve urgent problems. A thousand polluted sites have been remediated to date. Among them are highly problematic ones; although there is still much work to be done (around 3 000 sites still to be remediated), it can be said that the process is on track.

The time has now come to analyse whether it is possible and realistic to integrate the management of polluted sites and soils into a single public policy.

The general objective of such a policy is to assess chemical soil pollution, irrespective of its origin, solely on the basis of its risks to humans, animals and plants. The need for measures should be orientated towards the current use of the soil concerned. FOEN is currently preparing a first proposal for an integrated and comprehensive management for chemically polluted soils. Based on current knowledge on the pollution of Swiss soils, the financial, social and environmental impacts on the various stakeholders and on the economy and society as a whole must be assessed.

The analysis of the situation in Switzerland, from the implementation of the legal bases to the current problems, provides an interesting insight into the key points for an optimised management of polluted sites and soils and can potentially provide useful practical information for other countries. It highlights how a systematic analysis, based on a tool such as the politico-administrative program, can highlight gaps, but also the strengths of a specific sectoral policy.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.8. Persistent organic pollutants in soils of the Veneto Region

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Abstract

A survey on the concentration of PCDD-PCDFs, PCBs and PAHs in soils of Veneto (total area 18.407 km², 8.100 cultivated) conducted on 148 samples, was a chance to establish some reference values related to the presence of such compounds in regional soils. Differences between areas with different land use (agricultural, urban or industrial) were highlighted to better evaluate results coming from further investigations.

Keywords: POPs, soil, reference values

Introduction, scope and main objectives

In order to increase the knowledge on content in dioxins, furans, polychlorobiphenyls and polycyclic aromatic hydrocarbons in soils of the region and to develop reference values for these organic compounds in the soil, the Environmental Protection Agency of Veneto region (ARPAV) carried on a soil monitoring, not linked to incidental events, that could provide useful elements to understand the phenomena of enrichment due to atmospheric fall out or diffuse contamination.

During the activities carried out by ARPAV for the investigation of impacts due to factory fires, or to cement factories or incinerators, some reference values are useful to better understand the concentration of these organic pollutants in different kind of areas (near potential sources of pressure, urban or agricultural).

Dioxins and furans (PCDD/PCDFs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are organic pollutants (so called Persistent Organic Pollutants – POPs) that persist in the environment and bioaccumulate, thus posing a danger to human health and the environment. These substances are organic compounds mostly of anthropogenic origin, characterized by high lipo-affinity, semi-volatility and resistance to degradation. These characteristics make them extremely persistent in the environment (APAT, 2006).

These substances tend to bioconcentration and present a process of biomagnifications (i.e. the accumulation of increasing quantities passing from prey to predators, occurs through food, more easily for highly lipophilic compounds and for terminal predators) thus reaching potentially toxicologically relevant concentrations.

The accumulation in the soils can occur through different ways; the most important are:

- atmospheric deposition;
- spreading sludge, compost and other organic soil fertilizers;
- deposit of sediments from contaminated areas;
- accidental release on the ground.

POPs mobility in soil is low as they are generally adsorbed by organic carbon; once adsorbed, they remain relatively immobilized and, due to the low solubility in water, do not show tendencies to deep migration (California Environmental Protection Agency, 2012).

Knowledge on the content of organic pollutants in soils can therefore provide useful information regarding the level of widespread pollution and elements to assess any risks related to the management of both agricultural and urban soils. Agricultural soils should have the minor anthropogenic impacts and for this reason allow us to define reference values with which to compare situations of greater impact (urban soils, industrial areas, areas near incinerators and / or cement works, etc.).

Methodology

For the execution of the new samplings, a series of points to be performed in the vicinity of particular sources of environmental pressures have been selected (figure 1).

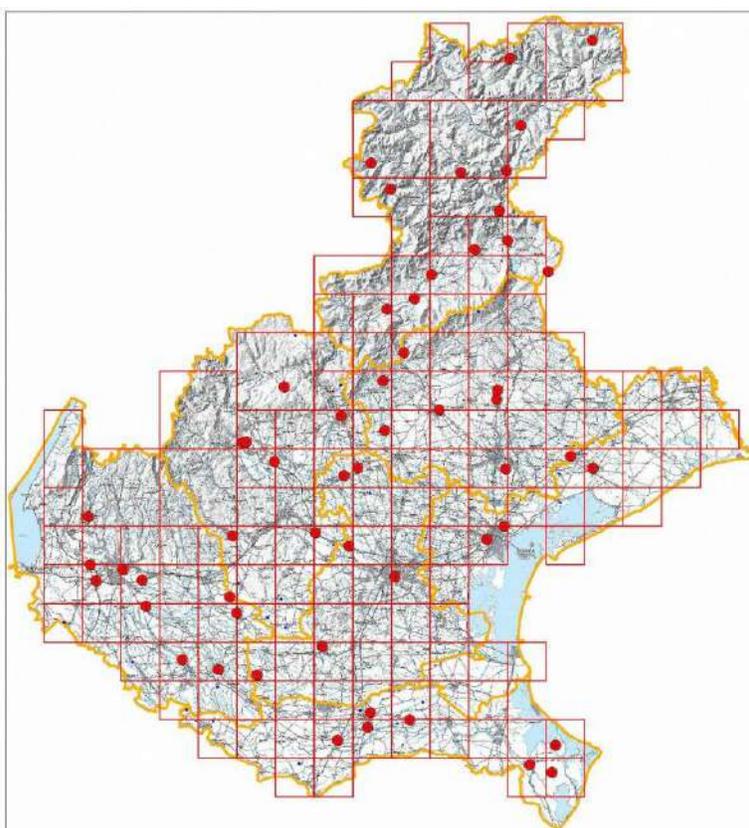


Figure 1. Sources of environmental pressures points to be monitored (in red); the red grid was indicative of the sampling density for the remaining regional area.

The main types of sources present in the regional territory have been included:

- waste disposal: incineration of municipal waste;
- combustion: for the production of energy and heat;
- high temperature processes: production of cement, asphalt and lime;

- melting, processing and ennobling metals: primary and secondary metallurgy operations, iron ore sintering, steel production;
- uncontrolled combustion: fires.

In the remaining regional the sample grid has a density of about 1 sample per 100 km² (Figure 2).

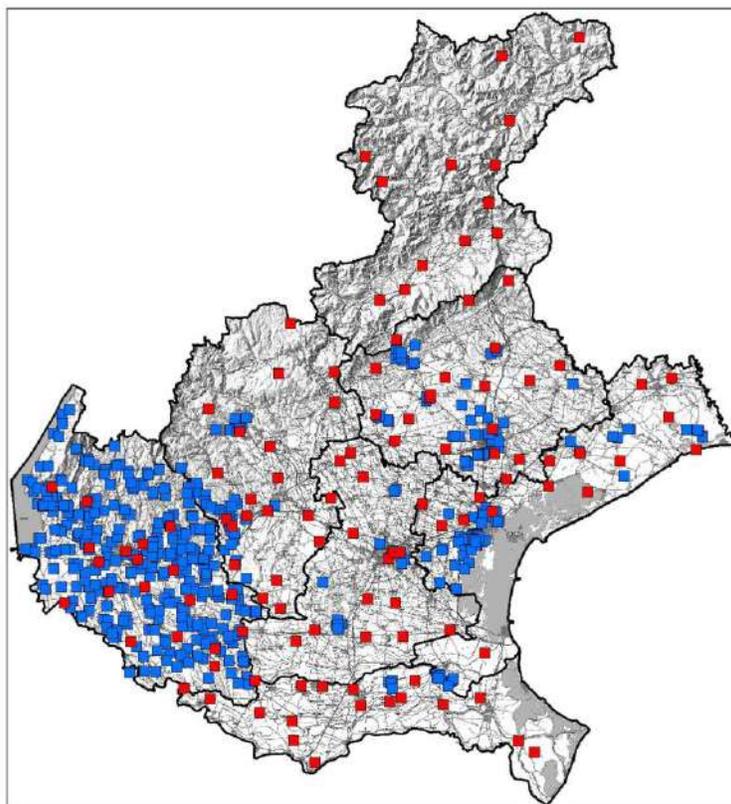


Figure 2. Data on POPs in soils; in blue the data available before the start of the monitoring project and in red the data collected during the project; all analytical results are stored in a database prepared specifically for the project.

On all the samples, in addition to the analysis on organic pollutants, pH, texture, organic carbon, total limestone, cation exchange capacity and heavy metals were also determined, in order to have useful elements to establish the natural origin or not of samples and to better understand the behavior of organic compounds in the soil.

Sampling took place through the identification of areas that were as homogeneous as possible for cultivation and pedological characteristics.

Within each selected site, a systematic sampling was carried out on an area of about 4000 square meters according to the following steps: division of the area into cells, collection of elementary samples, one per cell, by means of a manual drill, pallet or punch in the case of superficial samples (0-5 or 0-10 cm) and mixing of the elementary samples taken for each depth and formation of the final sample.

Sampling depth has been different in relation to the use of the soil and to the possible mixing of the superficial horizon due to plowing in agricultural area; in the plowed lands the superficial

horizon stands above the plowing depth, while the deep horizon to a layer of depth between 70 and 100 cm; on natural soils (stable meadows, public green, grassy vineyards) the surface sample has involved the first few centimeters of soil (generally 0-5 cm) while the deep one has been harvested at an indicative depth between 15 and 40 cm, to evaluate the possible effect of atmospheric deposition and the mobility of pollutants within the soil (ARPAV, 2016).

All the samples were analyzed by ARPAV laboratory.

Data were processed on descriptive statistics both on the whole dataset and on homogeneous groupings for land use/pressure source; for each variable average, median, minimum, maximum, percentiles (5th, 25th, 75th, 90th and 95th), standard deviation, standard error, asymmetry coefficients (skewness) and kurtosis (kurtosis) have been determined, in addition to various tests for normality (Soliani, 2003).

For some congeners in particular of PCDD/Fs and PCBs the number of "non-detected" values (hereinafter ND), i.e. at concentrations below the detection limit (Detection Limit, hereinafter DL), was very significant. ND samples were set equal to 0.

Results

Dioxins and Furans (PCDD/PCDFs)

129 sites were sampled and analyzed, 19 sites have samples even in the deep horizons for a total of 148 samples.

The spatial distribution of PCDD/PCDFs contents in the soils of the Veneto region is shown in Figure 3. The exceeding of the legal limit for residential areas (10 ng/kg I-TE (NATO/CCMS, 1988)) is limited to 2 cases, detected on the same site both in surface that in depth, less than one percent of the samples; this finding reassures the good quality of Veneto soils, with limited contamination to well-defined areas.

About 50% of the samples collected within the project have concentrations lower than 0.5 ng/kg I-TE a value close to the detection limit. In the class of values above 5 ng/kg I-TE only few samples occur.

Some values determined in the collected samples are worthy of attention, because although below the limits there have anomalous concentrations with respect to the population of the entire database. Among these it is worth noting two samples taken in the pre-alpine area (Asiago plateau and Cansiglio plateau) under the forest that showed significant concentrations of dioxins, especially in the first few centimeters of organic soil; in these samples the organic surface layer (humus), with thicknesses of a few centimeters, had concentrations of dioxins between 5 and 6 ng/kg instead mineral underlying horizon showed lower but still significant values (1.8 and 3.9 ng/kg I-TE). This phenomenon is observed, even if mitigated, also in samples collected in other pre-Alpine stations and is confirmed by other studies carried out in the alpine environment (Offenthaler *et al.*, 2009).

Other anomalous concentrations have been found in two agricultural samples, the first around an incinerator and the second in the province of Padua. Both values could be linked to the widespread practice of combustion in the field of agricultural residues and to the subsequent dispersion of the ash produced.

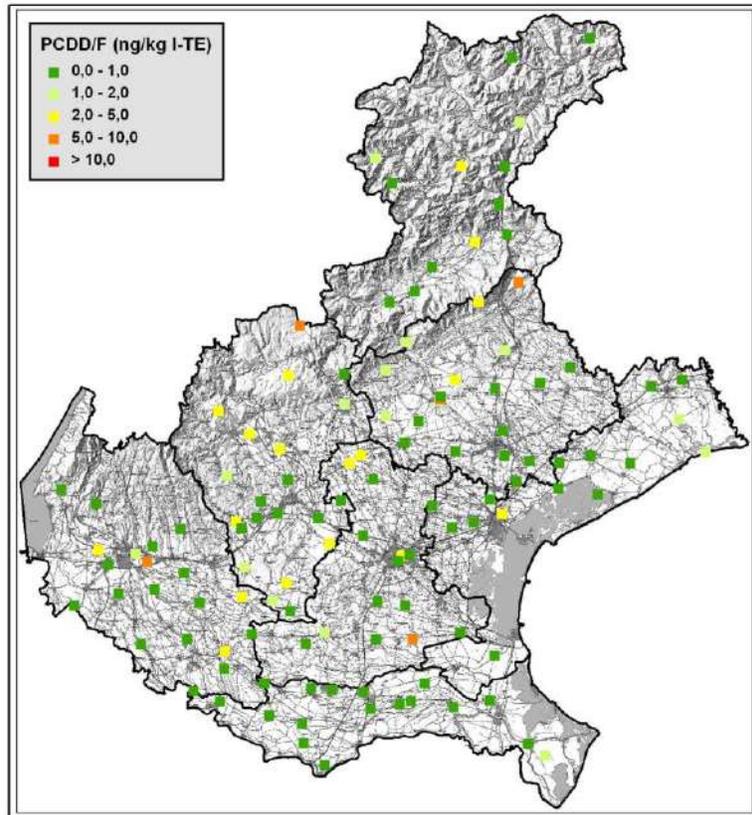


Figure 3. Content in dioxins and furans, expressed as equivalent toxicity (I-TE ng/kg).

Policlorobiphenyls (PCBs)

113 sites were sampled for a total of 128 samples analyzed, including 15 deep horizon samples. The territorial distribution of the new data made it possible to cover the entire regional territory in a homogeneous way. Previously, data were available only for some regional areas (ARPAV, 2003).

Distribution of results in concentration classes is reported in figure 4.

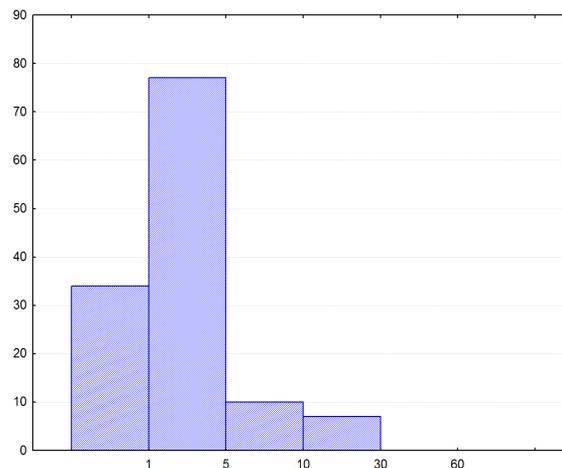


Figure 4. Frequency classes of PCB concentration (sum as µg/kg).

Most of data are lower than 0,005 mg/kg that means very near to the detection limit, all data are lower than 0,03 mg/kg. the Italian law limits for residential area is 0,06 mg/kg.

Policyclic Aromatic Hydrocarbons (PAHs)

131 sites were sampled and analyzed, 19 of which with samples even in the deep horizons for a total of 150 samples.

No exceedance of the legal limit for the sum of the PAHs was observed (10 mg/kg; figure 5).

The highest values were found: in the Asiago plateau near a biomass plant (4.1 mg / kg), in the Cansiglio area (where, however, the entire amount (5.6 mg/kg) is attributable to a single compound: Benzo(b)fluoranthene), and in Ospitale di Cadore near a former foundry (0.97 mg/kg). Only 12 other samples have concentrations greater than 0.1 mg/kg.

As far as the individual compounds are concerned, some exceedances of the limits for the residential areas have been found for benzo(a)pyrene in 4 samples, 3 of which with concentrations just above the legal limit; in the sample where the compound was present in highest concentrations (0.91 mg/kg) there were also overruns for benzo(a)anthracene (0.75 mg/kg) and dibenzo(g,h,i)perylene (0.64 mg/kg).

Discussion

In order to take correct decisions, it is important to be able to distinguish, only on the basis of concentration values, a hotspot contamination from a widespread contamination. This would prevent the risk of giving undue responsibilities to a specific source. For this reason, starting from the results of soil monitoring, attention thresholds have been defined for the different territorial contexts. Exceeding these values would indicate that in the investigated site one or more sources of contamination may be present.

The 95th percentile of the data observed in the different populations can reasonably be identified as attention threshold value. These thresholds do not refer to risk limit values for human health or for the environment, but represent a reference value above which it is useful to proceed with some more detailed investigations.

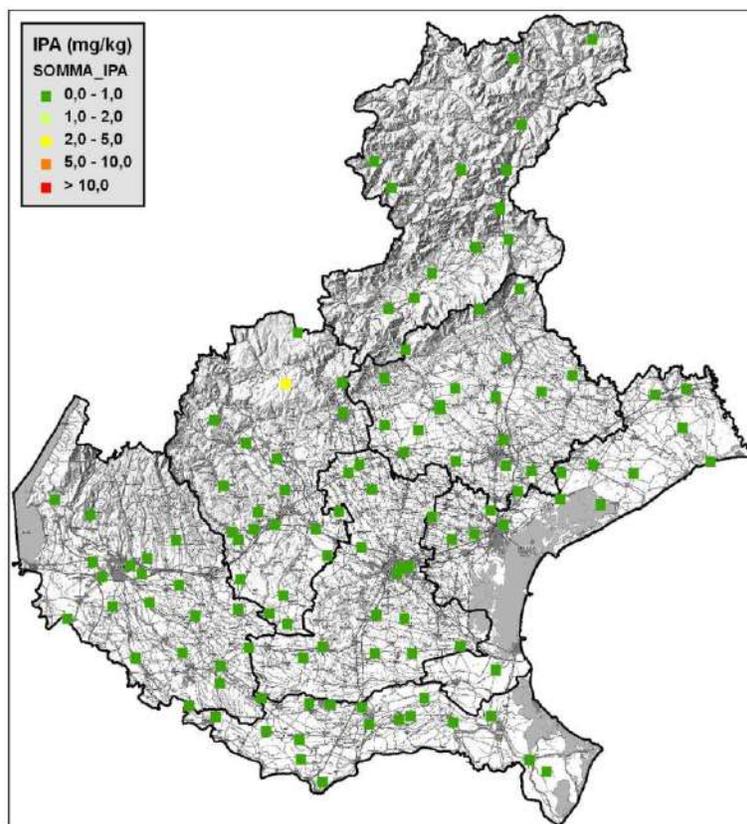


Figure 5. Content in PAHs, expressed as mg/kg.

For PCDD/PCDFs the attention threshold for agricultural soils is equal to 2,5 ng/kg I-TE but is reduced to 1,1 by eliminating outliers recognized by box-plots graphic method.

Also for soil sampled near foundries the 95th percentile value is equal to 1.9 ng/kg I-TE after elimination of the outliers (2 upper) while without such removal the value would be significantly higher and equal to 9.9 ng/kg I-TE.

The 95th percentile for the soils of urban areas is 3.1 ng/kg I-TE while for soils near incinerators it is equal to 3.8 ng/kg I-TE.

For PCBs attention threshold value in agricultural soil is 4.0 µg/kg, in soil near foundries is equal to 5.5 µg/kg, while for the soils of urban areas is 13.2 and in wooded areas or pastures is 12.4. Higher values in these areas is probably due to the lack of mixing through plowing in the agricultural soils.

All values are well below the most restrictive legal limits.

For PAHs specific attention thresholds could not be defined for the different areas because the concentrations were always extremely low; however, it was decided to provide a reference value for all the dataset. Exceeding this value indicates the probable presence of significant IPA contributions. The threshold can reasonably coincide with the 95th percentile of the sampled data or with the inflection point of the cumulative frequency distribution. The value of the 95th percentile of the sum of the PAHs is equal to 0.25 mg/kg and it is very close to the inflection point identified by the cumulative frequency distribution.

Conclusions

The concentration of POPs in soils of Veneto region is quite low if compared with the most restrictive regulatory limits. Almost all samples range between 0,1 and 5 ng/kg I-TE of PCDD/PCDF and between 1 and 30 µg/kg for PCBs. For PAHs only one third of the total samples showed a detectable concentration.

To have more effective elements in order to highlight if in a specific situation there is a possible ongoing contamination by POPs it is important to establish an attention threshold calculated on the basis of a widespread soil monitoring initiative; this was done with the investigation promoted by EPA of Veneto region, that through data elaboration, removing of outliers and calculation of the 95th percentile of remained population, indicated some attention threshold values for soils in agricultural, urban and industrial areas.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.9. Uranium, a new villain among the dirty dozen in soil protection

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Abstract

Widely unknown is that through use of mineral phosphate (P) fertilizers significant quantities of uranium (U) are charged to agricultural land. Worst case scenarios for Germany for instance estimate this amount to 239 t U annually. Data for 28 EU states range from 3 to 116 t/yr. Not extracting U during fertilizer production results in ca. 80-90% of U accumulating in the final fertilizer product. When mineral P fertilizer is then applied to land this has detrimental effects on the environment.

Keywords: uranium, heavy metals, soil pollution, phosphate fertilizers

Introduction

Agriculture is a main contributor to environmental loads of nearly all elements of the periodic system, for instance by applying waste-based fertilizer materials such as sewage sludge, and mineral fertilizers.

Particularly mineral P fertilizers contain significant amounts of elements which affect the quality of the environment and food plants. Primary phosphorus resources, phosphate ores and in particular sedimentary phosphate ores contain U in relevant concentrations (mean 259 mg U kg⁻¹ P₂O₅) which accumulates in soils.

Soil pollution with U from mineral P fertilizers

The Institute for Crop and Soil Science of the Julius Kühn-Institut (JKI) estimates for the time span from 1950/51 to 2016/2017 annual average loads of the elements As, B, Cu, Li, Mo, Ni, Pb, U and Zn to agricultural land in Germany exclusively through the application of P fertilizers of:

38 t/yr As, 1,575 t/yr B, 170 t/yr Cu, 71 t/yr Ni, 50 t/yr Mo, 14 t/yr Pb, 167 t/yr U and 604 t/yr Zn. Some of these elements are essential for plants and higher organisms, for instance B, Cu and Mo. Other elements such as As, Pb and U show a significant toxicity for life processes.

There are two major pathways through which elements enter the food chain: either through uptake in crops and forage plants or through leaching in potable ground and surface water bodies. Transfer factors (TF) for the elements in question give an idea to which extent these elements may enter the food chain through the soil/plant pathway when applied with fertilizers. Compared to this entry of elements into the food chain that into drinking water is direct. Groundwater resources are prone to anthropogenic contaminations not only depending on their depth in the ground and shielding by low permeable geological strata, but also by the site-dependent translocation of the individual elements, which is mainly affected by physical, biological and chemical properties of the soils to which fertilizers are applied.

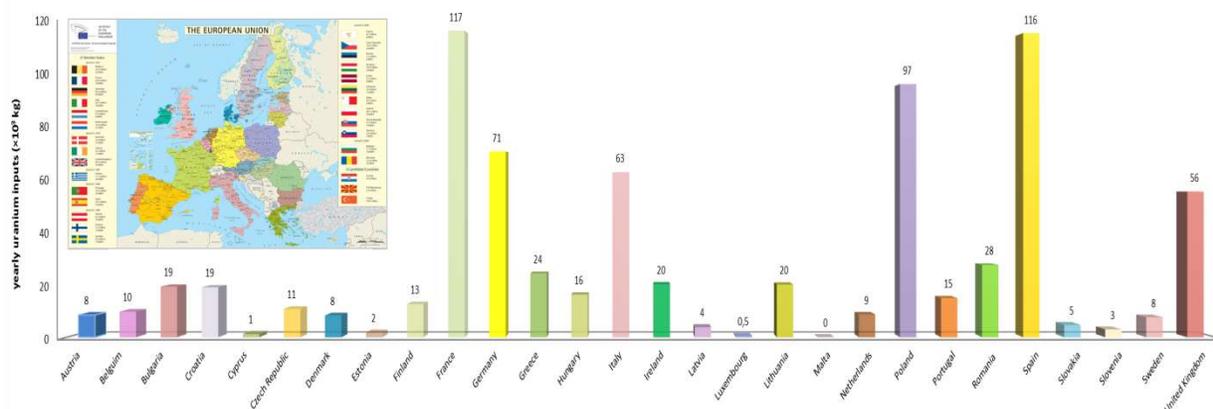


Figure 1. Estimated annual U input to agricultural soils with mineral P fertilizers in the European Union (based on FAO data 2002-2013)

Fertilizer-derived U pollutes drinking water resources

Fertilizer-derived U is primary a risk for the quality of groundwater and drinking water. Up to > 90% of the daily U intake of humans is by drinking water. Fertilizer-derived U already pollutes drinking water in such a way that not only the legal limit value of 2 µg/L U for the preparation of baby food is exceeded, but also the designated general limit value of 10 µg/L in drinking water and the proposed action value of 20 µg/L U suggested by the Federal Environment Agency (UBA) may be met.

Table 1. Evidence for fertilizer-derived U in groundwater - U and nitrate concentrations in neighboring shallow (7-9m) and deep (70-90m) wells of two waterworks in southern Germany (data from 2008).

Location	Well type	U (µg/L)	NO ₃ (mg/L)
Straubing	shallow	2.8	40.0
	deep	< 0.2	2.8
Rehlingen	shallow	10	22.0
	deep	1.6	8.2

At an annual application rate of 9 g/ha U applied with 22 kg/ha P a steady state concentration of 22 µg/L U is expected in the percolating water.

According to the amount of P₂O₅ consumption data provided by FAO, about 707 tons U per year are added to agricultural soils in European countries through the application of mineral P fertilizers. These initial rough estimation clearly highlights the chance and need for U recovery from phosphate rocks at the European scale. The removal of U from mineral P fertilizers does not necessarily involve higher costs for agriculture if the value of the resource U for nuclear power and the resulting reduction of CO₂ emissions are taken into account next to the prevention of costs for the removal of U from drinking water. Quite the contrary, a consistent extraction of U from rock phosphates will provide added value to P fertilizers, which exceeds distinctly the price for fertilizers.

Uranium - the hidden treasure in phosphates

On an average during the last 10 years in Germany alone 167 t U were spent every year with mineral P-fertilizers. To compare: in the German repository for nuclear waste "Bergwerk ASSE II" are stocked "only" in total 102 t slightly enriched U in wastes which is equivalent to approximately 201 t natural U. 167 t U contain enough energy to supply 2,350,000 average sized German households and equals the energy of firewood harvested from 5,600,000 ha forest.

From 10 g U (corresponding to a P fertilization of 22 kg/ha P according to GAP) 500 kW of energy can be produced. Compared to the same amount of energy derived from coal this saves a total of 500 kg CO₂. At a CO₂-tax of 0.08 €/kg this equals a value of 40 €/ha.

The monetary value of 10 g U (as yellow cake) amounts actually (28.1.2010) 1.11 €, the costs of the 22 kg P 32 €. In this context U retrieved from mineral P fertilizers protects not only soils and waters from this toxic element, but is also an unconventional contribution of agriculture to climate protection!

Conclusion - proposed action to protect soils and water bodies from fertilizer-derived uranium.

Limit the input of U to soils by fertilization through regulation of U in mineral P fertilizers to 1 g/ha**a* U at GAP (standard P fertilizer rate in good agricultural practice = 50 kg/ha**a* P₂O₅) as follows:

for fertilizers with < 5% P₂O₅:

- limit for declaration: 1 mg U per kg fresh material
- limit for trading: 1.5 mg U per kg fresh material

fertilizers with > 5% P₂O₅:

- limit for declaration: 20 mg U per kg P₂O₅
- limit for trading: 50 mg U per kg P₂O₅

Removing U from mineral P fertilizers not only protects soils and waters but can feed the world's nuclear energy cycle for an extra 350 years and it contributes to a cleaner atmosphere and last but not least increases the profitability of fertilizer manufacturing.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.10. Sustainable management of the DDT contaminated site in Lâm Hoá site, in Quang Binh province Viet Nam

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Abstract

To sustain the results of the 2009 – 2015 GEF/UNDP project with the title “Building capacity to eliminate POP-pesticides stockpiles in Viet Nam” the sustainable management of a POP pesticides (DDT) contaminated sites site near the Lâm Hoá village in the Quang Binh province is implemented. This site is an abandoned former military logistical centre annex field hospital from the North Vietnamese Army.

The site is located on the Hồ Chí Minh Trail. This trail was used for distribution of strategic goods including DDT for Malaria control, to the troops in South Viet Nam. It is very likely that there are more DDT contaminated sites as the Lâm Hoá site on the Trail.

The site management of the Lâm Hoá site is implemented in line with Vietnamese Guidelines. These Guidelines are divided into five (5) successive phases. Currently the phases involving site

investigation and the removal of 48 tons DDT waste are successfully completed. The remediation of the remaining DDT contaminated soil is being prepared and will be implemented soon.

Based on the experiences gained on the Lâm Hoá site it is concluded that the Guidelines provide enough technical basis to technical sustainably manage contaminated sites. But sustainable management of contaminated sites is a multidisciplinary area of expertise. As soil remediation is developing activity in Viet Nam, well-defined detailed requirements related to all areas of expertise involved, among others: health and safety, stakeholder involvement and chemical analyses, should be in each site remediation project Terms of Reference. During implementation, enforcement of these requirements and capacity building should go hand in hand.

Keywords: Sustainable Management - POP pesticides contaminated sites – Risk reduction

Introduction

In the scope of the 2009 – 2015 GEF/UNDP project, “Building capacity to eliminate POP-pesticides stockpiles in Viet Nam”, Guidelines on the sustainable management of POP pesticides contaminated sites (1) (hereafter referred as the Guidelines) were drafted. The Vietnamese ministry Of Natural Resources and Environment (MONRE) has published these Guidelines and country wide implementation is under way.

To sustain the results of the initial capacity building program a follow-up GEF/UNDP project, “The sustainable management of the POP pesticides (DDT) contaminated Lâm Hoá site in Quang Binh province Viet Nam” was initiated. In the scope of this project, the sustainable management of a DDT contaminated site in Lâm Hoá according the Guidelines is implemented. The main project objectives are to:

- Facilitate the country wide implementation of the sustainable management of POP pesticides contaminated sites;
- Remove and dispose all known stocks of POP pesticides from the Lâm Hoá site; remediate the contaminated soil; and implement Monitoring and Aftercare;
- Record the lessons learned and formulate recommendations for improving the implementation of sustainable management of POP pesticides contaminated sites.

The guidelines

The Guidelines are divided into five (5) successive phases. By following these phases for each individual site, the site investigator can quickly determine what is needed and what the following actions for the site will be. The phases and deliverables are:

- Phase 1 – Preliminary Site Assessment:
 - Initial Conceptual Site Model (ICSM);
 - Preliminary Risk Assessment;
- Phase 2 –Site Assessment:
 - Gap Analyses of the ICSM;

- Site survey and analysis;
- Updated Conceptual Site Model (CSM);
- Risk Assessment;
- Phase 3 –Site Remediation Assessment:
 - Selected best/ preferred site remediation option;
 - Preliminary design of the preferred remediation option;
- Phase 4 –Site Remediation Management:
 - Remediated site;
 - Updated Conceptual Site Model;
 - Design of the Monitoring and Aftercare;
- Phase 5 –Site Monitoring and Aftercare:
 - Site monitored and taken care of;
 - Periodical updated CSM.

Phase 1 is a quick review of the site status to establish the presence of contamination, the necessity of additional investigation and the urgency for these actions. The practice the first task of Phase 1 is to identify contaminated sites by establishing the (potential) presence of contamination components such as:

- Stockpiles of POP pesticides;
- Buried pesticides waste;
- Contaminated buildings;
- Contaminated hotspots in the soil;
- Contaminated soil and groundwater.

The next step is to preliminary assess whether or not there are potential risks for human health, ecosystem and/or off-site migration of the contaminants (hereafter referred as environmental risks). Knowing the potential environmental risks makes it possible to prioritize sites and site components based on risks. This prioritization allows using the limited time and funds available for site remediation on the sites and site components with the highest environmental risks in the more cost and time consuming next phases. The results of the Preliminary Site Assessment are an ICSM describing the suspected source(s) of contamination, the suspected receptor pathway(s) and the potential receptor(s) and a Preliminary Risk assessment.

Phase 2, is only implemented when there are potential environmental risks identified during Phase 1. The objectives of the Site Assessment are to establish quantitatively the contamination situation

of a site and the associated environmental risks. The Site Assessment report describes the CSM including the source(s) of contamination, the receptor pathway(s) and the receptor(s) and the results Tier 2 Risks Assessment using the applicable Vietnamese limit values. The Phase 2 report concludes with recommendations for the site including necessity for site clean-up.

Phase 3 comprises of the conceptual design of a least three feasible remedial options, the selection of the best remedial option and the preliminary design of this option. In general, the objectives of the best option are to:

1. Remove the direct environmental risks on the short-term;
2. Reduce and remove the potential environmental risks on the mid-term;
3. Contain and monitor the latent environmental risks on the long-term.

The selection of the best remedial option is based on the highest risk reduction, with the best environmental merits at the lowest cost. The results of this phase are reported in a site Remedial Plan; the input for Phase 4.

Phase 4 is the implementation of the site clean-up and contains supervision, monitoring and reporting of the factual clean-up works. Phase 4 is completed when the short-term remediation measures are completed and the mid and long-term remediation measures to mitigate the remaining environmental risks, are installed.

Phase 5 is only implemented when the remediation campaign of Phase 4 is completed and a residual contamination remains at the site. The objectives of this phase are to make sure and prove that:

1. No unwanted contaminant spreading develops from the residual contamination;
2. The environmental risks remain under control and gradually reduce;
3. The residual contamination is also remediated.

Results sustainable management Lâm Hoá site

The Lâm Hoá site is an abandoned former military logistic center annex field hospital on the Hồ Chí Minh (HCM) Trail operated by the Group 559 (the logistics and transportation corps in charge of the supply routes of the Ho Chi Minh Trail on land) (2). The site was used by the North Vietnamese Army in the Viet Nam - US war (1960 - 1975). There were numerous smaller and larger of such facilities that provided support to the warfare in the form of storage and distribution of strategic goods including DDT for Malaria control. DDT was important because at least ten (10) percent of the casualties along the HCM trail were from such illnesses as Malaria (3). The former Lâm Hoá military logistics center was located on a narrow strip of land (3 - 4.5 hectares large) close to the steep slopes of the outcropping limestone rocks. The whole strip was suspected to have remains of DDT, especially close to the rocks. Because it was suspected that the DDT at the Lâm Hoá site is causing environmental risks the remediation was included in the GEF /UNDP program 'Vietnam POPs and Sound Harmful Chemicals Management'.

The Phase 1 preliminary site assessment was carried out in October 2015 (Tauw report with Reference R021-1217441BFF-los-VO2-NL, 13 November 2015). And identified at least nine (9) hotspots, including a cave where the military field hospital was located, with remains of DDT in bags and as lumps of DDT (hereafter referred as DDT) and DDT contaminated soil.

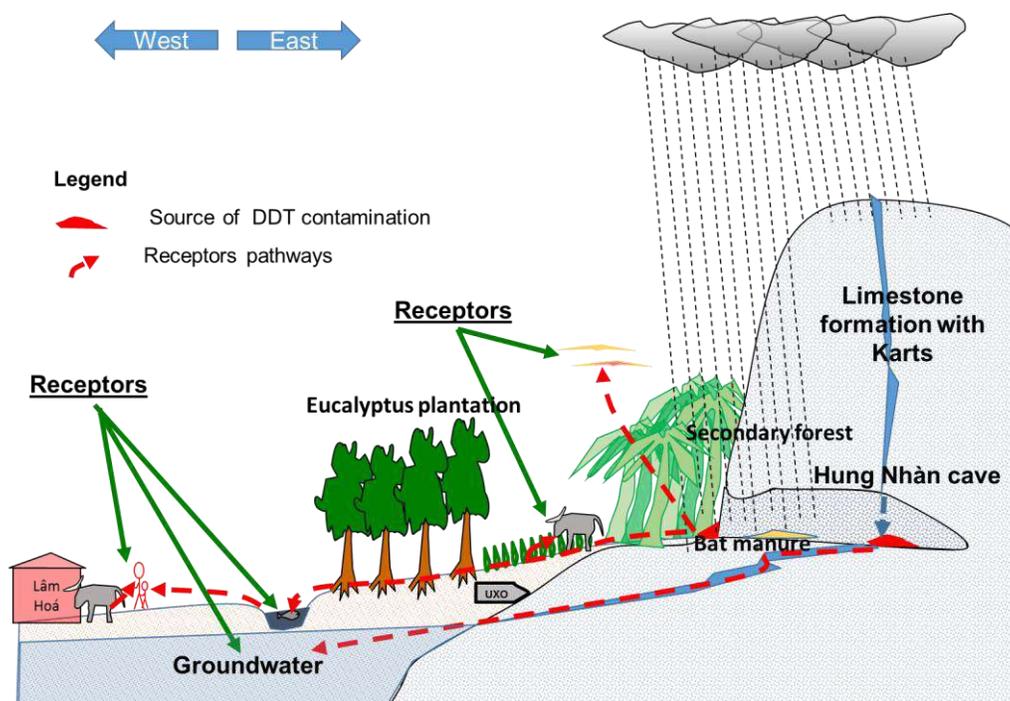


Figure 2. Illustration (not on scale) of the ICSM Lâm Hoá site (From Tauw, 2015)

Phase 1 concluded that there are environmental risks. The main cause for concern is the presence of DDT. Through direct contact with the ecosystem and migration by rainwater runoff, the DDT at the site can end up in the food chain. Villagers collect bat manure in the cave and thus come into contact with the DDT stockpiles. The site has also direct risks (injuries/fatality) related to Unexploded ordnances (UXO's) and therefore any further on-site activity could only be carried out after the area was searched and cleared of UXO's.

Based on the preliminary site assessment it was concluded that an immediate site clean-up of the hotspots and stockpiles was needed, followed by a more detailed investigation of the soil and groundwater of the area. Essentially Phase 2 and a part of Phase 4 (removal of the DDT) of the guidelines were planned to be executed parallel to each other. The field work of the Phase 2 and partly Phase 4, the removal of the DDT were carried out in December 2017. The Phase 3, is currently executed and the remaining part of Phase 4, the soil remediation, is expected to be implemented in May 2018.

Site Investigation and preliminary clean-up

After the UXO clearance and vegetation removal, the DDT could be mapped at the identified hotspots. To establish the exact spreading of the DDT narrow trenches were dug across the hotspots. The trenches were dug beyond the deepest DDT remains, visibly present in the soil profile (see figure 2). Based on these observations the contours of the DDT in the soil were indicated with colored ropes (see figure 2). As the vegetation was removed, the DDT was more exposed resulting in increased risk for spreading of the materials. Therefore the DDT was excavated, packed and sent for destruction by co-processing in a cement kiln. Integrating the removal of the DDT in the site investigation speed up the clean-up operation, avoided enhanced migration of contamination after the removal of the vegetation and made it easier to map the remaining DDT contaminated soil. In total 48 tons of DDT were collected and removed.



Figure 3. Left: Shallow trench to map the DDT. Right: Hotspot indicated with colored rope (From Tauw, 2015)

After the DDT from the hotspots was excavated, packed in bags and removed off-site, the remaining DDT contaminated soil was mapped. For the soil mapping an Edelman auger of 1.20 m long was used (see figure 3). The survey strategy was to install boreholes in a raster of 5 x 5 meter, till a minimum depth of 0.5 meters below surface. The boreholes cuttings were described and sampled. The sampling strategy was to make composite samples from the topsoil where the DDT was excavated. These composite soil samples are made by five (5) grab samples from the 5 x 5 meter area. The topsoil and subsoil of all borings outside these hotspots were individually sampled.

The baseline quality was established by analyzing two representative composite soil samples from 0.0- 0.1, 0.1 - 0.2 and 0.4 - 0.5 meter minus surface. The soil was sampled in all other boreholes at the same depths. To avoid cross contamination the baseline boreholes were installed and sampled first, followed by the boreholes around the hotspot. The boreholes inside the hotspots were installed and sampled last. The individual samples were taken direct from the auger, the grab samples were collected on a clean steel tray, mixed and sampled.

One (1) hotspot is bomb crater that was used to dump DDT and medical waste. The contaminated soil in the bomb crater was mapped with four (4) transacts of boreholes 1 to 2 meter apart from each other (see figure 3). The first bore hole was installed outside but very close to the edge of the filled crater. The second borehole was installed at the nearest location to the edge of the crater where waste was encountered. The third borehole was installed in between these two boreholes. Depending on the profile of the third borehole, the border of the waste dumped could be determine with an accuracy of plus or minus 50 % of the distance between the third borehole and the first borehole or the third and the second borehole. In practice this was plus/minus 50 cm.



Figure 4. Left: Soil sampling. Right: Transect to map the bomb crater (From Tauw, 2015)

The DDT (48 tons) were excavated using hand tools by a team of trained villagers. Differentiation in the field between DDT and fragments of limestone, roots and others proved difficult. The only difference is the specific weight (see figure 4). To avoid packing rock and the other material looking like lumps of DDT the team used handpicking to take out as much as possible lumps of DDT. The 48 tons of DDT was packed in bags and transported to for co-processing in a cement kiln.



1. Piece of a wild banana tree
2. Not weathered piece of a the limestone rock
3. Weathered piece of a the limestone rock
4. Fungus
5. Lump of DDT
6. Piece of a plastic bag used to pack the DDT

Figure 5. Left: Left Soil sampling a hotspot. Right: Transect used to map the bomb crater (From Tauw, 2015)

The soil at the hotspots is contaminated till a maximum depth of around 0.5 meter. The DDT concentrations in the soil vary from a few ppm to a few hundred ppm. The concentrations of DDT in the baseline soil samples are all below detection limit, which is 0.002 mg/kg dry matter.

The sediment in the creek draining the Lâm Hoá site and its surroundings was sampled to see if the run-off rainwater has impacted the sediments. The downstream creek was sampled at four (4) locations. To establish baseline quality two (2) location in the creek upstream of the Lâm Hoá site were also sampled and analyzed for DDT. The concentrations of DDT in the baseline samples and the samples downstream are all below detection limit, which is 0.002 mg/kg dry matter.

The update CSM

With the mapping data and other site information the CSM is completed, meaning that the sources of contamination, the receptor pathways and potential receptors have been established. Table 1 summarizes the results carried out site activities.

Table 1. Results site activities

Hotspot	Area in m ²	Tons of DDT removed	Estimated m ³ of contaminated soil	Expected origin DDT
1	70	1.8	50	Iron boxes with DDT left behind after the war were emptied
1a	35	2.5	1.8	Spilled during handling/transport
2	25	3.5	28	Probably storage of bags with DDT
3	10	7.2	7.5	
4	16	7.1	4	
5	Identified during Phase 1, not be recollected during Phase 2			
6	12	2.5	1.2	Probably storage of bags with DDT
7	15	4.4	1.5	
8		1	no contaminated soil as the cave floor is limestone	Remains DDT stock in the military field hospital
9	18	1.8	1.5	Spilled during handling/transport
10*	20	5.8	9.6	Dumped in the bomb crater by villagers after the war

* Identified during Phase 2

The **sources** of contamination are the nine (9) hotspots (see table 1)) with a total volume of 122 – 130 m³ DDT contaminated soil. The contaminated soil is mainly topsoil but reaches in the inside the contour of the hotspot, where the DDT was removed, a maximum depth of around 0.5 meters below surface level.

The identified **receptor pathways** are the people entering the site for whatever reason (working in the gardens, collection forest product and hunting) bringing contaminated soil into their houses. Also the cattle roaming freely around is a receptor pathway. Besides that the rainwater run-off spreads the contaminants especially the contaminated soil receiving run-off from the bordering bare rock outcrops. The run-off did not impact the sediments in the downstream part of the creek draining the site.

The **receptors** are the people working on the adjacent Eucalyptus plantations, the women collecting forest products, among others bamboo shoots, wild bananas and all kinds of leaves, the farmers collecting the bat manure in the cave and the family members eating these forest products. Also the consumption of products of the cattle roaming around expose families to the DDT. Besides this the surrounding ecosystem (birds etc.) is one of the main receptors.

With the results of the CSM and by comparing the analytical results with the Vietnamese risk based limit values the environmental risks are established. An overview of the source, the receptor pathways and receptors in the risk assessment is given in figure 5.

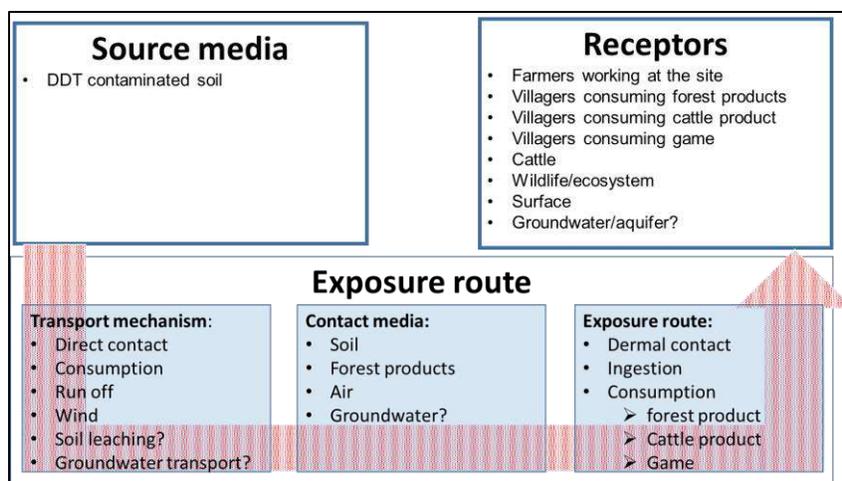


Figure 6. Overview of the source, the receptor pathways and receptors in the risk assessment for the Lâm Hoá site

The Vietnamese, risk-based limit values for soil have been determined for four (4) land use classes. Table 2 provides these values for DDT. The land-use of the contaminated soil at the Lâm Hoá site is currently Class 2, Perennial agriculture. The average DDT concentration in the top soil till maximum 0.5 meter below ground level ranging from 20 to 100 mg/kg dm with some spots reaching to 400 mg/kg dm.

The results of the Phase 2 will be used to select the most cost effective site remediation and design the mid and long term remediation measures to mitigate the environmental risks (Phase 3). One of the best options is most likely land farming for the mid-term (around 1 – 2 years), followed by phyto-containment and Monitoring and Aftercare for the long-term.

Table 2. Vietnamese limit values (mg/kg dm) for DDT in soil

Contaminant	background limit value*	Limit value#			
		Class 1 Agriculture	Class 2 Perennial agriculture	Class 3 Public	Class 4 Industrial
DDT/DDE/DDD (sum)	0.01	1.10	16.50	4.70	50.00

*QCVN 15:2008 /BTNMT #QCVN 54:2013/BTNMT

Discussion

If Viet Nam continues to enforce the soil protection and remediation as recently adapted in their legislation, the soil remediation market will develop. The Guidelines provide enough technical basis to technical sustainably manage contaminated sites. But sustainable management of contaminated sites is a multidisciplinary area of expertise. As Franks said *“Dealing with contaminated sites: When you have a wide scientific knowledge concerning contaminant fate and transport processes in soil and groundwater, site characterization, Human Health Risk Assessment, Ecological Risk Assessment and Groundwater-related Risk Assessment, AND have experience with designing cost-efficient Risk Management solutions AND have a creative personality AND have good communication qualities AND are in a position to take policy decisions: Go ahead. Otherwise: Build a team”* (4).

Because site remediation is developing in Viet Nam, well-defined requirements should be in project Terms of Reference and during implementation, enforcement and capacity building should go hand in hand.

Conclusions

- The Guidelines provide enough technical basis to technical sustainably manage contaminated sites;
- Phase 1 should focus on identifying high risk sites like the Lâm Hoá so that limited resource are spent on contaminated sites with high risk profile;
- The POP-pesticides removal does not necessarily need to be subjected to a Phase 3 remediation assessment. At the Lâm Hoá the packaging of the DDT (Phase 4) was done parallel to the mapping of the DDT (Phase 2) and turned out to be cost effective. The Guidelines should mention that the Phase 3 can be skipped in such situations as encountered on the Lâm Hoá site;
- Based on the experiences gained it is expected that there are more high risk sites as the Lâm Hoá site on the former Ho-Chi-Minh trail in Viet Nam, Laos and Cambodia.

Recommendations

- To carry out mid and long-term remediation measures to remediate the DDT contaminated soil at the Lâm Hoá site;
- To guarantee the Monitoring and Aftercare (Phase 5) at the Lâm Hoá site by involving the community of Lâm Hoá in the future activities;
- To initiate a regional inventory (Viet Nam, Laos and Cambodia) of the former Ho-Chi-Minh trail to identify other high risk sites like the Lâm Hoá site.

Acknowledgements

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.11. Radionuclide Soil Pollution

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Abstract

In the last years soil contamination concern from natural and artificial radionuclides has become increasingly important. Natural radionuclides have terrestrial and cosmic origin, while anthropogenic radionuclides mainly derive from air leakage and subsequent fall-out following the accidents in the nuclear power plants at Chernobyl and Fukushima. In the present work the importance of studying their presence in the soil is highlighted, and in particular the radionuclide gamma emitter ^{137}Cs for its environmental consequences due to the long half-life of about 30 years. Numerous studies carried out in radioecology and radioprotection allowed to assess the mechanisms of radionuclides transfer from soil to plants, and to analyze the food chain and the biological cycle in humans. Following the Chernobyl accident, in Italy the “National Surveillance Network for Monitoring of Environmental Radioactivity” (RESORAD) has been established with the following aims: measure the radionuclides concentration in numerous environmental, food and animal matrixes; highlight some particular and interesting radiocontamination bioindicators; standardize methods and protocols for the data reliability and comparability; and obtain the first maps of soil deposition of ^{137}Cs in Italy. The latter are of particular interest in the agri-environmental sector. In this work, concentration data and trend over time of ^{137}Cs in soils of different Italian regions are shortly summarized. These results have been obtained from about thirty years of monitoring activity. Monitoring is still very important to measure the pollution level, and consequently to identify any uncontaminated soils that can be used for agriculture and livestock farming.

Keywords: [radionuclides, ^{137}Cs , ^{134}Cs , ^{40}K , soil pollution, agricultural]

Introduction, scope and main objectives

Natural radionuclides of the uranium and thorium families as well as ^{40}K , all gamma-emitters, are present in the soil. ^{40}K has a half-life equal to $1,277 \times 10^9$ years. It is ubiquitous on Earth and its concentration depends partly on fertilization with potassium, but mostly on the parent material. The natural radioactivity of terrestrial and cosmic origin is homogeneously distributed in the soil profile, and varies from site to site in relation to the geological conformation, the characteristics of soils and the bedrock from which they were derived. The radioactivity of terrestrial origin is due to “primordial radionuclides” (^{40}K , ^{238}U , ^{232}Th , ^{235}U), present in different quantities in the inorganic materials of the earth's crust (rocks, minerals) since its formation. The second source is constituted by cosmic rays. These sources represent the “natural background of radiation”. Natural radioactivity provides the highest contribution to the collective dose received from the world population; the contribution due to cosmogenic radioisotopes is much less relevant.

Artificial radionuclides present in the soil can contribute significantly to population exposure. They mainly come from radioactive fall-out following nuclear explosion (Hiroshima and Nagasaki), nuclear tests and incidental situations (military, health and energy applications). In fact, since the mid-1940s, for about twenty years and following the test of nuclear weapons in the atmosphere, there were 520 atomic explosions with nuclear fission or thermonuclear fusion for a power of 545 megatons. More significant consequences followed after the accidents that occurred at the nuclear power plants of Three Mile Island (USA - March 28, 1979), Chernobyl (Ukraine - April 26, 1986) and Fukushima Daiichi (Japan - March 11, 2011).

In particular, the Chernobyl's is the most serious nuclear accident, and it was classified as well as Fukushima Daiichi as catastrophic, with degree 7 of the INES scale (International Nuclear and Radiological Event Scale). During the nuclear reactor incident, radioactive materials were emitted with a total activity of 11×10^{18} kBq, in particular with the contributions of the radionuclides ^{131}I , ^{137}Cs , ^{134}Cs , and ^{90}Sr , all of which gamma-emitters. The contamination mainly affected the territories of the former Soviet Union (Ukraine, Russia and Belarus) and the majority of the Northern Hemisphere (Poland, Sweden, Finland, Germany, France, Holland, United Kingdom and Greece, and later Japan, China, India and finally the United States and Canada) (Spezia 1996). As far as the Russian Federation is concerned, the agricultural land of 21 regions suffered from radioactive contamination, and in an area of 800 thousand hectares the contamination density of ^{137}Cs was higher than 185 kBq/m². In the Republic of Belarus the area contaminated by radionuclides (over 37 kBq/m² of ^{137}Cs) involved about 46,000 km² (23% of the total area) and 2.1 million inhabitants (over 20% of the population). Agricultural land underwent radioactive contamination in an area of over 1,800,000 ha, of which 264,000 ha were excluded from agricultural production. On the European territory the fall-out, followed a "leopard spot" pattern from a scale of kilometers to a regional scale and has concentrated in the geographical areas subject to particularly heavy rainfall in the days following the event.

In 2011, after the Fukushima incident, there was a dispersion in atmosphere containing several radionuclides, in particular the Cesium isotopes (^{134}Cs , ^{137}Cs) and iodine (^{131}I , ^{132}I , ^{133}I). In the most contaminated areas (30 million Bq/m² of ^{134}Cs and ^{137}Cs) it was necessary to evacuate the population. The radionuclides were transported and dispersed to Europe where traces of ^{131}I , ^{134}Cs and ^{137}Cs in atmospheric particulate were detected (Rannou *et al.* 2011). In Italy, after the Fukushima accident, the radionuclide concentrations found in the food production cycle were not radiologically relevant and the dose assessments to the population had no consequences. (Trotti *et al.* 2016)

Even today, 32 years after the Chernobyl event, we find levels of ^{137}Cs since its half-life is 30.25 years, while ^{134}Cs , with a half-life of 2.07 years, is not found in the Italian territory and in Central Europe, unless further accidental contamination. In Italy in the months following the event many measurements were made on particle deposition, (Aromolo *et al.* 2015 a), environmental matrixes (soils, drinking water, sediments, S.M.O.D. (Fontana *et al.* 1997), sands, etc.) and agricultural and zootechnical products (wheat, potatoes, broad-leaved vegetables, milk, fruit, mushrooms, fodder, honey, meat, etc.), to evaluate the impact of the radioactive fall-out and determine the "Zero Point". That is, to establish a concentration value of the various radionuclides that can allow to calculate any variations in the concentration of radioactivity over time, and go back to the actual concentration in case of a possible new deposition on the soil.

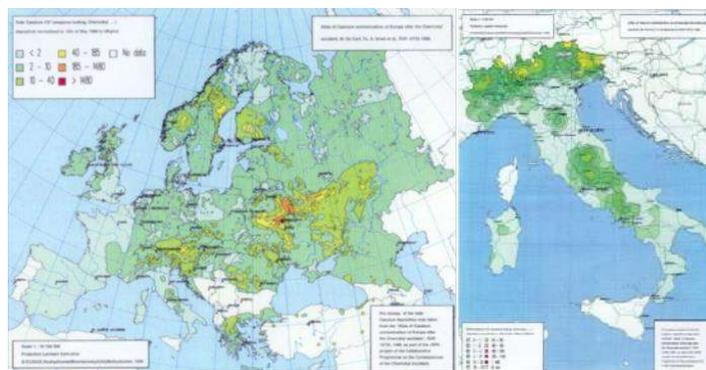


Figure 1. Distribution of ^{137}Cs in Europe and in Italy after the fall-out. (De Cort *et al.* 1996)

Methodology

Radiocontamination of the environment occurs through irradiation (exposure), inhalation (breathing) and ingestion (eating or drinking). The control of environmental radioactivity in Italy is regulated by the Legislative Decree n. 230 of 1995 and subsequent amendments. The decree incorporates the directives 89/628/Euratom, 90/641/Euratom, and 96/29/Euratom concerning ionizing radiation. According to article n. 104 of Legislative Decree 230/95, the control of environmental radioactivity is exercised by the Ministry of the Environment and the Protection of the Territory and the Sea; the control of food and drinks for human and animal consumption is exercised by the Ministry of Health.

The whole of the controls is divided into National and Regional Surveillance Networks. The RESORAD, coordinated by National Center for Nuclear Safety and Radioprotection (ISPRA), consists of the twenty-one Regional and Provincial Agencies for Environmental Protection (ARPA/APPA), the Italian Red Cross (Environmental Radioactivity Measurements Service) and three Experimental Zooprophyllactic Institutes. The overall system of surveillance of the Italian radioactivity is subjected, as for all the Member States of the European Union, to periodic checks by the European Commission (Article n. 35 Treaty EURATOM 1957).

Network Laboratories have carried out research of fundamental importance on the various radionuclides and their absorption by the different types of soil, the modalities of transfer, the influence of agrochemical and agrotechnical factors, and their transfer from soil to plants. The analytical procedures used for the measurement of radionuclide concentrations, for the sampling and for the treatment of the soils are performed according to specific National Guidelines (ISPRA 2012). The samples are properly treated and are placed in special containers, the “Marinelli beaker”, and analyzed by gamma ray spectrometry (Gordon *et al.* 1998) using high purity Germanium detectors (HPGe); the unit of measurement is Bq/kg or Bq/m².

Results and discussion

In Italy numerous studies have been performed since 1986 to evaluate the presence of radionuclides in the soil. The Italian regions most affected by the deposition were the Northern regions but also the Central regions, particularly Campania and Lazio, where, in the city of Rieti, there was a high concentration of ^{137}Cs . (Fontana *et al.* 2000a). The pluviometric data of the weather stations following the days of the accident confirmed that the highest concentration of ^{137}Cs occurred in the regions where rainfall was higher. In 1995 the National Network (regional Laboratories and Italian Red Cross) (ISPRA, 2001), conducted a campaign that used bryophytes

as bioindicators of soil contamination. 106 stations have been characterized and results have allowed to elaborate the first national deposition map of ^{137}Cs on the soil. (Figure 2).

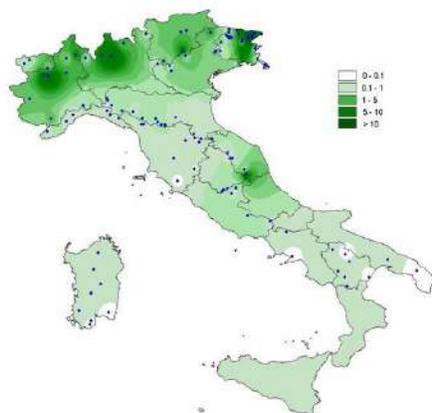


Figure 2. Soil deposition map of ^{137}Cs (kBq/m²) in mosses (year 1995) (ISPRA, 2001)

Approximately 25 years after the Chernobyl fall-out, the data developed by the RESORAD Network have been grouped into three macro areas: North, Central and South of Italy. Of particular interest was the highest concentration of ^{137}Cs in soils in Northern Italy (Lombardy, Friuli Venice Giulia, Piedmont, and Valle D'Aosta), (JRC Technical Reports 2015; Giovani *et al.* 2007). The maximum values of ~ 40 kBq/m² for ^{137}Cs were measured in mountain soils and the minimum values ~ 6 kBq/m², in the plain areas. Furthermore, the tendency towards a higher concentration of this element in forest soils compared to agricultural lowland soils has emerged. In the latter soils, ^{137}Cs has a tendency to dilute after tillage operation that homogenize the soil. Forest land, on the other hand, remains unaffected since atmospheric deposition is intercepted by vegetation.

It was also reported a trend of ^{137}Cs to migrate in the soil. Today, it is mainly found in the first 10 cm, in particular in the layer ranging from 5 cm to 10 cm, and its migration in depth is lower for the sampling sites located at higher altitudes. Usually, at greater depths, minimum concentration values are found ~ 0.4 Bq/kg at 80 cm depth. Data on recent sampling of pasture land (2016 - 2017) show that ^{137}Cs has a very low concentration between 3 Bq/kg and the Minimum Detectable Activity, (MDA).

The atmospheric fall-out deposition concerns the surface of the ground, but then there are factors that involve a different penetration in the underlying layers depending on the deposited radionuclide, the nature of the soil, the vegetation cover (different for distribution and type of cultivation), and factors of horizontal migration on the surface, due to the conformation of the ground, with possible effects of local accumulation.

Moreover the vegetation can have an important “dynamic” role, (Aromolo *et al.* 2015 b) with the effect of radical absorption, redistribution to the aerial parts of the plant (Rossi *et al.* 2004) and finally restitution to the ground with the death of the plant.

In addition, the scientific research carried out in recent years shows that in the soil-plant-animal system the foods at higher risk of contamination are berries, potatoes, salads, honey, milk and mushrooms. The latter, because of their high accumulation capacity (even millions of Bq/kg), are excellent radio contamination indicators for which they should be monitored to avoid potential accumulation risks for ingestion (Fontana *et al.* 2000b). The importance of monitoring the

contamination of fodder as a food source for cattle has also emerged, because of the possible contamination of milk radionuclides, given its importance in the human diet and in particular in that of children.

Finally we can state that the monitoring of radioactivity is still important today in Italy, as it allows to detect in real time, in case of possible cross-border incident, any contamination and to adopt the appropriate countermeasures for the population. In this regard, in February 2017 abnormal levels of Iodine-131 found in Finland were measured in the air in Italy (Lombardy ARPA 2017). In September 2017 the passage of a cloud of Ruthenium-106 coming from an area between the Volga and the Urals was detected. Traces of Ruthenium-106 were also found in Italy, Lombardy, Piedmont, Friuli, Tuscany, Emilia Romagna and Friuli Venice Giulia (ARPA FVG 2017).

Conclusions

Numerous activities conducted in Italy following the Chernobyl accident in radioecology and in radioprotection, have also provided a significant contribution in the agricultural sector. In Italy, the Fukushima accident, even if it did not imply environmental consequences, represented a test, confirming the importance of a monitoring network in emergency situations, and giving evidence of immediate response, data acquisition in the air and on the soil in real and continuous time. In the last 30 years the concentration of ^{137}Cs in the many samples analyzed by the RESORAD Laboratories, has allowed to obtain the soil distribution maps of this radionuclide on the national territory on a medium and small scale. A more complete analysis of the data collected in different measurement campaigns will be used to complete and harmonize the soil monitoring system, and the actual extent of local and diffuse contamination that is not yet clearly known. Therefore it's important to continue the studies to define how to use radioactivity indicators many years after a possible deposition, and to study the application of radioactive deposition models on soil with the development of a dedicated software. Despite considerable progress has been made from Chernobyl (1986) to Fukushima (2011), the contaminated areas still represent a great problem both due to the impossibility of using large areas of land and the crisis in the agricultural and industrial economy of populations involved, that in extreme cases are forced to leave their territories.

Finally, it would be important to disseminate current knowledge (Fontana *et al.* 2016) and inform the operators in the agricultural sector about the risks and possible contamination of soil and agricultural products.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.12. Halogenated technosoils within oil and gas fields of Ukraine

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Abstract

The objective of this article is to study the properties and characteristics of halogenated technosoils within oil and gas fields of Ukraine. The salinization formed as a result of air dissemination of emergency water and gas blow-out from the wellhead during a workover. The chemical composition of produced waters (PWs) from the Svyrydivske gas condensate field was determined in the course of the study. Based on the composition, PWs type refer to chloro-sodium brines and content of particular components. Dark grey type of technosoils have been investigated. Visual color change and soil structure in the field of emergency flood were evident, and it was possible to clearly identify two zones – impact focus and dispersion area. Based on the salt amount, the soils under study are highly salinized. In the control soils adjacent to the halo salinity, observed trend of higher concentrations of total and toxic salts and high content of chloride anions and cations sodium in aqueous solution. Ba predominate in the upper layers of halogenated technosoils (0-30 cm) which is a direct indicator contamination from drilling operations. Most of the elements under study accumulate in the 30-60 cm soil layer. Li⁺ has accumulated primarily in the arable layer both in the impact focus and area of dispersion. With an increase in depth the Sr²⁺ concentration ratio increased by 7 times. Based on the ascending geochemical mobility, the triad of alkaline-earth elements in the impact focus is as follows: Sr→Ca→Mg and Mg → Ca → Sr for the periphery.

Keywords: halogenated technosoils; control, produced waters; PWs; exchangeable cations; toxic salts; geochemical composition; concentration ratios

Introduction, scope and main objectives

Ukraine is one of the most agriculturally developed countries in the world. As of January 1, 2017, the land fund of Ukraine is 60.3 million hectares, or about 6 percent of the territory of Europe. At the last time, the processes of degradation of soil cover due to man-made pollution have intensified. The greatest danger to the environment is the pollution of soils. The issue of soil pollution and geochemical composition transformation has become particularly acute in the development zone of fertile agricultural soils to which a significant fraction of Ukraine's oil and gas production sites is confined. The losses caused by disusing the soil bodies affected by emergency PWs spills between 1980 and 2017 were quite significant. With intensive development and exploitation of oil fields in the environment undergoes significant human impacts, often leads to pollution and ecosystem degradation. Produced waters (PWs) are one of primary

environmental pollutants in oil and gas fields resulting from emergencies, pipeline leakages, repair operations and due to some other reasons (Pichtel 2016). PWs have unique polycomponent continuously changing composition, high geochemical reactivity and toxicity (Vengosh *et al.* 2014; Brantley *et al.* 2014). The technogenic halogenesis is the most typical soil transformation process occurring within oil and gas fields as a result of emergency PWs spills. PWs contain heavy metals the concentration of which varies depending on geological age (Fontenotet *et al.* 2013; Jackson *et al.* 2013; Vengosh *et al.* 2014; Sangadzhieva *et al.* 2013). Differences in the composition of PWs result in some additional chemical elements introduced into soils and/or encourage an increase in the content of chemical elements occurring in micro-quantities in natural, non-polluted soils or being completely uncharacteristic of such soils.

The objective - is to study properties and characteristics of halogenated technosoils within oil and gas fields.

Methodology

The soil was studied at site being emergency PWs spill locations. The layout of key sites was determined based on visual changes in colour and structure of the soil cover at the emergency spill locations. Control plots were selected in the near-by fields located beyond the impact zone (fig.1).

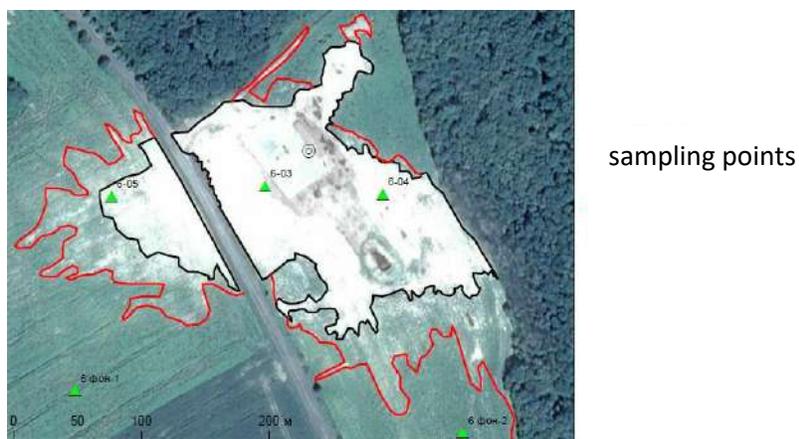


Figure 1. The points of soil sampling

Site is located in trans-accumulative landscape environment of the Svrydivske field in the north of Poltava (Ukraine). The salinization formed as a result of air dissemination of emergency water and gas blow-out from the wellhead during a workover. The salinization has a more complex shape due to peculiarities of the relief and stretches out in the form of linear flows downslope the adjacent hollow. The soil is of dark grey leached sandy loam type on glacial deposits.

The surface of the soil in the zone of influence of the halo is covered with gray dry powder, soil compacted. The sampling of soil was carried out in April 2016 and 2017. The study of chemical characteristics included the sampling of the soil at the depth of 0–30 cm and 30–60 cm (number of sampling points $N = 5$). Soil samples were taken using a handle steel soil sampler. Attach sampling point which was 30×30 cm in surface, three sub-samples were taken at the levels of 0–30 cm and 30–60 cm, mixed to obtain a bulk sample (1 kg of soil per sample) for each depth. These depths were selected in order to achieve contrasting samples for the topsoil and deeper horizons.

The salt composition of the soil water extract (1:5) was determined in accordance to NSTU 7908, NSTU 7909, NSTU 7943 and NSTU 8346, exchangeable cations NSTU 7604, NSTU 8345. Chemical composition of the soil and PWs samples was determined by emission photometry. The obtained data was processed statistically following the conventional procedures. Based on the chemical composition determination results, concentration ratios of chemical elements in technosoils as compared with the control soil (Perelman *at al.* 1999.).

Results

Produced water of the studied oil-gas-fields refers to Cl-Na brines with total dissolved solids up to 250 g/L. Chloride usually takes more than 90 % among anions while sodium varies in between 50–70 % among cations sharing the prevalence with calcium (table 1). Buried originally in marine deposits, produced water contains high concentrations of such components as Sr²⁺, Li⁺, B⁺, Br⁺, I⁺.

The study of make up of the control soil water solution from site under study has revealed dominance of calcium bicarbonate, the soils are non-saline, with the content of toxic salts equaling 0.01%, pH (6.5 ± 0.2). The PWs entry into soils has caused formation of specific halogenated technosoils with different content of both total salt and toxic salt amount. Toxic salts content depends on the distance from source of pouring and varies from 0.1 to 0.4% (fig.2). It is possible to clearly identify two zones – impact focus (p. 6-3) and dispersion area (p.6-4 and p. 6-5). In different zones pH varies from 7.0 to 8.2 (±0.3). It has been noted that there is a prevalence of sodium chlorides in the cation-and-anion composition of the technosoils water extract.

Table 1. Chemical composition of produced waters

Value	Concentration, mg L ⁻¹									
	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Sr ²⁺	Li ⁺	TDS
min	40	24800	2	2300	880	11500	28	13	0.35	40 570
max	480	148000	790	30300	3400	60600	1600	720	4.9	238 120
mean	174	96043	160	16429	1487	41214	648	365	2.6	156 520

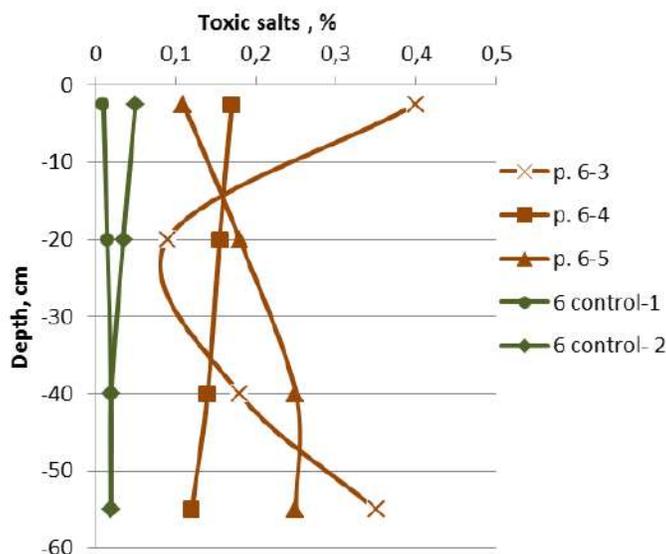


Figure 2. Distribution of toxic salts in the soil profile

Content of exchangeable cations showed a predominance of calcium cations (82-88 %), the content of magnesium is significantly lower and steady (5-11 %). The content of sodium cations (2-4 %) and potassium (1,5-2,9 %) in control soil. In halogenated technosoils exchangeable sodium is predominant (41-65 %), the content of exchangeable calcium is 25-50%, exchangeable magnesium (4-6 %), exchangeable potassium is (2-5 %).

The study focused also on accumulation in the soil :Ba, Ni, Na, P, Sr, Si, Zn, Mg, K, Pb, Ca, Al, Ti, Fe, S, Cu, Mn. The objective - to identify the patterns of accumulation using the concentration ratios. The spatial variation of elements within the studied control plot was not significant - coefficient of variation (C.V.) was less than 30%, elements showed a little variations according to soil depths (C.V. was less than 30%). The fact indicated the homogeneity of the soil over its entire thickness. The spatial variation of elements within the studied halogenated technosoils according to soil depths and distance from source of pouring was significant (C.V. was more than 35%). Concentration ratios more than 1.0 for Na, Mg, Si, P, Sr, Ti, Ni, Pb, with the highest value for Ba (2.0-3.0).

Discussion

The PWs entry into soils has caused formation of specific technogenic alkali soils with different degree of salinization. In technosoils of dark grey soils the ingress of PWs, has resulted in a 100 times increase in the total toxic salts in the 0-30 cm soil layer in impact focus one as compared with the control soils. There is also a 11 to 17 times decrease in the content of toxic salts in the tehnozem profile farther from the impact focus in dispersion area. Based on the salt concentration distribution over the profile, there is a clear differentiation with salts tending to primarily accumulate in the 0-30 cm soil layer. Based on the salt amount, the soils under study are highly salinized. In the control soils adjacent to the halo salinity (p.6-control-2), observed trend of higher concentrations of total and toxic salts and high content of chloride anions and sodium cations in aqueous solution, which may indicate the spread of contamination on adjacent spots territory, probably due to the diversity of its agricultural machinery surface during cultivation, wind sprinkling activity or during an emergency ejection.

The high content of exchangeable sodium in halogenated technosoils was due to strong salinization, especially in impact focus zone. It is not significantly reduced in dispersion area.

The highest concentration in impact focus (layer 0-30 cm) were for Ba (2.0) and Ni (1.7) and lower (30-60 cm) - Ba (2.0), Ti (1.8) and Fe (1.4). In dispersion area Ba concentration in layer 0-30 cm was higher (3.0), fixed high concentration for Ni and Pb, lower (30-60 cm) - Ti, Ba, Fe, K, Mg, Al. The high Ba content may be due both to the receipt of an element in the PWs and to soil contamination by the components of the drilling mud during the construction of the well. In dispersion area for soils adjacent to the halo salinity in the chemical composition dominated Ti and Mn (layer 0-30 cm), but in the subterranean horizon (30-60 cm) there is again a high content of Ba, which is a direct indicator contamination from halo salinity.

Was found that increased solution concentrations of ions brought in with the saline waters are responsible for selective accumulation of mobile fractions of separate alkaline and alkaline-earth metals in the soils (Zhuravel *et al.* 2017). Most of the elements under study accumulate in the 30-60 cm soil layer. Sodium is an active migrant in any geochemical environment; it forms readily soluble salts and can accumulate in soils in significant amounts. With an increase in the distance to the focus, sodium concentration ratios decrease by 5 times in the layer 0-30 cm and by 7 times in the layer 30 -60 cm. K⁺ accumulates primarily in the arable soil layer in the spill focus. However, there was minor variance between the concentration ratios measured in the arable

layers of soil types both from the spill focus and dispersion area. Li^+ is marked by weak mobility in any environment and accumulates primarily on an evaporation geochemical barrier (Perelman *at al.* 1999). Li^+ has accumulated primarily in the arable layer both in the impact focus and area of dispersion. Ca^{2+} , Mg^{2+} and Sr^{2+} being similar in geochemical behaviour, differ in mobility. Strontium is the most active migrant leaving behind both calcium and magnesium in terms of geochemical mobility (Perelman *at al.* 1999). With an increase in depth the Sr^{2+} concentration ratio increased by 7 times (from 24 to 160). Based on the ascending geochemical mobility, the triad of alkaline-earth elements in the impact focus is as follows: $\text{Sr} \rightarrow \text{Ca} \rightarrow \text{Mg}$ and $\text{Mg} \rightarrow \text{Ca} \rightarrow \text{Sr}$ for the periphery. The Ca/Sr ratio equals 0.2-0.4 in the spill focus and 0.9 in the periphery.

Conclusions

The study completed has established that the entry of AWs into soils caused formation of specific technogenic soils with high salinization degrees. The salinity increase can be traced both to the total and toxic salts content. The highest toxic salts content are noted in the area of the impact focus. Ba predominate in the upper layers of technosoils. Most of the elements under study accumulate in the 30-60 cm soil layer. There is a differentiation in the accumulation and enleaching of alkaline-earth and alkaline metals depending on the PWs properties and distribution by technogenic zone. The salinity of the halo is dynamic, because it depends on the diversity of its agricultural machinery during the cultivation and windbreaking activity. In view of the growing environmental risks, it is necessary to use special complex reclamation activities.

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1.2.13. Best Management Practices Reduce Soil Pollution and Improve Health of All: a review

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Abstract

Soil is an essential, nonrenewable resource providing vital supporting, regulating, provisioning, and cultural ecosystem services. Contamination of soils by inorganic and organic pollutants can result in a decline in soil quality and its capability to support ecosystem functions. Soil pollution occurs when soil contains chemicals that are toxic or otherwise dangerous for humans and other living things. The chemicals may be foreign to the area, or they may be naturally occurring materials that pollute the soil by being present in dangerously high amounts. Soil pollution can have many harmful effects on human health (organ damage, bioaccumulation & cancer etc.). In addition to endangering human health, soil pollution can also cause economic damage. For example, in some parts of China, soil that is polluted with heavy metals is nevertheless used to grow grain. The grain grown in these soils is often polluted with heavy metals. According to China Dialogue, an estimated 12 million tons of polluted grain must be disposed of each year, costing Chinese farmers up to 20 billion yuan, or about USD2.57 billion U.S. Soil pollution has increased over the last decades and may pose a risk for human and ecological health. The main causes of soil pollution are associated with human activities, resulting in the accumulation of contaminants in soils that may reach levels of concern. Entry of pollutants directly (release of effluents on land) or indirectly (use of polluted water as irrigation to crops) has been reported to contaminate vast area of soil resources and groundwater bodies, affecting crop production as well as human and animal health through food contamination. The amount of chemical fertilizer used in agriculture fields, total population and total grain yield achieved from the crops are the three most important socio-economic factors that contribute to soil heavy metal pollution. Composts and sewage sludge from municipal wastewater sources, may contain excessive amounts of heavy metals, such as Sn, Zn, Cd, Pb, Mn, Fe, Co, and Si, which in high concentrations can be toxic. The higher toxic elements in sewage may be leached into groundwater and surface water, creating threats not only to the soil but the whole ecosystem too. Policies on soil protection in relation to soil pollution include two basic strategies: (1) a preventive approach and (2) a remediation or cleanup approach.

Keywords: polluted soils, integrated management, remediation

Management of polluted soils

In cases of soil pollution by heavy metals, it is important to identify the available and unavailable forms of the heavy metals to ensure that the soil is managed in such a way as to prevent the unavailable forms from becoming available (Aydinalp & Marinova, 2003). Bioremediation has been used worldwide, including Europe, with varying success (Zouboulis, Moussas & Nriagu, 2011). Bio-decomposition of remains of poultry and livestock, and land application of the resulting product is used throughout the U.S. and Canada for management of routine poultry, swine, and

cattle mortalities, and is often cited as being more environmentally friendly than burial since it recycles nutrients and other potential pollutants into the topsoil and crop production cycle, rather than placing them deeper in the ground and closer to groundwater (Glanville *et al.*, 2009). Land application of biosolids, such as sewage sludge or compost, has a great incentive in view of its fertilizer and soil amendment values, unless they contain toxic elements (Park *et al.*, 2011; Kacprzak *et al.*, 2014; Grobelak, 2016). Cleaning soil pollution is far from easy because site managers may often have little knowledge of how the pollutant is behaving beneath the surface. Different pollutants have different properties, resulting in varying types of behavior and dispersal. Numerous attempts are being made to decontaminate polluted soils, including an array of both in situ (on-site, in the soil) and off-site (removal of contaminated soil for treatment) techniques. None of these is ideal for remediating contaminated soils, and often, more than one of the techniques may be necessary to optimize the cleanup effort.

Best management practices (BMPs) are individual or combinations of management, cultural and structural practices that researchers (academic or governmental), have identified as the most effective and economical way of reducing damage to the environment (Cestti, Srivastava, & Jung, 2003). To ensure food safety and food supply, many management techniques have been applied, for example non-tillage systems, direct seeding, pesticide and drought-resistant GMO crops and organic amendments application to increase soil organic content. Biological control is urgently needed, opening increasing possibilities for biopesticides (Popp, Petó, & Nagy, 2013).

Remediation strategies such as application of soil amendments (adding materials to soils to improve their quality) and phytoremediation (remediation of soils using plants) can reverse the soil quality (Fangueiro *et al.*, 2018). Plant wastes are being increasingly used to produce compost, which is an important amendment to improve the properties of degraded soils (Grobelak, 2016). Addition of organic matter into the soil can result in decreased mobility of heavy metals (Wuana & Okieimen, 2011; Grobelak & Napora, 2015). Compost made from sawdust, wood chips, bark, straw, plant wastes, and food waste from households are commonly used as organic matter in the soil (Kuo *et al.*, 2004).

Integrated crop management (ICM) is something that affects everyone - not only farmers but also consumers - and it presents a realistic solution to many of the problems facing agriculture. ICM is a method of farming that balances the requirements of running a profitable business with responsibility and sensitivity to the environment. It includes practices that avoid waste, enhance energy efficiency and minimize pollution. ICM combines the best of modern technology with some basic principles of good farming practice and is a whole farm, long term strategy.

ICM is a 'whole farm approach' which is site specific and includes:

- The use of crop rotations
- Appropriate cultivation techniques
- Careful choice of seed varieties
- Minimum reliance on artificial inputs such as fertilisers, pesticides and fossil fuels
- Maintenance of the landscape
- The enhancement of wildlife habitats

Integrated Soil Fertility Management is an approach based on the following principles:

- (1) Neither practices based solely on mineral fertilizers nor solely on organic matter management are sufficient for sustainable agricultural production,
- (2) well-adapted, disease- and pest-resistant germplasm is necessary to make efficient use of available nutrients, and
- (3) good agronomic practices - in terms of planting dates, planting densities, and weeding - are essential for ensuring the efficient use of scarce nutrient resources. There is also a need to target nutrient resources within crop rotation cycles, preferably including legumes, thus going beyond recommendations for single crops.

Integrated nutrients management can play a role in improving plant growth, dry matter partitioning and total crop biomass (Amanullah and Khalid, 2016; Amanullah and Hidayatullah, 2016; Amanullah *et al.*, 2016), including root biomass (Amanullah and Stewart, 2013) in the soil have a significant impact on the efficiency of phytoremediation processes of degraded soils (Grobela, A. 2016). Maintaining organic carbon-rich soils, restoring and improving degraded agricultural lands and, in general terms, increasing the soil carbon, play an important role in addressing the three-fold challenge of food security, adaptation of food systems and people to climate change, and the mitigation of anthropogenic emissions (Paris Agreement, 2015). For achieving the pollution free world, the Voluntary Guidelines for Sustainable Soil Management (FAO, 2017) which include integrated or organic pest management practices are recommended worldwide. Moreover, the IPM encouraging crop rotations which encourage low or no pesticide use, which can lower the need for pesticides (Garcia-Préchal *et al.*, 2004).

The Role of Biofertilizers: Biofertilizers are known to play many vital roles in soil fertility; crop productivity and profitability. Biofertilizers are the products containing living cells of different types of beneficial microbes (bacteria, fungi, protozoa, algae and viruses). Some of the commonly used beneficial microbes in agriculture include Rhizobia, Mycorrhizae, Azospirillum, Bacillus, Pseudomonas, Trichoderma, Streptomyces species etc. Beneficial microbes are essential for decomposing organic matter in the soil and increase essential macro-nutrients (nitrogen, phosphorus, potassium, sulfur, calcium and magnesium) and micro-nutrients (boron, copper, chlorine, iron, manganese, molybdenum and zinc) availability to crop plants. Beneficial microbes also play significant role in solid wastes and sewage management. Beneficial microbes increase plants tolerance to different environmental stresses (drought, heat, cold, salinity etc.) and increase plant resistance to insects and diseases attacks. Beneficial microbes not only improve crop growth and productivity by increasing photosynthesis and producing hormones and enzymes, but also improve crop quality by controlling different insects and various plant diseases. Beneficial microbes reduce the use of chemical fertilizers and thereby reduce environmental pollution caused by chemical fertilizers. Beneficial microbes reduce cost of production and so increase grower's income and profitability. Beneficial microbes are therefore very important for increasing crop productivity, profitability and sustainability. Applications of organic manures such as crop residues, animal manures, chicken manures, green manures, composts, farm yard manure, biochar, ash etc. increases the beneficial microbes in the soil and improves soil health and sustainability (Amanullah, 2015).

Integrated Pest Management (IPM) is a program that should be based on prevention, monitoring, and control which offers the opportunity to eliminate or drastically reduce the use of pesticides, and to minimize the toxicity of and exposure to any products which are used. IPM does this by utilizing a variety of methods and techniques, including cultural, biological and structural strategies to control a multitude of pest problems.

Integrated weed management (IWM) is the control of weeds through a long-term management approach, using several weed management techniques such as: physical control, chemical control, biological control and cultural control.

The increasing need for remediation of contaminated soils has led to the development of new technologies that emphasize on the biological detoxification and destruction of the (organic) contaminants (Zouboulis, Moussas & Nriagu, 2011). **Bioremediation** is among these technologies that destroy or render harmless various contaminants, using the biological activity of certain microorganisms. Bioremediation relies on the microbial growth and activity; its effectiveness is highly dependent on the applied environmental parameters that influence the microbial growth and the degradation rate. Bioremediation is considered as a very promising technology with great potential when dealing with certain types of contaminated sites (Zouboulis, Moussas & Nriagu, 2011).

Plantation of trees having good resistance to high levels of toxic substances and having a high capacity to collect, and store pollutants are good for phytoremediation process in soil (Paz-Alberto & Sigua, 2013). According to Wisłocka *et al.* (2006), the most popular trees exhibiting a high capacity to accumulate heavy metals are: silver birch (*Betula pendula*), alder (*Alnus tenuifolia*), black locust (*Robinia pseudoacacia*), willow (*Salix* sp.), and conifer trees. Selected energy crops, like *Miscanthus giganteus*, have excellent adaptability to change habitat conditions and the possibility to gradual reclamation of degraded land and the ability to prevent the migration of heavy metals into the soil and groundwater.

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1.2.14. Nutrient-rich top soils as potential sources of trace metals in domestic and urban landscapes in Cape Coast, Ghana

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Abstract

Contamination of soils with trace metals is a topmost concern for environmental and human health worldwide. In Ghana, landscaping of homes and public spaces relies heavily on nutrient-rich top soils (commonly called ‘black soil’) supplied by dealers. There is little information on the trace metal contamination of these ‘black soils’ widely used for horticultural purposes. This study therefore assessed the status of arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) in 40 ‘black soil’ samples collected from homes, hostels, schools and other sources in Cape Coast. The samples were analyzed for the trace metals using the standard method of Aqua Regia and a PDV6000 plus Trace Metal Analyzer. The index of geoaccumulation (Igeo) and modified degree of contamination (mCd) were calculated. The results show that the black soil samples were strongly contaminated with the trace metals. Median values of Igeo showed that about 50% of the samples were strongly contaminated with As, Hg and Pb but moderately to strongly contaminated with Cd. The mean mCd was 10.87 (indicating very high degree of contamination). Large number of samples had As and Hg concentrations below the Canadian Environmental Quality Guidelines (CEQG) values for

agricultural and residential/parkland soils. However, substantial number of samples exceeded the CEQG value for Cd and Pb in agricultural and residential/parkland soils. The results show that the black soils can be potential sources of trace metal contamination of residential and urban landscapes, and pose potential ecological and health risks to end users. There is the need for a wider study to underpin the regulation of mining and safe use of black soils and development of a strong growth media industry to support horticultural development in Ghana.

Keywords: chemicals of concern; trace metals; soil contamination; arsenic; lead; cadmium; mercury; pollution indices.

Introduction

Trace metals are amongst the largest contaminants in soils and water (Science Communication Unit 2013; Huber 2012). Trace metals of significant biological toxicity or adverse effects on human health include Arsenic (As), Cadmium (Cd), Lead (Pb) and Mercury (Hg) (Su *et al.* 2014; Armah *et al.* 2013), which are among the ten leading chemicals of concern identified by WHO (Brevik and Burgess 2014). The impacts of these four trace metals on human health include neurological, heart, liver, kidney, mental and pregnancy disorders (Peralta-Videa *et al.* 2009). Some trace metals are also carcinogenic. Trace metals in soils can enter into the human body through skin absorption, inhalation of dust, geophagia, consumption of food grown on contaminated soils, or drinking of water affected by contaminated soil (Peralta-Videa *et al.* 2009). Common anthropogenic sources of trace metals in soils include mining, agriculture (pesticides and fertilizers), smelting, industrial activities, and improper disposal of municipal waste, paint, batteries, electronic waste and sewage (Armah *et al.* 2013, Peralta-Videa *et al.* 2009).

Good plant growth depends on the capacity of soils or growth media to supply especially nutrient and water (Adu *et al.* 2016; Yawson *et al.* 2010). In Ghana, nutrient-rich top soils (popularly known as 'black soil') are used mainly for domestic and urban landscaping purposes. Recently, black soils are also used as top soil for home gardens, urban farming, and in pot experiments. The sources of the black soils vary widely, including refuse dumpsites, fallowed or idle lands covered with bushes, pristine areas, and top soils scrapped off from construction sites. These soils are normally collected and sold by dealers to end users upon request. A booming construction sector, together with non-existent or weak growth media industry, creates excess demand for black soils for domestic and urban landscaping in Ghana (Yawson *et al.* 2018). Given the sources and areas of use of these black soils, they can pose potential environmental and health risks to end users. However, there is paucity of information on the trace metal contamination of black soils widely used for horticultural purposes in Ghana. This paper therefore assessed the contamination status of four trace metals in black soil samples at various locations in Cape Coast (Ghana).

Methodology

Soil Analysis

The soil sampling protocol has been described in Yawson *et al.* (2018). In all, a total of 40 soil samples were collected for this study. Soil samples were collected from homes landscaped with black soil (25), hostels (2), schools (7), and heaps for pot experiment (2). In addition, two samples were collected from dealer vehicles transporting black soil and two homes that have not been landscaped with transported black soil in Cape Coast. Representative samples were obtained by repetitive bulking and fractioning of two or three samples randomly collected from each location. The soil samples were oven dried at a temperature of 105 °C to constant weight. The dried soil samples were then crushed, ground into powder and sieved to reduce clump sizes and to obtain a fine earth fraction for analysis. The standard method of using aqua regia (ISO 1995) as an

extracting agent was employed in the current study. Here, 1 g of previously dried and ground samples were acid digested with heated hydrochloric and nitric acid solution in a fume chamber. The digested sample was then filtered with a Whatmann paper into a volumetric flask. The filtrate was then diluted with deionized water to the 250 ml mark. Blank samples were then prepared in the same procedure with deionized water. The trace metal concentrations of the soil samples were determined with the Anodic Stripping Voltammetry (ASV) method using PDV6000 plus Trace Metal Analyzer. The final values represent the means of three replicates for each sample.

Indices of contamination

Indices of contamination were calculated using the observed concentration values and background concentration values obtained from literature. The indices of contamination calculated were geoaccumulation index (I_{geo}), contamination factor (C_f^i), and the modified degree of contamination (mC_d). These indices normally indicate the extent to which the observed values exceed background values, giving an indication of whether remedial action is necessary or urgent for the site under consideration. Index of geoaccumulation was calculated as [18, 19]:

$$I_{geo} = \log_2 \left(\frac{C_o}{1.5C_b} \right) \quad (1)$$

where C_o and C_b are the observed and geochemical background concentrations, respectively. The factor 1.5 is used to minimize the effect of possible variations in the background values due to lithological variations in the samples [20]. The I_{geo} has seven classes of contamination: uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} < 1$), moderately contaminated ($1 < I_{geo} < 2$), moderately to strongly contaminated ($2 < I_{geo} < 3$), strongly contaminated ($3 < I_{geo} < 4$), strongly to extremely contaminated ($4 < I_{geo} < 5$), and extremely contaminated ($I_{geo} > 5$) (Abraham and Parker 2008).

The contamination factor (C_f^i) was calculated using equation two (Abraham and Parker 2008):

$$C_f^i = \frac{C_o^i}{C_b^i} \quad (2)$$

Where C_o^i and C_b^i are the mean observed and background concentration values, respectively. The contamination factor values were used to calculate the modified degree of contamination mC_d , which produces an overall average degree of contamination for the contaminants under consideration. The mC_d was calculated using equation three (18, 20):

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (3)$$

where n is the number of analysed contaminants, $i = ith$ contaminant and C_f^i is the contamination factor. The seven classes for the modified degree of contamination are: nil to very low degree of contamination ($mC_d < 1.5$), low degree of contamination ($1.5 \leq mC_d < 2$), moderate degree of contamination ($2 \leq mC_d < 4$), high degree of contamination ($4 \leq mC_d < 8$), very high degree of contamination ($8 \leq mC_d < 16$), extremely high degree of contamination ($16 \leq mC_d < 32$), and ultra high degree of contamination ($mC_d > 32$).

For mineral or arable soils, the background values are suitable if obtained from soils formed under similar conditions or soil forming processes and are uncontaminated. Due to the varied sources and nature of the black soils in the current study, it is difficult to classify them entirely as mineral

soils or arable soils. For example, black soils collected from old refuse dump might have minimal lithological influence on the trace metal concentrations. However, due to paucity of relevant values, we used the maximum value of the range of global average background values for each of the trace metals in uncontaminated soils reported by Alloway (2013). In addition, the observed trace metal concentrations were compared with those in the Canadian Environmental Quality Guidelines for soils used for agricultural and residential/parkland purposes.

Results

Out of the 40 samples, Arsenic (As) was found in 38 samples, Cadmium (Cd) was found in 39 samples, Lead (Pb) was found in 37 samples, and Mercury (Hg) was found in 35 samples. The observed concentrations of As in the samples ranged from 0.00 to 21.20 mg kg⁻¹ soil, with a mean of 6.37 mg kg⁻¹ soil (Table 1). The mean values for the other trace metals were 7.14 (Cd), 58.12 (Pb) and 1.93 (Hg) mg kg⁻¹ soil, with maximum values of 19.45, 182.50 and 10.50 mg kg⁻¹ soil for Cd, Pb and Hg, respectively. All the trace metals studied were positively skewed, with negative kurtosis except Hg. All the kurtosis values were less than three, indicating that the histogram of the distribution of the data has short tails and most of the observations are tightly clustered around the mean.

For all the samples, the mean and maximum index of geoaccumulation (Igeo) for As lied in class 5 (strongly contaminated) and class 7 (extremely contaminated), respectively (Table 1). The mean Igeo for Cd was 1.33, indicating a moderately contaminated samples, while the maximum indicated strongly contaminated samples. For Pb and Hg, the mean Igeo values indicated that the samples were extremely contaminated and moderately contaminated, respectively. The median values of Igeo for As, Pb and Hg indicated that 50% of the samples were, at least, strongly contaminated with these trace metals. The median for Cd indicated that about 50% of the samples were moderately to strongly contaminated. Even though the Igeo values for all the trace metals exhibited a negative skew, the kurtosis values showed that most of the observed values tightly clustered around the mean. Integrating all the trace metals studied, the modified degree of contamination index (mC_d) had a mean of 10.87 (class 5, very high degree of contamination). The maximum mC_d was 44.41 (class 7, ultra-high degree of contamination). The median mC_d indicated that 50% of the samples had high degree of contamination by the four trace metals studied.

Table 1. Descriptive statistics of the trace metal concentrations (mg kg⁻¹ soil), index of geoaccumulation (Igeo) and modified degree of contamination index (mC_d) in the soil samples (n = 4-0)

	<i>Arsenic</i>		<i>Cadmium</i>		<i>Lead</i>		<i>Mercury</i>		<i>mC_d</i>
	<i>Conc.</i>	<i>Igeo</i>	<i>Conc.</i>	<i>Igeo</i>	<i>Conc.</i>	<i>Igeo</i>	<i>Conc.</i>	<i>Igeo</i>	
Mean	6.37	3.64	7.14	1.33	58.12	6.73	1.93	3.14	10.87
Std. Error	0.99	0.39	0.96	0.34	9.80	0.66	0.43	0.43	1.74
Median	4.20	4.16	6.72	2.16	21.75	7.95	0.66	3.45	7.01
Std. Dev.	6.29	2.45	6.05	2.17	61.96	4.18	2.72	2.73	11.00
Kurtosis	-0.96	-1.25	-1.07	2.79	-0.92	-1.39	2.41	-1.42	1.88
Skewness	0.57	-0.44	0.43	-1.46	0.71	-0.63	1.77	-0.06	1.59
Minimum	0.00	-1.00	0.00	-6.23	0.00	0.00	0.00	-1.58	0.54
Maximum	21.20	6.73	19.45	3.70	182.50	11.01	10.50	7.45	44.41

With the mC_d, 11 of the samples belonged to class 5 (very high degree of contamination), while 10 belonged to class 3 (moderate degree of contamination) (Table 2). Four samples showed nil to

very low degree of contamination while four samples showed ultra high degree of contamination. With I_{geo} , five of the samples were uncontaminated with As while 18 were extremely contaminated. For Cd, 10 samples were uncontaminated, 11 were moderately to strongly contaminated while 9 were strongly contaminated. None of the samples was extremely contaminated with Cd. However, as many as 27 samples were extremely contaminated with Pb and only 3 samples were uncontaminated with Pb. For Hg, 11 samples were uncontaminated while 12 were extremely contaminated.

Table 2. Frequencies of the index of geoaccumulation (I_{geo}) and modified degree of contamination index (mCd) for all the samples ($n = 40$).

Class	mCd Interpretation	mCd Freq.	I_{geo} Class Interpretation	I_{geo} Frequencies			
				As	Cd	Pb	Hg
1	Nil to very low	2	Uncontaminated	5	10	3	11
2	Low	2	Uncontaminated to moderately contaminated	4	8	5	1
3	Moderate	10	Moderately contaminated	5	2	4	4
4	High	6	Moderately to strongly contaminated	3	11	0	3
5	Very high	11	Strongly contaminated	3	9	1	3
6	Extremely high	5	Strongly to extremely contaminated	2	0	0	6
7	Ultra high degree	4	Extremely contaminated	18	0	27	12

Comparison of observed trace metal concentrations with environmental permissible concentrations provides immediate impression of the scale of risk posed by the trace metals studied. The observed trace metal concentrations were compared with the respective guidelines indicated in the Canadian Environmental Quality Guidelines (CEQG). For As and Hg, the CEQG thresholds for both agricultural and residential/parkland soils were 12 and 6.6 mg kg⁻¹ soil, respectively. Thirty samples had As concentration values below the CEQG threshold (Figure 1, A) while 35 samples had Hg concentration values below the CEQG value (Figure 1, F). For Cd, 33 samples exceeded the CEQG guideline of 1.4 mg kg⁻¹ for agricultural soils (Figure 1, B), while 15 samples exceeded the CEQG guideline of 10 mg kg⁻¹ for residential and parkland soils (Figure 1, C). For Pb, 17 samples exceeded the CEQG guideline of 70 mg kg⁻¹ for agricultural soils (Figure 1, D), while only 7 samples exceeded the guideline of 140 mg kg⁻¹ for residential/parkland soils (Figure 1, E).

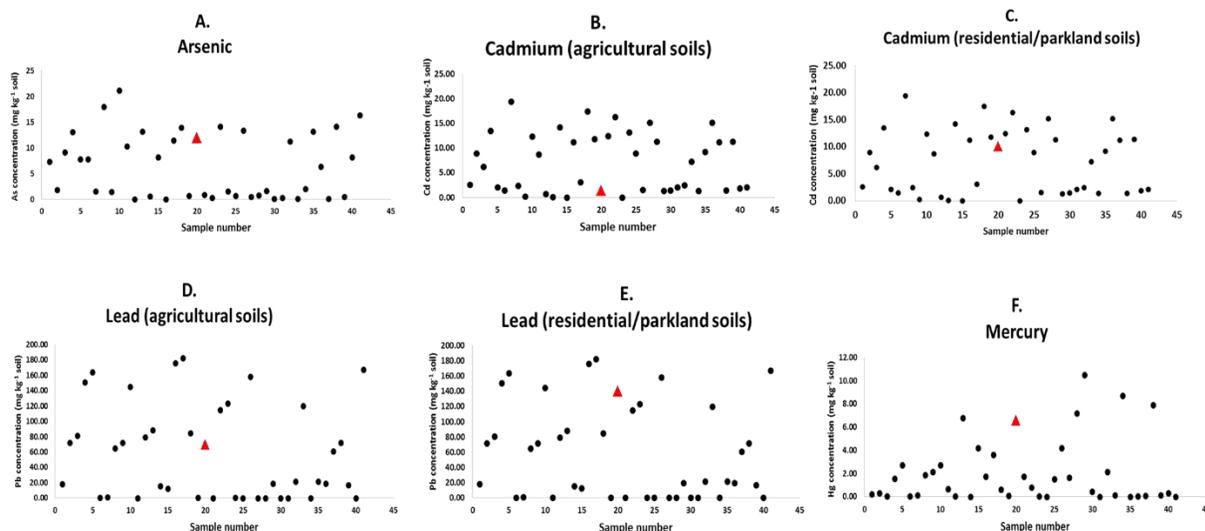


Figure 1. Comparison of trace metal concentrations in the samples with the guideline values (triangle, solid red fill) prescribed by the Canadian Environmental Quality Guidelines: (A) Arsenic in agricultural and residential/parkland soils; (B) Cadmium in agricultural soils; (C) Cadmium in residential/parkland soils; (D) Lead in agricultural soils; (E) Lead in residential/parkland soils; (F) Mercury in agricultural and residential/parkland soils.

Discussion

In Ghana, the so-called black soils are widely used for horticultural purposes due to their perceived rich nutrient contents and properties, absence of a strong growth media industry, the informality of the landscaping industry, and poor understanding of the risks associated with use of the black soils. The current study shows that use of black soils can pose potential ecological and human health risks. Based on the index of geoaccumulation (Igeo), the black soil samples were highly contaminated with As and Pb, and moderately with Cd and Hg (Table 1). The modified degree of contamination index (mCd), which integrates all the trace metals studied, also showed that about 50% of the samples had high degree of contamination (Table 1). Overall, high degrees of contamination were observed for As and Pb in most of the soils (Table 2), with comparable lower values for the two non-black soil samples. The average Igeo values for the trace metals in the current study are higher than those observed in agricultural soils around Dhaka Export Processing Zone in Bangladesh (Rahman *et al.* 2012). However, the average mCd reported by (Rahman *et al.* 2012) is much larger than in the current study. This is probably due to the larger number of trace metals they considered.

The current study focused on four trace metals (As, Cd, Hg and Pb) considered among the ten leading chemicals of concern by the WHO (Brevik and Burgess 2013). Permissible levels of trace metals in soils vary across jurisdictions and are context-dependent. In the current study, permissible trace metal concentrations in agricultural and residential/parkland soils specified by the Canadian Environmental Quality Guidelines (CEQG) were used due to the absence of such fine classifications in the Ghana standards. Arsenic and Mercury had the highest number of samples exceeding permissible guidelines for both agricultural and residential/parkland soils (Figure 1). In soils, lateral and vertical migration of As is very limited (Alloway 2013). Hence, As can remain harmful in top soils for a long time. A review by (Rajae *et al.* 2015) indicated high As concentrations for both mining and non-mining soils in Ghana. Though Hg was banned in Ghana about 30 years ago, it is still widely traded in both formal and informal markets (Rajae *et al.* 2015). For Cd, approximately 83% of the samples exceeded the guideline value for agricultural soils. None of the trace metals considered had all the samples below specified guidelines for agricultural and residential/parkland soils. This suggests that the use of black soils can be a potential source of trace

metal contamination or pollution in domestic and urban landscapes in Ghana and can pose potential ecological and health risks to end users. It is therefore important to regulate black soil mining, assess its safety for use, and develop a strong growth media industry in Ghana.

Conclusions

The current study assessed the concentrations of four trace metals (As, Cd, Hg and Pb), among the ten leading chemicals of concern, in nutrient-rich top soils (commonly known as 'black soil') widely used for horticultural purposes in Ghana. The results showed that the black soil samples used had high degrees of contamination as the trace metal concentrations in large proportion of the samples exceeded the environmental quality guideline values for agricultural and residential/parkland soils. This suggests that use of black soils can pose potential ecological and health risks and help pollute non-agricultural landscapes. It is important to regulate black soil mining, ensure its safety for use, and develop a strong growth media industry for the horticultural sector in Ghana.

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1.2.15. Sources and levels of soil pollution by PCBs in Belarus: achievements and problems of management

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Abstract

In the paper the results of PCB-contaminated sites investigation in Belarus caused by leakages from PCB-containing equipment considered as the main sources of soil pollution are discussed. It is shown that revealing of PCB-contaminated sites simultaneously with the inventory of PCB-containing equipment is an effective approach for data base creation and future management.

More than 90 sites were investigated and more than 600 soil samples were collected and analysed. At the moment more attention is paid to electrical substations where PCB-containing capacitors were installed and in some cases are used or stored in open air. The surface (up to 20 cm) layers of soil and in some cases subsoil horizons were tested. GC-MS method for 7 PCBs congeners (PCB-28, 52, 101, 118, 153, 138 and PCB-180) determination was applied.

Extremely high PCBs content (grams or dozen grams per kilogram) were revealed as a results of PCBs leakages. Very mosaic and heterogeneous spatial structure of PCB-contaminated soil as well as spreading of PCBs beyond the places of PCB-containing equipment usage or storage was established. Different sizes of hot spots (from less than one to dozens square meters) and depth of pollution (from centimeters up to meter) were established.

It is shown that identified PCB-contaminated sites are only a small part of potentially contaminated sites, which could be formed at all 800 owners of PCB-containing equipment.

The problems of PCB-contaminated sites management are connected with increasing rates of PCB-containing equipment out of service for temporary storage; absence of technology for PCBs destruction and soil remediation; poor investigation of soil pollution in places with PCB-containing transformers used or stored. The problem is typical for CIS countries.

In spite of progress in PCB-contaminated sites management, concern about future actions should be increased to avoid preservation or even loss of hot spots as the long-term secondary sources of PCBs.

Keywords: Polychlorinated biphenyls, persistent organic pollutants, PCBs leakages, soil pollution, Belarus

Introduction, scope and main objectives

Polychlorinated biphenyls (PCBs) are the group of persistent organic pollutants (POPs) regulated by Stockholm Convention on POPs since 2001. At present, 182 countries are Parties to the Convention, indicating recognition of the need for joint efforts and the environmentally sound management of POPs at the global level. To protect human health and the environment, Parties to the Convention shall eliminate the usage of polychlorinated biphenyls in equipment by 2025, and dispose of PCBs in an ecologically sound manner as soon as possible but no later than 2028 (The Stockholm Convention..., 2009). Identification of POPs-contaminated sites is an essential element in the management of POPs and one of the obligations of the Stockholm Convention. According to the para 6 Convention, each Party... “endeavour to develop appropriate strategies for identifying sites contaminated by chemicals listed in Annex A, B or C; if remediation of those sites is undertaken it shall be performed in an environmentally sound manner”. The measures for soil remediation should be taken if the content PCBs equal to 50 mg/kg and more (Technical Guidance..., 2017).

Up to now, PCB-contaminated sites caused by manufacture of this chemicals and PCB-containing articles/equipment are well known in the countries because of very limited number (Toolkit..., 2013); many activities have been undertaken regarding their investigation and remediation.

Revealing of PCB-contaminated sites related to PCBs leakages from PCB-containing equipment is not an easy task because of different sphere and long history of their usage as well as wide geographical distribution of owners. There is a huge amount of PCB-containing equipment globally, especially in developing countries and countries with transitional economic, including CIS countries (Treger 2011; Sukhorebra *et al.* 2011; Implementation Plan..., 2014; Report by the United..., 2017).

Identification and ecologically sound management of PCB-containing equipment as well as detection and remediation of PCBs-contaminated soil (sites) are the two tight connected tasks. Successful decision of the second task depends on the results of the first one because PCB-containing equipment was and is still the main source of soil pollution (Weber *et al.* 2008; Kukharchyk *et al.* 2011). About 60% of the total volume of PCBs was used as dielectric fluids in

transformers and power capacitors globally (Breivik *et al.* 2007). Filled with virtually pure PCB, power transformers and capacitors pose the greatest threat in terms of impact on human health and the environment, especially in emergency situations and other cases following the leaks of hazardous chemicals. According to (National Plan ..., 2006; Kukharchyk 2006; Gumanova 2008; Kukharchyk *et al.* 2011), high levels of soil contamination with PCBs were detected in sites where PCB-containing equipment was used or stored.

Belarus acceded to the Stockholm Convention on POPs in February 2004 in accordance with Decree of the President of the Republic of Belarus of December 23, 2003 No. 594. Since then a lot of efforts were undertaken related to PCBs, including identification of PCB-containing equipment and its owners, its labeling, reporting, decommissioning, secure temporary storage and disposal.

The purpose of this article is to show the specific features of soil pollution caused by leakages from PCB-containing equipment, possibility of new hot spot formation after PCB-containing equipment dismantling, main gaps and tasks for future ecologically sound management of contaminated sites.

Methodology

Revealing of PCB-contaminated sites in Belarus has been started in 2003 simultaneously with the inventory of PCB-containing equipment in the country. The main tasks for PCB-contaminated sites and hot spots were identification/localization of sites where PCB-containing transformers and capacitors were in use or stored, including damaged equipment and PCB waste; identification of PCBs leakages; sampling of soils and chemical-analytical determinations of PCBs (Kukharchyk *et al.* 2007).

The main attention was paid to the study of places where PCB-containing capacitors were installed or stored in open air because of high risk of PCBs discharges directly into soil. The research was carried out repeatedly at a number of substations to determine the changes that had occurred as a result of capacitors dismantling, changes in storage conditions and other factors (Kukharchyk *et al.* 2018).

More than 90 sites were investigated and more than 600 soil samples were collected and analysed. The surface (up to 20 cm) layers of soil and in some cases subsoil horizons were tested. GC-MS method for 7 PCBs congeners (PCB-28, 52, 101, 118, 153, 138 and PCB-180) determination was applied.

Results

Contaminated soils were found at almost all enterprises which are used PCB-containing equipment that confirmed PCBs leakages and indicated PCBs source. The sum of 7 PCBs congeners varies from micrograms to grams or even dozens grams per kilogram. The highest levels of PCBs are detected directly under capacitors installations or within storage areas of dismantled equipment. In a number of cases, the extremely high PCBs content in soil was detected visually, i.e. "burned" vegetation, oiled soil and a specific odor. Extremely high levels of soil pollution (with PCB content more than 500 mg/kg) were revealed in 80% of investigated sites.

Generally, in most cases PCBs content in soils is very heterogeneous; the levels of pollution and the structure of anomalies depend on the type of leakage, time of PCB-containing equipment operation or storage and processes of PCBs migration. The size of hot spots is different; most of them were less than one square meter, but sometimes the area of extremely polluted soils reached

up to 50 m² or even 1000 m². It was supported, that larger area of hot spots was created as a result of capacitors explosion and PCBs spraying.

The investigated sites also differ significantly in the depth of PCB migration. More often extreme levels of pollution are found in the upper soil levels – up to 10 cm. However, in cases of easily identifiable hot spots of PCBs spills high levels of PCBs pollution were found at the depth of 0.5 m or even 1 m (Kukharchyk 2006; Kukharchyk *et al.* 2007, Kukharchyk *et al.* 2008).

It was established that even after 10-15 years or more after dismantling and removal of PCB-containing equipment from the places of their installation and storage contaminated sites are still existing (Table 1).

Table 1. The sum of 7 PCBs congener content in soil in impact zones of PCB-containing equipment installation or storage, mg/kg (substation Minoity, Grodno region)

Site of investigation	Year	Sampling site	Depth of sampling, cm	The sum of 7 PCBs
Territory of PCB-containing capacitors installation	2004	5 years after capacitors dismantling, no visual leakage	0-5	29 -383
		the same, visual leakage (hot spot 1)	0-3	6333.5
			40-50	83.3
	2005	6 years after capacitors dismantling, visual leakage (hot spot 2)	0-3	3769.2
			10-20	2088.2
			40-50	443.1
			90-100	2036.7
	2011	12 years after capacitors dismantling, visual leakage (hot spot 3)	0-2	9604.2
			18-26	0.19
			70-80	0.23
the same, visual leakage (hot spot 4)		7-15	38.13	
The storage of PCB-containing capacitors	2005	10 m from storage	0-2	80.05
		between concrete slabs, visual leakage	0-3	12461
		near the concrete slab	0-5	412.86
	2011	near the damaged container with PCB-containing capacitors, visual leakage	0-2	78440

The data given in Table 1 demonstrate only the situation within one electrical substation, where PCB-containing capacitors were installed for more than 20 years and then were stored about 10 years. The trends of PCBs content in soil were not considered in the study; the samples from different hot spots were collected to illustrate the spatial structure of pollution. The formation of new contaminated site after PCB-containing capacitors dismantling and moving for the temporary storage was more important issue.

The absence of vegetation in places of PCBs leaks, which haven't restored in 15 years or more, as well as oily soil, hampered the development of pedological processes including humus and podzolic horizons formation. In many cases the coloring of soil horizons to a depth of 40-50 cm was due to PCB leakages. Traces of vertical infiltration of PCBs (firstly on the roots of plants and tracks of soil animals) in widths from a few centimeters to 10-20 cm were clearly indicated.

It was also shown that mechanical processes of contaminated soil redistribution away from contaminated sites is important. It was confirmed by the results of soil samples collected from molehills and ant tracks as well as deposits caused by wind and run off (Table 2). Of course, vapors and secondary emissions should be also taken into account.

Due to such redistribution, on the one hand, the increasing of heterogeneity of pollution, but on the other hand, the formation of secondary anomalies are possible.

As a results of investigation data base including 68 PCB-contaminated sites (with PCBs content 50 mg/kg and more) and 23 potentially contaminated sites was developed. The data base containing the following information: territory name, enterprises name, Ministry name, area, locality, geographical coordinates, type of use, source of pollution, years of investigation, undertaken measures for soil remediation, priority for future remediation.

Table 2. The content of 7 PCB congeners in soil and deposits at former site of PCB-containing equipment installation (12 years after dismantling), mg/kg (substation Minoity, Grodno region)

Site of sampling	Depth of sampling, cm	PCB-28	PCB-52	PCB-101	PCB-118	PCB-153	PCB-138	PCB-180	Sum of 7 PCBs
Deposits on concrete tracks (caused by wind)	0-1	0.072	0.04	0.052	0.038	nd	0.007	0.004	0.213
Soil from molehill	0-15	0.188	0.037	0.024	0.019	0.007	0.004	0.001	0.281
Soil from ant tracks	0-1	0.265	0.033	0.013	0.024	0.004	0.023	0.002	0.363
Run off deposits near the substation	0-2	0.003	0.01	0.003	0.002	nd	nd	nd	0.018

Discussion

Revealing of PCB-contaminated sites is still very acute because of PCB-containing equipment use and storage. According to the results of the inventory (Kukharchyk and Kakareka 2008), 1.5 thousand tons of PCBs were revealed in Belarus (total amount according to rough estimates), 55 per cent of which were concentrated in power transformers, and 44 per cent – in power capacitors. By the beginning of 2017, the total stocks of PCB-containing equipment in Belarus decreased only by 17% due to the removal for disposal within the framework of the GEF project.

The process of PCB-containing equipment dismantling, especially equipment located in open air, creates the prerequisites for soil remediation. At the same time new potentially polluted sites are formed because of absence of technology for PCBs destruction and necessity of long-time storage. To date, the number of sites with installed PCB-containing capacitors in substations of electric networks has decreased by 2/3 or more than 70 sites. At the same time, 23 new sites for storing PCB-containing equipment have appeared. In some cases, storage is organized within the same substations where they were used.

Among the remediation measures, excavation of mostly polluted soils at 22 substations has been undertaken. About 44 tons of excavated soil are stored on the territories of those facilities where it was excavated. Even packed in containers, it is a source of pollution of the environment due to the processes of evaporation of PCBs and their dispersion (there is a strong specific smell in the places where the contaminated soil is stored).

As the main concern it should be highlighted that the majority of sites where PCB-containing equipment used and stored are not investigated. There are only preliminary data regarding the soil pollution within the places of power transformers location. In spite the fact that in most cases

they are installed in buildings, PCBs leakages during dismantling, transportation and other activities are not excluded. The volume of PCBs in transformers varies from 240 to 4400 kg therefore the current risk of huge amount of PCBs discharges is very high.

It should be noted that PCB-containing transformers as a source of PCBs are more rarely used than capacitors because of their specific purpose (for enterprises with high risk of fire hazard). For comparison, in Belarus there are 40 enterprises where PCB-containing transformers and more than 760 enterprises where PCB-containing capacitors are used.

It seems, that all of the 800 enterprises in Belarus (owners of PCB-containing equipment) should be considered as potentially contaminated sites. Therefore, the database of PCB-containing equipment owners developed in Belarus in 2007 and annually updated, is extremely important for PCBs management in future.

Conclusions

The problems of PCB-contaminated sites management in Belarus (and probably in many other countries, firstly in CIS) are connected with the following reasons: increasing rates of PCB-containing equipment out of service for temporary storage; absence of technology for PCBs destruction and soil remediation; poor investigation of soil pollution in places with PCB-containing transformers use or storage. When PCB-containing equipment is dismantled the risk of pollution sites loss is occurring, therefore the system of PCBs management should be created.

Based on the experience, a few steps may be recommended for PCB-contaminated sites revealing: identification of PCB-contaminated capacitors and transformers location, revealing the substations where PCB-containing capacitors are used in open air; revealing the places of equipment storage; inspection of enterprises and investigation of soil where PCB-containing transformers are used or stored. Legislative documents relating to the management of contaminated sites should be developed as soon as possible.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.16. Soil contamination in kitchen gardens of urban areas: the need for comprehensive approaches.

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Abstract

Collective gardens were studied in four different areas in Europe within the “Urban Soils” project: the Walloon region, Brussels, Paris and Manchester. Our study aimed at deciphering relationships between gardener practices, soil quality and perception of services provided by collective urban gardening. Three questionnaires dedicated respectively to motivation, usage and perceptions were set up and filled with the stakeholders: the garden management on the one side and the gardeners on the other side. Soil samples were taken on a voluntary basis in order to characterize soil fertility and metal contamination. Although every case study appeared specific, some soil results ask questions about safety of urban gardening. If investigations of sanitary risks can conclude to the need of remediation strategy in some situations, however, urban gardens also provide ecosystem services and health benefits that are not taken into consideration by sanitary assessment. We therefore plead for the development of more comprehensive approaches.

Keywords: Urban gardens, allotment, contaminations, ecosystemic services, sanitary risk, health benefits

Introduction, scope and main objectives

Urban agriculture and green infrastructures have been spreading worldwide in recent years due to a shift of the balance between urban and rural areas as living place for the people. More than a half of the population now lives in cities and population projections indicate that this pattern is expected to continue during the next 35 years (EUROSTAT, 2017). Simultaneously to the need to feed the urban people, there is a growing demand for self-production by the city dwellers, some for financial reasons others for social or environmental purposes. The development of urban gardens in Europe has faced at least four phases driven by industrialization, world wars, economic crisis and more recently need to reconnect with nature (Keshavarz and Bell, 2016). In that context, allotment

gardens have become a strategic stake in urban planning regarding economic, political, social and environmental issues (Eizenberg *et al.*, 2016).

The access to land for crop production is limited in most cities and collective gardens are typically places that allow people to practice agriculture. These places are owned by public authorities, private agencies or communities and can take a variety of forms. Besides food production, urban agriculture would contribute to ecosystemic services (Camps-Calvet *et al.*, 2016; Langemeyer *et al.*, 2016) and human health and well-being (Tzoulas *et al.*, 2007, Calvet-Mir *et al.*, 2016), through physical activity, healthy food consumption, stress reduction, and development of social contacts (Schram-Bijkerk *et al.*, 2018).

Ecosystemic services and soil quality are tightly linked as soil properties determine functions that soil can fulfill and contribute to human well-being through ecosystemic services (Adikhari and Hartemink, 2016). Classical structuration of services include provisioning, regulation, cultural and supporting services (MA, 2005). Food and fiber production, climate regulation, water regulation, pollination, recreation, regulation of nutrient cycles are examples of known services from urban agriculture. More and more research have been dedicated to the quantification of soil ecosystemic services and methods were proposed such as Rutgers *et al.* (2012) or Calvet-Mir *et al.* (2016). However, links between soil properties and soil functions/services are not always straightforward, soil data are often scarce and quantification of holistic functioning therefore faces strong difficulties which implies simplification of described processes.

The legal framework of gardens might also appear unclear. According to Schwartz *et al.* (2013) more than 50 articles of law applied on this specific kind of land use in France. However, health assessment is crucial in urban environment which are potentially contaminated (Schwartz, 2013; Swartjes, 2015) and there is no common set of standards nor methodology in Europe to evaluate sanitary risks linked to gardening on contaminated land.

Methodological framework are moreover needed to link urban green areas, ecosystem and human health (Tzoulas *et al.*, 2007). The Urban Soil Project, financed within the Snowman network, aimed at studying relationships between socio-economical drivers of collective urban gardening, agronomical practices, soil quality, ecosystemic services and dysservices and human health in some gardens of Western Europe (fig.1). This paper presents the first results of the field work (soil characterisation and questionnaire survey) and stresses the need for comprehensive consideration of the various issues in the decision-making processes about urban agriculture development.

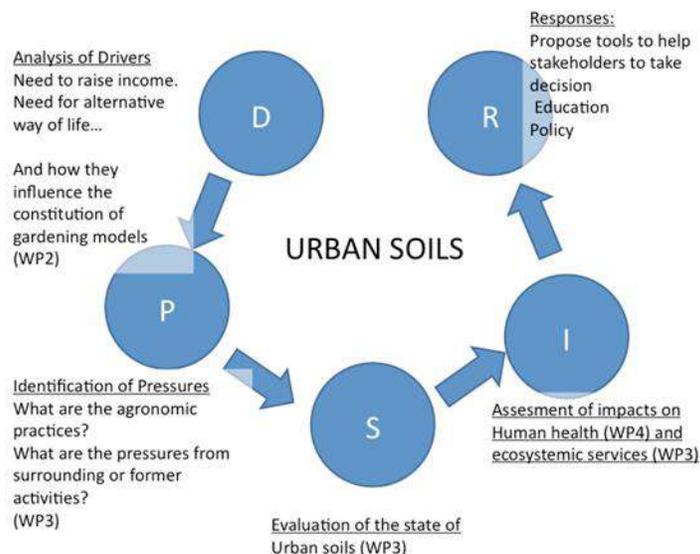


Figure 1. DPSIR framework of the URBAN SOILS project.

Methodology

The general methodology consisted in selecting study cases, surveying soil quality and gardeners view, gathering information in a database, producing status reports and analysing links between data in order to assess services and dysservices of gardens. Four study cases were selected according to the importance of collective gardening and of former or present industrialization of the urban centers and also depending on project feasibility: Brussels, Paris, Manchester and the Walloon region, which included two main industrial cities (Liège and Charleroi) and some smaller cities.

Gardens and plots within gardens were selected on a voluntary basis. Questionnaires were built in order to survey motivations, practices and feelings of gardeners about their activities and the environmental issues of urban gardening. Interpretation grids of the questions were also built. Fields were visited and soil samples taken by our team while questionnaires were either directly filled in during the visit or left to gardeners who had to send it later. The number of participants to the survey varied largely according to the study case and the diversity of type of collective gardens as well. Due to practical feasibility, only family gardens were surveyed in Paris and Manchester. Sixty-four, 16, 10 and 5 gardens were surveyed in Wallonia, Brussels, Paris and Manchester, respectively and more than 370 plots were soil sampled.

Soil analysis covered fertility - pH in 0,1N KCl, total organic carbon (TOC in g.100g⁻¹), available Ca, Mg, K and P (CH₃COONH₄+EDTA at pH 4.65) - and metal contamination – pseudototal (aqua regia) As, Cd, Cr, Cu, Hg, Ni, Pb and Zn and available Cd, Cu, Pb and Zn (CH₃COONH₄+EDTA at pH 4.65).

Soil interpretation was realized on the basis of standards for crop soils for fertility (Genot *et al.*, 2009) and of the legislation of the Walloon region related to soil contamination (SPW, 2009). References for residential use were taken (table 2).

The database was built under access software (Henquin, 2016).

Results and discussion

Soil Quality

The results for soil fertility are given in table 1. They indicate usually a pH close to neutral and high levels of organic matter and available nutrients. Differences of soil properties were very high between gardens and between study sites. Imbalanced cation ratios were numerous, higher than 90% of situations, indicating lack of knowledge from gardeners related to soil and agronomical practices (Schwartz, 2013; Schwartz *et al.*, 2013). Whatever the study case considered, the soil quality reflected the intensive nature of fertility management by gardeners which produce crops on small surfaces.

Table 1. Soil fertility status in collective garden plots: pHKCl, Total Organic Carbon, Available Ca, Mg, K and P. Proportion of nutrient imbalanced ratio

	pH	TOC (%)	P	K	Mg	Ca	Imbal. (%)
mg.100g ⁻¹							
<i>Walloon region (N=206)</i>							
Min.	4,17	0,68	1,1	6,2	7,8	91	92
Median	6,63	3,54	17,7	25,7	19,4	517	
Max.	7,37	14,2	106	206	99,2	3363	
<i>Brussels (N=50)</i>							
Min.	4,77	1,16	1,4	3,8	5,8	114	90
Median	6,54	2,02	18,5	22,0	12,4	414	
Max.	7,25	4,56	76,9	59,3	47,6	4105	
<i>Paris (N=90)</i>							
Min.	5,98	1,31	3,1	13,7	13,4	213	100
Median	7,20	2,46	12,3	31,2	30,0	1822	
Max.	7,46	6,54	72,8	88,7	67,6	4981	
<i>Manchester (N=22)</i>							
Min.	4,07	2,2	4,1	8,4	5,1	91	95
Median	5,82	5,8	14,1	23,9	15,1	366	
Max.	6,93	19,1	32,5	47,2	26,6	615	

The soil contamination status is summarized in table 2 for the entire dataset. Again variation is important between and within study cases according to origin of contamination (industrialization or gardeners practices). At some places in the Walloon region, the levels of contamination were so high that a detailed risk assesment had to be done at the end of the project. One of the most crucial metal was Pb content (Fig. 2).

Table 2. Interpretation values for metal contamination (total content in mg/kg): VR = reference value indicative of natural natural levels, VS = level above which a risk assesment is needed, VI: intervention value above which remediation operations should be implemented. Proportion of plots higher than thresholds.

Metals	VR	VS	VI	> VS (%)	> VI (%)
As	12	49	300	0	0
Cd	0,2	3	30	3	0
Cr	34	125	520	0	0
Cu	14	110	290	5	1
Hg	0,05	1	6	9	0
Ni	24	150	300	0	0
Pb	25	200	700	17	2
Zn	67	230	710	18	4

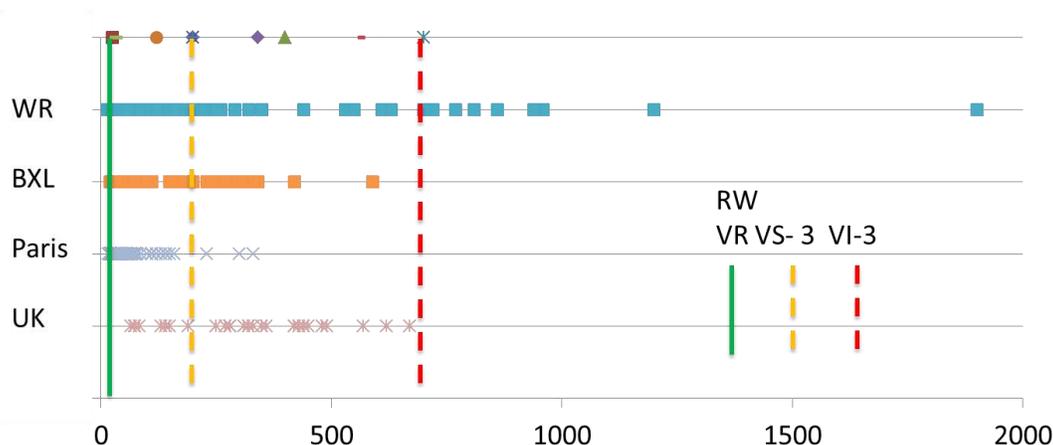


Figure 2. Pb content of Topsoil (mg.kg-1) in the 4 study cases of collective gardens according to Walloon Region limits for gardening: WR = Walloon Region, BXL = Brussels, UK = Manchester.

Gardens and gardeners

The results of the questionnaire were analyzed only for Wallonia and Brussels as only family plots were investigated in Paris and Manchester. Most of gardens are rather recent as 80% were installed less than 10 years ago. They cover a surface smaller than 5000m² and usually include less than 15-20 plots. The social importance of the project is affirmed (important motivation for 2 gardeners over 3). Finally, a typology of urban gardeners in collective gardens has being made available. It confirms that people are diverse but dominantly from higher education, either active or retired, male or female. Even if shared infrastructures exist, most plots are managed only by one or two persons at a time. One third of the gardeners do not till the soil. They use soil mulching and cover crops in winter. Organic fertilizers are widely used: composts, manure, natural organic conditioners and green manure. Eighty percent of gardeners declare following the regulation for organic agriculture. Most of them look for accessing food of better quality, social links, practicing physical activity and reducing stress (fig. 3).

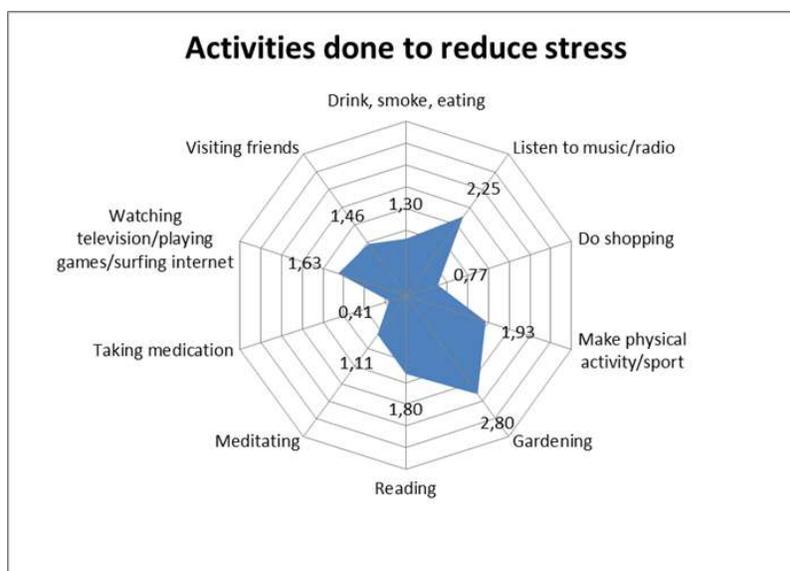


Figure 3. Activities done to reduce stress by gardeners from Wallonia and Brussels on a scale from 0 (never) to 4 (always).

Services and human health

Despite the potential dysservices of gardens to environment due to overfertilization and to human health due to soil contaminations, the gardens fulfill a lot of ecosystemic services which largely counterbalance these dysservices: production of food, climate regulation, soil structure improvement, health benefits of physical activity, social links... which confirms other studies (Boulianne *et al.*, 2010; van den Berg *et al.*, 2010; Boukharaeva and Marloie, 2015; Dennis and James, 2017). We made a semiquantitative assesment of ecosystem services on the basis of questionnaires and results of soil analysis (fig. 4). The methodology should be improved but first results show the importance of services other than food production.

Regarding health consideration, all the indicators that we used to assess physical health, physical activity, healthy food consumption, psychological health and community health (modified from Schram-Bijkerk *et al.*, 2018) tend to confirm the high levels of benefits for gardeners.

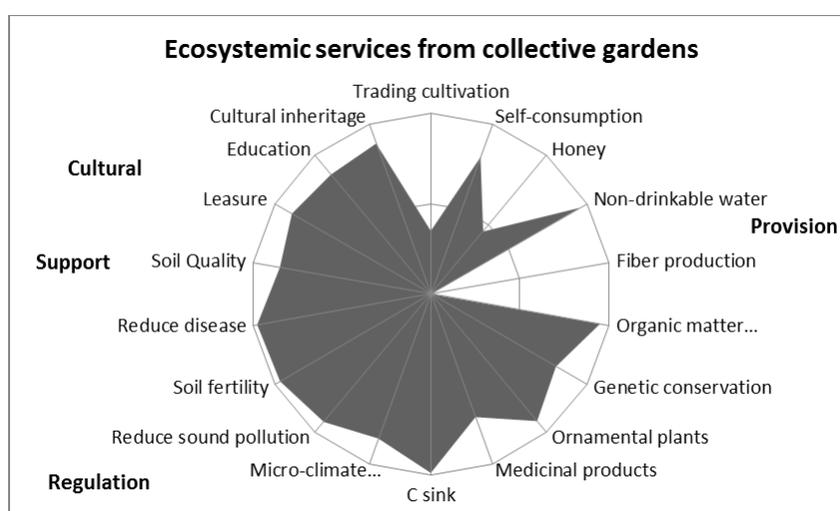


Figure 4. Assesment of ecosystemic services from collective gardens in Wallonia and Brussels on a scale from 0 to 100 (log scale) according to answers to questionnaires and soil analysis.

Conclusions

Our study focussed on collective gardens in urban environment in Wallonia, Brussels, Paris and Manchester. Through a questionnaire and soil survey, we got insights on the relationships between drivers of gardening, agronomical practices, state of soils and perceptions. It is clear that an approach based on a qualification of soils based on comparisons to environmental threshold values is not sufficient as social and health benefits are real even if they are difficult to quantify.

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1.2.17. Study of the spatial and temporal dynamics of heavy metals under the effect of hydrological erosion, wind and soil properties. J. Ressas mining environment case study in Tunisia

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Keywords: Heavy metals, mining activities, physic and chemical, Soil properties and quality.

Tunisia is a country with a long mining tradition, for several centuries. This activity is the result of a very extensive and extremely varied geological context (Phosphates, Lead / Zinc, Iron etc.). Important quantities of mine tailings made up of concentrated residues and waste rock are abandoned in several areas without worrying about their rehabilitation. Agricultural lands around many former Tunisian mines, despite the high risk of heavy metal contamination, are occupied by various plants and crops (Chakroun 2012).

The region of J. Ressas in Mornag holds an important mining past. In spite of the complete cessation of any activity of extraction of metals, this mining can pollute a long time the environment of the site under the effect of water and wind erosion causing soil dynamics. The physic and chemical analyses of soil of this region show a heavy metal effect and an important contamination, which pose problems that must be resolved.

The objectives of this study is to evaluate the Impact of mining project on soil quality and the effect of erosion on the movement of heavy metals on agricultural soils, fluvial transport and transfer of trace elements in the environment.

-The characterization of polluted soils downstream of the old jebel Ressas mining and the nature of this pollution.

-The environmental consequences of erosive processes on the transport of pollutants solid particles (soil), to rivers (Robert, 1996).

-The evaluation of the mobility of heavy metals and the risks of pollution.

- Evaluation of the spatial and temporal dynamics of heavy metals according to the physic and chemical properties of soils.

At the scale of agricultural catchments, the major processes and phenomena that influence the dynamic of heavy metals are alteration, erosion, runoff, physic and chemical parameters of the soils and finally the actions of agricultural practices.

Action 1: Characterization of the ETM pollution of agricultural soils J.ressas mining.

Action 2: Spatio-temporal natural dynamics of ETM in agricultural soils under the effect of erosion.

Methodology

It is important to know as the physical and chemical characteristics of the land using a sampling campaign; samples were taken from agricultural soils and residues in the mining site. The information obtained, at the surface of soil, provides a better understanding of the migration phenomena of the contaminants present. The main elements to be known and identified in the field are the surface features, the presence of buried structures, the geological and hydro geological context and the characteristics of the contamination (eg solubility, miscibility, etc.).

- 45 samples were carried out systematically in the form of a regular square grid of 250 meters. This method allows for uniform coverage of the field and facilitates data mapping and interpretation of analysis results by, for example, allowing longitudinal and cross-sectional profiles of contamination to be plotted. Geostatistics allows the analysis of linear data, correlated in space.

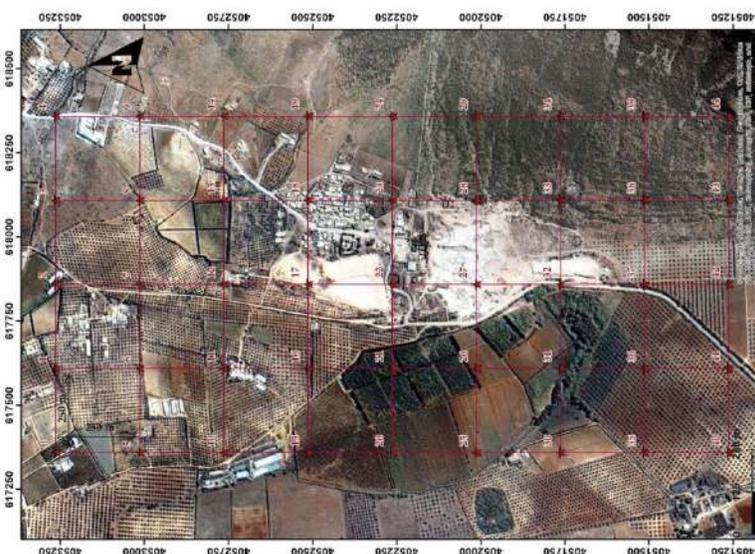


Figure 1. Sampling Plan

Laboratory studies focus on physical analyzes (Texture analysis, determination of total limestone and active limestone, and organic matter content), chemical (pH, conductivity, heavy metals) on representative soil samples at the mine tailing level and in soils.

Results

The spatial analysis of heavy metals in the sediment level shows a longitudinal evolution of this contamination by a clear increasing gradient towards tailing and the mountain contents. Pb, Zn, Cd are abnormally high. Downstream, the situation is gradually improving and leads to a decrease in the metal pollutant concentration. The spatial distribution maps obtained show that the lead pollution is greater spatially and quantitatively around the site. All the samples taken show that the Zn contents (up to 470 ppm), Pb (up to 5465 ppm) and Cd (up to 185 ppm) compared to the save soil (202 ppm Zn, 125 ppm Pb and 0.4 ppm Cd).

It can be noted, however, that samples taken from agricultural soils under NE-SW dominant wind directions revealed the highest levels.

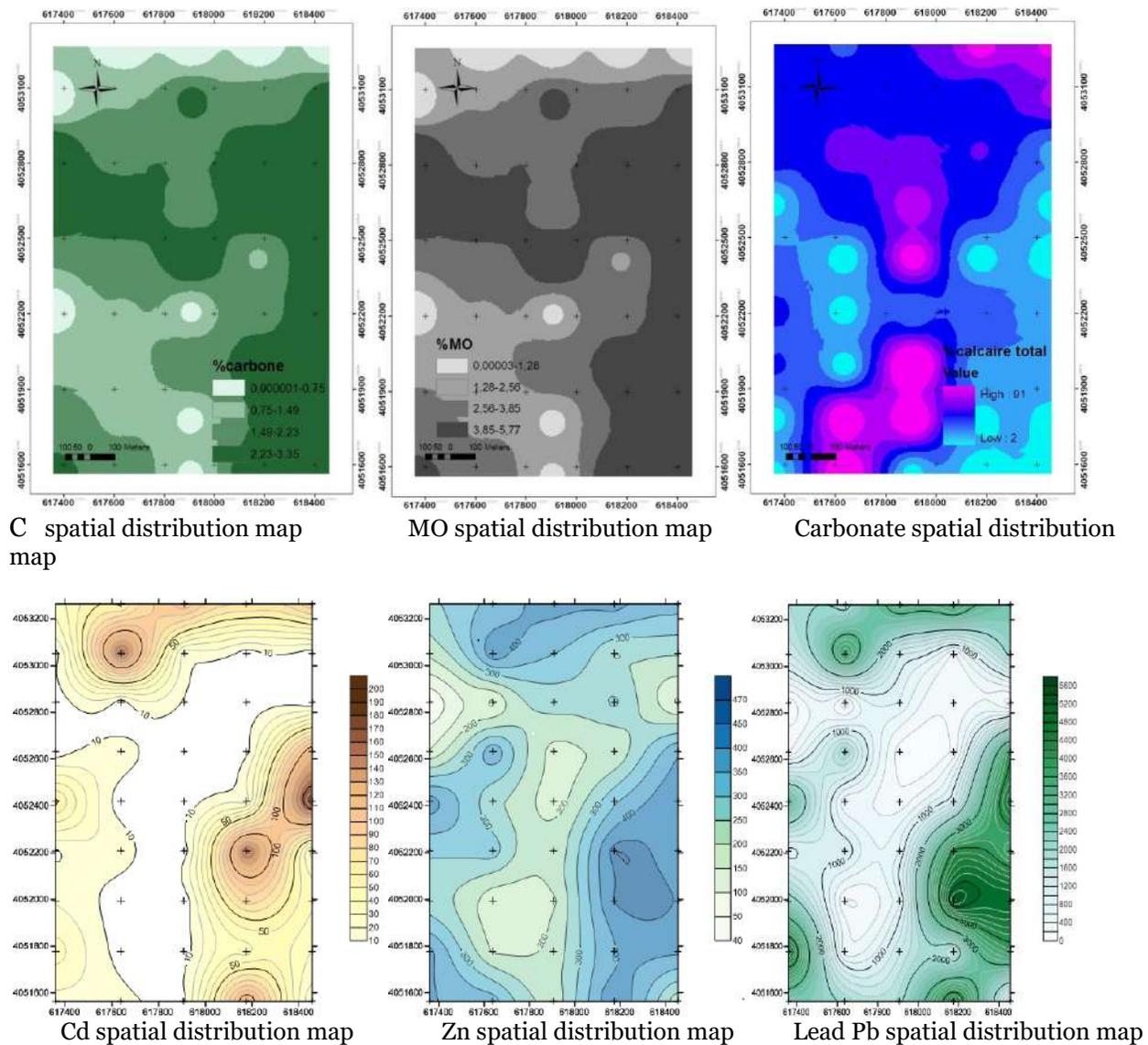


Figure 2. Thematic Maps were elaborated for each parameter

Conclusion

- The dynamics of the metallic trace elements is strongly influenced by the topography and the water circuit.
- These situations are good examples to illustrate the relationship between the functioning of the soil and the biogeochemical cycle of metals, in particular Zn (relatively mobile) and Pb (not very mobile).
- Indeed, when the contamination is moderate, these two elements are essentially accumulated in the plowed horizon

-Rehabilitation plan must project and applied in this are to ensure environmental and health protection.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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1.2.18. Effectiveness of hydroxyapatite, hematite and maghemite nanoparticles to reduce the available and dissolved As, Pb and Sb content in mine soils from Iberian Pyrite Belt (Portugal)

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Abstract

São Domingos mine is an abandoned mine in the Iberian Pyrite Belt (SW, Iberian Peninsula), which has large amounts of waste deposited in tailings. Weathering, causes sulphide oxidation, acid mine drainage, leaching of high levels of potentially hazardous elements (PHEs) and, consequently, environmental degradation of other ecosystems and surrounding areas. The use of hydroxyapatite (HANPs), hematite (HMNPs) and maghemite (MNP) nanoparticles (NPs) for the recovery of those degraded soils was assessed in this research. The extractable contents of As, Pb and Sb were determined in soils both treated with each NP and non-treated. Three different extractants based on CaCl₂ (0.01M), low molecular weight organic acids (LMWOA - 10mM) and ultrapure water were used. The extractable contents of Pb, As and Sb in the soil samples with NPs decreased and the HANPs retained most of the available and dissolved Pb. In addition, before and after being applied to the soil samples NPs were characterised in shape, size and elemental composition using High Resolution Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy (HR-TEM/EDS). As they were identified NPs associated to As, Pb and Sb in the soil samples, the high decrease in their availability was possible due to their association with the NPs, therefore these NPs can be used to reduce the mobility of PHEs in mine soils.

Keywords: Technosols, pollution, nanoremediation, potential hazardous elements, mobility, HR-TEM/EDS.

Introduction, scope and main objectives

Iberian Pyrite Belt (IPB) is a volcanogenic massive metallic sulphide ore deposits (Saez *et al.* 1999). As a result of mining activities in this area, weathering of metal sulphide-rich waste causes acid mine drainage and solubilisation of high levels of PHEs towards surface and subsurface waters, agricultural crops and living beings. The abandoned mine of São Domingos (Alentejo, Portugal) is one of the most important contaminated areas from IPB and an example of the consequences arose in this area. As a result, large nearby areas present degraded soils (Abreu *et al.* 2011).

Ecosystem restoration is advisable and possible in a long term; although, in the case of large disturbances, to go back to previous natural conditions is difficult or even impossible. Several techniques have been developed to address the problem of cleaning, restoring, rehabilitating or recovering contaminated soils. (Mirsal 2008, Singh and Prasad 2015).

Nanoremediation has emerged as a possible way for recovering contaminated soils. The higher efficiency and rate to recovery contaminated soils with the use of nanoamendments compared to the traditional amendments is due to a greater reactivity of NPs, as well as their easy distribution between soil pores (Liu and Lal 2012). Phosphate and iron NPs could be used as modifiers to act on

soils with high levels of PHEs as the general NPs characteristics -high reactivity, small size, large specific surface area and ease for being spreading in soils- suggest that they are possible tools for attaching PHE from soil solution thus reducing availability and mobility (Micháľková *et al.* 2014, Qiao *et al.* 2017). There are already studies focussed on using Fe oxide or phosphate NPs for water treatment (Gu *et al.* 2015, Hu *et al.* 2004) but for soil remediation they are still on process (Arenas-Lago *et al.* 2016, Qiao *et al.* 2017).

The objectives of this study are i) to study the usefulness of hydroxyapatite (HANPs), hematite (HMNPs) and maghemite (MNPs) nanoparticles to attach the available and dissolved PHE contents in soils from São Domingos mine, ii) to define the interactions between the NPs and PHEs by means of HR-TEM/EDS and iii) to assess the use of these NPs as possible option for recovering degraded soils.

Methodology

Material

This study was carried out with soils from São Domingos mine. Three different areas were selected and samples of soils developed on *gossans* and sulphide-rich wastes were taken from surface horizons (< 20 cm) (G1, G2, G3) (Fig. 1). Samples were split up for soil characterization and NPs treatment.

Three different NPS were applied to soil samples in order to investigate their influence on PHE availability: hydroxyapatite (HANPs) [MKN-HXAP-020P $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 20 nm], hematite (HMNPs) [NO-0055-SG-0500 Iron(III) oxide, 20-40 nm] and maghemite (MNPs) [NO-0053-HP-0500 gamma Iron(III) oxide, 20-40 nm].



Figure 1. Location of study area

Soil characterization

Soil samples were analysed for pH (Slattery *et al.* 1999); organic matter (Walkley and Black 1934); effective cation exchange capacity (ECEC) (Hendershot and Duquette 1986); oxide contents (Sherdrick and McKeague 1975); and pseudototal concentrations of PHEs by acid digestion (HNO_3/HCl) (1:3 v/v). Extractions were measured with ICP-OES.

Soil treatment with NPs

Suspensions of NPs were prepared (5 g NPs/L) following Liu and Lal (2012) and Liu and Zhao (2007). Soil samples were mixed with NPs (Ratio NPs:Soil=5%). Mixtures were shaken for homogenization for 10 days and stored in darkness. Each mixture was then dried (30 °C) and divided into three parts.

Extractable PHE content

Nine treated soil samples (dried mixtures of G1, G2 and G3 with HANPs, HMNPs and MNPs) and three non-treated soil samples (G1, G2 and G3) were analysed for determining the so-called available and soluble contents of PHEs.

0.01M CaCl₂ solution at soil pH according to Houba *et al.* (2000) and 10mM LMWOA (Feng *et al.* 2005) were used for extracting the so-called available content of PHEs and UPW was applied for the extraction of the soluble one. PHE concentrations in extracts of treated and non-treated soil samples were determined by ICP-OES.

The difference between the concentration of PHEs in the extracts of G1, G2 and G3 (no treated) and that from the treated samples was assumed as the quantity of PHEs attached to or retained by each corresponding NPs.

High Resolution Transmission Electron Microscopy (HR-TEM)

Samples were evaluated by HR-TEM with Energy Dispersive X-ray Spectroscopy (HR-TEM/EDS) in STEM mode with Z-contrast. Samples were prepared according to Yang *et al.* 2014.

Statistical analysis

Results were analysed using SPSS. ANOVA and Duncan's multiple range tests were used to compare the differences between soils. Kolmogorov-Smirnov and Levene tests were applied to check the normality and homogeneity of variances, respectively, in order to test their homoscedasticity. Data not satisfying these assumptions were analysed using Kruskal Wallis test ($p < 0.05$) and the Man-Whitney U-Test for comparison among areas.

Results

Soil characterization

The concentration of PHEs in soils and their characteristics are shown in Table 1.

Table 1. Soils characteristics.

Properties/Soil		Units	G1	G2	G3
pH(H ₂ O)			5.13b	4.17c	6.29a
Organic matter		mg kg ⁻¹	1.26a	0.43c	0.65b
FeOx		g kg ⁻¹	249.7a	261.2a	81.2b
MnOx			0.03a	0.02a	0.002b
AlOx			2.05a	2.04a	0.59b
ECEC		cmol(+)kg ⁻¹	7.80b	1.22c	11.85a
Exchangeable	Na ⁺	cmol(+)kg ⁻¹	0.34a	0.20a	0.26a
	K ⁺		0.14b	0.10b	1.97a
	Ca ²⁺		7.03a	0.53b	5.67a
	Mg ²⁺		0.28b	0.20b	3.95a
	Al ³⁺		0.01b	0.19a	<DL
Pseudototal content	As	mgkg ⁻¹	9575b	10799a	2548c
	Cr		20.03a	20.18a	18.62a
	Co		6.37a	6.42a	2.46b
	Pb		20506b	23003a	3052b
	Sb		475.3a	510.7a	137.0b
	Zn		93.91b	99.58a	25.21c

FeOx: Iron oxides, MnOx: Manganese oxides, AlOx: aluminium oxides, ECEC: Effective cation exchange capacity. DL: Detection limit. Values followed by different letters differ significantly with $p < 0.05$.

PHE extractable contents before and after treatment with NPs

Concentration of As, Pb and Sb removed from soil samples after the extraction with UPW, 0.01M CaCl₂ and LMWOA are shown in Table 2. Those of Cr, Co and Zn were below the detection limit, therefore they are omitted in the table.

Table 2. Extractable PHEs contents in soils: untreated (Ut) and treated with the different nanoparticles

PHE	Treatment	Extracted with	Extractable PHEs content (mg kg ⁻¹)			
			G1	G2	G3	
As	Ut	UPW	71.1(0.8)	7.5(0.5)	105.5(6.2)	
	HANPs		29.0(1.2)	0.1(<0.01)	54.6(7.3)	
	HMNPs		<DL	<DL	0.2(0.1)	
	MNPs		<DL	<DL	1.0(0.6)	
Pb	Ut		144.5(10.7)	131.3(3.7)	19.8(2.2)	
	HANPs		<DL	<DL	0.2(<0.01)	
	HMNPs		<DL	0.2(0.01)	0.5(0.1)	
	MNPs		2.9(0.7)	4.8(0.5)	2.0(0.1)	
Sb	Ut		20.8(3.1)	<DL	3.3(0.7)	
	HANPs		1.2(0.3)	<DL	<DL	
	HMNPs		0.2(<0.01)	<DL	0.1(<0.01)	
	MNPs		0.5(0.2)	<DL	<DL	
As	Ut		CaCl ₂	6.2(0.9)	<DL	26.2(2.1)
	HANPs			0.8(0.4)	<DL	18.9(0.2)
	HMNPs			0.7(<0.01)	<DL	1.0(<0.01)
	MNPs			0.1(<0.01)	<DL	<DL
Pb	Ut	4.4(0.4)		221.4(4.1)	<DL	
	HANPs	<DL		<DL	<DL	
	HMNPs	<DL		83.7(2.8)	<DL	
	MNPs	3.8(0.4)		210.0(1.3)	<DL	
Sb	Ut	0.8(0.01)		0.4(0.1)	0.8(0.1)	

	HANPs		0.7(0.2)	0.2(0.1)	0.2(0.1)
	HMNPs		0.7(0.2)	0.2(0.1)	0.1(<0.01)
	MNPs		0.2(<0.01)	0.1(<0.01)	0.5(0.2)
As	Ut	LMWOA	23.1(0.8)	28.3(0.5)	221.4(9.2)
	HANPs		20.1(0.5)	8.2(4.0)	163.0(3.3)
	HMNPs		3.5(0.6)	0.7(0.2)	20.6(0.7)
	MNPs		3.9(0.7)	1.3(0.2)	41.1(0.2)
Pb	Ut		21.2(1.2)	376.9(13.9)	4.1(0.2)
	HANPs		<DL	<DL	<DL
	HMNPs		7.8(0.2)	78.0(12.7)	<DL
	MNPs		7.2(0.7)	147(2.8)	<DL
Sb	Ut		5.5(0.6)	6.9(0.6)	2.7(0.1)
	HANPs		4.8(0.2)	2.0(1.1)	2.5(0.4)
	HMNPs		3.8(0.2)	3.5(0.2)	2.4(0.3)
	MNPs		4.2(0.2)	3.3(0.4)	1.4(0.1)

Mean values (n=3) and standard deviation in brackets. DL: detection limit.

HR-TEM/EDS

To prove the effectiveness of NPs retaining PHEs and for determining the location, size, morphology and interaction of NPs with PHEs, both NPs alone and treated samples were examined by HR-TEM/EDS.

Fig. 2 shows the HR-TEM images and the respective EDS of samples of NPs used.

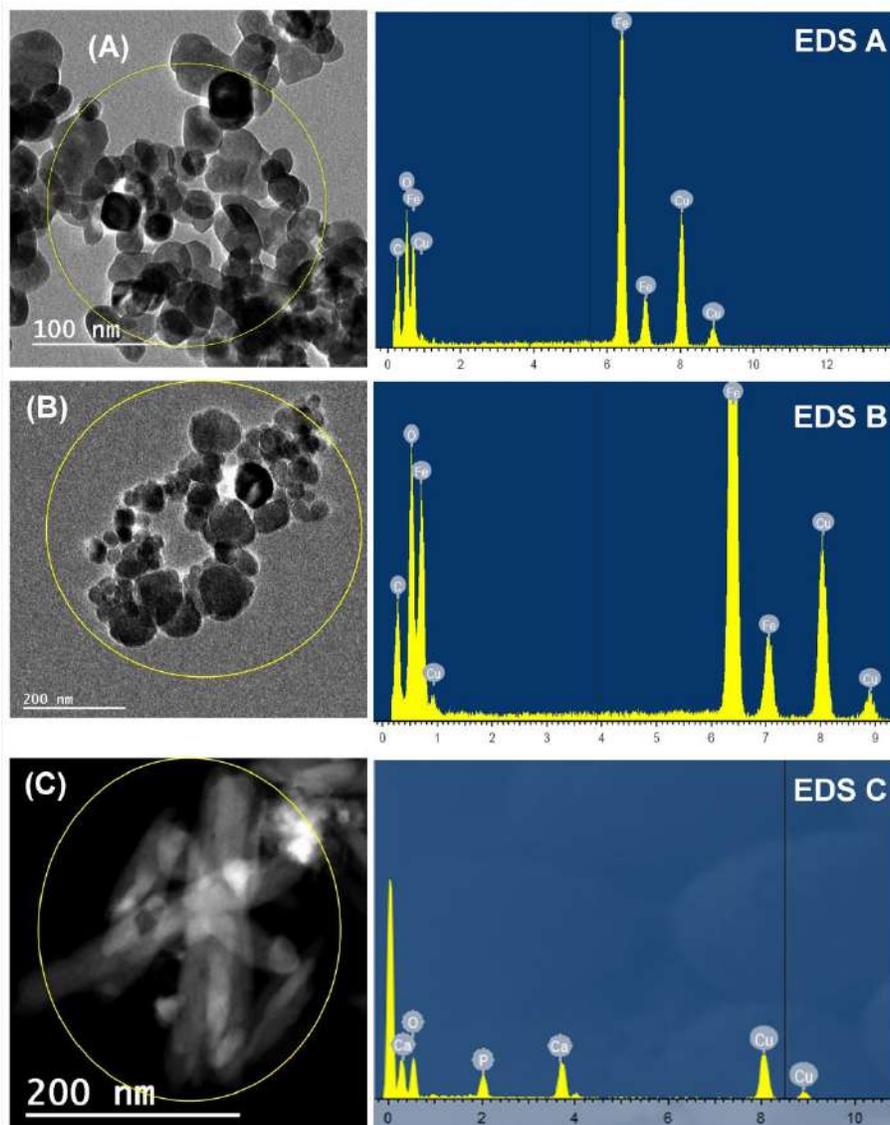


Figure 2. HR-TEM images and its corresponding EDS of: A) HMNP; B) MNP and C) HANP.

Figures 3 and 4 are illustrative examples of HR-TEM images of soil samples with NPs retaining PHEs.

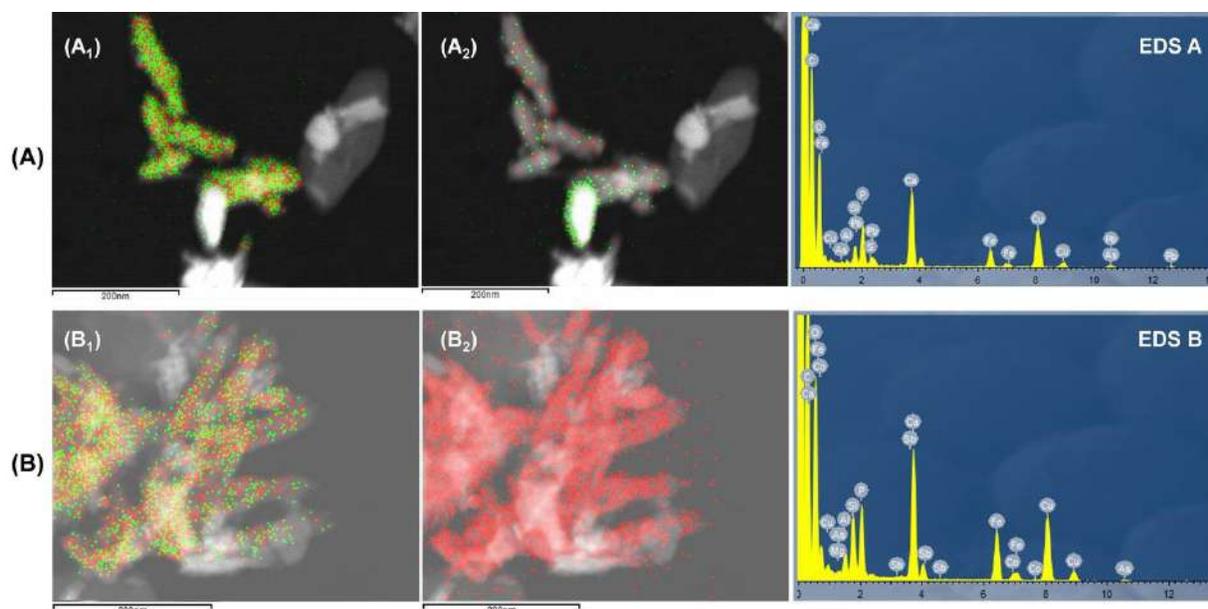


Figure 3. HR-TEM/EDS results from: (A) G1 using H₂O as extractant with: (A₁) HANP in the soil (Ca: red dots; P: green dots and their overlapping: yellow dots) and (A₂) HANP in the soil with PHEs distribution (As: red dots; Pb: green dots); (B) G1 using H₂O as extractant with: (B₁) HANP in the soil (Ca: red dots; P: green dots and their overlapping: yellow dots) and (B₂) HANP in the soil with Sb distribution (red dots).

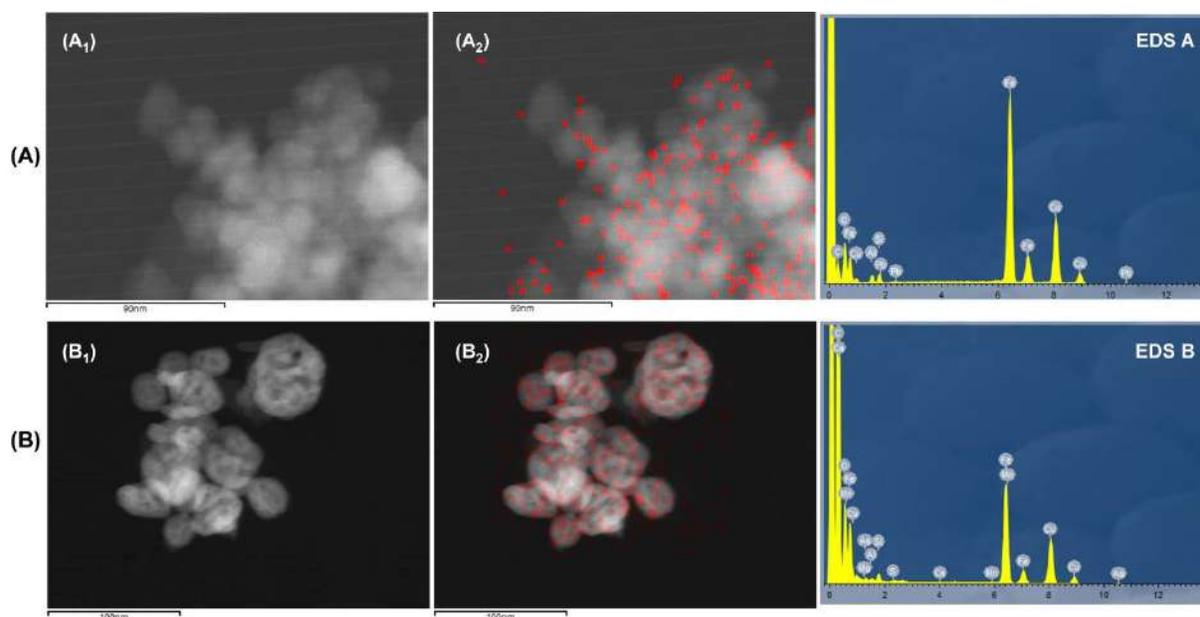


Figure 4. HR-TEM/EDS results from: (A) G2 using LMWOA as extractant with: (A₁) HMNP in the soil, (A₂) HMNP in the soil with the distribution of Pb (red dots); (B) G3 using H₂O as extractant with: (B₁) MNP in the soil and (B₂) MNP in the soil with the distribution of As (red dots).

Discussion

PHE concentrations analysed in soils are very high, mainly for Pb, Sb and As, in G1 and G2. Soil pH indicates that G1, G2 and G3 soils are strong, extreme and slightly acidic, respectively and ECEC are low (<12 cmol₍₊₎ kg⁻¹). Organic matter and Mn and Al oxides contents are low while Fe oxides are very high in all samples. These characteristics do not favour the development of an optimal vegetation cover in São Domingos mine (Perez-Lopez *et al.* 2008).

The fractions defined as available and dissolved (removed by the three different reactants) were low when comparing with the corresponding pseudototal content (<9% in all cases) but the amount released is high. Nevertheless, the oxidizing conditions, the high sulphide content and the low pH of soils and *gossans* of São Domingos favour the mobilization of high PHE contents causing pollution problems in nearby rivers and aquifers (Abreu *et al.* 2011). After the extraction with UPW, CaCl₂ or LMWOA, the average concentration of As released was 54.4 mg kg⁻¹ and the maximum 221.4 mg kg⁻¹. The average concentration of Pb released was 102.6 mg kg⁻¹ and the highest concentration corresponded to G2 with LMWOA (376.9 mg kg⁻¹). For Sb, the average of the amount released (4.6 mg kg⁻¹) was lower than for Pb and As, and only the concentration released from G1 after UPW extraction is higher than 10 mg kg⁻¹. These results agree with those of Fu *et al.* (2016) who found differences in mobility and bioavailability between As and Sb in soils and tailings from China, suggesting that mobility of Sb was lower than that of As.

After treatments with the NPs, results showed that, generally, the operationally defined soluble and available contents of As, Pb and Sb were significantly reduced, regardless of the extractant and the kind of NPs. The decrease of Pb availability was found higher than 99% in HANPs-treated soils regardless of extractant used, indicating the effectiveness of these NPs to fix Pb.

Although in a lesser extent, the availability of Pb after the treatment with HMNPs and MNPs was reduced ranging between 61-99% after the extraction with LMWOA and between 5.1-99% after CaCl₂ extraction. Moreover, between 90-100% of dissolved Pb content, determined after UPW extraction, was removed from the soil solution when HMNPs and MNPs were applied. These results indicate that iron oxides NPs are effective for reducing the availability of different PHEs in polluted soils (Michalkova *et al.* 2014, Shipley *et al.* 2013).

When soils were treated with HMNPs or MNPs more than 81% of the dissolved and available contents of As decreased. Accordingly to this, Shipley *et al.* (2011) indicated that MNPs can be used to remove As from contaminated soils, being a partial irreversible sorption the main mechanism to retain As.

HANPs seem to have different effect as after being applied the As concentration extracted with LMWOA was reduced by 13% (G1), 26.4% (G3) and 71% (G2) and the one extracted with CaCl₂ by 27.9% (G3) and 87.1% (G1). Although higher than with LMWOA or CaCl₂ extractions, As released after HANPs treatment and UPW extractions accounts for 48.3% (G3), 59.2% (G1) and 98.7% (G2).

The concentration of Sb in the aqueous extract was reduced between 94% (G1 and HANPs) and 100% (G3 and HANPs or MNPs) regardless of the NPs used. Instead, after CaCl₂ or LMWOA extractions, the available contents of Sb were within a wider range. According to CaCl₂ extractions, the highest availability reduction (>70%) happened in G3 when was treated with HANPs or HMNPs; and in G1 and G2 when were treated with MNPs. Taking into account results from LMWOA experiments, the highest availability reduction of Sb occurred in G2 after being treated with HANPs (Table 2) and the lowest decrease (<20%) was detected in G1 after both HANPs and HMNPs treatment. Focussing on data from CaCl₂ extractions the Sb available contents in G1 and G3 samples after HANPs treatment and in the latter after HMPNs treatment are similar to those without treatment (less than 20% of availability reduction).

In spite of this low decrease of availability and because the pseudototal contents of Sb, especially in G1 and G3, are low when comparing with those of As or Pb, in general the NPs applied have reduced the available or dissolved contents of PHEs in the soil samples. As an average and regardless NPs treatment, the concentration of As, Pb and Sb in UPW extractions was reduced by

89.4, 97.8 and 98%, respectively. After 0.01M CaCl₂ and LMWOA experiments the available contents were reduced respectively by 83-71.5% (As); 63.5-85.5% (Pb) and 52.8-34% (Sb).

The above results were confirmed with the analysis of NPs and treated soil samples with NPs by HR-TEM/EDS. Figure 2 shows the different NPs used in this study. Figure 2A shows a semi-spherical shape ranging from 20-40 nm diameter of HMNPs and the Fe and O peaks EDS spectrum demonstrate their elemental composition. Figure 2B shows a set of MNPs, with similar description as HMPNPs. HANPs are filamentous with a size varying between 20-150 nm with Ca, P and O in its composition according to the peaks from the EDS spectrum (Figure 2C).

Figure 3A₁ shows the location of HANPs in G1 soil and the red and green points are Ca and P of NPs as both signals overlap (yellow areas). Additionally, in the same areas of HANPs they were identified (Figure 3A₂) signals of As (red dots) and Pb (green dots) supporting that they are associated with NPs after treatment. EDS confirmed the elemental composition of the NPs, as well as the presence of Pb and As. There are visible areas not related to HANPs with As and Pb still associated with other components of the soils. Figure 3B₁ shows HANPs in G1 soil, the distribution of Ca (red dots) and P (green dots) from the NPs and the interaction of both signals (yellow dots). Figure 3B₂ shows signals from Sb (red dots) and its distribution is related with HANPs. The EDS indicated the elemental composition of the nanoparticles (Ca, P and O peaks) and the presence of Sb in the HR-TEM image, therefore the association between HANPs and Sb was confirmed.

Figure 4A₁ shows the results obtained from G2 sample after LMWOA treatment with HMNPs and MNPs. The semi-circular shape and size of the HMNPs did not change after treatment and the distribution of Pb (red dots in Figure 4A₂) is in the same area as the HMNPs. The EDS indicates the presence of Pb and Fe from NPs composition. Figure 4B₁ shows the HR-TEM image of MNPs in G3 soil after UPW treatment. NPs did not change after treatment and the distribution of As (red dots) and their location are related to the area of the MNPs (Figure 4B₁) what indicates that released As is retained by the MNPs.

The HR-TEM/EDS technique allowed understanding the association of the most readily available As, Pb and Sb with studied NPs since it was possible to visualize the agglomerates or precipitates as already indicated Arenas-Lago *et al.* (2016). Results shown that As, Pb and Sb can either be surface adsorbed, co-precipitated or incorporated into the nanoparticles (Fe)-oxide structure.

Conclusions

The results obtained indicate that nanoremediation can be a tool for the in situ remediation of mine soils from Iberian Pyrite Belt or soils with similar characteristics. Besides, this technique could be complementary and combined with techniques of phytostabilization as indicated by previous studies conducted in the area. However, before its widespread application in-situ, more research is needed to know the possible impacts, as well as the environmental fate of these nanoparticles in mining areas, above all, deepening into the different associations, compounds or aggregates between PHEs and NPs, as well as their stability.

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Sub-theme 2.1: Soil pollution and food safety

2.1.1. Strategies for reducing cadmium and arsenic in rice

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Abstract

Rice (*Oryza sativa* L.) is a major dietary source of not only cadmium (Cd) but also inorganic arsenic (iAs) in populations that consume rice as a staple food. When rice is cultivated under aerobic conditions, Cd in the paddy soil is solubilized and is more likely to accumulate in the grain, whereas under flooded conditions, iAs is more likely to accumulate. The application of intermittent irrigation, consisting of three days of flooding and several days of drainage, during the heading stage of rice growth was effective for simultaneously decreasing Cd and iAs accumulation, without negative effects on grain yield and quality. An alternative and promising strategy is a combination of water management and soil amendment to reduce Cd and iAs absorption. Growing a low-Cd accumulating cultivar under aerobic conditions is the most practical way to simultaneously reduce Cd and iAs contents in rice.

Keywords: Cadmium, Arsenic, Inorganic arsenic, Arsenite, Rice, Water management, Soil amendment, Low-Cd cultivar, OsPCS1

Introduction, scope and main objectives

Soil pollution by Cd has been of public concern since the 1970s, when chronic Cd poisoning (*Itai-itai* disease) was reported in the Cd-polluted Jinzu River basin of Toyama Prefecture, Japan (Aoshima, 2016). In this region, as part of an intervention program, soil replacement of polluted rice paddy fields was conducted from 1980 until completion in 2012 (Toyama Prefectural Itai-itai Disease Museum, 2012). Cd is toxic to humans at lower concentrations than it is to plants because its effects on humans are cumulative. Rice is a staple crop in Asia, and it is the principal source of dietary Cd intake in the Japanese population; therefore, minimizing Cd intake from rice is an important health issue. Approximately 40% of the Japanese Cd intake is derived from rice (Ministry of Agriculture, Forestry and Fisheries of Japan, 2016).

As is a metalloid with diverse organic and inorganic forms that are widely distributed in water, soil, and air. iAs is a nonthreshold, class 1 carcinogen in humans, based on epidemiologic studies in groundwater-contaminated regions. While there is concern about the health risks associated with high levels of iAs in drinking water in many parts of the world, rice is the largest dietary source of this compound for populations not affected by elevated iAs levels in water. A market-basket study indicated that, in Japan, cereals contributed the most to the total daily intake of iAs and that 97% of the iAs intake from cereals originated from rice and rice cake consumption (Oguri *et al.* 2014).

When rice plants are cultivated under aerobic conditions, Cd in the paddy soil is more easily solubilized and accumulated in the grain. In contrast, under flooded conditions, more iAs accumulates in rice (Arao *et al.* 2009) because paddy cultivation mobilizes it in the soil through the reductive dissolution of iron (Fe) oxide, and the subsequent reduction of As(V) to the more

bioavailable As(III) (Takahashi *et al.* 2004). We examined the abilities of different water regimes, agricultural materials, and rice genotypes, to simultaneously reduce Cd and As in rice grains.

Methodology

Water management

Field experiments were conducted to investigate the optimal soil Eh and pH conditions for simultaneously decreasing Cd and iAs accumulation in rice (Honma *et al.* 2016). Water management during the experiments included continuous flooding and intermittent irrigation at different intervals after midseason drainage.

Amendments

We applied three Fe-bearing materials, including zero-valent iron (ZVI), non-crystalline iron hydroxide (FH), and steel converter furnace slag (SCS), to paddy fields with submerged cultivation and examined the possibility of a simultaneous decrease in Cd and As in the rice grains (Makino *et al.* 2016). The effects were analyzed in relation to the As concentration in the soil solution, as well as brown rice yield and quality.

Rice cultivars that absorb little amount of Cd

A japonica rice mutant with nearly undetectable Cd levels in the grain was produced (Ishikawa *et al.* 2012). The name 'Koshihikari Kan No. 1' was chosen for the cultivar, and in 2015, it was registered in Japan. This cultivar and its parent 'Koshihikari', the most popular cultivar in Japan, were grown in paddy fields with different soil properties under three water regimes: flooded conditions (FLD), with flooding for 2 or 3 weeks before and after heading; alternate wetting and drying conditions (AWD), with re-flooding of the soil just after the disappearance of ponding water; and water-saving conditions (WAS), with irrigation water re-applied after the drying of the soil surface (Ishikawa *et al.* 2016). For WAS, the duration of the dry-soil period in one cycle ranged from 2 to 7 days, depending on the water-holding capacity of the soil at each site.

Results

Water management

Intermittent irrigation with three days of flooding and five days of drainage was effective at simultaneously decreasing Cd and iAs accumulation in rice grains (Honma *et al.* 2016). The Eh, pH, and dissolved As, Cd, and Fe(II) concentrations were strongly affected by the water management practices. Neither the grain yield nor the rice plant growth significantly differed among the plots. Water management did not affect grain quality. In practical situations, the efficiency of the water management practices may be affected by the size of the paddy field due to a possible delay in drainage. Further research is needed to confirm if the optimal irrigation interval is widely applicable across different soil types, weather conditions, and Cd and As concentrations in soils.

Amendments

In experiments conducted in paddy fields in six regions in Japan, the As concentration in the soil solution during the cultivation period decreased in the following order: control > SCS > FH > ZVI (Makino *et al.* 2016). Arsenic concentrations in brown rice followed the same order, with the application of ZVI achieving a particularly strong reduction. Cd concentrations were low due to the submerged cultivation conditions. The application of Fe-bearing materials slightly and non-

significantly reduced the grain and straw yields. The application of these materials did not have a significant negative impact on rice quality. These data indicate that the application of Fe-bearing materials effectively reduces As concentrations in the soil solution and rice grain without negative effects on yield and quality and with a particularly powerful effect of ZVI, which is possibly explained by As sulfide formation.

Rice cultivars that absorb little amount of Cd

The application of FLD for several weeks before and after heading significantly increased the grain As concentrations in both rice cultivars. The AWD regime, whereby the soil was re-flooded just after the disappearance of ponding water, reduced the grain As concentrations by an average of 27% relative to those under FLD for both cultivars. The WAS regime, with irrigation after the drying of the soil surface, decreased the grain As concentrations by an average of 43-48% compared with FLD. Although WAS remarkably increased grain Cd concentrations in the 'Koshihikari' cultivar, the 'Koshihikari Kan No. 1' cultivar had nearly undetectable levels of grain Cd in all treatments (Fig. 1, Ishikawa *et al.* 2016). Although aerobic conditions such as WAS had slightly adverse effects on grain yield and quality, growing the low-Cd cultivar aerobically was the most practical way to simultaneously reduce Cd and As contents in the rice grain.

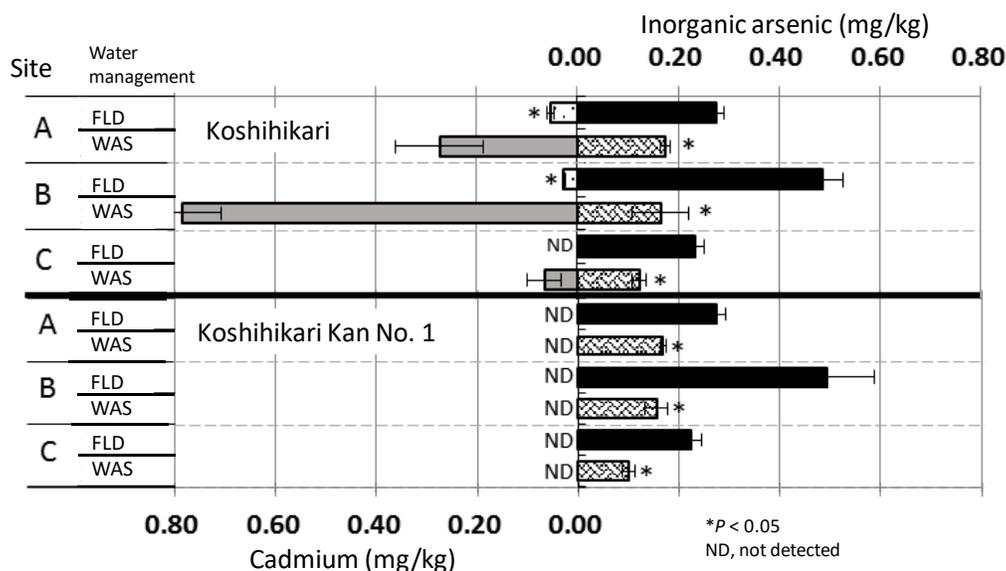


Figure 7. Effects of the water regimes (FLD: flooded conditions; WAS: water-saving conditions) on inorganic arsenic and cadmium concentrations in brown rice grains of 'Koshihikari' and 'Koshihikari Kan No. 1' cultivars.

Discussion

Air-filled porosity (AFP) of soil is a key to reducing dissolved Cd and As concentrations in paddy soils (Nakamura *et al.* 2018). Intermittent irrigation practices which realize a maximum AFP slightly above the threshold value for As immobilization have the potential to immobilize dissolved As while minimizing the development of dissolved Cd. Extensive field studies are in progress to verify the relationships between temporarily varying AFP and dissolved Cd and As concentrations, and to examine whether water management strategies based on AFP are feasible under field conditions for reducing Cd and As concentrations in rice grains.

The daily management of water supply and drainage in rice fields with intermittent irrigation is a heavy burden for farmers. A new water control system that allows the remote control and the automatic monitoring of water supply and drainage in rice paddy fields using a smartphone or PC has been developed (Institute for Rural Engineering, NARO. 2017). With this system, saving labor in water management can be possible.

The selection and breeding of low As-accumulating cultivars is also a practical option for reducing the risk of As contamination in rice. We produced transgenic lines over-expressing the phytochelatin synthase gene *OsPCS1*, and these lines were cultured in paddy soil or hydroponics. The result showed that total As levels in grains were significantly lower in the *OsPCS1* over-expressing lines than in the wild-type (Hayashi *et al.*, 2017). We may be able to create low-As rice without the control of a strong constitutive promoter (*CaMV 35S*) if the gene-editing can modify the endogenous *OsPCS1* expression.

Another important finding is the effect of high air temperature after heading of rice on the iAs concentration of grain (Arao *et al.* 2018). Global warming will increase temperatures in rice-growing areas, which could result in higher concentrations of iAs in rice grain. Late or early transplanting to avoid high air temperatures around the heading stage of rice could be a countermeasure.

Conclusions

To reduce Cd and As levels in rice, we proposed three strategies: I) intermittent irrigation, II) application of Fe-bearing materials to paddy fields with submerged cultivation, and III) aerobic growth of the low-Cd cultivar. Strategy III is the most practical way to simultaneously reduce Cd and As contents in the rice grains.

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2.1.2. Prevalence of Antibiotic Resistant Bacteria in poultry litter based manures and potential threats on food safety for carrot (*Dacus carotova*)

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Abstract

Due to high antibiotic usage in poultry industry there is a risk of contaminating soils with antibiotic resistance determinants when poultry manure (PM) is applied. Vegetables like carrot (*Dacus carotova*) that use in fresh-cut produce could be linked to spread of antibiotic resistance along food-chain. A study was conducted to investigate the abundance and diversity of antibiotic resistant bacteria (ARB) in freshly removed poultry litter (PL) and PM, and root environment of carrot grown in PM treated soils. The presence of ARB in carrot sold in market and traits of selected ARB isolated from PL, PM and carrots were also studied. Freshly removed PL from 36 broiler farms and five PM piles were sampled and analyzed for bacteria resistant to 10 ppm tetracycline (TC) and enrofloxacin (EN). Soil samples were collected from two adjacent fields (Soil type: Typic Paleudults) with different manure application histories (3 years-SH; 10 years-LH) and used in a pot experiment to assess the effect of antibiotic inputs (as PM and TC) on TC resistant epiphytic and endophytic bacteria (EEB) in carrot. TC resistant endophytic bacteria were analyzed in carrot collected from sales points in Kandy municipal area (n=30). Selected isolates were characterized for minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC), and multiple drug resistance (MDR). ARB in PL resistant to 10 ppm TC and EN ranged from 3.58 to 10.48 log₁₀ CFU/g and 0.96 to 9.86 log₁₀ CFU/g, respectively. Application of PM increased the abundance of TC resistant EEB significantly in LH compared to SH. MDR prevalence was higher among ARB from PL (30%) than carrot roots (12%). High MIC and MBC (>128 ppm) were observed for majority of ARB. The study confirmed that poultry litter and manure are carriers of antibiotic resistance to soils and continuous application of PM to soil increase prevalence of antibiotic resistant EEB in carrot.

Keywords: Antibiotic resistant bacteria, Poultry litter, Tetracycline, Endophytes, Epiphytes, Carrot

Introduction, scope and main objectives

The increase of bacterial resistance to antimicrobial drugs is one of the most serious emerging threats to public health globally. Excessive use of antibiotics in hospitals, households and agriculture creates a selective pressure for the emergence and spread of antibiotic resistance traits among microorganisms (Van Boeckel *et al.*, 2014). The antibiotic residues and the antibiotic resistant gut-flora excreted by farm animals could serve as determinants of spread of antibiotic resistance in the environment (Martinez 2009; Marti *et al.*, 2013). Thus, the use of animal manure has serious implications on safety and quality food for human consumption, especially for vegetables that are consumed raw such as carrot (Marti *et al.*, 2013).

Approximately 80% of poultry farms in Sri Lanka operate at commercial scale and use variety of antimicrobials. The bedding material (poultry litter) disposed with each batch of broiler chicken (at 42 days) is either burnt or sold to farmers who cultivate vegetables (Herath *et al.*, 2015). The common practice is to keep poultry litter (PL) piled up for one to two months to cure in the field or at poultry farm before applying to field as poultry manure (PM) (Herath *et al.*, 2015). Therefore, if the litter contain antibiotic resistance determinants these could spread in the environment with surface runoff and leaching from the pile even before incorporating to soil with the application of PM (Martinez 2009). When the agricultural produce is sold away from the point it is produced the contaminants can spread across geographic barriers. However, the background resistance levels and resilience of microbial communities in soils to antibiotic resistance determinants could play an important role in transmitting antibiotic resistance traits in the environment (Schmitt *et al.*, 2006; Popowska *et al.*, 2010).

The PM used by farmers from intensive vegetable based cropping system in Nuwara Eliya in upcountry of Sri Lanka originates from the PL disposed from poultry farms in Kandy, Kurunegala and Gampaha districts located in the mid and low country of Sri Lanka. The exotic vegetables like carrot (*Dacus carotova*) is largely produced in Nuwara Eliya and sold throughout the country. Therefore, to assess the contribution of PM in antibiotic resistance development in the environment and develop policies to better manage antibiotics in animal husbandry it is important to study the level of contamination of PL and PM with antibiotic resistance determinants and the potential risk of transferring these determinants that enter to soil through food chain.

Thus, a study was conducted with following objectives: 1) investigate the abundance of antibiotic resistant bacteria (ARB) in freshly removed PL from commercial scale broiler farms and PM available in farm fields; 2) assess the effect of PM usage on populations of ARB colonizing the root environment of carrot; 3) assess the prevalence of ARB in endo-rhizosphere of carrot sold in market; 4) characterize the antibiotic resistance traits of selected bacterial isolates obtain from PL, PM and carrot root environment.

Methodology

Fresh PL samples were collected from 36 commercial scale broiler farms (22 buy back farms and 3 closed house farms operating under six large companies and 11 medium scale farms selling the produce locally) distributed in Kandy, Gampaha and Kurunegala districts, Sri Lanka during September to November 2015. A questionnaire survey was conducted with the poultry farmers to gather information on antibiotic usage and their knowledge about residual effects and other impacts of antibiotics. Manure samples were collected from five PM piles in five fields ready for vegetable cultivation in Kandy district. Farmers purchased PL from medium scale broiler farms located in Kandy district and allowed to cure them in the field in piles. The abundance of ARB in PL and PM were assessed by enumerating bacteria in Tryptic Soy Agar (TSA) spiked with 0 and 10 ppm tetracycline and enrofloxacin separately.

Soil samples were collected at 0-20 cm depth from two adjacent fields (Soil type: Typic Paleudults) with different manure application histories (3 years-SH and 10 years-LH) representing vegetable based intensively cultivated cropping system in Nuwara Eliya district, Sri Lanka. Soils were treated with PM (10 % w/w) and tetracycline (10 and 100 ppm) and used in a greenhouse pot experiment. An un-amended soil was used as control. Nutrients were supplied equally in all treatments considering the amounts added through PM. Carrot was seeded and seedling were thinned to one plant per pot, and 3 months after germination epiphytic and

endophytic bacteria (EEB) of carrot roots were enumerated on TSA plates spiked with 0, 1, and 10 ppm tetracycline (Surette *et. al.*, 2003; Yrjala *et al.*, 2010).

Different vegetable sales points in Kandy municipal council including supermarkets, small boutiques and roadside vendors were visited over a period of two weeks in September 2015 and 30 carrot samples (each about 250 g) were collected. Endophytic bacteria were enumerated on TSA plates spiked with 0 and 1 ppm tetracycline (Surette *et. al.*, 2003). Selected bacterial isolates from PL (n=24), PM (n=6) and carrot root environment (n=24) were characterized for antibiotic resistance. Gram staining and basic morphological characterization was performed. Minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) of tetracycline was assessed (Andrews, 2001). Multiple drug resistance (MDR) was determined via disk diffusion test (Tetracycline-30µg; Enrofloxacin-5µg; and Neomycin-30µg) following standard procedures.

MINITAB (version 16) statistical software was used for statistical analysis. Analysis of variance (ANOVA) with GLM procedure was used to determine significance of the effect of history of manure application and treatments on measured parameters of EEB populations in carrot and Tukey's mean comparison was performed at $P < 0.05$.

Results

Antibiotic resistant bacteria in poultry litter and manure

All poultry farmers participated in the study used antibiotics as a sub-therapeutic measure. The feed given to broilers contained as per the information provided in the label by the manufacturer. However, only 56 % of buy back and medium scale farmers knew about the use of in-feed antibiotics while the rest were unaware about in-feed antibiotics/growth promoting antibiotics they were giving to the animals. In addition to in-feed antibiotics, Amoxicillin, Enrofloxacin and Thylosin were observed as other antibiotics used in broiler farms associated with large scale companies and Tetracycline, enrofloxacin and amoxicillin were commonly used by medium scale farmers who sold the produce locally. Broiler farms associated with large scale companies indicated that they have discontinued the use of tetracycline as it is no longer effective.

Results indicated that all PL and PM samples contained ARB (Table 1). Tetracycline resistant (10 ppm) bacterial populations in buyback and closed house broiler farms were significantly higher than medium scale farms that continue the use of Tetracycline (Table 1). Although the enrofloxacin resistant population was always less than the tetracycline resistant population the abundance followed the same trend as the latter.

Table 1. Abundance of antibiotic resistant bacteria in poultry litter and poultry manure.

Environment	Bacteria population (\log_{10} CFU/g)		
	Control (0 ppm antibiotic)	Tetracycline (10 ppm)	Enrofloxacin (10 ppm)
Poultry manure (n=5)*	7.14±0.31	4.78±0.12	1.77±0.90
Poultry litter			
Closed house farms of large companies (n=3)#	11.44±0.08	10.01±0.47	9.33±0.53
Buy back farms linked with large companies (n=22)#	11.54 ±0.49	9.88±0.47	9.13±0.50
Medium scale farms that sells produce locally (n=11)*	6.73±0.52	4.26±0.46	2.97±0.42

*From Kandy district

#Distributed in Gampaha and Kurunegala districts

Effect of poultry manure application on endophytic and epiphytic bacteria in carrot

Total culturable epiphytic bacterial population (2.45 to 2.91 log₁₀ CFU g⁻¹ dry carrot) was significantly higher than the endophytic bacterial population (1.72 to 2.42 log₁₀ CFU g⁻¹ dry carrot). Epiphytic bacteria are capable to live in interface of soil and root. Therefore, they have narrow ecological niche. The diversity of epiphytic bacterial community depends on the external environmental conditions. Interestingly PM and tetracycline application did not affect total culturable epiphytic bacterial populations in carrot grown in LH and SH soil but 10 ppm tetracycline and PM increased the endophytic bacterial population in carrot grown in LH soil only. However, tetracycline resistant epiphytic bacteria (1 and 10 ppm) and endophytic bacteria (10 ppm) were significantly higher in carrot grown under PM amended LH than SH. The endophytic bacteria resistant to 1 ppm tetracycline significantly increased with application of tetracycline and PM compared to control only in LH. Thus, the soil with a longer history of PM application (LH) was more responsive to the addition of antibiotics and PM.

Since endophytic bacteria resistant to 1 ppm tetracycline were responsive to PM addition this concentration was used to assess the prevalence of tetracycline resistant endophytic bacteria in carrot sold in open market. The carrot samples collected from Kandy municipal area contained tetracycline resistant (1 ppm) endophytic bacteria. The bacteria resistant to 1ppm tetracycline was significantly less than the total culturable endophytic bacteria in the sample.

Antibiotic resistance traits of ARB from PL, PM and Carrot roots

MIC and MBC of tetracycline were observed in the range of 0.5 to 1024 ppm and 4 to 1024 ppm respectively. The MIC and MBC of tetracycline of the bacterial isolates used in this study significantly correlated ($r = 0.76$). The prevalence of MIC and MBC ≥ 128 ppm among ARB isolates was 56 % and 79% respectively. 13 isolates (24 %) had MBC ≥ 1024 ppm of tetracycline. Multiple drug resistance prevalence was higher among ARB from PL (30%) than carrot roots (12%).

Discussion

The mode of operation of poultry farms affected the ARB in PL since it determines the quality of inputs, availability of antibiotics and frequency of administration. Thus, the release of ARB to the environment via PL may be system specific and is not consistent among poultry farms. Results reinforce the importance of increasing awareness among poultry practitioners about antibiotics and potential threats to environment. As indicated by the large resistant bacterial populations, the broiler farms associated with large scale companies will have to consider suitable alternatives for enrofloxacin before it too become ineffective in disease management. The origin of PL to produce PM via curing in piles in the farm fields was from medium scale broiler farms in Kandy District who were not linked with large-scale companies. This may be a reason for the observed similarities in bacteria population sizes among PM and PL from Kandy District.

Residual antibiotics and gut microorganisms excreted into PL can affect soil microorganisms by imposing a selection pressure facilitating resistance development, inhibiting some microorganisms, and changing community composition (Popowska *et al.*, 2010). Maintenance of antibiotic resistance in soil is governed by natural background resistance, introduction of antibiotic resistant genes, and pressure exerted by antibiotics (Schmitt *et al.*, 2006; Popowska *et al.*, 2010). Epiphytic bacteria are capable to live in interface of soil and root. Therefore, they have narrow ecological niche. The diversity of epiphytic bacterial communities is highly affected by

external environmental conditions. Interestingly PM and tetracycline application increased the endophytic populations in carrot grown in LH but did not have any effect on epiphytic bacteria in carrot roots.

Tetracycline resistant epiphytic bacteria (1 and 10 ppm) and endophytic bacteria (10 ppm) were significantly higher in carrot grown under PM amended LH than SH. Hence the effect of antibiotic resistance determinants added via PM on soil bacteria is not universal across soils (Schmitt *et al.*, 2006; Popowska *et al.*, 2010). The two soils were not significantly different with respect to basic soil chemical and physical characteristics, and they were from adjacent fields in same geographic region. Since the two fields shared similar intensity and duration of cultivation, the difference observed in response to the treatments may be directly linked with biological characteristics of soils that are influenced by the history of management practices (mainly PM application). The reason for EEB in carrot grown in LH was more responsive to PM addition may be because the exposure of microbial communities to similar material in LH is higher than in SH. Therefore, some members in microbial communities in LH may be better adapted to harness the resources and seize competitive advantage.

In poultry industry, antibiotics are used as growth promoters at sub-therapeutic concentrations (50 - 100 mg/ kg) in feed (Apatha, 2012). Thus, high prevalence of ARB having MIC and MBC higher than 128 ppm indicate the potential risks associated with disease management in recent future. More importantly, prevalence of MIC and MBC ≥ 128 ppm among ARB isolates from carrot roots were 46% and 83%, respectively. Further studies on virulence traits of the EEB inhabiting fresh-cut produce like carrot and the potential of those bacteria in sharing antibiotic resistance determinants (genetic information) with different target groups such as plant growth promoting rhizobacteria, gut microbiome and microorganisms on skin/ facial tissues are required to ascertain the threat of ARB on food-chain contamination.

Conclusions

The study confirmed that poultry litter and manure are carriers of antibiotic resistance to soils. However, the degree of soil contamination by poultry litter or manure cannot be generalized as antibiotic resistance determinants may present in PL and PM to different levels depending on the intensity or the mode of operations in poultry management. Further the effect of PM on antibiotic resistant populations of root colonizing bacteria of carrot is not universal across soils because antibiotic resistant endophytic bacteria in carrot is high under soils with repeated exposure to PM than under soils with less exposure to poultry manure. Carrot sold in market away from place of produce contained antibiotic resistant bacteria. Majority of bacteria isolates from PL, PM and carrot had MIC and MBC values greater than 128 ppm. Hence, virulence traits of these bacteria and the potential to transmit genetic information to other microbial communities in the environment need to be studied further. The findings emphasize the importance of enforcing mechanisms to pretreat PL prior to release to the environment and use in vegetable cultivation. System specific unique features contributing to occurrence of antibiotic resistance determinants should be considered in policy making to facilitate better management of antibiotic usage in agriculture.

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2.1.3. First results on the bioavailability of some metals in the soils of the emilia-romagnola plain

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Abstract

In 2013 the Geological, Seismic and Soil Service of the Emilia-Romagna Region in collaboration with the Institute of Biometeorology of the national Research Council of Italy, mapped the background content (ISO DIS 19258: 2005) of eight potentially toxic metals and metalloids (As, Cu, Cr, Ni, Pb, Sn, Zn, V) in the agricultural soils of the plain; metal content was determined by aqua regia extraction (UNI EN 13346).

It is known that the risk related to the presence of a potentially toxic element in the soil is not only due to its total or pseudo-total content, but also to the bioavailable fraction, i.e. that available for absorption by living animal and plant organisms (ISO17402: 2008).

The bioavailable fraction depends on the soil functions that are considered; in this study we focused on biomass production, thus determining the exchangeable fraction that can be absorbed through the plant roots (ammonium nitrate extraction, UNI-EN 12457-2; 2004).

As for food biomass production, bioavailability in soils must be compared with the content of metals in plants to fully understand the actual risk of transition to the food chain. The purpose of this study is to understand the extent of potential bioavailability in soils and to which extent it depends on their intrinsic properties, further than the nature of metals.

The bioavailability data were related to the pseudo total contents for different types of soil by calculating the extraction percentage to assess whether the soils have different behaviors linked to their intrinsic characteristics, and to identify a "bioavailability hierarchy" of the individual metals.

To evaluate the results ammonium nitrate data were compared with those of the German legislation (BBodSchG, 1998), while eluates data were compared with MD 5 February 1998

Keywords: background content, bioavailability, soil functions, heavy metals, biomass production, groundwater protection

Introduction, scope and main objectives

As part of the "*Pedogeochemical Maps of Emilia-Romagna plain*" the background content (ISO DIS 19258: 2005) of eight potentially toxic metals and metalloids was mapped at 1: 250.000 scale (As, Cu, Cr, Ni, Pb, Sn, Zn, and V). The study used an integrated approach (pedological, geochemical, and land use driven), including over 700 analytical data from aqua regia extraction and ICP-MS determination (UNIEN13346 + EPA6020). The soils units defined in the 1: 50,000 soil map were grouped into 13 Genetical Functional Units (GFU) on the basis of: parent material provenance, texture, degree of alteration, and geochemical analysis (Fig. 1).

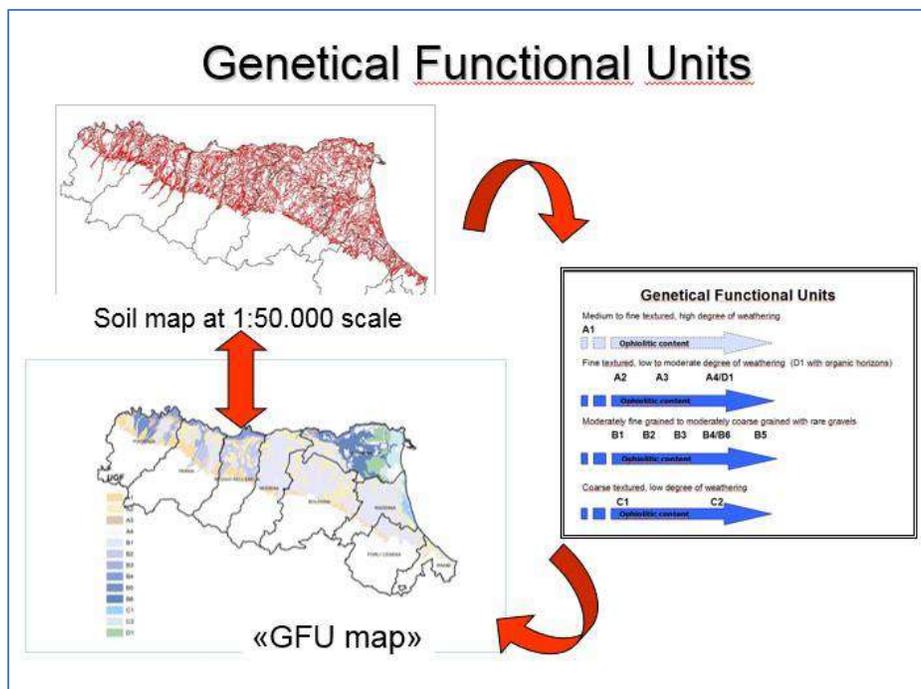


Figure 1. Genetical Functional Units

The risk related to the presence of a potentially toxic element in the soil is not only due to its total concentration, but also to the bioavailable fraction, i.e. that available for absorption by living animal and plant organisms (ISO17402: 2008), potentially harmful if we consider the function of the soil to produce biomass. Therefore, since 2013 it has been started a cognitive framework of the bioavailable fraction by choosing samples already analyzed by aqua regia extraction and subjecting them to bioavailability analysis: currently 242 site samples were analyzed on 5 agricultural districts and in the next three years we plan to complete all the plain.

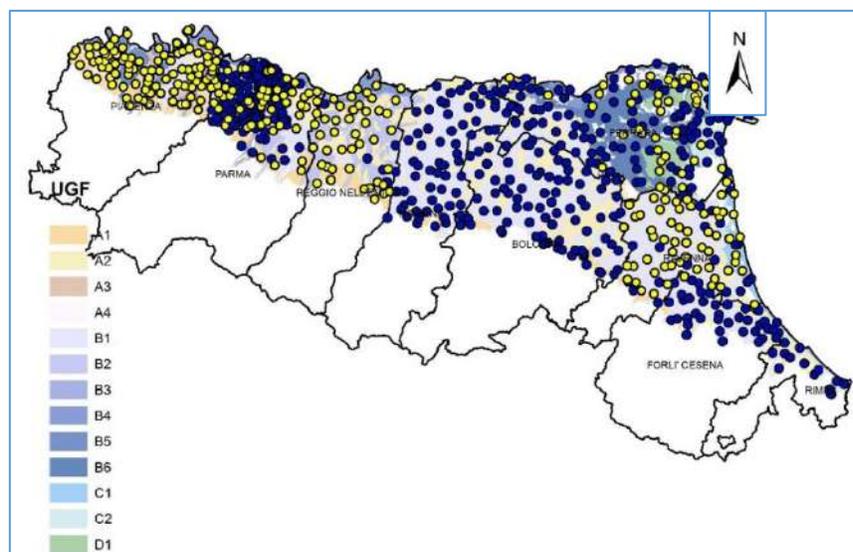


Figure 2. Bioavailability sampling sites (yellow) vs total sampling sites (blue).

Methodology

To date 210 samples were analyzed with the DIN 19730:2008 method (ammonium nitrate), i.e. one of the reference method for the soil-plant pathway. To describe the soil bioavailability, we compared the average extracted values with the average values of the aqua regia contents for each GFU, calculating the extraction percentage.

In the Italian legislation there aren't threshold values for the bioavailable content of metals in soil and it is therefore difficult to assess the environmental significance of the concentrations found without the help of references. We used then the German legislation (Bodenschutzgesetz, 1998) which establishes trigger values in soils for plant pathway determined with the DIN 19730: 2008 method.

Results

Table 1 shows that copper is the most mobile metal towards plants with values higher than all the others except in the case of peaty soils (GFU D1); the background content of copper is largely due to anthropogenic contribution in the superficial horizons of agricultural soils (as evidenced by the regional cartography) since copper is contained in manure and phytosanitary products (Bordeaux mixture). It is therefore plausible to hypothesize that a large part of what has been added by means of agronomic management in soils is potentially available for plants, and especially in the coarse soils of the coast (UGF C2),

Table 1. Percentage of extraction by DIN 19730:2008 (ammonium nitrate)

UGF	Cr	Ni	Cu	Zn	As	Sn	Pb
A1	0,002	0,124	0,200	0,065	0,034	0,039	0,005
A2	0,002	0,065	0,296	0,021	0,064	0,035	0,007
A3	0,002	0,036	0,217	0,029	0,048	0,037	0,004
A4	0,008	0,017	0,092	0,017	0,018	0,031	0,007
B1	0,002	0,053	0,360	0,020	0,036	0,039	0,008
B3	0,002	0,039	0,288	0,025	0,040	0,051	0,006
B4	0,001	0,045	0,507	0,017	0,061	0,047	0,007
B5	0,001	0,031	0,233	0,041	0,035	0,027	0,002
B6	0,007	0,036	0,241	0,029	0,046	0,038	0,009
C2	0,012	0,123	3,091	0,051	0,257	0,073	0,014
D1	0,009	0,312	0,073	0,342	0,052	0,032	0,038
average	0,004	0,080	0,509	0,060	0,063	0,041	0,010

From the average values of extraction with respect to the average value of total content of the GFU it results the following sequence of metals mobility: Cu > Ni > As > Zn > Sn > Pb > Cr; this is independent from total concentrations.

Chromium and nickel are influenced by the soil acidity conditions in the pathway to plants (Figure 3): the extraction data in NH₄NO₃ in relation to the pH show that below pH 5 significant percentages of Nickel become bioavailable while Chromium release to plants increases below pH 6 but with lower values.

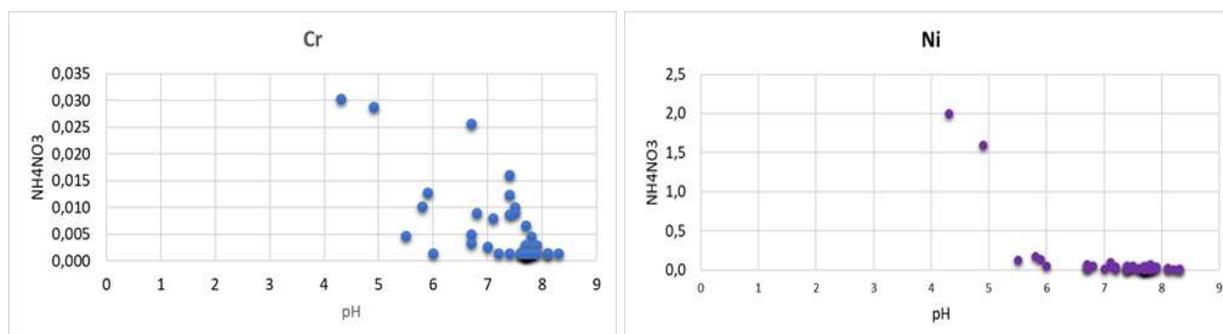


Figure 3. Ammonium nitrate values for Cr and Ni (mg/kg) vs pH in the soils of ancient Po delta

Table 2. Maximum values in mg / kg for GFU of metals with ammonium nitrate extraction: in red those exceeding the trigger value of the German standard (Bodenschutzgesetz, 1998).

	Cr	Ni	Cu	Zn	As	Sn	Pb
A1	0,009	0,265	0,258	0,326	0,008	0,001	0,002
A2	0,008	0,242	0,729	0,109	0,025	0,001	0,002
A3	0,008	0,105	0,281	0,045	0,011	0,001	0,002
A4	0,015	0,052	0,093	0,030	0,004	0,001	0,002
B1	0,002	0,059	0,696	0,038	0,005	0,001	0,002
B2	0,004	0,088	1,130	0,032	0,013	0,001	0,002
B3	0,003	0,061	0,278	0,047	0,006	0,001	0,002
B4	0,003	0,063	0,790	0,017	0,013	0,001	0,002
B5	0,003	0,188	0,151	0,055	0,004	0,001	0,001
B6	0,015	0,132	0,393	0,057	0,012	0,001	0,005
C2	0,025	0,105	3,000	0,047	0,061	0,001	0,002
D1	0,030	1,997	0,103	2,122	0,016	0,001	0,057
<i>trigger values agriculture</i>		1,50	1,00	2,00	0,40		
<i>trigger values agriculture plant quality</i>							0,10

Discussion

The first data on bioavailable fractions allow us to make some considerations: a) copper is by far the most mobile metal towards the plants, particularly in sandy soils; this is confirmed by literature and European studies (Kabata Pendias, 1994; ENV. A.2./ETU/2001/0024, 2004), and means that copper added to the soil enters the food chain with ease; b) notwithstanding a high content of chromium (mainly of natural origin) Cr is the least mobile metal in the biosphere; c) pH, texture and organic carbon content are confirmed as discriminating factors for metal mobility. For this reason, in the revision of the legislation regarding the use of sludge wastewater in agriculture, it would be advisable to maintain the prohibition for soils with pH <5. In the case of Ni, Zn and Cu soils have some values above the trigger values according to the German legislation but so far metal trends are below, bearing witness to the sustainable management of soils.

Conclusions

The comparison of the bioavailable fraction with the aqua regia content allows to identify which are the most mobile metals, in relation to the type of soils. The conclusions drawn in the light of the first analytical results do not claim to have a universal value, but are limited to the regional area that has its peculiarities. As such they represents the current conditions resulting from ordinary agronomic management, and an estimate of the concentrations potentially available to plants with the aim of allowing a better soil protection in the perspective of food safety.

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2.1.4. Heavy metals concentrations in composts and substrates used to production of vegetables in Cuba's urban agriculture

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Abstract

The urban agriculture has been improving food security in Cuba by providing fresh vegetables within and on the outskirts of cities, in the last three decades. However, organic fertilizers and substrates that are used in urban agriculture systems can be contaminated by heavy metals and metalloids and hence to pose risks to human health. This study was carried out to measure the concentrations of cadmium, lead, arsenic, selenium, mercury, nickel and chromium in composts and substrates used in Cuba's urban agriculture, as well as in vegetables grown in this cropping system to assess risks to human health. Extraction of heavy metals from samples was performed with a mixture of nitric and hydrochloric acid in a microwave oven, according to EPA Method 3051A. Cadmium, lead, nickel and chromium were determined by optical emission spectrometry (ICP-OES), and arsenic, selenium and mercury were measured using an atomic absorption spectrophotometer coupled with a hydride generation system (FIAS-AA). The results demonstrated that concentrations of heavy metals in organic fertilizers, with the exception of compost from municipal solid waste, were within permissible values and do not pose risk for human health. By contrast, the compost produced from municipal solid waste and the substrates prepared with this material presented cadmium and lead concentrations above maximum permissible limit; therefore they should not be used for food production. This work represents the first national wide survey of heavy metals in Cuban urban agriculture. With this result, the use of municipal solid waste compost for food production was forbidden in Cuba.

Keywords: Heavy metals; food security; sustainable agriculture.

Introduction

Urban agriculture has been practiced in Cuba for the last three decades (Febles-González *et al.* 2011). The use of compost as fertilizer is a sustainable recycling practice due to its beneficial effects on the properties of the soil, as well as on plant growth (Mylavarapu and Zinati 2009 and Sharif *et al.* 2016). However, the ongoing monitoring of heavy metals in composts is essential to guarantee an agroecological agriculture that protects human health and the environment (Nogales *et al.* 2014). The objectives of this work were to determine the concentration of Cd, Pb, Hg, As, Se, Ni and Cr in composts and substrates used in urban agriculture, assess the uptake of Cd and Pb for vegetables cultivated in these substrates, and evaluate the risks associated with the consumption of vegetables grown in urban agriculture. This result can assist management authorities in eliminating or avoiding major metal sources in order to guarantee food quality and safety.

Methodology

We sampled 11 types of compost used for vegetable production on 60 organic urban farms (so-called organopónicos) and 11 waste-processing centers throughout Cuba. The composts were sampled in the following provinces: La Habana (n = 50), Guantánamo (n = 10), Pinar del Río, Artemisa, Mayabeque, Matanzas, Villa Clara, Ciego de Ávila, Camagüey, and Granma y Guantánamo (n = 11). The 10 composts sampled in Guantánamo were obtained from the waste processing centers of Sur Isleta, Los Cocos, and Vilonio. The first two centers process municipal solid waste without previous sorting that is then classified manually before forming the compost piles; the Vilonio waste center processes only crop residues. Eight replicates of each compost were analyzed for pH, electric conductivity, and percentage of organic matter according to the methodology described in ISO-11464 (1999). The values' ranges were the following: pH (6.59–7.88), electric conductivity (1.09–7.45), and organic matter (39.3–69.5).

Four species of highly consumed vegetables in Cuba were analyzed for heavy metals concentrations in their edible parts: lettuce (*Lactuca sativa*), chard (*Beta vulgaris*), radish (*Raphanus sativus*), and bell pepper (*Capsicum annuum*).

These species were grown on four different substrates in single and successive croppings. These substrates were prepared with a 1:1 mixture of soil and either cow manure or municipal solid waste composts as commonly used in the organopónicos. Two soils were used. They were classified as Typic Kandiuustalf and Rhodic Eutrodox according to Soil Taxonomy (Soil Survey Staff 1999). Substrates with municipal solid waste compost were cultivated in two successive croppings: (1) lettuce followed by bell pepper and chard (Typic Kandiuustalf) and (2) lettuce followed by radish and chard (Rhodic Eutrodox). Substrates with cow manure underwent a single cultivation of lettuce and chard.

Samples of the leafy vegetables were divided into leaves and stems, and the bell pepper samples were separated into leaf, stem, and fruit parts.

Samples of soil, composts, substrates, and vegetables were digested with 9.0 mL of HNO₃ and 3.0 mL of HCl in a microwave oven (USEPA 1998). The concentrations of Cd, Pb, Ni, and Cr were determined via inductively coupled plasma (ICP-OES/Optima 7000, Perkin Elmer), and the concentrations of Hg, Se, and As were determined via atomic absorption coupled with a hydride generation system (FIAS100/Flow Injection System, Perkin Elmer). Descriptive statistics (mean, medians, minimum and maximum values, and standard deviation) for the raw data were established using the statistical package StatPoint, Inc., VA, USA.

Results and discussion

Heavy metals concentrations in composts and substrates

The concentration of heavy metals in the studied composts was within the regulatory levels (Table 1), ensuring their safe use. However, heavy metals contamination in municipal solid waste compost raises concerns about risks to human health; all of the elements assessed exceeded the permissible limits. The high level of Ni and Cr in the earthworm humus and in crop-residue compost is probably due to the unusually high natural concentration of Ni and Cr in soils of Cuba (Rodríguez *et al.* 2015). Municipal solid waste compost contains heavy metals a consequence of plastics, metal objects, solvents, paints, papers, wood and petroleum products, Cd-Ni batteries, and other discarded materials. The results indicated that the manual separation of significant trace-element enriched materials was not effective at reducing the concentration of trace elements in the municipal solid waste compost.

Table 1. Heavy metals concentrations for composts sampled from organopónicos in Cuba.

Compost	Heavy metals concentration (mg kg ⁻¹)						
	Cd	Pb	Hg	As	Se	Ni	Cr
1	0,7±0,1	41,8±13,0	0,02±0,00	2,5± 0,5	3,4±0,8	61,3±10,9	39,9±5,0
2	0,7±0,4	34,7±24,6	0,03±0,02	1,7±0,9	3,7±2,9	34,1±8,7	40,3±15,2
3	0,7±0,5	45,4±31,0	0,02±0,01	3,0±2,1	4,3±3,2	58,9±24,5	47,8±19,4
4	0,6±0,0	34,9±0,0	0,03±0,00	2,8±0,0	2,9±0,0	46,9±0,0	52,1±0,0
5	0,8±0,5	34,9±6,5	0,03±0,02	1,4±0,9	5,7±4,7	60,2±22,2	57,6±21,2
6	0,9±0,8	58,5±0,8	0,04±0,02	1,2±0,1	2,8±0,0	26,0±0,0	33,8±8,0
7	1,5±0,3	48,0±12,5	0,04±0,01	2,7±1,5	3,8±0,4	62,7±11,2	113,0±3,5
8	1,0±0,5	47,8±17,8	0,06±0,04	14,9±2,1	4,6±1,9	160,4±45,4	152,6±40,9
9	0,5±0,1	61,9±7,4	0,02±0,00	14,3±2,8	2,6±0,9	150,9±21,5	177,0±15,0
10	0,6±0,3	45,0±7,2	0,03±0,02	16,3±2,8	4,3±0,8	206,4±97,5	176,4±34,8
11	4,9±0,9	545,1±93,8	1,9±0,6	62,1±22,9	141,0±42,1	253,3±26,5	221,7±46,3
Range	0.2–6.2	13.5–551.1	ND–2.8	ND–98.0	0.8–204	10.6–455.7	16.7–297.3
RL^a	3	150	1	20	80	70	200

1: filter-cake compost (n = 5), 2: horse manure + crop-residue compost (n = 6), 3: horse manure + soil – 1:1 (n = 14), 4: rabbit-manure compost (n = 1), 5: cow-manure compost (n = 5), 6: cow manure + crop-residue compost (n = 3), 7: cow manure + soil – 1:1 (n = 5), 8: earthworm humus (n = 5), 9: crop-residue compost (n = 4), 10: crop residue + soil – 1:1 (n = 23), 11: municipal solid waste compost (n = 6); RL^a: regulatory levels (Brasil, 2006).

The concentrations of heavy metals in soils and substrates that did not receive municipal solid waste compost were within permissible levels for agricultural soils (Table 2), except for Ni and Cr. The high concentrations of Ni and Cr in Cuban soils are natural and inherent to the parent soil material (Rodríguez *et al.* 2015). On the other hand, the use of municipal solid waste compost increased the concentrations of Cd, Pb, As, Se, and Hg

above the limits considered safe for soil cultivation. Achiba *et al.* (2009) also reported that the addition of municipal-solid-waste compost increased Cd and Pb concentrations in the soil.

Table 2. Heavy metals concentrations in soils and substrates (soil + compost, 1:1 ratio).

Substrate	Heavy metals concentration (mg kg ⁻¹)						
	Cd	Pb	As	Se	Hg	Ni	Cr
TK soil	0.8±0.1	24.3±4.3	15.1±1.1	1.3±0.1	0.07±0.0	183.0±9.6	191.9±12.6
RE soil	0.4±0.1	36.9±5.0	6.2±0.9	1.4±0.2	0.03±0.0	276.5±8.8	154.9±16.2
TK+Cow Manure	0.4±0.1	66.5±7.1	18.0±4.3	2.4±0.1	0.07±0.0	178±10.0	179±14.6
RE+Cow Manure	0.4±0.1	98.1±9.1	19.4±6.2	1.4±0.8	0.07±0.0	186±7.6	198±12.2
TK+MSWC	9.1±1.0	352.0±12.1	62.4±9.1	143.1±8.1	12.45±1.08	285±8.8	245.2±23.1
RE+MSWC	8.6±0.9	1501.5±23.2	75.8±12.1	149.0±12.2	14.09±1.37	298±9.5	228.4±32.0
PL ^a	3	180	35	5	12	100	150
PL ^b	8	300	20	80	2.5	175	500

TK: Typic Kandiuistalf, RE: Rhodic Eutrodox, MSWC: municipal solid waste compost, PL^a: permissible level in soils (CONAMA, 2009) and PL^b: permissible level in substrates (Brasil, 2006)

Cadmium and lead concentrations in vegetables

The concentrations of Cd and Pb in the edible parts of vegetables grown on substrates that received cow manure (Fig. 1) were below the maximum allowable concentration of these elements (Codex Alimentarius 2016).

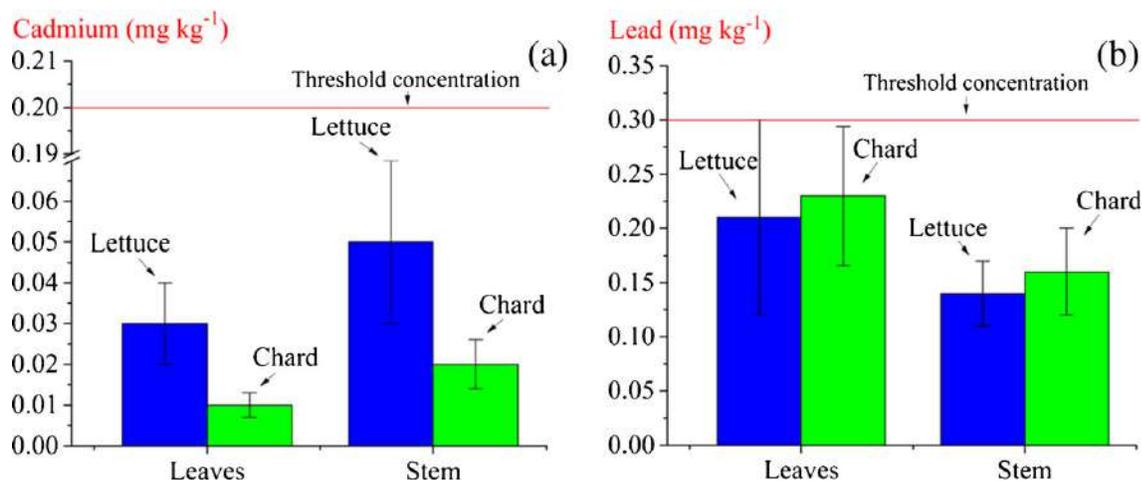


Figure 1. Concentrations of Cd (a) and Pb (b) in edible parts of lettuce and chard grown on the substrate with cow manure. Threshold concentration (Codex Alimentarius 2016)

Therefore, the cow manure used in Cuban urban agriculture does not pose risks regarding the uptake of Cd and Pb by vegetables. In general, cow manure presents low

concentrations of potentially toxic elements, and it can even be used to alleviate phytotoxicity and heavy metals uptake in plants (Rehman *et al.* 2016).

We found that the use of municipal solid waste compost obtained from the three waste processing centers studied poses a serious risk to human health due to the transfer of heavy metals present in the municipal solid waste compost into the edible parts of vegetables cultivated in successive cropping: lettuce, bell pepper, and chard (Fig. 2a, b) and lettuce, radish, and chard (Fig. 2c, d).

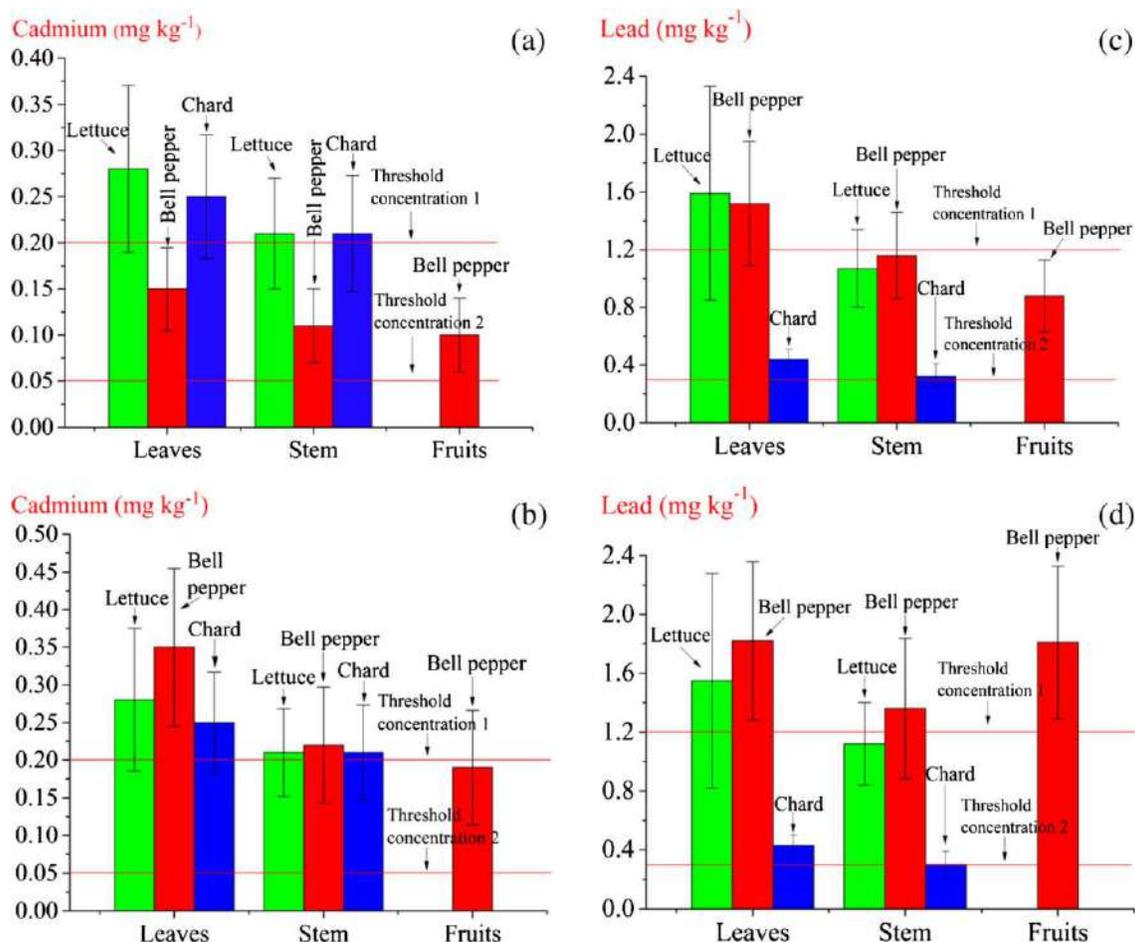


Figure 2. Concentration of cadmium (a and c) and lead (b and d) in edible parts of vegetables grown successively (lettuce—bell pepper—chard and lettuce—radish—chard) on substrate with municipal-solid-waste compost.

TC (1) and TC (2) threshold concentration in leaves and fruits, respectively (Codex Alimentarius 2016)

In all cases, the highest concentrations of Cd and Pb were observed in leaves. With the exception of bell pepper fruits, the lowest metal concentrations were found in plant stems. However, the concentrations of Cd and Pb in leaves of lettuce and chard and the fruits of bell peppers were above the permissible limits set by the Codex Alimentarius, which renders these edible parts unsuitable for human consumption. It is important to point out that unacceptably high concentrations of Pb and Cd associated with municipal solid waste compost application in our

work were observed in leaves and fruits harvested, even in the third cropping. This fact clearly highlights the potential health risks associated with the use of such composts for food production.

Conclusions

The concentrations of Cd, Pb, As, Se, Hg, Ni, and Cr in organic fertilizers used for composting in Cuban urban agriculture were within permissible limits. Therefore, these fertilizers do not constitute a risk to human health. However, the composts produced from municipal solid waste yielded values above the permissible concentrations in organic fertilizers for all of the heavy metals that we studied. Plants cultivated with municipal solid waste composts absorbed Cd and Pb in concentrations higher than the limits considered safe for human health.

As a result of our study, municipal solid waste composts have been forbidden by Cuban authorities for food production until strategies to achieve lower trace-element concentrations in municipal-solid-waste compost from waste processing centers are implemented.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.1.5. Transfer of trace elements from a substrate of titanium ore landfill into edible crops and poplar

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Abstract

Urban gardening has recently experienced rapid development; however, the risk of the transfer of toxic elements from neighboring industry needs to be evaluated. We performed a multi-elemental analysis with several common edible crops (cucumber, pepper, cabbage and lettuce) and poplar grown directly on a titanium ore landfill as a maximized scenario of exposure. Despite elevated concentrations of soil Ca, Fe, Mn, and Ti resulting from the industrial process, we did not register higher accumulation of these elements in the edible parts of crops or in poplar leaves grown on red gypsum compared with the control soil. Only S concentrations were higher in plants grown on the red gypsum, especially for cabbage. The correlation matrix among elements for plants grown on red gypsum indicated that S and Mn have similar accumulation patterns and are negatively correlated with Cd, Cu and Zn uptake. The poplar clone had a significantly higher transfer of S and Cr than the control and is a suitable tree species for monitoring element transfer to vegetation in this industrial context. By comparing our data with tolerable daily intake (TDI) recommendations, we demonstrated the low risk of cultivating edible crops directly on an industrial substrate in a maximized scenario of exposure, except for Cr, for which the toxicity depends on the bioavailable form. However, we did not consider the cumulative effects of the various elements because there are no current guidelines, and further research is needed to address this question.

Keywords: Titanium industry, Urban gardening, Trace metals, ICP-AES, Transfer, Tolerable daily intake, Vegetable crops, Poplar

Introduction, scope and main objectives

Accumulation of Trace metals (TMs) in soils can have adverse effects on environmental health, crop growth, and food quality and is a major concern because of the potential health risk to the local population if directly ingested or transferred through food (Hough *et al.*, 2004; Bermudez *et al.*, 2011).

Plants can take up TMs from soil through their root systems, transport them through the xylem to their shoots and accumulate them in the tissues of all organs. TM sources, accumulation, transfer, health risk and the effects of TMs on the nutritional status of food plants have been widely studied and recently reviewed (Khan *et al.* 2015). In most cases, TM transfer to the edible parts of vegetables is poor. For instance, McBride *et al.* (2014) found a weak relationship between vegetables and soil metal concentrations (Pb, Ba and Cd), while soil characteristics, such as pH, organic matter content, and other soil properties, were the most influential on metal bioavailability. Douay *et al.* (2012) reported heterogeneous TM contents when comparing different crop species exposed to Cd, Pb, and Zn in urban gardens in northern France. Moreover, Finster *et al.* (2004) found that the Pb content depended on the edible part of the vegetables.

When humans consume metal-enriched food plants, the metal contents can exceed the food safety limits set by authorities. An important factor of human contamination is the direct ingestion of particles from the plant growth substrate from unwashed or poorly washed vegetables (Izquierdo *et al.*, 2015). For washed vegetables growing on potentially polluted substrates, contradictory results have been reported. Several studies addressing the consumption of vegetables grown on, or near, contaminated sites concluded that exposure through vegetable consumption can lead to an intake above toxicological threshold levels (Cui *et al.*, 2004; Xu *et al.*, 2013). Highly studied TMs, such as Cd, can be transferred to the edible part of plants and become potentially toxic (Jolly *et al.*, 2013). Conversely, studies on other elements indicate that this exposure does not result in intake above the safety limit, even in areas with significant pollution (Sipter *et al.*, 2008; Pelfrène *et al.*, 2013; Adamo *et al.*, 2014). However, many authors concluded that garden soils should be analyzed for TM contents before cultivating vegetables.

Potential transfer from soil to vegetable edible parts is commonly described for Pb, Cd, Zn and As (Finster *et al.*, 2004; Defoe *et al.*, 2014; Massaquoi *et al.* 2015, Xu *et al.* 2015), but other elements, such as Cr, Ti and S, are less studied. Pollution by Ti and its impact on human health are poorly documented, although Ti is widely used in micro-technics, cosmetics and pigments in paints. The extraction of Ti by the sulfuric process (Cristal Company in France) leads to the production of red gypsum, produced by limestone neutralization of waste water from the TiO₂ plant, which contains mainly gypsum (CaSO₄), Fe oxides/hydroxides and other metal (e.g., Mn, Cr) oxides/hydroxides. Red gypsum is stored in open landfills, and TMs contained in red gypsum may be emitted into the air, largely as aerosols or associated with the particulate fraction (Alloway, 2004) and further deposited in neighboring suburban/urban areas by precipitation in rainfall or by gravitational fallout. Air, therefore, provides a route for the contamination of adjacent gardens used for the production of edible vegetables.

The major objective of our study was to compare the accumulation patterns of TMs in different vegetables grown directly onto red gypsum to maximize the exposure route. In this context, we designed an experiment with two leafy vegetables (lettuce and cabbage) and two fruit vegetables (pepper and cucumber). In addition, as one of the major ecological concerns around the TiO₂ industrial site is the reduction of dust emission enriched in TMs, a large-scale field trial using woody species (including poplar) has been recently implemented onto the industrial site, to test the impact of the woody cover on the phytostabilisation potential. However, as there was no background

information on uptake of TMs from such a substrate, we have added poplar to the list of studied plants. We will also consider poplar as a control to test whether this model plant would reflect the transfer of TMs in the different vegetables. Poplar proved indeed to be a useful bio-indicator to assess pollution of the urban environment (Laureysens *et al.*, 2004; Celik *et al.*, 2010; Sluchy, *et al.*, 2014). We hypothesized that the pattern of TM accumulation could vary among vegetable species exposed to red gypsum. We monitored the major macronutrients, micronutrients and TMs to further estimate the exposure risk and compared our data with the recommended tolerable daily intake (TDI) values provided by public agencies.

Methodology

Substrate preparation and physico-chemical analyses

Red gypsum was collected on a landfill. This enriched substrate was diluted with sand (1/1, v/v) prior to use to limit compaction in pot experiments and this sand/red gypsum mixture is referred to as “red gypsum” throughout the text, tables and figures. The control substrate was composed of loam (Brill soil GmbH, Germany) and sand (1/1, v/v) and is referred to as the “loam” control substrate throughout the text. Fertilizers (N/P/K 11/11/18, Heerlen, Netherlands) were added to each pot (1.5 g/pot) at the beginning of the experiment to ensure non-limiting plant nutrition in the different substrates. Substrate sub-samples were collected before adding fertilizers and dried for further physico-chemical analysis.

The physico-chemical characteristics that were measured included the particle size fractions (French Norm), pH (French Norm), organic status (French Norm). To determine the available fractions of elements from the two substrates (Table 1), five grams of 2-mm sieved soil was dried at 60°C for 48 h and incubated with 50 mL of 10 mM calcium chloride under agitation (40 rpm) for 2 h at room temperature. The mixture was first filtered with ash-free filters, passed through a 0.45-micrometer mesh and acidified at 2% (v/v) with HNO₃ prior to inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fischer Scientific, Pittsburg, USA) analysis.

Growth and sampling conditions

Seeds from food crops, lettuce (*Lactuca sativa* Batavia kamikaze), cabbage (*Brassica oleracea* var Mozart F1), cucumber (*Cucumis sativus* var Raider F1), and pepper (*Capsicum annuum* var Alby F1) were allowed to germinate for 2 weeks in a loam substrate, and planted after clearing the roots. Poplar cuttings (*Populus trichocarpa* x *Populus maximowiczii* var Skado) were directly planted in the new substrate. Twelve plants per species were planted in 0.5 L pots in both loam and red gypsum substrates. The climatic conditions of the growth chamber were as follows: day light for 16 h (250–300 μmol m⁻² s⁻¹); day temperature of 22 C°; night temperature of 18 C°; day and night humidity of 30%. One half of the plants were collected after 32 days of growth and the other half after 56 days. The whole leaves of the five species and the fruits for cucumber and pepper were sampled. The fruit and leaf tissues were carefully washed in deionized water to remove potential substrate particles, placed in separate paper bags, and dried at 40°C before analysis.

Elemental analysis

The extraction of TMs from plant tissues (using 1.75 mL HNO₃ + 0.5 mL H₂O₂) and substrates (using 2 mL HNO₃ + 5 mL HCl) was performed after milling the samples (125 mg) and mineralization in closed tubes placed in a block digestion system (DigiPREP, Courtaboeuf, France). Gradual heating was used to achieve a final temperature of 100°C (total run of 265 min). Then, ultrapure water (Millipore Milli-Q Integral 3 system, Molsheim, France) was added to a final volume of 12.5 mL. Finally, filtration to 1 μm was performed. The element concentrations were determined using

inductively coupled plasma atomic emission spectrometry (ICP-AES, Radial ICAP 6500 Model, Thermo Fischer Scientific, Courtaboeuf, France), and all samples were analyzed in triplicate with certified reference materials, including oriental basma tobacco leaves (INCT-OBTL-5, Molsheim, France), *Cucumis sativus* fruits (IPE-817, Molsheim, France), and loamy clay soil (CRM052, LGC, Molsheim, France).

Statistical analysis

All statistical analyses were performed using R 3.2.0 software (R Development Core Team, 2015). All tests were considered significant when $p < 0.05$. Differences in element contents among species, sampling dates, organs (leaf and fruit), and soil types were analyzed by a two-way ANOVA followed by Tukey-Kramer mean comparison test. To respect the postulates of ANOVA, the element contents were log transformed.

For the correlation matrixes and principal component analysis, all data from the fruits and leaves were pooled into two data frames (one per soil type), and data below the LQ were excluded from the statistical analysis. For the correlation matrixes, data were normalized to a mean of 0 and a variance of 1 for comparison among elements, and a normal distribution was obtained by log transformation. Correlation matrixes were drawn using the Pearson R correlation coefficient.

Results and discussion

Substrate characterization

The macronutrients Ca and S, the micronutrient Mn and the TMs Cr and Ti were found at much higher concentrations in red gypsum than those in the loam substrate (4 and 24 mg/kg D Wt for Cr and Ti, respectively). However, in red gypsum, a detectable CaCl_2 -extractable fraction was found only for Cr. Only 4% of the total S content of the red gypsum was measured in the CaCl_2 -extractable. Among all micronutrients, only Fe showed a quantifiable CaCl_2 -extractable fraction (Table 1).

There was no significant difference in pH, ranging from 7.6 to 7.9, between loam and red gypsum.

Element concentrations in plant tissues

We observed significantly higher concentrations of S in the leaves of all plant species, from 2-10 g/kg D Wt for plants grown on loam to 3-24 g/kg D Wt when grown on red gypsum. This result is in agreement with the bioavailability of S in red gypsum (Table 1). Cabbage had a significantly higher S concentration than other species, reaching 24 g/kg D Wt after 32 days of growth. Plants from the *Brassicaceae* family, i.e., cabbage, are known for their capacity to accumulate S compounds (e.g., Ishida *et al.*, 2014).

Cr was significantly differentially accumulated among species and substrates (Table 2 and 3). The Cr concentrations in plants (leaves and fruits) were at detectable levels when grown on red gypsum and were below the LQ (0.6 mg/kg D Wt) in most of the samples grown on the loam substrate. Cr was partly CaCl_2 -extractable on the red gypsum. When measured in detectable amounts, Cr was significantly higher in cucumber fruits after 56 days of growth (26 mg/kg D Wt) than for other plants and sampling times (Table 2 and 3). Concerning Ti, we observed a 14-fold increase in the red gypsum compared with loam, although the maximum increase in plants was found for cucumber leaves with a 1.7 fold increase in Ti content, when grown on red gypsum (Table 3). The plants do not seem to accumulate significant amounts of Ti, which is generally

considered as poorly bioavailable (Cornelis *et al.*, 2014). However, these data need to be taken with caution, as there are no certified Ti in the reference materials.

Table 1. Mean element concentrations (mg/kg) \pm standard deviation in the red gypsum and in the loam, CaCl₂-extractable fractions (nd: not determined), and worldwide means in soils reported from Kabata-Pendias (2011): † or Logsdon (2008): *, na: no available data. The number of replicates is indicated in brackets. <LQ below the limit of quantification.

	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Si	Ti	Zn
Red gypsum (5)	5,384 \pm 64	125,524 \pm 2,020	<LQ	19.6 \pm 0.3	174 \pm 2	49.9 \pm 0.3	45,799 \pm 655	584 \pm 10	977 \pm 9	2,955 \pm 33	48.7 \pm 0.7	21.0 \pm 0.1	103 \pm 3	90,869 \pm 858	328 \pm 20	6,245 \pm 90	99.5 \pm 0.8
CaCl ₂ - extractable fraction in the red gypsum (5)	<LQ	nd	<LQ	<LQ	1.09 \pm 0.02	<LQ	0.245 \pm 0.04	112.8 \pm 3.4	7.03 \pm 0.12	<LQ	10	<LQ	<LQ	3,714 \pm 122	nd	nd	<LQ
Loam (4)	2739 \pm 470	21753 \pm 1277	0.23 \pm 0.02	4.2 \pm 0.49	4.11 \pm 0.83	23.36 \pm 2.05	5839 \pm 1317	1889 \pm 82.34	1081 \pm 45.87	219.4 \pm 17.06	193.7 \pm 10.6	6.29 \pm 1.07	705.29 \pm 53.89	1640 \pm 81.81	504.1 \pm 13.52	23.61 \pm 2.84	35.53 \pm 6.41
Indicative world means in soils	10,000- 50,000 †	400- 35,000 *	0.41 †	11.3 †	60 †	38.9 †	35,000 †	400- 5,000 *	600-15,000 *	488 †	na	29 †	100- 5,000 *	100- 10,000 *	257,000 †	7,038 †	70 †

Table 2. Significance of the mains and the interactives effects of the 2-way ANOVA for substrate, species and experiment duration effects, on the element concentrations in leaves and fruits of the studied species collected after 32 and 56 days of growth.

Effect	Macronutrients						Micronutrients						Metallic trace elements				
	Ca	K	Mg	Na	P	S	Co	Cu	Fe	Mn	Ni	Si	Zn	Al	Cd	Cr	Ti
Substrate type	ns	*	ns	ns	***	***	ns	***	***	ns	***	***	***	ns	ns	***	**
Species	***	***	***	***	***	***	***	***	***	***	ns	***	***	*	***	***	***
Experiment duration	ns	ns	ns	ns	ns	ns	***	ns	ns	ns	ns	**	***	*	ns	***	***
Substrate × species	ns	ns	ns	*	*	***	ns	**	ns	ns	ns	***	ns	**	ns	ns	**
Substrate × duration	*	*	**	ns	ns	ns	ns	ns	***	***	ns	*	ns	ns	ns	***	ns
Species × duration	**	ns	ns	ns	**	ns	**	**	*	*	ns	***	**	ns	ns	ns	*
Substrate × species × duration	ns	**	**	ns	ns	***	ns	**	**	***	ns	***	ns	ns	***	ns	***

Tolerable daily intake of elements

Ti has no toxicological reference values due to a lack of data. However, carcinogen and genotoxic effects on reproduction have been proposed and require further investigation (ANSES, 2014). For S, the absence of a TDI is because, until 2014, no toxic effect was demonstrated due to ingestion of this element. The risk of ingestion of Ti has not been clearly established to date and should consider the same species that accumulate S.

Approximately 600-1000 g fresh mass of cabbage consumption would be necessary to reach the TDI for Ca and Mn. This value did not significantly change for plants grown on the red gypsum compared with the control (Table 4). These results indicate a species effect and not an effect of excess Ca and Mn in the polluted substrate. Despite of its high concentration in red gypsum, the Fe (with a low bioavailability) concentrations did not reach the TDI in vegetables. Cr reached the TDI, particularly in cucumber, but the toxicity of this element is highly dependent on its redox state, which was not addressed in the present study. For the other measured elements with high concentrations in the red gypsum, consumption of more than kilograms of vegetables per day would be required to reach the TDIs (Table 4). We therefore did not find any risk to human health resulting from direct ingestion of the studied food crops for the analyzed elements, for which a TDI has been defined by public agencies. Our results are in agreement with Adamo *et al.* (2014), who did not find a risk to human health due to vegetables grown in soil containing a high concentration of toxic metal for a set of agricultural and polluted soils.

In contrast with the antagonism found in food crop species for S and Cd, poplar leaves significantly accumulated S compared with plants growing on loam, and a high transfer of Cd (on loam and red gypsum) was found. This is in agreement with previous studies, where poplar leaves were proposed as suitable monitors of TM transfer at the seasonal level in plants (Madejón *et al.*, 2004; Abreu *et al.*, 2008; Migeon *et al.*, 2009).

Table 3. Median (min-max) concentration values of trace elements (mg/kg) in the leaves of food crops and poplar and in the fruits of cucumber and pepper. Data are shown as a function of substrate type (loam or red gypsum mix) after 32 and 56 days of growth. Different letters indicate significant differences among categories for the element. Italics: the category was removed from the statistical analysis (Helsel, 2010); <LQ: below the limit of quantification.

Species	Substrate	Organ	Age (days)	Al	Cd	Cr	Ti
Poplar	Loam	Leaves	32	<i>2.97</i> $n=1$ <LQ $n=5$	0.41 (0.36-0.65) a	<LQ	1.02 (0.84-1.05) h
			56	<i>4.14</i> $n=1$ <LQ $n=5$	0.23 (0.20-0.42) abc	<LQ	1.05 (0.86-1.31) gh
	Red gypsum	Leaves	32	4.3 (4.0-4.8) bc	0.41 (0.32-0.52) a	<LQ	1.1 (0.7-1.2) gh
			56	<i>4.7</i> (3.2-21.1) $n=3$ <LQ $n=1$	0.28 (0.27-0.39) abc	4.8 (3.4-8.1) bc	1.8 (1.5-1.9) bcdef
Cabbage	Loam	Leaves	32	6.7 (5.1-7.1) abc	0.07 (0.06-0.18) e	<LQ	2.2 (2.1-2.3) abc
			56	4.9 (3.8-6.2) bc	<i>0.06</i> (0.05-0.07) $n=2$ <LQ $n=4$	<LQ	2.2 (2.0-2.3) abc
	Red gypsum	Leaves	32	5.7 (5.0-7.2) abc	0.07 (0.06-0.08) e	2.5 (2.2-4.6) c	2.5 (2.3-2.9) ab
			56	<i>8.4</i> (7.5-9.4) $n=2$	<i>0.06</i> (0.05-0.06) $n=2$	<i>11.6</i> (4.8-18.4) $n=2$	<i>3.9</i> (3.4-4.3) $n=2$
Lettuce	Loam	Leaves	32	4.8 (4.1-49.3) abc	0.15 (0.14-0.17) cde	<LQ	1.2 (1.1-4.4) defg
			56	6.1 (4.4-22.1) abc	0.13 (0.09-0.81) bcd	<LQ	1.8 (1.6-2.3) abcde
	Red gypsum	Leaves	32	3.8 (3.4-5.0) c	0.21 (0.18-0.24) bcd	<i>0.89</i> $n=1$ <LQ $n=5$	1.2 (1.0-1.4) fgh
			56	4.4 (3.6-5.6) bc	0.1 (0.08-0.13) de	6.1 (4.4-13.1) bc	2.0 (1.5-2.3) abcde
Pepper	Loam	Leaves	32	4.4 (3.0-5.3) bc	0.16 (0.11-0.24) cd	<LQ	1.3 (1.2-1.5) efgh
			56	7.0 (5.8-8.3) abc	0.18 (0.17-0.27) bcd	<LQ	2.1 (1.7-2.3) abcd
	Fruits	56	<i>5.2</i> (3.8-6.5) $n=2$ <LQ $n=3$	<LQ	<LQ	<LQ	
			Red gypsum	Leaves	32	6.5 (5.6-8.9) abc	0.33 (0.24-0.40) ab
		Fruits	56	<i>3.50</i> $n=1$ <LQ $n=1$	<i>0.08</i> (0.07-0.09) $n=2$	<i>4.7</i> (4.4-5.0) $n=2$	<i>0.8</i> (0.6-1.0) $n=2$
Cucumber	Loam	Leaves	32	5.2 (4.4-5.4) bc	<LQ	<LQ	1.7 (1.5-1.9) cdef
			56	11.1 (7.4-14.5) a	<LQ	<LQ	2.5 (2.0-3.0) ab
		Fruits	32	6.3 (5.2-8.8) abc	<LQ	<i>2.18</i> $n=1$ <LQ $n=4$	<LQ
			56	<i>4.8</i> (4.3-4.9) $n=3$ <LQ $n=1$	<LQ	<i>0.66</i> (0.64-0.69) $n=2$ <LQ $n=2$	<LQ
	Red gypsum	Leaves	32	6.9 (5.9-11.2) abc	0.19 (0.07-0.27) cd	<i>1.12</i> (0.91-1.33) $n=2$ <LQ $n=4$	2.3 (1.8-2.7) abc
			56	6.9 (5.4-8.5) abc	<LQ	9.3 (5.3-15.3) bc	2.6 (2.5-3.3) a
		Fruits	56	10.3 (6.9-15.1) ab	<LQ	20.3 (12.3-49.0) a	2.4 (1.8-3.2) abc

Table 4. Fresh mass (kg) to be eaten daily by an adult of 60 kg to reach the tolerable daily intake (TDI) for each element. The value and source of the TDI used for the calculation are shown at the bottom of the table. The water contents (cabbage: 84%, lettuce: 93%, cucumber: 95%). Data are shown after 56 days of growth, except for cabbage (32 days) because it did not grow sufficiently on the polluted substrate (n<6). When at least one measurement was <LQ, the fresh mass is noted as higher than the fresh mass for the mean of quantifiable data; when all data were <LQ, the fresh mass is noted as higher than the fresh mass for LQ. Total Chromium was only measured in this study, but it is separated into Cr VI and Cr III because the two forms have highly different TDIs. Shading indicates <1 kg of fresh mass. Italic numbers indicate the dry mass (g) of airborne deposits of the polluted soil to be accidentally ingested daily by an adult of 60 kg to reach the TDI for each element.

	Substrate	Al	Ca	Cd	Co	Cr VI	Cr III	Cu	Fe	K	Mg	Mn	Na	Ni	P	Si	Zn
Cabbage Fresh mass (kg)	Loam	77	0.568	4.2	>1.4	>2.19	>938	24	11	1.644	1,019	0.936	5	>8	6	9	10
	Red Gypsum	36	1.184	>2.2	>1.4	0.467	200	16	10	1.504	1,015	0.635	7	>8	6	11	12
Lettuce Fresh mass (kg)	Loam	97	2.198	3.6	>3.2	>5.00	>2,143	41	14	3.165	1,564	1.285	7	>19	10	17	20
	Red Gypsum	19	1.651	8.6	>3.2	0.408	175	26	7	1.902	2,385	1.605	10	6	12	21	21
Cucumber Fresh mass (kg)	Loam	>77	3.189	>7.1	>4.4	>1.25	>3,000	30	22	2.269	1,802	5.311	82	30	7	18	13
	Red Gypsum	116	1.546	>7.1	>4.4	0.164	67,644	15	6	1.582	1,149	6.899	82	5	9	25	9
Dry air bone (g)	Polluted soil	60	2,500	0.06	0.084	0.21	90	8.4	30	5,000	530	10	2,000	0.72	3,000	84	25
TDI	<i>mg / day / 60 kg corporal mass</i>	60	2,500	0.06	0.084	0.21	90	8.4	30	5,000	530	10	2,000	0.72	3,000	84	25
	Source	FAO/ WHO 1989	EFSA 2006	EFSA 2009	Baars et al. 2001	INERIS 2005	Baars et al. 2001	EFSA 2006	EFSA 2006	EFSA 2006	SCF 1993	WHO 2003	WHO 2005	EFSA 2006	SC 2007	EFSA 2006	

Conclusions

With regard to our data, we could postulate that the selection of edible plants for urban gardening in the vicinity of industry should favor those plants that do not accumulate Cr and S, which have the strongest potential to transfer to the edible tissues. We effectively observed differences among species for these elements, but none of the tested species could be selected for gardening because of the low transfer of Cr. A detailed speciation of Cr forms would be required in this industrial context to precisely assess the risk of ingestion. In addition, the risk of direct ingestion should be investigated in further studies. In addition, the patterns of element transfer to poplar leaves indicate that this tree species is a suitable candidate to monitor element transfer to vegetation in this industrial context. The present data on poplar will be very useful for further interpretations of the large-scale field trial, and are also clearly of relevance for comparisons with edible plant species.

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2.1.6. Animal and anthropogenic pressures on agricultural soils from Shiga Toxin producing *E. coli* (STEC): impact on food safety and food security

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Abstract

Shiga/Vero-Toxin producer *E. Coli* (STEC/VTEC), the so called top 5+1 strains (O157, O26, O111, O103, O145 and O104:H4) are recognized as priority zoonotic agents, due to their ability to cause the onset of severe Hemorrhagic Diarrhea (D), and life-threatening Hemolytic Uremic Syndrome (HUS) in humans. The disposal on agriculture soil of manure and run-off water from ruminants slaughterhouses has been proven to cause the contamination of vegetables and ready-to-eat foods - drinking water included, leading to reported food-borne outbreaks. Nowadays, the recovery of organic carbon and water from urban wastewater treatment plants for agriculture may represent a driver for the anthropogenic contamination of soil with pathogenic *E. Coli* as well with human enteric viruses (Norovirus, Hepatitis A), no more confined as etiological agents of inter-human epidemics. The potential impact of the aforesaid anthropogenic pressures on food safety/food security, relies on: a) the possibility that former inter-human pathogenic strains could be responsible of food-borne exposures; b) the possibility that due a genetic assortment of virulence factors (*vtx1*, *vtx2*, *eae*, *aggR*, *aaiC*, *lt*, *sth*, *stp*, and *ipaH*) in biosolids microflora, new hybrid pathotypes characterized by antimicrobial-resistance, soil persistence (months), and less sensitive to pasteurization treatments, could arise. Such potential emerging risk suggest to shift from the current diagnostic tools based on the identification/isolation of the top 5+1 serogroups in food, to a genomic-based approach focused on the identification of the virulence and resistance factors. This would allow a sharper definition of the good agriculture practices able to prevent such emerging risk, as well to limit false negative results that could affect both food safety, and food security.

Keywords: STEC, pathogenic E. Coli, soil contamination, food safety, food security, genomics, virulence

Introduction, scope and main objectives

The recovery of organic matter from sludges originating from civil wastewater treatment plants (WWTPs), as well of the remediated waters as top soil improvers and for irrigation of agriculture soils supports the overall productivity and sustainability of the food production systems with respect to the carbon and water footprints (Kumar V., *et al.*, 2017). However, the recovery of such former wastes may represent the port of entry of emerging microbial, pharmaceutical, and chemical hazards, whose combined presence can be transferred to food producing animals and livestock through pasture, fodders, vegetable, and crops, and ultimately drinking/well water, due to the lack or impairment of adequate sanitization process (EFSA, 2017; Pico *et al.*, 2017, Gigliucci *et al.*, 2017). In this paper we provide evidence about the presence of virulence genes present in human and animal pathogenic *E. coli* strains in the organic matter originating from WWTPs and used as top soil improvers. Given the high genomic plasticity of the *E. coli* species, the finding of the presence of such genomic features may account for the emergence of hybrid *E. coli* strains

with shuffled virulence properties, potentially driven by the contemporary presence of inputs of human and animal origin on agriculture soil and irrigation waters. The set-up of diagnostic tools based on genomics would allow to identify emerging pathotypes, to design the end-of-waste criteria for the agriculture use of biosolids as well to evaluate the efficacy of the management options able to reduce/abate the risk for food safety and food security.

Methodology

Hazard Characterization. Pathogenic *E. coli* are characterized by a set of mobile genetic elements encoding virulence factors, that alone, or in combination, are able to provoke human illnesses, with symptoms not always confined to the digestive tract (Pasqua *et al.*, 2017). Enteroinvasive *E. coli* (EIEC), Enteropathogenic *E. coli* (EPEC), Enteroaggregative *E. coli* (EAggEC), have been frequently associated to inter-humans epidemics, and represent a leading cause of diarrhoea, often with high mortality rates, in developing countries (Ifeanyi1 *et al.*, 2015). Enterotoxigenic *E. coli* (ETEC) are a known cause of traveller's diarrhea while Shiga toxin-producing *E. coli* (STEC) are the etiological agents of foodborne diseases in humans, with ruminants being regarded as the main animal reservoir. Associated diseases span from mild to severe diarrhoea, up to haemorrhagic colitis (HC) in adults and to the life-threatening haemolytic uremic syndrome (HUS) in children and the elderly, as matter of the presence of mobile genetic elements encoding the production of Shiga toxins 1 and 2 (Stx1, Stx2) (Lawal *et al.*, 2015).

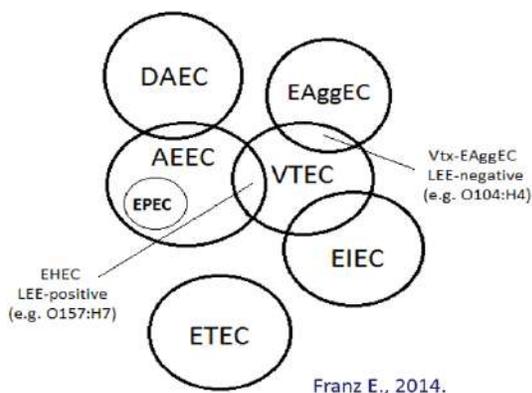


Figure 1. Re-assortment of virulence genes between different *E. coli* pathotypes of human and ruminant origin, leading to new hybrid strains able to cause HC and HUS. From Franz *et al.*, 2014.

Human pathogenic *E. coli* isolates reveal also the presence of AMR genes as additional virulence factors (Odetoyin *et al.*, 2016). Other factors enabling pathogenic *E. coli* to cause food-borne diseases rely on the environmental persistence in agriculture soils for months (Vogeleer *et al.*, 2014). Finally, the ability to form bio-films that make pasteurization treatments less effective in abating the potential infectious dose (Li and Gänzle, 2016), and the ability to enter into the cells of vegetables in contact with contaminated soils and/or water (Wright *et al.*, 2017) also confer pathogenic potential. The characterization of the *E. coli* pathotypes (human, animal, and hybrid) by Real Time Polymerase Chain Reaction (RT-PCR) allows to identify the virulence-associated genes (Tozzoli *et al.*, 2017).

Such approach proved to be effective to characterize their presence in biosolids, amended agriculture soils, waste-waters, food commodities of vegetable and animal origin, and in human specimens, before and after a selective enrichment, as tool to assess the presence of living bacteria. Additionally, the metagenomics characterization proved effective in identifying the virulence associated genomic features of pathogenic *E. coli*. Moreover, such an unbiased approach provided an analytical framework to detect Anti-Microbial Resistance (AMR) genes (Gigliucci *et al.*, 2017; Sharma *et al.*, 2017)

Results

The risk assessment/risk characterization about the role of anthropogenic pressures on the food safety and food security has been proven on genomic and epidemiological basis through the outbreak assessment of the most relevant food-borne outbreaks reported in Europe (Table 1). The genotyping of the different virulence factors/strains agents of *E. coli* infections, or Norovirus serotypes indicates the probable use of sludges as top soil improvers on agricultural soil. Within this context, we can also frame the large outbreak occurred in Germany in 2011, caused by the consumption of sprouts produced with contaminated seeds. In the latter case, the etiological agent, a strain of STEC O104:H4 could have evolved from a human EAggEC O104:H4 following the uptake of a *stx2*-phage of bovine origin. It is proposed that also the typical STEC isolated from food-borne cases of HC and HUS, could have evolved from an EPEC or EPEC-like strains following an event of *stx*-phage acquisition (Whittham *et al.*, 2005). In fact, these strains share with EPEC the capability to colonize the intestinal mucosa with the “Attaching and Effacing” mechanism governed by the presence in the STEC genome of a pathogenicity island termed the locus for enterocyte effacement (LEE) (Franz *et al.*, 2014) (Figure 1). The molecular methodologies, including PCR and Whole Genomic Sequencing, applied to the screening of different soils improvers originating from WWTPs in Italy (Gigliucci *et al.*, 2017; Tozzoli *et al.*, 2017) support the hypothesis that the contemporary presence of human and animal contributions at level of WWTPs can be responsible for the re-assortment of the virulence factors, particularly facilitating the transfer of *stx2*-phages to human *E. coli* pathotypes (e.g. EAggEC, EPEC). In a study, it was described that after the routine aerobic stabilization of sludges (> +55 °C, 5 days), it was still possible to observe growth of some *E. coli* pathotypes. Owing to the above, the systematic dressing of agriculture soil may transfer the contamination of such emerging pathogens to fodder, vegetable, crops, and farmed animals (as reservoir), thus possibly causing new epidemiological water- and food-borne cycles.

Table 1. Most relevant food-borne outbreaks reported in the European Union, from hazards related to anthropogenic pressures

Year	Hazard	Food	Reference
2014	Human Epatitis A Virus	Frozen berries	ECDC 2014
2012	Human Noroviruses	Frozen Strawberries	Höhne <i>et al.</i> , 2015
2011	<i>E. coli</i> 104/H4	Seeds and Sprouts	EFSA, 2011

Discussion

Pathogenic *E. coli* should be considered priority microbial hazards, for the virulence and resistant factors above reported able to re-assort in new pathotypes and proved as cause of severe outbreaks in humans, as well problems in the trade of food commodities. This implies the definition of the appropriate risk management options able to reduce or abate the risk that should be tailored case by case. Indicatively, these could be identified as: 1) abatement of the microbiological load allowing the sludge/manure to have an aerobic fermentation able to reach +75 °C for a prolonged time, or applying a thermolytic treatment; 2) measures to limit or avoid the amended soil to come in contact with leafy vegetables; 4) restriction in the possibility to amend soils to the dry season, to prevent the run-off of the contamination in fresh- and ground-water; 5) procedures to keep separate human from animal sludges, especially in urban/rural environments, to prevent the re-assortment of virulence genes.

Conclusions

The sustainability of food production through the recovery of organic carbon from animal and human sludge, as well from remediated waters, should be based on an extensive risk assessment focused on the so-called end-of-waste criteria supporting both food safety and food security.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.1.7. Transfer of contaminants from agricultural contaminated soils to crop plants: a field study at Brescia-Caffaro SIN (Italy)

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Abstract

The Site of National Interest (SIN) “Brescia-Caffaro” is a highly contaminated site located in the industrial area of Brescia (north Italy). The former PCBs production caused a widespread contamination from the city centre (where the factory was located) until the southern agricultural lands, affecting more than 100 ha of soil. Since 2001, several studies showed the transfer of contaminants (mainly PCBs) into the food chain, with very high levels of PCBs detected in different agricultural products (meat, milk) and in the inhabitants’ blood. This led to the issuance of a mayor decree which ordered limits and prohibitions on the soil use within contaminated area, preventing agricultural activities. The present project aimed to investigate the transfer of contaminants (POPs and heavy metals) from the soil to crop plants within the SIN. Seven different plant species (maize, common wheat, barley, triticale, soybean, sunflower and hemp) were tested in experimental plots 10 x 10 m, in triplicate, for a total of 21 plots. Contaminants concentrations were measured, for each parcel, both in soil and plant products. A great spatial variability of contamination levels in soils was observed (e.g. PCBs range: 400 - 17000 µg/kg d.w.), despite the relative proximity of the 21 plots. As regards crop plants, the results showed the absence of correlation between the concentrations in the plant biomass and those in the soil; in particular, both POPs and heavy metals concentrations in the grains were always close to the instrumental detection limit, regardless of the level of soil contamination. dl-PCBs values were higher than the action thresholds set by EU reg. 277/2012 only in hemp stem samples. This study could therefore lead to a follow up analysis of local and national regulations, allowing selected agricultural productions in contaminated lands under strictly controlled and defined conditions aimed at safeguarding human health.

Keywords: Caffaro, PCBs, POPs, heavy metals, contaminated soils, agriculture, food chain, grains

Introduction, scope and main objectives

The Site of National Interest (SIN) “Brescia-Caffaro” is a contaminated site located in Brescia, an industrial city in northern Italy. The contamination of the SIN originated from the past activities of the Caffaro factory, which was one of the worldwide largest producers of PCBs between 1930s and 1980s. The process waters were discharged into a widespread network of irrigation channels thus transferring the contamination to the south of the factory, on several hundred hectares of agricultural soils. The state of contamination was initially detected in 2001 by analysing the concentration of contaminants (mainly PCBs and heavy metals) in local agricultural products (vegetables, meat, milk) and inhabitants blood (Donato *et al.* 2006; Turrio-Baldassarri *et al.* 2007; Turrio-Baldassarri *et al.* 2008; Turrio-Baldassarri *et al.* 2009): the results showed very high level of contaminants concentrations and this led to the issuance of a mayor decree (Municipality of Brescia 2017) which ordered limits and prohibitions on the agricultural soil use within an extended area, even beyond the SIN borders. Since 2015, also due to the presence of an Extraordinary Commissioner, several activities were undertaken with the aim to better investigate

the relationship between soil contamination and agricultural activities, with special focus on the transfer of contaminants into the food chain and therefore human health.

The present work, carried out during 2015-2016, aimed to provide further data on the effects of soil contamination on crop plants, with a final purpose of eventually allowing agricultural production without any impact on human health.

Methodology

Among the crop plants commonly cultivated in the study area both from the economic and environmental point of view, the following 7 species were selected:

- Common wheat (*Triticum aestivum*);
- Barley (*Hordeum vulgare*);
- Triticale (\times *Triticosecale*);
- Maize (*Zea mays*);
- Soybean (*Glycine max*);
- Hemp (*Cannabis sativa*);
- Sunflower (*Helianthus annuus*).

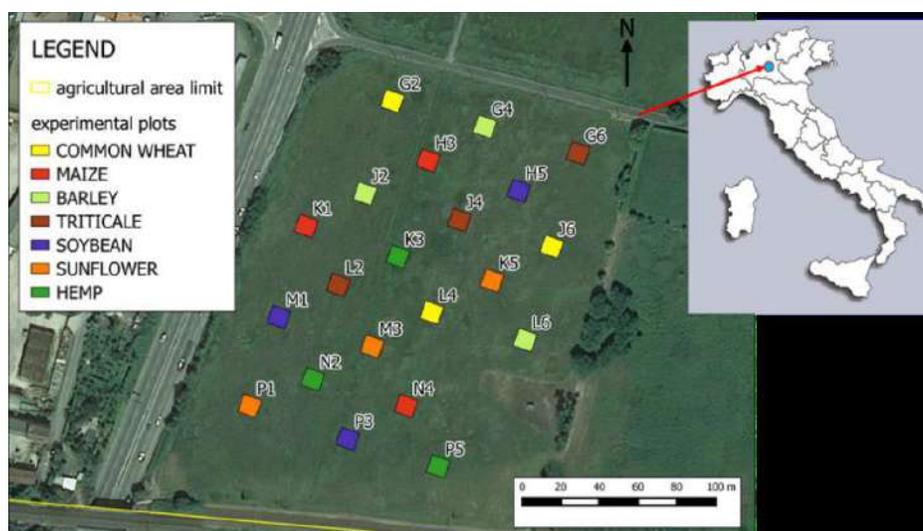


Figure 1. Territorial framework and layout of experimental plots.

Study area was selected based on the results of previous characterizations to let crop plants growing on highly contaminated soils; the experimental plan was designed by experimental plots 10 x 10 m, in triplicate, for a total of 21 plots (Fig. 1). For each plot, an initial sampling survey was carried out for soil analysis in order to obtain detailed information on the concentration levels of the specific contaminants: PCBs, PCDDs, PCDFs, As and Hg (“Caffaro contamination”). Further sampling and analysis were performed for vegetable biomass grown in the experimental plots; in particular, for each species, only the commercial part of the plant (e.g. grains, seeds, chopped

maize) was sampled and analyzed. The harvest time for each species was therefore fixed in coincidence with the right maturation degree of the commercial product to be obtained.

Soil sampling

For each plot, a composite soil sample was obtained through the collection and subsequent mixing of n. 13 sub-samples taken by manual drilling with a 40-mm diameter gouge until a depth of 40 cm. The soil sample for the laboratory was prepared by sieving the material with a 2 mm mesh, using the incremental sampling method of the Japanese Slab Cake (Gy *et al.* 1978; Gy 1982).

Crops cultivation

The sowing of cool-season cereals (common wheat, barley and triticale) was carried out at the beginning of November 2015 and their harvest at the end of June 2016; the other crops (maize, soybean, hemp and sunflower) were sown in May 2016 and their harvest was carried out between September and October 2016.

Vegetables biomass sampling

The collection of vegetable biomass was carried out by simulating the common techniques used, and so neither washed, in order to obtain data referred to conditions closer to reality but also according to the mayor decree on cutting height: several studies showed that a higher cutting height and therefore a greater distance from the ground decreases the probability of a telluric contamination on the products and, consequently, limits the contact with the soil pollutants (Pecoraro and Camera 2008). In general, several studies highlighted that the direct ingestion of soil particles during grazing, rather than the presence of contaminants in feed, represents a risk factor for the intake of organic contaminants by animals (Fries 1982; Schulz *et al.* 2005).

Therefore, chopped maize was cut to about 40-50 cm from the ground level while the hemp to about 20-30 cm. The vegetable biomass sampling was carried out through the collection of incremental samples to obtain a representative sample for each plot sent to the laboratories for the analysis of the total content of PCBs, PCDDs, PCDFs, As and Hg.

Results and discussion

The results allowed to deepen the knowledge on soil-plant relationships at a field scale and on the transfer of contaminants from agricultural contaminated soils to crop plants. The concentration values of the contaminants found in the different matrices were compared with the reference values shown in Table 1. Regarding agricultural products, the concentration values of the pollutants were compared with the limits for livestock feed fixed by EU Reg. 277/2012.

Table 1. Reference values for contaminants concentrations in the different matrices

MATRIX	CONTAMINANT	ACTION THRESHOLDS	MAXIMUM CONTENT
<i>EU Reg. 277/2012</i>			
CROP	DL PCBs <i>ng IEQ/kg</i>	0.35	n.a.
	PCDD/Fs <i>ng IEQ/kg</i>	0.50	0.75
	PCDD/Fs+DL PCBs <i>ng IEQ/kg</i>	n.a.	1.25
	NDL PCBs <i>µg/kg</i>	n.a.	10.00
MATRIX	CONTAMINANT	TABLE 1 Col. A (public green use)	TABLE 1 Col. B (industrial use)
<i>D.Lgs. 152/06</i>			
SOIL	PCBs <i>µg/kg</i>	60	5000
	PCDD/Fs <i>ng IEQ/kg</i>	10	100
	As <i>mg/kg</i>	20	50
	Hg <i>mg/kg</i>	1	5

The analysis of the results, shown in Table 2, led to several considerations based on the principle of the maximum precaution; this table does not show the heavy metal content (As and Hg) in plant products as it was always close to detection limits in all the different materials analyzed.

All the analyzed soils showed a very high spatial variability of contamination levels despite the relative proximity of the 21 plots all placed within a homogeneous area (e.g. PCBs range: 400 - 17000 µg/kg d.w.) (Fig. 2).

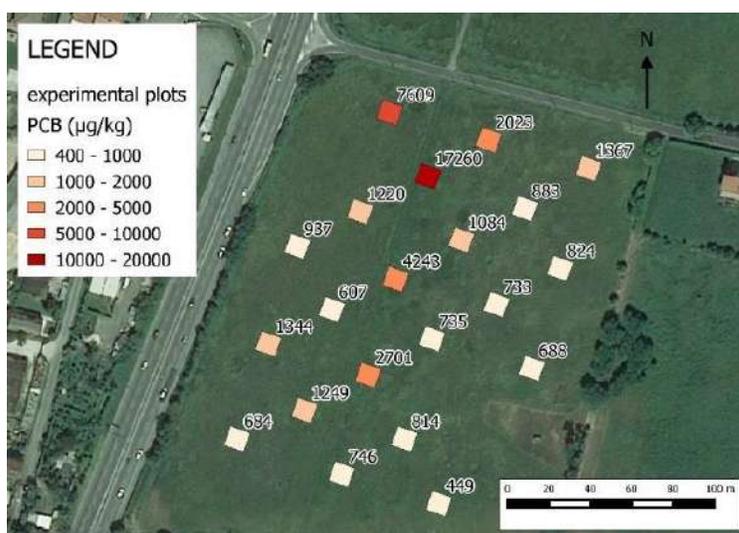


Fig. 2. Spatial distribution of PCBs content in the experimental plots.

Barley, triticale and common wheat grains and sunflower seeds showed a total content of each analytes equal to the detection limit of the instrument, regardless of the level of soils contamination (Table 2). In plot H3, characterized by high levels of contamination (total concentration of PCBs = 17260 µg/kg; total concentration of PCDD/Fs = 313 ng Teq/kg), chopped maize showed a concentration of Non-Dioxin-Like (ndl)-PCBs of 4.93 µg/kg, below the maximum content of 10 µg/kg but higher than chopped maize grown in 2 different plots, N4 and K1, where soil contaminant concentrations were significantly lower (respectively, 814 µg/kg of PCBs and 46 ng Teq/kg of PCDD/Fs; 937 µg/kg of PCBs and 55 ng Teq/kg of PCDD/Fs). As reported in previous studies (Webber *et al.* 1994), this behavior was not found for the Dioxin-Like (dl)-PCBs and PCDD/Fs whose content in the agricultural product did not show significant variations despite the considerable differences in the levels of soil contamination. These results showed that soil contamination had a limited direct impact on the final product of chopped maize cultivation.

The soybean grown on the plot M1 showed a higher level of pollutant concentration than that cultivated in the other 2 plots which, however, did not exceed the detection limit of the instrument. In the case of PCBs, these results could be explained by a correlation with soil contamination (1344 µg/kg), while this behavior was not detected for PCDD/Fs whose soil concentrations were relatively low (56 ng Teq/kg). This variability could be linked to some eventual anomaly in the sampling phase; however, this possibility seems to be unlikely due to the rigorous procedures applied in the specific sampling method.

The concentration values of the contaminants in the hemp grain were measured below the action thresholds, which was instead exceeded in the stem for the dl-PCBs, even considering the extended measurement uncertainty. The maximum content for the sum of PCDD/Fs and dl-PCBs would be exceeded if the measurement uncertainty was considered in excess; therefore, for an assessment on food safety, this result would require further study by collecting a larger number of samples to increase the statistical significance of the data (NB: EC Reg. 589/2014 for maximum content specifies that the uncertainty should be removed).

Table 2. Summary of main analytical results on soil and plant samples of experimental plots

CROP	PLOT	Crop contamination (values expressed with a moisture content of 12%)				Soil contamination			
		DL PCBs ng IEQ/kg	PCDD/Fs ng IEQ/kg	PCDD/Fs +DL PCBs ng IEQ/kg	NDL PCBs µg/kg	PCBs ⁺ µg/kg	PCDD/Fs ng IEQ/kg	As mg/kg	Hg mg/kg
Triticale grain	J4	0.14	0.17	0.31	3.00	1084	52	38	1.03
Triticale grain	G6	0.14	0.17	0.31	3.00	1367	69	37	1.50
Triticale grain	L2	0.14	0.17	0.32	3.00	607	23	24	0.41
Barley grain	J2	0.14	0.17	0.32	3.00	1220	42	27	0.81
Barley grain	G4	0.14	0.17	0.31	3.00	2023	100	42	2.01
Barley grain	L6	0.14	0.17	0.31	3.00	688	38	27	0.81
Wheat grain	J6	0.14	0.17	0.31	3.00	824	55	29	1.04
Wheat grain	G2	0.14	0.17	0.32	3.00	7609	153	32	2.26
Wheat grain	L4	0.15	0.17	0.32	3.00	735	42	31	0.87
Maize chopped	H3	0.16	0.17	0.33	4.93	17260	313	46	2.87
Maize chopped	N4	0.25	0.17	0.42	3.00	814	46	27	0.94
Maize chopped	K1	0.15	0.17	0.32	3.00	937	55	44	1.02
Hemp stem	K3	1.01 +/- 0.40	0.18	1.19 +/- 0.47	3.15	4243	128	42	1.54
Hemp grain	K3	0.22	0.18	0.40	3.00	4243	128	42	1.54
Hemp stem	N2	1.01 +/- 0.40	0.18	1.20 +/- 0.47	3.36	1249	33	23	0.61
Hemp grain	N2	0.18	0.19	0.37	3.00	1249	33	23	0.61
Hemp stem	P5	0.72 +/- 0.29	0.18	0.90 +/- 0.35	3.00	449	31	26	0.62
Hemp grain	P5	0.29 +/- 0.12	0.18	0.47 +/- 0.18	3.05	449	31	26	0.62
Soybean grain	H5	0.14	0.17	0.32	3.00	883	59	36	1.28
Soybean grain	P3	0.14	0.18	0.33	3.00	746	93	31	0.82
Soybean grain	M1	0.31	0.44	0.75	4.51	1344	56	34	1.27
Sunflower seed	K5	0.15	0.17	0.32	3.00	733	55	29	0.67
Sunflower seed	M3	0.14	0.17	0.32	3.00	2701	225	29	1.54
Sunflower seed	P1	0.25	0.17	0.42	3.00	684	29	32	0.90

in bold the exceeding of reference values shown in Table 1

* 33 congeners: 28, 52, 77, 81, 95, 99, 101, 105, 110, 114, 118, 123, 126, 128, 138, 146, 149, 151, 153, 156, 157, 167, 169, 170, 177, 180, 183, 187, 189, 194, 196, 203, 209

Table 3 shows, as an example, the calculation of the Pearson correlation index among the dl-PCBs values measured in the soil and those in cereal grains and hemp stems. This analysis confirmed the absence of correlation for cereals grains with soil contaminants content while a moderate

correlation was evident for hemp stems; this last result would seem to support the hypothesis of the telluric contamination of agricultural products.

Table 3. Pearson correlation index among DL PCBs values in soil, cereal grains hemp stems

	CONTAMINANT	Pearson Correlation Index
<i>Cereal grains vs soil</i>	DL PCBs	-0,20
<i>Hemp stems vs soil</i>	DL PCBs	0,70

Conclusions

The analysis of plant products grown within the “Brescia-Caffaro” SIN, although showing the conformity of all products for zootechnical use, showed differences in contamination levels even within the same species. This data is worthy of deepening because it could depend on several factors: for example, a different radical absorption or a possible contact with soil during cultivation or harvesting.

Based on the analytical results obtained in this project, the hypothesis of restitution of the “Brescia-Caffaro” SIN soils to an agricultural use could currently allow the reintroduction of the cultivations of wheat, barley and triticale for the grains production and sunflower for the seeds with the restriction to carry out the contamination level analysis of the product confirming its suitability for zootechnical use. Chopped maize could be also reintroduced with the restriction to cut over 50 cm from the ground, as carried out during the present test. The analytical variability recorded in soybeans deserves a specific analysis and therefore at the moment it is not possible to evaluate its reintroduction in the SIN area. Both seeds and stems of the hemp showed some critical points which do not recommend the reintroduction in the SIN area.

Therefore, in heavily contaminated areas such as the SIN it is essential to restrict as far as possible the exposures of agricultural operators to the pollutants by inhalation and dermal contact and limit the air pollution distribution for the population and environment protection. Several factors linked to agricultural activities can lead to situations of greater risk: for example, soil manipulation activities (e.g. tillage) determine the raising of dust and the acceleration of oxidation processes of the organic substance (in particular, PCBs and PCDD/Fs are linked to the soil organic carbon); moreover, the manipulated soils are more easily exposed to erosion, surface run-off and washout with consequent transport of potentially contaminated material outside the SIN. In this perspective, the application of conservative agriculture practices, such as minimum tillage or no-till farming, should be considered as a potential alternative to conventional farming techniques.

From a regulatory point of view, the human health risk in contaminated agricultural areas is a problem not yet been solved in Italy in the absence, for example, of specific reference values for agricultural soils or standards quality for irrigation water (only some maximum limits for few analytes have so far been regulated by law). While awaiting the issue of the Italian Ministerial Decree on the “Regulations relating to remediation, environmental restoration and emergency safety measures, operational and permanent, of agricultural and breeding areas” (D.Lgs. 152/06 art. 241) the analytical monitoring of food products obtained from contaminated soils is essential in order to guarantee food safety.

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2.1.8. The bioavailability of cadmium and lead in soil and bioaccumulation in barley from a contaminated soil.

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Abstract

Cadmium and lead are among the most environmentally toxic heavy metals. The bioavailable heavy metal fraction, that is potentially assimilated by biota or liscivable, is of great interest in soil contamination studies because it is the most environmentally mobile. In assessing the dynamics of metals in the soil-plant system, it is to be considered that plant species show a different ability to absorb heavy metals from the soil depending both on the type of metal and the plant. Moreover, in the presence of high concentrations of heavy metals in the soil, most plants put radical barrier mechanisms in place thus limiting their toxicity on the plant organism.

This study aims to evaluate the capability of barley (*Hordeum vulgare L.*) to bioaccumulate cadmium and lead from an artificially contaminated soil and translocate them from roots to shoots (straw and grain). Plants were cultivated on soil contaminated with cadmium (100 mg kg⁻¹) or lead (300 mg kg⁻¹) sulphate. Soil and plant samples were collected at maturation.

The concentrations of cadmium and lead in soil (total and bioavailable) and plant extracts were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP). The bioaccumulation factor (BCF: heavy metal concentration in plant/ heavy metal concentration in the soil) and the translocation factor (TF: heavy metal concentration in the shoots/ heavy metal concentration in the roots) were elaborated.

The results obtained show that lead in the soil is less bioavailable than cadmium. Despite the high concentrations of cadmium and lead in the soil, the BCF and TF values show that barley activates biochemical defence mechanisms that limit the bioaccumulation of the two metals from soil to roots and their translocation to shoots, especially in the case of lead. The roots are the main organs involved in the accumulation of cadmium and lead.

Keywords: Barley, cadmium, lead, bioaccumulation, soil contamination, heavy metals.

Introduction, scope and main objectives

The global production of barley during the 2017-2018 campaign is estimated at 144 million tonnes by the International Grains Council. Its cultivation is more frequent in East Asia, in particular in Nepal and Tibet, but also in China, Korea, and Japan, areas where the use of barley in food is more widespread, while its frequency decreases towards the West (Europe, North Africa, Asia Minor and America).

The main anthropogenic sources of heavy metal contamination include industrial activities (eg: vulcanization, tanning and fusion), domestic (eg: heating, motorized traffic), agricultural (eg: phosphate fertilizers for cadmium, fungicides and insecticides containing arsenates for lead) and the effluents resulting from these activities (eg. sewage sludge).

Defining the limit values for the concentration of heavy metals in agricultural soil, taking into account the phytotoxicity threshold for crops and the health risk for humans, is particularly complicated because the dynamics of each metal in the soil-plant system is regulated by complex chemical-physical-biological factors. The bioavailable heavy metal fraction that is potentially assimilated by biota or liscivable is of great interest in soil contamination studies because it is the environmentally most mobile (Rossi *et al.* 2002a; Stephen, 2009). In assessing the dynamics of metals in the soil-plant system, it is to be considered that plant species show a different ability to absorb heavy metals from the soil, depending both on the type of metal and the plant. Moreover, in presence of high concentrations of heavy metals in the soil, most plants put in place radical barrier mechanisms, limiting their toxicity on the plant organism. Plants can take up these toxic metals and have evolved defense mechanisms to avoid or minimize damage (Rossi *et al.* 2002b; Lina Liu *et al.* 2009; Rascio and Navari-Izzo 2011; Ferraz *et al.* 2012; Hladun *et al.* 2015). The translocation of heavy metals from roots to shoots is controlled especially by species specific physiological mechanisms (Kalis *et al.* 2008).

Cadmium and lead are among the most toxic heavy metals. Cadmium derived from anthropic activities is more environmentally mobile and bioavailable than that of natural origin (Naidu *et al.* 1997; Rafiq *et al.* 2014). In agricultural soil, sources of contamination by cadmium are the phosphate fertilizers and the use of sewage sludge as amendment, (McBride 1998; McLaughlin and Singh 1999).

Many authors emphasize that the toxicity of Cd on various commercial crops particularly affects the root system (Seregin and Ivanov 1998; Page and Feller 2015) and chemical affinity of the cadmium to zinc (electronic configuration) seems to be one of the factors that influence the transfer to the vegetable due to the phenomena of vicariance between the two elements (Herren and Feller 1997).

Lead is released into the environment from different sources: industrial waste, fuels, fungicides and insecticides containing arsenates and sewage sludge (Mahar *et al.* 2015). Lead is not very mobile in the soil where it forms bonds with the organic component. This behavior could create problems of pollution in the food chain linked to its bioaccumulation by plants. Also the possibility of the return of lead from the first layers of the soil to atmospheric dust with consequent risks of ingestion and inhalation is a problem for the environment and for human and animal health. Plants will accumulate heavy metals from the soil with the amount of uptake depending on a wide range of factors including soil chemical-physical and biological characteristics, agricultural management practices and crop genetics.

This study aims to evaluate the capability of barley (*Hordeum vulgare L.*) to bioaccumulate cadmium and lead from an artificially contaminated soil and translocate them from roots to shoots (straw and grain) and its suitability for use in phytoremediation techniques.

Methodology

The trial was conducted in greenhouse conditions in Rome (Italy). The barley (*Hordeum vulgare L. cv Robur*) was cultivated in pots (7.4 kg soil pot⁻¹). Soil was characterized according to the official methods of the Italian Ministry of Agriculture (MIPAF 1999).

The main physico-chemical characteristics of agricultural soil utilized were: pH 6.7; C.E.C. 30.05 meq 100g⁻¹; texture (ISSS) SL; O.M. 0.43 %; total N 0.6 g kg⁻¹; total P 20 mg kg⁻¹; total Cd 1.8 mg kg⁻¹; DTPA – Cd 0.5 mg kg⁻¹; total Pb 70 mg kg⁻¹; DTPA-Pb 4.7 mg kg⁻¹.

The “natural” cadmium and lead content in soil was increased with 100 mg kg⁻¹ Cd or 300 mg kg⁻¹ Pb in the form of sulphates.

The experimental design was: control soil C (not artificially contaminated); soil + 100 mg kg⁻¹ Cd (Cd₁₀₀); soil + 300 mg kg⁻¹ Pb (Pb₃₀₀). Each thesis was replicated three times (3 replicates) in a randomised block design.

The plants were watered using the same volume of water for each plot avoiding leaching phenomena.

Soil and plant samples were collected at maturation at the same time from all the pots.

Soil total cadmium and lead were extracted by wet digestion with a HNO₃-HClO₄ mixture (2.5:1 ratio) at 140 °C for 40 hours. The bioavailable forms of cadmium and lead in soil were extracted with a DTPA-TEA solution (pH 7.3) in accordance with the Lindsay and Norwell procedure (Lindsay and Norwell 1978). Extraction of Cd and Pb from soil by DTPA is thought to give an estimate of bioavailable heavy metals in soils, either alkaline or neutral (Haq 1980). The soil concentration of bioavailable Cd and Pb were analysed because it is of great interest in studies of soil contamination as it is the most environmentally mobile fraction.

At maturation (harvesting time), collected plants were separated into roots, straw and grain. Vegetable samples were rinsed accurately, oven dried at 80° C and weighed. For each plant part, three subsamples were mineralised in HNO₃ (Campbell and Plank 1998).

Cadmium and lead concentrations in plants and soil extracts were determined by Inductively Coupled Argon Plasma Spectroscopy (ICP-OES).

The results obtained were compared with the Least Significance Differences Test (LSD) at a confidence level of 95% to test significance (P≤0.05).

The bioaccumulation factor (BCF) and the translocation factor (TF) were elaborated. The bioaccumulation factor (BCF) is defined as the ratio of the metal concentration in a plant to that in soil and is elaborated to illustrate the heavy metal accumulation efficiency in the plants from the soil. The TF is defined as the ratio of the metal concentration in the shoots to that in the roots and is used to evaluate the effectiveness of a plant in translocating the heavy metal from roots to shoots.

Results and discussion

In figure 1 the total and bioavailable concentrations of cadmium and lead in soil are shown.

Elaborating the percentage ratio between the bioavailable (B) and total (T) form, it was highlighted that cadmium and lead show different dynamics in the soil; in fact, 74.5% of the total cadmium is bioavailable whereas in the case of lead it is only 48%. What makes Pb less mobile than Cd is its ability to form more stable bonds with the organic substance of the soil.

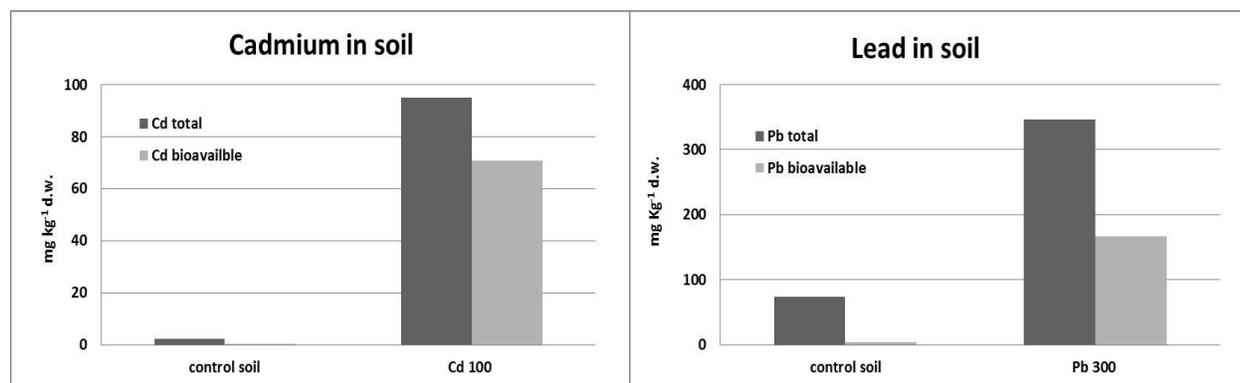


Figure 1. Total and bioavailable cadmium and lead concentrations in soil (mg kg⁻¹d.w.).

In table 1 the concentrations of cadmium and lead in plants are reported. In control C, the values of cadmium in grain were below the limit of detection. In the artificially contaminated treatments (Cd₁₀₀; Pb₃₀₀), the cadmium and lead concentrations in roots and shoots showed different dynamics. With regard to cadmium, plants grown in soil contaminated with cadmium (Cd₁₀₀) showed concentrations significantly higher than C in the roots, straw and grain. In barley cultivated on soil enriched with 300 mg kg⁻¹ of lead (Pb₃₀₀), lead concentrations were significantly higher than C in roots and grain. Instead, in straw no significant differences were found between C and Pb₃₀₀.

A different distribution of cadmium and lead in barley plants was observed in C, Cd₁₀₀ and Pb₃₀₀. In control soil C, 67% of cadmium was in roots, 33% in straw and 0% in grain. In the case of lead, always in C, 61% of lead was in roots, 38% in straw and 1% in grain. In plants grown in soil contaminated with cadmium (Cd₁₀₀), 91% of cadmium was analyzed in roots, 8% in straw and 1% in grain. In plants grown in soil contaminated with lead (Pb₃₀₀), 89% of lead was analyzed in roots, 11% in straw and 0% in grain.

Table 1. Concentration of cadmium and lead in barley at maturation (mg kg⁻¹d.w.).

Thesis (cadmium)	Roots	Straw	Grain
C	0.03 a	0.06 a	n.d.
Cd ₁₀₀	30.13 b	2.76 b	0.34
Thesis (lead)	Roots	Straw	Grain
C	19.7 a	12.0 a	0.2 a
Pb ₃₀₀	107.2 b	13.1 a	0.3 b

For each column, different letters indicate significant differences ($P \leq 0.05$; $n=12$) - n. d. = not detectable (< 0.05 ppm)

The BCF (the ratio of the metal concentration in a plant to that in soil) and TF [the ratio of the metal concentration in the shoots (straw+grain) to that in the roots] were elaborated for both heavy metals in control and contaminated soil (tables 2 and 3).

The BCF values show that the barley bioaccumulates cadmium from highly contaminated soil. In fact BCF value in Cd₁₀₀ was 9 times higher than C. Instead, in the case of lead, Pb₃₀₀ has a BCF value lower than control (C).

Table 2. Bioconcentration factor (BCF)

	C	Cd ₁₀₀	C	Pb ₃₀₀
BCF	0.04	0.35	0.43	0.35

Table 3. Translocation factor (TF)

	C	Cd ₁₀₀	C	Pb ₃₀₀
TF₁ (shoots/roots)	2.00	0.10	0.62	0.12
TF₂ (straw/roots)	2.00	0.09	0.60	0.12
TF₃ (grain/roots)	0.0	0.01	0.01	0.002

As regards the plant's capacity to translocate the two heavy metals from the roots to the shoots, the translocation factor values in soil contaminated with cadmium or lead were lower than the control (table 3). In Cd₁₀₀, TF₁ value is 20 times lower than C. In Pb₃₀₀, TF₁ value is 5 times lower than C. Approximately the same orders of magnitude have been observed in TF₂ elaborated as straw/roots for both, cadmium and lead. The translocation factor elaborated as grain/roots (TF₃) was very low, especially in the case of lead. These results indicate that in polluted soil the barley probably will absorb higher amounts of cadmium than lead. However it seems that, in the presence of high concentrations of these heavy metals in soil, the barley implements physiological mechanisms that limit their translocation to the shoots.

Conclusions

The results of this study suggest that, in soils highly contaminated by cadmium and lead, the barley plant activates physiological and biochemical mechanisms at the soil/root interface -in the case of lead- and at the root level -for both heavy metals- limiting the bioaccumulation of the two heavy metals from the soil to the roots and their translocation into the shoots (straw and grain). The roots are the main organs involved in bioaccumulation of cadmium and lead from soil. In polluted soil, the translocation of two heavy metals from the roots to the grains was low compared to the straw. Nevertheless, the barley plants grown on contaminated soil should, in any case, be considered as possible means of entry for the cadmium and lead into the trophic chain.

Some authors report that plants with both translocation factor (TF) and bioconcentration factor (BCF) greater than one (TF and BCF > 1) have the potential to be used in phytoextraction. Besides, plants with bioconcentration factor greater than one and translocation factor less than one (BCF > 1 and TF < 1) have the potential for phytostabilization (Yoon *et al.* 2006; Rezvani and Zaefarian 2011).

In this case study, barley does not seem to be a species that can be used in phytoremediation techniques.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.1.9. Food Safety and Soil Health: An FDA Perspective

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Abstract

The United States Food and Drug Administration is implementing the Food Safety Modernization Act. FSMA transforms the United States' food safety system by shifting focus from response to prevention of foodborne illness. FDA has finalized seven major rules as part of the implementation of FSMA. Here we present an overview of one of those rules; the Produce Safety Rule, which provides standards for growing, harvesting, packing, and holding produce for human consumption. Special emphasis will be given to provisions associated with usage of Biological Soil Amendments of Animal Origin and Human Waste (Subpart F contained in 21 CFR Part 112). Specifically, we will discuss risk assessment and quantification of human illness linked to use of untreated Biological Soil Amendments of Animal Origin (e.g. manure) for production of fresh fruits and vegetables. Objectives include: (1) overview of the scientific data underpinning new rules; (2) explanation of what FDA has done and where we are now; and (3) proposing international initiatives aimed at achieving globally implemented improvements for production of fresh fruits and vegetables for human consumption.

Additionally, we will discuss how integration of molecular sequencing technologies (i.e. Whole Genome Sequencing) is revolutionizing risk assessment and predictive modeling of microbial risks associated with agricultural waters, soils, and produce microbiomes. For example, the evaluation of agro-ecologies and anthropogenic farming practices has identified unintentional enrichment of ecological niches that support persistence of foodborne pathogens such as *Salmonella* in field environments. Multiple environmental surveys within agricultural land use regions have consistently found *Salmonella* in surface waters. These data have been used to direct new recommendations that appear to have mitigated risk of *Salmonella* transfer in at least one high risk crop environment. FDA will present case studies on how the integration of genomic technologies has resulted in new insight and novel approaches to the safe and responsible stewardship of fresh fruits and vegetables.

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2.1.10. Bio-solids from Bugolobi Wastewater Treatment Plant, Uganda do not meet the minimum standards for land application.

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Abstract

Land application of bio-solids is the cheapest and most convenient method of disposal of bio-solids worldwide but it was unclear if the bio-solids in Uganda were safe for land application. We established the impact of ageing on quality and safety of bio-solids from Bugolobi Wastewater Treatment Plant (BWTP) for land application. Nine out of 14 beds in each of the four blocks (Block 1: fresh bio-solids; Block 2: settling bio-solids; Block 3: maturing bio-solids and Block 4: mature bio-solids) were randomly sampled for quality and for bio-safety. For quality, bio-solids were analysed for electrical conductivity (EC); N, P and K concentrations and their respective stocks; organic matter (OM) content and bio-solid organic carbon (BOC) stocks. For bio-safety, bio-solids were screened for *E. coli* and *Salmonella*. Data were subjected to ANOVA after checking for normality and equal variance assumptions, using Genstat statistical package 14th edition. Means were separated using Fischer's protected LSD at two standard deviations. Ageing of bio-solids had a significant impact on EC; N, P and K concentrations; OM and *E. coli*. The EC was highest in the mature bio-solids (4556±173) $\mu\text{S cm}^{-1}$ and smallest in fresh bio-solids (3494±124) $\mu\text{S cm}^{-1}$. These EC values exceed the maximum permissible limits. Similarly, microbial counts were highest for *E. coli* in the mature sludge (3946±86) '000' CFU g⁻¹ and smallest in the fresh bio-solids (633±22.9) '000' CFU g⁻¹. Out of the 36 bio-solid samples, one tested positive for salmonella. The bio-solids are not safe for land application nor general release into the environment.

Keywords: Bio-solids, bio-solid organic carbon (BOC), Electrolytic conductivity (EC), E. coli, land application, maximum permissible limits (MPL), Salmonella, wastewater

Introduction, Scope and Main Objectives

Wastewater contains high levels of organic matter, germs, nutrients and toxic compounds which can pollute soils, with potentially serious human and environmental health hazards. Wastewater treatment is therefore, recommended to ensure that pollutants from the resulting sewage sludge (hereafter, bio-solids), do contaminate the food chain via polluted soils (UN-HABITAT 2008; Tukar *et al.* 2011; Rawlinson 2012).

Since the early 1970s, the US Environmental Protection Agency (USEPA) and wastewater treatment industries have promoted the recycling of bio-solids (EPA Victoria 2004; Suzanne *et al.* 2007) to cope with increasing volumes of wastewater (NETWAS UGANDA 2011). By early 2000, approximately 1,500 km³ of wastewater was generated annually worldwide, about six times the water in all rivers in the world (UNWWAP 2003). Land application for agriculture; large-scale landscaping, lawn gardening; remediation of abandoned mining sites; and soil-surface re-vegetation is the commonest method for disposal of bio-solids worldwide. In the USA e.g., over 40% of bio-solids produced annually are disposed of by land application (Evans 2009) as are hundreds of thousands of metric tonnes of bio-solids produced annually in Australia (Rawlinson 2012).

The bio-solids, should meet the minimum standards for disposal by land application. With respect to pathogen levels, bio-solids are classified in two ways each with its own application rules: Class

A and Class B bio-solids. Class A bio-solids should ideally, not have detectable levels of *Salmonella* sp, enteric viruses, and viable helminth ova and less than 1,000 CFU faecal coliform bacteria g⁻¹ (USEPA 1995) and can be land applied without any pathogen-related restrictions except when used in bulk (Suzanne *et al.* 2007). For class B bio-solids, site restrictions on land application are aimed at minimising the potential for human and animal contact until environmental factors have suppressed pathogens to undetectable levels. Faecal coliform bacteria should be < 2 million CFU g⁻¹ and the potential to attract vectors that can transport pathogens should be reduced (USEPA 1995).

South Africa has included Class C bio-solids (Table 1) with no pathogen reduction targets preferably destined for incineration (UN-HABITAT 2008). Class B restrictions target 99% pathogen reduction. Australia has established four treatment grades (T1 to T4) of bio-solids with maximum permissible limits (Table 2) (EPA Victoria 2004). Grade T1, the highest quality bio-solids are suitable for unrestricted use whereas Grade T4 bio-solids are not suitable for land application unless subjected to site-specific risk assessment (EPA Victoria 2004).

Table 1. Classification of bio-solids by the South Africa standards as a guide for their suitability for land application (UN-HABITAT 2008). Restrictions for Class A and Class B bio-solids are derived from USEPA (1993).

Bio-solid class	Faecal coliform target value (CFU g ⁻¹)	Faecal coliform maximum permissible value (CFU g ⁻¹)
Class A	< 1000	< 10000
Class B	< 1000000	< 10000000
Class C	No target set	>10000000

Table 2. Classification of bio-solids by the Australian standards as a guide for their suitability for land application (EPA Victoria, 2004).

Treatment grade	E-coli	Salmonella
T1	< 100 MPN/g dw	< 1salmonella/5g dw
T2	<1000 MPN/g dw	< 10 salmonella/50g dw
T3	< 2000000 MPN/g dw	
T4	Nil	Nil

In Uganda, we could not find a single study indicating whether or not; the bio-solids meet the minimum standards for land application. We conducted this study to establish safety of the bio-solids from Bugolobi Wastewater Treatment Plant (BWTP) that treats wastewater from Kampala City, central Uganda (Fig. 1) for land application. Specifically, we evaluated the impact of ageing on the quality of the bio-solids and examined the safety of the bio-solids for land application to test the hypothesis that the bio-solids do not meet the minimum standards for land application.

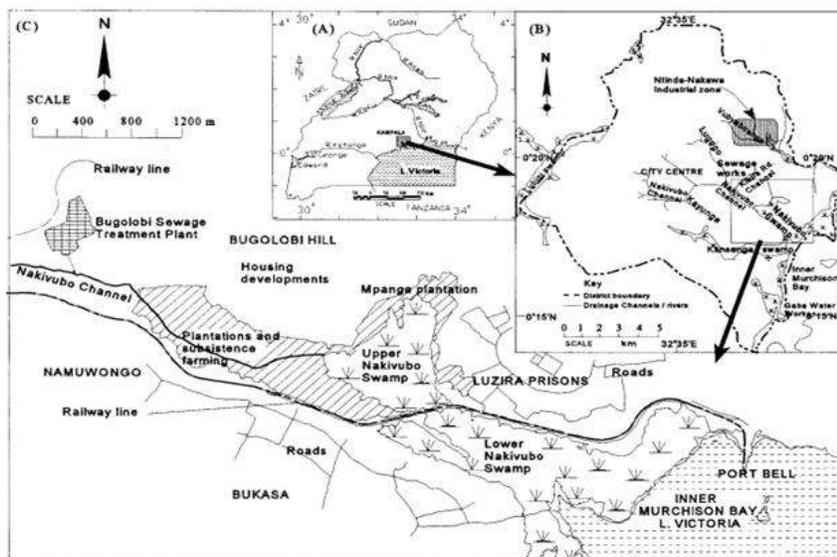


Figure 1. Location of Bugolobi Sewage Treatment Plant. Inset A is the Map of Uganda showing the location of Kampala City whereas Inset B shows the extent of Kampala City, with the Nakivubo Swamp, Murchison Bay and the location of the Bugolobi Sewage Treatment Works (Kansiime and Nalubega 1999).

Methodology

Bio-solids sample collection and handling

We sampled nine out of the 14 beds denoted by numbers 1 to 9 in each of the four bio-solid blocks with the age of bio-solids as the basis for blocking: Block 1 (fresh bio-solids), Block 2 (settling bio-solids), Block 3 (maturing bio-solids) and Block 4 (mature bio-solids) (Fig. 2). In each of the selected beds, bio-solids sampling was done for quality (EC; OM and bio-solid organic carbon (BOC) stocks; and N and P concentrations and their respective stocks) and bio-safety (*E. coli* and *Salmonella*). For quality and biosafety, four sampling spots were randomly located in each of the selected beds. From each of the sampling spots, the caked layer on the surface of the bio-solids was carefully scrapped off. Bio-solid samples were thereafter carefully scooped mid-way the freshly exposed surface and the bottom of the bio-solids drying bed using a trowel. Each of the four bio-solid samples scooped was emptied into a plastic basin from which the samples were manually homogenised and quarter-sampled to get a representative composite sample per bed, giving a total of 36 composite samples (4 blocks * 9 beds * 1 composite sample). Each composite sample was immediately split into two: one for quality and the other for bio-safety tests. Each of the samples for bio-safety analyses was carefully emptied into a well-labelled and sterile zip-lock polyethylene bag, fastened tightly (to minimise moisture loss) and packed into an ice cooler box.

1		3	5	9		7
	2		4		6	8

Block 1

1		3	5	9		7
	2		4		6	8

Block 3

1		3	5	9		7
	2		4		6	8

Block 2

1		3	5	9		7
	2		4		6	8

Block 4

Figure 2. Sampling design for wastewater bio-solids from four blocks: Block 1 (fresh bio-solids); Block 2 (settling bio-solids); Block 3 (maturing bio-solids) and Block 4 (mature bio-solids ready for disposal) at Bugolobi Wastewater Treatment Works on March 27, 2014. Numbers 1-9 in each block represent the beds from which bio-solid samples were collected for laboratory analyses.

The second batch of 36 samples for quality tests were also similarly packed but in a separate ice cooler box. For samples for estimation of stocks of N, P and BOC in the bio-solids at BWTP annually, the dimensions (length, width and depth) of bio-solids in each of the selected beds were taken. An open-ended plastic PVC tube of internal diameter 0.05 m was then used to extract core bio-solid samples from three spots randomly located in each of the selected bio-solid beds by driving the PVC tube into the bio-solids from top to bottom of the bio-solids bed, followed by carefully trimming the top part of the PVC tube so that the exact space left was that occupied by the bio-solids. Each of the bio-solid samples extracted using the PVC tube from each spot were emptied into a large polyethene bag and fastened tightly to minimize moisture loss. This gave a total of 108 samples (3 core samples x 9 beds x 4 blocks). Fresh weights of the samples were taken using a digital weighing scale.

Bio-solids sample processing and laboratory analyses for quality

For biosafety, the bio-solids samples were immediately transported to the Microbiology Laboratory College of Veterinary and Biosciences, Makerere University. Here, the bio-solid samples were tested for *Escherichia coli* and *Salmonella typhi* and *Salmonella* following the standard procedures described by (Refai 1979; USEPA 2003; USEPA, 2011). Samples for bio-solid quality and for estimation of total bio-solids generated and moisture content were transported to the Soil, Water and Plant Analytical Laboratory in the College of Agricultural and Environmental Sciences, Makerere University. The samples for chemical analyses were tested for EC, organic matter content (OM) and subsequently, organic carbon stocks and N, P and K concentrations following the methods compiled by Okalebo *et al.* (2002).

Estimation of the N, P and K stocks and moisture content of bio-solids

The core bio-solid samples were oven-dried at 60 °C to constant weight and cooled in a desiccator before the dry weights (W_d) were taken. The density of bio-solids (B_d) was estimated by dividing respective W_d of the bio-solids by volume of the PVC tube (V_{pvc}). V_{pvc} was estimated using the formula:

$$V_{pvc} = \frac{\pi d^2}{4} * h \quad (1)$$

Where: h : height = 0.3 m, d : diameter of the PVC = 0.05 m, $\pi = 22/7$

To estimate the total mass of bio-solids generated at BWTP, the volume of each of the beds (V_b) was estimated from the formula:

$$V_b = l * w * h \quad (2)$$

Where: l = length of the bed = 10 m, w = width of the bed = 10 m, and h = height of the bed = 0.3 m

The mass of the bio-solids in each of the beds was estimated by multiplying respective B_d by volume of the beds (in equation 2). The total mass of bio-solids was obtained by multiplying the mass in one bed by 14 (the total number of beds in each block) and by 4 (the total number of blocks). To correct for moisture content of the bio-solids, the weight of moisture was subtracted from total weight of bio-solids in each block using the formula:

$$DMY = w - (w * \%m) \quad (3)$$

Where; DMY = Dry matter yield, w = estimated total weight, $\%m$ = percentage moisture of bio-solids

Consequently, the nutrient stocks (NS): N, P and K were estimated by multiplying the total dry matter yield (DMY) of the bio-solids by the respective percent nutrient concentration ($\%N$) as follows:

$$NS = DMY * \%N \quad (4)$$

Estimation of organic carbon stocks of the bio-solids

We modified the equation that Olupot *et al.* (2015, 2017) used to estimate soil organic carbon (SOC) and soil organic nitrogen (SON) stocks for estimation of bio-solid organic carbon (BOC) stocks:

$$BOCstock = \sum_{Block_i}^{Block_n} (BOC * DMY) \quad (5)$$

Where, BOCstock is the BOC stock ($t \text{ cycle}^{-1}$); $Block_i$ is the block with fresh bio-solids whereas $Block_n$ is the block with mature bio-solids; BOC is the BOC concentration (% bio-solids on dry weight basis).

Results

Impact of ageing on electrolytic conductivity (EC) of bio-solids

Age of bio-solids had a significant impact on EC with the highest (4556 ± 173) $\mu\text{S}/\text{cm}$ in the mature bio-solids and smallest (3494 ± 124) $\mu\text{S}/\text{cm}$ in the fresh bio-solids (Fig. 3), pointing to increasing salinisation of the bio-solids with ageing. The impact of ageing of bio-solids on OC concentration was also significant, with a progressive decrease in OC concentrations from the fresh bio-solids (46.6 ± 0.92 %) to mature bio-solids (42.2 ± 1.44 %) (Table 3). However, there was no significant impact of ageing on bio-solid organic carbon (BOC) stocks (Fig. 4).

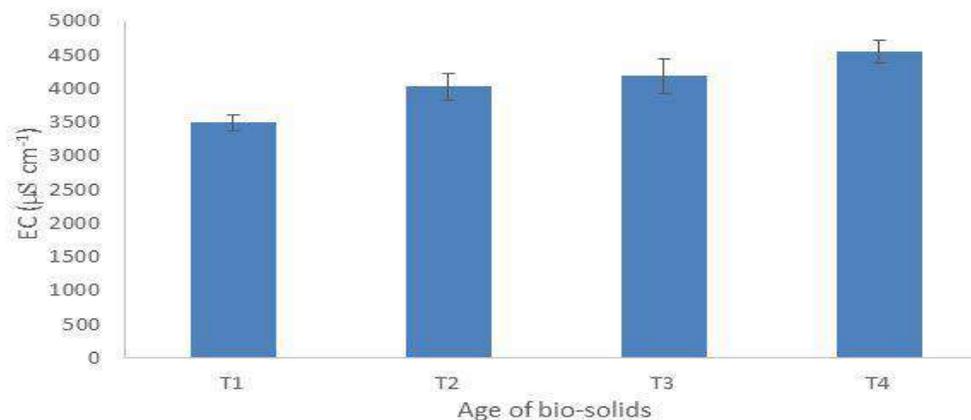


Figure 3. Effect of age of bio-solids (x-axis) on electrolytic conductivity, EC (y-axis) from Bugolobi Wastewater Treatment Plant as of March 27, 2014. T1, T2, T3 and T4 denote: fresh, settling, maturing and mature bio-solids, respectively.

The ageing of bio-solids had no significant impact on concentrations and stocks of N, P and K with the bio-solids being generally low in nutrient concentrations (Table 3). Despite the low nutrient

concentrations, the nutrient stocks stockpiled in these bio-solids in excess of 400 kg N yr⁻¹ (Fig. 5) and 1,000 kg P yr⁻¹ (Fig. 6), potentially threaten the Wetland meant to naturally treat the effluent from BWTP where these bio-solids are located before its discharge into Lake Victoria.

Table 3. Effect of age of bio-solids (x-axis) on % OM, %N, %P and % K of bio-solids from Bugolobi Wastewater Treatment Plant as of March 27, 2014.

Age of bio-solids	Parameters of bio-solids measured			
	%OM	%N	%P	%K
Fresh	46.6±0.92 ^b	0.29±0.01 ^a	0.74±0.02 ^b	0.87±0.05 ^a
Settling	44.1±0.82 ^{ab}	0.28±0.02 ^a	0.71±0.04 ^{ab}	0.79±0.04 ^a
Maturing	43.8± 0.96 ^{ab}	0.28±0.02 ^a	0.67± 0.01 ^a	0.77±0.03 ^a
Mature	42.2±1.4 ^b	0.26±0.01 ^a	0.68±0.01 ^{ab}	0.77±0.03 ^a

Means with the same letter within a column are not significantly different ($P < 0.05$)

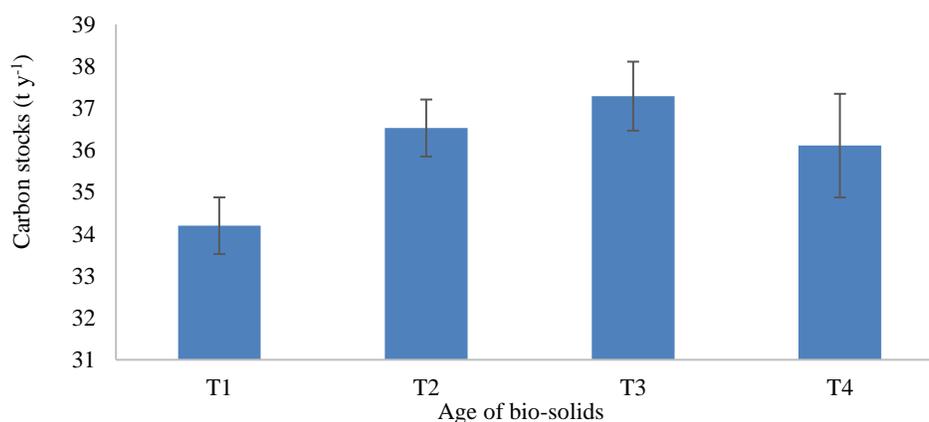


Figure 4. Effect of ageing of bio-solids (x-axis) on bio-solid organic carbon stocks (y-axis) from Bugolobi Wastewater Treatment Plant as of March 27, 2014. T1, T2, T3 and T4 denote: fresh, settling, maturing and mature bio-solids, respectively.

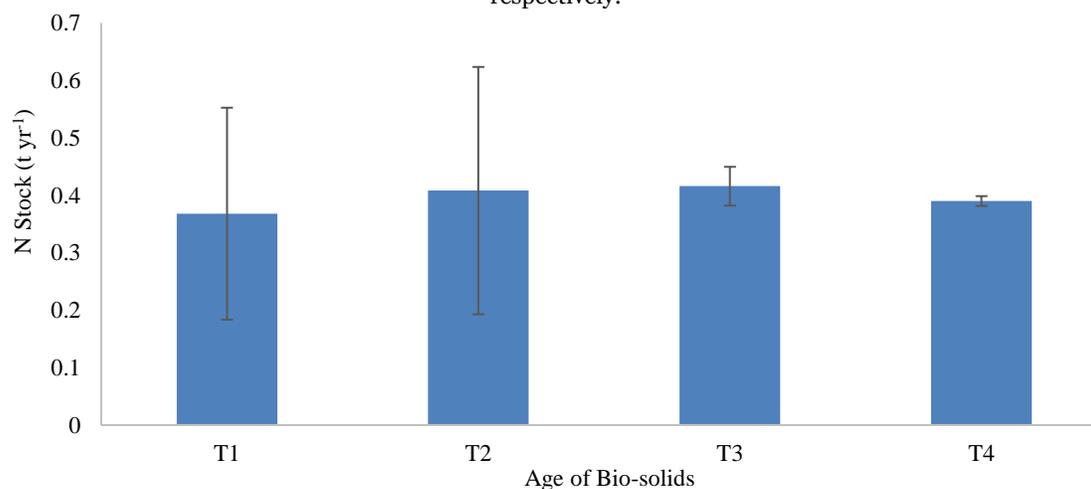


Figure 5. Effect of ageing of bio-solids (x-axis) on bio-solid organic nitrogen stocks (y-axis) from Bugolobi Wastewater Treatment Plant as of March 27, 2014. T1, T2, T3 and T4 denote: fresh, settling, maturing and mature bio-solids, respectively.

The impact of ageing of bio-solids was also significant on *E. coli* with the highest populations in the mature bio-solids (3946 ± 86) '000' CFU g⁻¹ and smallest in the fresh bio-solids (633 ± 229) '000' CFU g⁻¹ (Fig. 7). One out of the 36 bio-solid samples tested positive for *Salmonella*, implying that the bio-solids are not safe for land application.

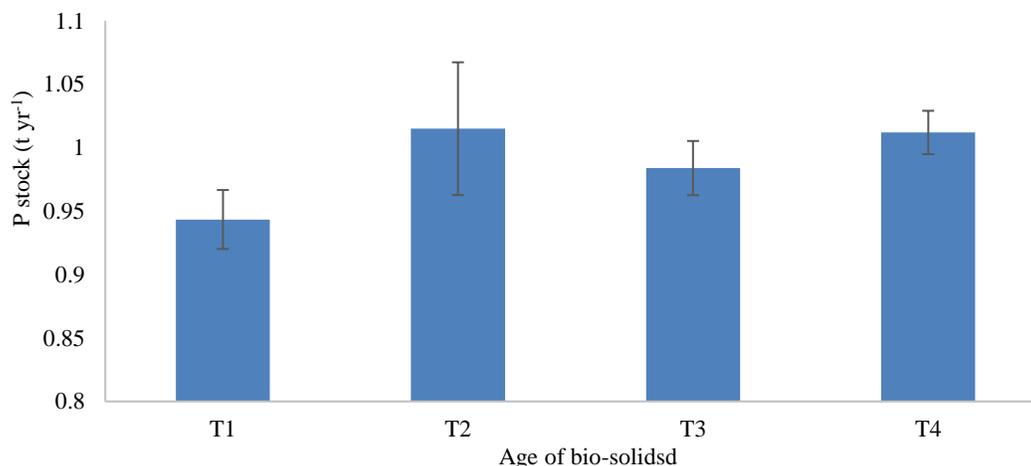


Figure 6. Effect of ageing of bio-solids (x-axis) on bio-solid phosphorous stocks (y-axis) from Bugolobi Wastewater Treatment Plant as of March 27, 2014. T1, T2, T3 and T4 denote: fresh, settling, maturing and mature bio-solids, respectively.

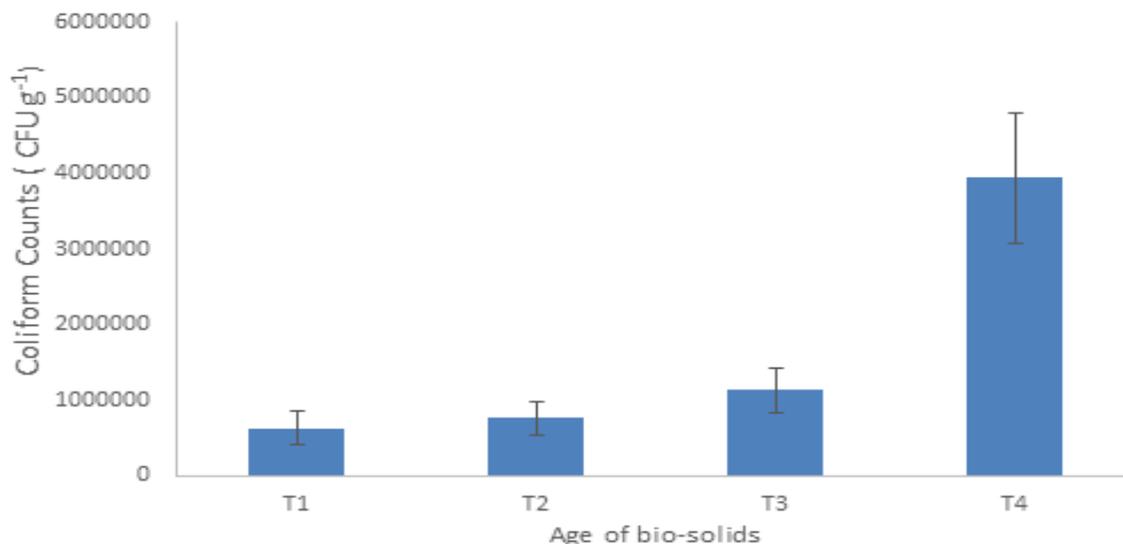


Figure 7. Effect of age of bio-solids (x-axis) on *E. coli* x 10¹ (y-axis) from Bugolobi Wastewater Treatment Plant as of March 27, 2014. T1, T2, T3 and T4 denote: fresh, settling, maturing and mature bio-solids, respectively.

Discussion

The EC values of the bio-solids tested in this study exceed the 4000 $\mu\text{S cm}^{-1}$ MPL for soils (USDA 2011) especially for the settling, maturing and mature bio-solids. Salt tolerance limits of even the most tolerable plants are 3000 $\mu\text{S cm}^{-1}$ (Doulaye *et al.* 2010). The EC > 4000 $\mu\text{S/cm}$, restrains plant growth by inducing high osmotic pressures in the roots (Garrido *et al.* 2005). The increase in EC with ageing of bio-solids could be due to (i) increasing solubilisation and mobility of ions of salts (Kiely 1998; Ngole *et al.* 2006); (ii) Increasing organic matter humification and formation of carboxyl and phenolic functional groups onto which cations could be adsorbed (El-Naim and El-Houseini 2002) and (iii) the inevitably increasing dewatering with ageing of bio-solids which

concentrates total solids. According to Irene *et al.* (2001) the final solid content of bio-solids increases almost linearly with salinity. In most cases, where the possibility of recycling bio-solids into agriculture exists, the salt content is often a limiting factor. Continued use of the bio-solids at BWTP without de-salinisation could lead to soils salinisation, a chemical type of toxic soil pollution (Byron and Calvin 2012).

The decrease of OM with ageing of bio-solids occurs naturally due to humification and mineralization of the bio-solids-derived OM by the microorganisms (Leifeld *et al.* 2001). These processes convert organic material in the sludge to inorganic forms resulting in a reduction of the amount of OM accumulated with age. The initial tendency of carbon stocks to increase with ageing of the bio-solids could be due to dewatering which has been found to concentrate solids to between 50 and 90 % (Bresters *et al.* 1997). This OM can potentially improve soil physical and biological properties: water retention capacity and soil organic matter (FAO 2003), soil aggregation, buffering of soil pH, increased cation exchange capacity and rejuvenation of microbial populations and activities in the soil (USEPA 1995; Leonie *et al.* 2009). However, if not disposed of well, it could also be a source of greenhouse gases and atmospheric pollution.

Although the N and P nutrients of the BWTP bio-solids are generally low, they can become formidable enough in stockpiles of bio-solids to trigger eutrophication. Eutrophication had devastating impacts on hydropower, water transport, fisheries and water supply sectors of Lake Victoria in the early-to-mid 1990s (NEMA 1996). The presence of *E. coli* in water is a pointer to presence of pathogenic bacteria, including strains of *E. coli*, viruses and protozoa (USEPA 2002; Stevens *et al.*, 2003) that can pose serious human and environmental health risks (Saha *et al.*, 2011). All the counts for *E. coli* in the bio-solids we analysed were above the 10000 CFU g⁻¹ MPL for *E. coli* in wastewater (WHO 1998; NEMA 1999; UNBS 2014). Unregulated use of these bio-solids could be the reason for sporadic outbreaks of cholera in and around Kampala City especially during heavy rains.

Conclusions

In their current state, the bio-solids from the Bugolobi Wastewater Treatment Plant do not meet the minimum standards for land application and general release into the environment. In particular, the bio-solids contain high concentrations of salts and therefore could potentially lead to soil salinisation with repeated application. The microbial load is also way above the maximum permissible limits. One in 36 bio-solid samples tested positive for *Salmonella*. Without desalinization to lower the EC to MPL and disinfection to eliminate or lower potentially pathogenic organisms such as *E. coli* and *Salmonella sp* to recommended MPL, alternative disposal methods for the bio-solids to land application for agricultural and related purposes should be sought.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.1.11. Soil contamination policy: increasing students' awareness

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Abstract

Soil pollution is considered as a major challenge for healthy environment and human health. One of the key points in the soil contamination policy is the education and public awareness of the problem caused by soil pollution. Today's students will be tomorrow's soil guardians. Education influences decisions regarding to soil care. It is important to convey to students that the three types of soil pollution (biological, chemical and radioactive) should be avoided in industrial, agricultural, forest and urban soils. Knowledge of soil properties, soil functions, soil pollution, human health and ecological risk assessment is the foundation for achieving sustainable soil management. Spreading knowledge about soil health and environmental and human risk relationship requires a very conscientious education/training at both undergraduate and graduate level. Universities should be aware of the need to promote the collaboration between industry, research and education in order to train individuals to become highly-competent professionals in Soil Pollution. In addition, because we live more and more in a globalized world, students should know the regulations of soil and groundwater contamination in other countries and be fully aware of the social responsibilities in this issue. Moreover, students should keep in mind the need to help developing countries. This

article provides some practical guidelines to raise awareness and sensitize students at University level about the importance of having clean and healthy soils for the development of the humanity. Furthermore, it provides a broad and deep view of the knowledge that is taught in subjects related to soil pollution.

Keywords: soil pollution, soil remediation, human health risk, ecological risk, enhancing student learning, educational experience.

Introduction

Soil is an important constituent of the earth surface system and essential to life processes in the terrestrial ecosystems. It is also indispensable for agricultural and farming production and therefore for human life. During the last few decades, there has been a fast development of industrialization, urbanization, and agricultural intensification. Unfortunately, in some cases, large amounts of anthropogenic emissions of different types of pollutants have entered the soil environment through multiple pathways, causing soil pollution (Luo and Tu 2016). Land contamination is a worldwide phenomenon that is faced by both developed countries and developing countries (Zhao 2017). Currently, there is an increase in pressure on soil safety and health, and the social demand for the control and remediation of polluted soils is extremely urgent (Luo and Tu 2016). The main objective of soil contamination policy is to protect or restore the functions of the soil on a permanent sustainable basis, and for that, we should transmit the need to protect clean soil, monitor soil quality, clean up all contaminated sites and optimize the use of contaminated soil. Soil pollution not only has negative effects on food safety but can also result in increased health risks (Lu *et al.* 2015; Carré *et al.* 2017, Rodrigues and Römken 2018). It is clear that to avoid the problems for human health and ecosystems associated with soil pollution we need to have a regulatory system, develop sustainable and environment-friendly techniques not only in the industrial processes but also in the agricultural field, increase basic and applied research, and develop industrial support on soil pollution and remediation (Luo and Tu, 2016).

Furthermore, it is necessary to raise awareness of the entire population about environmental degradation, and specifically about the importance of having healthy soils.

As the 2003 World Youth Report points out 'Young people constitute a large part of the world's population' and 'strengthening the participation of youth in environmental protection is partly a matter of increasing opportunities in governmental organizations, established NGOs and restoration projects'. Students at university level constitute an important group of the population concerned with environmental protection as can be deduced from different studies (He *et al.* 2011; Ramirez 2017; Onokala *et al.* 2018). Students that participate in learning activities related with Soil Pollution could increase their concern about this problem and have more tools for analytical and creative thinking. They are able to propose affordable and workable solutions, not only during their studies but also in also in their future career.

The main objectives of this paper is to bring experiences and ideas through different activities that can increase student's awareness of the soil pollution problem.

Methodology

This article is based on the educational experience in the teaching of subjects related to soil contamination in the Degree of Environmental Science (subject: Soil pollution and waste treatment) and in the Master's Degree in Industrial Engineering (subject: Waste and contaminated site management). A range of activities was used to support student learning and to raise the awareness of students about the problem of contaminated soils. Among them, we have used audiovisual aids

(e.g. series of fiction and documentaries), case studies (Table 1), participation in on-line forums, and use of a computer simulation model to predict nitrate leaching.

Audiovisual aids

A documentary about lindane (HCH) was used in the class. The documentary is accessible in RTVE (Spanish TV). After watching the documentary, the students answered some questions about soil contamination and the influence of the documentary on their critical attitude to this problem.

Case studies

Case studies of soil contamination sites used in classroom are reported in Table 1.

Table 1. Case studies

Location	Type of contamination	Year	Location	Cited by
Aznalcollar	Chemical	1998	Spain	Madejón <i>et al.</i> 2018
Sabiñánigo	Chemical	From the late 1970s on	Spain	Gómez-Lavín <i>et al.</i> 2018
London Olympic Park	Chemical	Since XIX century	United Kingdom	Hellings <i>et al.</i> 2012; Mead <i>et al.</i> 2013
Love Canal	Chemical	1970s	USA	Phillips <i>et al.</i> 2007
Lekkerkerk	Chemical	1970s	Netherlands	Brinkmann 1982
Fukushima	Radioactive	2011	Japan	Yasunari <i>et al.</i> 2011
Chernobyl	Radioactive	1986	Ukraine	Steinhauser <i>et al.</i> 2014 Yoschenko <i>et al.</i> 2018

Computer simulation model

An important goal in order to face soil pollution problems is the ability to simulate contaminant transport, diffusion and transformation processes for reliably estimating their impact and forecasting the effects of chemicals in soil and water. Calibrated and validated simulation models can be useful tools for evaluating different fertilizer and pesticide application scenarios and as support systems for the recommendation in the manage of these products. One of these models is LEACHM (Leaching Estimation and Chemistry Model). LEACHM is a process-based, one-dimensional model that simulates water and solute movement, and related chemical and biological processes, in the unsaturated soil (Wagenet and Hutson, 1989). LEACHM has four different modules: LEACHN describes nitrogen transport and transformation and it is the one used with our students; LEACHP deals with pesticides; LEACHC describes flow of inorganic ions and a fourth one; LEACHW describes water transport only. This model was used as an awareness of the relation between soil contamination and groundwater contamination.

Results and discussions

On the one hand, Soil Pollution is a very broad area of knowledge inside Soil Science, and on the other hand interacts with many other areas as Chemistry, Physics, Biology, Geology, Civil Engineering, etc. As it is illustrated in Figure 1 and without being exhaustive, good knowledge of Soil Pollution involves many concepts, methodologies, processes, etc.

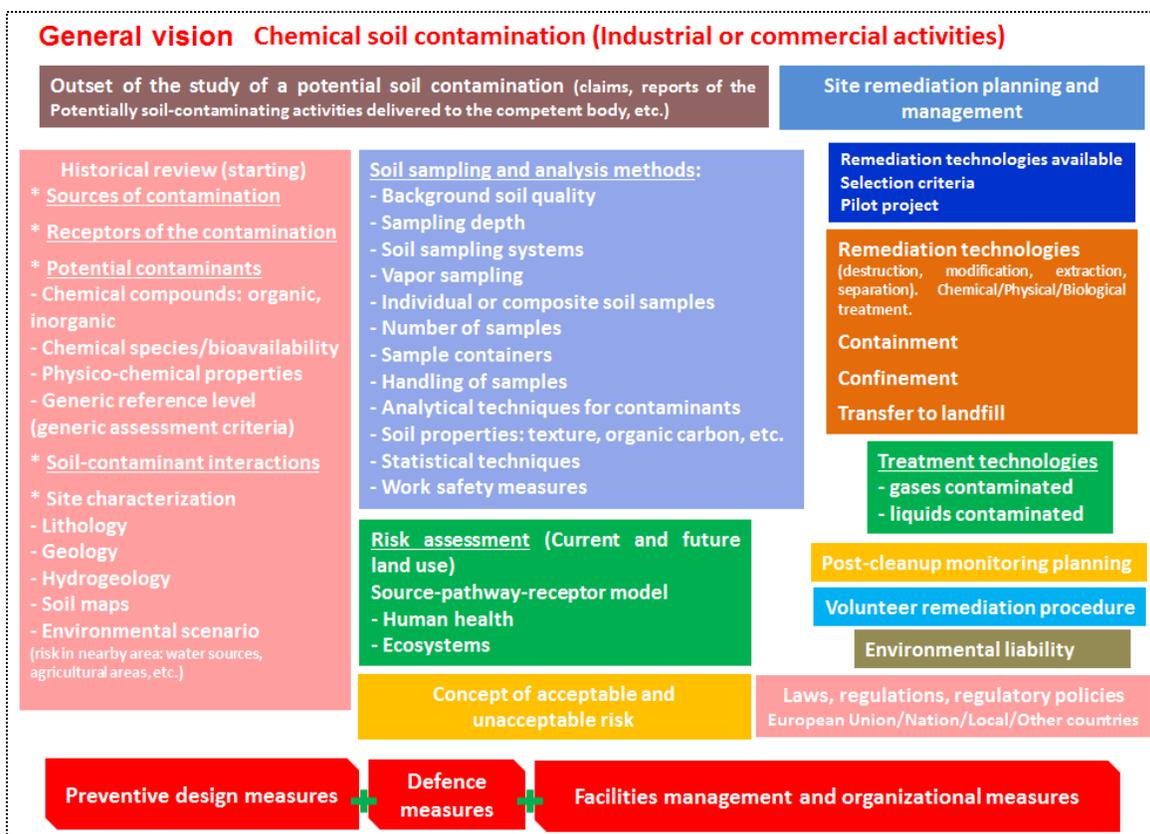


Figure 1. Core body of knowledge of chemical soil contamination

We teach not only chemical soil contamination but also biological and radioactive contamination. In the case of the use of sewage sludge as a fertilizer and the reuse of wastewater for irrigation of crops, forest, gardens, etc., soil could be contaminated by organic compounds and heavy metals, and by microorganism, when regulations are not followed. Currently, the Spanish regulation (the same as the European regulation) of the use of sewage sludge in farming only takes into account heavy metals as potential harmful compounds. For this last reason, it could be interesting that students work in the classroom more advanced regulations (see Christodoulou and Stamatelatou 2016) like the Decree 453/2013 that aims to regulate the use of sewage sludge in agricultural soils in the Basque Country and takes into account metals, organic compounds and microorganisms.

In the case of radioactive soil contamination, it could be intriguing to encourage students based on Fukushima or Chernobyl accidents to characterize radioactively contaminated sites for remediation purposes. In Spain, we have the case of Palomares but there is not much information available. Briefly, on 17 January 1966, due to an aircraft accident, two nuclear weapons detonated and the result of these detonations was the fragmentation of the weapons, and the dispersion of their content. This dispersion produced a clear contamination of plutonium isotopes in the zone. The most contaminated areas, the upper 10 cm layer of soil and the associated vegetation was collected, stored in drums and sent to the USA for disposal (Jiménez-Ramos *et al.* 2006).

The first goal in the classroom is to get the attention of the students, and this is not difficult in the topic of Soil Pollution because there is a close relationship between soil contamination and risks for humans and for ecosystems, and nowadays most of the students are concerned about the degradation of the environment. Therefore, the first steps to encourage them in this subject could

be to talk about the pairing soil contamination-risk (Figure 2) illustrating this coupling with case studies (Table 1). The case studies Love Canal (USA) and Lekkerkerk (Netherlands) are very interesting for them, first because it is clear the relation between waste-soil contamination-health/environmental problems, and secondly due to the fact that after these cases were enacted the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in the USA, and the Soil Clean-Up Act 1983 in the Netherlands. At the end of the semester, students should know which is the action plan and the working plan for a case study. Other case studies that could be used in classroom can be found in the document 'European achievements in soil remediation and brownfield redevelopment' (Payá and Peláez, 2017).

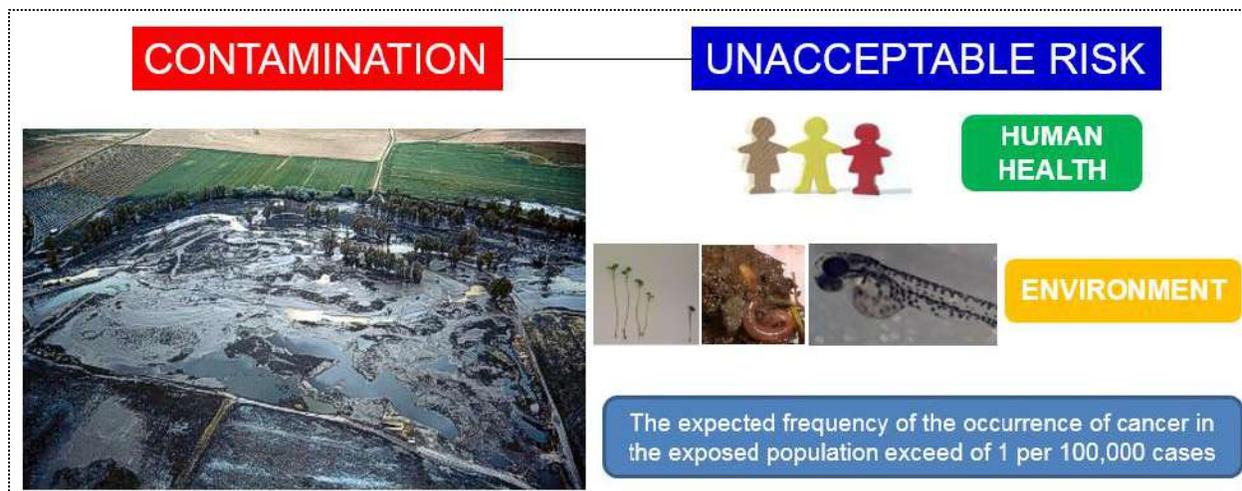


Figure 2. First step in the awareness of students: relationship between land contamination and risk

Appealing to their sense of responsibility with the environment and future generations, we could explain the Soil Pollution Principles (Figure 3). Specifically, the Prevention principle and the Rehabilitation-Reclamation Principle. The Prevention principle has a crucial role; it underpins much of the legislative and policy basis for a better soil preservation in the European Union. Steps need to be taken to minimise the creation of additional contaminated sites and to prevent the further contamination of already contaminated sites which can occur either as a result of accidents or of ongoing poorly managed industrial, agricultural or commercial activities (CRC CARE 2013). Students should be awarded that the industry should use the so called 'Best Environmental Management Practice', using preventive design measures (e.g. floors of bulk storage facilities should be designed to withstand the hydrostatic pressure exerted when tanks are full), defense measures (e.g. alarm systems in case of leakage), and facilities management and organizational measures (e.g. emergency plans, maintenance and inspection programs).

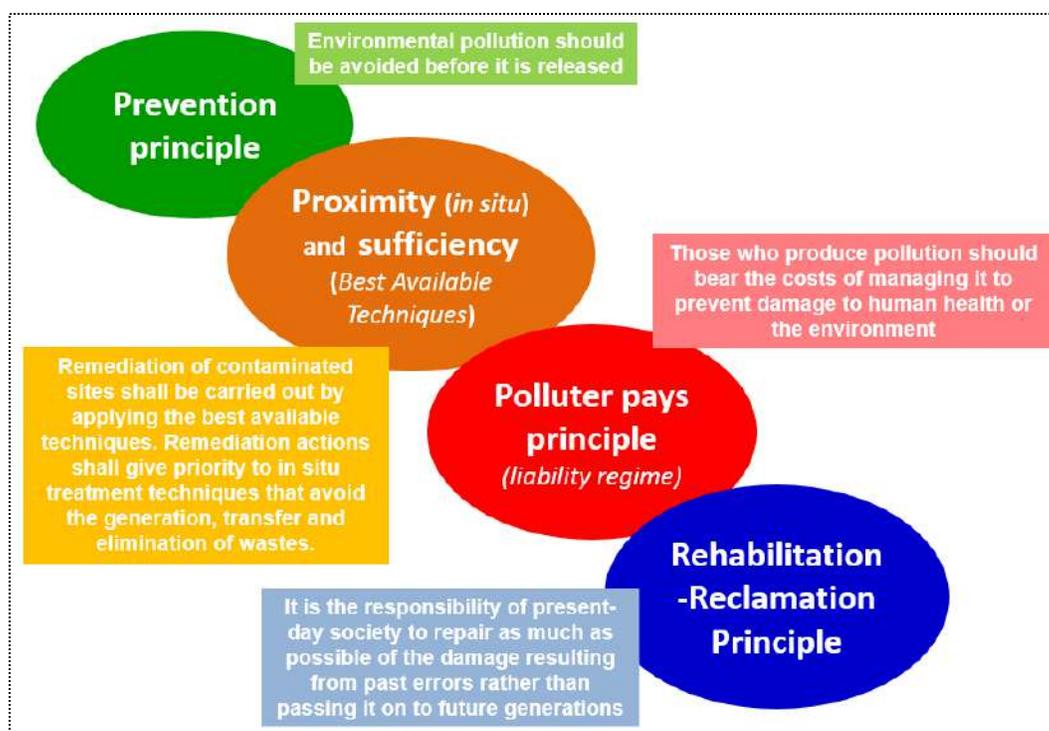


Figure 3. Basic principles in soil contamination policy

An on-line forum is set up for the students to share and discuss information about companies working in activities linked to soil contamination and, real cases of soil remediation carried out by companies. They search for companies that offer: i) exploratory study of contaminated soils, ii) detailed study of contaminated soils, iii) risk study of soil and groundwater pollution, iv) preparation of decontamination projects, v) direction and execution of soil and groundwater decontamination, vi) supply and manufacture of decontamination equipment, vii) probes and piezometers and suppliers, viii) development of ecotoxicological tests, ix) software for risk analysis assessment, etc. The contact with the labour market makes a subject more interesting and this is what students express.

The use of audio visual aids encourage teaching learning process and make it easier and interesting (Rasul *et al.* 2011). We used two documentaries to support the case study of Sabiñánigo (Table 1; RTVE 1 and 2), a site contaminated with lindane (listed in Annex A of the Stockholm Convention on POPs in 2009 because of their environmental persistency and bioaccumulation potential (reported by Gómez-Lavín *et al.* 2018)). Previously, we discussed with the students the role of the documentaries. As Ambrós and Breu (2012) point out the documentary is a construction about reality and it is interpretation and persuasion, and it is necessary to keep in mind that the filmic discourse can make a series of affirmations, but it does not mean that they are true or real. It will have to be analyzed. After watching it, students were asked about the effect of the documentary on their critical thinking, awareness of the risks of soil pollution and if it had given them new ideas to support and argue their own opinions. In this last question and in a questionnaire of 5 points, all the students claim that agree or strongly agree. Nowadays, very well-informed documentaries about different soil remediation techniques made by companies can be found on the Internet (e.g. thermal desorption by Emgrisa, soil bioremediation by Kepler Engineering and Ecogestion, soil washing by FCO). They are an aid too in the lecture-class.

Soil plays a pivot role in assessing the quality of water. The presence of contaminants in soil vary according to their degree of mobility in it and their bioavailabilities are regulated by physical, chemical and biological processes as well as interactions between them (Teh *et al.* 2016). Students use the LEACHN module to study the connection between soil and groundwater. Nitrogen is a vital nutrient that helps plants and crops to grow, but high concentrations are harmful to people and nature, and agricultural use of nitrates in organic and chemical fertilizers can be a major source of water pollution (91/676/EEC). The 1991 Nitrates Directive is one of the earliest pieces of EU anti-pollution legislation. Students quantify the losses of nitrate for different fertilization practices. They should take into account that the fertilizers applied should be consistent with good agricultural practice, soil conditions, soil type and slope, climatic conditions, rainfall and irrigation, land use and agricultural practices. With this activity, they are more aware that land contamination does not recognize its boundary and that easily goes unnoticed. Therefore, it can happens that by the time we realized, damage has already been caused.

Conclusions

Teaching soil pollution is a challenge but we have many tools to encourage our students to be as enthusiastic as we are with this topic. We can raise environmental consciousness in our students by many ways as stated above. This paper is only one attempt to highlight the importance of teaching and active learning to ameliorate soil contamination through student awareness. Students are asking for activities as case studies, current examples, use of audio visual aids, greater participation in the classroom, classroom activities that make them think, more field trips, etc. This year the World Soil Day 2018 is 'Be the solution to soil pollution!'. Many things can be done from the research and companies point of view but also in the field of education or training in all the levels of education.

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2.1.12. Legal approach to measures to prevent soil contamination and increase food safety for the consumer

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Abstract

The aim of this paper is to carry out an analysis of the Spanish legislation that protects the ultimate recipient of the products: the consumer, in the cases in which there has been a contamination that has affected the crop, as well as the penalty regime foreseen in the criminal matters regarding offenses of an ecological nature.

Keywords: soil, contamination, legislation, security, consumer, food safety

Introduction, scope and main objectives

The Spanish Constitution of 1978, in its article 43 recognizes the right to health protection, and proclaims the competence of public authorities to protect public health by means of preventive measures. Similarly, article 45 states the right to enjoy an environment suitable for the development of the person, and the duty to preserve it. It indicates that the public authorities will ensure that natural resources be used rationally, with the aim of protecting and improving the quality of life and preserving and restoring the environment.

We cannot forget that in many occasions the use of highly polluting products in the agricultural field produces harmful and undesirable effects on human health and the environment, with the consequent degradation of the soil (Cabello 2017). This contamination is not limited to the medium itself, but also occurs in the feed and food chain (Fonseca *et al.* 2005). Therefore, the chemical compounds that have produced a contamination in the land and in water can be harmful, in many occasions, for the crops that grow in these lands causing the food to be affected in its quality and safety for the consumer (Repetto *et al.* 2008; Wing 2008; Pérez *et al.* 2011; Agabo 2014; Reyes *et al.* 2016).

Eutrophication is a widespread environmental problem that can lead to highly undesirable changes in ecosystem structure and function (Smith *et al.* 1999) and aquatic pollution (Gutiérrez 2012; Guadarrama and Galván 2015). Eutrophication in rivers and seas can be caused by increased nitrogen and phosphorus losses from agriculture. Carpenter (2005) states that slow flux of phosphorus from overfertilized soils is an important source of this nutrient for maintaining eutrophication of lakes in agricultural regions and that this type of eutrophication is not reversible unless there are substantial changes in soil management. Preece *et al.* (2017) highlighted a potential food-borne exposure route to humans due to the accumulation of microcystins (toxin produced by harmful cyanobacteria blooms) in coastal seafood due to high nutrient conditions (often associated with eutrophic waters) and combined with other factors such as climate change.

The main objectives of this paper are as follows: determine the Spanish legislation that can be applied to soil pollution, relate the previous legislation with the field of food safety, and determine which legislation would be the best for the protection of the consumer and user of the products.

Methodology

The methodology used was firstly to analyse Spanish national legislation to determine what is meant by contaminated soil and altered soil, indicating the differences that exist in the legislation studied. Secondly, to determine what is the risk that the legislation contemplates in relation to soil contamination and human health. Thirdly, to determine what are the precautionary measures and recovery of contaminated soil to avoid damage to human health. Fourthly, to point out the principles to avoid soil contamination, according to the legislation, and finally, to determine the legal instruments regulated in the legislation to control the quality of the soil.

Results

The Spanish legislation has been oriented to establish guidelines to avoid contamination in the soil, and to pursue the safety of food in order to ensure that the products are safe for consumption (Ramón, 2012). In fact, article 51 of the Spanish Constitution stipulates that public authorities shall guarantee the defence of consumers and users, protecting, through effective procedures, safety and health. However, we lack a specific national legislation that focuses especially on soil contamination and food safety jointly, this is why we must extrapolate the measures contemplated in the environmental liability legislation.

In 2007 was approved the Environmental Liability Law 26/2007, of 23 October (BOE No. 255, of 24 October 2007). It transposed into Spanish Law the Directive 2004/35/EC of the European Parliament and of the Council on environmental liability in relation to the prevention and repair of environmental damage. The Law of Environmental Responsibility develops article 45 of the Constitution, regarding the rational use of natural resources. Two fundamental principles of Community legislation on the environment are made effective: the principle of prevention and the "polluter pays" principle. With this law is intended that companies respond to the damage caused to natural resources as soil, water, wildlife and protected habitats, riverbanks and rivers, but damage to people is not contemplated in this text. In 2008 the Government adopted the Royal Decree 2090/2008, of 22 December, which enacts the partial implementation regulations of Environmental Liability Law 26/2007, and in 2014 the Government approved the Law 11/2014, of 3 July, amending Law 26/2007, on Environmental Liability (BOE No. 162, of 4 July 2014). Law 11/2014 introduces in the article 3 a new section (number 6). In this section indicates that in the case of public works of general interest, competence of the General State Administration, this law shall be applied to damage caused to waters and soils, among others, when they were caused by economic or professional activities listed in its Annex III, even if there is no fraud, fault or negligence.

In 2015 was adopted the Royal Decree 183/2015, of 13 March, amending the Regulation on the partial development of Spanish Law 26/2007 adopted by Royal Decree 2090/2008.

The quality of the soil and the measures to avoid its contamination are expressly indicated in the Royal Legislative Decree 7/2015, of 30 October, by which the consolidated text regarding the soil and urban rehabilitation law is approved (BOE No. 261, of 31 October 2015). In its article 3.2 indicates that under the principle of sustainable development, the public policies related to the regulation, management, occupation, transformation and use of land must promote the rational use of natural resources by harmonizing the requirements of the economy, employment, social cohesion, equal treatment and opportunities, health and the safety of people and the protection of the environment, contributing in particular to the prevention and minimization, as much as possible, of air, water, soil and subsoil contamination, among other measures.

And regarding the field of security and health, we must observe the General Health Law 14/1986, of 25 April (BOE No. 102, of 29 April 1986), to determine the protection in that sense.

Together with this, we should indicate that food safety is related to traceability, therefore, with all the evolution of the chain of production, and thus the product should be observed from its collection in the field to its subsequent production process (Mesa and Ramón, 2016).

In 2016 was approved the Royal Legislative Decree 1/2016, of 16 December, approving the Recast Text of the Integrated Pollution Prevention and Control Act (BOE No. 316, of 31 December 2016). The aforementioned Royal Legislative Decree aims to prevent, reduce and control atmospheric, aquatic and edaphological pollution, through the establishment of a preventive system and integrated control of pollution, in order to achieve global environmental protection.

In addition, taking into account the Spanish autonomic configuration, we must also point out that recently it has been legislated in the Foral Community of the Basque Country the Law 4/2015, of 25 June, for the prevention and correction of soil pollution in the Basque Country (BOE No. 176, of 24 July 2015). The purpose of this regulation is the protection of the soil in this Autonomous Community, preventing the alteration of its chemical characteristics that are derived from actions of anthropic origin. A legal regime is established that is applied to contaminated soils for the preservation of the environment and human health, in such a way that a series of obligations are established for activities that are potentially polluting.

Another related aspect is the sanctioning aspect in applicable legislation to determine which is the responsibility of both civil, criminal (crime or misdemeanor) and administrative through fine or sanction, which proceeds in the case of incurring any activity contrary to the norm applicable in relation to soil contamination.

The commercialization of the products in relation to its contamination involves the application of the Royal Legislative Decree 1/2007, of 16 November, approving the revised text of the General law for the protection of consumers and users and other complementary laws (BOE No. 287, of 30 November 2007). And also the application of the Law 3/2014, of 27 March, for which is modified the restated text of the General law for the protection of consumers and users and other complementary laws, approved by the Royal Legislative Decree 1/2007, of 16 November (BOE No. 76, 28 March 2014).

This must be also related to the regulations of waste and effluents. Law 22/2011 of 28 June (BOE No. 181, 29 July 2011) regulates waste and polluted soil, and Royal Decree 9/2005, of 14 January, which establishes a list of potentially soil contaminating activities and criteria and standards for declaring that sites are contaminated (BOE No. 15, 18 January 2005). Finally, we should mention Law 5/2013, of 11 June, that modifies Law 16/2002, of 1 July, of Integrated pollution control and prevention and Law 22/2011.

Discussion

It is debated whether the legislation we have indicated contains sufficient tools to prevent soil contamination and guarantee food security. We must bear in mind that the dispersion of the legislation hinders the application of a single regulatory framework, since legislation has been legislated on aspects related to the prevention and integrated control of pollution, at the national level, but we also have a territorial norm such as is in the case of the recent Law for the prevention and correction of soil contamination in the Basque Country.

Conclusions

We consider that the legislation applicable to soil contamination and food safety does not adequately address the aforementioned problems. It would be necessary to have a national legislation on soil pollution in a specific way, in a similar way to that applied in a territorial way in the Basque Country Foral Community (Law 4/2015). This norm indicates the potentially contaminating activities of the soil, either by the handling of harmful substances or by the generation of waste. Bearing in mind that they must have contact with the soil. This Law differences between contaminated soil and altered soil. Altered soil is the one that exceeds the concentrations of pollutants according to the reference values, but is not in a situation of contamination. A series of applicable principles are also established in this Law (e.g. conservation of the natural functions of the soil, maintenance of the same, recovery of the soil, priority of solutions that imply reusing the soil, environmental solutions in relation to the urban management, and the application of the principle of that the polluter pays and who damages responds).

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2.1.13. Policy Research on Soil contamination to Achieve Food Safety

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Abstract

Conceptual models are used in the study of politics and public policy analysis that use Majchrzak method of policy research, which documented knowledge about an issue and evidence to understand the causes and consequences of the issues and how to solve them. In this study, the aim was to investigate the current situation of soil policies and its relation to food safety. For data collection four groups with policy-making experience in the fields of: soil and food safety, standard, health, environment and agriculture, were interviewed. These four groups were selected using snowball sampling. According to the questions of the Majchrzak method, the interview was semi-structured.

Data analysis was carried out using open coding, axial coding and selective coding processes in MAXQDA2010, then the themes were identified by establishing relationships between themes and

casual conditions, contextual conditions, intervention/ intermediate conditions, strategies and consequences.

Results showed that a complementary political intervention (intervention in different aspects in a coordinated and concurrent manner) in the public policy of education, soil and food safety should be used. This includes using a holistic approach to integrate policies addressing soil and water pollution for achieving food safety, motivational intervention of farmers and industrials in environmental management for food safety, the establishment of a promotional training system and technology with environmentally-friendly and sustainable process and production, the mobilization of resource needs and the green supply chain management from farm to plate.

Keywords: Policy Research, Grounded theory, Soil, Food Safety

Introduction, scope and main objectives

Soils play a central role in food safety as it determines the possible composition of food and feed at the root of the food chain (Tóth et al 2016). Soil contamination may lead to the degradation of water quality and a series of negative impacts on the environment (Mulligan et al 2001; Rattan et al 2005).

Environmental pollution and food safety are two of the most important issues of our time. Soil and water pollution, in particular, have historically impacted on food safety which represents an important threat to human health. The increasing negative effects on food safety from water and soil pollution have put more people at risk of carcinogenic diseases, potentially contributing to ‘cancer villages’ which appear to correlate strongly with the main food producing areas (younlong et al 2015).

A sustainable food system is one that efficiently meets the current and emerging demand for food without jeopardizing the availability of scarce natural resources. At present, resource use in agriculture is unsustainable. For example, as much as 85 percent of global water use goes to agricultural irrigation, 20 of which 15–35 percent is thought to be unsustainable. Furthermore, nearly a quarter of all global land has been affected by environmental degradation. We can avoid sacrificing the environment for food security and nutrition by focusing on sustainable intensification whereby increased food production goes hand in hand with more efficient use of natural resources and reduced environmental impacts. Sustainable intensification strategies can help promote soil health and sustainable land management, which are key to producing a sustainable food supply; ensuring ecosystem services, such as habitats for beneficial insects and pollinators; and promoting human health (Shenggen 2015).

However, until recently, the impacts of soil pollution were not known. In addition, the science involved is complex. Various policies regarding water, waste, chemicals, industrial pollution, nature protection, pesticides and agriculture all contribute to soil protection. For this reason, the European Commission has adopted the Soil Thematic Strategy (Commission Communication COM (2006) 231) and proposals for a Soil Framework Directive (Commission Proposal COM (2006) 232) specifically to protect soils. Among the goals of these instruments, of particular relevance to this report, is the protection of soils from a number of threats, including contamination. Following over 200 years of industrialization, soil contamination has become a widespread problem in Europe. The most frequent contaminants are heavy metals and mineral oil. According to estimates by the European Environment Agency (EEA, 2007), the number of sites where potential polluting activities have been carried out in the EU is approximately three million and, of these, an estimated 250,000 sites may need urgent remediation. The main causes

of contamination are past and present industrial and commercial activities, and the disposal and treatment of waste, but these categories vary widely across Europe.

One issue that increases the challenge of assessing the state of soils across Europe is that there is currently no legal requirement to collect information in a harmonized manner, if at all. Many European countries have mapped soils used for agriculture or forestry, but this data may be several decades old. This is an important consideration when discussing the potential impacts (including health impacts) of pollutants on soil. Some countries do have detailed soil monitoring networks to measure soil quality, however, these may reflect national or regional priorities and standards, so comparing results between countries is difficult. Other nations do not have systems in place for systematic soil data collection. Recent improvements in data collection mean that the number of reported contaminated sites could increase by as much as 50% by 2025 (EEA, 2007) (SCU 2013).

In Iran, like in many other countries, soil is under threat by a combination of mismanagement and changing natural conditions. Soil pollution, erosion and salinization are three problems that have put Iran's environmental sustainability at risk. Contaminated soils can endanger the entire food chain (Pouran 2015). Currently in Iran, food safety policies are not integrated with soil and water pollution management policies (Damari 2016).

In this study, integrated policies addressing soil and water pollution for achieving food safety are suggested to provide a holistic approach. As a result, the country simply cannot afford to lose any more available land or water due to increasing problems with pollution. Historically soil and water pollution have been considered separately by environmental policy makers. It is imperative, however, that integrated policies, addressing both soil and water pollution, are formulated for the protection of agricultural production and human health.

Methodology

The term policy research refers both to a skillful process and to an outcome. The process is a set of activities to perform and outputs to produce. The outcome is documented knowledge about a problem and about ways to solve the problem combined with carefully reasoned recommendations for action.

Majchrzak method for policy research is for studies that want to make a difference in problems of truly global proportions, such as climate change, war, disease, famine, economic crisis, or water pollution or address problems that affect an entire country, such as persistent unemployment or deal with issues that are more local in scope.

Policy research involves using evidence to understand the causes and consequences of problems and the advantages, disadvantages, and risks of different ways of dealing with problems. Evidence can include data already assembled by others and new evidence collected especially for policy research purposes. Evidence means facts, data, and experience—as opposed to assumptions, theories, opinions, and values. But, of course, assumptions, theories, opinions, and values—we call them meaning—are ever-present and affect both the production of evidence and its interpretation and use. So policy research involves working with both evidence and meaning to create outcomes that help to change the world.

This method has different phases: 1- make a difference with policy research, 2- launch the policy research process, 3- synthesize existing evidence, 4- obtain new evidence, 5- design policy

recommendations, 6- expand stakeholder engagement and 7- reflect on the policy research process (Majchrzak, 2014).

Based on this model, with the study of documents, rules and regulations and interviewing soil policymakers and food safety with snowball sampling. The question that was answered involved the Policy Problem Change Wheel and Policy Solution Change Wheel. Based on grounded theory, data analyzing was done using open coding, axial coding and selective coding processes in MAXQDA2007. To identify the themes, relationships between themes and casual conditions were established, contextual conditions, intervention/ intermediate conditions, strategies and consequences (Corbin and Strauss 2008).

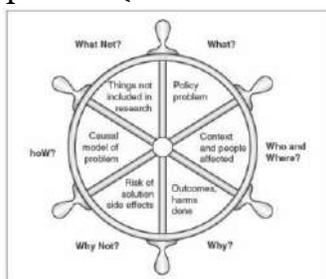


Figure 8. The Policy Problem Change Wheel

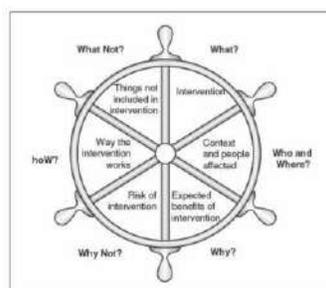


Figure 2. Policy Solution Change Wheel

Results

Based on the synthesis of existing evidence and new evidence, the questions on the policy problem change wheel and policy solution change wheel were answered in table 1 & 2.

Table 1. Answer for question of the Policy Problem Change Wheel

Question	Description	Answer
What	situation to improve or the problem to solve	food safety
What not	scope of research by excluding certain aspects of the problem	another aspect of food security
Who & where	what effect the context may have on the problem	policy makers every where
How	refers to theory, or causal model, of how	unsafe production from farm to plate

	the policy problem occurs.	
Why	why the policy problem needs to be improved	
Why not	possible reasons for not trying to fix the policy problem	reduce production and risk the public's access reduce

Table 2. Answer for question of the Solution Change Wheel

Question	Description	Answer
What	question means describing the interventions themselves	policies to protect soil and water quality for safe food production
What not	question identifies interventions that are deliberately leaving out further analysis	A new method for safe food production
Who & where	describe the context specifically for the interventions	policy makers every where
How	describes the ways in which the interventions are believed to work; it provides the causal model or theory of the interventions	provide a comprehensive and integrated policy model
Why	reasons the interventions should be implemented	maintain community health
Why not	risks that must be minimized when implementing the interventions	Cause worries for small producers and farmers.

Based on New data obtained from interview in format of grounded theory, core categories of soil policies and their relation to food safety include (figure 3):

1. Holistic approach to integrated policies addressing soil and water pollution
2. Motivational intervention of farmers and industrials in environmental management
3. Establishment promotional training system and environmental technology for sustainable process and production,
4. Fulfilling resource needs
5. Green supply chain management from farm to plate.

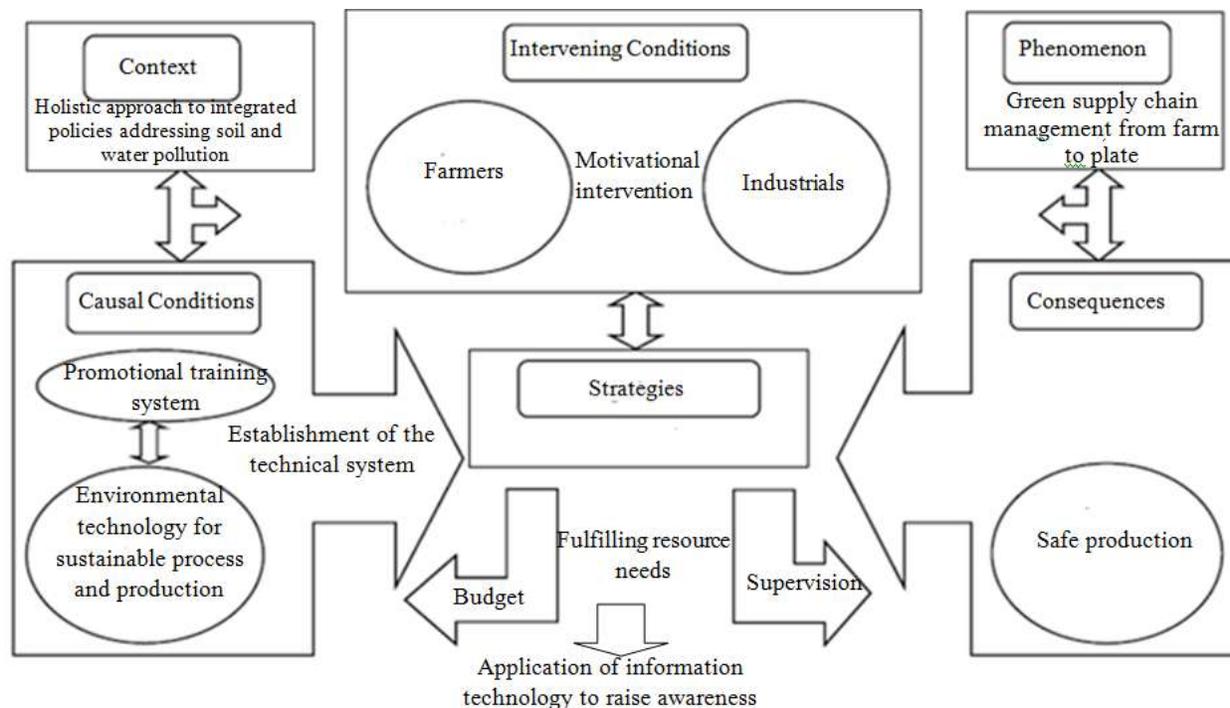


Figure 3. Concept Map of Soil Pollution Policy Research

Discussion

Soil governance in this review is understood as the sum of all formal and informal institutions (e.g. legal prescriptions, regulation, market incentives, rules, norms, habits, attitudes) that concern soil-related decision-making processes of state and non-state actors' at all decision-making levels. Soil governance shapes the way soils are used and thus reflects the needs and interests in soils of current and future generations to ensure long-term soil vitality. Furthermore, soil governance regulates the use of soils in order to avoid and manage conflicts between stakeholders about soils. The “soil governance landscape” is highly fragmented and has been characterized as a multi-level and multi-actor system. This fragmented governance structure parallels the multi-scale character of soil management challenges.

Now, among all types of pollutants reported, heavy metals are considered to present the greatest risk to food safety in Iran. The main sources of heavy metals in farmland soils include mining and smelting, sewage irrigation, sludge reuse and fertilizer application. Policy implementation is challenging as a result of the lack of availability of good quality water, and this results in farmers using sewage for irrigation, which causes pollution of soils and agricultural production systems. We should therefore have a holistic approach to integrated policies addressing soil and water pollution.

Governing the soil requires national collaboration between governments, local authorities, industries, farmers and citizens to ensure implementation of coherent policies that encourage practices and methodologies that regulate usage of the resource to avoid conflict between users to promote sustainable land management. Motivational and voluntary intervention of farmers and industrials is necessary especially in environmental management.

Soil is recognized as a non-renewable resource, but in Iran, its governance is maintained at the national level, unlike other non-renewable and climate sensitive resources. Soil governance

mechanisms are usually encapsulated within the context of land governance, with a focus on urban and industrial soil governance that have rapid urbanization rates; thus, soil governance is not highly interlinked with other atmospheric and anthropogenic issues. The establishment of promotional training systems and environmental technologies for a sustainable process and production system are useful for the relationship between the different aspects.

On the other hand, for the implementation of policies, it is necessary to fulfill resource needs such as: budget, supervision and application of information technology to raise awareness. To achieve these goals, policies concerning soil and food safety should be implemented in the context of the Green supply chain management from farm to plate.

Conclusions

Soil governance refers to the policies, strategies, and the processes of decision-making employed by nation states and local governments regarding the use of soil. Soil governance has been criticized for not being effective, efficient, and legitimate in governing soils in a way that sustains their long-term protection and maintenance. In the context of the transition towards increased food safety, the question of how soil governance should be organized has not been sufficiently addressed. There is some agreement in the literature that novel instruments and tools are needed in the transition towards more sustainable food safety. However, how these novel instruments and tools could be designed to be more successful in ensuring sustainable soil use and management is unknown. The allocation of decision-making authority between different decision-making levels and between various actors within a multi-scale governance system is an important aspect in this context. So far, no comprehensive overview exists that summarizes the current knowledge on these issues within the existing multi-level soil governance system.

A disparity between scientific knowledge and traditional, indigenous knowledge about soil management practices has been diagnosed. It has been argued that the field of agricultural sciences should stop assessing the scientific correctness of local knowledge. Instead, more integration and dialogue between different knowledge systems is suggested. The points of overlap of different mental models should be used to allow communication between farmers and scientists.

To increase the awareness of soil issues and to provide a mental model for soil policy, suggest the establishment of a promotional training system.

The existing soil policy is mandatory but not sufficient in order to achieve food safety. It is necessary to integrate different aspects within this policy, especially water quality. The integrated policy between soil, water, food safety, technology awareness and resource needs is necessary for food production for a healthy community.

Acknowledgements

We would like to managers in the ministry of agriculture, department of environment, *ministry* of health and medical education and National *Standards* Organization for interview and their valuable comments.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Sub-theme 2.2: Risk assessment of soil pollution on the environment and human health

2.2.1. Ecological impacts of wetland utilisation in the Upper Ewaso Ngiro Basin, Laikipia, Kenya

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Abstract

Land use changes in Upper Ewaso Ngiro basin has undergone significant transformation in the past 100 years, from nomadic communal grazing land before 1900, large scale ranching up to early 1970s to small-scale farming from 1990s. The later change has been accompanied by increased food crop and horticultural cultivation that is geared towards both domestic and commercial needs by migratory agrarian communities from humid regions. Due to the arid nature of the basin, cultivation mainly involves irrigation of dry land or farming in the several wetlands in the basin upon draining. Lack of clear legal framework (*draft wetland policy*) has resulted in severe degradation of wetlands ecosystem with wetland area reducing by ca. 80%. Although the wetlands ecosystem renew themselves significantly annually during the long rains through excessive flooding regaining exploited soil fertility, the cumulative impact of anthropogenic effect is reflected mainly in vegetation change. Farming is characterised by recurrent losses, food crop and finances due to a combination of low farming inputs and poor market access, which further limit resources input for land and soil management. This results in sustained low food production and continued agricultural resource degradation.

Keywords: transformation, wetlands, small-scale, farming inputs, degradation

Introduction

In Kenya's arid and semi-arid land (ASALs), wetlands occur in relatively small but widely distributed patches, providing critical watering points for pastoral communities and grazing areas for both wildlife and livestock. The Ewaso Ngiro basin stretches from 2600 m (ASL) in the south and falls to below 1000 m ASL in the north. Annual rainfall range: 500-1000mm per annum: Temperature vary between 20-37 C annually. In spite of aridity it has numerous permanent riverine wetland attributed to geology, tectonic earth movement and topography. Rivers forming these wetlands originate from humid areas of Mt Kenya and Aberdare ranges.

Land use changes in Upper Ewaso Ngiro basin has undergone significant transformation in the past 100 years, from nomadic communal grazing land before 1900, large scale ranching up to early 1970s to small scale farming from 1990s. Population growth has been rapid since 1960s at one point reaching over 7% per annum. There has been Extensive degradation of wetland ecosystems due to high rate of population growth.

Main objectives

- Inventory of Upper Ewaso Ng'iro basin wetlands detailing their bio-physical components and map land use/cover changes overtime
- Assess the impact of wetland utilisation in the basin on water resources and soils

Materials and site description

The Upper Ewaso Ng'iro North Basin stretches from a semi-humid area at the foot of the Aberdare ranges and Mt Kenya through the arid regions of Laikipia County (eco-climatic zone 3), to the more arid Samburu and Isiolo Counties (eco-climatic zone 4). The nature of the physiographic features that are characterised by plateau formation has encouraged wetland formation along the Ewaso Ng'iro river artery. The uppermost wetland is Lake Ol'Bolossat in Nyandarua County, which forms the headwaters of the main river, the Ewaso Ng'iro, that receives water from rivers draining from both Mt Kenya and Aberdare ranges catchments.

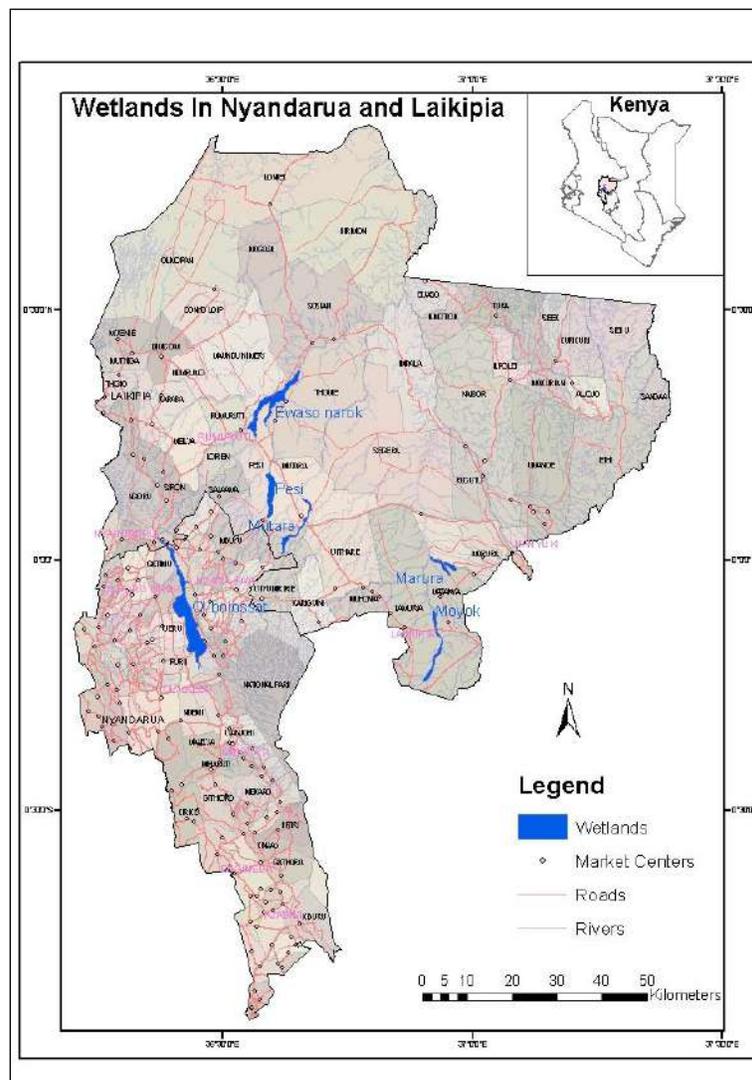


Figure 9. Distribution of Wetlands in Upper Ewaso Ng'iro Drainage

Methodology

- Planning Meeting and Reconnaissance
- Ecological
 - o Water- insitu and exsitu- water quality
 - o Soil- fertility and bulky density
 - o Flora rapid inventory
 - o Fauna- spot inventory
- Land cover
 - o Changes between 1980s and 2010 - dry season images

Soil Chemistry Dynamics

Since wetland soils are found in low-lying areas, their soil forming factors are strongly influenced by the presence of water, vegetation and drainage. This results in hydromorphic soils that are rich in humic acids and hemicelluloses. The soil characteristics also reflect the geology of the area and the prevailing human activities. For example, land-use patterns and vegetation cover have a strong influence on soil fertility variation in the swamp, with farming leading to reduced organic matter in the soil while the geological set-up influences soil composition.

Results and discussions

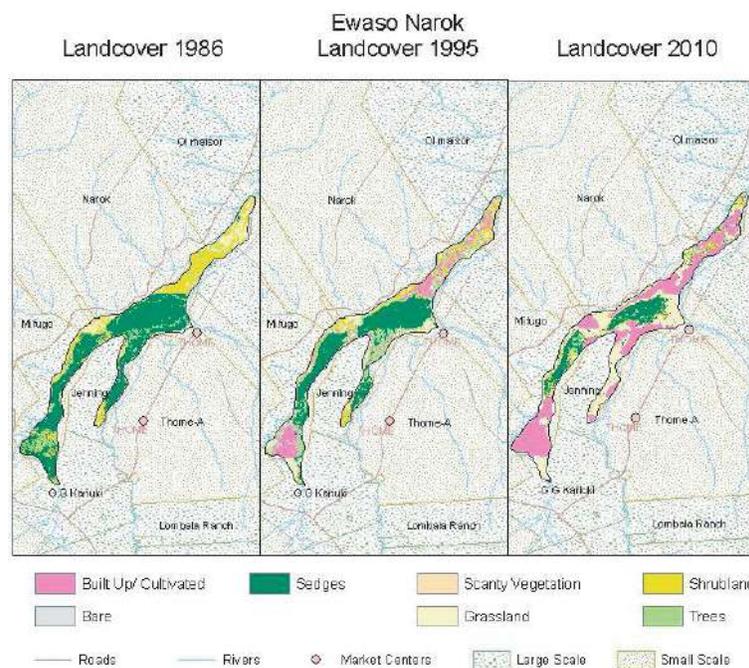


Figure 2. Land cover change in Ewaso Narok wetland between 1986-2010 Note increase in cultivated and reduction of sedges

Impact and consequences of changes on water resources

Increasing demand for water (especially for irrigation) and declining river water flow leading to:

- Competition and user conflicts arising from;
- Water inadequacy/ Dry season/ Drought
- Upstream – downstream conflicts
- Farmers fighting over irrigation water
- Overuse of inadequate water
- Wildlife destruction

Table 1. Soil characteristics in Ewaso Narok Wetland

Ewaso Narok - Western									
GPS	pH	pH 0.01 M	ds/m	%		Cmol/Kg			ppm
Sample description	Water	CaCl ₂	EC 25°C	C	N	K	Na	CEC	P
272	6.5	5.6	0.4	3.2	0.26	2.75	2.50	23.2	3
273	6.1	5.4	0.2	3.1	0.38	3.50	1.50	24.6	2
274	6.82	5.7	0.3	3.7	0.34	2.25	1.50	22.4	3
275	6.12	5.8	0.2	4.5	0.37	1.75	0.50	35.6	10
276	6.34	5.87	0.2	2.9	0.24	2.25	2.00	32.6	4
277	6.1	5.2	0.3	3.5	0.32	2.75	4.50	22.4	3
279	6.47	5.43	0.2	2.1	0.25	2.75	1.25	28.4	5
280	5.95	5.7	0.2	2.9	0.21	3.75	1.25	35.6	2
Mean	6.3	5.587 5	0.25	3.252 5	0.296 3	2.718 8	1.875	28.1	3.843 8
Ewaso Narok -Eastern									
	pH	pH 0.01 M	ds/m	%		Cmol/Kg			ppm
	Water	CaCl ₂	EC 25°C	C	N	K	Na	CEC	P
281	5.82	4.8	0.2	5.1	0.45	3.00	0.50	32.8	2
282	5.44	4.54	0.2	1.7	0.15	3.00	2.50	31.6	15
283	5.8	4.7	0.2	5.5	0.48	3.00	2.00	36.6	7
285	7.7	6.8	0.4	4.7	0.37	3.50	3.00	33.6	1
286									
288	6.61	5.3	0.3	3.3	0.22	4.50	1.25	26.8	2
290	6.2	5.1	0.2	3.6	0.21	2.50	1.50	25.8	4
291	6.11	5.3	0.2	5.1	0.24	3.50	1.25	27.4	2
Mean	6.24	5.22	0.2428 6	4.122 9	0.302 9	3.285 7	1.714 3	30.65 7	4.607 1

The soil pH values in Ewaso Narok wetland were found to be slightly acidic (mean 6.2), which is high considering that the study was done in a wet season. Much lower pH values have been previously recorded in Ewaso Narok (Thenya, 1998). The tendency towards acidity results from the reduction processes that release hydrogen ions in anaerobic reactions. Some areas were observed to have relatively high pH, especially where cultivation has taken place, due to reduced anaerobic environment (GPS 274 western side, GPS 285 and 288 on highly cultivated eastern side). This tendency towards alkaline soil pH in the disturbed eco-type was due to the accumulation of carbonates of calcium and magnesium (Jones, 1987; Mbuvi and Mainga, 1991, Thenya 2005). This is because of the reduced anaerobic conditions and the high decomposition rates. These results are in line with swamp pH values observed in other parts of the country such as the Laikipia wetlands (Mbuvi and Mainga, 1991).

The results obtained in the Ewaso Narok swamp indicate high average CEC values, 28 Cmol/kg and 30 Cmol/kg in the western and eastern sides respectively. The CEC values obtained in the Ewaso Narok swamp were within the range of other studies in the tropics (Mbuvi and Mainga, 1991; Thenya, 1998; Thenya, 2005). This means that the soils are able to attract and retain positively charged elements as plant nutrients (FitzPatrick, 1988), especially in the less disturbed eco-types.

The ability to retain nutrients decreases with ecological disturbance, resulting in leaching tendencies. Ewaso Narok swamp experiences heavy flooding during the wet season, which helps to rejuvenate the soil fertility as this acts as a fallow period. Similar observations have been made previously in Ewaso Narok, meaning that the ecosystem has a high potential of recovering from disturbance (Thenya, 1998). This is complemented by high values of potassium and sodium and high hydraulic dynamics.

Conclusions

The impact of several years of farming in the wetlands is visible in the dramatic change in the land cover, with the wetlands having recorded at least a 50% increase in built up or cultivated areas between 1986 and 2010. The increase in human activities is confirmed by decrease in sedge vegetation, which represents the natural wetland ecosystem, by the same percentage. However, the ecosystems indicated minimal change in soil fertility (ca. CEC 29 Cmol/Kg) and water quality (pH 7.8), which can be attributed to water flow from the humid Aberdare and Mt Kenya ecosystems.

During the wet season these wetlands are heavily flooded and human activities are totally curtailed, resuming again in the dry season, which allows ecosystem self-recovery. However, the wetlands need management plans, as farmers would like to continue living in the wetlands where farming is feasible because of the availability of water.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.2.2. Past, present and future exposures to natural elements

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Full text here http://www.fao.org/fileadmin/user_upload/GSP/GSOP18/Bengtsson_Environmental_full.pdf

Abstract

Humankind has always been exposed to elements from the periodic system. These contributions have since millennia been enhanced by human activities employing elements extracted from the earth's crust. Over the last century the anthropogenic component has increased strongly, mainly due to fossil fuel combustion and production and use of extracted elements. The current analysis discusses past unavoidable exposures, last century exposures as integrated in European topsoils, present exposures as demonstrated in sewage sludge, and projected future exposures. All estimates are uncertain and subject to further verification.

The natural mean dietary intake over large population groups could for most elements be predicted from the topsoil concentration.

The average topsoil concentration of 13 elements has been measurably increased in European topsoil with drivers being fossil fuel combustion and element production over the last century. It is estimated that by 2045, the concentrations of 10 more elements will be significantly enhanced, with gold being multiplied, a cause for concern.

Element levels in sewage sludge are often enhanced beyond the inevitable contributions from human excreta. Mean German sewage sludge levels were in the year 2011 enhanced more than 100 times for 19 elements. The highest enhancement refers to tungsten and scandium at almost 600 times the diet-related level. These and several other elements can be tied to emissions from fossil fuel burning, but also production and use of the element is a driver. Assuming typical sludge amendment 1960-2011, agricultural soil concentrations of 6 elements might have been more than doubled.

Soil concentrations of some elements (Cd, Hg, Pb) have already been shown to entail some environmental effects. If several additional elements may reach similarly enhanced soil concentrations, further effects might be anticipated. Further studies and preventive measures are recommended to minimize such effects.

Keywords: natural elements, topsoil, sewage sludge, dietary intake, human enhancement, global production, fossil fuel combustion

Introduction, scope and main objectives

Anthropogenic material turnover via mining and other extraction from the earth's crust is a prerequisite for modern society and its agriculture, building, transportation and other endeavours. For about one-third of all elements, the anthropogenic scale is larger than that of natural processes such as weathering and volcanic eruptions. For rare elements like osmium and iridium, anthropogenic mobilization may be more than a million times the natural mobilization (UNEP 2013). This mobilisation upsets natural balances and may for instance lead to depletion of natural resources, climate change and toxic effects on humans and environmental organisms.

The current paper aimed to:

- give a generalized model for normal human intake of elements from the topsoil (past exposures).
- illustrate how natural levels of elements in European topsoil (past exposures) and sewage sludge (present exposures) have been amended by contributions due to human activities.
- relate the enhanced elemental content in topsoil and sewage sludge to emissions from production and use of the elements and from fossil fuel combustion.
- forecast how the elemental content in topsoil and sewage sludge will develop in broad terms over the next human generation (future exposures).

Because of the many generalizations and simplifications, the results are expected to be useful to generate hypotheses about the exposures rather than giving accurate descriptions.

Methodology

Existing data were reviewed using data gathered on the following parameters:

- relevant elements
- the topsoil composition for these elements
- potentially important chemical properties of the elements
- mean human dietary intakes over large population groups for the elements
- anthropogenic emissions over the last century due to fossil fuel combustion and to production, fabrication, use and discarding management of elements
- topsoil enhancement of element concentrations
- concentrations of elements in sewage sludge
- chemical parameters of elements that might inform interpretation of findings on human intakes, and soil and sludge concentrations.

Data were critically selected and analyzed across most of the periodic system elements.

Normal human intake

The objective of this part of the review was to find the normal human intake

- to establish a background level of intake and of excretion to sewage sludge
- for all selected elements in the periodic system of elements
- disregarding contributions from elements extracted from the earth's crust by man.

Dietary studies can give data on normal human intakes. It was hypothesized that the overall transfer of elements to humans might depend on the mean concentration of the corresponding element in the topsoil, combined with some rather simple chemical properties. The relevant

transfer factor might then be the mean dietary intake of an element over large population groups divided by the mean concentration of the corresponding element in the topsoil.

The analysis set out from 73 elements of the periodic system, excepting elements that are gaseous or have no stable isotopes. Mean topsoil concentrations across about 800 European sample sites were available for 57 elements sampled near the year 1999 (FOREGS 2005). Several sources gave measured topsoil concentrations for the lacking 16 elements. For 13 elements, the topsoil concentrations were significantly enhanced, as discussed under Results. For these, the topsoil concentrations were reduced to correspond to a non-enhanced level.

Data were reviewed from hundreds of sources on the mean dietary intake of adults (average of males and females) over larger regions in at least one country. Care was taken to use as far as possible, for all elements, only data on intakes that would be free of anthropogenic enhancement.

A special analysis was made for the relation of the transfer factor from soil to diet and the first three ionization energies of the element. The analysis was guided by the character of the oxidation states of the elements.

Enhanced element levels in European soils

An extensive set of soil element concentrations was used (FOREGS 2005) sampled in 1998-2001. This set contained data on total element concentrations in 0-25 cm topsoil and in a 25-cm thick subsoil section within a depth range of 50 to 200 cm. The topsoil has integrated the deposited elements over the last century, when most of the emissions to date from fossil fuel combustion and production and use of elements have occurred. For many elements, the mean penetration depth according to the penetration equation of Bengtsson (2015) was calculated to be 8-10 cm. This is not sufficient to give any major loss from the top 25 cm of a soil, if there is little downward displacement of the metals due to soil management procedures. Sulfur does not fall into this general pattern. Several field studies suggest that added sulfur is largely lost through leaching (Andersson et. al. 2015, Kirchmann et. al. 2000, Sakadevan et. al. 1993).

The ratio of mean topsoil to mean subsoil element concentration was studied for the 57 elements included in the FOREGS data set. A minimum excess concentration was found for baseline elements with comparatively low global production volumes. For elements with larger volumes of use, excesses smaller than 2 standard deviations among the baseline elements were deselected. This left 13 elements with significant mean concentration excesses in topsoil over subsoil.

For those elements, historical data on global fossil fuel combustion and on consumption were identified and simple relations for air emissions were sought.

- For fossil fuel, Mylona (1996) has traced the emissions of sulfur dioxide in Europe back to 1880. It seems likely that the overall cumulative emission fraction for sulfur has been about 0.8. The same emission factor was assumed for other elements in coal. The main source for the mean coal concentration of elements was Nalbandian (2012). Coal consumption data for the countries behind the FOREGS data were obtained from Mylona (1996).

- Historical global production data of elements were mainly obtained from USGS (2017), and consumption in the FOREGS countries was mainly obtained by scaling global production with the gross domestic product in constant US dollars given by the World Bank (2017).

The air emission fraction used to calculate mean excess of topsoil/subsoil concentrations among elements was adjusted to 0.06 to give a calculated mean excess equaling the mean measured excess.

Enhanced element levels in sewage sludge

The sludge ash contents of 54 elements (Krüger and Adam 2014) were used to assess pollution from sewage sludge. Their ash samples were obtained in 2011 from 22 sludge incinerators representing 97 % of German sludge ash. Samples were digested with perchloric acid. In this case two assumptions are needed to translate ash levels of elements to dry sludge levels: a retrieved mass fraction to ashes of 0.8, based on mass balances given by Krüger and Adam 2014, and an ash weight fraction of 0.38 of the dry sludge mass, based on loss on ignition data by Eriksson (2001) supported by limited information from Krüger and Adam (2014). The concentration in dried sludge is then assumed to be $0.38/0.8$ or 0.475 of that of ashes.

Trends in sludge concentrations were derived using a preliminary compilation of measurements of 69 elements in 2012-2016 representing approximately 50 % of the population of Sweden (Finsson private communication 2017). The sludge was collected from 41 sewage treatment plants applying the Swedish sludge quality system REVAQ. Samples were digested with nitric acid or aqua regia. Results for 4 elements (Ru, Rh, Re, Ir) were deselected because none or few of the results were above the detection limit. The data were compared with those of a previous national survey (Eriksson 2001). The macroelements (Al, C, Ca, Cl, Fe, K, Mg, N, Na, P, S and Si) were deselected since they are also released with the outgoing water or added in-plant as part of the sewage plant process.

The purposes of the assessments were to elucidate:

1. Pollution enhancement. Enhancement of the element concentration in comparison with that derivable from human dietary intakes. The average dry sludge mass was assumed to be 70 g per person and day (Almqvist et.al. 2007, Statistics Sweden 2018), half of which is due to urine and feces (Almqvist et.al. 2007, Rose et.al. 2015), and the mean dietary intakes discussed above were applied.

2. Environmental burden. Estimation of the increase in the natural soil concentration due to sludge amendment. The simplified annual application rate of 1 ton of sludge per hectare was used, assuming no loss from the 25-cm topsoil of density 1200 kg/m³.

3. Extrapolation to elements, for which the concentrations in sludge were not measured. The total sludge level of an element was assumed to be

$$T=H+a*P+b*C \quad (1)$$

T = total sludge concentration of an element

H = mean contribution to the sludge concentration of the element from natural human intake

P = country consumption of the element

a = fraction of the consumed element that reaches sewage sludge per unit sludge mass. This fraction was assumed to be approximately constant across elements

C = country consumption of the element in coal (concentration*mass)

b = fraction of the element consumed in coal that reaches sewage sludge per unit sludge mass. This fraction was assumed to be approximately constant across elements.

Calculations according to Equation 1 were performed for 45 elements. The ratio of the measured net sludge concentration T-H and that calculated according to Equation 1 was derived for all measured elements. The fractions a and b were adjusted so that the geometric standard deviation of the ratio was minimized, while the geometric mean of the ratio was kept equal to 1. The obtained values of a and b were used to calculate hypothetical sludge concentrations for elements for which the concentrations had not been measured.

Future exposures

The global production of elements, mainly retrieved through USGS data (2017) exhibits rather clear trends with a doubling over about 20 years, so it seems likely that this trend will continue over the next 30 years.

For 9 elements, air emissions in Europe have been reported (EMEP 2018). In the period 1990-2015, the emission reductions have more than offset the increased use of elements. Additional depositions beyond 2015 were predicted, assuming the average fractional emission reduction would continue. All estimates are uncertain, not the least since some sources may not have been accounted for.

Results and discussion

Normal human intake

The human dietary intake over large population groups was for many elements clearly related to the soil element concentration and the atomic number (Figure 1).

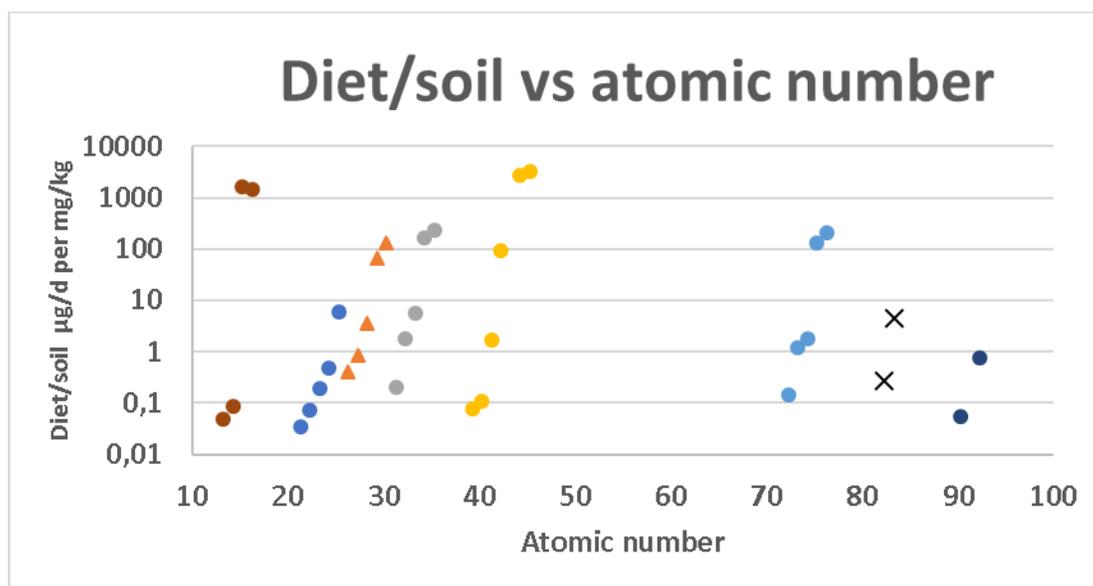


Figure 1. Ratio of mean dietary intake of elements over large population groups and corresponding mean soil concentrations versus atomic number.

For all example series except elements 26-30 (triangles), the maximum oxidation state is steadily increasing with atomic number. The equations of the straight lines are of the form $d=k \cdot e^{a \cdot n}$,

where d is the described ratio, k is a highly variable parameter, a is a series constant (1.3 – 2.8, meaning the ratio multiplies 4-16 times to next atomic number) and n is the atomic number.

The deviation of the points in the diagram from a corresponding exponential function trendline is typically less than a factor of 2 while the uncertainty of the diet data is usually less than a factor of 3. The coefficient of determination R^2 is in the range 0.93 – 1 except for the series 31-35 where it is 0.73. Similar trends and R^2 apply for the diet/soil ratio for

- alkali metals versus first ionization energy
- alkaline earth metals versus geometric mean of first and second ionization energies
- groups 14 – 16 of the periodic system versus geometric mean of first three ionization energies

Enhanced element levels in European topsoil

The calculated excess concentrations of elements in European topsoil over subsoil were compared with measured excesses (FOREGS 2005). The result for elements with significant measured excesses is given in Figure 2. It shows that 11 elements have mean excess topsoil concentrations above 10 %, excluding Hg and S for which calculation was not relevant. In many soils, local excesses of more than 10 times the mean excesses should be expected, judging by detailed analyses for mercury, cadmium and lead (UNECE 2007). In such soils, the natural concentration for these 13 elements may thus be more than doubled. Two pieces of information may give perspective on the significance of a doubling:

- In the subsoil, the 90th percentile of the concentration distribution is approximately twice the mean (FOREGS 2005)
- A doubling of trace elements in agricultural soil has been proposed as a limit for sludge amendment by the Swedish Environmental Protection Agency (Naturvårdsverket 2013).

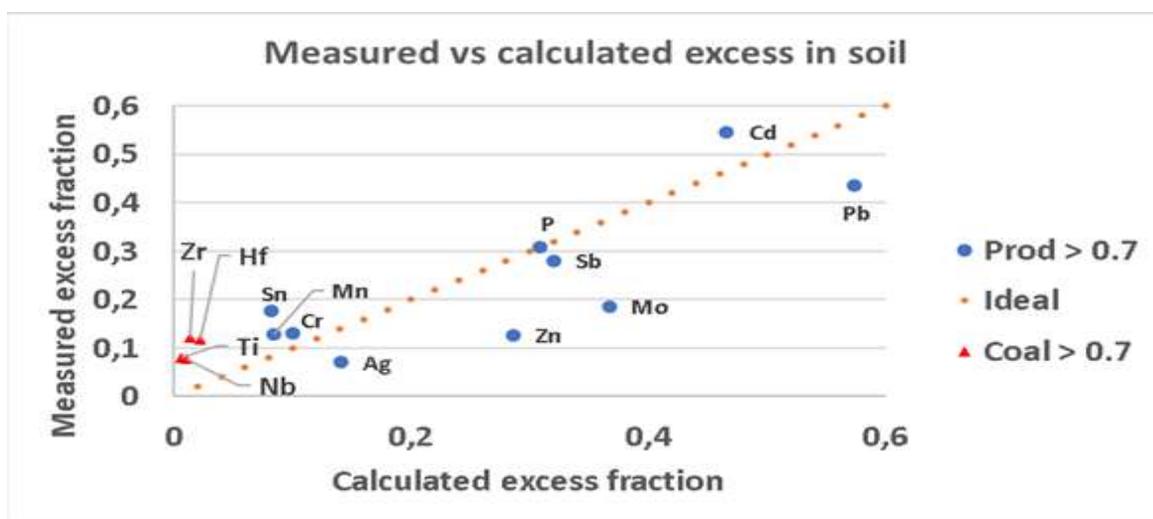


Figure 2. Measured versus calculated mean excesses of elements in European topsoil around the year 2000.

The triangles relate to elements where the calculated contribution from coal combustion exceeds 70 % of the total. For the circles the contribution from element production and use exceeds 70 %. The straight line applies if the calculated excess equals the measured one.

Existing contamination levels have already been associated with some effects on health and the environment (UNECE 2007):

- Effects on the decomposition of organic matter
- Impairs the recycling of important forest nutrients
- Reproductive problems in birds and other wildlife
- Wildlife also harmed by mercury in fish.

In addition, there is the potential for cumulative or synergistic effects if the concentrations of many elements are enhanced (Cedergren 2014).

Calculations were made for elements that were not measured. They suggest that mean excess concentrations of 10-50 % might have been expected in 1999 for Ge and Ir and beyond 50 % for 6 other elements (Rh, Re, Pd, Au, Pt, Ru) of which Re would have a calculated excess of 3.0 and Rh of 4.2 times the mean concentrations.

Additional depositions for the period 2000-2045 were estimated, based on measured emissions 1990-2015 (EMEP 2018) for 6 elements (Cd, Hg, Pb, Se, Zn, S). The additions were judged to become smaller than the depositions already accumulated. This is also expected to hold for the 7 other measured elements (P, Sb, Mo, Sn, Mn, Zr, Hf). In addition to the 13 (measured) plus 8 (calculated) elements exceeding 10 % excess in 1999, 2 new elements (Ag and Cu) might be added to that list in the period 2000-2045. In that period, concentrations of Au and possibly Ru and Pd might attain several-fold enhancement which may be of concern. Gold has been considered to be of low toxicity but effect levels of gold nanoparticles for aquatic organisms cover a similar range as those for silver (Moreno-Garrido *et al.* 2015). One silver compound (silver zinc zeolite) has a harmonized classification as very toxic to aquatic organisms (European Commission 2017). Ionic gold further appears to be considerably more toxic than gold nanoparticles (Botha *et al.* 2015).

The contamination of European soil parallels that of Tibet ice (Beaudon *et al.* 2017) and Ontario soils (Sheppard *et al.* 2009), as shown in Figure 3.

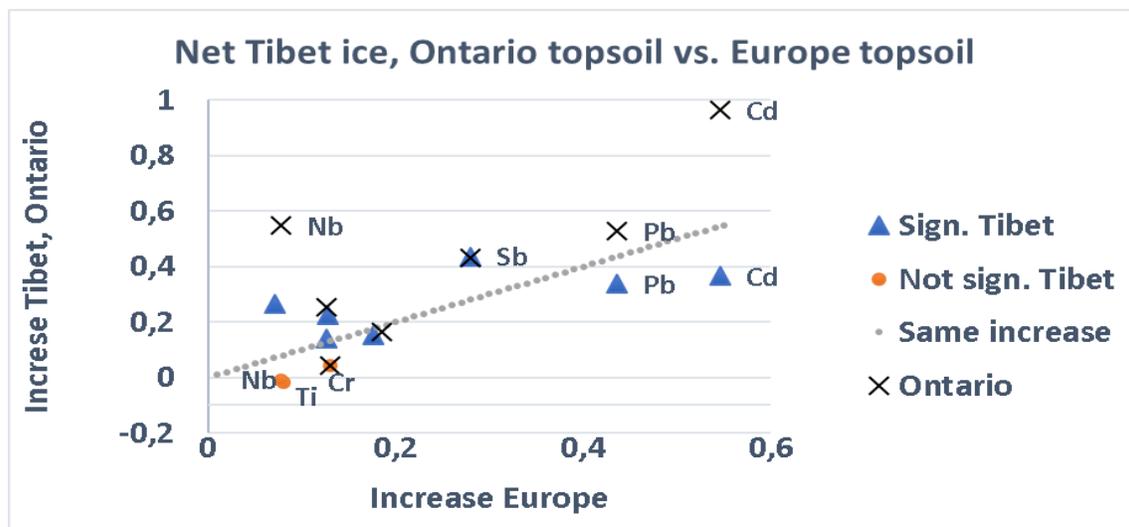


Figure 3. Fractional increases over the last century in measured element concentrations in European topsoil and Tibet ice.

Some Tibet measurements (Ti, Nb, Cr) were not significantly different from zero. The dotted line represents equal excesses for Tibet, Ontario and Europe.

Enhanced element concentrations in sewage sludge

The element concentrations in sewage sludge from Germany (Krüger and Adam 2014) were compared with the minimum concentrations deriving from human excreta. Nineteen elements (Sc, Ti, V, Cr, Ga, Sr, Y, Zr, Sb, Ba, La, Ce, Gd, Hf, Ta, W, Pb, Bi, Th) had measured levels more than 100 times the minimum, at most almost 600 times for tungsten and scandium. Calculated sludge concentrations compared with measured ones are given in Figure 4. The figure shows that it is possible to align result from simple calculations with measured ones, thus lending credibility to calculated concentrations for elements for which there are no corresponding measurements.

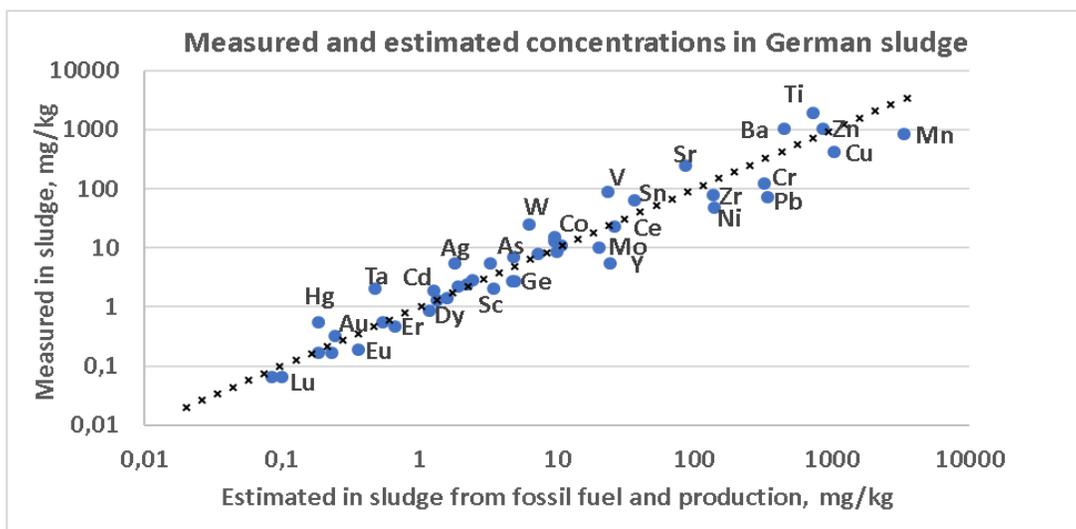


Figure 4. Measured and estimated element concentrations in German sewage sludge.

The emission fraction for the estimation was chosen to make the points fall around the straight line.

Agricultural soils are often amended with sludge at an annual rate of 1 ton per hectare. After 100 years of amendment, a doubling of the natural soil concentration is attained if the dietary intake alone is above 2100 µg/day per mg/kg of the element in the initial soil, assuming 70 g of sludge/person per day and 300 kg topsoil per m² of agricultural land, and no loss from the topsoil. There are ample margins to a doubling for elements like scandium but none for No. 44 ruthenium and No. 45 rhodium (see Figure 1).

Cumulative concentrations after 1960 may typically correspond to 300 years of the levels of 2011 (based on Umweltbundesamt 2012, and Kirchmann et. al. 2017). Continuous amendment through 2011 would then have resulted in doubling or more of the soil content of Ag, Cu, Mo, Sb and Zn, disregarding macroelements. For the not measured element Au, also more than a doubling is predicted.

In the years 2011 to 2045, the concentration of most elements in sewage sludge would be expected to decrease and soil concentrations of elements from sludge amendments be marginally increased. In Swedish sewage sludge, namely, the median concentration in 2016 (based on Finnson private communication 2018) was 0.7 of that in 1999 (Eriksson 2001), with a range between elements of 0.2- 5. From 2012 to 2016 (based on Finnson private communication 2018), there was a decrease by a few percent per year for most elements but a minor increase for a handful of elements like Cu and Zn. Additional broader platinum group elements (Pd, Re, Os, Ir, and Pt) have generally not been measured but their consumption has increased strongly in recent decades. There is thus a potential for future increases in their sludge concentrations, but a doubling until 2045 appears unlikely.

Conclusions

Concentrations of many element in European soils have increased over the last century. Concentrations in sewage sludge are already enhanced more than a hundred-fold for many elements. It is possible that continuous sludge amendment in German soils might have more than doubled the mean soil concentrations of 6 elements (Ag, Au, Cu, Mo, Sb and Zn). Over the next generation significant increases but not a doubling might be incurred for some additional platinum group elements, bearing in mind that all estimates are quite uncertain. Locally much higher concentrations can be expected, and cumulative or synergistic effects cannot be excluded. To minimize this extensive soil pollution, more studies are necessary as well as further preventive measures.

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2.2.3. Emerging contaminants in soil and sediment of Mediterranean catchments (Valencia, Spain)

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Abstract

According to the Stockholm Convention on persistent organic pollutants, these compounds are resistant to chemical, biological, and photolytic environmental degradation, and could pose significant impact on human health and the environment. The screening of emerging persistent organic pollutants (ePOPs) in soils and sediments is crucial to understand their transport, accumulation and fate. The Jucar and Turia basins (including L'Albufera Natural Park, Valencia, Spain) are areas severely threatened by land use changes, soil and water pollution, high population density, etc. The concern about the occurrence and distribution of ePOPs is rising since they are one of the factors adversely affecting fragile agricultural systems, dominant in the area. In this study, 98 samples including agricultural soil, sediment, influent and effluent from wastewater treatment plants (WWTPs) were collected (2010-2016). Considered ePOPs, 21 perfluoroalkyl substances (PFASs) and 9 organophosphate flame-retardants (PFRs), were extracted by solid phase extraction and determined by liquid chromatography triple quadrupole mass spectrometer.

PFASs and PFRs were detected in all the matrices. It is remarkable the high occurrence and concentration of short-chain PFASs (C<8), intended to replace the long-chain ones in several industrial applications. Perfluorooctane sulfonate was also detected together with tris(2-chloroisopropyl) phosphate. WWTPs were identified as an important but not unique source. High levels of target compounds (mainly PFASs) in wastewater effluents suggest the presence of precursors and their poor removal through the treatments. Despite concentrations found in this study can be considered low, monitoring of ePOPs in zones under the threat of global change, as the Mediterranean, is required, particularly in the development of Special Action Plans in situations of alert and temporary drought in which contaminant concentrations could be increased.

Keywords: persistent organic pollutants; perfluoroalkyl substances, organophosphorus flame retardants; analytical determination; Mediterranean wetland

Introduction, scope and main objectives

According to the Stockholm Convention on persistent organic pollutants (UNEP, 2009), these compounds are resistant to chemical, biological, and photolytic environmental degradation. POPs are stable and persistent, long-distance transportable, bioaccumulative, biomagnifiable in the food chain, and could pose significant impact on human health and the environment (Campo *et al.* 2016).

Among ePOPs, perfluoroalkyl substances (PFASs) have been used since 1950 in a number of industrial and commercial applications as surfactants and stain repellents (examples of products containing PFASs or precursors are anti-fire foam, alkaline detergents, paints, nonstick cookware, carpets, upholstery, textile fibers, shampoos, floor polish, smoke inhibitors, semiconductors, pesticide formulations, food packaging, tapes, denture cleaners, etc. (Lorenzo *et al.* 2015). On the other hand, flame retardants are chemicals added to materials both to prevent combustion and to delay the spread of fire after ignition. Since the ban on some bromine-containing flame retardants, phosphorus flame retardants (PFRs) have been proposed as alternatives. PFRs are widely used as plasticizers and anti-foaming agents in a variety of industries including plastics, furniture, textile, electronics, construction, vehicles and petroleum industries (Wei *et al.* 2015).

Despite the attempts to reduce PFAS and PFR release to the environment, a clear declining trend in their levels has not been observed yet since there is a still growing demand for substances with their unique properties, and short-chain PFASs are replacing long-chain ones (Llorca *et al.* 2012). PFRs are the recent replacement of brominated flame retardants (BFRs) and do not have any substitute yet.

The screening of emerging persistent organic pollutants (ePOPs) in soils and sediments is crucial to understand their transport, accumulation and fate in sensitive areas. The Jucar and Turia catchments (including L'Albufera Natural Park, Valencia, Spain) are areas severely threatened by water pollution, disturbances of the water regime, industrial pressures, high population density, etc. The concern about the occurrence and distribution of ePOPs is rising because they are one of the factors that adversely affect fragile agricultural systems, dominant in the research area.

This work presents the results of up to authors' knowledge, the first comprehensive PFASs and PFRs monitoring survey conducted in soil and sediment matrices in the Jucar and Turia River catchments. The objectives of this study were: (i) determine concentrations, profile patterns and spatial distribution of PFASs and PFRs in these Mediterranean catchments and; (ii) to identify their possible sources as well as their fate.

Methodology

Study area is located in the Spanish Mediterranean. The Jucar River's catchment (21578 km²) and the Turia's one (6393 km²) are mainly agricultural areas although industrial activities are not negligible (i.e. car's factories). Big cities are also present in the watersheds, as Cuenca in the former, and Teruel and Valencia in the latter. Both rivers drain to L'Albufera de Valencia, a large coastal lagoon and marshy area where important protected wetlands (Natural Park included in the Ramsar convention) and agriculture (mainly rice, citric and orchards) share the same area (Fig. 1).

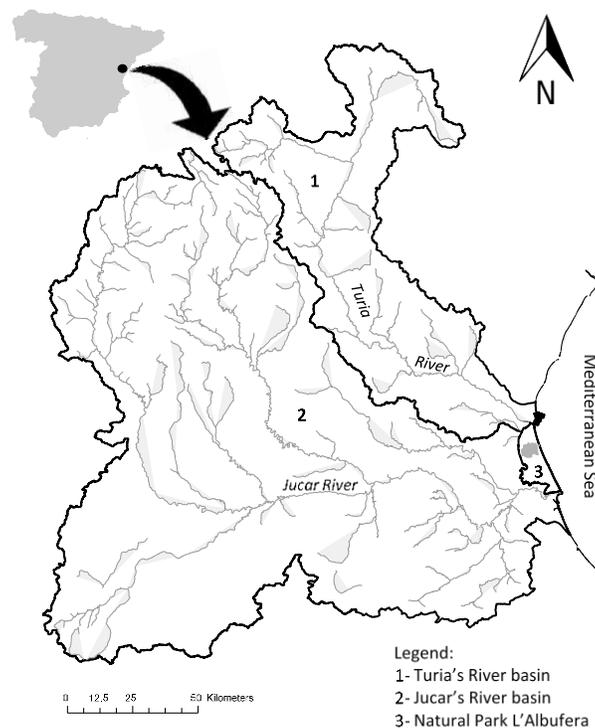


Figure 10. Study area

Samples have been collected from riverine areas through different campaigns: in 2010, 15 sediment samples from Júcar catchment; in 2012 and 2013, 21 and 26 soil samples, respectively, from Turia basin; and in 2016, 19 sediment samples from L'Albufera Natural Park and the surrounding area. Influent (IN) and effluent (OUT) samples from WWTPs were also collected: 4 (2010: 2 WWTPs) and 13 (2016: 10 WWTPs). Samples were always collected in October. Considered ePOPs (21 PFASs in all samples, and 9 PFRs in 2016 samples, Table 1) were extracted by shaking and ultrasonication with methanol followed by solid-phase extraction with STRATA-X cartridges (Lorenzo *et al.* 2015). Determination was made by high-performance liquid chromatography-tandem mass spectrometry. Data were processed using MassHunter Workstation Software for qualitative and quantitative analysis (internal standard methodology based on peak areas).

Table 1. Studied compounds and acronyms

Compound	Acronym
Perfluoroalkyl substances	PFAS
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluoro-7-methyloctanoate	ipPFNA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnDA
Perfluorododecanoic acid	PFDoDA
Perfluorotridecanoic acid	PFTTrDA
Perfluorotetradecanoic acid	PFTeDA
Perfluorohexadecanoic acid	PFHxDA
Perfluorooctodecanoic acid	PFODA
2H-Perfluoro-2-decenoic acid	FOUEA
Perfluorobutane sulfonate	PFBS
Perfluorohexane sulfonate	PFHxS
Perfluoroheptane sulfonate	PFHpS
Perfluorooctane sulfonate	PFOS
Perfluoro-7-methyloctane sulfonate	ipPFNS
Perfluorodecane sulfonate	PFDS
Organophosphate flame retardants	PFRs
Trippropyl phosphate	TPP
Tris(2,3-dibromopropyl) phosphate	TDBPP
Tris(2-ethylhexyl) phosphate	TEHP
Tricresyl phosphate	TMPP
Triphenyl phosphate	TPhP
Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP
Tris(2-chloroethyl) phosphate	TCEP
Tris(2-chloroisopropyl) phosphate	TCIPP
Cresyl diphenyl phosphate	CDP

Results

The results show the presence of PFASs and PFRs in all the samples analysed. In 2010, 11 PFASs were detected in sediment samples, through the whole Jucar River watershed, with frequencies ranging from 7% (PFNA) to 100% (PFBA). PFOS was also found (67%). Short-chain compounds (C<8) presented the highest mean concentrations: 5.85 ng g⁻¹ dry weight (dw) of PFBA (maximum 10.7 ng g⁻¹ dw), and 11.5 ng g⁻¹ dw of PFBS (maximum 29.2 ng g⁻¹ dw). PFOA and PFOS showed similar average (2.47–2.57 ng g⁻¹ dw) and maximum (6.69–9.83 ng g⁻¹ dw) concentrations. In 2012, PFBA was predominant being found in a large number of Turia's basin soil samples (77%), followed by PFOA (59%) and PFOS (14%). PFBA was also the compound at higher concentrations (maximum of 17.96 ng g⁻¹), followed by PFOA (3.08 ng g⁻¹) and PFOS (2.74 ng g⁻¹). A similar pattern was observed in 2013, but with smaller frequencies and higher concentrations. PFBA was again prevalent (42%) and with the highest concentration (64.04 ng g⁻¹), followed by PFOA (31%, 6.96 ng g⁻¹) and PFOS (15%, 4.15 ng g⁻¹).

In 2016, 13 out of 19 samples from L'Albufera area were contaminated with at least one PFAS and 7 analytes were detected. PFOS was predominant (58%). The other PFASs were found in less than 32% of the sampling points. Mean values were from 0.01 ng g⁻¹ dw (PFTeDA) to 4.9 ng g⁻¹ dw (PFOS). Maximum concentration was for PFOS with 21.4 ng g⁻¹ dw. All the samples were contaminated with at least 4 PFRs and 7 of them were detected at concentrations above the limits of detection (LODs). TCIPP was ubiquitous (100%), followed by TCEP and TPhP (95%), TEHP (89%), and TDCIPP (79%). Mean concentrations for detected compounds were from 2.5 ng g⁻¹ dw (TDCIPP) to 53.8 ng g⁻¹ dw (TCIPP). Maximum concentration was for TCIPP, 246.5 ng g⁻¹ dw in a sample from a horticultural irrigation channel.

On the other hand, of the 21 PFASs screened in this area, 15 were detected in both influent and effluent samples collected in 2010 in Jucar's WWTPs. PFBA, PFPeA, PFOA, PFDA and PFUnDA were the most frequent compounds (100% in IN and OUT). PFOS was found in 1 out of 2 WWTPs. The highest concentration detected was for the PFDA, 128 ng L⁻¹ (IN) and 103 ng L⁻¹ (OUT), followed by PFOS with 52.5 ng L⁻¹ (IN) and 35.1 ng L⁻¹ (OUT). Removal efficiencies calculated were between -121% of PFBA, in Alzira's WWTP, and 82% of PFOA, in Cuenca's WWTP. Mass loads of individual PFASs (mg day⁻¹) were in the range of 0.70 (PFBS)–1.23*10³ mg day⁻¹ (PFOS).

In 2016, 13 PFASs were found in IN and 20 in OUT. PFOA was the most frequent (100%) in both wastewaters, followed by PFOS with 54% (IN) and 92% (OUT). The highest concentrations were for PFBS (101.3 ng L⁻¹) in Pinedo I's WWTP (OUT) and for PFOS (63.1 ng L⁻¹) in Perellonet's WWTP (IN). Some PFASs (i.e. PFHxA, PFHpA, PFHxS, PFOA, PFHpS, ipPFNS, PFOS and FOUEA) showed higher concentrations in OUT than in IN, and some others like PFBS, ipPFNA, PFNA, PFDA, PFUnDA, PFTrDA, PFHxDA and PFODA were only found in OUT samples. The remaining PFASs showed removal efficiencies between 8 and 100%.

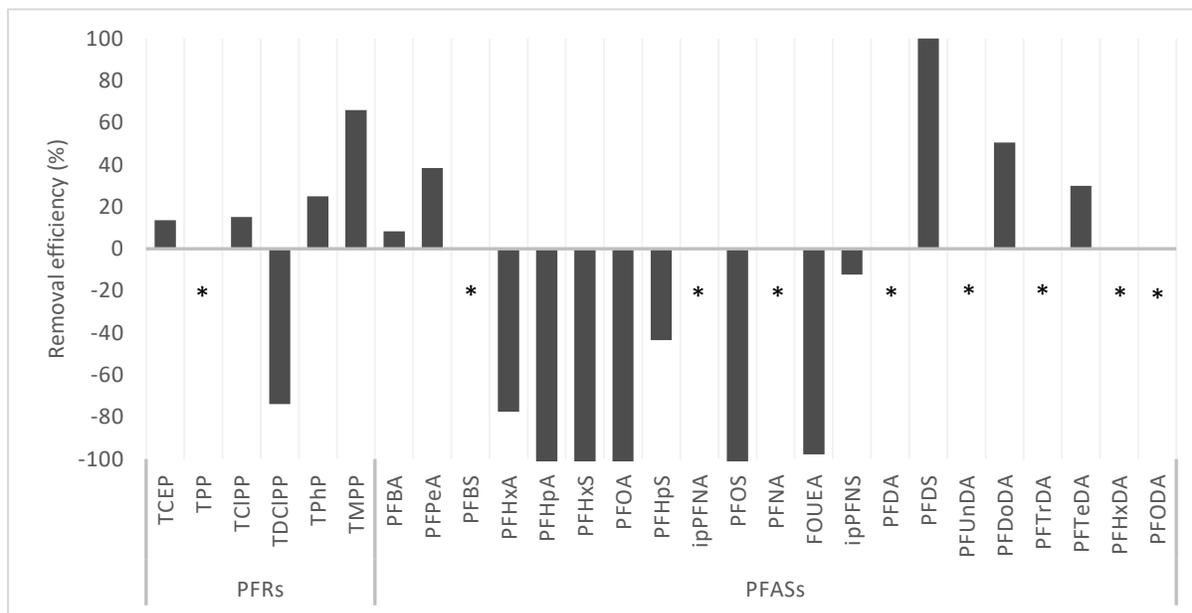


Figure 2. Mean WWTPs removal efficiency (%) of PFRs and PFASs in 2016 samples. Compounds with (*) were only found in effluent samples (Lorenzo *et al.* submitted).

Regarding PFRs, most frequent ones in WWTP's IN and OUT were TPhP (100% in both), TDCIPP (92% and 85%) and TCIPP (92% and 77%). The highest concentrations were found for TCIPP (1543.5 ng L⁻¹ in Pinedo I (IN) and 1908.5 ng L⁻¹ in Pinedo II (OUT)). WWTPs showed lower removal

efficiency for chlorinated PFRs (TCIPP, TDCIPP and TCEP) than for non-chlorinated such as TPhP and TMPP. Removal efficiencies ranged from 14 to 66% except for TPP which was only found in effluent samples and TDCIPP that was found in much higher concentrations in effluent samples (-74%).

Discussion

There are few articles about PFAS and/or PFR concentrations in soil and sediment (e.g. Boiteux *et al.* 2016; Matsukami *et al.* 2017). The main limiting factor to expand the number of studies is the complexity of these matrices and the low concentrations at which PFASs/PFRs are found. This work presents the results of up to authors' knowledge, the first comprehensive PFASs/PFRs monitoring survey conducted in soil and sediment matrices in the Jucar and Turia River catchments.

PFAS concentrations detected in sediments are in the same range than those reported elsewhere (Labadie and Chevreuil 2011, Beškoski *et al.*, 2013). Jucar River revealed PFASs accumulation in sediments downstream (Campo *et al.* 2016). It is important to highlight that PFOS, a compound added in May/2009 to Annex B as new POP at the Stockholm Convention (UNEP, 2010) was found in soil and sediment of both watersheds, and at high frequencies and concentrations. It is remarkable the high occurrence of short-chain PFASs (C<8), particularly in Turia's basin soils, which are intended to replace the long-chain ones in several industrial and commercial applications.

On the other hand, EU banned the use or manufacture of TCEP in 2001, classified as carcinogenic (cat. 2) and toxic to reproduction (cat. 1B) (EU Regulation, 2008). This compound has been replaced progressively by other flame retardants as TDCIPP and TCIPP. The former is also classified as carcinogenic (cat. 2) and the latter, although not yet classified, is a possible carcinogenic (EU Directive, 2014). All three compounds were found in the study area where they are accumulating and would pose significant impact on human health and the environment.

The occurrence of PFAS and PFRs is related to urban and industrial discharges associated to big cities in both basins. The high concentrations of these compound in effluents suggest that WWTPs are ineffective removing them (Campo *et al.* 2014, Lorenzo *et al.* under review). Furthermore, there is evidence that an additional source of these ePOPs in WWTPs is the biotransformation of their precursors during activated sludge treatment. Monitoring data (Arvaniti *et al.* 2012, Woudneh *et al.* 2015) suggest that WWTPs could be main sources of PFASs and PFRs contamination to surface water and contribute to increase the concentration of these compounds in the soils and sediments of the study area. Such result points out the need of these type of studies and their environmental forensics utility, since they could help to identify ePOPs sources to the environment.

Conclusions

Samples of the Jucar and Turia River basins and of L'Albufera Natural Park were all contaminated with at least one PFAS or PFR. PFBA and PFBS were the most predominant analytes confirming the current replacement of long-chain PFASs by short-chain ones in industrial and commercial applications, and their increasing accumulation in environmental matrices. WWTPs were identified as an important but not unique source of ePOPs to the environment. High levels of target compounds (mainly PFASs) in wastewater effluents suggest the presence of precursors within plants and their poor removal through the treatments.

Despite concentrations found in this study can be considered low, monitoring of these compounds in zones under the threat of global change, as the Mediterranean, is required in order to manage and predict their possible effects on ecosystem services, particularly in the development of Special

Action Plans in situations of alert and temporary drought in which contaminant concentrations could be increased.

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2.2.4. Application of Health Belief Model in pesticide pollution: a case study from Nepal

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Abstract

Indiscriminate use of pesticides is an emerging problem in developing countries including Nepal, which results in environmental pollution and increased health risk. This study assesses end user's perception on impacts of pesticide use on the environment as well as human health applying the constructs of Health Belief Model (HBM). We focused on their awareness and perceived threats of pesticide use on the environment. The study revealed that farmers applied pesticides much higher than the recommended dose, at an average of 2.9 kg a.i. ha⁻¹ per crop per season. Pesticide users perceived pesticide as "medicine" rather than "toxin", i.e., minimal perceived threats of pesticides on the environment and human health, leading to excessive use of pesticides in farming. Changes in farmers' perception on the pesticide threats, along with awareness on the good agricultural practices are necessary for reducing soil pollution from pesticide use.

Keywords: Health Belief Model; pesticides and human health; environmental health; vegetable; Nepal

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2.2.5. Cadmium management in New Zealand agricultural soils

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Abstract

Soil cadmium (Cd) concentration is the primary indicator through which fertiliser-derived Cd is currently managed under the New Zealand Cadmium Management Strategy (MAF 2011). Specifically, the Tiered Fertiliser Management System (TFMS) aims to minimise Cd accumulation in soil by imposing increasingly stringent fertiliser management practices as Cd concentrations increase. Previous work has identified that soil Cd concentrations to support compliance with food standards are likely to be a primary trigger for managing soil Cd and that New Zealand-specific research was required (MPI 2012; Cavanagh 2013).

This paper describes research on:

- Cultivar and soil property influence on Cd uptake into food crops

- Risks to pastoral systems – Cd uptake in pasture species, impact on rhizobia, and uptake by livestock

Findings from this research will assist with managing the risk of exceeding food standards in food crops and livestock products in New Zealand and aid further strategy development. The key findings were:

- The soil trigger values in the TFMS are insufficient to manage the risk of exceeding food standards in some food crops
- Management of Cd in potatoes and wheat appears likely to be most effectively achieved by cultivar management, as there was an absence of identified relationships with soil properties
- Management of soil pH may be sufficient to ensure compliance with food standards for onion, while the addition of compost may reduce Cd uptake in bunching spinach
- Regional variation in plant uptake of Cd may be linked to differences in soil type although detailed soil property analyses did not identify the critical soil properties
- There is minimal risk of negative impact from soil Cd on the clover–rhizobia symbiosis, or plant nitrogen content until Cd concentrations are markedly higher than current concentrations in pastoral soils
- Cadmium was elevated in the liver of lambs grazed on feed crops with elevated Cd (chicory) and warrants further investigation

Keywords: Cadmium, rhizobia, food crops, livestock, pasture, food standards

Introduction, scope and main objectives

The strategy document ‘Cadmium and New Zealand Agriculture and Horticulture: A Strategy for Long Term Risk Management’ was released in February 2011. This strategy outlines a risk-based approach for managing cadmium in New Zealand agricultural soils:

To ensure that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years.

Soil cadmium (Cd) concentration is the primary indicator through which fertiliser-derived Cd is currently managed under the New Zealand Cadmium Management Strategy (MAF 2011). Specifically, the Tiered Fertiliser Management System (TFMS) aims to minimise cadmium (Cd) accumulation in soil by imposing increasingly stringent fertiliser management practices as Cd concentrations increase. The soil Cd concentrations used as trigger values in the TFMS were agreed to by the Cadmium Working Group (CWG), following international review and recommendations are from a variety of sources (MAF 2011³).

However, there is a lack of New Zealand-specific data on the soil Cd concentrations that actually pose a risk for New Zealand agricultural systems and how these risks might be managed. A number of research priorities, including the development of risk-based soil guideline values specific to New

³ A full description of the Tiered Fertiliser Management System is available from:
http://www.fertiliser.org.nz/Site/resource_center/Tech_Papers.aspx

Zealand, have been identified to address these issues as part of the strategy (MAF 2011). Previous work has identified that soil Cd concentrations to support compliance with food standards are likely to be lower than soil Cd concentrations causing detrimental effects on ecological receptors and that New Zealand-specific research was required to inform the use of soil management tiers, the risk posed by Cd concentrations in agricultural soils and how any risks might be managed (MPI 2012; Cavanagh 2013). Furthermore, food standards have previously been reported to have been occasionally exceeded in potatoes (Kim 2005) and wheat grown in New Zealand (Gray *et al.* 2001).

Pastoral land is the dominant land use in New Zealand with elevated soil Cd concentrations in some regions (Cavanagh 2014). Ryegrass/clover systems are the dominant pasture species, although other species such as chicory and plantain, or forage crops, such as kale and fodder beet are increasingly used to improve the resilience of the pastoral system. As grazing animals take up Cd mainly via consumption of herbage (e.g. Loganathan *et al.* 1999), increased herbage Cd may lead to food standards being exceeded, particularly in kidneys sold as offal for human consumption.

Rhizobium leguminosarum is the rhizobia species most commonly associated with pasture legumes (i.e. white clover) and previous studies have shown that N-fixation by rhizobia is sensitive to Cd (e.g. Broos *et al.* 2004). However, most studies have been focused on heavily contaminated sites, where Cd has accumulated from industry, mining, or application of sewage sludge to land. The effects of relatively lower levels of Cd contamination on rhizobia and the rhizobia:legume symbiosis in agricultural soils is not well understood

This paper describes research undertaken over the past three years on Cd uptake in food crops and risks to pastoral systems (Cd uptake by pasture, forage species and livestock and impact on rhizobia) to inform further strategy development, including the development of New Zealand specific soil-guideline values, and outlines recommendations for further research to manage risk.

Methodology

Food crops

Investigation of Cd uptake in food crops was undertaken in two stages 1) uptake in a range of commonly-grown cultivars of wheat, potatoes, onions, and lettuce at a limited number of sites; and 2) uptake in one or two higher accumulating cultivars of wheat, potatoes, onions, lettuce and spinach in the main growing areas of each crop across New Zealand.

As a general overview, soil and plant samples were collected from existing industry trials and/or commercial fields. At each site plant and soil samples were taken from each of three or four replicate plots per cultivar/species. A sample was a composite sample of soil or the edible/millable portion from several individual plants within a plot. The plot size differed, depending on the crop being sampled. Multiple soil cores (2.5 × 15 cm for crops) provided a composite sample for each plot. A summary of samples collected for each crop is provided in Table 1, with locations shown in Fig.1.

In the laboratory, soil samples were oven-dried (35°C) sieved, through a 2mm sieve and sent to a commercial laboratory for analysis of Olsen P, pH, CEC and to Lincoln University for Cd using inductively-coupled-plasma mass-spectrometry (ICP-MS), other elements (e.g. Zn, Al, Fe) using ICP-OES and total carbon and chloride analysis. Plant materials were oven-dried to a constant weight (60°C) and sent to Lincoln University for Cd analysis via ICP-OES.

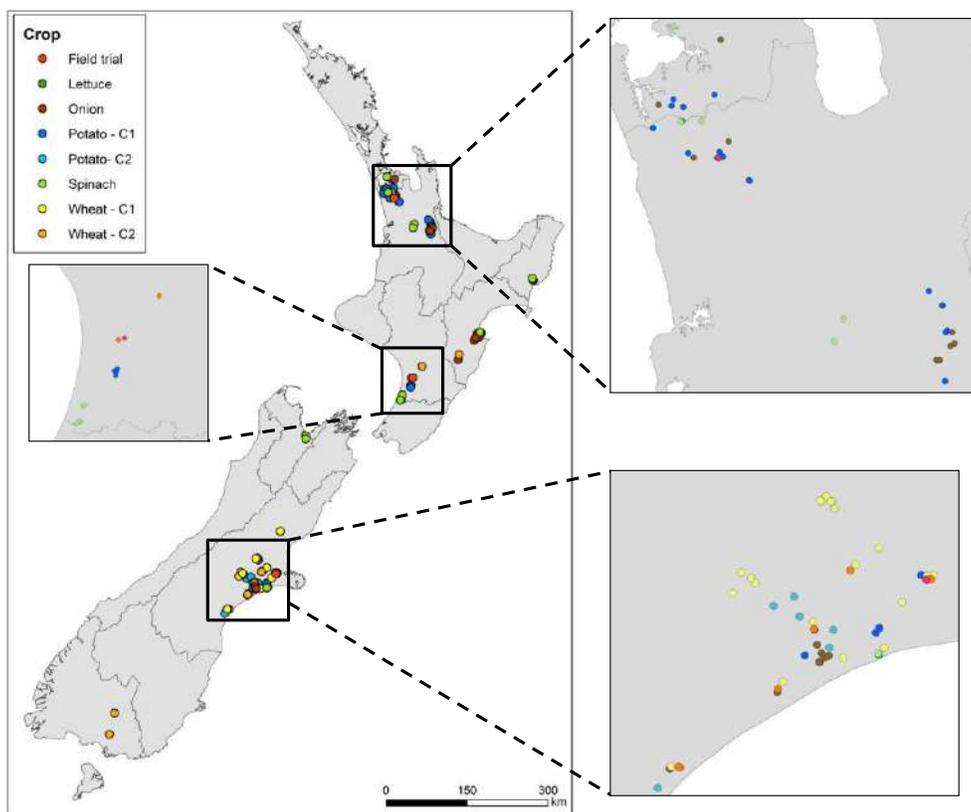


Figure 11. Sampling location for different crops during the field survey over 2016 and 2017, and during a previous study (one wheat site for C1 and three sites for C2, three potato sites for C1, one for C2, three onion sites, two lettuce sites). C1 and C2 are separate cultivars (Cavanagh *et al.* 2017).

Table 1. Summary of cultivars and number of sites used in the two studies. Three to four replicate plots were sampled for crop and soil samples at each site.

Crop	Cultivar study	Soil study - Cultivar
Wheat (<i>Triticum aestivum</i>)	Bread wheat – 8 cultivars, 1 location	C1 – bread wheat Site <i>n</i> = 26
	Feed and biscuit wheat 6 cultivars, 2 locations	C2 – biscuit wheat Site <i>n</i> =9
Onions (<i>Allium cepa</i>)	4 cultivars, 3 locations	C1 / Site <i>n</i> = 28
Potatoes (<i>Solanum tuberosum</i>)	10 cultivars across 3 sites	C1 / Site <i>n</i> =28
		C2 / Site <i>n</i> =7
Spinach (<i>Spinacia oleracea</i>)	Not sampled	Baby leaf / Site <i>n</i> =10 Bunching / Site <i>n</i> =11
Lettuce (<i>Lactuca sativa</i>)	3 cultivars of crisphead lettuce, 2 locations	8 types across 3 sites

Pasture and forage species

Soil and plant samples were collected as described above except soils were sampled to 7.5 cm for pasture species. Species tested were Chicory (*Chicorium intybus*), Plantain (*Plantago major*), Ryegrass (*Lolium perenne*), White clover (*Trifolium repens*), Lucerne (*Medicago sativa*), Maize (*Zea mays*), Fodder beet (*Beta vulgaris*), Kale (*Brassica olearaeae*), Sunflower (*Helianthus sp.*). The sampling was undertaken at one or two sites for each species.

Rhizobia-legume symbiosis

A 96-well format, respiration-inhibition assay (MicroResp) was used to quantify the effect of Cd on growth of *R. leguminosarum* isolated from two soils with high and low soil Cd, and the dominant commercial strain TA1 (Wakelin *et al.* 2016). Pottle-based assays with vermiculite and nutrient solution were used to quantify the effects of increasing Cd concentration on the growth of white clover seedlings (shoot dry weight) in the presence and absence of rhizobia and effect on plant N following Wakelin *et al.* (2016).

Cadmium uptake in lambs

At four commercial farms recently weaned (14–16 weeks), pasture-fed only, Romney composite lambs (Highlanders) were mustered. Lambs were randomly divided into groups of 15 using the ‘odds and evens’ drafting technique to determine whether they were grazed on pasture or forage crop. Liver biopsies were taken on 3 or 4 occasions over December 2016 to March 2017, with soil and plant samples also collected. All procedures using animals were approved by the Massey University Animal Ethics Committee (approval number 16/116).

Table 3. Field locations and forage treatments, and number of liver samplings at each location

Location	Forage crop	Number of animals	Number of times sampled
Tangimoana	Ryegrass, lucerne	30	3
Waipukurau	Ryegrass, lucerne	30	4
Taihape – township	Ryegrass, plantain	30	3
Taihape – rural	Ryegrass, plantain, chicory	45	3

Biopsy samples were immediately chilled and frozen for Cd analysis with Cd analysed by graphite furnace atomic-adsorption-spectroscopy (GFAAS). The detection limit for total Cd analysis was 0.00026 mg/kg DM. Soil and plant samples were analysed as described above.

Results

Cadmium uptake in food crops

A 2.4-fold difference in wheat grain Cd concentrations between different cultivars was observed, with the highest concentrations found in feed wheat cultivars. Cadmium concentrations in wheat bran were higher than wheat flour in the selected cultivars analysed. Assessment of two cultivars across 35 sites found few significant relationships between soil properties or site management factors (nitrogen fertiliser application, irrigation status) and wheat grain Cd concentrations, with relationships observed sometimes being contradictory between cultivars.

Differences in Cd concentrations in onion cultivars were not consistent across sites. Assessment of a single onion cultivar across 28 sites revealed that pH and total Cd were significant predictors of onion Cd, although only explaining 38% of the variation. Inclusion of region in the regression relationships explained a greater proportion of variation (50%).

Differences between cultivars of crisphead (iceberg) lettuce were not consistent across sites nor were differences in Cd concentrations between different lettuce types (e.g. cos, iceberg). Concentrations were very low (<0.04 mg/kg FW). Observed regional differences in lettuce Cd were not related to soil Cd concentrations – i.e, higher concentrations were found regions with

lower soil Cd. In contrast, Cd concentrations in both baby leaf and bunching spinach were close to, or above, the FSANZ food standard of 0.1 mg/kg FW, with Cd concentrations higher in bunching spinach. Soil carbon and soil Cd were identified as key factors influencing Cd uptake in bunching spinach, explaining 48% of the variation in spinach Cd. In contrast, zinc, total phosphorous and exchangeable calcium, but not soil Cd, explained 57% of the variation in baby spinach Cd.

There was a 2.3-fold difference in potato Cd concentrations between different cultivars. No relationships between soil properties and tuber Cd concentrations were identified. With the exception of one site, potato Cd concentrations were remarkably uniformly low and much lower than the FSANZ food standard of 0.1 mg/kg FW. Soil properties at the exceptional site were similar to those at other sites, other than potatoes being the first crop grown after conversion from long-term pasture.

Cadmium in pastoral systems

Pasture Cd concentrations were highest in chicory and plantain and lowest in ryegrass and clover. Leaf Cd concentrations of all forage crop species were higher than other plant components.

Cadmium was demonstrated to have negative effects on the growth of rhizobia isolated from New Zealand pastures, with the current commercial strain, TA1 being most sensitive. Conversely, *Rhizobium leguminosarum* TA1 appears to mediate the toxicity of Cd to clover: a minimum tolerable concentration of Cd for white clover in the absence of rhizobia was 0.040 mg/kg Ca(NO₃)₂-extractable Cd, and 3.34 mg/kg in the presence of rhizobia. These concentrations are markedly higher than current environmental concentrations of Ca(NO₃)₂-extractable Cd up to 0.00068 mg/kg (Reiser *et al.* 2014). No effect on nitrogen content in clover was observed in clover/rhizobia exposed to extractable Cd concentrations up to 5 mg/kg.

Increased liver Cd concentrations were observed in lambs grazed on crops with higher Cd (plantain and chicory), with the highest liver concentration occurring in lambs grazed on chicory.

Discussion

The primary purpose for undertaking this research was to inform future management of cadmium to manage risks associated with soil Cd and is discussed below.

Implications for crop management

The absence of identifiable relationships between soil properties and Cd in wheat grains, and the proximity of grain Cd concentrations to the food standards, suggests that the use of low-Cd-accumulating cultivars will be most effective to manage Cd in wheat grain. Similarly, management of Cd in potatoes is also likely to be most effective by using low-Cd-accumulating cultivars, given the absence of identified relationships with soil properties. As tuber concentrations are generally much lower than the FSANZ food standard, a less restricting approach ensuring that high-Cd-accumulating do not become widely grown could provide an appropriate management approach. We found that variation in Cd uptake by different cultivars varied across sites, highlighting the importance of assessing cultivars at a number of sites.

Maintaining soil pH at around 6 appears to be sufficient to ensure Cd concentrations in onions comply with food standards. Further assessment is required to determine if this advice is more generally applicable to a wider range of onion cultivars.

Cadmium concentrations in baby, and particularly bunching, spinach (i.e. close to or above FSANZ food standard) suggests that management actions should be implemented to reduce Cd uptake. As soil pH is typically managed to around 7 for spinach crops, lime addition offers limited value in reducing Cd uptake in spinach. Given the dependence of Cd concentrations in bunching spinach on soil carbon, the addition of compost may help to reduce Cd uptake, although the extent to which it is reduced needs to be determined.

It is notable that the EU food standards for both wheat and spinach are double those of the FSANZ food standards (0.2 mg/kg FW vs 0.1 mg/kg FW). Cd concentrations in these crops are close to the food standards in low Cd soils, and management options are limited. As the standards are established based on being as low as reasonably achievable while ensuring protection of human health, it may be relevant to review the applicability of the FSANZ food standards for wheat and spinach to determine whether this principle is being met.

Soil cadmium management implications

Soil Cd concentrations in the majority of sites fell into Tier 0 of the Tiered Fertiliser Management System (TFMS), for which only 5-yearly monitoring of soil Cd is required. However, for wheat and spinach and some regions, managing to the soil trigger values in the TFMS is clearly insufficient to ensure crops comply with applicable food standards.

Provisional soils guideline values to support compliance with food standards were developed using identified relationships based on regression analyses for onion and bunching spinach. These relationships explained a low to moderate proportion of the variation in onion (38%) and bunching spinach (42%), indicating factors other than those assessed are also influencing plant uptake. The onion relationship under-predicted observed high onion Cd concentrations, suggesting caution needs to be applied in using these values to support compliance.

Table 4. Provisional Cd soil guideline values (pFS-SGV) to meet EU maximum limits for onions (0.05 mg/kg FW) and the FSANZ standard for leafy greens (0.1 mg/kg FW), as a function of soil properties (38% and 42% of variation in plant Cd was explained by soil Cd and pH or soil C, respectively)

Onions		Spinach	
soil pH	pFS-SGV (mg/kg)	soil C	pFS-SGV (mg/kg)
5.5	1.7	2	0.24
6	2	3.5	0.36
6.5	2.2	5	0.48

The plant uptake factor (PUF, $\frac{Cd_{plant} (mg/kg (DW))}{Cd_{soil} (mg/kg)}$) was also used to provide a first approximation empirical estimate of the soil concentrations to support compliance with food standards at individual sites. This approach assumes that site conditions, including soil properties and management (and therefore PUF), do not change. Mean values for individual crops ranged from 0.3 to 4.7 mg/kg (range 0.14 to 16 mg/kg) for different crops, with clear regional differences.

Conclusions

The findings from this study will inform the ongoing management of Cd in New Zealand agricultural soils, including the development of New Zealand-specific risk-based guideline values, as part of the National Cadmium Management Strategy. Provisional soil guideline values to support compliance with food standards (plant crops and livestock products) were developed. Further data is required

to develop robust guideline values, but these values nonetheless provide insight into the Cd concentrations at which management to mitigate the risk of exceeding food standards should be considered. These studies also provided insight into crop and soil property factors that may also support compliance with food standards. Further monitoring and field studies of plant crops, including a range of cultivars, is required to verify the wider applicability of these findings.

Further assessment of Cd uptake by livestock grazed on pastoral or forage species with elevated Cd is also required to more fully establish the risk of non-compliance with livestock product food standards, and to identify relevant management options. Finally, there appears to be minimal risk of negative impact from soil Cd on the clover–rhizobia symbiosis, and subsequent effects on plant nitrogen content until Cd concentrations are markedly higher than current concentrations in agricultural soils.

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2.2.6. Environmental fate and off-site impacts of pesticides – a case study of the S. Lourenço do Bairro sub-basin, Portugal

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Abstract

Vineyards are highly dependent of pesticides to fight diseases such as downy mildew and powdery mildew. In 2015-2017 we assessed the environmental impacts of pesticide use in vineyards in the S. Lourenço do Bairro sub-basin. The degree of soil contamination by pesticide residues was evaluated and the toxicity of the most relevant residues in soils (in both frequency and concentration) was tested on a battery of aquatic species. The soil surveys (fall 2015, fall 2016) revealed that the fungicide dimethomorph (DIM), the herbicide glyphosate (GLY) and its metabolite AMPA were by far the most common compounds in soils, reaching concentrations of 0.45, 7.84 and 4.29 mg/kg, respectively. The individual and combined toxicity of DIM, GLY and AMPA was tested using standard aquatic species: *Raphidocelis subcapitata*, *Lemna minor*, *Chironomus riparius*, *Daphnia magna* and *Gambusia holbrooki*. Uncontaminated soils were spiked with pesticide median field concentrations (DIMf: 0.05 mg/kg, GLYf: 0.85 mg/kg, AMPAf: 0.81 mg/kg) and with the predicted concentrations by EFSA (DIMp: 0.86 mg/kg, GLYp: 6.62 mg/kg, AMPAp: 6.18 mg/kg), and aqueous soil extracts were prepared based on solids concentrations in the S. Lourenco stream (0.26 g TSS/L). Overall, exposure to single compounds resulted in the highest toxicity to organisms. *R. subcapitata* and *L. minor* were mostly sensitive to DIM (maximum growth inhibitions of 6 and 14%, respectively), *C. riparius* to GLY (maximum mortalities and feeding inhibitions of 15 and 32%, respectively) and *D. magna* and *G. holbrooki* to AMPA (maximum mortalities of 10 and 40%, respectively and feeding inhibitions of 74 and 32%, respectively). A higher pesticide concentration in soil was not always translated into a higher toxicity, with GLYf being more toxic to aquatic biota than GLYp. These results reinforce that the intensive pesticide use compromises soil quality and that soils are potential sinks of pesticides to downstream areas, threatening aquatic ecosystems.

Keywords: pesticides, environmental impacts, soil contamination, particle transport, ecotoxicological assessment, non-target species

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2.2.7. Interactions between land use, fluxes of water and sediments, and the spread of bacterial contaminants in the uplands of northern Lao PDR

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Abstract

Over the past two decades, throughout the uplands of mainland Southeast Asia, both forested land and land traditionally used for food production have extensively been converted to commercial tree plantations, most often at an unforeseen environmental cost. In the uplands of Northern Laos, the M-TROPICS program (<https://mtropics-fr.obs-mip.fr/>) thus found that the conversion of rice-based shifting cultivation to teak tree plantations, while doubling overland flow contribution to stream water, resulted in a six-fold increase in sediment yields.

In the absence of management guidelines, most farmers burn the litter and suppress understorey that naturally occurs under the trees, directly exposing soil to raindrop energy and inducing the formation of an impermeable surface crust. Soil crusting in turn reduces rainwater infiltration and enhances overland flow, with adverse consequences such as increased soil detachment and erosion, gully formation, slope failure and eventually, yield declines.

In addition, mammalian presence combined with land uses that induce high overland flow play an important role in determining stream water loads of fecal indicator bacteria, potentially pathogenic to humans. The interplay between land use and the transfer of bacterial pathogens therefore represents a serious - although currently much underestimated - public health hazard.

Optimal vegetation structures that combine minimum height of the lowest layer (to reduce raindrop velocity at ground level) and maximum coverage (to intercept the largest amount of rainfall), need to be promoted amongst farmers to alleviate the adverse externalities of tree plantations.

Overall, conserving understorey under plantation trees appears an economically and environmentally sound management practice that conserve soils resources and minimizes the risk of pathogenic contaminations of downstream populations. Such conservation practices should be recommended to farmers via the relevant government agencies.

Keywords: land-use change; soil erosion; overland flow; vegetation structure; fecal indicator bacteria (FIB).

Introduction, scope and main objectives

Over the past two decades, economic development and population growth have induced profound changes in land-cover management and agricultural practices of Southeast Asian montane catchments (Sidle *et al.*, 2006; Valentin *et al.*, 2008). In particular, commercial tree plantations have expanded, resulting in the massive conversion of both forested land and land traditionally used for food production (Ziegler *et al.*, 2009). In the uplands of Northern Laos, teak and rubber tree plantations have thus increasingly replaced traditional rain fed rice-based systems as part of the national effort to eradicate slash-and-burn cultivation (Lestrelin & Giordano, 2007). In the absence of relevant information and explicit management guidelines, most farmers remove the litter and suppress understorey that naturally occurs under the trees, directly exposing soil to raindrop energy and inducing the formation of an impermeable surface crust. This paper summarizes the main findings of the long-term monitoring conducted under the umbrella of the M-TROPICS program (<https://mtropics-fr.obs-mip.fr/>) with the aim of characterizing the hydro-sedimentary response of a small headwater catchment of Northern Laos to the gradual conversion from shifting cultivation to teak plantations. In particular, it examined how crop structure influences the amount, size and velocity of through fall raindrops, and how the drops kinetic energy upon impact on the ground leads to soil crusting, influencing local runoff and inter-rill soil loss. This work also characterized the seasonality in FIB loads and identified during which hydrological periods (e.g. storm or base flow periods) the highest FIB contamination levels are observed.

Methodology

Study sites and land uses.

The Houay Pano catchment (0.6 km²) is located 10 km south of Luang Prabang in northern Laos (Fig. 1a). The mean annual temperature is 25.3 °C (Ribolzi *et al.* 2011a). The tropical monsoon climate is characterized by high seasonality, with 80% of annual rainfall occurring from May to October (Ribolzi *et al.*, 2011b). Soils consist of deep (> 2 m) and moderately deep (> 0.5 m) Alfisols, except along crests and ridges where Inceptisols prevail (Ribolzi *et al.*, 2008). Main land uses include annual crops (upland rice and Job's tear), fallow, teak plantations and secondary forests (Patin *et al.*, 2012; Lacombe *et al.*, 2016). The slash-and-burn cultivation system that dominated between 2002 and 2007 has gradually been replaced with teak tree plantations (Fig. 2b). Land-use mapping was conducted each year to compute areal percentages of each land use (±10%) using QGIS (<http://www.qgis.org/>). Water and sediment fluxes were monitored at the outlet of the catchment (Fig. 1b) since 2002. During the rainy season in 2014, fluxes were monitored at the outlet of two zero-order headwater nested catchments (see below, paragraph *Impact of land-use change on sediment yields*). The specific analysis of the effect of land use and hydrological processes on *Escherichia coli* concentrations in stream water was conducted in 2015. The specific study of impact of vegetation structure on soil crusting and runoff was carried out in Houay Dou, another catchment located about 15 km south of the city of Luang Prabang, because of its wider diversity of crops and land covers (Lacombe *et al.*, 2017).

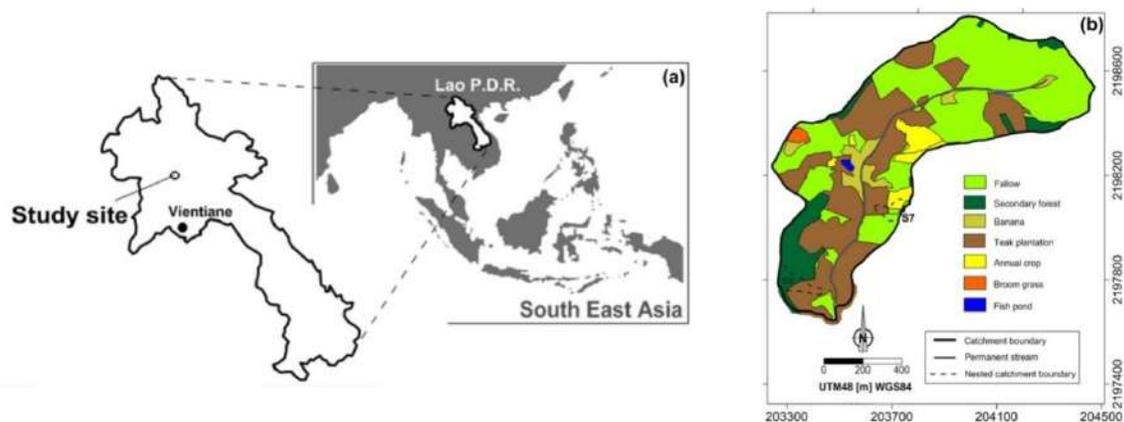


Figure 12. Experimental site location (a) and land use map of Houay Pano catchment in 2014 (adapted from Ribolzi *et al.*, 2017)

Impact of land-use change on sediment yields.

Paired zero-order sub-catchments with different land uses but similar soil characteristics were monitored to investigate the impact of land-use change on sediment yields. These sub-catchments had similar soil characteristics, surface areas (0.60 and 0.57 ha) and mean slope gradients (62 and 54%) but contrasted land uses. The main land use in one (hereafter referred to as S7) consisted of teak monoculture with an abundant understorey (22% of surface area), and typical shifting cultivation mosaics (i.e. upland rice 23%, Job's tears 14%, fallow 34%, secondary forest 7%), while the other sub-catchment (hereafter referred to as S8) was covered with teak monoculture with a degraded soil surface downslope (42% of the total surface), and secondary forest (58%) upslope. As it is very challenging to find two identical catchments (Zégre *et al.*, 2010). This synchronic approach was complemented with a diachronic investigation at the scale of the whole catchment, over a 13 years period (2002-2014, see below, paragraph *Hydro-meteorological measurements and water sampling*).

Interactions between vegetation structure soil surface conditions, runoff and soil loss

Ten land uses with contrasted vegetation structures, were selected to assess the impact of crop heights and canopy densities on soil crusting, runoff and inter-rill soil loss. These ten land uses included: banana trees (*Musa ssp*); broom grass (*Thysanolaena latifolia*); fallow; job's tears (*Coix lacryma Jobi*); banana trees intercropped with maize (*Zea mays*); rubber trees (*Hevea brasiliensis*) on gentle slope; rubber trees on steep slope; mature teak trees (*Hevea brasiliensis*); young teak trees + fallow; vernicia trees (*Vernicia montana*). Through fall Kinetic Energy, TKE ($\text{J m}^{-2}\text{mm}^{-1}$) and maximum diameter of through fall raindrops, D_x (mm) were measured with a disdrometer (RD 80, LTD) under seven of the ten selected land uses with a dense crop cover, and for non-intercepted rainfall. Each land-use plot was instrumented with three micro-plot replicates, i.e. 1-m²square metal frames inserted into the soil at a depth of approximately 10 cm and connected to a bucket to collect runoff water and suspended sediments. Soil loss is the total weight of the sediments collected during the wet season, after flocculation, filtration and oven dehydration. Runoff coefficient is the ratio between surface runoff depth (including suspended sediments) and total rainfall depth cumulated during the rainy season. Both, runoff coefficient and soil loss were corrected by the cosine of the slope angle of the micro-plots to remove the influence of the slope on the intercepted area (Janeau *et al.*, 2003). Vegetation cover was described in a representative of 18-m²area encompassing the three micro-plot replicates: mean plant height and plant cover of each vegetation layer was assessed; spacing between cultivated

plants was measured; observed plant species and their abundances were listed.

Characterization of soil surface types.

The percentage areas of different soil surface types were assessed at least 3 times per year using the methodology of Casenave and Valentin (1992). Soil surface crusting has been found as the best predictor of overland flow in these catchments (Valentin & Bresson, 1992; Patin *et al.*, 2012; Podwojewski *et al.*, 2008; Janeau *et al.*, 2003) and we therefore used it as a proxy of overland flow (Patin *et al.* 2012). The soil surface crusting rate ascribed to each land use and vegetation cover was assumed to be homogenous for each land use type across catchments.

Hydro-meteorology and hydro-sedimentary sampling.

Daily rainfall was measured every 6-min using an automatic tipping-bucket gauge (Campbell ARG100, 0.2 mm capacity tipping-buckets) and 6 manual gauges (maximal spatial variability of annual rainfall: 20%). Stream discharge was calculated from the continuous monitoring of the water level since 2002, with a 1-mm vertical precision at a minimum of 3-minute time interval using a water level recorder (OTT, Thalimedes) connected to a data logger within V-notch weirs. A control-rating curve (the relationship between water level and discharge) was determined using the velocity area method at each station. The estimated accuracy of stream discharge (Q_{sw}) is $\pm 10\%$. Suspended sediment was collected using automatic samplers during each flood event (samples collected every 2-cm water level increase during the rising stage and every 5-cm decrease during the falling stage). An average of 20 river water samples (600 mL) was collected ~10 cm below the river surface during each flood event. The concentration of total suspended solid (TSS; uncertainty: $\pm 10\%$) was determined for each sample after filtration on 0.2 μ m porosity cellulose acetate filters (Sartorius) and evaporation in an oven at 105 °C for 48 h. Suspended and bed load sediments were estimated following the approach described by Valentin *et al.* (2008). The contributions of surface (*i.e.* overland flow) and sub-surface flow (*i.e.* groundwater) to river water at the catchment outlet were assessed by measuring water electrical conductivity (comparable, although easier to implement than the $\delta^{18}O$ isotopic method; Ribolzi *et al.*, 2000; Ribolzi *et al.*, 2016). Temperature and electrical conductivity (EC; uncertainty: $\pm 5\%$) of stream water were measured using a Multi Probe System (YSI 556 MPS). Infiltration rates were estimated from the difference between rainfall and overland flow divided by the duration of the rainfall event. Total sediment fluxes correspond to the export of both, bed load and suspended sediment (uncertainty: $\pm 10\%$). The contributions of surface and sub-surface soil sources to stream sediment exports at the catchment outlet were discriminated by measuring the activity of ^{137}Cs emitted by thermonuclear bombs in the 1960s in the sediment transiting the river (Ritchie & McHenry, 1990). With a half-life of 30 years ^{137}Cs shows highly contrasting activities between the surface of cultivated soils exposed to atmospheric fallout and gully/channel bank material sheltered from this fallout (Olley *et al.*, 2013; Gourdin *et al.*, 2014; Evrard *et al.*, 2016). All hydro-sedimentary data are available on-line (<https://mtropics-fr.obs-mip.fr/>).

E. coli determinations.

The standardized microplate method (ISO 9308-3) was used for *E. coli* number determinations (Causse *et al.*, 2015; Ribolzi *et al.*, 2016; Rochelle-Newall *et al.*, 2016). Each sample was incubated at four dilution rates (*i.e.* 1:2, 1:20, 1:200 and 1:2000) in a 96-well microplate (MUG/EC, BIOKAR DIAGNOSTICS) and incubated for 48 h at 44 °C. Ringers' Lactatesolution was used for the dilutions and one plate was used per sample. The number of positive wells for each microplate was noted and the MPN was determined using the Poisson distribution.

Results

Land-use change.

The proportion of secondary forests in the catchment decreased from 16% in 2002 to 8% in 2014 (Fig. 2b). During this period, the respective proportions of fallow (29-69%) and annual crops (4-42%) were negatively correlated, with large inter-annual variations, corresponding to slash-and-burn rotations (2 to 6 year cycles) (Fig. 2b). From 2008 onward, the fractional area of teak plantations continuously increased, almost linearly, from 4% to reach 36% in 2014 (Fig. 2b). Accordingly, the monitoring period was divided into a first sub-period (2002-2007) dominated by slash-and-burn rotations, and a second sub-period (2008-2014) corresponding to the expansion of teak tree plantations and the concomitant reduction of annual crops. During the last five years of this second sub-period, most of the teak plantations were > 3 years old and characterized by sparse understorey vegetation cover.

Rainfall and runoff.

Between 2002 and 2014, annual rainfall (Rain) depth varied from 978 mm (2012) to 1,884 mm (2011), with a mean of 1,271 mm (SD: 271 mm, CV: 20%) (Fig. 2a). Only 32% of rainfall events, with a mean annual depth of 404 mm (SD: 118 mm; CV: 28%) triggered floods (Rain_F). Annual runoff showed large inter-annual variations (SD: 52 mm; CV: 67%; mean: 77 mm; range: 13-174 mm) (Fig 2a). In 2014, runoff from the hollow valleys strongly differed ($p < 0.0001$) between S7 (32 mm) and S8 (200 mm).

Infiltration rate, overland flow and sediment yield.

The annual median values of infiltration increased from 9 to 20 mm h⁻¹ during 2002-2007 sub-period and decreased back to 4 mm h⁻¹ from 2008 to 2014. The annual median overland flow contribution to total stream flow during floods increased significantly ($p = 0.004$) between 2010 and 2014, following the decrease in understorey vegetation cover from 31 to 16% before and after 2010 (Fig. 2d). Similarly, annual sediment yields (SY) significantly increased between the two sub-periods, from 98 to 609 Mg km⁻² ($p = 0.003$) (Fig. 2e). Bed load contribution to these total annual losses fluctuated between 9 and 42%, with similar averages during the first and second sub-periods. In the paired sub-catchments in 2014, cumulated sediment yields were 127 and 2,499 Mg km⁻² in S7 and S8, respectively ($p < 0.0001$). The annual median overland flow contribution to the total stream flow during floods was positively correlated to the surface area of >3-year-old teak tree monocultures and negatively correlated to the sum of fallow and forest areas ($p < 0.05$).

Effects of rainfall intensity and land uses on throughfall.

The throughfall rate, i.e. the ratio between throughfall and rainfall ranged from 48% (broom grass) to 116% (banana trees). Rainfall intensities exceeding 50 mm h⁻¹ (mid-May to mid-July) coincided with the greatest throughfall rates. Dx and TKE were the lowest under broom grass and banana trees. Broom grass was the only land use that reduced TKE (by 45-50%), while vernicia and rubber increased TKE and Dx. TKE was the main driver of soil crusting across the ten studied land uses. Larger crusted area locally enhanced runoff, which further removed soil particles detached by splash over non-crusted areas. Best protection against soil erosion was provided by land uses that minimized TKE by reducing the velocity of raindrops and/or by preventing an increase in their size (Fig. 3)

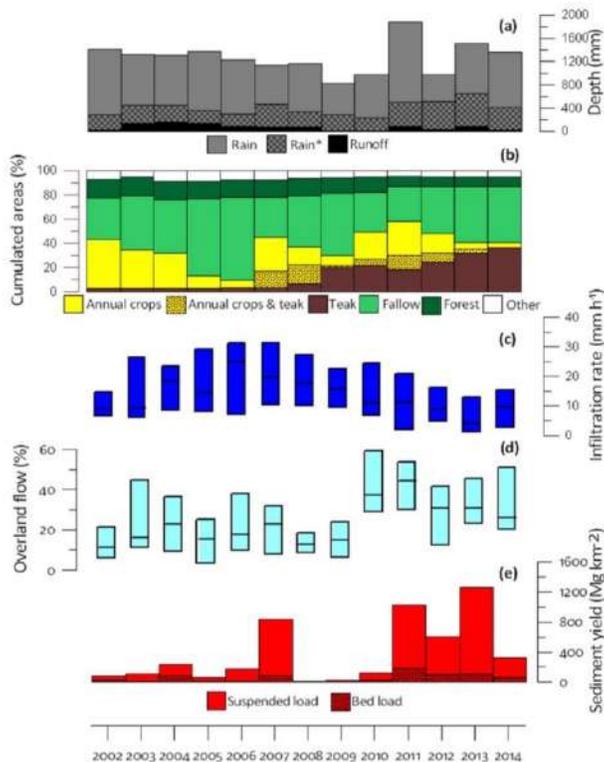


Figure 2. Annual hydro-sedimentary and land-use changes in Houay Panocatchment: (a) Total rainfall depth (Rain), flood-triggering rainfall depth (Rain*) and total stream flow depth (Runoff); (b) Areal percentages of the catchment covered by the main land uses; (c) Box plots (25th and 75th percentiles and median) of infiltration rates; (d) Box plots of overland flow contribution to total depth of flood events; (e) Annual sediment yield including suspended load and bed load contributions. From Ribolzi *et al.*, 2017.

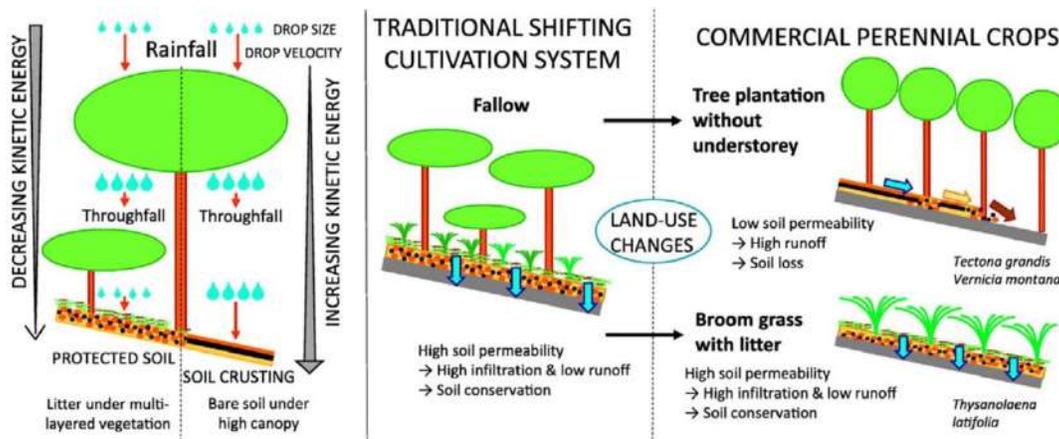


Figure 3. Relationships between vegetation structure, throughfall and soil crusting. From Lacombe *et al.*, 2017.

Contamination of stream water with E. coli.

In the upper areas of the watershed, *E. coli* concentration was <1 MPN 100 mL⁻¹ (Causse *et al.*, 2015) but FIB concentration increased as the density of poultry and humans settlements increased in downstream areas (human occupancy: 548 ±120 people/days). Soil surface crusting

and high human presence interacted to yield stream water *E. coli* concentrations that were quite high during storm-flow (Rochelle-Newall *et al.*, 2016). *E. coli* concentrations in stream water were over two orders of magnitude higher during the monsoon than during the dry season. During the monsoon, *E. coli* concentrations varied between 78 and 14,000 MPN 100 mL⁻¹ and increased concomitantly with high discharge, TSS and low EC. TSS and *E. coli* concentrations were over two orders of magnitude higher in storm-flow than during the base flow period (Fig. 4).

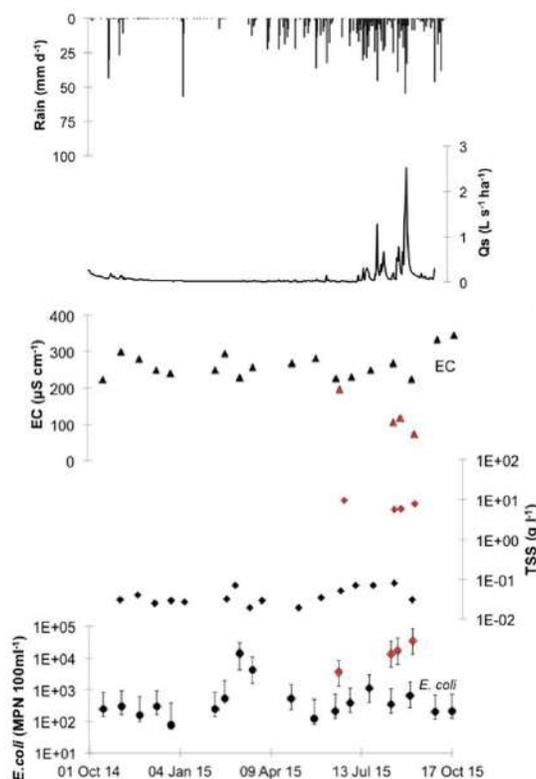


Figure 4. Comparison of base flow and storm flow Rainfall intensity (daily time step; mm d⁻¹); stream specific discharge (Q_s , L s⁻¹ ha⁻¹); electrical conductivity (EC, μ S cm⁻¹); total suspended solids (TSS, g L⁻¹); *E. coli* concentration in stream (*E. coli*, MPN 100 mL⁻¹). Black-filled symbols: base flow samples, red-filled symbols: storm flow samples. Adapted from Rochelle-Newall *et al.*, 2016.

Discussion

The work reported in this paper established that recurrent burning of the litter and understorey that naturally occurs under teak trees directly exposes soil to raindrop energy. The large leaves of teak canopies concentrate rainfall, which affects the soil with greater kinetic energy, clogging the soil surface porosity and disturbing soil surface structure, both processes contributing to crusting and the associated reduction in infiltration rates. The subsequent increase in overland flow detaches more soil particles and washes out large quantities of faecal matter into the stream from the soil surface (Causse *et al.*, 2015; Shehane *et al.*, 2005), such a process explains why *E. coli* concentrations were over two orders of magnitude higher during the wet season than during the dry season (Mitch *et al.*, 2010; Isobe *et al.*, 2004). Hence, there is little or no transfer of faecal matter into the waterways during the dry season, although it should be borne in mind that humans and animals can cause the local resuspension of soil or sediment particles when they use or cross the stream during dry periods (Ribolzi *et al.*, 2011). Clearly, the consumption of contaminated stream water holds some health risks (Soller *et al.*, 2015): for many of the sample dates, *E. coli*

numbers exceeded the limit of 500 colonies 100 mL⁻¹ above that the World Health Organization considers that there is a 10% risk of gastro-intestinal illness after one single exposure (WHO, 2003). Therefore, the use of water from sites with high FIB numbers poses a serious threat to public health. We did not conduct epidemiological studies in parallel with this work; however, it would be interesting in future studies to investigate this health threat.

Conclusions

We show that land use, vegetation cover and hydrology, strongly control *E. coli* concentrations in tropical, rural streams in Southeast Asia. The interplay between land use, farming practices and the transfer of bacterial pathogens therefore represents a serious - although currently much underestimated - public health hazard. The maintenance of adequate vegetation structures that combine minimum height of the lowest layer (to reduce rain drop velocity at ground level) and maximum coverage (to intercept the largest amount of rainfall), together with the use of management practices that reduce erosion, will not only reduce soil losses and increase soil carbon storage, it will also contribute to better surface water quality thereby, reducing the risks to the human populations using the water resource.

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2.2.8. Plastics in terrestrial ecosystem: effects of macro- and micro-plastic residues on wheat growth

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Abstract

Plastic residues from mulching after harvest remain and accumulate in soil leading to serious environment problems. The effects of macro- and micro-plastics on crop growth and their interaction with earthworms in agroecosystem are still unclear.

Therefore, we performed a mesocosm experiment to assess the effects of low density polyethylene (LDPE) and biodegradable plastic (Bio, made of polyethylene terephthalate, polybutylene terephthalate, pullulan) macro- (5 mm², Ma) and microplastics (50 µm-1 mm, Mi) on wheat growth and assessed potential synergetic effects with earthworms. We used 1% w/w plastic, according to a field survey. The experiment was carried out over 4 months in sandy soil and consisted of 10 treatments (10 replicates): 5 treatments LDPE-Ma, LDPE-Mi, Bio-Ma, Bio-Mi and Control with presence of earthworms and homologous 5 treatments in the absence of earthworms. Above- and below-ground vegetation characteristics, tillering, fruit number, and chlorophyll content were assessed.

The results showed that plastic residues presented negative effects on both above- and below-ground parts for both vegetative and reproductive development. The development process of wheat in all the treatments with plastic residues was delayed relative to the Control. The presence of earthworms positively altered wheat growth status and chiefly alleviated the impairments made by plastic residues. Wheats in Bio-Ma and Bio-Mi without earthworms started tillering two weeks later than in all other treatments. With the presence of earthworms, the total wheat biomass in LDPE-Ma, LDPE-Mi, Bio-Ma, Bio-Mi was significantly lower than in the control (5.5%, 14.6%, 26.1% and 33.7%, respectively). This effect was even stronger for treatments in the absence of earthworms (13.5%, 15.7%, 39.9% and 48.2%, orderly). Further studies about their effects on soil properties and rhizosphere microorganisms are needed to illustrate the underlying mechanism of their inhibition on plant growth.

Keywords: Plastic residues; Biodegradable mulch film; Wheat growth and development; Microplastics in agroecosystem

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2.2.9. Assessing background values of metals and metalloids in soils of the Veneto Region

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Abstract

A survey on the concentration of some metals and metalloids in soils of Veneto (total area 18.407 km², 8.100 cultivated) carried on 4131 samples, of which 2337 topsoil (10-40 cm) and 1794 subsoil (70-100 cm), allowed to define the background values for investigated metals. Particularly for some metals and in areas of volcanic substrates natural background values are often above threshold concentrations of contamination defined by the Italian environmental legislation.

Keywords: metals, soil, background level

Introduction, scope and main objectives

Sustainable land management needs to be based on reliable data that allow planning economic and social development. Soil is part of this necessary information, as it is an essential component of environment, which is subjected to increasing pressures that can lead to accumulation of contaminants and metals among these (Hooda, 2010).

In order to assess soil contamination by metals it is necessary to know natural content due to the composition of the minerals in parent material. Actually, such concentrations, especially for some metals, can vary greatly depending on the material from which the soil has developed (Alloway, 1995; Kabata Pendias, 2001, Adriano, 2001). In Italy, rocks of very different origin and composition determine concentration of metals in soil quite different throughout national territory (Ottonello & Serva, 2003).

During the realization of regional soil map, throughout several years, ARPAV determined also the concentration in soil of some metals and metalloids, with the aim of defining a basic information level for the regional territory.

This activity has been carried out since the first survey in 1995 and then during the implementation of the regional soil map at 1:250,000 scale (ARPAV, 2005) and of the soil maps at 1:50.000 scale of the provinces of Treviso (ARPAV, 2008), Venice (ARPAV, 2008), Padua (ARPAV, 2012), Vicenza and Rovigo (ARPAV, 2018).

Methodology

Determination of metal background values in soil was carried out as specified by ISO 19258:2005 (Soil Quality - Guidance on the determination of background values), the international reference for sampling, analysis and data elaboration.

According with ISO standard pedo-geochemical background content represents the concentration of elements generated by the characteristic features of pedogenesis, such as composition and alteration of the rock and any movement in soil. On the other hand, background content refers to the concentration of an element in a specific type of soil, located in an area or region, resulting

from both natural, geological and pedological processes and including diffuse source inputs, such as atmospheric deposition and agricultural practices.

The choice of sampling sites was carried out following the "typological approach" of ISO 19258:2005, i.e. depending on the parent material, soil types and land use. Homogeneous areas were defined by parent material composition. For the plain, where soils have been formed from alluvial deposits, homogeneous areas were defined considering the origin of the sediments (Ungaro *et al.*, 2008; Amorosi & Sammartino, 2006); these areas were called "*depositional units*". For mountain region, areas were defined considering the prevalent parental material together with the type of pedogenetical processes, and these were called "*physiographic units*".

Two sampling depths were used, depending on soil horizon arrangement, following different strategies for plain and mountain areas: in plain, the first sample was taken within upper horizon, up to a maximum depth of 40-50 cm (ploughed layer) and the second in the subsoil within the first soil horizon starting below 70 cm, that usually excludes a possible anthropogenic contribution. In mountain areas the first sample was taken within upper horizon, that has variable thickness, and the second in the subsoil within the first soil horizon starting below 70 cm, or, if soil was thinner, within the deeper layer.

4131 samples were analyzed: 2337 from upper layer and 1794 from deeper. In the plain 1906 samples from upper layer and 1480 from deeper, while in mountain areas 431 from upper and 314 from deeper. The survey density is about 0,183 obs/km² in the plain and 0,061 obs/km² in hilly and mountain area.

The "pseudo-total" fraction through *aqua regia* extraction of antimony, arsenic, beryllium, cadmium, cobalt, chromium, copper, mercury, nickel, lead, selenium, tin, vanadium and zinc were determined. All analysis were performed at the ARPAV Laboratories of Treviso, with ICP-AES detection, on the size fraction less than 2 mm.

Statistical analysis was worked out for the whole dataset and for each depositional/physiographic unit. Some descriptive statistics were performed, keeping separate values of upper horizons from the ones of deeper; for each variable were determined mean, median, minimum, maximum, percentiles (5th, 25th, 75th, 90th and 95th), standard deviation, standard error, skewness and kurtosis, normality tests. Once removed outliers, unit background value was determined by means of 95th percentile value.

Results

In tables 1 and 2 the 95th percentile values are reported, subdivided between upper and deeper layers.

Pedo-geochemical and background values are in many cases above the Italian law limits for gardens and residential sites.

During data processing, land use was not distinguished, due to the lack of significant statistically differences, except for vineyard; these soils show very high concentrations of copper regardless the physiographic/depositional unit. This is due to the repeated copper-based treatments that since the second half of nineteenth century are made against *Plasmopara viticola* and other fungal parasites of the vine, which determined the accumulation of the element in the soil.

Data collected in Veneto vineyard show values of 300-400 mg/kg and more, very high if compared to other land uses and pedo-geochemical background values. 284 mg/kg of copper is the usual

background value determined for vineyards; this value can be used as a reference for vineyard soils. For this reason, the utmost attention must be paid to land use changes from vineyard to other agricultural uses and vice versa.

Table 1. Background content (mg/kg) in depositional and physiographic units of Veneto region: 95th percentile value in the upper layer. In bold values exceeding law limits. In the last row law limits for residential sites.

Depositional and physiographic units	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
Tagliamento river (T)	1.1	14	1.5	0.5 9	12	68	0.26	39	30	83	0.76	3.1	65	90
Piave river (P)	1.0	13	1.6	0.6 8	15	61	0.26	44	37	19 2	0.51	3.9	86	12 0
Brenta river (B)	2.0	37	1.9	0.9 0	15	60	0.51	37	56	110	0.36	6.3	79	143
Adige river (A)	1.6	40	1.5	0.9 3	18	92	0.21	78	57	97	0.68	4.2	80	15 0
Po river (O)	1.3	28	1.7	0.5 4	19	16 0	0.08	12 1	34	66	0.91	3.7	89	111
North-eastern Coast (DP)	0.6	11	0.6	0.2 5	6	32	0.37	19	38	45	0.32	2.0	43	70
South Coast (DA)	1.0	23	1.0	0.2 6	16	4	0.13	96	42	48	0.68	4.7	70	15 8
Calcareous river fun (CC)	0.8	13	1.3	0.9 2	22	3	0.21	67	42	14 1	0.40	3.7	84	113
Astico river fun (CA)	3.3	25	1.5	0.7 4	25	84	0.20	66	65	101	0.45	7.2	19 0	15 0
Leogra-Timonchio river fun (CL)	2.7	26	1.5	0.7 4	27	90	0.18	42	90	90	0.37	6.0	12 2	19 5
Agno-Guà river fun (CG)	1.9	15	1.3	0.6 6	50	6	0.10	16 0	88	3	0.42	3.4	15 1	16 0
Hills (RR)	1.1	16	1.5	0.9 0	26	93	0.23	64	48	112	0.59	3.6	99	141
Calcarene hills (RA)	3.2	62	1.3	0.8 0	10	21 6	0.14	47	60	86	0.54	6.2	20 1	25 2
Berici Hills (RB)	4.7	40	2 4	1.5 8	30	0	0.15	10 0	77	91	0.59	4.4	17 6	15 4
Prealps on calcarenite (LC)	1.8	29	2 2	1.6 8	39	16 7	0.11	13 6	42	10 3	0.74	3.3	14 6	137
Prealps on basalts (LB)	1.6	14	1.7	0.5 6	68	0	0.15	21 1	57	99	0.47	3.8	20 1	17 7
Prealps on marly limestones (SD)	2.6	17	2.1	1.9 2	35	5	0.28	118	13 3	86	0.81	3.4	13 8	19 7
Prealps on hard limestones (SA)	3.3	25	2 3	3.4 0	36	121	0.33	82	10 1	96	1.10	4.9	17 5	21 2
Alps on werfen formation (MW)	2.3	31	2.1	2.0 0	19	74	0.59	36	14 0	34	1.21	2.6	10 2	23 6
Alps on silicatic rocks (MS)	1.7	11	1.5	0.8 4	31	72	0.29	32	61	64	-	-	18 0	114
Alps on crystalline and metamorphic rocks (MA)	2.0	15	1.1	0.5 3	19	66	0.40	42	97	41	-	-	72	15 5
Alps on dolomite rocks (MD)	2.2	21	1.5	1.7 0	18	74	0.23	53	84	37	0.52	2.9	10 1	15 9
<i>Threshold values for residential areas</i>	<i>10</i>	<i>20</i>	<i>2</i>	<i>2</i>	<i>20</i>	<i>0</i>	<i>1</i>	<i>12</i> <i>0</i>	<i>10</i> <i>0</i>	<i>12</i> <i>0</i>	<i>3</i>	<i>-</i>	<i>90</i>	<i>15</i> <i>0</i>

Table 2. Pedo-geochemical background content (mg/kg) in depositional and physiographic units of Veneto region: 95th percentile value in the deeper layer. In bold values, exceeding law limits. In the last row, law limits for residential sites.

Depositional and physiographic units	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
Tagliamento river (T)	1.1	15	1.8	0.4 7	11	68	0.0 9	43	21	24	0.4 2	2.8	88	78
Piave river (P)	0.9	14	1.5	0.4 5	14	62	0.14	51	24	31	0.3 8	2.7	80	95
Brenta river (B)	1.8	46	2.1	0.9 3	16	63	0.17	38	38	40	0.2 7	4.8	84	12 9
Adige river (A)	1.5	39	1.3	0.5 7	19	12 4	0.0 8	10 3	44	53	0.7 5	3.1	73	116
Po river (O)	0.9	19	1.6	0.2 5	20	16 2	0.0 6	13 0	21	46	0.7 6	3.3	85	10 4
North-eastern Coast (DP)	0.5	9	0.3	0.2 5	5	20	0.1 0	15	11	15	0.1 0	1.1	22	46
South Coast (DA)	0.9	20	1.1	0.2 5	16	16 6	0.0 6	10 5	18	35	0.4 6	3.0	56	84
Calcareous river fun (CC)	0.7	13	1.6	0.7 2	21	99	0.11	81	32	43	0.2 0	2.5	84	92
Astico river fun (CA)	1.5	19	1.8	0.3 8	19	61	0.0 8	43	37	33	0.3 4	3.1	16 6	10 4
Leogra-Timonchio river fun (CL)	2.4	28	1.9	0.5 4	20	62	0.14	47	60	41	0.2 9	3.2	12 9	14 4
Agno-Guà river fun (CG)	1.5	21	1.5	0.3 9	48	19 0	0.0 9	14 5	22	48	0.3 7	2.5	15 1	119
Hills (RR)	1.0	18	1.7	0.5 7	27	10 2	0.14	66	41	76	0.4 2	3.2	10 0	111
Calcarene hills (RA)	4.2	11 6	2. 2	0.9 6	16	38 6	0.12	74	47	26	0.5 6	2.6	35 8	16 8
Berici Hills (RB)	2.8	38	3.1	1.6 4	29	22 1	0.13	118	47	50	0.5 6	4.1	22 8	13 4
Prealps on calcarenite (LC)	2.1	36	3. 0	1.75	34	16 9	0.15	117	22	34	0.7 0	3.3	16 6	112
Prealps on basalts (LB)	1.4	12	2.1	0.2 7	79	31 3	0.14	25 1	28	71	0.4 3	4.2	21 2	16 1
Prealps on marly limestones (SD)	1.1	15	2. 3	2.1 5	33	17 5	0.2 2	14 8	52	88	0.5 8	2.7	10 9	16 3
Prealps on hard limestones (SA)	2.5	27	2.7	3.8 4	35	12 3	0.2 9	92	67	76	0.6 6	4.0	16 1	22 0
Alps on werfen formation (MW)	1.7	18	2.1	1.47	17	71	0.6 9	34	72	28	0.3 1	0.6	63	125
Alps on silicatic rocks (MS)	2.9	15	2. 4	0.4 8	32	71	0.16	37	32	110	-	-	18 8	12 3
Alps on crystalline and metamorphic rocks (MA)	1.4	21	1.7	0.4 1	25	67	0.3 2	49	35	50	-	-	55	13 9
Alps on dolomite rocks (MD)	1.8	19	1.2	0.8 5	25	85	0.15	53	30	39	0.2 3	2.0	78	92
<i>Threshold values for residential areas</i>	<i>10</i>	<i>20</i>	<i>2</i>	<i>2</i>	<i>20</i>	<i>15</i> <i>0</i>	<i>1</i>	<i>12</i> <i>0</i>	<i>10</i> <i>0</i>	<i>12</i> <i>0</i>	<i>3</i>	-	<i>90</i>	<i>15</i> <i>0</i>

Discussion

Antimony, mercury, lead, copper and selenium pedo-geochemical background values do not exceed the threshold concentrations for residential sites in any depositional or physiographic units. Tin has not a regulatory limit now.

For copper, 2 units exceed law limits only for background values, in the unity of the Piave (P) and in that of the calcareous river fan (CC), probably due to the spread of pesticides in vineyards, at least in the past. For the vineyards, a specific copper background value of 284 mg/kg has been defined.

For cadmium, both, for pedo-geochemical and background values exceeding limits occurs only in prealpine area on hard limestone (SA) and on marly limestones (SD) due to the natural content in the parent material.

Lead has background values above the limit only in the prealpine area, both on hard and marly limestone (SA and SD) and in mountain areas in the Alps unit on the formation of Werfen (MW) probably due to atmospheric deposition from next industrial plain area.

Arsenic, beryllium, cobalt, chromium, nickel, vanadium and zinc values exceed the threshold concentration in many units both in upper and deeper layers, involving a significant area within the region.

The units with the highest number of both, pedo-geochemical and background values, exceeding the threshold limits are the Prealps on basalts (LB) and Prealps on limestones units (SA e SD) in mountain area and the Agno-Guà (CG) and the Leogra-Timonchio (CL) river fan units in the plain, which receive alluvial deposits from the alteration of basalts; basaltic rocks contain high concentration of zinc, nickel, chromium, cobalt and vanadium compared to sedimentary rocks (Alloway, 1995; Kabata Pendias, 2001).

Arsenic exceeding of law limit occurring in Adige, Po and Brenta sediments, both for pedo-geochemical and background values, is very significant because of both the size of the area and the toxicological characteristics of element.

In the agricultural areas, the metals showing the largest increases, due to land use, are lead, copper, selenium and zinc with surface concentrations of 30-50% higher than the deeper horizon.

Conclusions

This study aimed and lead to define pedo-geochemical background and background values (as defined by ISO 19258:2005) of 14 elements in soils of the Veneto Region. Physiographic and depositional units, defined as homogeneous area whit the same parent material, demonstrate a good tool to represent the distribution of heavy metal concentration in soils.

In some units (depositional or physiographical) the background values was found to exceed law thresholds because of an high natural content or diffuse source inputs, such as atmospheric deposition or agriculture practices.

For many elements, no significant difference between concentration in upper and deeper layer was found, as evidence than deposition and accumulation processes are not so diffuse in regional territory. For some, such as copper, lead, selenium, mercury and zinc, some cases of upper/deeper

layer concentration ratio higher than 30-50% occur, mainly due to diffuse pollution through deposition of traffic emission or fertilizer and pesticide distribution by farmers.

Other aspects, such as effective bioavailability of metals for plant uptake and microorganisms assimilation, still have to be investigated in order to better identify risk exposure for animals and humans.

Studies about risk evaluation for human health are necessary for units with high contents, also if due to natural processes. In the same units, the probability that metals are transferred on foods must also be investigated, together with further biological availability and bioaccessibility tests.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.2.10. Evaluation of pesticide risks to soil organisms and functioning – A module in the FAO Pesticide Registration Toolkit, addressing pesticide regulators in low and middle income countries

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Abstract

To support member countries in implementing effective pesticide evaluation and registration, FAO has placed on-line, and is further developing, a Pesticide Registration Toolkit, which is a decision support system for pesticide registrars in developing countries. A specific module of this Toolkit is presently under development to advise regulatory authorities about the options for risk assessment of pesticides to soil organisms and functioning.

An *ad hoc* technical working group, consisting of experts in soil ecology and ecotoxicology as well as pesticide regulators, has advised FAO on appropriate methods and procedures to evaluate the risks of pesticides to soil organisms and functioning, which can be applied with limited staff and technical resources.

Various methods were proposed, based on the following approaches: i. bridging of risk assessments conducted by other regulatory authorities or scientific institutions, ii. generic risk assessment models, and iii. locally specific testing and risk assessment methods.

It is expected that this module in the Toolkit will lead to more sustainable pest management and less adverse impact on soil organisms and functioning.

Keywords: pesticide, adverse effects, soil organisms, biodiversity, risk assessment, pesticide registration

Introduction, scope and main objectives

The International Code of Conduct on Pesticide Management (FAO/WHO, 2014) defines pesticide registration as: “the process whereby the responsible national government or regional authority approves the sale and use of a pesticide following the evaluation of scientific data aimed at

demonstrating that the product is effective for its intended purposes and does not pose an unacceptable risk to human or animal health or the environment under the conditions of use in the country or region”.

To support member countries in implementing effective pesticide evaluation and registration, FAO has placed on-line, and is further developing, a Pesticide Registration Toolkit (FAO, undated). This Toolkit is a decision support system for pesticide registrars in developing countries. It assists registrars in the evaluation and authorization of pesticides. The Pesticide Registration Toolkit can be considered as a web-based registration handbook intended for day-to-day use by pesticide registrars. Registration staff can use the Toolkit to support several of their regular tasks, including finding data requirements, evaluating technical aspects of the registration dossier, choosing an appropriate pesticide registration strategy and procedures, reviewing risk mitigation measures and getting advice on decision-making. The Toolkit also links to many pesticide-specific information sources such as registrations in other countries, scientific reviews, hazard classifications, labels and pesticide properties.

The assessment of the hazards and risks of a pesticide to soil organisms and functioning is one of the key aspects of the registration process in many countries. Risks of pesticides to soils are of particular importance as they may directly or indirectly affect agricultural production (FAO/ITPS, 2017). However, so far, few low and middle-income countries are conducting dedicated risk assessments for this compartment of the environment. This may be due to the lack of appropriate risk assessment procedures and models, lack of expertise, and/or limited time or human resources available at the pesticide registration body.

Guidance and models for risk assessment of pesticides in soils are available, however, from various sources, in particular from industrialized regions such as the European Union and North America (e.g. EFSA, 2017). While some of these risk assessment methods and models are relatively generic, others focus specifically on local cropping situations and ecosystems. However, pesticide use conditions in low and middle income countries, which often have sub-tropical, tropical or semi-arid agro-ecosystems, may be very different from those encountered in industrialized (generally temperate) countries. Environmental conditions that drive the pesticide exposure to soil organisms may vary considerably, soil inhabiting species may be different as well as their ecological interactions. The key question therefore is to what extent existing risk assessment models and procedures can be applied to the situations in low and middle-income countries, how to use or adapt existing methods and interpret their outcomes, and how to extrapolate risk assessments conducted in industrialized countries.

A specific module of the FAO Pesticide Registration Toolkit is presently under development to advise regulatory authorities in low and middle-income countries about the options for risk assessment of pesticides to soil biodiversity.

Methodology

To develop the module, a small *ad hoc* technical working group was established consisting of experts in soil ecology and ecotoxicology, pesticide regulators and FAO technical staff. Participants came from both industrialized and low/middle income countries.

The main objective of the working group meeting was to advise FAO on appropriate methods and procedures, intended for pesticide registration in low and middle income countries, to evaluate the risks of pesticides to soil organisms and soil biodiversity.

More specific, the working group discussed:

i. Appropriate approaches, methods and models for testing and risk assessment of pesticides to soil organisms, which can be used by registration authorities with limited resources.

ii. Possibilities to bridge risk assessments between countries and situations, e.g. between resource-rich registration authorities such as the EU, Canada or Australia and resource-poor countries; but also among developing countries: What are the key factors that need to be taken into account? Can generic exposure scenarios be applied? Can one extrapolate between species?

iii. Pesticide registration data requirements for soils in low and middle income, often tropical or hot semi-arid, countries: Should they be different from the “standard data set”?

iv. Moving from protection of soil species towards protection of soil biodiversity and ecosystem services. What pragmatic approaches can low and middle income countries take?

The working group met physically once, from 23-25 April 2018, at FAO HQ in Rome and further collaborated on-line.

Results

In the Assessment Methods module of the FAO Pesticide Registration Toolkit, hazard and risk assessment methodologies for pesticides are presented at different levels of complexity. They range from relatively simple assessment methods requiring very limited human resources at the regulatory authority, to intermediately complex methods, requiring more staff and technical capacity, to complex evaluation methods, often requiring locally relevant risk assessment models, a wide range of data and specialized risk assessment staff.

Pesticide regulatory authorities can choose from these methods depending on their national priorities, technical capacity and time available for conducting the evaluations. The strengths and weaknesses of each of the proposed methods are outlined in the Toolkit, to allow an informed choice by the regulatory authority.

With respect to the evaluation of pesticide risks to soil organisms the working group made the following suggestions for risk assessment approaches to be included in the Toolkit:

- Pesticide effects on soil organisms are difficult to link in a quantitative manner to expected effects on long term soil functioning, due to lack of relevant data. Therefore, in risk assessment the focus is on effects on soil organisms which should be combined with knowledge about functional ecology of these organisms.

- Very few data are presently available about the fate and effects of pesticides in tropical and hot semi-arid environments.

- Hazard assessments specifically for soil organisms often do not reflect real impacts and are not considered complete, although a general hazard assessment as part of initial screening of a pesticide may provide useful information about potential risks.

- Tier-1 (worst case) risk assessment applied in temperate climates can be conducted also for tropical and semi-arid climatic conditions using the standard ecotoxicological and fate data and generic soil exposure models.

- The tier-1 ecotoxicological dataset consists as a minimum of an earthworm reproduction test, a collembola reproduction test and a nitrogen transformation test (for soil micro-organisms).

- Existing tier-1 tests need to be adapted to tropical or semi-arid situations in terms of soils and test conditions (e.g. temperature).
- Bridging of soil risk assessments conducted by other regulatory authorities or scientific institutions can be conducted and key parameters to include in such bridging were identified.
- Since no standard laboratory toxicity tests are yet available for tropical soil organisms, higher tier risk assessments may be based on semi-field and field studies conducted in tropical or semi-arid conditions.
- There is an urgent need to conduct a critical quantitative review of pesticide fate and effects in different soil types, to get a better understanding of the influence of soil types and testing conditions on fate and toxicity endpoints, which could be used to facilitate extrapolation of results obtained in temperate conditions to (sub-)tropical situations, and possibly reduce future testing requirements.
- Identification of reference countries in the regions for bridging based on global soil classification maps. Which countries can be clustered together?

Conclusions

The main objective of the FAO Pesticide Registration Toolkit is to make relevant and reliable information and methods available to pesticide registration authorities, literally “at their fingertips”. This to ensure that optimal use is being made of existing information from reputable sources, avoid duplication of work and facilitate informed decision making about the approval of pesticides in a country.

The development of the Toolkit module on evaluation of pesticide risks to soil organisms and functioning should help regulators conduct better pesticide risk assessments for soils. This in turn is expected to reduce the number of high-risk pesticides that are approved for registration and lead to more sustainable pest management and less adverse impact on soil organisms and functioning.

Acknowledgements

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.2.11. Pollution of agricultural soils with heavy metals through irrigation water in Eastern Georgia

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Abstract

Pollution of soils with heavy metals Cd, Cu, Zn and Pb was studied on arable lands in Kvemo Kartli region, Eastern Georgia. The results have shown that soils of the selected plots are affected contaminated irrigation water, the quality of which is deteriorated due industrial activities in upstream areas of the rivers from which irrigation canals are fed.

Keywords: soil pollution, heavy metals, water pollution

Introduction, scope and main objectives

Soil degradation by chemicals has become a major concern because of the soil's finite capacity to act as a sink for pollutants. Due to the soil's limited resilience with regard to binding and containing chemicals, these substances can accumulate in soils and become mobile and bioavailable to plants, animals and humans [Urushadze 2007]. Increasing quantities of certain heavy metals are being released into the environment by anthropogenic activities, primarily associated with industrial processes, manufacturing and the disposal of industrial and domestic refuse and waste materials [Ross 1994, Ghambashidze 2006].

Water quality degradation is one of the major issues caused by industrial activities in Georgia [Withanachchi 2018] affecting chemical composition of surface water bodies, especially rivers as the main receivers of treated or untreated discharged waters. Deterioration of river water quality has direct impact on agricultural soils, while rivers are the main source of irrigation water being essential for agricultural production in some regions of Georgia.

Current study was conducted in Kvemo Kartli region, Eastern Georgia, where river water is contaminated with heavy metals due to open pit mining activities in upstream areas, causing elevation of concentrations of heavy metals in irrigation water, and, finally, in soils of arable lands of lowland areas intensively used for cultivation of vegetable crops and requiring considerable amount of water to ensure a profitable production.

Demand on irrigation water shows an increasing tendency due to observed long draughts during vegetative period in last years, which may lead to not only increase in amount of water used for irrigation but also in extension of area of irrigated lands. Therefore, it is essential to assess current status of irrigation water quality as well as degree of soil contamination by heavy metals already being under irrigation.

Three arable plots were selected for this study from exiting irrigated lands as potentially affected areas to evaluate heavy metal concentrations in soils and assess their bioavailability.

Methodology

Soil samples were collected from the selected plots from 0-10, 10-20 and 20-40 cm depth for heavy metal determination. Individual soil sampling locations was selected randomly to ensure complete coverage of the plot. In total 9 composite soil samples were taken from three plots and analysed in the Laboratory of Soil Research of the Soil Fertility Research Service.

Total concentration of four heavy metals Pb, Cd, Zn and Cu were determined in *aqua regia* extracts using flame atomic absorption spectrometer (Cu and Zn) and graphite furnace atomic absorption spectrometer (Pb and Cd).

Mobile or potentially bioavailable fractions of selected elements were extracted using ammonium acetate buffer (pH 4.8) solution and final measurements were done on ICP-MS.

In addition to heavy metals general properties of soils such as pH, organic matter, cation exchange capacity, texture and calcium carbonate content were also determined.

Results

The results of laboratory analysis (Table 1) were compared to guide values established in Georgia for heavy metals in agricultural soils. The comparison has shown that studied soils on all three plots are polluted with Cu, Cd and Zn. The concentration of Pb is slightly elevated from the local background, but is under recommended guide value.

Table 1. Concentration of heavy metals in soils of irrigated arable lands

Plot name	Depth in cm	pH _{H2O}	OM %	Cd	Cu	Pb	Zn
				mg/kg			
Plot #1	0-10	7.04	4.50	6.07	730.17	49.52	770.74
	10-20	7.59	5.21	6.27	740.00	46.37	767.84
	20-40	7.17	4.57	6.50	744.28	41.83	791.53
Plot #2	0-10	7.12	4.04	5.87	758.90	41.71	734.71
	10-20	7.30	4.27	8.38	741.01	41.96	687.20
	20-40	6.79	3.60	4.44	539.53	36.04	450.70
Plot #3	0-10	7.18	2.53	4.11	362.25	24.95	319.66
	10-20	7.39	3.20	4.17	392.62	27.22	316.26
	20-40	7.66	2.92	3.81	317.77	24.19	225.29
Guide values* GEO		-	-	2	132	130	220
Limit values** EU		-	-	3	140	300	300

*Guide values for soils with pH>5.5

**Upper limit values established in European Union

The concentration of mobile forms of studied heavy metals were above maximum permissible concentrations on the 1st and 2nd plot in nearly all samples in case of Cu and Zn. All samples were under MPC value in case of Pb. No limits for mobile forms of cadmium is established currently (Table 2).

Table 2. Concentration of mobile forms of heavy metals in soils of irrigated arable lands

Plot name	Depth in cm	Cd	Cu	Pb	Zn
		mg/kg			
Plot #1	0-10	1.480	26.51	0.333	53.01
	10-20	1.577	29.04	0.463	50.07
	20-40	1.885	35.94	0.597	46.96
Plot #2	0-10	1.603	34.18	0.303	49.80
	10-20	1.543	31.58	0.356	49.18
	20-40	0.891	17.97	0.284	22.41
Plot #3	0-10	0.462	5.20	0.154	7.24
	10-20	0.467	3.33	0.188	6.23
	20-40	0.213	1.57	0.126	0.95
MPC values* GEO		-	3	6	23

*Maximum permissible concentration of mobile forms of heavy metals

Discussion

The study of heavy metals concentrations in soils of irrigated arable lands shown that the impact of polluted irrigation water affected by industrial activities is considerable. The higher concentrations for total and mobile forms of Cu, Zn and Cd indicate the direct influence of copper-gold mining site located in the upstream areas.

Conclusions

The studied agricultural lands are polluted by Cu, Zn and Cd and there is a risk of translocation and accumulation of those metals in edible parts of crops grown on these plots. Therefore, additional sampling sites and monitoring of metal concentrations in foodstuff produced in the area is essential to ensure food safety and human health.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.2.12. Assessment of heavy metal pollution in the cultivated area around mining. Tunisia case study Medjredah Watershed.

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Abstract

Large dumps results from the accumulation of solid mining wastes after treatment of the Pb-Zn are within the borders of mining area. Exposed to different meteoric factors, heavy metal are mobilized and affects soils, vegetables reaching food chain consumed by people conducting to impact on the environment.

This work based on identification and assessment of nature and spatial distribution of the heavy metal on the soil (surface, depth) around mining and their dynamic in low compartments of the landscape by the processes of streaming of surface, runoff and wind movement. The study concerns different parts of Medjredah Watershed (10 pilot areas were selected, 4 areas were tested). Over than 90 samples were analysed. The strategy of sampling was defined by taking into account the position of the mine site, the topography, distribution of cultivated soil in the study area and factors that influence the dispersion of metals.

For The Site of the Khanguet Kef Tout mining district the value varies from 15 to 308 ppm for Zn, from 4 to 432 ppm for Pb From 0,1 to 4,6 ppm for Cd in soil surface. For the site Fedj El Adoum Area, the value varies from 36 to 3485 ppm for Zn, from 37 to 3844 ppm for Pb from 1 to 15 ppm for Cd. For Touiref mining district the value are 5837 ppm for Zn, 5205 for Pb ppm, 63,4 ppm for Cd.

The speed of this pollution depends on several factors: the slope, the soils properties, the position of the mine the intensity of rains and wind direction.

This results can lead to establish a contamination tendency in Medjerdah watershed, to compare pollution process and factors in different site, to determine Tunisian standard regulations for heavy metals in Tunisian cultivated lands and to propose Control measure pollution.

Keywords: Mine El Akhouat, Rejects mining, heavy metals, cultivated area, contamination, plants, Tunisia.

Introduction, scope and main objectives

Various plants and crops occupy agricultural lands around rejects Tunisian mining, despite their high level of heavy metals. This manifests itself in the extensive studies that have been carried out on the lands of certain mines (Ckaroun, etc.). Two problems result, a localized pollution of these lands but also a diffuse pollution, which is implemented in the lower compartments of the landscape by the processes of surface run-off but also the underground infiltration of certain metals under the effect of the rains. The speed of this pollution depends on several factors including the slope, the soil properties and especially the quantity and intensity of the rains.

This work is based on the identification and evaluation of the nature and spatial distribution of heavy metals in agricultural soils (surface, depth) around mining operations and their dynamics in the compartments of the great Medjerda watershed by surface diffusion processes, runoff and wind movement.

Methodology

The study focuses on the different hydrological units of this system (Medjerda) through an in-depth study of spatio-temporal monitoring to evaluate the natural dynamics of these metals; (10 pilot areas were selected, 4 sites were tested). About 90 samples were analyzed. The sampling strategy was defined taking into account the position of the mine site, the topography, the distribution of soils grown in the study area and the factors that influence the dispersion of the metals.



Figure 13. The mine of El Akhouat , NorthWestern Tunisia



Figure 2. Khanguet Kef Tout mining district



Figure 3. Fedj El Adoum Area

Results

Table 1. The mine of El Akhouat results

	Zn (ppm)	Pb (ppm)	Cd (ppm)
Les sols de l'Akhouat	9780	2394	43
Echantillon (témoin)	42	0,45	37
Council of the European communities (CEC),1986	300	300	3
OMS	90	35	0,35

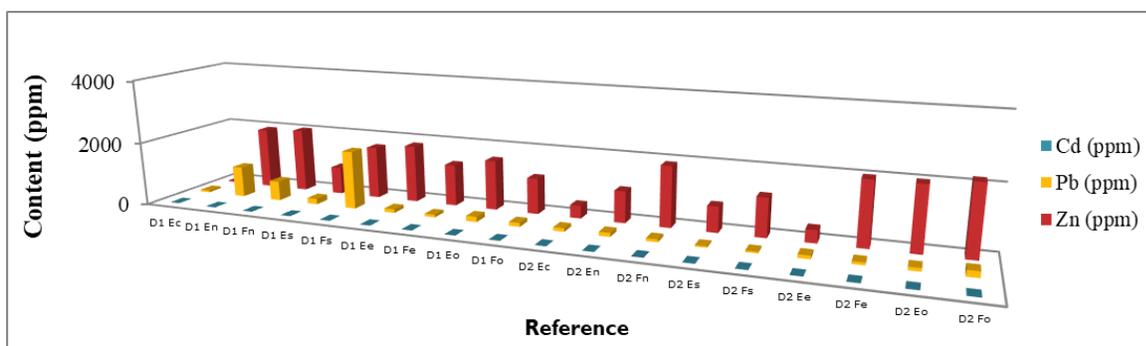


Figure 4. Fedj El Adoum Area results

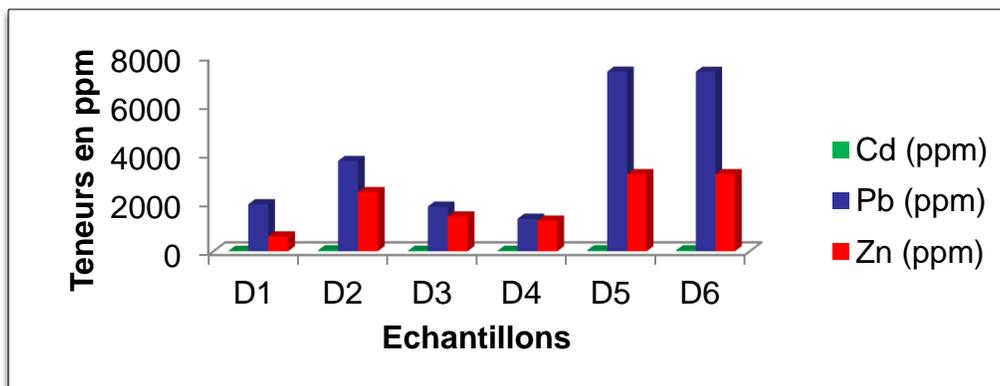


Figure 5. Khanguet Kef Tout mining district results

Discussion

The mine of El Akhouat, which is located in North Western Tunisia, dealt mainly lead ore and zinc. Abundant tailings have been stored without any rehabilitation of the environment. Mineralogical characterization of these discharges has revealed the presence of lead sulfide (PbS: Galena), sulfides (ZnS: sphalerite) and iron disulfides (Fe₂S: Pyrite and Marcasite) and other minerals: carbonates (dolomite, calcite), silicates (quartz) and iron oxides (goethite).

Geochemical characterization of mine waste shows high levels of trace elements: Pb (4184 ppm), Zn (10 070 ppm) and Cd (46 ppm). Alkaline pH soils resulting primarily from the high levels of carbonates are characterized by high levels of Pb, Zn and Cd up to 2572 ppm Pb, 8906 ppm Zn and 43 for Cd. Similarly, there were relatively high levels in polluting elements (Pb, Zn and Cd) in certain plants of the region. Same characterizations were conducted in the other sites.

For Khanguet Kef Tout mining district the value varies from 15 to 308 ppm for Zn, from 4 to 432 ppm for Pb. From 0,1 to 4,6 ppm for Cd in soil surface. For Fedj El Adoum Area, the value varies from 36 to 3485 ppm for Zn, from 37 to 3844 ppm for Pb from 1 to 15 ppm for Cd. For Touiref mining district the value are 5837 ppm for Zn, 5205 for Pb ppm, 63,4 ppm for Cd.

Conclusions

The speed of this pollution depends on several factors: the slope, the soils properties, the position of the mine the intensity of rains and wind direction.

This results can lead to establish a contamination tendency in Medjerdah watershed, to compare pollution process and factors in different site, to determine Tunisian standard regulations for heavy metals in Tunisian cultivated lands and to propose Control measure pollution.

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2.2.13. Biomonitoring soil health in agricultural volcanic areas – an integrative approach

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Abstract

Volcanic soils are unique fertile resources, with unusual andic properties that place them as highly suited, as well as vulnerable, to agricultural practices. This study emerges as an integrative approach to provide advanced knowledge about the health status of volcanic soils. Key indicator species, exposed in situ/ex situ to agricultural volcanic soils, were selected and sensitive biomarkers were determined at different levels of biological organization (molecular, subcellular, cellular and tissue level), to integrate information about the presence (biomarkers of exposure), bioavailability and biological effects (biomarkers of effect) of soil pollutants in agricultural systems. The results clearly reveal that the unique chemical heritage observed in the agricultural volcanic soils, resulting from the volcanic parent material (geogenic origin) and modulated by agricultural land use history (anthropogenic origin), leads to stressful conditions to the resident biota, compromising the local soil health status and provision of soil-based ecosystem services. Meanwhile, the degree of such stress and its effects are related not only with soil physicochemical properties, management practices, type and/or amount of agrochemicals input, but also with the organism in which those stress is measured and its ecological role in these humanized (agro)ecosystems. Each of the selected indicators (soil physicochemical characteristics, biomarkers from belowground biota and small mammals) had a specific and relative contribution to the overall soil health “puzzle”. The implications of this study outcomes go far beyond the warning about the impact of agricultural practices in soil biology, by setting the scientific foundations upon on which management risk actions should be erected, as well as defined agricultural and land use policies adjusted to volcanic soils particularities.

Keywords: Soil Health; Volcanic Soils; Agrochemicals; Biological Indicators; Integrative Biomarker Response.

Introduction, scope and main objectives

Although volcanic soils only cover 1–2% of the world’s land surface (approximately 124 million hectares), they yet support 10% of the world’s population (Takahashi & Shoji, 2002; Neall, 2009). They are often among the most fertile soils and therefore are the foundations for some of the most densely populated areas of the world (Arnalds *et al.*, 2007). When volcanic materials are exposed to weathering, colloidal materials are rapidly formed, giving to the soils distinctive properties (e.g. high SOM content, high water retention capacity, low bulk density, etc.). These andic properties historically allowed the establishment of non-shifting agricultural practices in many volcanic areas (McDaniel *et al.*, 2012). Nevertheless, these soils also enclose a more unknown aspect, the presence of nanominerals derived from the weathering of the tephra material, providing distinctive features to these resources, namely greater binding properties to metal cations. Therefore, the long-term use of agrochemicals (anthropogenic input) in agricultural volcanic soils can lead to the silent increase of the natural trace metal background up to critical loads, triggering undesirable effects to the resident biota, compromising the soil associated ecosystem goods and services, and thus the well-being. Herein lays a deeper and undisclosed aspect of volcanic soils, simultaneously acting as

ecosystem sink and a source of toxic substances, an unusual soil feature that can assume particular relevance in areas where agriculture is the primary sector of economic activity and income.

In spite of soil health being a concept widely defined, (e.g. Doran *et al.*, 1996) there is no universally applicable formula to measure it. Several authors highlight an ongoing need for the development of more integrative indices that involve combinations of several indicators (Bastida *et al.*, 2008), including those chosen to reflect key soil-based ecosystem services (Zornoza *et al.*, 2015). Although many studies have been conducted on soil health assessment (e.g. Burges *et al.*, 2015; Trivedi *et al.*, 2016), a general methodology to characterize soil health and define the set of indicators, is yet missing.

Given the complexity of volcanic agroecosystems, understanding the links between soil biological indicators is of particular importance to assess the effects of both natural and anthropogenic pressures in soil health. Hence, volcanic areas would benefit from a formulation and evaluation of realistic agricultural and land use policies, fine-tuned to the particularities of volcanic soils. For this goal, an integrative soil health assessment in agricultural volcanic areas is urgently needed to assist a well-balanced ecosystem supporting of local, regional, and global environmental health.

This study emerges as the first effort towards bringing together agroecosystem bottom-up soil health data to provide advanced knowledge about the health of volcanic soils. The study was outlined to integrate soil physicochemical properties, biomarkers from belowground biota (soil microbial communities) and small mammals (mice), to assess soil health status in agricultural volcanic areas, using agricultural soils from São Miguel Island (Azores archipelago, Portugal) as a study models.

Methodology

The selected study area in São Miguel Island corresponds to the Picos Fissural Volcanic System (200 km²) and is the most recent geologic unit, being the oldest subaerial outcrops dated from about 50,000 yr. ago (Moore, 1990). For this reason, the primary edaphic properties are expected to be more evident in this geologic unit. According to Ricardo *et al.* (1977) two main associations of soil types can be observed in the studied area: (1) thin allophanic soils and thin Andosols, the latter over lava flows, and (2) thin allophanic soils and coarse Regosols, the latter mainly associated with basaltic pyroclastic deposits. The Picos Fissural Volcanic System has gone through significant farming development during the last decades, with the transformation of the majority of smallholdings, whose soils were usually managed traditionally (where agrochemicals were frequently used without official restrictions), into farms for commercial purposes, where intensive agriculture is practiced following the EU directives, either when using agrochemicals (conventional farming) or not (organic farming). Soil samples were collected from two conventional farms, two organic and one traditional and characterized for physicochemical properties, trace metal content and microbial activities.

Soil physicochemical properties [particle size fractions, soil organic matter, pH (H₂O) and electric conductivity] were carried out following nationally recommended procedures and the Portuguese official methods (LNEC, 1967a,b). Trace metal (Li, P, K, V, Cr, Mn, Ni, Cu, Zn, As, Mo, Cd, Ba, Pb and Hg) contents in soil were determined by inductively coupled plasma mass spectrometry (ICP/MS) and inductively coupled plasma optical emission spectrometry (ICP/OES). Enrichment factors were calculated to distinguish the geogenic and anthropogenic contribution to trace metal contents in agricultural soils. An ensemble of multivariate statistical analyses (Principal Component Analysis and Factorial Discriminant Analysis) was performed to reduce the multidimensional space

of variables and samples, thus defining a set of metals as tracers of distinct agricultural farming systems.

Soil microbial activities were determined in soil sample, as follows: the β -glucosidase activity was determined according to the procedure described by Dick *et al.* (1996); the acid phosphatase activity, according to Dick *et al.* (1996); the dehydrogenase activity, according to Rossel *et al.* (1997) method. Soil basal respiration was determined by quantifying the carbon dioxide (CO₂) released in the process of microbial respiration during 8 days of incubation at 25°C, according to Jenkinson and Powlson (1976) method. The microbial biomass C was calculated as 0.33 times the difference in extractable organic C between the fumigated and unfumigated soils (Sparling and West, 1988). The metabolic quotient was calculated as the ratio of basal respiration to microbial biomass C (Anderson and Domsch, 1990). To associate the soil microbial responses to soil trace metal contamination, non-parametric correlations (Spearman correlation, $p \leq 0.05$) were used. The soil microbial activities were integrated in an effect-based soil index [Integrated Biomarker Response, Beliaeff and Burgeot (2002)] to score soil health status in trace metal contaminated agricultural soils.

To untangle the link between agricultural practices and male reproductive impairment due to chronic exposure to xenobiotics (such as agrochemicals) in farming environments, male wild mice populations (*Mus musculus*) from sites representing two distinct farming practices (conventional and organic farming systems) were used as bioindicators for observable effects of testicular damage. For each specimen, testicular histological sections (5 per testicle) were randomly chosen for relative volumetric density determination of different spermatogenic stages (spermatogonia, spermatocyte, early spermatids, late spermatids, spermatozoa) and interstitial space, using the M168 Weibel Multipurpose Test System (Weibel, 1979). The seminiferous tubules injury was evaluated and scored according with criteria based on the percentage of luminal area occupied by spermatozoa and germinal epithelium structural organization (adapted from Ferreira *et al.*, 2015). For each specimen, the hepatic trace metal content was determined ICP/MS. Biomarkers and trace metal hepatic contents were further explored under Principal Component Analysis. Testicular damage biomarkers were combined into the Integrated Biomarker Response index, as described by Beliaeff and Burgeot (2002), to evaluate testicular stress.

Results and discussion

Results from this study, demonstrate that present-day agricultural volcanic soils have a unique chemical heritage, set by the nature of the parent material (geogenic origin) and modulated by agricultural land use history (anthropogenic origin). Through a multivariate approach, the observed V, Ba and Hg soil loads were associated to the volcanic nature of the parent material; while, Li, P, K, Cr, Mn, Ni, Cu, Zn, As, Mo, Cd and Pb were associated with agrochemicals use. Globally, different soil management practices triggered negative effects on the local soil microbial communities, by decreasing soil microbial biomass, microbial respiration (decreased soil basal respiration) and their catabolic activities (i.e. decrease of acid phosphatase and dehydrogenase activities). Meanwhile, the most severe effects were observed in soil microbial communities under conventional management practices, suggesting that local soil-based ecosystem services can be compromised in these agroecosystems. Moreover, the use of the Integrated Biomarker Response index (IBR), as a measurement of the combined effect of soil management practices and trace metal soil contamination on soil microbial functionality, allowed the discrimination of soil health status in agricultural volcanic soils as follow: organic > traditional > conventional. Results from the analysis of the testicular damage biomarkers in wild mice populations (*Mus musculus*) indicate that chronic exposure to conventional farming environments entails higher risks to male fertility. Mice chronically exposed to conventional management practices displayed higher Pb hepatic

accumulation, further associated with disruption in seminiferous tubules, increased interstitial tissue, lack of sperm cells in luminal space and higher amount of germinal cells undergoing apoptosis. Applying the IBR, the pool of testicular damage biomarkers was summarized into a single stress value, ranked as: conventional > organic.

Conclusions

Overall, the results clearly reveal that agricultural management practices in volcanic soils, leads to stressful conditions to the resident biota, compromising the local soil health status and provision of soil-based ecosystem services. All the biological endpoints measured in the selected biological indicators were sensitive to anthropogenic activities (land use type and soil management) and/or stressors (agrochemicals) present in soils, validating their applicability as tools to assess soil health status in volcanic areas. The use of an Integrated Biomarker Response to assess and score soil and animal health, proved to be an useful multi-biomarker approach to discriminate, score and rank farming systems, based on their ecotoxicity to the exposed organisms. At the regional level, the implications of this thesis outcomes go far beyond the warning about the impact of agricultural practices in soil biology, by setting the scientific foundations upon on which should be erected management risk actions, as well as defined agricultural and land use policies adjusted to volcanic soils particularities. This study is the first scientific attempt to open the soil black box in agricultural volcanic areas, highlighting the soil functionality and its wider concept of health, critical for agricultural productivity and environmental sustainability. Although with a regional focus, the integrative approach of the research results represent a major advance in the international arena and a great contribute to soil science, in general.

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2.2.14. Assessing soil pollution and application of water-waste-soil nexus solution for improved land use management

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Abstract

Soil pollution occurs in many countries within many farmlands among other land uses. While air or water pollution is visible and assessed by science-based evidences, soil pollution is invisible and often overlooked in both resources and sustainable management strategies. The trade-off between the exponentially increasing request for food provisioning and the progressive global water scarcity is the unfortunate platform in which many countries must optimize their land use management at the minimum cost for both humans and natural ecosystems. By using the wastewater reuse as case study in Latin America, China and MENA Region as well Europe, the main objective of our work is three folded:

- 1) Raise awareness on the pressing problems of soil pollution in different Region of the World and at a global scale
- 2) Suggesting monitoring strategies aiming at the foundation of a sustainable land management strategy that could increase resources use efficiency and preserving at the same time the irreversible pollution of soil ecosystems while reusing wastewater for irrigation purposes
- 3) Show how data gathering on soil pollution have shaped policy interventions

Keywords: Soil pollution, wastewater, irrigation, land use management, soil-water-waste, Nexus Approach, reuse

Introduction, scope and main objectives

Soil pollution occurs in many countries within many farmlands among other land uses. While air or water pollution is visible and assessed by science-based evidences, soil pollution is invisible and often overlooked in both resources and sustainable management strategies. Soil has not been explicitly factored in to the Sustainable Development Goals (SDGs) and despite it encompasses the agricultural value chain and ecosystem services, the recognition of soil as critical resource is still neglected. Consequently, the knowledge about global soil pollution and thus the management strategies to keep soils “healthy” is still poor in many regions the World.

Anthropogenic pollution is the result of the increased human activities globally and now seen as one of the biggest threat for the renowned resilience of soils. Is not a isolated case that China reported to have 16.1% of all soil and about the 19.4% of overall farmland polluted with organic and inorganic

contaminants at varying degrees (Zhang and Schwärzel 2017), or that the land used for agriculture with untreated wastewater in the Mezquital Valley, Mexico, will reach its capacity for heavy metal pollution in less than three farming generations (Caucci and Hettiarachchi 2017).

Immediate action is required to buffer the foreseen negative impact on soil uses and land management. No action is possible if no awareness raises, monitoring strategies and sustainable options for soil managements are identified.

The introduction of integrated natural resource management (water-soil-waste nexus) aiming at a better allocation of socio-economic-ecological return to the society spotlighted that water supply, pollution control, and soil management have been wrongly independently approached and that now, this approach need to be reconsidered as one complex approach (Hettiarachchi and Ardakanian 2016 a). Despite the promising nature of such approach, challenges are facing its sustainability and data gathering is one of the biggest bottleneck for its implementation. The use of wastewater for sustainable land use management is the perfect representative. In such a practice, the risks associated with the different routes of exposure, to concentrations of physicochemical and microbiological parameters and type of exposed land might strongly impacts soil ecosystem functioning and services (Hettiarachchi and Ardakanian 2016 a) if not properly Managed.

China and Mexico are not an exception. The trade-off between the exponentially increasing request for food provisioning and the progressive global water scarcity is the unfortunate platform in which many countries must optimize their land use management at the minimum cost for both humans and natural ecosystems.

The main objective of our work is three folded:

- 1) Raise awareness on the pressing problems of soil pollution in different Region of the World and at a global scale
- 2) Suggesting monitoring strategies aiming at the foundation of a sustainable land management strategy that could increase resources use efficiency and preserving at the same time the irreversible pollution of multiple soil ecosystems.
- 3) Show how data gathering on soil pollution have shaped policy interventions

Methodology

This work makes use of a blended variety of knowledge recovered from own scientific research work, in field-testing and multiple-stakeholder's participation. Data on soil pollution resulting from non-sustainable land use management from Latin America, China and, MENA Region as well Europe will be described in the optic of strategic monitoring planning and adoption of water-soil-Waste Nexus Approach as path for the implementation of sustainable land use management strategies. This work will also highlight the bottleneck to be overcome to reach harmonized and as possible complete data recollection on the health of anthropogenically impacted soils.

Conclusions

Previous mitigation strategies for soil pollution were mainly focused on the identification and controlling of the major sources of soil pollution and water centric legislations on wastewater ensuring higher water quality standards or soil remediation and management measures. However, such solutions did not included the reuse possibilities that wastewater and sludge have respectively

as rich nutrient and water pool and soil conditioner of agricultural soils. Tailormade wastewater quality that would preserve soils while being used for irrigation practices can be reached if knowledge on the health status of soil are present and wastewater treated in the optic of its final reuse. This could, on the one hand, consolidate the solutions for controlling water and soil pollution and at the same time recycle the nutrients present in the wastewater, decrease soil nutrient depletion and water provisioning thus enhancing safe crop production, soil health and ultimately increase food security. More cases addressing the biophysical and socioeconomic benefits from applying nexus approach in preventing soil pollution and more sustainable land management practices are needed. Moreover, enabling policy and capacity development are crucial to encourage the adaptation of such strategies.

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2.2.15. Bacterial microbiota of soils managed with Methyl Bromide, Methyl Iodide and Dimethyl Disulfide

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Abstract

Methyl Bromide (MeBr) or Bromomethane is a broad-spectrum biocide that kills fungi, nematodes, weeds, insects, and rodents. It has been applied to soils around the world in copious quantities for decades as a fumigant for pre-harvest field preparation of crops. MeBr was listed as an ozone depleting substance in 1992 and the Montreal Protocol was established in 1987 with the goal of phasing out the use of all materials that deplete ozone. While impact on ozone is clearly of enormous concern, the impact of a broad-spectrum biocide on soil microbiota and agro-ecosystems is also of huge concern to long-term soil health and fertility. Macro and micro drivers of diversity work in many directions, shifting ecologies in ways that have the potential to impact the flow of infectious disease, soil fertility, nitrogen fixation and a myriad of other potentially dysbiotic interruptions of agricultural biospheres. Through efforts to produce the best crop, we may unintentionally destroy ecological niches that are vital to healthy agriculture but currently remain poorly described. At the time of this study, Dimethyl Disulfide (DMDS) and Methyl Iodide (MI) were proposed alternatives to use of Methyl Bromide (MB) so all three materials were applied to soils in randomized complete block design for four months. All soils, Control (C), MB, MI and DMDS soils, were profiled using 16S rRNA gene amplicons. Control soils supported a much more diverse bacterial profile with almost double the number of species (~1,500) than any of the treated soils (~700). One commonly reported trend in human microbiome research has been the correlation of low diversity ecosystems (gut) with dysbiotic systems and high diversity with healthy systems. Following chemotherapies, low gut microbial diversity has been one of the most highly correlated data points with mortality. Among bacteria that were depleted in MB treated soils compared to controls were two poorly studied Actinobacteria genera; *Actinomadura* and *Actinoallomurus* of the family Thermomonosporaceae. Other significantly depleted taxa was *Mucilaginibacter*, a recently proposed novel genus in the Sphingobacteriaceae. The paucity of information on the most depleted organisms highlights the fact that we are destroying organisms with roles in soil ecologies and soil systems that we have yet to even understand.

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2.2.16. On the contribution of wastewater reuse in agriculture to the potential impact on soil pollution and crop contamination with antimicrobial resistant bacteria and genes

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Abstract

The spread and contamination of agroecosystems with antibiotic resistant bacteria and genes (ARB&G) is currently considered a relevant public health challenge. While studies on animal husbandry and manure amendment of agricultural soil have already started to get attention, the impact that wastewater reuse irrigation might have on soil pollution and consequently to food/feed contamination is still in its infancy. ARB&Gs spread and evolution in agroecosystems can be affected by changes in environmental conditions caused by agricultural practices such as fertilization, wastewater reuse and climate change. Accordingly, a microbial and antimicrobial resistance risk assessment must be defined. Unfortunately, no guidelines for risk assessment can be generated if not both the baseline of ARG&B and the status of agroecosystems is performed.

Within this work, we will try to understand the diversity, persistence of ARGs in the soil and food/feed using multiple case studies based in Europe, MENA Region and Latin America.

Keywords: Soil pollution, wastewater, irrigation, reuse, antibiotic resistance, ARB&G, agriculture

Introduction, scope and main objectives

The spread and contamination of agroecosystems with antibiotic resistant bacteria and genes (ARB&G) is currently considered a relevant public health challenge. Hotspots for the spread of antibiotic resistance in the environment have been identified and are in most of the cases connected to humans or anthropogenic related-activities. While studies on animal husbandry and manure amendment of agricultural soil have already started to get attention (Ruuskanen *et al.*, 2017) by both scientific community and International organization, the impact that wastewater reuse irrigation might have on soil pollution and consequently to food/feed contamination is still in its infancy.

Water scarcity, foreseen to aggravate, pushes for maximum utilization of non-conventional water globally. Alternatively, WW contaminated water is used as irrigation of food crops obligating farmers to unplanned wastewater reuse (Caucci, S. and Hettiarachchi, H. 2017). Such practice if not monitored could be an additional source of risk for humans and animals that could be infected by resistant microorganisms via raw vegetable/forage ingestion (Caucci, 2016).

It is already known that wastewater treatment plants (WWTP) effluents have a considerable impact on the resistome of freshwater ecosystems, traditionally considered the downstream environment for WWTP effluents. Previous studies have shown that traditional municipal wastewater treatment plants failed to completely remove ARB&G in their effluents (Caucci *et al.*, 2016). ARB&G are actively selected in human bodies because of increased antibiotic consumption, concentrate in WWTP and released via WWTP effluents and could risk becoming newer routes for indirect ARB&G reintroduction in human bodies (Piña *et al.*, 2018).

Within this context agroecosystems are unique settings where pathogenic and potential resistant bacteria from humans are constantly in contact in the soil due to irrigation practices and in crops harvested for food feed/production. Knowledge on the actual effects of wastewater reuse regarding these aspects is currently not consolidated. ARB&Gs spread and evolution in agroecosystems can be affected by changes in environmental conditions caused by agricultural practices such as fertilization, wastewater reuse and climate change. Accordingly, a microbial and antimicrobial resistance risk assessment must be defined. Unfortunately, no guidelines for risk assessment can be generated if not both the baseline of ARG&B and the status of agroecosystems is performed.

Within this work, we will try to understand the diversity, persistence of ARGs in the soil and food/feed using multiple case studies based in Europe, MENA Region and Latin America.

Methodology

Surveys, Reviews and experimental work based on culture dependent and independent methods have been employed to assess the status and accumulation of ARG&B in soils and crops as well as in wastewater effluents used for crop irrigation. Results are showing that resistant bacteria and ARGs abundance decreases overtime in soils. The degree of reduction is influenced by climatic condition and type of wastewater used wastewater reuse practices. Crops irrigated with wastewater carry ARG&B but not at critical level (unless untreated wastewater is used) if wastewater practices are managed. Not clear is if the degree of ARB&Gs reduction would prevent the spread and thus the persistence of ARB&Gs in soils.

Conclusions

Additional studies should address the potential of ARG transfer between soil-related microorganisms and wastewater bacteria in order to determine the spread and accumulation of ARGs in soils. Wastewater reuse guidelines should be followed and the destination use of food/feed followed accordingly. Due to the characteristic of soil as natural reservoir of antibiotic resistance genes and agricultural practices are known to disseminate ARGs to the environment, the natural and intrinsic soil resistome should be also targeted to allow the definition of ARGs baseline for agroecosystems irrigated with wastewater.

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2.2.17. Soil pollution issues in a tropical agricultural wetland in India

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Abstract

The Vembanad-Kol wetland, a designated agricultural wetland in India is facing serious environmental problems associated with the pollution of soil and water. In addition to climate change and anthropogenic activities, failure in an agricultural development project deteriorates the rich soil. The region has become inhospitable to humans and other living organisms and people try to migrate to safe locations. Soil and water degradation leads to several health issues and socio-economic issues such as hiking price of food and water and conflicts over allocation. The traditional and indigenous below sea-level farming practices now faces many challenges, threatening food security in the State.

Keywords: soil pollution, agricultural wetland, India, policy

Introduction, scope and main objectives

Soil degradation as a result of anthropogenic activities and climate change create food and water crises in the Vembanad-Kol wetland agriculture region in the tropical coastal State of Kerala in India. This wetland ecosystem, a large Ramsar site has been declared as Globally Important Agricultural Heritage Systems (GIAHS) for traditional and indigenous below sea-level farming practices. The region faces serious environmental problems from rising population, encroachment, industrial development, urban development and drawbacks in development projects, making the region inhospitable to living organisms and affecting the livelihood of wetland dependent communities. Most of the area of the wetland lies nearly one metre below sea

level. Rice farming in this rich rice cultivation area is made possible by constructing dikes and pumping out water. Measures to multiply crop production cause concentration of pesticides and fertilizers on logged water, poisoning soil and water as natural flow is controlled by regulators. The projects to prevent brackish water intrusion and flood control produced negative results. The ponds, wells and canals in the wetland area on which the majority of population once depended for all domestic purposes are now highly contaminated. The study analyses the impact of increasing soil pollution in the wetland, basic reasons behind it and the associated various socio-economic issues. Conservation of the wetland is important as the State is facing a serious shortage of rice and is depending on neighboring states for its food requirements.

Methodology

Analysis of the concentration of different types of pollutants in soil and water has been carried out using samples collected from selected locations. Impact of increasing population, climate anomalies and failure in development projects on the ecology of wetlands has been assessed. Data and reports from the national meteorological service, state department for water and state research institutes have been used for the study.

Results

Kerala receives more than 300cm rainfall annually. Rainfall over the wetlands region is slightly higher than the state average. Rainfall is becoming more seasonal and intense, adding to the severity of floods. This also leads to increased transport of sediments into wetland. The increasing duration of rainless days further reduces the water quality, affecting soil characteristics. The wetland has a total area of 1100Km², of which 500km² are 0.6 to 2.2 m below sea level. Five rivers flow through the wetland to join the Arabian Sea. From these rivers, 10,000Mm³ water flows into the wetland in a year and in extreme years it is up to 15,000Mm³ (Nair, 1987). Steep slopes in the eastern hills where the rivers originate cause fast flow of water in rainy season and results in flooding in the wetland. This acts as a natural flushing system that removes the wastes and wastewater in the wetlands into the Arabian Sea.

Measures to multiply the agricultural production and protect crops from floods in the wetlands now produce adverse results. Rice cultivation was carried out by constructing temporary dykes in lowlands and pumping out water. Floods and salinity intrusion resulted in heavy losses. To avoid this and to make double cropping possible, three major projects – the Thottappally Spillway to evacuate floodwater during monsoon, the Thannermukkam barrage to prevent saline water intrusion during dry season and the AC Road for easy access to help development activities - were planned and implemented for the overall development. Failure in the completion of leading channels and failure in foreseeing the rising sea level in fact increased flood risk and resulted in crop failure. Barrage affected the natural flushing, the road obstructed water flow, and the concentration of pollutants multiplied. Rapid urbanization is increasingly polluting wetlands. Accumulation of pollutants in the wetlands makes life difficult in the thickly populated area.

The rivers carry tremendous amount of pollutants en route, into the wetlands. This leads to the contamination of both soil and surface and groundwater resources, including traditional sources like ponds and wells. Major source of pollution is from agriculture and industries. All the rivers carry hundreds of tons of pesticides and fertilizers including organochlorine and organophosphorous (Jospeh, 2010). Their use is very unscientific and is lot more than actual requirement. As the rivers flow through thickly populated regions, there is tremendous input of detergents and bio wastes from households. There are several small factories and vehicle servicing centres in this region that empty wastewater containing oils and chemicals. In the lowland areas,

coir making is the livelihood of many low-income people and the coconut husk retting in freshwater has deteriorated the water in ponds and canals. The wetland receives nearly 0.105M m³/day of wastes containing organic wastes of the order of 260 tons/day. The rivers joining the wetlands carry a fertilizer load of 30000 tons/year. Trace metals in estuarine sediment had a post - monsoon enrichment of iron with 740 mg/g in the northern and southern limbs of the wetland. Presence of manganese, zinc, copper, nickel, cobalt etc is also high. Recent study reveals the presence of mercury beyond safety limit. Water logging makes soil and water unsafe, making the region inhospitable. Weeds and mosses grow fast and, promoting the spread of mosquitoes and water-borne diseases. Many species of fishes, reptiles and birds have disappeared from the wetland in the last few years. There is a considerable reduction of migratory birds that visit Siberia for nesting and breeding even from far away.

Discussion

Safe soil and water is becoming scarce resources in the wetlands area. Trends in climate and population indicate that water availability in Kerala will be drastically reduced from the present 3000m³ to 1800m³ in two decades. Actually available usable water will be much less than this. Domestic or public pipe water facility is inadequate and many people have to depend on the local water resources. Soil pollution contaminates the groundwater resources. Changing rainfall seasonality results in flooding and summer water crisis. The proposed schemes for river linking and water diversion will further deteriorate the environment of all wetland. Encroachment and land reformation processes contracts the wetlands area.

Increasing pollution leads to several socio-economic issues such as migration, hiking price of reliable food and water and conflicts over allocation. Water-borne and vector-borne diseases have become common. Polluted soil and water result in serious health issues such as the increasing number of cancer patients.

Current management practices and conservation measures are inadequate. The national water policy, state water policy or state-level adaptation strategies are not appropriate in addressing the issues. State level wetland policy is weak and with loopholes to protect vested interests. Rules and regulations become farce because of poor administration and political interference.

Conclusions

Soil and water in the Vembanad-Kol wetland are facing degradation. Impacts of anthropogenic activities and natural climate change pose serious challenges to them, to the wetland dependent communities and to the habitats. Urban, agricultural and industrial expansion and failure in development projects deteriorate the wetlands and their ecology. Large inflow of untreated effluents and release of solid wastes highly degrades the wetland. Proper implementation of the conservation projects, urgent measures to control point and non-point pollution, efficient water treatment plants, strict implementation of the existing rules to control land and water degradation, proper public awareness and people's participation in wetland development programmes could create better environmental conditions in the wetlands. State urgently needs an appropriate policy for the wetlands and its effective implementation.

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2.2.18. A global review of water pollution from agriculture

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Abstract

Population growth and changes in consumption patterns, including new dietary preferences, require increased and diversified food production. This, in turn, is driving agricultural expansion and intensification leading to unprecedented environmental externalities, including impacts on water quality.

Water pollution is a global challenge that has increased in both developed and developing countries, undermining economic growth and the physical and environmental health of billions of people. Agriculture accounts for 70 percent of global water withdrawals and plays a major role in water pollution. Farms discharge large quantities of agrochemicals, organic matter and sediments into water bodies. The resultant water pollution poses serious risks to aquatic ecosystems, human health and productive activities, costing billions of dollars annually.

Agricultural pollution is the major factor in the degradation of inland and coastal waters. For example, in the United States of America, agriculture is the main source of pollution in rivers and streams, the second main source in wetlands and the third main source in lakes (US EPA, 2016). In China, agriculture is responsible for a large share of surface-water pollution and is responsible almost exclusively for groundwater pollution by nitrogen (FAO, 2013). Large loads of untreated municipal and industrial wastewater in low-income countries are major concerns and nitrate from agriculture is the most common chemical contaminant in the world's groundwater aquifers.

This presentation is based on the forthcoming FAO-WLE/IWMI publication “More people, more food... worse water?: a global review of water pollution from agriculture”, using Drivers-Pressures-State-Impact-Response (DPSIR) framework to analyse and synthesize the best available information on the causes and effects of water pollution from agriculture (including livestock and aquaculture) to identify pollution hotspots and key remedial actions.

Introduction, scope and main objectives

Agricultural pressures on water quality come from cropping and livestock systems and aquaculture, which have all expanded and intensified to meet increasing food demand related to population growth and changes in dietary patterns. The need to produce more food implies an increase in land clearing for food production and in the productivity of agricultural lands. The required rise in agricultural production cannot continue to occur, however, at the expense of the environment, which has been the case in the last decades. Business as usual may be insufficient to meet growing needs and cannot be sustained.

In the last few decades, the global growth of crop production has been achieved mainly through the intensive use of inputs such as pesticides and chemical fertilizers. The trend has been amplified by

the expansion of agricultural land, with irrigation playing a strategic role in improving productivity and rural livelihoods while also transferring agricultural pollution to water bodies. At the same time, the livestock sector is growing and intensifying faster than crop production in almost all countries, and the associated waste, including manure, has serious implications for water quality (FAO, 2006). In the last 20 years, a new class of agricultural pollutants has emerged in the form of veterinary medicines (antibiotics, vaccines and growth promoters [hormones]), which move from farms through water to ecosystems and drinking-water sources. Zoonotic waterborne pathogens are another major concern (WHO, 2012). There has also been a dramatic and rapid increase in aquaculture worldwide in marine, brackish-water and freshwater environments (FAO, 2016b). Fish excreta and uneaten feeds from fed aquaculture diminish water quality. Increased production has combined with greater use of antibiotics, fungicides and anti-fouling agents, which in turn may contribute to pollute downstream eco-systems.

Water pollution from agriculture has direct negative impacts on human health, and pesticide accumulation in water and the food chain has demonstrated ill effects on humans, led to the widespread banning of certain broad-spectrum and persistent pesticides (such as DDT and many organophosphates). However, some such pesticides are still used in poorer countries, causing acute and likely chronic health effects. Aquatic ecosystems are also affected by agricultural pollution; for example, through eutrophication caused by the accumulation of nutrients in lakes and coastal waters has impacts on biodiversity and fisheries, and water-quality degradation may also have severe direct impacts on productive activities, including agriculture. In Organisation for Economic Co-operation and Development (OECD) countries alone, the environmental and social costs of water pollution caused by agriculture probably exceed billions of dollars annually (OECD, 2012a).

Diagnosis, prediction and monitoring are key requirements for the management of aquatic ecosystems and the mitigation of harmful impacts on them. If they are to design cost-effective measures for preventing pollution and mitigating risks, managers, planners and lawmakers need to know the state of aquatic ecosystems, the nature and dynamics of the drivers and pressures that lead to water-quality degradation, and the impacts of such degradation on human health and the environment. Therefore, the objective of this paper is to analyse and synthesize the best available information on the causes and effects of water pollution from agriculture (including livestock and aquaculture) to identify pollution hotspots and key remedial actions.

Methodology

Based on a literature review of recent work on agricultural water pollution, and following the logic of the Drivers-Pressures-State change-Impact-Response (DPSIR) framework (Figure 1), this paper presents a summary of causes and effects of water pollution in agriculture as well as possible responses to prevent pollution and mitigate its impacts.

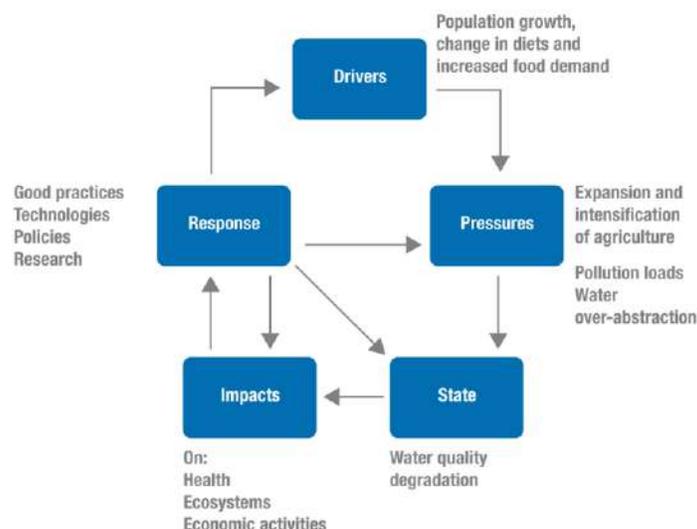


Figure 14. DPSIR framework for analysing water pollution in agriculture

Results

Population growth, changes in diets, and increasing food demand

The global population is projected to reach 9.8 billion people by 2050 (UNDESA, 2017). Population growth and changes in consumption patterns, including new dietary preferences (Figure 2) require the production of more (and more diverse) food. This, in turn, is driving agricultural expansion and intensification and bringing new environmental externalities, including impacts on water quality. Average calorie intake has increased as populations have become richer (despite the continuing large number of people living in absolute poverty). Diets are changing from those based mostly on grains and carbohydrates towards those with larger proportions of meat, eggs, dairy, oils and other resource-intensive products (Figure 3) (FAO, 2009). Excessive consumption (which is leading to overnutrition and obesity, even in middle and low-income countries) and post-harvest losses and waste draw down scarce resources and increase environmental footprints, including the degradation of water quality (FAO, WFP and IFAD, 2012). The need to produce more food implies an increase in land clearing for food production and in the productivity of agricultural lands. The required rise in agricultural production cannot continue to occur, however, at the expense of the environment, which has been the case in the last decades. Business as usual may be insufficient to meet growing needs and cannot be sustained.

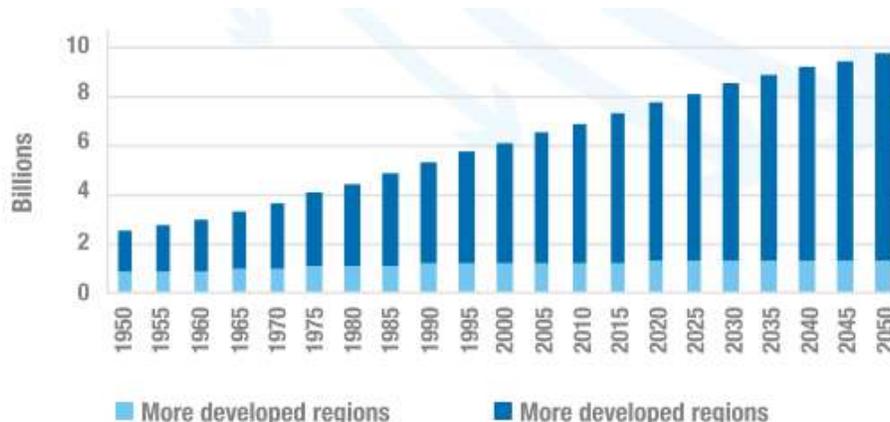


Figure 2. Past and expected global population, by developed and developing countries

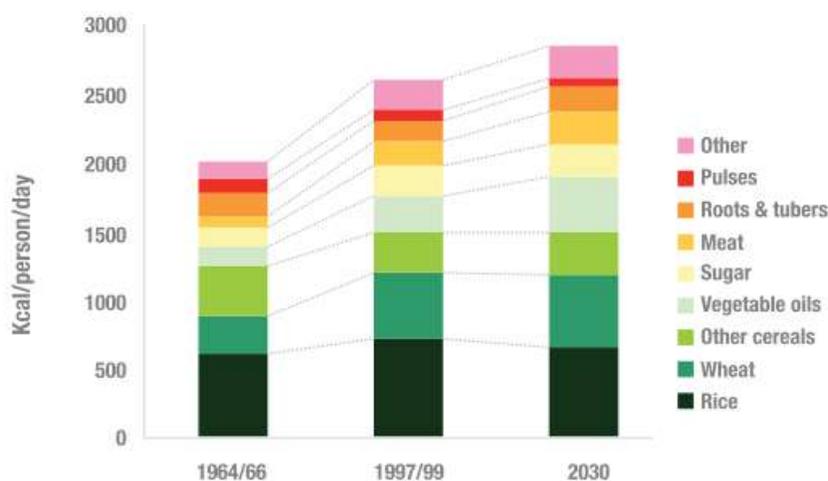


Figure 3. Global food consumption patterns, 1964–2030; Source UNDESA 2017; FAO, 2009

Expansion and intensification of agricultural systems

Agricultural systems have expanded and intensified in response to the ever-increasing demand for food. In absolute terms, land clearing and agricultural expansion have contributed to higher pollutant loads in water, but probably the biggest impacts have been caused by certain unsustainable patterns of agricultural intensification. The overuse and misuse of agrochemicals, water, animal feeds and drugs designed to increase productivity have resulted in higher pollution loads in the environment, including rivers, lakes, aquifers and coastal waters.

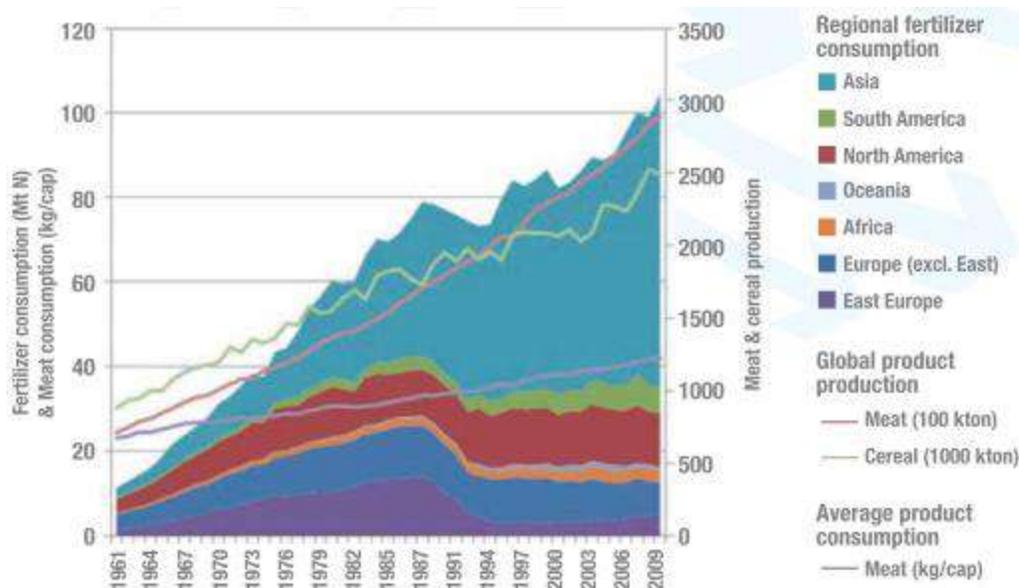


Figure 4. Total mineral fertilizer consumption in major world regions, global cereal and meat production, and per capita meat consumption, 1961–2009; Source Sutton *et al.*, 2013

Irrigation is a major factor in agricultural intensification. Big irrigation projects have been important means for increasing food security globally and particularly in developing countries. Nevertheless, irrigation and drainage have often been associated with a loss of water quality caused by salt, pesticides and fertilizer runoff and leaching.

Mineral fertilizers have been used since the nineteenth century to supplement natural nutrient sources and recycling to raise crops and animals, but the use of such fertilizers has increased dramatically in recent decades (Figure 4). Today, the world consumes ten times more mineral fertilizer than it did in the 1960s (FAO, 2016a). Rockström *et al.* (2009) suggested that the mobilization of nutrients could already have exceeded thresholds that will trigger abrupt environmental change in continental-to-planetary-scale systems. Fertilizer use has not grown evenly worldwide. Major disparities exist between those parts of the world with too many nutrients and those with insufficient. Key regions where excess nutrients are being transferred to water bodies include North America, Europe, and parts of South and East Asia.

In the trajectory of land-use intensification, countries have increasingly adopted a pest management approach based on the use of synthetic pesticides. Today, pesticide production is a multibillion-dollar industry, with the global market worth more than USD 35 billion per year (nominal) (Figure 5; FAO, 2016). Several upper-middle-income countries (e.g. Argentina, Brazil, Malaysia, South Africa and Uruguay) and lower-middle-income countries (e.g. Cameroon, Cape Verde, Nicaragua, Pakistan and Ukraine) have experienced double-digit growth in the intensity of pesticide use, albeit sometimes from a low base. Costa Rica, Colombia, Japan and Mexico have the highest pesticide use intensities worldwide (Schreinemachers and Tipraqsa, 2012).

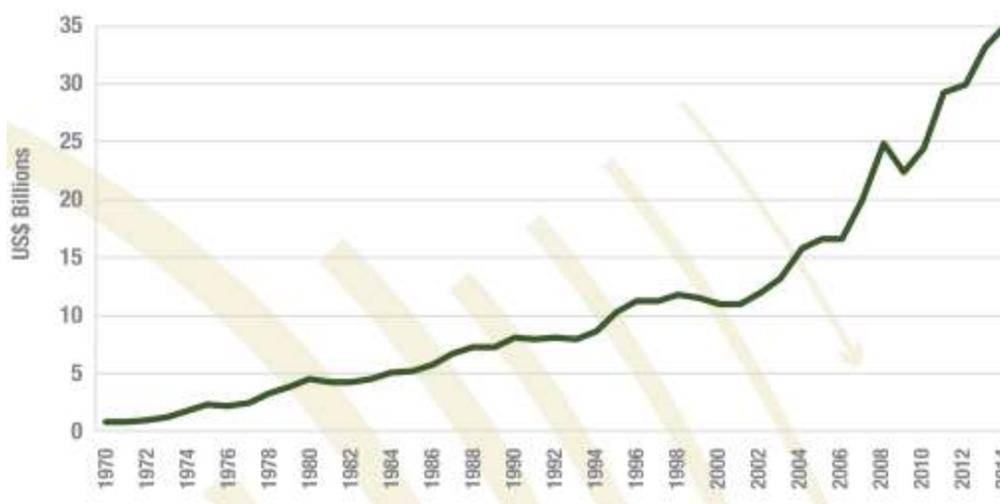


Figure 5. Value of global pesticide trade, 1970–2014; Source FAO, 2016

In general, the proportion of herbicides in pesticide global consumption increased rapidly, while the proportion of fungicides and insecticides declined (Zhang, Jiang and Ou, 2011). In developing countries, the fast rate of growth in pesticide use, reliance on broad-spectrum pesticides, weak institutional frameworks, weak rule enforcement, and limited knowledge and awareness among farmers on the use of hazardous chemicals pose enormous challenges to the safe and sustainable management of pesticides.

Livestock Production

Livestock production accounts for 70 percent of all agricultural land and 30 percent of the land surface of the planet. The livestock sector is one of the top three contributors to the most serious environmental problems, including water-quality degradation, at every scale from local to global (FAO, 2006). Demand for and the production of livestock products are increasing rapidly globally, but the following regions take centre stage: central and eastern United States of America; southern Brazil, Uruguay and northern Argentina; Europe; India; and China.

The major structural changes occurring in the livestock sector are associated with the development of industrial and intensive livestock production systems, which often involve large numbers of animals concentrated in relatively small areas. Intensive livestock systems increasingly depend on feed concentrates that are traded domestically and internationally. These changes are exerting growing pressure on the environment and particularly on water quality. Most of the water used for livestock drinking and servicing returns to the environment in the form of liquid manure, slurry and wastewater. Livestock excreta contain considerable quantities of nutrients, oxygen-depleting substances and pathogens and, in intensive systems, heavy metals, drug residues, hormones and antibiotics. When livestock is concentrated, the associated production of wastes tends to go beyond the buffering capacity of surrounding ecosystems, thereby polluting surface waters and groundwater.

Aquaculture Production

Demand for fish and shellfish for food, feed and other products has grown faster than for any other agricultural commodity in the last several decades. Wild fish catches plateaued in the 1990s and all increases in fish production, therefore, have derived from aquaculture, which has expanded dramatically and now produces nearly half the total quantity of fish consumed. Total

global aquatic animal production reached 167 million tonnes in 2014 (FAO, 2016b), of which an estimated 146 million tonnes was consumed directly by humans.

Overwhelmingly, the growth of aquaculture has taken place in developing countries, which produce 91 percent of global output; the greatest concentration of aquaculture is in low-income developing nations. Asia is by far the larger producer of aquacultural output, with almost 90 percent of world production, with output from China dominating at 45.5 million tonnes per year (FAO, 2016b).

There has also been a steady increase in the proportion of fed species in aquaculture that require externally produced foods; this form of production accounts for 70 percent of total production, compared with 50 percent in 1980. Fed and intensive aquaculture can result in export of faeces, uneaten feed and drugs to water bodies. Carnivorous species are of high value in aquaculture, and these require large inputs of fishmeal and other pelleted feeds. Many types of non-fed aquaculture (e.g. mussel farming) can filter and clean waters, but other types (e.g. intensive caged crab culture) may disrupt natural nutrient cycles and result in the degradation of water quality.

Market pressures and differentiation are increasing the intensity of production and leading to increased concentrations of single species. These trends have resulted in an increase in the use of medicines (e.g. antibiotics, fungicides and anti-fouling agents), which in turn contribute to downstream pollution.

Discussion

Agricultural pollutants: sources and effects

Major agricultural contributors to water pollution (and the main targets for water-pollution control) are nutrients, pesticides, salts, sediments, organic carbon, pathogens, metals and drug residues. The importance of different forms of agricultural pollution varies with individual situations, and negative impacts such as eutrophication (which may include sediments, nutrients and organic matter) arise from combinations of stressors.

In crop production, water pollution from nutrients occurs when fertilizers are applied at a greater rate than they are fixed by soil particles or exported from the soil profile (e.g. by plant uptake or when they are washed off the soil surface before plants can take them up). Excess nitrogen and phosphates can leach into groundwater or move via surface runoff into waterways. Phosphate is not as soluble as nitrate and ammonia and tends to be adsorbed onto soil particles and enter water bodies through soil erosion. In livestock production, feedlots are often located on the banks of watercourses so that (nutrient-rich) animal waste (e.g. urine) can be released directly into those watercourses. Manure is usually collected for use as organic fertilizer, which, if applied in excess, will lead to diffuse water pollution. In many cases, too, manure is not stored in contained areas and, during significant rainfall events, it can be washed into watercourses via surface runoff.

Together with other stressors, high nutrient loads can cause the eutrophication of lakes, reservoirs, ponds and coastal waters, leading to algae blooms that suppress other aquatic plants and animals. Despite data gaps, 415 coastal areas have been identified worldwide as experiencing some form of eutrophication, of which 169 are hypoxic (WRI, 2008). The excessive accumulation of nutrients may also increase adverse health impacts, such as blue-baby syndrome, due to high levels of nitrate in drinking-water.

Insecticides, herbicides and fungicides are applied intensively in agriculture in many countries (Schreinemachers and Tipraqsa, 2012). When improperly selected and managed, they can pollute

water resources with carcinogens and other toxic substances that can affect humans. Pesticides may also affect biodiversity by killing weeds and insects, with negative impacts up the food chain. In developed countries, although considerable use of older broad-spectrum pesticides persists, the trend is towards the use of newer pesticides that are more selective and less toxic to humans and the environment and which require lower quantities per unit area to be effective.

New agricultural pollutants, such as antibiotics, vaccines, growth promoters and hormones have also emerged in the last two decades. These can reach water via leaching and runoff from livestock and aquaculture farms, as well as through the application of manure and slurries to agricultural land (OECD, 2012b). Residues of heavy metals in agricultural inputs such as pesticides and animal feed are also emerging threats. Today, more than 700 emerging pollutants and their metabolites and transformation products are listed as present in European aquatic environments (NORMAN, 2016). Agriculture is not only a source of emerging pollutants, it also contributes to the spread and reintroduction of such pollutants into aquatic environments through wastewater (re)use for irrigation and the application of municipal biosolids to land as fertilizers. An estimated 35.9 Mha of agricultural lands are subject to the indirect use of wastewater (Thebo *et al.*, 2017). The potential risks to human health posed by exposure to emerging pollutants via contaminated agricultural products needs attention.

Conclusions

Water pollution in agriculture is complex and multidimensional, and its effective management requires a comprehensive package of responses. Such responses need to act on key drivers of agricultural expansion and intensification, such as unsustainable dietary shifts and food waste and loss; limit the export of pollutants from farms; protect water bodies from agricultural pollution loads; and help restore already-affected water bodies. Responses for influencing both farm- and landscape-scale practices may include regulation; the use of economic instruments; education and awareness raising; cooperative agreements; and research and innovation.

The contributions of crops, livestock and aquaculture to water pollution are not well known, particularly in developing countries. Quantifying these contributions is essential if national governments are to understand the full extent of the problem and to develop meaningful and cost-effective responses. The polluter-pays principle cannot be applied if the source of pollution is unclear. A sustained research and modelling effort, supported by water-quality monitoring, is needed to better understand pollutant pathways and the links between pollution causes and effects.

The pathways of, and the health and environmental risks posed by, emerging agricultural pollutants such as animal hormones, antibiotics and other pharmaceuticals are growing areas of research that require more attention. For example, greater understanding is needed of the contributions of animal medicines to the increasing problem of antimicrobial resistance among pathogens. There are opportunities for more innovation in practices and technologies to reduce the use of nutrients and pesticides on farms and the movement of pollutants from farms to sensitive aquatic ecosystems. Research is needed to evaluate policies and instruments for reducing source loads and minimizing pollution along flow paths to the sea. More work is also required to quantify the effectiveness of different approaches in reducing the economic impacts of water pollution in agriculture.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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2.2.19. Effect on growth and development of *Eisenia foetida* of a broad spectrum herbicide

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Abstract

Eisenia foetida is one of the epigeas species used in the biodegradation of organic waste, favoring the availability of nutrients as well as the physical and chemical properties of soils.

Epigeas species live on the organic horizon or near the surface of the soil so they are affected by all the changes and disturbances that occur mainly because of the effect of fertilizers, herbicides and pesticides.

There are numerous studies that show the quantity of these products and the active matter that can appear in the vegetal products, as well as in waters, crops and soil, and scarce the studies on the effects in the fauna, provoked by these applications. In this paper we study the effect of a pesticide that presents in its composition N-Fosfonometilglicina on the fauna epigea composed by *Eisenia foetida*, in the experiment it is observed that the number of worms descends mainly after the application Of the herbicide although large numbers of adult individuals are kept at low dose, decreasing by increasing the dose against the witnesses. With regard to the variation of the earthworm biomass by the effect of the herbicide in relation to the number of individuals, it is observed that in all the variables studied glyphosate is a herbicide that at low doses does not affect the development of earthworms in the soil.

Keywords: Epigeas species, biodegradation of organic residues, herbicides and pesticides

Introduction

The culture of intensive cultivation has promoted the use of an increasing number of pesticides.

Agrarian intensification processes, coupled with a decrease in the amount of potentially arable land, have caused an increase in the amount of herbicide applied per surface unit (AEPLA, 2010), which considerably aggravates the problem. Environmental impact on soil fauna where earthworms are found. According to Boroukhovitch, (1992) the misuse of pesticides can cause bioecological problems and environmental pollution. Among the first mentions the elimination of natural enemies of pests and diseases, resistance to them, emergence of new species such as pests and elimination of useful fauna, among others.

The isopropylamine salt of N-(Fosfono methyl) Glycina is a non-selective, systemic action herbicide of broad spectrum and suitable for the control of many weed species in postemergence treatments to foliage. It is indicated that it does not act on the seeds nor is absorbed by the roots, as well as it is not of prolonged residual action and that it is not or acts like soil sterilizing herbicide.

In this context, the main objective of this work was to evaluate the effect of the aforementioned herbicide applied at different doses on earthworms and their different stages, as well as on the number and weight.

Methodology

For research, the same bed was used for the development of earthworms made from a mixture of rabbit dung and garden pruning residues mainly grass (1:3, V/V).

The substrate was placed in polyurethane containers 15 cm x 30 cm. Three of them were used as witnesses where 100 *Eisenia foétida* worms were added. Always performing three replicates per sample or application of herbicide in treatments. The application of a herbicide whose active principles is the isopropylamine salt of N-(Fosfono methyl) Glycina is performed. Applied to two doses at 2.5 and 5%. Watering was carried out each week to maintain the humidity between 70 and 75%.

At the end of the experiment, earthworm eggs, adult and juvenile worms were counted and weighed.

The respiration rate of the soil was determined by measurement of O₂ consumption due to soil microorganisms, used Respirómetros OxiTop-C (Roca-Pérez *et al.*, 2005), the incubation time was a maximum of 15 days at 20° C and in darkness.

Results

The side effects of glyphosate on soil wildlife are indicated to be non-existent or almost nil. Glyphosate is adsorbed and quickly fixed on the ground. The organic matter, the clay, the sediment and the sand contained in the soil, and the pH thereof, influence the process in a minimal way.

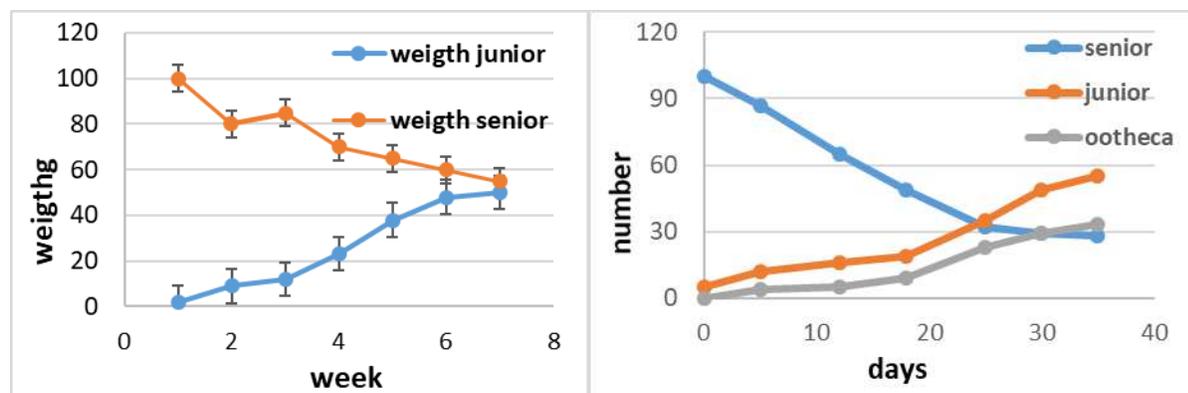


Figure 1. Weight and number of senior worms, juniors and eggs in samples

The adsorption of glyphosate correlates with the number of phosphate binding sites available, and appears to occur by ligation of the phosphonic acid fraction. In laboratory experiments in which glyphosate was added to aqueous sample suspensions, the adsorption coefficient K_S/L was 18 to 377 DM^3/kg .

The biological activity measured as the respiration rate of the microbiota soil is a parameter employed by several authors in order to determine soil quality. The results obtained expressed as the O_2 consumed in different incubation periods in the samples of the experiments studied are presented in table 1. The results obtained in the study of respiration expressed as the O_2 consumed in different incubation periods in the samples of the experiment are presented in table 1. The number of worms correlates with the biological activity and the dose of the herbicide.

Table 1. Respiration rate ($mg O_2 g^{-1}ss$.) of samples for different incubation periods.

Sample	Days of incubation		
	1	10	15
D2,5	718±47	3317±117	6874±323
D5	324±6	632±25	1499±12

Conclusions

Glyphosate is adsorbed and quickly fixed on the ground. Glyphosate affects adult worms, while young worms are easily adapted to the doses used. The biological activity of the soil is affected by the high doses of glyphosate, while at lower doses it is not affected.

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2.2.20. Mining and sustainability - a study case in Minas Gerais, Brazil

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Abstract

Mining practices nowadays are performed with the intention to be sustainable, however the sustainability is a real challenge, since the materials are not renewable; however, through sustainable practices it is possible to make it more sustainable. The study case refers to the disaster on the November 2015, where a large dam burst in the Fundão dam in the district of Bento Rodrigues, Mariana-MG, causing 19 dead, hundreds of homeless families and contaminating with heavy metals a distance of 680 km until the ocean. Two years after the disaster the environmental, economic and social problems still persists. The recovery will need to include a wide range of technologies that can stabilize and rebuild the minimum ecological conditions necessary to restore the resilience of the environment. This study highlights the main points in which mining could improve their approach to become more sustainable. A series of sustainable development goals are attempted to cover be supported here, goal number 15 about land and diversity restoration, goal number 6 of improving water quality through reduction of pollution, goal number 12 about supporting sustainable consumption and production patterns by information and awareness campaigns, encouraging companies to adopt sustainable practices

and disrupting the consumers perception. In the CEFET, Brazil, a research project is performed on this subject, in cooperation with the Leuphana University in Germany. Now an awareness campaign is being launch on the socio legal and environmental problematic, different alternatives to food security are being proposed and a test site is being implemented for phytoremediation in order to remove the heavy metal contamination and restore the soil. This study shows proof of the global responsibility, states the most important factors towards mining sustainability and proposes alternatives for phytoremediation from an ecological and economically point of view and gives some preliminary results.

Keywords: Minas Gerais, Land Restoration, Phytoremediation, Social awareness, sustainable consumption, pollution reduction, Biomass valorization.

Introduction, scope and main objectives

On November 5, 2015, 34 million cubic meters of iron ore tailings were dumped from the mining complex operated by Samarco after the rupture of the Fundão dam. This episode represented the greatest environmental catastrophe in the history of Brazil, one of the most impacting in the world, bringing environmental consequences in the human, water, soil, fauna and flora of the region directly and indirectly affected. Carmo *et al.* (2017) reports that since the beginning of the operation, in 2008, the Fundão dam had presented several anomalies related to drainage construction defects, upwellings, mud and water management errors and saturation of sandy material.

Brazilian Institute of the Environment and Renewable Natural Resources -IBAMA reported that thousands of fish and other animals died, including endemic and other species in the list of endangered animals (ICMBIO 2016). Also, several studies have shown that both water and sediments present high levels of heavy metals, such as Fe, Mn, Cd, As and others (IBAMA 2015; Embrapa 2015; Maia 2017; IGAM 2018).

Soils contaminated with heavy metals have been studied intensively and it has been identified that some plant varieties degrade toxic compounds in contaminated soils (EPA, 1999, Dushenkov *et al.* 1999; Watanabe, 1997, Szczygłowska 2011; Schneider 2016; Newman *et al.* 1997, Volk and Daley 2016; Wu *et al.* 2011) and for the reconstruction of the fertility and ecological functions (phytoremediation) (Robinson *et al.* 1998; Wong 2003; Stumpf *et al.* 2014)

The recovery strategy that is proposed here includes social, environmental and economic contributions so that at least part of the ecosystem could be rebuilt and restore the resilience of the environment. This study wants to make a holistic visualisation of the problem in a disaster area and for that, an academic alliance between two universities and the community is proposed. The social and legal part is being studied through an awareness campaign that allows reclaiming the social responsibility at a global scale, the environmental part is being analysed by a screening of the best plants to remediate the land and the economical would be a powerful driver in which get interested the mining industry into remediation since it visualize the best way in which the resulting biomass could be valorised. Additionally, this approach presents a pedagogical exercise in which two seminars of two educational institutions collaborate in working packages with the intention of defy together the problem of sustainability of mining after a disaster. The students worked together with their lectures towards the mobilization for the social reintegration of the affected residents and alternatives for the recovery of the areas affected by the disaster.

Methodology

During the winter term of 2017-2018, an interdisciplinary group of students from the Leuphana University together with their lecturer from the discipline “Mining and sustainability” worked together in order to visualise the best way to support the community in Minas Gerais after two years of the disaster. The case of the disaster was no longer talked of and it was important to launch an aggressive awareness campaign that reopened the case of the dam burst in MG, the information regarding the disaster was gathered and documented in the form of a webpage, some stickers were printed and distributed. Strategies were drawn to make possible to establish a relationship between the minerals extracted in Brazil and the everyday consumer items following the supply chain of the minerals. There was a launching awareness party, an online social media campaign and the participation in a Conference week at Leuphana University. The best available technology for land remediation was looked at, by interviewing experts, literature review and the preliminary results from this study allowed to produce a tentative screening list of the best phytoremediation plants for the region. Finally, the best economic and environmental alternative to utilise the biomass produced after the remediation was proposed.

Between 2016 and 2017, students of the Environmental and Sanitary Engineering of the Federal Center of Technological Education of Minas Gerais, during the discipline "Recuperation of Degraded Areas", made visits to the site of the disaster. As evaluation activities, the students carried out works covering the environmental aspects (collection and physical-chemical analysis of tailings samples, evaluation of three different species of grasses for vegetation recolonization with generation of income to the families of those affected and elaboration of Environmental Recovery Plan) and socio-economic: video presenting the interviews with the affected residents and authorities of the municipality of Mariana-MG, Exhibition of photographic material produced by the students during the visits to the site of the disaster and production of a technical report sent to Leuphana, who subsidized the realization of awareness campaign.

September 2016 and January 2017, in campus I of CEFET-MG, municipality of Belo Horizonte an experiment was carried out, under normal environmental conditions. A 4 x 2 factorial scheme was used, with seedlings of three species of aromatic plants (*Chrysopogon zizanioides*, *Cymbopogon citratus* and *Cymbopogon winterianus*), transplanted in polypropylene pots, filled with tailings and fertilized with four doses of organic compost (0, 0.5, 1 and 2 kg), with or without *mycorrhizae*, with four replicates. These species were chosen for the potential of income generation, for the extraction of aromatic oils and for erosion control and retention of the tailings, preventing them from continuing to sediment the rivers of the Rio Doce watershed. The iron ore tailings were collected in the district of Bento Rodrigues, municipality of Mariana-MG, approximately nine months after the rupture of the Fundão Dam. The organic compound was produced with residues from the preparation of the meals of the restaurants of campuses I and II, CEFET-MG, in the second half of 2015 (Figure).



Figure 1. Plants with potential for recovery of degraded areas and production of essential oils

Results

The case of the disaster in Minas Gerais, was re-open in direct communication person to person and to a broad public in Germany by an exhibit party and a student's conference week, where posters of the tragedy were exposed and talk about. Additionally, a social media campaign was launched, using diverse platforms using technologies of the information. A special webpage, Facebook and Twitter pages were design, which collected information about mining in general and the disaster in Minas Gerais in particular. The webpage may be accessed in the following link: <https://samarcodisaster.jimdo.com>. The platform is setup to contribute in the sensibilisation of the consumers, the government and ultimately the companies involved in mining and start an open conversation on the topic of Mining and sustainability. Stickers were created and sent to different parts of the world to serve as a silent propaganda that instils curiosity to learn more about the mining conflict.

The prospection of the best hyperaccumulators gave as interesting plants for this particular region temperature the following plants: *Brassica juncea*, which is reported to extract Cadmium, reduce 28% of Lead, up to 48% Selenium and Zinc, Mercury and Copper (Dushenkov *et al.* 1999; Szczygłowska 2011). *Vetiveria zizanioides* that is a hyper accumulator good for removal of Lead and Cadmium (Schneider, 2016; Saeb *et al.* 2015; Khan 2006, Roongtanakiat 2008, Wu 2010). For multi-element contaminated soils the *Helianthus annuus* showed a high extraction capacity independent of the inoculation with bacteria while the phytoremediation of *Agrostis capillaris* was very high in combination with microbial consortia (Langella *et al.* 2014). **Error! Reference source not found.**

Figure 2 proposes a long-term reclamation plan involved the characterisation of the soil, prospection and selection of the best plants for phytoremediation. The growing of the plans in a greenhouse and posterior field planting. Depending on the type of chosen plant, the technique would be phytostabilisation or phytoextraction. The phytoextraction involves the harvesting of the biomass and have various possibilities, amongst them: the cultivation of plants with capacity to produce essential oils to be used in the cosmetic industry; to dry and chipped the biomass and posterior pyrolysis process for producing energy generation gas, leaving the char with the heavy metals, which could be recovered by smelting process and another part to be Terra Preta. Another possibility could be for the biomass to be composted to reduce the volume and extract the metals, which would be leached and posterior smelting process, leaving another part of the biomass as a

fertiliser. Additionally, it is important that the mining companies design a strategy to collaborate with the local farmers to support this method as parallel industry to mining. This way the farmers will become the guardians of the land and the miners will get incentives for sinking carbon dioxide and land remediation.

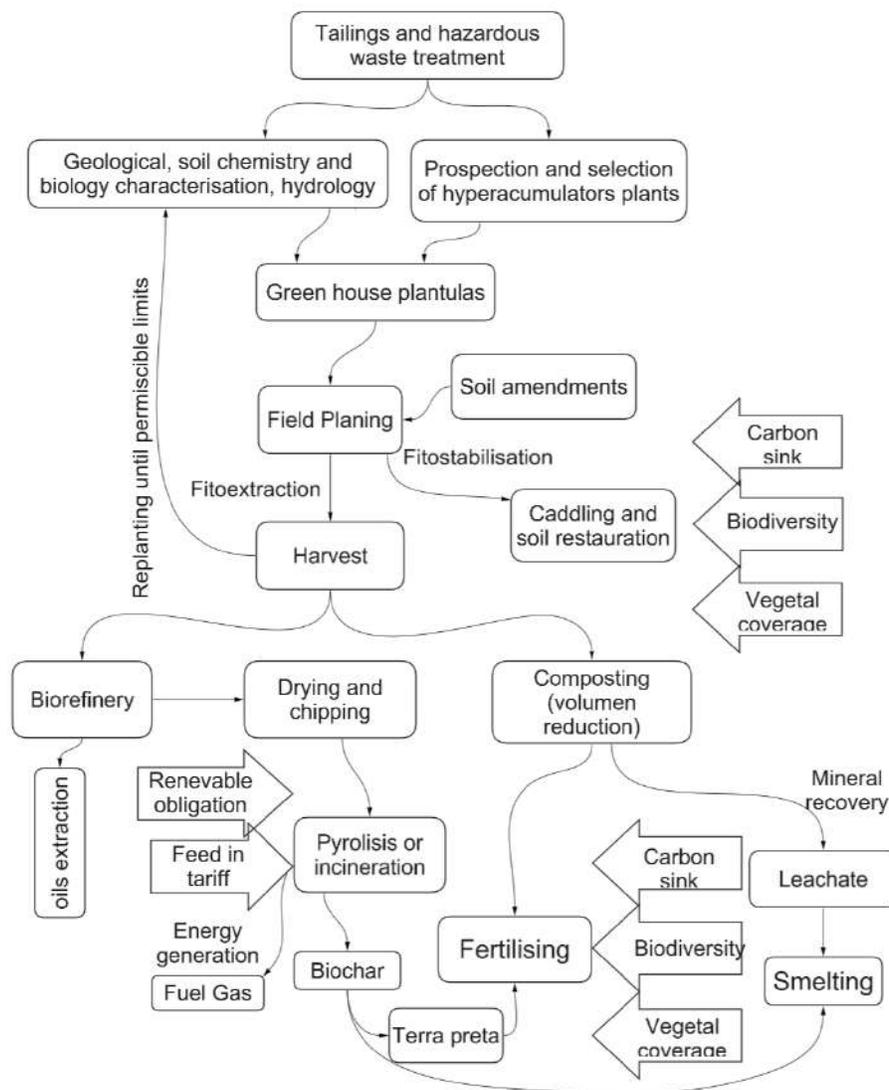


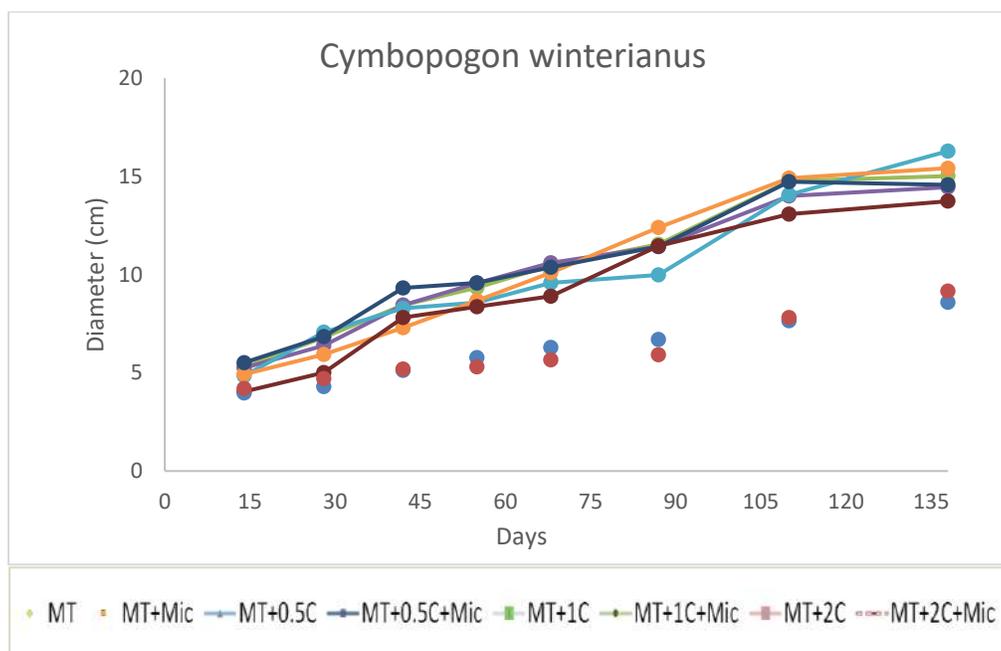
Figure 2. Best available technology for land remediation on Minas Gerais

The samples presented a granulometric composition of: 89, 22; 7,04; 3,74 % of sand; silt and clay, respectively. The chemical analyzes are presented in Table 1.

Table 1. Chemical analyses of samples of iron ore tailings from the dam of Fundão, Bento Rodrigues district, Mariana-MG, Brazil, collected in August 2016.

Tailings sample	Content	Unit
pH (H ₂ O)	8,0	
H + Al	0,64	cmolc/dm ³
Al ³⁺	0,03	
Ca ²⁺	1,06	
Mg ²⁺	0,02	
Na	0,22	
P	9,8	
K	12	
Cu	0,90	
Mn	176,40	
Fe	164,10	
Zn	1,8	
Organic Matter	1,06	dag/kg
C	0,62	
N	0,06	

The use of organic fertilization aided the development of species *Cymbopogon winterianus* and *Chrysopogon zizanioides* (Figure 3, Table 2). However, the species did not show good development (data not shown).

**Figure 3.** Biomass productivity as growing diameter for of *Cymbopogon winterianus* with time. MT: tailings mixtures; Mic: Mycorrhizae; Dosis of organic compost: 0,5C; 1C and 2C

The analysis of variance showed a significant effect ($p < 0.05$) of the doses of organic compound in relation to the treatment with the rejects only, but there was no significant difference between the doses with compound for Vetiver plants (*Chrysopogon zizanioides*). However, for the

parameters analyzed, no difference was observed regarding inoculation with the mycorrhizal cocktail (Table 2).

Table 2. Cumulative growth of Vetiver plants (*Chrysopogon zizanioides*)

Mycorrhizae	Compost's dosis (kg.pot ⁻¹)	Diameter (cm)	Number of tillers	Height (cm)
No inoculated	0	13,65 b	2,25 c	78,15 b
	0,5	15,67 ab	6,25 b	128,825 a
	1,0	17,31 a	10,25 ab	128,225 a
	2,0	17,90 a	10,75 a	144,475 a
Inoculated	0	11,99 b	3,00 c	77,45 b
	0,5	14,36 ab	6,75 b	111,35 a
	1,0	15,65 a	6,25 ab	145,2 a
	2,0	16,71 a	8,5 a	159,525 a

Note: Equal letters do not differ by Tukey's test ($P < 0,005$)

Discussion

Worldwide environmental problems could only be tackled successfully through international cooperation. The most important legally binding agreement is still not in force and corresponds to the protocol on civil liability and compensation for damage caused by the transboundary effects of industrial accidents on transboundary waters recognized in Kiev, 21 May 2003, which, after ratification, would ensure compensation and address physical damage, damage to property, loss of income, the cost of reinstatement and response measures (United Nations 2003).

The company responsible for the dam burst is Samarco Mining, which is a joint venture of the two mining giants BHP Billiton and Vale SA. Parents companies however are not legally liable for the mistakes of the subsidiaries. However, through responsible consumption is it possible to encourage the consumer to an ethical consumption. The investigations of this research exposed the link between the Brazilian ores and Germany imports. Between 2013 and 16, Germany imported 39% of Iron ores from Brazil (Ober 2018) and in 2017 imported 7 million metric ton of steel by 2017 (Global Steel Trade Monitor 2017). The ThyssenKrupp provides steel for several manufacturer industries in Germany, interestingly the majority of its iron comes from Brazil (Kier 2017). It is however not possible to establish clear links to allow to trace down the connection from manufactures to the ores from the broken dam. This is because it is a general practice to mix the ores, making it impossible to trace the origin. However, ThyssenKrupp and Vale have joint ventures (Handelsblatt 2016). Kier, also reports that in 2017, Volkswagen awarded ThyssenKrupp for their commitment as a supplier. Public image is a strong motivator for companies to become more sustainable. On February 2018, the Health Ministry reported 545 cases of yellow fever, which lead to the death of 164 people, there are ongoing investigations on the possible link of the disease outbreak and the lost on ecosystem services of the region (AgenciaBrasil 2018).

The scheme proposed to long-term reclamation of the affected area involves first the characterization and the prospection of the best hyperaccumulators plants and phytoremediators (Figure 2). The preliminary plants presented has been selected taking into account that are plants that could thrive on the Brazilian tropical weather and additionally with the possibility to mix various crops: trees, bushes and grasses that also serve as vegetal cover for erosion and stabilization of the terrain.

The best economic alternative to utilise the biomass produced after the remediation step was studied, so that the economic barriers posed by the cost of remediation would be able to overcome. A function-orientated approach was adopted by focusing on the farmland, so that the community could reclaim their territory, the essential oils production would foster more the small farmer and the creation of a community union that will empower them.

It must be reinforced the idea of the phytostabilisation, as carbon dioxide sinking strategic policy. Therefore, governments should legislate accordingly to promote this focus instead of the biomass for energy, which receive several incentives such as feed in tariff and renewable obligation. The production the essential oils involve the extraction of the oils and posterior use of the biomass leftover.

The analysis of the conditions of the MT reported in Table 1 were low in nutrient contents (Ca, Mg, P, K) and organic matter, carbon and nitrogen are very low for the crops. Additionally, Arsenic and Cadmium are above the permissible limits as above noticed, according to (IBAMA 2015). The sodium content is also extremely high, typical of a saline soil. It can be observed in the pot experiment that the plants had a compromised development when grown only on the MT. The low levels of nutrients present in the tailings, as well as high levels of Fe, Mn and Na could have affected especially the species *Cymbopogon citratus*. The species *Chrysopogon zizanioides* showed the highest growth in the experiment in pots, even growing only in the presence of MT. *Chrysopogon zizanioides* is widely used in reclamation projects in degraded areas. This species is considered as one of the most versatile crops of the millennium based on its numerous qualities (Khan 2006; Wu *et al.* 2011; Saeb *et al.* 2015).

Conclusions and Recommendations

Sustainable mining practices need to have a heuristic approach on prevention of disasters but also on ecosystem remediation. Therefore, good practices such as community preparedness, consumption reduction, fair trade, supporting additional industries parallel to mining, investing on community education and health are necessary as well as managing the mining waste in environmental sound way, effective contingency plan and a compulsory insurance for the mining companies are necessary as a prevention measure so that in case of a disaster, the impact would be minimal.

After a disaster it is necessary the characterisation of the soil and water and remediation of the contaminated water and soil. The search for technologies for the recovery of degraded areas due to the rupture of the Fundão Dam and the deposition of millions of tons of iron ore waste in the Bento Rodrigues district is extremely relevant from the environmental, social and economic point of view. One of the most used techniques is the revegetation with pioneer species; however, its cost is very high, still more in the immense area affected. Thus, the use of less fertile plants, associated with the use of low cost fertilizers, such as composting of urban or rural organic waste, can make a significant contribution to the gradual recovery of the recovery potential of that area. The *Chrysopogon zizanioides* to field in local disaster conditions is suggested, helping to control soil erosion and can generate economic income for the affected residents.

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2.2.21. Soil pollution and children in rural and urban areas

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Abstract

The risk of potential toxic chemical elements in the soils of schoolyards could be important, because these elements can enter human body via skin, mouth or nose. The concentration of toxic chemical elements in the soils of schools of Mashhad city was investigated in this research. A statistical population of 20 schools from different parts of urban and rural areas of Mashhad were selected. Three mixed homogenized soil samples were randomly collected from each school and the concentrations of metals were measured in those samples using an ICP-OES instrument after dry acid digestion. It is found that the main metal composition of the soil is nearly constant for all of the schools, while there are differences in minor metals such as Pb and As concentrations between urban and rural areas. These differences are mostly because of different land-use and activities in urban and rural areas, namely transport (Pb) and agricultural activities (As).

Keywords: Mashhad, soil, contamination, metal, urban, rural, school

Introduction, scope and main objectives

Soil is one of the important components of the environment in rural and urban areas. Mining and related activities, industrial waste resulting from the production of various materials such as pesticides (insecticides, herbicides etc.), household waste and the use of sewage sludge as fertilizers can cause contamination of agricultural land and urban soils to heavy metals. Apart from the natural discharge of heavy metals into soils, there are numerous anthropogenic sources and activities releasing heavy metals into the soil. Nevertheless, in general, five major sources of soil pollution include mineral extraction and mining, industrial-agricultural activities, atmospheric sediments and waste products (Hamidian, 2018).

Heavy metal contamination not only directly affects the physical and chemical properties of the soil, but also reduces biological activity of soil. The biological nutrient uptake in soils poses a serious risk to human health, especially to children, through entry into the food chain and causes environmental health risks through penetration into groundwater (Hamidian, 2017). Nerve disorders (Parkinson's, Alzheimer's, depression, schizophrenia, various types of cancers, nutrient deficiencies, and disturbance of hormonal balance) are the effects of heavy metals entering the human body. On the other hand, school playgrounds should provide safe and secure environment for children and students. More than thousands of students and children are spending their education in schools and other places in the country. They suck up the soil and sometimes eat snacks even after touching the soil. The risk of potentially toxic elements for children is very important because these elements enter the body through the skin, or breathing (Namavar and Salehi, 2018).

The application of metals in various industries, agriculture and household has led to an increase in the concentration of these contaminants in various terrestrial and aquatic ecosystems. It directly contaminates soil and indirectly poses health risks to the consumers of agricultural products (Chitsaz *et al.*, 2016).

This research was conducted by selecting a statistical society consisting of 10 elementary schools scattered randomly in rural areas of Mashhad and 10 elementary schools located in Mashhad city. The purpose of the study was to investigate and compare the soil pollution in urban area, dominated by industries and municipal activities, with rural areas, which are mostly dominated by agricultural activities.

Methodology

Study area

Mashhad is a metropolis in northeastern Iran and is the capital of Khorasan Razavi Province. Mashhad with an area of 351 square kilometers is the second largest city in Iran after Tehran. The city of Mashhad has spread over the Kashafrud river basin and in Mashhad plain between the mountains of Hazrat Mosque and Binaloud. The city of Mashhad has a changing climate, but it is mild and temperate and has warm and dry summers and cold and humid winters. The height of the city from the sea level is about 1050 meters (maximum 1150 meters and at least 950 meters).

Sampling

Soil samples were randomly collected from 10 primary schools throughout Mashhad and 10 primary schools in rural areas around Mashhad. Three sampling locations were selected randomly in each school. From each location three samples were collected in sunny days and the samples were mixed together in order to obtain three soil samples from each school. Samples were collected from the surface with 5-10 cm depth. The samples were dried and sieved, then transferred to the laboratory of environmental pollution in the University of Tehran (Hamidian, 2014).

Total concentration of metals

After transfer to the laboratory, soil samples were air-dried and passed through a 2 mm sieve. To determine the total concentration of metals in soil samples, the samples were then weighed and ashed. The ISO 11466 method was used for sample preparation. First, 1 gr of each sample was added into an Erlenmeyer flask, and then 3.5 ml of nitric acid and 10.5 ml of hydrochloric acid (aqua regia method; ratio 1:3) were poured into the flask, and the liquid was kept at laboratory temperature for 16 hours. Afterwards, the liquid was placed for 2 hours in an oven at 130°C and then passed through Whatman filter paper grade 42. Afterwards, the volume of solution was increased to 50 ml with nitric acid 1%. The blank and recovery samples were simultaneously prepared. The metal concentrations were measured using ICP-OES (VARIAN, 725-ES) device (Dalvand *et al.*, 2016). The chemical experiments were conducted in the laboratory of environmental pollution of the University of Tehran.

Results

The statistical society was selected somehow to illustrate the distribution of the mineral pollutants throughout the urban and rural areas of Mashhad in order to predict the metal pollution and its distribution for the whole area. The Max and min metal concentrations in urban and rural areas of Mashhad are summarized in Table 1.

Table 1. The Max and min metal concentrations (ppm, dw) in urban and rural areas of Mashhad

		As	Ba	Ce	Co	Cr	Cu	Ga	La	Mo	Pb	Rb
Urban	min	N.D.	623	12	15	31	47	14	6	31	40	74
	Max	21	1041	67	22	193	121	21	48	36	125	115
Rural	min	6	588	8	14	32	39	14	8	30	7	58
	Max	41	1102	92	28	341	115	24	71	34	34	121
		Sr	S	Sn	Sb	Th	V	W	Y	Zr	Zn	U
Urban	min	442	N.D.	N.D.	N.D.	N.D.	88	N.D.	38	142	36	N.D.
	Max	669	1421	29	29	3	117	31	54	212	135	N.D.
Rural	min	547	N.D.	N.D.	N.D.	N.D.	78	N.D.	32	141	68	N.D.
	Max	845	1654	27	24	4	162	30	58	214	628	N.D.

Discussion

The Pb containing particles from the exhaust of cars, will enter directly or indirectly (after rainfall or water runoff) into the soils. These mechanisms are the major routes of soil Pb pollution, especially in urban areas. The Pb concentration was significantly decreased by increasing distance from the roads. The Pb has serious effects on human poisoning, which especially affects the brain and nervous system. The children are more vulnerable to Pb poisoning and its damages. It seems that the agricultural areas are better off of highways and the related vehicles, air pollution and consequent Pb contamination (Panahi *et al.*, 2016).

In addition, the results of this study showed that the concentration of arsenic in sampling locations in some areas of the city of Mashhad is less than the limit specified by the US Environmental Protection Agency. From an environmental point of view, arsenic concentrations in rangelands are in the range of 0.1 to 222 ppm, which is higher than the range of N.D. to 41 ppm found in the current research. However, considering that long-term exposure to arsenic causes different types of cancerous diseases, arsenic contamination in terms of the general health and the well-being of children must be regarded as alarming and important. Considering the ability of some plants to prove the adsorption of arsenic, the use of new methods such as phytoremediation and expansion of green-space in urban and rural areas can be a good solution to remove arsenic from soil at high points.

The measurement of soil metallic compositions showed that the average percentage of major soil compositions in all schools was almost constant. The main percentages of soil compositions are silicon oxide (56%) and aluminum oxide (7%). The high percentage of calcium oxide was detected in comparison with other soil compositions such as pyrophosphate, mannoxide, titanium oxide, potassium oxide and sodium oxide due to the presence of two different soil types in the region, namely clay and calcareous. An increase in calcium carbonate content and its percentage of calcium oxide in the analysis up to 16% was due to the presence of calcareous soil in the sample. The clay consists of aluminosilicate compositions that contain various cations such as mycelium in their structure. For this reason, a strong dependence was found between the compounds of alumina oxide, silicon oxide and mannitrile oxide, and this is a reciprocal relationship between silicon oxide and the oxide monoxide and the direct between silicon oxide and alumina oxide (Alloway, 1995).

The well-known dependence between di-sodium oxide, ferric oxide, and manganese oxide and titanium oxide compounds are thought to be due to the replacement of various cations in the crystalline structure of the soil. The dependence of di-sodium oxide on all of these compounds is reversed. Calcium oxide and Aluminum oxide also have a strong reverse correlation, due to two different types of soil. By increasing the percentage of clay in the sample, the concentration of

aluminum oxide increases and vice versa. With increasing calcium content in the sample, the concentration of calcium oxide increases.

Concentrations of barium, strontium, zirconium, zinc, vanadium, chromium and copper are about one to two degrees higher than other heavy metals. In addition, the dispersion of these metals in different samples of each elementary school is very high. The concentration of arsenic in different locations is very different. For example, the average arsenic concentration in five primary schools is higher than the standard of 12 ppm and in the rests is lower. The average barium concentration in all schools is about 1.8 times higher than the standard. Chromium concentrations were lower than standard only in two primary schools and in the rest of the schools contained a concentration of 2.3 times higher than the standard value. The concentrations of copper in seven schools were lower than the standard and in other classes of primary schools about slightly twice higher than the standard.

The mean concentration of vanadium in all primary schools is about 3 times lower than the standard. Zinc concentrations were higher than the standard only in one elementary school. Molybdenum concentration in all samples from different primary schools is about 6 times lower than the standard. Antimony concentrations were detected in all schools below the standard levels.

Conclusions

According to these measurements and statistical analysis, it can be concluded that the main cause of soil contamination of some schools is the arsenic of agricultural activities. Low concentrations of lead in rural areas and its high concentrations in urban areas of Mashhad is due to traffic congestion highlighted that the transportation has not created any threat to the environment of the rural areas, but is a serious threat in urban areas. In addition, the geological structure of the region also contributes to the presence of copper and is relatively high up to approximately twice of the standard in some schools.

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2.2.22. Arsenic contamination in groundwater in parts of West Bengal and elsewhere in India and its influence on the water-soil-plant-animal-human continuum due to the entry of the toxin in the food-web

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Abstract

Widespread arsenic contamination in groundwater in West Bengal (India) and Bangladesh has remained mostly confined to the Bengal delta basin, bound by the rivers Bhagirathi and Padma. However, spread (detection) of groundwater arsenic contamination has been reported from several states of India, as well as certain other parts of the Indian subcontinent. Whereas the safe limit for arsenic in drinking water has been prescribed by the World Health Organization (WHO) to be $10 \mu\text{g L}^{-1}$ (with the permissible limit in India and Bangladesh being $50 \mu\text{g L}^{-1}$; recently revised), arsenic contamination in the groundwater to the tune of 50 to $3700 \mu\text{g L}^{-1}$ has been reported from the states of West Bengal, Assam, Bihar, Uttar Pradesh, Madhya Pradesh, Manipur, Jharkhand, Chhattisgarh, Punjab, Tripura and Nagaland.

The source of such arsenic contamination in groundwater is believed to be of geogenic origin. However, large-scale withdrawal of groundwater to support the irrigation of summer (*boro*) paddy during the lean period (January-May) is believed to play a role. Primary attention so far has been primarily directed towards solving the problem of contaminated groundwater-based drinking water, *notwithstanding* the fact that the groundwater in the affected belt is predominantly used in the agricultural sector rather than for drinking purposes. Despite these, large number of systematic studies is yet to be conducted to explore the influence of arsenic in groundwater, used as irrigation source, on soil-plant-animal continuum. It is only rather recently (during the last 15 years or so) that interdisciplinary, inter-institutional studies, led by Bidhan Chandra Krishi Viswavidyalaya (BCKV), West Bengal, India as well as others have given important leads as to the source of this toxin in groundwater, its accumulation in soils and crops grown in the affected belt of West Bengal and in the animal tissues and products in the area of study. However, much more research work remains to be done in this field, especially in the other parts of the affected belt mentioned above. This issue assumes particular importance in view of the fact that what remains essentially a *point-source* of contamination, as in the case of drinking

water, becomes a *diffuse-source* of contamination of uncertain extent and spread when arsenic finds its way into the human food-web through the contaminated groundwater being used for agricultural irrigation, coupled with the possibility of *bio-magnification* up in the food-chain. The present talk has examined these aspects along with the mitigation options. The present article has made an attempt to take stock of this issue of considerable and long-standing environmental impact, as well as the appropriate mitigation options.

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Sub-theme 3.1: Monitoring soil pollution

3.1.1. Assessing arsenic distribution and metabolism genes abundance in soils from Pakistan

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Abstract

Microbe-mediated arsenic (As) biotransformation in soils determines the fate of As in soils and its availability in food chain, yet little is known about the metabolism genes involved in As biotransformation. The objectives of the study were to determine the level of As and its species, abundance of As metabolism genes and their relationship with soil physicochemical properties from the different sites of Punjab and Sindh province Pakistan. As was significantly different among different sites. The higher concentration of inorganic As was recorded at the site M4 (Multan) (34.50 ± 5.50 $\mu\text{g}/\text{kg}$), mono-methylated As at the site A4 (Agriculture) (2.55 ± 0.46 $\mu\text{g}/\text{kg}$); di-methylated As at the site S5 (Sialkot) (2.19 ± 0.32 $\mu\text{g}/\text{kg}$) and Tri-As at the site M5 (Multan) (1.86 ± 1.15 $\mu\text{g}/\text{kg}$) as compared to other sites. Comparison among different sampling locations revealed that Rawalpindi has more As level than the Sialkot, Karachi, Multan and Agriculture areas. The higher abundance of *arsM* and *arrA* genes were recorded at the R1 site; While *arsC* gene abundance higher at the site A4. Redundancy analysis (RDA) results suggested that methylated As species in soil occur due to microorganisms, and As methylation in soil was influenced strongly by the soil physicochemical conditions. The results will be helpful to develop management strategies of these sites.

Keywords: As, Soil, Biotransformation Genes

Introduction, scope and main objectives

Arsenic (As), a ubiquitous toxin originating in the environment through natural processes and anthropogenic activities (fertilizers and untreated poultry manure) posed worse impacts on the soil quality and public health. As can generally occur in four oxidation states as arsine (-3) As^{-3} , arsenic metal (0) As, arsenite (+3) As^{+3} , and arsenate (+5) As^{+5} . Methylation of As in soil influences its behavior and transfer into food chain, but little is known about the factors affecting As methylation. As metabolism includes dissimilar forms of genes encoding proteins helping the transportation and biotransformation activities (Xiao *et al.*, 2016). Primarily, As metabolism genes consisting of four types: *aio* genes (As(III) oxidation), *arr* genes (As(V) respiration), *ars* genes (As(V) reduction related), and *arsM* genes (As(III) methylation) (Yin *et al.*, 2011). Although As biotransformation mechanisms have been well studied in microbial pure cultures (Ye *et al.* 2012) and distribution, diversity and abundance of genes responsible for As metabolism in paddy soils (Zhang *et al.* 2015), but there are scarce information regarding soils. High concentration of As in water over Pakistan has been well documented (Podgorski *et al.*, 2017). However, there is scarce information regarding the distribution of As ($\mu\text{g}/\text{g}$) and metabolism genes in soils from Pakistan. The objectives of the study were to determine the level of As and its species from different sites of Punjab and Sindh province Pakistan; to understand the As metabolism genes in soil and the relationship between soil physicochemical properties, As species and metabolism genes.

Methodology

Pakistan is the second largest South Asian country, which is located within latitude 24° to 37°N and longitude 62° to 75°E (table 1). Few studies had been done in Pakistan to screen the soil contamination levels in various ecological matrices. However, there is scarce information of soil As contamination from Pakistan. Punjab (Sialkot with sites S1-S5, Rawalpindi with sites R1-R5, Multan with sites M1-M5 and Agriculture areas with sites A1-A5) and Sindh (Karachi with sites k1-k5) provinces of Pakistan were selected for soil sampling because of industrialization, agriculture activities dumping sites of chicken manure and irrigation of As contaminated water. Soil samples were collected from the 0 to 20 cm depth with five replicates (500 g each subsample) through stochastic sampling technique was used for selection of different sites from Punjab and Sindh province on 15 August 2016 with soil auger. Soil samples were placed in sterile polythene bags and transferred to the test laboratory on ice. All samples at temperature of -20 °C were stored for DNA extraction. After being processed through a 2.0 mm sieve, the soils were used for subsequent analysis of chemical properties. For the analysis of total As content, 1.0 g freeze-dried samples was digested with 10 ml 1:1 aqua regia at temperature of 100 °C for 2 h with water bath. Solution was cooled and diluted to 50 ml and then total As was regulated by utilization of an Atomic fluorescence spectrometer (AFS-9130, Beijing Jitian Instrument Company, China). Spectrometry (HPLC-ICP-MS, NEXION300XX, PerkinElmer, Inc., USA) was used to determine the concentrations of As species. The freeze-dried samples were first separated using 10 mL orthophosphoric acid (2%) via ultrasonic extraction. HPLC separation of As species was done on an anion exchange PRP X-100 HPLC column (250 × 4.1 mm I.D., 10 µm, Hamilton, Reno, NV). The mobile phase consisted of 8 mM (NH₄)₂HPO₄ and 2 mM NH₄NO₃ at a pH 6.2 and run isocratically at a flow rate of 1 ml min⁻¹ for the entire 10 min. Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) was used to compute the As species at m/z (mass/charge) 75 corresponding to As using the standard techniques. The concentrations of the As species were estimated by combining the corresponding chromatogram peak ranges. Each sample was reiterated thrice with three HPLC injections. DNA was executed from 0.5 g of samples using the FASTDNA SPIN Kit for soil (MP Biomedicals, USA) as recommended by the producer's instructions. PCR amplifications of aioA, arrA, arsC and arsM metabolism genes were executed with the primers. The four replicates of DNA excuted were PCR amplified in 25 µl reaction mixtures (0.25 µl Ex Taq™ (Takara Bio Inc., Japan), 2.5 µl 10 × buffer, 2 µl dNTP, 1 µl each 10 µM primer pair, 1 µl DNA template (< 500 ng). The PCR thermal cycling parameters for genes were: 95 °C for 5 min followed by 40 cycles at 95 °C for 30 s, 60 °C for 35 s, 72 °C for 1 min; after the cycles the reaction mixtures were further incubated at 72 °C for 10 min. The abundance of aioA, arrA, arsC and arsM genes from forty (40) samples was projected using the primers illustrated above by quantitative real-time polymerase chain reaction (qPCR) executed on an iQTM5 Thermocycler (Bio-Rad, USA).

Results and discussion

Most of the soil samples were alkaline in nature collected from different sites of the Punjab and Sindh province, Pakistan. Soil texture was Sandy silty. Table 1 depicted the arsenic species for the different sites sampled from Pakistan. Results indicated that As species were significantly (0.01, 0.05) different among different sites. However, the higher concentration of iAs was recorded at site M4 (34.50±5.50 µg/kg), MMA at the site A4 (2.55±0.46 µg/kg), DMA at site S5 (2.19±0.32 µg/kg) and Tri-As at the site M5 (1.86±1.15 µg/kg) as compared to other sites. Comparison among different sampling locations revealed that Rawalpindi has more As level than the Sialkot, Karachi, Multan and Agriculture areas, suggesting it may be due to industrialization and dumping sites of chicken manure in this area. The other studies reported similar level of As (5.40 µg/kg) for paddy soil Khairpur (Baig *et al.*, 2011) and 98.3 µg/kg in soils from Khushab (Khan *et al.*, 2017),

Pakistan. However, reported in soil were lower for MMA from Bangladesh (0 µg/kg), China (1.3-2.3 µg/kg), UK (0 µg/kg) and US (14 µg/kg) reported by Zhao *et al.*, (2013). Baig *et al.*, 2011, reported higher level of TriAs (3.08-52.1 µg/Kg) from Khairpur, Pakistan.

Table 1. Descriptive statistics of As species (mean±S.E) of different soil samples (µg/kg)

Sites		Land use type	IAs	MMA	DMA	TriAs
	S1	Industrial, Urban, agricultural	5.94±0.05	0.32±0.02	1.01±0.02	0.62±0.02
	S2		15.23±0.23	0.14±0.01	1.50±0.06	0.00±0.00
Sialkot	S3		12.50±0.50	0.97±0.01	1.84±0.14	0.63±0.03
	S4		8.40±0.60	0.22±0.01	1.70±0.30	0.191±0.01
	S5		11.00±1.00	0.11±0.12	2.19±0.32	0.27±0.07
	K1	Industrial	15.54±0.47	10.13±9.88	1.53±0.48	0.47±0.07
	K2		14.14±0.17	0.10±0.10	1.20±0.20	0.27±0.03
Karachi	K3		4.55±0.46	0.35±0.50	1.84±0.17	0.28±0.02
	K4		14.03±2.03	0.40±0.01	1.72±0.28	0.58±0.02
	K5		13.49±0.51	0.38±0.03	1.69±0.31	0.69±0.04
	R1	Urban	25.00±2.00	0.22±0.02	1.25±0.18	0.28±0.08
	R2		18.50±0.50	0.20±0.00	1.50±1.00	0.30±0.25
Rawalpindi	R3		26.50±0.50	0.35±0.01	1.33±0.10	0.63±0.01
	R4		33.50±3.50	0.25±0.05	1.88±0.13	0.01±0.01
	R5		18.50±0.50	0.25±0.05	1.74±0.19	0.00±0.00
	M1	Urban, agricultural	28.50±3.50	0.23±0.03	2.02±0.02	0.00±0.00
Multan	M2		31.50±4.51	0.00±0.00	2.53±0.48	0.01±0.01
	M3		32.39±6.61	0.50±0.37	2.43±0.56	0.78±0.22
	M4		34.50±5.50	0.49±0.06	1.52±0.48	0.26±0.03
	M5		27.00±8.00	0.23±0.02	1.85±0.16	1.86±1.15
	A1	Agricultural	15.00±5.00	1.52±0.48	0.73±0.28	1.07±0.93
	A2		12.00±4.00	2.49±0.51	0.21±0.15	0.62±0.39
Agriculture areas	A3		15.50±1.50	1.84±0.17	0.78±0.22	0.00±0.00
	A4		24.00±4.00	2.55±0.46	0.82±0.18	0.77±0.21
	A5		18.00±2.00	2.00±0.00	0.00±0.00	0.35±0.31
	Total		19.01±1.31	1.05±0.40	1.47±0.09	0.44±0.07
	Analyses of variance		0.00	0.00	0.445	0.00

Biotransformation genes (arsM gene, aioA, arrA and arsC) results indicated that the genes abundance was significantly (0.01, 0.05) different among different sites. However, the higher copies number/g of arsM and arrA genes were recorded at R1 (5.44×10^4 , 9.00×10^3); While arsC gene 8.41×10^3 copies number/g at site A4 as compared to the other sites of Punjab and Sindh province. Zhang *et al.*, (2015) reported the abundance of aioA genes copy number in paddy soils from southern China was higher. Several factors influence the abundance of genes in soil such as As level, soil physicochemical properties, climate, soil aerobic and anaerobic conditions and water level tc (Zhao *et al.*, 2013). RDA indicated that arsC, MMA and EC were correlated at Agricultural sites; arrA correlated with OM; inorganic As was influenced by sand at Multan; aioA gene was correlated with pH, TriAs and clay at Sialkot and arsM gene correlated with DMA and silt at Sialkot and Karachi. The results were similar to the study by Zhao *et al.*, (2013) quoted that As

methylation concentration was found to be significantly correlated and non-significant correlation with the soil pH, but positively correlated with OM. The most important clusters of As oxidizing bacteria, i.e., the Rhizobiales and Burkholderiales in α -Proteobacteria and β -Proteobacteria, were typically rhizospheric bacteria (Zhang *et al.*, 2015). These microorganisms have been shown to contribute considerably to the As³ oxidation in soils under aerobic and anaerobic conditions (Jia *et al.* 2012). Previous studies suggested that the abundance of As³-oxidizing bacteria might rise As³ oxidation level to As⁵ in the rice rhizosphere, resulting in reduced As motion and bioavailability because As⁵ can be appropriated on Fe/Mn hydroxide/oxyhydroxide in rhizosphere soil and on rice roots (Ye *et al.*, 2012).

Conclusions

Present study providing baseline information for the As concentration in soils from different area of Pakistan as there has been no research work recorded in this perspective until now. The results obtained in present study established that significant variations of As species and abundance of metabolism genes in different soil samples were recorded. Soil physicochemical properties had obvious influence on distribution of As species. RDA results expressed clustering for OM and EC, which revealed the significant relationship for sandy and clay soil with aioA genes for paddy soil sites. The accumulation of As in soils rises by fertilization, which cause affect soil ecosystem and potential cause of cancer to human beings.

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3.1.2. Current hygienic state of agricultural soils based on soil monitoring system in Slovakia

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Abstract

The contaminants can reduce soil fertility, change the species composition of the flora and fauna, and endanger human health due to the enrichment of heavy metals in the food chain. Risk elements distribution on agricultural soils in Slovakia is evaluated in this contribution. The measured results have been obtained on the basis of soil monitoring system in Slovakia which is consistently running since 1993 year. Risk elements have been analysed in extraction by aqua regia (Cd, Pb, Cu, Zn, Cr, Ni, As, Se, Co) and Hg (total content using AMA analyzer). On the basis of the obtained results it may be said that the agricultural soils of Slovakia are not contaminated except some contaminated sites which are mostly situated on the industrial areas (anthropogenic impact) as well as on the areas situated under geogenic influence (mostly some mountainous regions). Their unfavourable state persists often a long period and agricultural land use of those affected fields is not recommended.

Keywords: soil monitoring, soil contamination, risk elements, Slovakia

Introduction, scope and main objectives

Conception of European soil policy and soil protection strategy, as well as its sustainable land use was established in the Proposal of the European Commission (EC) on the 6th Environmental Action Programme, which was accepted by European Council and the European Parliament on the 22nd of July, 2002, where one of the basic strategies is just soil and monitoring of its next development. The main aim of soil monitoring system is to obtain the knowledge of the most current state and development of soil properties according to main threats to soil including soil contamination. There are permanently monitored important parameters in connection to recommendation of EC for evaluation of current state and development of soils (van Camp *et al.* 2004). Monitored parameters are the basis for modeling and assessment of soil functions as well as for assessment of ecosystem services of agricultural land.

Governmental soil policy of Slovakia declares that the soil is and will be the basics of environmental, ecological, economical and social potential of Slovakia and therefore it must be carefully protected against damage. The new regulation concerning agricultural soils is the Act n. 220/2004 Z.z. on protection of agricultural soils and land use (MPRV SR, 2013) in effort to increase protection against degradation. Background soils contain native heavy metals concentrations plus an anthropogenic addition by the ubiquitous deposition resulting from diffuse heavy metal sources. The understanding of the potential risk elements behavior in the soil

system is one of the most important tasks in evaluation of their immobilization and transport. The objective of this study is the evaluation of current hygienic state of agricultural soils in Slovakia.

Methodology

The obtained results are evaluated on the basis of soil monitoring system in Slovakia, which has been running since 1993 year. Soil monitoring network in Slovakia is constructed on ecological principles and includes the important data of all main soil types and subtypes, soil substrates, climatic regions, emission regions, contaminated and non-contaminated regions as well as various land use. There are 318 monitoring sites on agricultural and alpine land in Slovakia. All soil monitoring sites are located in WGS 84 coordinates. The monitoring site represents the circular shape, with a radius of 10 m and an area of 314 m². The most important risk elements concerning soil contamination are included (Cd, Cr, Pb, Ni, Zn, Cu, Se, Co extracted with aqua regia) and Hg (total content – using AMA analyzer).

Results

The human influence on contamination of soils in Slovakia (former Czechoslovakia) was the most significant after the Second World War and especially during the industrial period in the second half of the 20-th century.

The geochemical anomalies occur mostly on volcanic and crystalline rocks, mainly in mountainous regions; this process is manifested in agricultural land with less intensity. The most extended areas of geochemical anomalies appear in Štiavnické vrchy, Low Tatras and Slovenské Rudohorie mountains. These regions are often characterized by high to very high concentrations of some risk elements, especially in all soil profile (Cd, Pb, Cu, Zn, As).

The distribution of risk elements on agricultural soils of Slovakia is given in the following tables 1, 2 and 3 and Figure 1.

Table 1. Content of risk elements (mg.kg⁻¹) extracted with aqua regia in agricultural soils (0 – 10 cm) in Slovakia

Elements Statistics	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg ¹
x	10.16	0.38	8.80	42.00	24.48	29.43	26.42	80.88	0.25	0.09
median	8.91	0.27	8.04	41.66	20.21	26.87	19.28	70.89	0.19	0.07
Xmin	1.00	0.07	1.00	0.99	0.39	0.24	3.45	19.80	0.04	0.01
Xmax	223.00	9.90	28.60	141.00	155.34	136.14	1238.00	1191.00	0.72	0.80
SD	7.14	0.39	4.15	19.47	14.97	14.21	37.79	46.34	0.11	0.06
Vc (%)	61.35	83.36	49.08	48.91	59.36	48.67	100.46	48.48	50.08	66.50
n	318	318	318	318	318	318	318	318	318	318

Explanations: x – arithmetic mean, Xmin – minimum value, Xmax – maximum value, Sd – standard deviation, Vc – coefficient of variability, n – frequency, Hg¹ – total content (AMA analyzer)

Table 2. Content of risk elements (mg.kg⁻¹) extracted with aqua regia in agricultural soils (35 – 45 cm) of Slovakia

Elements Statistics	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg ¹
x	9.55	0.41	10.02	42.87	23.09	32.10	22.70	71.22	0.21	0.05
Median	8.60	0.21	8.85	40.34	19.05	29.00	14.73	62.91	0.13	0.04
Xmin	0.77	0.01	1.00	1.99	1.33	0.29	4.10	3.80	0.02	0.01
Xmax	100.00	89.00	215.70	135.00	137.00	141.00	1941.00	1340.00	0.62	0.55
SD	6.40	1.57	7.36	21.50	14.93	16.64	45.41	44.24	0.10	0.04
Vc (%)	65.26	191.75	66.97	56.60	60.85	56.05	121.39	53.83	43.93	69.85
n	318	318	318	318	318	318	318	318	318	318

Explanations: see Table 1

Table 3. Average content of risk elements (mg.kg⁻¹) extracted with aqua regia in surface horizon (0 – 10 cm) of main soil types in Slovakia

Soils	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg ¹
FM	10.8	0.7	8.8	39.1	34.0	37.0	54.3	122.8	-	0.2
ČA	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.2	0.06
ČM	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.3	0.1
HM	9.2	0.2	10.0	41.5	22.9	32.6	19.7	68.8	0.1	0.05
LM+PG	9.9	0.3	9.7	42.8	17.0	23.3	24.2	66.7	0.2	0.07
KM	14.8	0.3	12.6	52.2	28.9	29.2	27.0	93.5	-	-
RM	3.4	0.1	2.0	19.5	17.0	12.0	7.7	41.0	0.3	0.03
RA	13.1	0.5	11.8	55.2	30.6	42.0	36.3	103.1	-	0.13

Explanations: FM – Haplic Fluvisols, ČA – Mollic Fluvisols, ČM – Chernozems, HM – Cutanic Luvisols, LM+PG – Albeluvisols and Planosols, KM – Cambisols, RM – Regosols, RA – Rendzic Leptosols, Hg¹ – total content (AMA analyzer)

Total content of the potential risk elements is one of the main parameter considered for soil sensitivity to the potential risk elements mobility. Distribution of soil contamination has been estimated as a surface contamination (Figure 1). Background levels of elements in soils depend on both the nature of the parent materials and on the soil texture since many elements are associated with the fine particles which have the ability to adsorb or form solid solutions with the element of interest. For this reason the values of the limits of soil potential risk elements according to Slovak Soil Law depend on clay fraction.

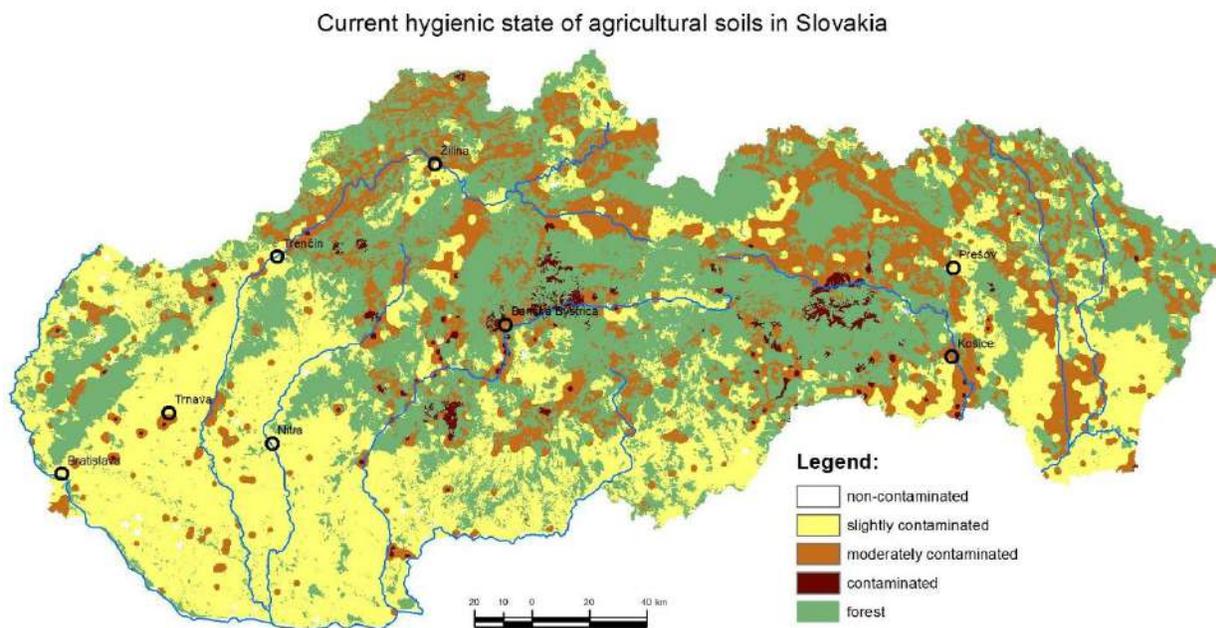


Figure 1. Current hygienic state of agricultural soils in Slovakia

The highest values of arsenic content occur on Cambisols especially with existence of geochemical anomalies (mostly Cambisols on granitic, metamorphic and volcanic rocks).

Average values of cadmium are the highest on Fluvisols (Table 3) as the result of its transport along the rivers where anthropogenic and geogenic influence can be mixed.

The variability of cobalt in the subsoil is higher opposite the topsoil. Finally, it may be said that anthropogenic input of cobalt in soils of Slovakia is not significant.

Difference of chromium content between topsoil and subsoil is very low. It means the content of chromium in soil profiles is even-tempered and reflects mostly the natural distribution of chromium in soils of Slovakia.

The highest concentrations of copper were determined in some Cambisols and Fluvisols (the areas with geochemical anomalies occurrence and alluvial deposits with accumulated soil-sedimentary material from those areas).

The average content of nickel is the highest on Fluvisols and Rendzic Leptosols (Table 3), what is in harmony with previous work (Čurlík, 2011).

The highest values of lead were determined in Fluvisols where Pb was often accumulated on alluvial deposits in lower part of rivers.

Zinc in conditions of Slovakia is common especially in areas with geochemical anomalies occurrence as well as in some alluvial deposits. The highest content of zinc was determined on Fluvisols – especially on alluvial deposits in lower part of rivers similarly as cadmium.

Selenium is characteristic with irregular distribution (Wedepohl, 1995) and low to high content in soils of Slovakia. Its occurrence is often common in soils on volcanic rocks. In individual soil

types exist evident differences in content of Se, while is indicated narrow relationship between soil forming substrates rich in Se and its content in soils (Čurlík, 2011).

Average content of Hg in agricultural soils of Slovakia is 0.09 mg.kg^{-1} what is the lower value than valid hygienic limit in Slovakia (MPRV SR, 2013). The high variability of Hg in evaluated soils of Slovakia is characteristic for this element (>60 %) (Table 1) caused by volatility of Hg.

Discussion

Distribution and behavior of risk elements in soils of Slovakia are often in harmony with other authors. Similar results were obtained also in soils of Czechia (Poláková *et al.*, 2011). Arsenic is an important component of arsenopyrite (FeAsS), which is the most extended arsenic mineral in Slovakia. Its migration in soil is limited (sorption with clay, hydroxides, oxides and with soil organic matter) – Čurlík, 2011). The distribution of risk elements depends on parent material, land use, soil type and potential source of elements origin (geogenic, anthropogenic, resp. mixed influence) (Wilcke *et al.* 2005). Concerning the measured values of risk elements presented in the Table 3 the slightly increased values of some risk elements (Cd, Cu, Pb, Zn) from among the evaluated soil types occur on the Fluvisols which could be transported from the catchments and accumulated on the alluvial deposits especially along lower parts of rivers (Kobza *et al.* 2014). Mean value of some risk elements on Cambisols could be also increased (As, Co, Cr, Cu, Zn) in areas influenced by geochemical anomalies. Unlike the soils with low to very low content of humus and clay fraction (Regosols) are characteristic with the lowest content of all risk elements, what it was already confirmed also in previous work (Wilcke *et al.* 2005).

Conclusions

In general, on the basis of our results it may be said that the hygienic state of agricultural soils in Slovakia is good except of some contaminated sites which are mostly situated in the industrial areas (anthropogenic impact) and in the areas influenced by geogenic impact – occurrence of geochemical anomalies (mostly mountainous areas). The area of contaminated agricultural soils is less than 1% of total area of soils in Slovakia. Their unfavorable state of these contaminated sites persists often a long period without significant change during soil monitoring period in Slovakia since 1993 year and therefore it will be necessary to monitor them also in the future.

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3.1.3. Source patterns of Zn, Pb, Cr and Ni potentially toxic elements (PTEs) through a compositional discrimination analysis: a case study on the Campanian topsoil data

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Abstract

This study presents a comprehensive discrimination analysis of four potentially toxic elements (PTEs) using the high-density Campanian topsoil data set. A workflow of compositional data analysis has been elaborated to identify their possible sources of contamination and enrichment. The investigated data set include 18 elements deriving from 3669 topsoil samples, collected at an average sampling density of 1 site per 3.2 km².

First, robust biplots and factor analysis were performed to get an overview of elemental associations and reduce the dimensionality of the data set. They revealed that the 4 PTEs belong to different groups. The multivariate regression analysis using alr-transformed (additive logratio) data proved the strong linear relationship between Fe, Mn (independent) and each investigated PTE (dependent), but also unveiled deviation trends in case of Zn and Pb.

Based on the multivariate regression result, a sequential binary partition was performed by means of 6 variables (the 4 PTEs, Fe, and Mn) to obtain balances. Balances are ilr-coordinates (isometric-logratio) which can be interpreted as ratios of specific groups of elements. They were used to generate interpolated map by using multifractal method to see spatial patterns and proportions of elemental associations.

A new index has been elaborated based on the bivariate regression of balances and their standardized residuals, which was particularly useful to identify and separate the sources of anthropogenic contamination and geogenic enrichment of respective elemental associations.

The large urban and industrial areas (e.g. Naples, Salerno) along the coastline are mainly contaminated by Pb and Zn due to heavy traffic and alloy production. Some Cr and Ni contamination was discerned in the Sarno Basin where the Solofra industrial district is likely to be the principal source through releases from tannery industry.

The large volcanic complexes (e.g. Mt. Somma-Vesuvius, Phlegraean Fields, Mt. Roccamonfina) are all characterized by geogenic enrichment of Zn and Pb. In contrast, Cr and Ni-geogenic enrichment is mainly related to the siliciclastic deposits.

Keywords: Campania Region (Italy), soil geochemistry, potentially toxic elements, compositional data analysis, discrimination index

Introduction, scope and main objectives

Geochemical survey aims to enhance mineralization and contamination through exploration and environmental geochemistry, respectively. For that, various geostatistical computations have been used to identify source patterns of different elements related to underlying geological features and/or anthropogenic activities (Cheng *et al.*, 1994, 1999; Lima *et al.*, 2003; Reimann and De Caritat, 2005). Graphical and statistical methods (e.g. classification using box-plots or cumulative probability plots) have been elaborated to study the elemental distribution and identify univariate outliers (Tennant and White, 1952; Sinclair, 1976, 1983; Kürzli, 1988; Reimann *et al.*, 2008). The detection of multivariate outliers using certain cut-off values on the Mahalanobis distance and observed covariance ratio were also successfully applied on compositional data (Bollen, 1987; Roosseuw and Van Zomeren, 1990; Filzmoser *et al.*, 2012; Buccianti *et al.*, 2015).

Background/anomaly separation by using various fractal methods (e.g. Concentration-Area) was given particular attention in mineral exploration, environmental health-risk analysis and regional topsoil studies (Cheng *et al.*, 1994, 1999; Agterberg, 2001; Lima *et al.*, 2003; Fabian *et al.*, 2014; Albanese *et al.*, 2015; Zuo *et al.*, 2015). In addition, the question of anthropogenic or geogenic origin has been always in the interest of investigations. Several indices have been invented to separate anthropogenic contamination from geogenic background values like Enrichment Factor (EF, Chester and Stoner, 1973) or Geo-accumulation Index (Müller, 1979). The critical reviews of these indices were made by Reimann and de Caritat (2005) claiming that their values vary and are dependent on the different parent rock materials and chosen reference media as well as reference elements. In addition, these indices do not take into account the different biogeochemical processes, which may have remarkable impact on elemental enrichment/contamination (Reimann and de Caritat, 2005).

In this study, the main objective is to identify the elemental associations and their interrelationships using robust compositional biplot and factor analysis on the high-density Campanian topsoil data set. In addition, a workflow of compositional data analysis has been elaborated to discriminate the possible sources of contamination/enrichment of Zn, Pb, Cr and Ni potentially toxic elements (PTEs). A new index has been elaborated based on bivariate regression analysis of balances (specific groups of elements) and their residuals, which was proven useful to reveal the sources and spatial patterns of the four investigated PTEs.

Methodology

The Campania Region is located in the southern part of Italy, covering an area of about 13,600 km² (Fig. 1A). The region is bordered by the Tyrrhenian Sea from the west, the Basilicata Region from the south, the Apulia Region from the east, and Latium Region from the north (Fig. 1A).

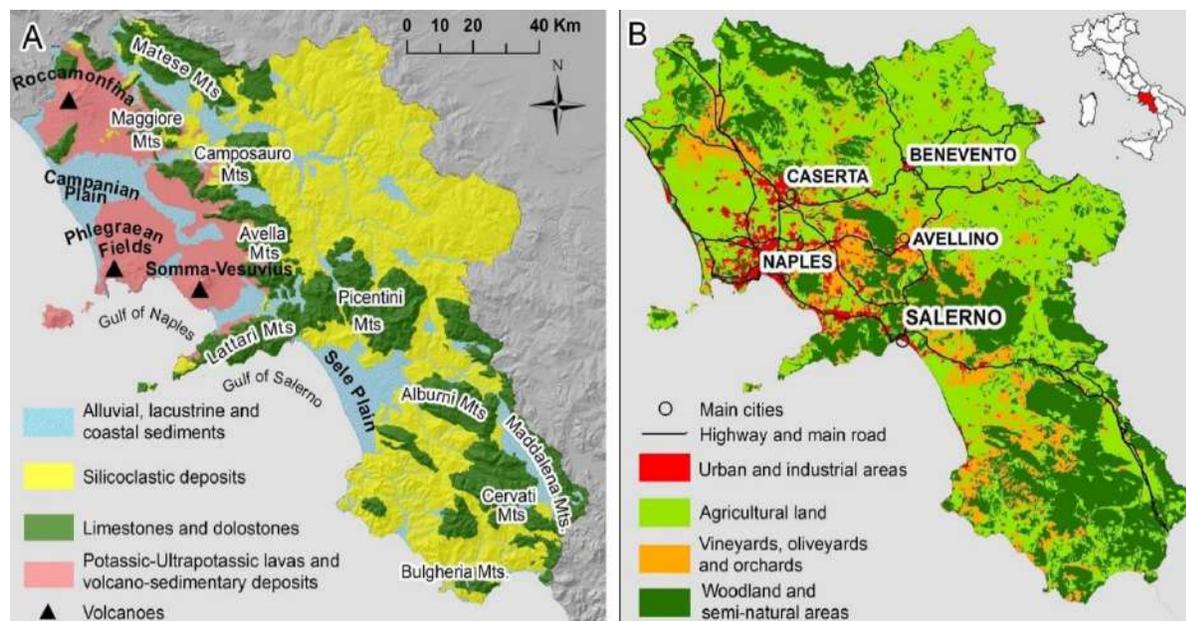


Figure 1. Simplified geological map (A) and land use (B) of the Campania Region (Italy).

Campania is one of the most populated regions of Italy with more than 5.8 million inhabitants (ISTAT, 2016). This high density of population is coupled with the presence of a large number of industrial activities, with the majority being involved in agriculture: vineyards and olive plantations - mostly in hilly areas - seasonal crops, and greenhouse products represent major resources for the region and the local economy (Albanese *et al.*, 2007). This intensive agriculture activity occupies more than 50% of the total land and occurs mostly in the coastal and mountainous areas, where fertile land is available (Fig. 1B). Unfortunately, such industrial activities are known to have a potential negative impact - if not properly managed - on the contamination of natural resources such as superficial and groundwater as well as soils. Campania is not immune to these problems, and some studies have already highlighted their existence and relation to its natural resources (Cicchella *et al.*, 2005; De Vivo *et al.*, 2016; Minolfi *et al.*, 2016).

From 2013 to 2015, 3669 samples were collected from topsoil of the Campania Region (13,600 km²) at a nominal density of one sample/3.2 km². Each top soil sample (from 0-20 cm) was made by homogenizing five subsamples at the corners and the center of a 100m² square, collecting approximately 1.5 kg in total. The sampling procedure followed the Geochemical Mapping of Agricultural and Grazing Land Soils (GEMAS) sampling procedure described by Reimann *et al.* (2014). At each sampling site, several physico-chemical parameters of the soil properties were measured, including pH, total water content, conductivity, total organic content and the geographical coordinates system recorded by geospatial positioning systems (GPS).

Chemical analyses were carried out at an international accredited Laboratory, Acme Analytical Laboratories Ltd (now Bureau Veritas, Vancouver, Canada). The samples were analysed after an aqua regia extraction, by a combination of inductively coupled plasma atomic emission (ICP-AES)

and inductively coupled plasma mass spectrometry (ICP/MS) for “pseudo total” concentration of 53 elements.

To better visualize the element distributions and possible natural or anthropogenic behaviour, robust compositional biplot and Factor analysis, and Discrimination computation were generated.

Results

The robust biplots explain 63.53% (PC1-PC2) and 57.84% (PC1-PC3) variability of the investigated 18 elements. They reveal several elemental associations related to the underlying geology and anthropogenic activities.

Al-Ti-Th, Fe, Mn, As, La, and Co elemental association (A_1) is characterized by the vicinity of their vertices and their rays point to the same direction (Fig. 2).

Sodium and K variables form clearly a separate association (A_2) because their vertices are located close to each other and they point to the same direction. Both variables display high communalities (the length of the ray (Fig. 2).

Zinc, Pb, Ni and Cr variables form another association (A_5); their vertices lay closer to each other and point to the same direction. They may be related to anthropogenic sources like vehicular emission and industrial activities (Fig. 2).

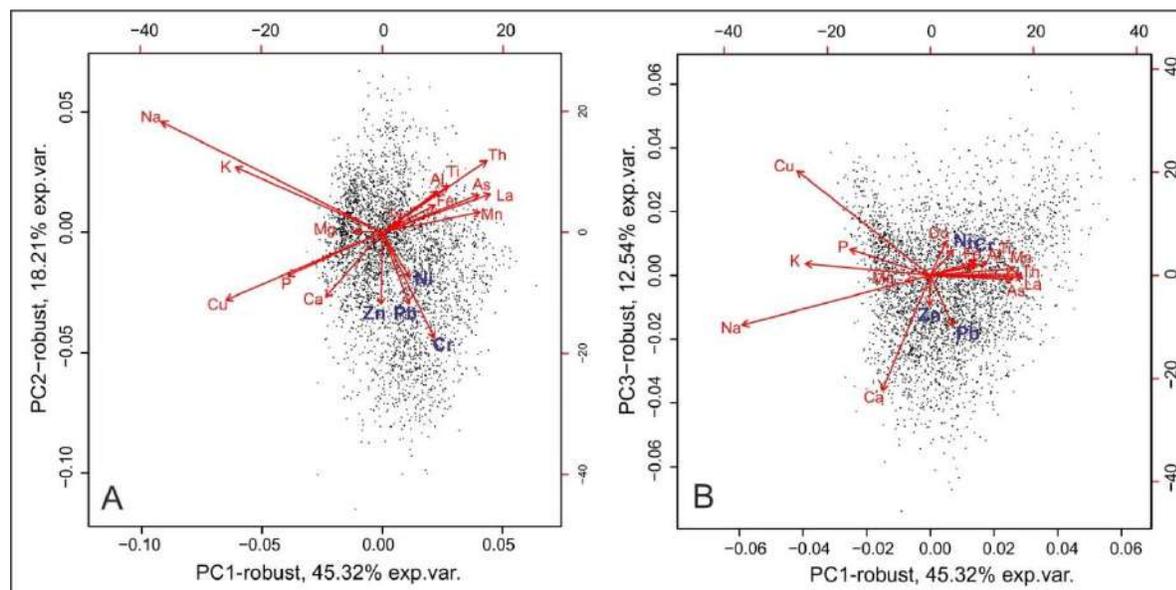


Figure 2. Robust biplots for the first and second principal components (A) and for the first and third principal components (B) based on the 18 investigated elements.

Factor analysis

The total variance of the 18 elements is 77.26 % in the four-factor model, which was chosen based on the break point on the scree-plot of all factors. The four factors, named F_1 , F_2 , F_3 and F_4 , account for 32.26%, 26.14%, 11.57% and 7.30% variability, respectively (Table 1). Variables with loadings over the absolute value of 0.5 have been considered to describe the main composition of each

factor. All variables hold communalities over 0.5 (50% of variability) meaning that the four factor models capture quite well the elemental interrelationships. The 18 elements of the four-factor model were separated by positive and negative loadings and sorted in descending order:

F₁: Ni, Co, Cr, Fe, Mn, - (Na, Ti, K); F₂: La, As, Th, Al, - (Cu, P); F₃: Al, Th, - (Ca, Mg); F₄: Al, K, - (Pb, Zn).

F₁: High factor scores (ranging from 2.88 to 5.09) are mapped in the eastern and southwestern parts of the study area where siliciclastic deposits prevail. High factor scores of the F₂ range from 1.73 to 2.75 and related to the positive correlation between Al, La, As, and Th in soils of the Mt. Roccamonfina and surroundings. The F₃ factor score map shows (particularly for Al and Th elemental association) elevated values (ranging from 1.26 to 2.39) close to the Mt. Roccamonfina.

The F₄ score map shows high positive values (ranging from 1.29 to 2.77) around the Mt. Somma-Vesuvius, where Al and K are the most congruent elements with the potassic pyroclastic composition (Peccerillo *et al.*, 2001; De Vivo *et al.*, 2010).

Table 1. Varimax-rotated factors of log ratio transformed (ilr) data, bold entries: loading values over absolute value of 0.5.

Variables	Factors				Communalities
	F1	F2	F3	F4	
Cu	-0.12	-0.77	0.23	-0.14	0.67
Pb	-0.28	0.10	0.09	-0.84	0.79
Zn	0.13	-0.21	-0.03	-0.83	0.75
Ni	0.90	-0.13	-0.28	0.09	0.91
Co	0.88	-0.10	0.01	0.37	0.92
Mn	0.69	0.41	0.04	0.05	0.65
Fe	0.79	0.31	0.20	0.27	0.83
As	0.01	0.72	0.25	-0.11	0.60
Th	-0.08	0.72	0.50	0.25	0.84
Ca	0.17	-0.17	-0.87	-0.06	0.83
P	-0.22	-0.72	0.00	0.03	0.57
La	-0.16	0.81	0.37	0.08	0.82
Cr	0.80	-0.08	-0.32	-0.20	0.78
Mg	0.20	-0.03	-0.82	0.14	0.73
Ti	-0.72	0.38	0.35	0.06	0.79
Al	-0.01	0.51	0.53	0.52	0.81
Na	-0.86	-0.24	0.17	0.14	0.84
K	-0.62	-0.46	0.30	0.50	0.94
Eigenvalues	5.81	4.71	2.08	1.31	
Total variance in %	32.26	26.14	11.57	7.30	
Cum. of total variance (%)	32.26	58.40	69.97	77.26	

In this session, we present the results of compositional data analysis used to discriminate the main sources of the investigated potentially toxic elements (Zn, Pb, Cr and Ni).

The higher proportion of Zn and Pb is associated with urban and industrial areas (e.g. Naples and Salerno) but also reaches higher abundance close to large volcanic complexes like Phlegraean Fields and Ischia (Fig. 3).

The residual map was overlain by those sampling points, which are related to different sources of contamination or enrichment based on the standardized residuals plot (Fig 3). The large positive residuals (>1.55, with red color) all indicate anthropogenic contamination of the four PTEs (Figs 3).

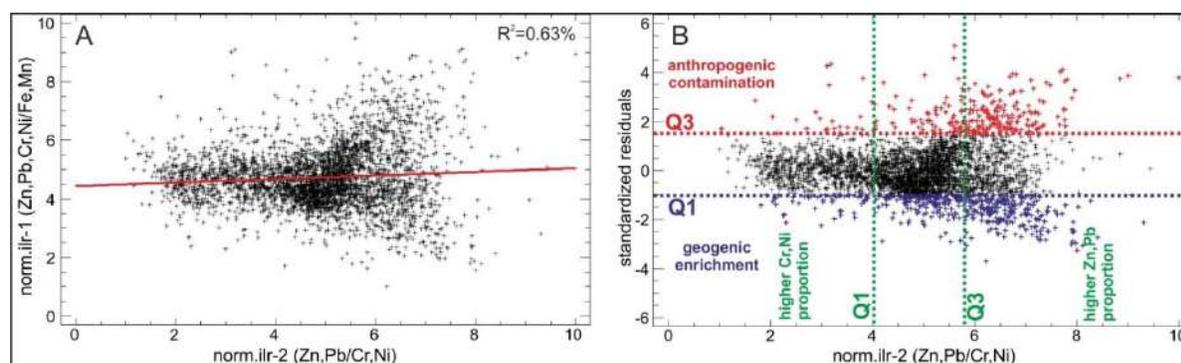


Figure 3. (A) Bivariate regression analysis between normalised ilr-2 (independent) and ilr-1 (dependent) variables. (B) Standardised residuals against normalised ilr-2. The plot was divided into more parts based on the classification of ilr-2 and residuals by means of Tukey's box-and-whiskers plot. Areas outside of lower (Q1) and upper quartiles (Q3) belong to geogenic enrichment and anthropogenic contamination of different elemental associations

Discussion

Compositional Biplot and Factor Analysis have shown:

- Al, Ti and Th element are possibly related to pyroclastic deposits, and Fe, Mn, Co, As, La tied to the coprecipitation of Fe-, Mn-oxy-hydroxides in siliciclastic deposits.

- Na and K may be associated with topsoils underlain by potassic and ultrapotassic rocks.

- Mixed behaviour of Cu and P, which are likely related to volcanic materials and phosphate fertilizers.

- Ni-Cr to the coprecipitation of Fe-, Mn-oxy-hydroxides in siliciclastic material

- Lead and Zn may be tied to anthropogenic sources such high rate of fossil fuel combustion, industrial and vehicular emissions release, a small portion in volcanic materials.

A compositional discrimination Analysis revealed:

- Contamination in the Solofra industrial district is linked to traffic emission (Pb), alloy production (Zn and Ni) and tannery (Cr and Ni) industries (Fig. 4). Cr and Ni may be influenced by not only the presence of Fe-, and Mn-oxy-hydroxide but also the organic matter and clay content.

- Zinc and Pb anomalies are located in the urbanized area of Naples and some parts of Ischia and Sorrento Peninsula where they are tied to intensive traffic (Fig. 4).

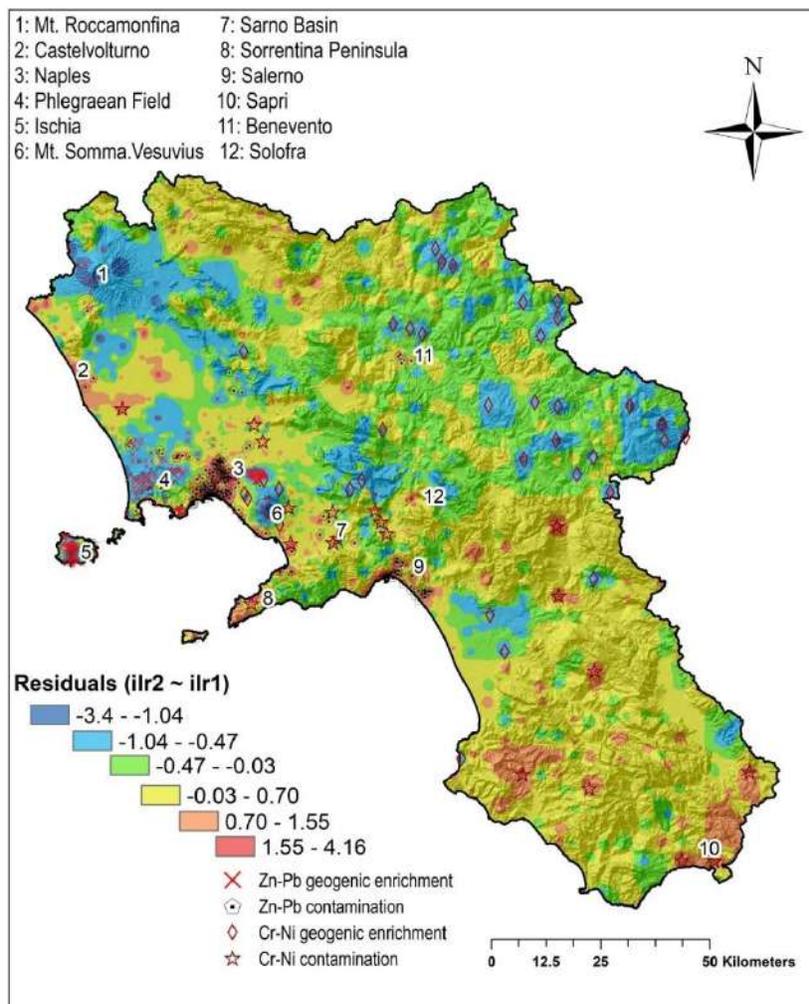


Figure 4. Classified standardized residual map indicating the contamination and enrichment areas. The map is overlain by those sampling points, which are related to anthropogenic contamination or geogenic enrichment of the respective four PTEs.

Conclusions

This study demonstrates a comprehensive discrimination analysis carried out on four PTEs (Zn, Pb, Cr and Ni) of the Campanian high-density topsoil data set. A workflow of compositional data analysis was implemented ranging from robust biplot and factor score maps to multivariate and bivariate regression analyses to discriminate the possible sources of contamination/enrichment.

The large urban and industrial areas (e.g. Naples, Salerno) along the coastline are mainly contaminated by Pb and Zn due to heavy traffic and alloy production. Some Cr and Ni contamination was discerned in the Sarno Basin due to the release of waste rich in Cr-Ni deriving from tannery industries (e.g. Solofra).

The large volcanic complexes (e.g. Mt. Somma-Vesuvius, Mt. Roccamonfina) are all characterized by geogenic enrichment of Zn and Pb. In contrast, Cr and Ni-enrichment are mainly related to the

siliciclastic deposits, where their proportion is not only influenced by Fe and Mn but also organic matter, clay content and dispersion mechanism.

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3.1.4. Detecting soil contamination in East Nile Delta, Egypt using remote sensing and GIS

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Abstract

Heavy metals are considered as one of the most critical contaminants in the environment, because of their toxicity, persistence and bioaccumulation. Heavy metal contamination in the East Nile Delta of Egypt was identified by using remote sensing, Geographical Information Systems (GIS), and Visible, near and Short Wave Infrared Spectroscopy (VNIR and SWIR) in the spectral range 400-2500 nm, were used to quantify various soil constituents simultaneously as the main research tools. Digital Elevation Model (DEM), Landsat 8 were used to map the landforms. Different physiographic units in the studied area. Field Spectroscopy was used for measured reflectance of 54 soil samples. Pb, Mn and Cd concentrations were measured and they all exceeded the average global concentrations identified. Stepwise multiple linear regression (SMLR) was used to construct calibration models. The concentrations of heavy metals were estimated with high accuracy where, the models were validated based on the independent validation. The results illustrated that, R² was recorded 0.94, 0.70 and 0.66 for Cd, Mn and Pb respectively. However, Remote Sensing and Geographic Information System (GIS) are provide detailed spatial information on soil contamination, it is rapidly and inexpensive. Contamination Factor, Pollution Load Index and Degree of Contamination indices were used to assess the environmental risks of heavy metal contamination from the soils. All analyzed metals pose some potential hazard and pollution levels were particularly high near Bahr El-Baqar drain and urban areas.

Keywords: soil contamination, Field Spectroscopy, SMLR, East Nile Delta, Egypt

Introduction

Heavy metal contamination of soils consider one of the major environmental problems in all over the world resulting from, the air (during combustion, extraction and processing), surface water (via runoff and release from storage and transport), rapid industrial development and urbanization, chemical fertilizers for Horizontal Extension Agriculture (HEA) and the residues of applied insecticides and pesticides. This affects the plant growth, crops or in pasture lands, and caused serious problems for food security and dangerous health (Tam and Wong, 2000; Erdoğan and Erbilir, 2007). Due to rapid increase in population, Egypt is expanding its agricultural land require reuse of agricultural drainage water for irrigation. Abu Zeid, (2011) showed that about one million acre in the Nile delta depends on drainage water for irrigation. And the physical and chemical properties of the soils effect on heavy metal levels in soil for instance; soil pH is a variable that influenced heavy metals adsorption, retention and movement (Matos *et al.*, 2001). Reusing this drainage water may cause adverse effects on soil, crop, animal, and human health. Abdel-Shafy and Aly, (2002) reported that one of the most polluted drains in Egypt is Bahr El-Baqar, East Nile Delta, which collect the effluents from two secondary drains: Belbeis drain and Qalyubia drain. The soils are affected by Lake Manzala and the Mediterranean Sea, and therefore, they were referred fluviomarine lacustrine flats. Soils are mostly clay to loam textures having high content of salts and ESP values. Almost simultaneously in the past few decades, large chunks of the lake have been sliced off to secure needed land for the agricultural, aquaculture, industrial, housing, and services sectors. It is estimated that the lake has shrunk from a total area of 300,000

to only 120,000 faddans in the span 30 years. Further evidence indicates that lake decreased in size at an average rate of 14.1 km² /year Ahmed *et al.*, (2000 and 2006). Some soils lie below sea level, and thus are badly drained and highly saline. Towards Lake Manzala there is vast clay swamps with conspicuous shore ridges of slightly higher elevation indicating former coast lines. Two soil orders were identified in the El-Matariya – Port Said region. These are Entisols comprising Vertic Torrifluvents, and Aridisols comprising Aquollic Saliorthids Hamdi *et al.*, (1978). Geochemical remote sensing technologies provide a fast, macro way to access to the Earth's surface chemical information, thereby has been widely used in many fields such as environmental geochemistry and soil sciences. As powerful tool for monitoring vegetation stress, hyperspectral remote sensing technique is increasingly being used, directly or indirectly to monitor the status of heavy metal pollution (Kooistra *et al.*, 2001; Kooistra *et al.*, 2003). Researchers have shown that they can accurately determine soil properties and heavy metals in visible-near-infrared (VNIR) spectroscopy in the spectral range 400-2500 nm under laboratory conditions. It can be almost continuously, and relatively less expensive and faster than traditional wet chemical measurements, and save time compared to standard laboratory tests (Yun, 2003). Zhang *et al.*, (2010) reported that the reflectance spectra and soil lead concentrations were measured in the laboratory and the study showed that bands centered around 838 nm, 1930 nm and 2148 nm are sensitive for soil lead content they reported that spectrometer data offers a powerful tool for predicting soil heavy metal contamination due to its high spectral resolution, and many continuous bands.

This research paper aimed mainly to develop a new method for quantitative prediction of heavy metals using quickly spectroscopy techniques as an alternative method to laboratory analysis in addition to describe the spectral characteristics of soil properties and soil contamination.

Material and Methodology

The study area is located between longitude 32°17' 39.56" and 32°17' 39.16"E and latitude 30°58'45.64"N 30°58' 34.56"N. It is situated north-east of Cairo, east of the Nile Delta, south of Manzala lake and west of Suez Canal as shown in Fig. 1. The study area has several environmental problems related to increasing soil pollution. The area attributed as an arid region where the minimum annualized temperature is 11.2°C and is recorded during January while the maximum annualized temperature is 31°C and is recorded during August. The relative humidity varies throughout the year, ranging from 67.2 to 82.87%. Visibility differs from ranged between 8.5 and 10.3 km. Where the lowest values are observed in December, whereas the highest values are recorded in July. The minimum annual wind speed is 12.3 km/hr., and is recorded during November while the maximum annual wind speed is 18.3 km/hr., and is recorded during March. The investigation area is described by (Mohamed *et al.*, 2011).

The total surface area of the study area is approximately (21641.59 Hectares). A reconnaissance visit was performed for the study area to get different landscape features; land-use and land-cover patterns. The extensive field surveys were guided with a Global Positioning System (GPS) receiver. Fifty eight different sites were selected randomly in southern Port-said Governorate where is found homogeneity in physiographic unites, and give each sample chance to represent population sample.

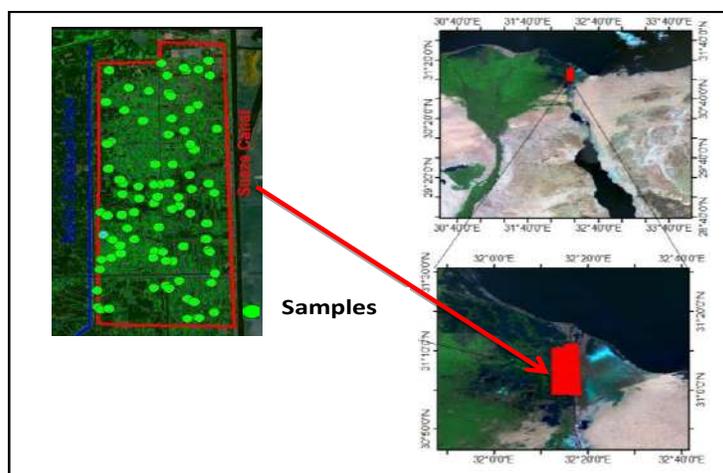


Figure 1. Location map of the studied area and Surface soil sampling.

Generation of digital elevation model (DEM)

Three topographic maps were rectified using georeferencing tool bar in Arc map 10.2, then about 2838 spot heights were digitized and their elevations in meters were put in the attribute table of a point shapefile. The inverse distance weighted, (IDW) tool was used in interpolation of these elevation points to produce DEM. This tool uses one of the deterministic interpolation techniques that create surfaces from measured points based on the extent of similarity between these points. (ESRI, 2015). Pre-processing of the DEM was done to remove sinks (small imperfections in the data) and this was implemented in ArcGIS 10.2. The fill tool in the spatial analyst was applied to the elevation grid (DEM) to fill all sink areas in the raster. This final sink-filled DEM was referred to as the 'corrected DEM' from which other terrain attributes (slope & Curvature) were extracted. Slope was extracted as a percent from the corrected DEM using the slope tool in ArcMap 10.2. The extracted slope image was then reclassified into five classes according to FAO (2006). The curvature was calculated from the corrected DEM using the curvature tool in ArcMap 10.2.

Laboratory Analyses

Soil Electric conductivity (EC), organic matter (OM), pH, soluble cations and anions, CaCO_3 , cation exchange capacity (CEC), and Particle size distribution was determined according to (Bandyopadhyay, 2007). Concentrations of selected heavy metals were determined using an atomic absorption spectrophotometer (Shimadzu, AA-6800).

Spectroscopy Analysis

The ASD FieldSpec FR spectroradiometer samples spectral radiance across the wavelength range 0.35–2.5 mm with spectral resolution of 0.003 mm at ffi 0.7 mm and 0.01 mm at ffi 1.4 and 2.1 mm. Its nominal noise equivalent changes in radiance (neL) are $1.4 \times 10^{-9} \text{ W cm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$ at 0.7 mm, $2.4 \times 10^{-9} \text{ W cm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$ at 1.4 mm and $8.8 \times 10^{-9} \text{ W cm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1}$ at 2.1 mm. The contact probe (Fig. 7) has a stable light source integrated with the mount for the spectrometer optic cable five spectra of each sample were obtained. All of the measurements were made with the sensor located directly over the center of the sample. The mean of the five spectra was determined to provide a single spectral value. ViewSpec software used to convert spectral data from DN data to reflectance data and export it to ASCII text files, which used easily in Microsoft Excel.

Multi Linear Regression (MLR)

The simplest way to express a relationship between variables is a linear relationship. The linear expression is as follows:

$$Y = a + b_1X_1 + b_2X_2 + \dots + b_nX_n$$

Where:

Y is the heavy metals concentration explained by wave lengths and soil properties X_1 , X_2 and X_n , a is intercept and b_1 , b_2 and b_n are the regression coefficients (Cohen *et al.*, 2003).

This can be tested first for linear regression analysis. This means if the independent variable (soil contamination, soil properties) decreases or increases then the depended variable (spectra) will either decreases or increase. The relationship should be tested for the following: ANOVA statistic, Collinearity Cook's distance and Centred Lever Value.

Results and discussion

Landform classification for southern part of Port Said

The produced physiographic map of the studied area was utilized to describe the dominant features of the physical earth surface, including processes responsible for their formation and evolution. These units were combined with the geological and topographic maps and the hill shaded map using the capability of GIS software to produce physiographic mapping units, Figure 2 show physiographic units in the studied area.

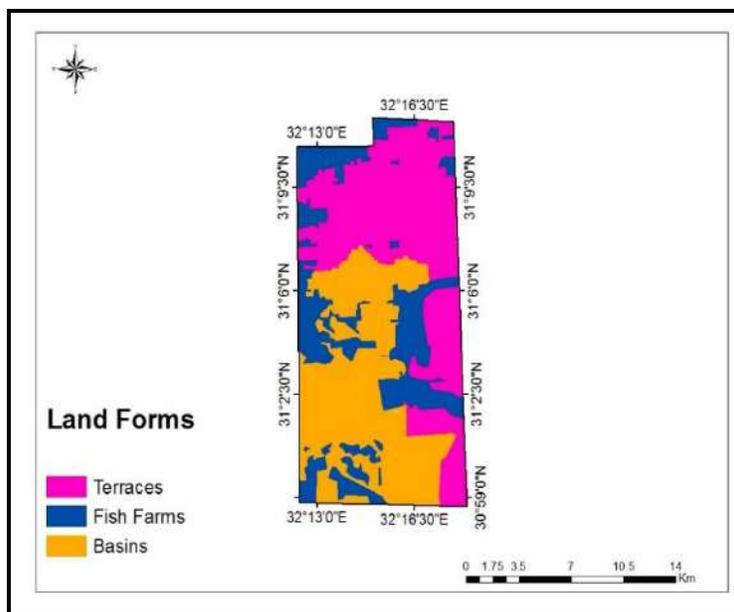


Figure 2. Physiographic map for the studied area

Physical and chemical properties for Soil in the studied area

Some physical and chemical characteristics and heavy metal levels in soil for each unites landform in the studied area. Figure 3 show soil mapping units in the studied area.

Soil of Terraces

Terraces landform represent 35.4 % from the total area it is covering about 76.60 km², which represent 35.3% of total area. The concentration of each heavy metal is always controlled by different soil parameters e.g. (soil pH, organic matter, calcium carbonates, cation exchange capacity, Manganese, Lead and cadmium), however the current ECe values ranged between 0.561 and 2.8 dSm⁻¹, which consider moderately salty soil of the study area. These results indicate the good management of these soils. The organic matter varied from 0.8 to 2.9 %. Soil organic matter plays an important role in not only iron oxidation and reduction but also it forms complexes with any soluble iron that is released. The organic matter extract, doubtless, chelates with iron and holds it for a time in a soluble condition and thus it can be transported within the plant tissues (Allison, 1973). The cation exchange capacity varied from 17.6 to 25.3 molc/kg⁻¹. The pH varied from 7.2 to 7.6 this indicate that the heavy metals in this soil is complex compound. The CaCO₃ percent ranged from 5.7 to 40.2 %, and the highest values related to their content the samples from shells in the field ,Manganese was under threshold which varied from 284.3 ppm to 474.8ppm,Lead was under threshold which varied from 3.38 ppm to 15.6ppm and cadmium was under threshold which varied from 1.4 ppm to 2.7 ppm .

Soil of Basin

Basin landform unit was lies in the southern part in the study area covering about 86.06 km² which represent 39.8% of the total area. ECe values ranged between 0.8 and 2.9 dSm⁻¹ which consider slightly salty soil of the study area. These results indicate the good management of these soils. The organic matter varied from 1.5 to 2.5 %. The cation exchange capacity varied from 19.5 to 24.1 molc/kg⁻¹. The pH varied from 7.2 to 7.5 this indicate that the heavy metals in this soil is complex compound. The percent of CaCO₃ ranged from 6.8 to 37.1 %, Manganese was under threshold which varied from 219.6 ppm to 441.3 ppm, Lead was under threshold which varied from 3.2 ppm to 14.6ppm and cadmium was over threshold which varied from 1.7 ppm to 3.2 ppm.

Soil of dry Fish Farms

Dry Fish Farmer landform unit was lies in the different part in the study area covering about 53.84 km², which represent 24.8% of the total area. ECe values ranged between 0.6 and 2.7 dSm⁻¹, which consider moderately salty soil of the study area. These results indicate the good management of these soils with leaching many times, as it used as fishponds. The organic matter varied from 0.5 to 2.5 %. These soils are used as fishponds and have some residual of organic feeding on soil surface, which is the reason of high OM. content. Soil organic matter plays an important role in not only iron oxidation and reduction but also it forms complexes with any soluble iron that is released. The cation exchange capacity varied from 17.2 to 24.5 molc/kg⁻¹. The pH varied from 7.2 to 7.6 this indicate that the heavy metals in this soil is complex compound. The percent of CaCO₃ ranged from 6.2 to 35.3 %, and the highest values related to their content the samples from shells in the field. Manganese was under threshold, which varied from 146.6 ppm to 448.2 ppm. Lead was under threshold, which varied from 2.5 ppm to 14.3 ppm and cadmium was over threshold which varied from 1.4 ppm to 3.9 ppm.

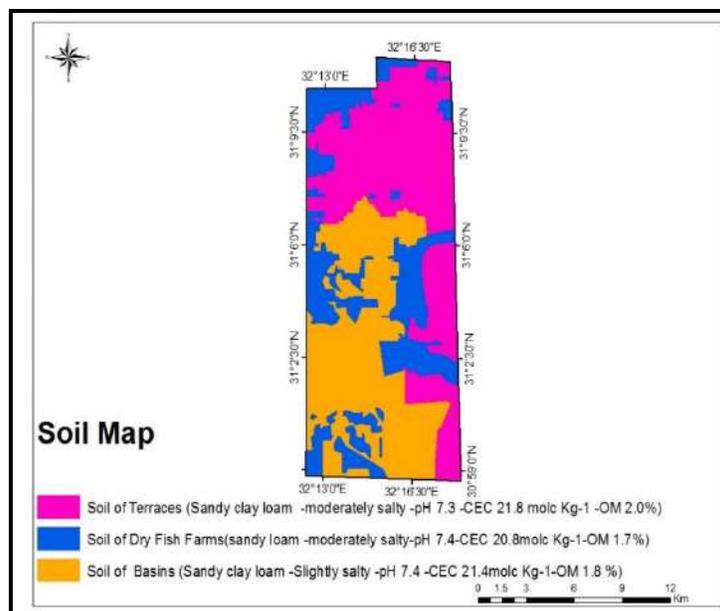


Figure 3. Surface Soil mapping of studied area

Relationships between reflection, soil contamination and soil properties

Reflectance spectrum analysis

The reflectance spectrum analysis was developing to prediction models for different soil contamination and soil properties. Two major processes were carried out calibration and validation. Calibration process was to develop a prediction model for soil contamination and soil properties. In this process, regression analysis was conducted using a stepwise MLR. Validation process was done to check if prediction model of calibration is reliable or not. The reflectance spectroscopy technique requires the selection of a representative calibration set that is chemically matched with the validation set. It is empirical, allows (actually requires) many combinations of samples and data manipulations to obtain optimal prediction. To keep the number of combinations to a manageable set, constant number and identity of samples were kept in both calibration and validation sets for soil contamination and soil properties. Only the data manipulation procedures (reflectance (R); absorption, (A); first derivative of absorption (A); Standardized R) in both the original and the compressed spectra were changed. The highest sum of squares of regression above the residuals was inspected to better estimate the prediction power of the selected routine (manipulation and wavelength compression). The highest R^2 of the validation set were selected to indicate the optimal data manipulation for obtaining the best analytical performance. In order to upscaling the models to multispectral images, for mapping the soil properties and soil contamination using field spectroscopy data as the reference spectra, using linear spectral immixing technique and geostatistical analysis for predicted parameters (soil properties and soil contamination) which obtain it from models and comparison between mapping from immixing technique and geostatistical analysis technique.

Calibration and validation processes

These processes were mainly carried out on 60% from number of soil samples which selected by randomly method. Firstly, extreme and outlier values had been taken out for soil contamination and soil properties. Secondly, Explore data to reduce error before start prediction, the histogram

applied to evaluate the normality of datasets, which indicate that the parameters follow extend the Gaussian's normal distribution for soil properties and soil contamination. Thirdly, run calibration process by stepwise multi linear regression procedure between the concentration of a given constituent for soil contamination and soil properties and the spectral response (reflectance, R; absorption, A; first order derivative of absorption, A; and standardized reflectance). In the multiple regression setting, the response variable y (soil contamination and soil properties) depends on not one but several explanatory variables: matrix x (spectral data). The mean response is a linear function of the explanatory variables:

$$Y=b+a_1*x_1+ a_2*x_2+...+a_n *x_n.$$

Where:

Y is soil contamination or soil properties element

(b) is an intercept

a_1, a_2, \dots, a_n are weighting factors for the spectral readings in various selected wavelengths 1 to

x_1, x_2, \dots, x_n are the values of the spectral parameters at wavelengths 1, 2, ... and could be either R, A, A', or standardized R.

For calibration based on multivariate statistics, a stepwise regression procedure was used in order to limit the number of input variables. Variables were entered or removed from the model depending on the tests for hypothesis. As illustrated in table 1, the ANOVA Test shows that the sum of squares of regression for all parameters are higher than residuals. In addition, the F test statistics, at confidence level of 95%, showed that silt, clay, CaCO₃, OM, EC, and Cd are higher than the number of samples selected, and at confidence level of 50%, for sand, CEC, Mn, and Pb are smaller than the number of samples selected. This means that the relationship is not coincident and that there is genuine relationship between the reflectance and silt, clay, CaCO₃, OM, EC and Cd, and not genuine relationship between the reflectance and sand, CEC, Mn and Pb. The values of Beta in all parameters are negative, which indicates that the relationship is an inverse one, meaning the spectral reflectance increase as the parameters content decreases. Tolerance (T) for Silt, lay, Sand, CaCO₃, OM, CEC, ECe, Mn, Cd, and Pb are 0.92, 0.84, 0.82, 0.52, 0.50, 0.58, 0.74, 0.77, 0.86 and 0.83, respectively, which if close to (1) indicate that 100% of the relationship cannot be explained by other variables. Variance Inflation Factors (VIF) for silt, clay, sand, CaCO₃, OM, CEC, ECe, Mn, Pb, and Cd are 3.4, 11.8, 4.09, 19.3, 20.08, 2.5, 24.5, 21.4, 22.1, and 26.5, respectively, bigger than (2) that indicated these variables are not collinear. Two or more predictor variables in a multiple regression model are not highly correlated. The statistical parameters from the calibration processes of the optimal combinations are given the best predictive equations were chosen as the equation by MLR with the highest R² as shown table 2.

Table 1. Test the hypothesis to select the best model

Parameter	ANOVA Test			Standardized Coefficients	Collinearity Statistics	
	Sum of Squares		F	Beta	Tolerance (T)	VIF
	Regression	Residual				
Silt%	2069.215	459.783	123.762	-1.604	0.92	3.4
Clay%	318.616	49.025	113.734	-2.835	0.84	11.8
Sand%	936.883	294.413	55.689	-1.460	0.82	4.09
CaCO ₃ %	916.858	100.034	160.396	-3.654	0.52	19.3
OM%	2.067	.428	86.852	-4.004	0.50	20.08
CEC mol _c Kg ⁻¹	71.044	27.556	29.220	-0.939	0.58	2.5
Ec dSm ⁻¹	4.474	.935	131.626	-4.417	0.74	24.5
Mn ppm	135895.315	36230.624	30.944	-2.585	0.77	21.4
Cd ppm	8.553	.821	118.019	-2.795	0.86	22.1
Pb ppm	478.304	443.898	14.277	-2.099	0.83	26.5

Table 2. Models have been extracted by MLR with R²

Parameters	Equations	Wavelengths	R ²	Spectral range
Sand	45.86+111.53*x1 142.105*x2	Where x1, x2, represent separately reflectance at wavelengths: 1680nm, 517nm	0.74	Green Short Wave Infrared) in
Silt	43.032 121.493*x1+133.194*x2	Where x1, x2, represent separately reflectance at wavelengths: 1680nm, 517nm	0.81	Green Short Wave Infrared
Clay	7.58+108.82*x1 117.39*x2	Where x1, x2, represent separately reflectance at wavelengths: 1694nm, 2498nm	0.82	Short Wave Infrared
Ec	2.574 15.470*x1+17.188*x2	Where x1, x2, represent separately reflectance at wavelengths: 1680nm, 1916 nm	0.82	Short Wave Infrared
CaCO ₃	2.289+241.06*x1 244.974*x2	Where x1, x2, represent separately reflectance at wavelengths: 1343nm, 1918 nm	0.85	Short Wave Infrared
CEC	19.266+12.09*x1 25.159*x2+15.702*x3	Where x1, x2, x3 represent separately reflectance at wavelengths: 490nm, 505 nm, 896nm	0.62	Blue Green –Near Infrared
OM (%)	1.65 11.14*x1+7.82 *x2+2.14*x3	Where x1, x2,x3 represent separately reflectance at wavelengths: 2467nm, 1674 nm ,494nm	0.82	Blue Short Wave Infrared
Pb (ppm)	13.39 33.8*x1+35.8*x2 96.0*x3+101.3*x4	Where x1, x2,x3,x4 represent separately reflectance at wavelengths: 505nm, 490 nm ,1679nm,1913nm 494nm	0.51	Blue Green Short Wave Infrared
Mn (ppm)	466.28 1937.4* x1+1002.53* x2+1389* x3 410.24* x4	Where x1, x2,x3,x4 represent separately reflectance at wavelengths: 1679nm, 506 nm ,1958nm,500nm	0.73	Green Short Wave Infrared
Cd (ppm)	1.45+32.6* x1 17.1* x2 17.09* x3	Where x1, x2,x3 represent separately reflectance at wavelengths: 1705nm, 1917 nm ,1161nm	0.91	Short Wave Infrared

The calibration processes of the optimal combinations are given the best predictive equations were chosen as the equation by stepwise MLR with the highest R² which indicated that cadmium

element was the best predicted model. Finally, for validation prediction models 40% from samples were not used in the calibration process were used to validate the prediction equations. The predicted concentration values were correlated to the chemical analysis results of the validation data set. The same as calibration, this process was run for each constituent until a relatively high prediction performance was obtained. At that point, the corresponding calibration equation was declared the preferred equation for predicting samples from the calibration and validation processes. Table 3 showed that the highest R^2 was 0.94 for Cd and the lowest was 0.53 for CEC that indicated the high accuracy model to predict the concentration was cadmium element and acceptant other models for all parameters.

Table 3. The values of R^2 for validation processing for soil contamination, soil properties.

Parameters	Silt %	Sand %	Clay %	Ec dSm-1	CaCO ₃ %	CEC molc Kg-1	OM %	Pb ppm	Mn ppm	Cd ppm
R^2	0.58	0.69	0.79	0.80	0.81	0.53	0.79	0.50	0.71	0.94

Conclusions

This search using spectral reflectance to detect soil contamination in southern district of Port-Said Governorate. Heavy metals have been predicted from spectral reflectance by using MLR. The result show Spectrum data which taken in Vis-NIR range (350-2500 nm) and could be used to estimate the soil contamination and soil properties with high accuracy the same in abstract. Therefore, Visible Near-infrared (Vis-NIR) reflection spectroscopy is cost and time-effective that could be alternatives to the traditional methods of heavy metals analysis. In addition, this paper highlights the environmental hazards occurred southern Port-said Governorate, the results showed concentration of soil contamination by Cd, Mn, and Pb are under the threshold. Except for an area contaminated with Cd covering 4532.6 Ha. Due to insecticides, fungicides, sludge, and commercial fertilizers us aye.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.5. UN Environment supports Serbian Environmental Protection Agency in the management of contaminated sites

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Abstract

In the frame of the project "*Supporting the Western Balkan Region in the Implementation of Multilateral Environmental Agreements through Strengthening of Institutional Framework and Capacity Building*", financed by the Italian Ministry of Environment, Land and Sea and implemented by UN Environment, ISPRA is assisting the Serbian Environment Protection Agency with a number of tasks related the management of contaminated sites. Activities include the preparation of two characterization plans for the industrial sites of Zorka (Šabac) and Viskoza (Loznica) and the organisation of a joint training for SEPA staff on selected topics such as characterization plans development, soil and groundwater sampling, risk assessment, remediation technologies and comparative risk assessment. Moreover ISPRA will assist in the frame of comparative risk procedure through the EEA software PRAMS to rank potential contaminated sites in Serbia in accordance with a risk based system.

Keywords: Contaminated site, Characterization plan, Sampling procedure, Soil, Groundwater, Hazardous Waste, Remediation technologies, Risk assessment, PRAMS

Introduction, scope and main objectives

The project "*Supporting the Western Balkan Region in the Implementation of Multilateral Environmental Agreements through Strengthening of Institutional Framework and Capacity Building*", financed by the Italian Ministry of Environment, Land and Sea and implemented by UN Environment Vienna Programme Office aims at supporting the Serbian Environment Protection Agency in dealing with a number of compelling environmental issues. Within the European panorama, neighbouring countries have different levels of expertise in dealing with environmental aspects. The correlation between quality of life and a healthy environment, the absence of specific legislation and the importance of environmental and sustainable development aspects in the political agenda are among them.

Since 2016, UN Environment is facilitating a strong capacity-building component between Italian and Serbian specialized institutions. This partnership saw the participation of ENEA, INAIL, ISPRA and ISS. In this frame, the Italian Ministry of Environment, Land and Sea decided to grant a co-financing to the UN Environment / GEF⁴ project "*Enhanced Cross-Sectoral Land Management through Land Use Pressure Reduction and Planning*". This initiative aims at strengthening national capacities and increasing technical knowledge with regards to soil monitoring and remediation, and is pivotal not only to the management of local industrial contaminated sites but also to the overall compliance to the EU acquis on environment and Serbia's accession path to the European Union.

The project is mainly looking at contaminated site management and in this framework, ISPRA in collaboration with the Serbian Environment Protection Agency, is developing two characterization plans for Zorka - Obojena Metalurgija site (Šabac) and Viskoza (Loznica). Both plans were developed based on the collection of

⁴ Global Environment Facility

preliminary data performed by a joint team of experts. The characterization plans were developed based on the Italian good practices and experiences on contaminated sites (SIN - Contaminated Sites of National Interest) that have comparable features in terms of extension and complexity to the two selected areas in Šabac and Loznica. A constant exchange and dialogue between ISPRA and SEPA experts during site inspections and the development of the characterization plans was necessary in order to guarantee the delivery of a consistent and coherent characterization plan to be applied to the Serbian legislative framework. This approach is necessary in order to allow SEPA to develop autonomously further characterization plans for additional complex areas.

Methodology

The methodology generally used for preparing a Characterization Plan for a contaminated site, consists of a desk study followed by an *in situ* inspection to verify the assumptions and collecting possible missing information. A “Site description” chapter summarizes the results of the investigation procedures. Further, the preparation of the investigation work plan is needed. Detailed information for soil and groundwater should be provided, including the analysis of additional aspects such as waste, asbestos containing materials, surface waters and sediments if present. The technical specifications on how to proceed are presented in an Annex of the Characterization Plan, with user-friendly plates, easy to understand and to apply in the field. The results of the site inspections are presented below.

Factory “Viskoza” is located in the outskirts of the city of Loznica, close to a settlement with 5,000 inhabitants at a distance of less than 300 m and 1 km away from the Drina river. Due to bankruptcy, production of viscose and cellophane has ceased in the beginning of 2010. Large quantities of substances that were once used in production line are now stored in the aboveground and underground reservoirs which are found to be in poor conditions. Lack of maintenance of factory inventory caused spillage and leakage of harmful substances from those reservoirs. No warning signs nor notices identify where hazardous waste was stored.

Hazardous substances identified include:

- Carbon disulfide (approximately 60 t partly stored in reservoirs and partly in sludge);
- Black liquor (approximately 600 m³ stored in cylindrical reservoirs of NaOH, Na₂S and lignin, in October 2013, app. 400 m³ of black liquor has leaked from the reservoir);
- Furfural (C₅H₄O₂), 200 t of coagulated furfural stored in two half-full reservoirs;
- Waste fuel oil, 20 t stored in reservoirs that have been positioned in the concrete bund;



Figure 1. Black Liquor reservoir in Viskoza - Loznica [Picture by Marco Falconi]

Previous investigations and soil analysis have shown exceedances in limit values of heavy metals (Pb, Zn, Cu, Ni, Hg and As), pH, sulphides, and sulphates. Analysis of soil samples was performed by the Public Health Institute of Belgrade in 2014. Soil samples were taken at three locations: next to the reservoirs from which black liquor has leaked previously, agricultural soil next to the wastewater treatment facility where the leakage also occurred, and a control sample on agricultural land at the 50m distance from the wastewater treatment facility. Soil screening performed in 2016 using handheld XRF device has shown elevated values of Ni, Co, Cr, Mo, Ba, Mo, V, and Th.

Factory “Zorka - Obojena Metalurgija” is located within the Zorka working zone “Istok” in the city of Šabac. The production process was shut down after bankruptcy was filed, but large amounts of substances from production can still be found in the facilities and in the surroundings. Due to the immediate vicinity of Sava river, groundwater is to be found at only one meter below the surface.

The possibility of groundwater contamination and contamination of Sava River is one of the major concerns for this site. An additional concern is the proximity of a large number of schools, health facilities and a residential area with approximately 10,000 inhabitants at a distance of about 1 km.

Problem areas and hazardous substances identified on the location include:

- Landfill of jarosite waste (estimated 330,000 t);
- Zinc sulfate ($ZnSO_4$), 4 t stored in factory facilities;
- Pyralene waste, large amount stored in factory facilities;
- Pb/Ag precipitate



Figure 15. PbAg precipitate in a pond inside Zorka - Obojena Metalurgija in Šabac [Picture by Marco Falconi]

In 2014, Public Health Institute of Belgrade performed analysis of soil samples collected at near the factory, the results showing that Pb, Cd, Zn, Cu, Ni have exceeded remediation values. On-site analysis of soil performed in 2016 using handheld XRF device shown elevated values of heavy metals such as Pb, Cu, Zn, Cd, Mo, As, Sb, Ag, Ba, Se, Th, and V.

Results

As of today only the characterization plan for Šabac has been prepared and is currently under revision by SEPA and UN Environment. The following figure can be used to summarize the main investigation needed. For each soil boring, three samples will be collected: first one from 0 to -1 meter below ground level, second in the capillary fringe zone and third one at an intermediate depth.



Figure 3. Proposed investigation in plant Zorka - Obojena Metalurgija in Šabac [From ISPRA]

Discussion

The characterization plan delivery and the training provided SEPA with a better understanding of conventional and innovative methods for investigating soil pollution, environmental reporting in accordance with EU standards, preparatory activities for remediation, risk assessment procedures with a specific focus on application of PRAMS methodology, on-site safety measures and personal protective equipment for field investigations.

The joint Italy-Serbia study visits and capacity building training were an excellent opportunity for international cooperation, learning and exchange of national experiences on soil quality deterioration and pollution monitoring. The project represents a further milestone of cooperation between UN Environment, the Italian Ministry of Environment, Land and Sea in the field of environmental protection and sustainable development in the Western Balkans.

Conclusions

A continuous capacity building process and exchange of experiences between Serbia and Italy should be granted with the support of public technical institutions and donors.

Positive outcomes represent a solid foundation for further intensifying cooperation and exchange from developed to developing countries in the field of environmental protection and sustainable development, in a joint effort for achieving goals set by the most recent international environmental agendas, that could be replicated also in other fields and/or with other countries.

Acknowledgements

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.6. Bioaccessibility of Pb and As in contaminated urban soil evaluated by chemical extraction and Vis-NIR spectroscopy

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Abstract

Urban soils are frequently contaminated with lead (Pb) and arsenic (As) causing a potential risk to human health. Soil plots at a suburban farm in New Jersey (USA) with elevated levels of Pb and As were amended with phosphates, iron oxide with elemental S, Mn sulfate monohydrate, manure compost, and raised bed soil to determine whether these treatments could change Pb and As bioaccessibility. Diffuse Infrared Reflectance Spectroscopy in the visible-near infrared (Vis-NIR) is an innovation in soil proximal sensing with a recent application in soil environmental protection. The aim of this research is to develop a diagnostic screening method for Pb and As bioaccessibility in urban soils using Vis-NIR. The use of VisNIR resulted in a good estimate of both total and bioaccessible (extracted with 0.4 M glycine) Pb and As. Total and bioaccessible elements were predicted by improving the 'cross' correlation between surface soil metal concentrations and Vis-NIR reflectance measurements via partial least-squares regression (PLSR) modelling. The two principal components (PC1 and PC2) accounted for 94% of the variation in the data. The plot of the first two principal components (PC1 and PC2) allowed identify five different clouds with different soil treatments. Both the PC1 and PC2 were correlated mainly with Vis wavelengths. These clouds depend mainly on similar adsorption in Vis range and related to several chemical soil components. The total and bioaccessible concentrations of Pb and As were qualitatively estimated (RPD>2). The two principal components likely indicate that bioaccessible Pb and As are linked to the form and distribution of the organic matter and the crystalline Fe oxides or Fe amorphous minerals. Therefore, the NIR spectroscopy provides a potential diagnostic screening method for bioaccessible Pb and As in urban soils.

Keywords: Vis-NIR spectroscopy, bioaccessibility, lead, arsenic, soil amendments, urban soil.

Introduction

Lead arsenate was first used as an insecticide in 1892 against gypsy moth (*Lymantria dispar*) in Massachusetts, USA (Peryea, 1997) and then extended in orchards and farms. The cumulative contamination of soils by Pb and As beginning in the late 1800s persists today, because Pb is quite immobile and As is only very slowly leached through soils (Veneman *et al.* 1983). As contaminated lands are converted to residential uses, the potential hazard to human health may be increased from direct or indirect exposure pathways arising from gardening and further transfer through the consumption of garden produce. Lead and As availability to plants, soil organisms and humans depends on their solubility. Lead solubility is controlled by adsorption of the Pb on soil minerals (particularly Fe oxides) and complexation with organic matter (Gustafsson *et al.* 2011). Soil pH is critically important in determining Pb activity in soil solution, as Pb adsorption and most

precipitation reactions are favoured by higher pH. Arsenic mobility depends on the oxidation states of this metalloid in soil environments in the forms of arsenate and arsenite species. Arsenate in most situations adsorbs more strongly than arsenite, behaving very similar to phosphate and chemisorbing most strongly on Fe oxide and silicate minerals in the pH range of 5.0 to 6.5 (Manning and Goldberg, 1996).

Different chemical behaviour of Pb and As in soils, coupled with the heterogeneities in contamination, limits the options for remediation. Organic and inorganic amendments are used to reduce metal mobility and toxicity in soils. These amendments modify soil metals to more geochemically stable phases via sorption, precipitation, and complexation processes (Hashimoto *et al.* 2009). The most commonly applied amendments include clay, cement, zeolites, phosphates, organic composts, and microbes (Wuana and Okieimen, 2011). Amendments that are mixed into soils are less expensive than excavation and removal of contaminated soils.

Generally, bioavailability of metals in soils is directly determined using bioassays, while bioaccessibility is estimated using chemical extraction tests. Many conventional methods of *in vivo* and *in vitro* assays are costly and time consuming. The rapid increase of urban gardening in recent years emphasizes the need of reliable *in vitro* bioaccessibility extraction methods to assess the risk of direct soil ingestion in moderately contaminated soils.

Diffuse reflectance spectroscopy (DRS) has been introduced for the determination of soil chemical properties. Simple non-destructive technology is a single scan, when combined with some multivariate statistics, can measure several properties simultaneously (Viscarra Rossel *et al.* 2006). In this study, DRS in the visible-near infrared (Vis-NIR) was applied to assess the impact of different amendments on the bioaccessibility of Pb and As in a moderately contaminated soil and compared with results from *in vitro* assay. Thus, the aim of the research is to develop a new diagnostic screening test for Pb and As bioaccessibility in urban soils using vis-NIR diffuse reflectance spectroscopy.

Methodology

Experimental design

This study was conducted at a community farm in New Jersey, USA, where elevated soil Pb and As concentrations were documented. A survey of the area performed by United States Department of Agriculture Natural Resources Conservation Service (USDA NRCS) showed that soil Pb and As were very closely correlated, with $R^2 = 0.83$ ($P < 0.001$), suggesting a single source of contamination, most likely due to past pesticide application of lead arsenate.

There were 25 sub-plots (1.2m x 1.2m each) (Fig. 1) including control, bone meal (Greenway Biotech Inc. 3-15-0, Ca-24%, derived from cooked bone meal), TSP (Hoffman, 0-46-0, derived from triple superphosphate), manure compost (Nature's Care Really Good Compost™), and raised bed soil (Nature's Care® Organic Raised Bed Soil 0.12-0.06-0.09, derived from poultry litter). Iron was supplied as Dr. Iron (Monterey, 22% Iron, non-staining, OMRI listed, 55% Sulfur, derived from elemental sulfur and iron oxide, phosphorous free) and Mn was supplied as manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, 32% Mn). In April 2015 each of phosphate-bearing amendments (both TSP and bone meal) was applied at single and double amounts while Fe and Mn amendments were each applied at 2500 mg kg^{-1} per plot.

Total, extractable and bioaccessible Pb and As concentrations

The samples collected (from the surface to a depth of 15-20 cm) were characterized for total organic content lost on ignition at 550 °C, total and extractable Pb, As, P, Ca, Al, Mn, and Fe, soil pH in water (1:1 by volume) and salts (1:2 by volume). Particle size fractions of <250 µm were utilized as this is the soil fraction that sticks to the hand of small children and is recommended by US EPA for bioavailability assessment (US EPA, 2000). For Vis-NIR-DRS analysis, the samples were oven dried and passed through 2 mm-sieve. Bioaccessible Pb and As were quantified following a modified version of the standard US EPA Method 1340: In Vitro Bioaccessibility Assay for Lead in Soil. This modified method involves extraction with 0.4-M glycine solution at pH 2.5 at 37°C for 1 hour.

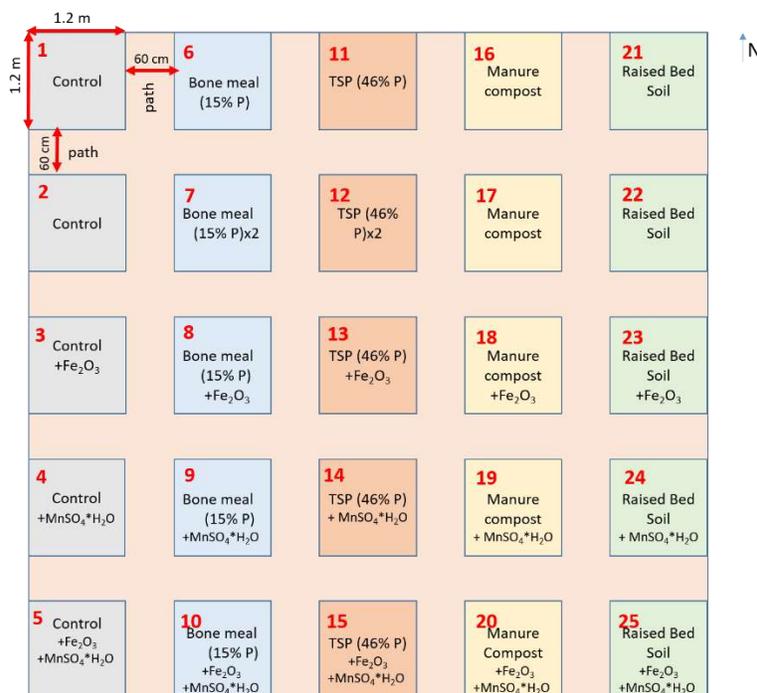


Figure 1. Experimental design used for 25 sub-plots: five amendments were applied with or without Fe and Mn.

Statistical analysis was carried out for 21 Vis-NIR samples. The spectra were transformed to apparent absorbance or $\log(1/\text{Reflectance})$ and Principal Component Analysis (PCA) was carried out taking into account both the response variables (As, Pb extracted) and the original predictor variables (namely Vis-NIR spectral) in order to compress the spectra into fewer principal components. We applied the leave-one-out cross-validation in PLSR to analyze the relationships between Pb and As bioaccessibility and the diffuse reflectance Vis-NIR spectral data. PLSR analysis was performed by CAMO software and used to relate spectra and soil attributes.

Results

Pb and As extractability with glycine

The 21 soil samples had a range of total Pb (132-276 mg kg⁻¹) and As (19-42 mg kg⁻¹) concentrations, with a linear correlation between Pb and As ($r = 0.78$) of the subplots. The variable concentrations among plots are likely due to the heterogeneities of Pb arsenate insecticide in soil. The Pb and As levels measured using the glycine in vitro assay (GL) were strongly dependent on the treatment but not on the total soil Pb and As concentrations. On average, glycine (PbGly) extracted about 30% of the total Pb but the bioaccessibility of Pb increased up to 50% in the Fe

amended soils (e.g., DF3, DF8, DF13) while significantly decreased in the soil amended with Mn (e.g., DF19 and DF20). The DF8 plot the highest Pb extracted with glycine (147.8 mg kg⁻¹), 55% of the Pbtot. Plots DF19 and DF24 (Mn and Mn+Fe treated) showed lower Pbgly, 25 and 21 mg kg⁻¹, respectively. Fig. 2 illustrates the pronounced effect of compost amendment (DF16-20) in reducing the efficiency of Pb extractability. In general, plots with phosphate treatments (bone meal and TSP) (DF6 to DF15) also had lower extractable Pb comparing to control plots (DF1 to DF5), suggesting the binding of phosphate with Pb to form stable pyromorphite mineral.

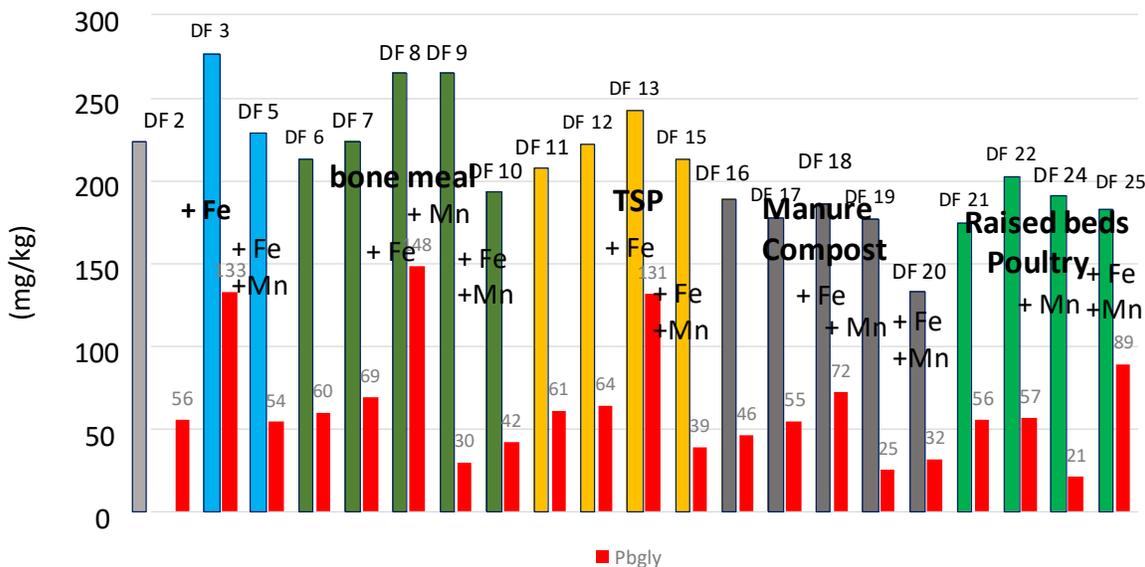


Figure 2. Total soil Pb (Pbtot), extractable Pb by glycine (Pbgly) (mg/kg) from the soils treated with Fe, Mn, P and compost amendments.

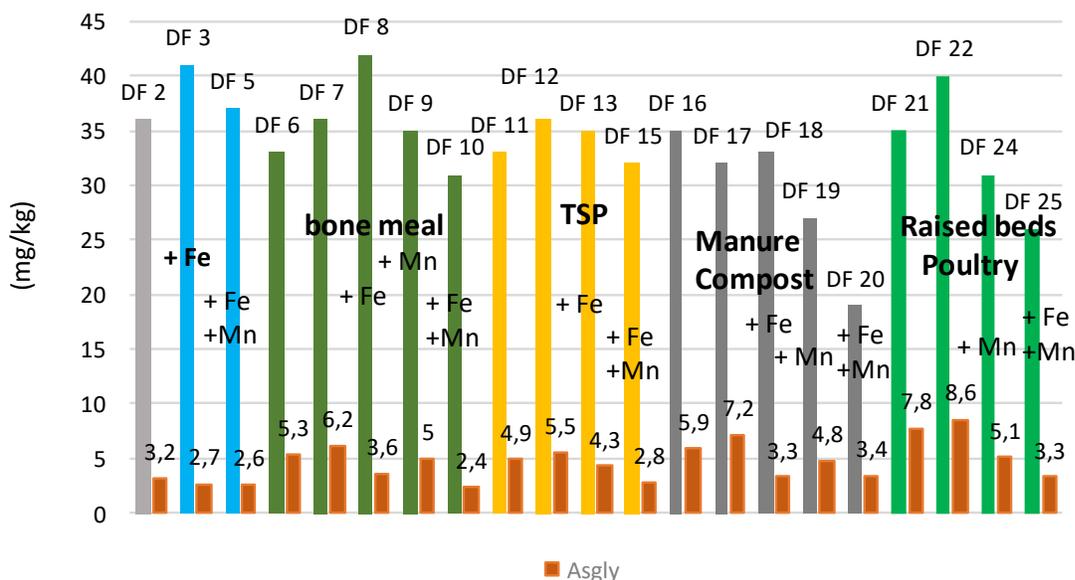


Figure 3. Total soil As (Astot), extractable As by glycine (Asgly) extracted (mg/kg) from the soils treated with Fe, Mn, P and compost amendments.

Glycine extracted about 14% of the total As (4.7 mg/kg) in the studied soils, which is about four times lower the extraction efficiency observed for Pb. However, the fraction of extractable As increased with compost addition to the plots DF21 and DF22, bone meal addition to plots DF5 and DF6, and TSP addition in the plots DF11 and DF12, with lower value of DF13 and DF15 in the Fe and Mn mixed TSP amended plots. The general trend seems indicates that the phosphate-bearing amendments increased the efficiency of As extractability in all the subplots.

Spectroscopy and chemiometric analysis

Soil Vis-NIR spectra showed a specific absorption peak at 1900 nm, due to the combinations of the H–O–H bond with the O–H stretches. Other differences of the different soil amendment were more manifest in the Vis regions with the change in slope of the spectra curves. Principal components analysis (PCA) have 4 eigenvalues that account for a 98.8% of the total variance. A large proportion of the variance can be explained by the first (PC1= 84%) and second (PC2 =12%), together, these two PCs account for 96% of the data variance.

The PC1/PC2 projection scatter plot showed four populations of the soil samples with important difference on the loadings values. The highest positive score values of PC1 and PC2 were observed in all the treated samples (DF3, DF5, DF8, DF9, DF13) with Fe and were located in the positive top right side of the projection. All samples treated with bone meal and TSP (DF6, DF7, DF11, DF15) were located in the negative side on the bottom right. The samples treated with compost and raised bed soil (DF17, DF22, DF25), characterized by higher amount of organic matter, were located in left side of the projection together with DF20. Finally, samples DF24, and DF19 treated with manure compost and raised bed soil with Mn were situated in the lower left side (Fig. 4)

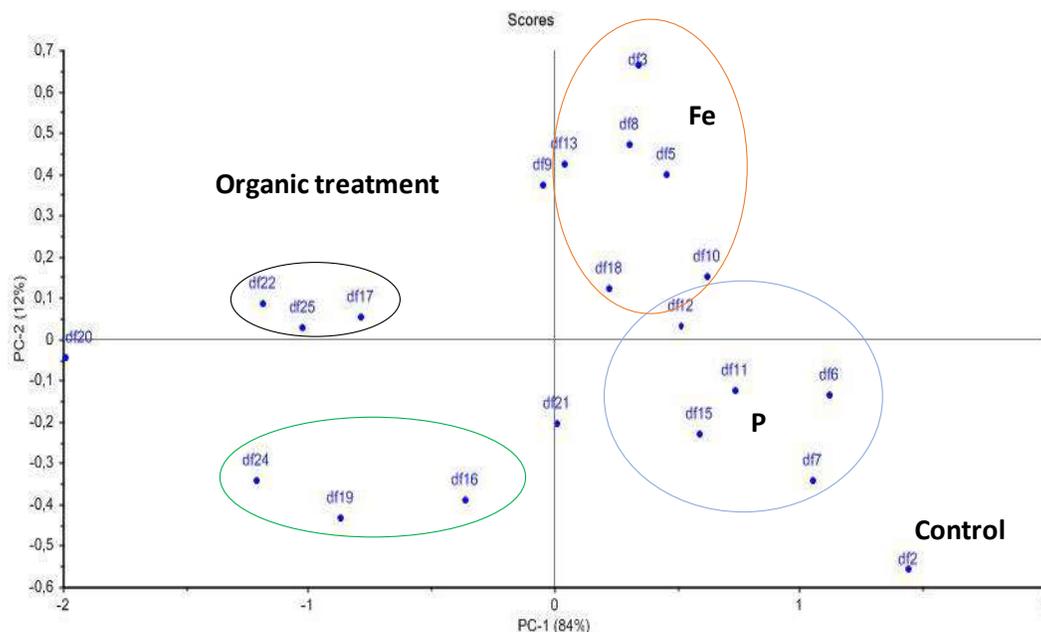


Figure 4. Factor coordinates of the samples in the principal plane of the first two principal components (PC1 and PC2, respectively X-axis and Y-axis) from PCA analysis.

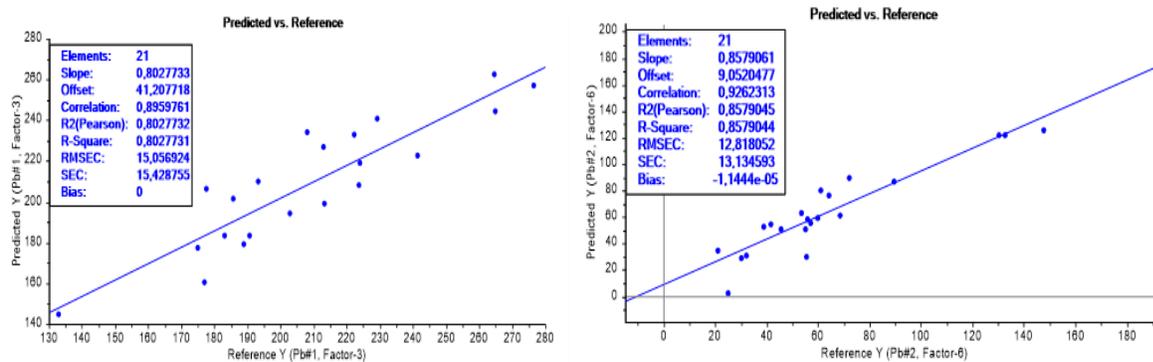


Figure 5. Observed vs. estimated values for Pb total (left) and glycine extracted Pb gly (right). The estimations were done by Partial Least Squares Regression (PLSR). Root mean square error (RMSE) and coefficient of determination (R^2), and bias for the validation data are shown for each Pb forms.

The Vis- NIR spectra were effective in estimating Pb concentrations of both Pb forms, i.e. total and bioaccessible (extracted with glycine) (Fig. 5). The PLSR analysis, performed on untransformed data, showed the highest $R^2 = 0.80$ for Pbtot, while Pb gly exhibited better R^2 values = 0.85 (Fig. 5). The RMSEs were also significantly lower for Pb gly, which was not expected since Ptot values were much higher compared to Pb gly. Good but lower performance in comparison with Pb were obtained for As with R^2 values of 0.47 and 0.80 for Astot and As gly, respectively (Fig. 6). Overall, these results emphasize that separate PLSR models generated from samples with different treatment have an important ability to predict Pb and As contents.

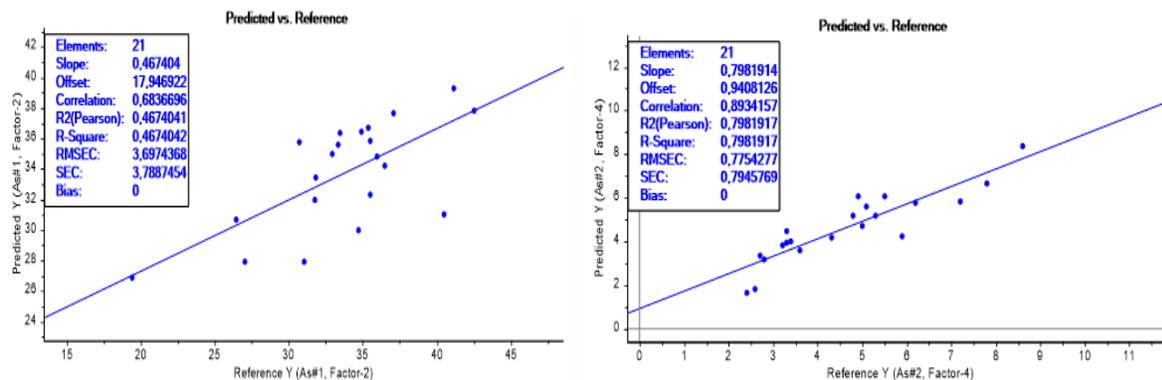


Figure 6. Observed vs. estimated values for As total (left) and glycine extracted As gly (right). The estimations were done by Partial Least Squares Regression (PLSR). Root mean square error (RMSE) and coefficient of determination (R^2), and bias for the validation data are shown for each As forms.

Discussion

The results of this research indicate that Vis-NIR-DRS is a promising technique for estimating Pb and As in moderate contaminate soils on the basis of R^2 value ($R^2 = 0.91$ or greater indicated an excellent prediction, values between 0.82–0.90 indicated a good prediction, while values between 0.66–0.81 indicated an approximate quantitative prediction). On one hand, by this standard, VisNIR-DRS showed a good prediction capacity for bioaccessible Pb and As, and an approximate quantitative prediction capacity for total Pb and As contents. In particular, the RPD values were greater than 2 for all Pb and As forms (Table 1), which is indicative of successful estimation of the prediction models (Chang *et al.*, 2001). Spectroscopic diagnostic screening for heavy metal

concentration, particularly Pb, zinc and copper, are possible because of their relationship with clay, Fe and organic matter.

Table 1. Partial least squares regression (PLSR) model performance in predicting the different Pb and As content forms using visible and near-infrared reflectance (Vis-NIR) spectroscopy for the 6 soil amendment treatment

PLSR	Pb tot	Pb gly	As tot	As gly
R ²	0,8	0,9	0,47	0,79
RMSEC	15,05	6,38	3,69	0,77
SEC	15,42	6,54	3,79	0,79
Bias	0	0	0	0
RP RPD	2,31	2,72	1,4	2,28

Conclusions

Vis-NIR spectroscopy coupled with PLS Regression was applied to develop the diagnostic screening tests for soil contaminants. The technique produced a good quantitative prediction with both Pb and As. The results obtained can be summarized as follows: 1) the PLSR models for Pb and As estimation on the basis of the VIS–NIR spectra generally give good results in terms of bioaccessibility of Pb and As among the soil samples with different treatments (high R² and mean of RPD > 2); 2) Fe and compost amendments seem to improve Pb availability measured by glycine; 3) the results showed a different effect of compost amendments in increasing the extractability of soil As; 4) since laboratory analyses of bioaccessible Pb and As are both costly and time consuming, the use of VNIR-DRS could result in significant reductions in cost and labor. Therefore, considering the promising results we conclude that VNIR-DRS estimations might offer a low cost alternative with reasonable accuracy for assessing Pb and As in polluted soil.

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3.1.7. Influence of irrigation waters on heavy metals pollution of agricultural soils in a Mediterranean alluvial plain (Valencia, Spain)

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Abstract

Heavy metals are unequivocal indicators of human activities, whose effects on health and biota are of increasing concern for the population. The dispersion by irrigation waters of these elements is one of the most important ways to reach agricultural soils and its production, reaching the food chain.

In this work, the target study area corresponds to the alluvial plain between the rivers Turia and Júcar (Valencia, SPAIN), with an extension of 486 km², which is characterized by its dense network of channels and ravines for irrigation one of the most productive agricultural areas of Spain and Europe. This area includes a wide zone of rice farming and a Natural Park (La Albufera). In this study area, 35 sampling zones for waters and 33 for soils were selected, covering the different water sources and agricultural uses, to monitor the levels of 15 heavy metals of different toxicities, characteristics and origins.

Total concentrations of the selected 15 heavy metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Rb, Sb, Tl, and Zn) were determined. Standard analytical methods were used to measure water and soil physical and chemical properties. Total content of the selected heavy metals was extracted by microwave acid digestion and determined by ICP-OES. The spatial distribution of these metals in the study area and the influence of the different soil uses and irrigation water types were also analyzed.

Metal levels obtained were, in general, below the limits established by the EU legislation, with maximum values in waters for Al, Fe and Tl with 1.02, 0.96 and 1.22 mg/L, respectively. In the case of Sb and Tl all samples showed values higher than those established in different legislations. Regarding soils, all values are under regulatory limits, assuming that for most of the studied metals there are not legislation. The highest values appeared for Al (45.64 g/kg) and Fe (28.99 g/kg). Li, Rb and Tl showed values over or around 100 mg/kg. In all cases, the major values were determined in zones with rice farming, mainly at the North of the study area.

Keywords: Heavy metals, toxic elements, Mediterranean alluvial soils, spatial distribution, irrigation waters, environmental influence

Introduction, scope and main objectives

Coastal zones of the world usually present a very high biodiversity and unique ecosystems. However, in the last 50 years, the increasing human pressure and the socio-economic development have caused serious damages to these ecosystems. In particular, in the Southern region of the

Mediterranean, 65% of the population (around 120 million inhabitants) is concentrated in coastal hydrological basins, where environmental pressures have increased (EEA 2015). In this sense, the Mediterranean coast of Spain has the fastest growing population in Europe, which increased up to 50% in the past decade, with around 1.7 million houses (Cundy *et al.* 2006; Andreu *et al.* 2016). This scenario have resulted in the need of resources to maintain population and infrastructures producing an increasing pressure on the hydrological and agricultural systems.

Related to these pressures, pharmaceuticals and heavy metals have been considered as potential indicators of human development in the different environmental media (Vystavna *et al.* 2013). Their effects, in general, on environmental and human health are relatively well known, representing a constant threat to be controlled. However, many of these elements have still been scarcely studied in soils or waters (Li, Ti, Tl, V, Rb, etc.), because of that, there are scarce legislation about their toxic levels, mainly in the case of soils in contrast to waters or atmosphere.

The objective of the paper is to establish the levels and distribution of 15 metals and metalloids (Al, As, Be, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Rb, Sb, Tl, and Zn) of different toxicities and biological functions, in soils and waters of the coastal alluvial plain comprised between Jucar and Turia rivers (Valencia, Spain). Their geo-spatial distribution and the possible influence of environmental factors (land uses, water sources, etc.) were also studied, together with the possible synergies between metals and with soil and water characteristics.

Methodology

Study site and sampling

The selected area (486 km²) is located in the Valencia (Spain) between the rivers Turia (to the North) and Jucar (to the South), that flow into the sea along a broad coastal plain (Figure 1). This landscape structure has a dense network of canals and ditches for irrigation. Agriculture is the main activity of the area, mainly rice farming (223 km², many of which are inside the limits of the Natural Park). However, there are also a large population, industrial and urban development pressures, surpassing population densities of 2000 inhabitants/km². Its characteristics and circumstances make it similar to the majority of the Mediterranean fluvio-littoral spaces in Europe.

Soils of this zone have been developed from organic black and gray silts and are affected intensely by agricultural practices. They show a basic pH, carbonated, with hydromorphic properties in places near the coast, and high salinity levels. The soils of this area can be grouped in three zones: (i) inner zone, devoted to orchard and citrus crops that present soils of calcic Luvisols, calcic Cambisols, haplic Calcisol types, (ii) a central part that comprises all rice farming with a very variable water table, with soils like calcareous Gleysols, calcareous Fluvisols and gleyic Fluvisols, and (iii) the coastal strip that shows the highest degree of anthropization with limited orchard points, is characterized by soils like hydric Anthrosols, calcareous Arenosols, gleyic Arenosols and urbic Technosols (IUSS Working Group WRB 2006).

Soil samples of the upper 0-30 cm depth layer were collected. From each of the 33 sampling zones, of 25 m each, five sub-samples were taken. Once in the laboratory, samples were dried and passed through a 2mm Ø sieve, and then, the sub-samples of each sampling point were homogenized to create a composite one. The composite soil samples were extended in a layer of approximately 1 cm thickness on polypropylene trays and air-dried in darkness at 20 °C to moisture content of approximately 3% water. Then, samples were stored in sealed plastic bag at 4 °C.

Surface waters were collected in 35 points in the study area (Figure 1) as close as possible to the soil sampling zones, covering the most important water channels and in the marsh. Before sampling,

polyethylene bottles (2.5 L) were washed successively with detergent, tap water, distilled water and the sample water finally. The bottles were filled to the top with the water to eliminate air bubbles and maintained at 4 °C until their arrival at the laboratory. Once in it, samples were filtered through glass microfiber GF/A filters prior to extraction, and stored in dark bottles at -20 °C until the analysis. Samples were extracted within 1 week.

Analysis

Total concentrations of 15 heavy metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Li, Ni, Pb, Rb, Sb, Tl, and Zn) were determined. Standard analytical methods were used to measure water and soil physical and chemical properties. Total content of the selected heavy metals was extracted by microwave acid digestion (U.S. EPA 1996) and determined by ICP-OES.

Statistics

IBM SPSS version 22.0 was used for statistical analyses. Analysis of variance (ANOVA) and Tukey's multiple range test at $\alpha=0.05$ were performed to detect differences in the variables between treatments.

Pearson statistical bivariate correlation analyses were applied, at 95% and 99% significance levels, between heavy metal concentrations and soils/water characteristics to determine possible relationships among them. When values of a variable showed a non-normal distribution, Spearman bivariate correlations were applied at the same significance levels. Multiple stepwise linear regression analysis, discriminant analysis and categorical PCA were used to confirm the weight and dependence between variables, differences and identifying possible behavioral patterns. To analyze spatial distribution of metals and zoning the area, geo statistical and spatial analysis tools were applied (Arc Info v. 10.3).

Results

A geostatistical analysis was made, considering land uses, water sources and human pressure, to sectorize the study area. As a result, nine landscape functional sectors (LFS) were obtained (Figure 1). It facilitated to understand the influence of the different environmental factors, on water and soils pollution. LFSs I, II, and III receive the influence of the Turia river waters including the influence of the Valencia city (almost one million inhabitants) with two of its waste waters treatment plants (WWTPs). Zones IV, VI and VII correspond to Jucar river waters, receiving LFS VIII the influence of both river waters. Zone V corresponds to the waters related to the Albufera lake, and Zone IX cover the littoral strip.

In the case of waters, Be, Cd, Co and Cr showed values under the limit of detection (LOD), while Al, Fe, Li, Tl and Zn had a 100% of apparition in the samples always above LOD. Maximum values were determined for Al, Fe and Tl with 1.02, 0.96 and 1.22 mg/L, respectively. It has to be pointed out that many of the studied elements showed values above those proposed by different legal regulations or benchmarks (WHO, FAO, EPA, etc.) for waters (Figure 2). It is the case of Al, As, Fe, Li, Pb, Sb and Tl. For many metals there are very scarce regulations, or none, about their toxic levels in waters, such as Be, Co, Li, Rb, Tl, etc. The highest levels of As, Fe, Sb and Tl were located in the lake and its surroundings, those for Cu, Ni, Pb and Rb were determined at the northern part of the studied area influenced by the Turia river waters. Al, Li and Zn major values are concentrated mainly at the south of the study area.

Statistics showed that there are not clear differences between LFS. Only differences at 95% of probability for As, Fe, Li and Tl were observed. Ni presented high significant differences, between

the lake and the waters corresponding to orchard zones irrigation (LFS I, II and IV). Regarding water types, Be, Cd, Co and Cr showed significant differences between their contents in rice fields waters and the remainder ones. Differences between river waters and those from channels for orchard irrigation were observed for Zn.

The analyses about the influence of waters intrinsic characteristics showed that there is a high significant relationship between the salts content (NaCl, Na, electric conductivity, etc.) and Li and Tl distribution. In the case of Cu, Ni and Rb these inverse strong relationships were observed with the nitrites levels, in the same way that between Al and Fe with the dissolved oxygen.

In soils, all the studied elements were detected in all samples, with values higher than the LOD. Al and Fe showed the highest levels in all cases, with maximum values of 45.64 and 28.99 g/kg, respectively. The majority of metals presented their highest values at the north of the study area (rice farming), only Al, Co, Cu and Fe show them at the southwestern part that is mainly dedicated to citrus and orchard crops.

In the case of soils there is an important lack of indications (recommendations, regulations, legal limits, benchmarks, etc.) regarding the toxic limits of many metals, usually, those are restricted to a limited group of them (As, Cd, Cr, Cu, Hg, Ni, Pb or Zn). In our case only 6 (Cd, Cr, Cu, Ni, Pb and Zn) from the 15 have these indications, and only Cr reach that (146.46 mg/kg).

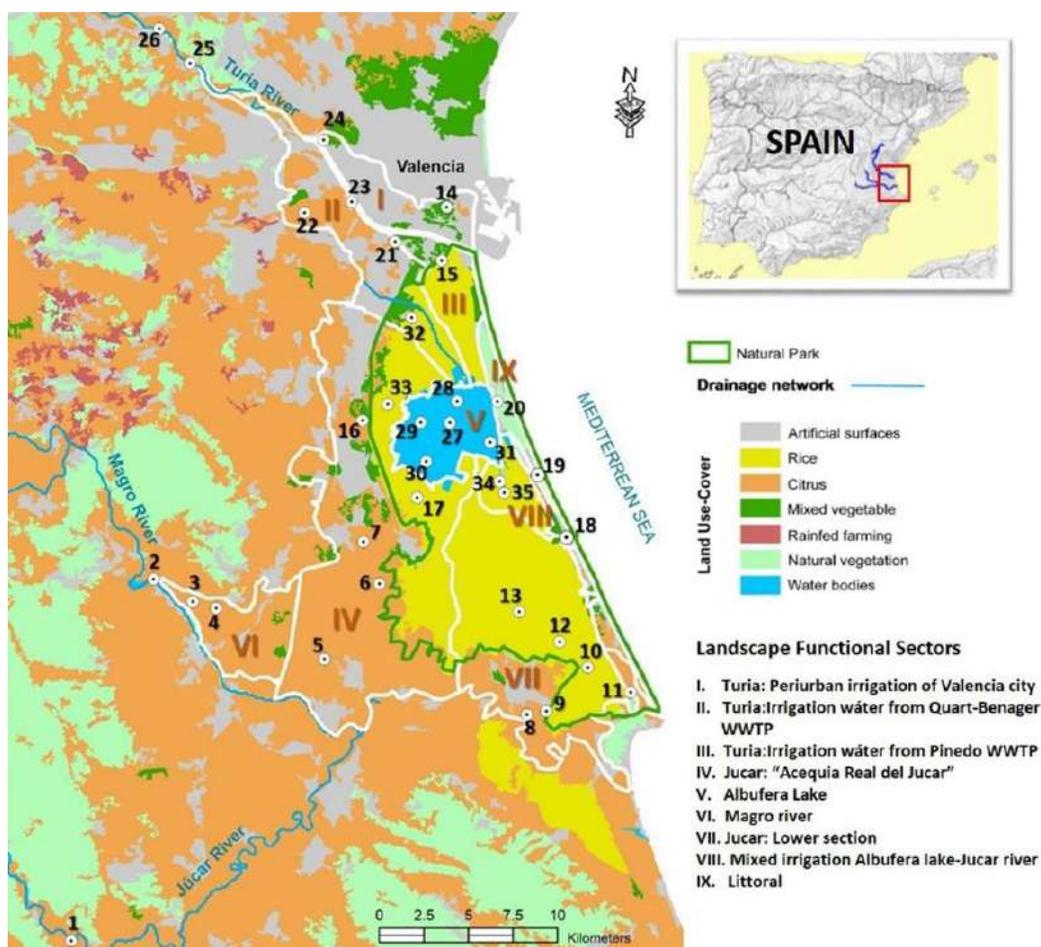


Figure 1. Location of the study area and its Landscape Functional Sectors, including sapling zones.

In general, the littoral strip (LFS 9) presented high significant dissimilarities with the other sectors for the majority of metals, mainly with LFS 3 (northern of the area) for Al, Be, Cr, Cu, Fe, Li, Ni, Rb, Sb, and Zn, and LFS 8 (rice farming south of the lake) for Tl. No differences were observed between water types. Regarding land uses, two significant tendencies were observed, high differences between natural vegetation and rice farming soils and the first with orchard soils. In general, the most influencing soil characteristic regarding the studied elements was the cation exchange capacity (Figure 3). Organic matter content has inverse significant relationships with Al, As, Cd, Fe and Li, and calcium carbonates have influence with Al, Pb, Tl and Zn. Li and Tl showed similar behavior in the soils of the study area; the same occurred with Cu, Ni, Pb and Zn. As did not present any relationship with the other metals, while Be, Sb and Rb show similar patterns.

Discussion

The framework for heavy metals depicted in the study area is of concern for soils and waters, and it is based in the high levels of particular toxic elements in both environmental compartments. The majority of metals showed values in waters below the limits established by national or international legislations, not only for irrigation or livestock waters (WHO, 2008) but also for drinking waters (Council of the European Unión, 1998), and even lower than those reported in the literature for natural coastal wetlands and lakes (Zeng *et al.* 2015; Engin *et al.* 2015). It is more evident for Be, Cd, Co and Cr, which show values <LOD.

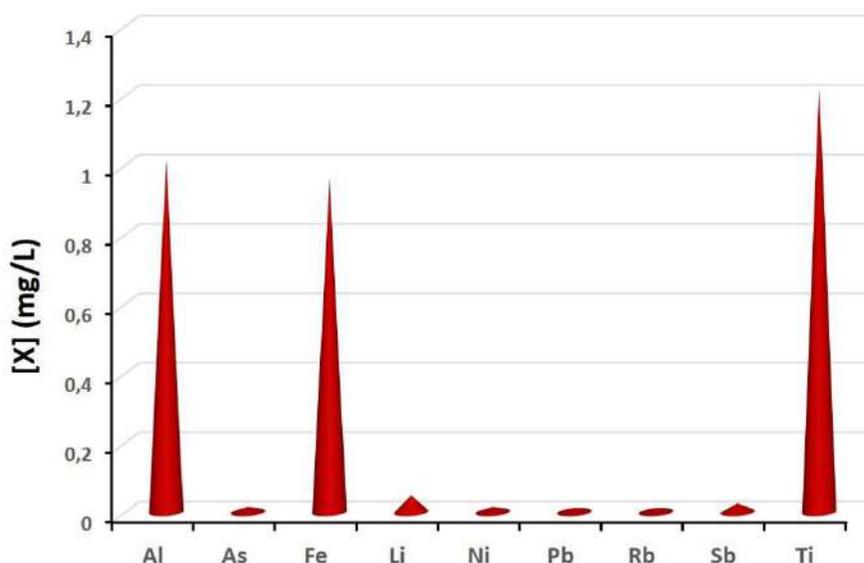


Figure 2. Maximum values of the studied metals that exceeded EU and WHO limits for waters.

However, Al, Fe, Pb, Sb and Tl presented mean levels that surpass the existent regulations. This is more evident for Tl with an average value of 0.36 mg/L, which is higher than values reported in the literature for rivers and groundwater (Karbowska 2016; Machado *et al.* 2017).

Regarding soils, it is difficult to evaluate properly their toxicity state because of the lack of official limits for many metals. Al and Fe showed by far the highest levels, with average values of 27.15 and 18.17 g/kg, respectively. These values could indicate a potential toxicity of these soils for plants growth and agriculture production (Singh 2017), even if the average pH of soils in the study area ranged from 7.06 to 8.70. However, Tl and Li levels also can produce toxic effects in crops development. The values of Tl in these soils are also of concern, with an average value of 52.47

mg/kg, higher than values reported by Vaněk *et al.* (2018) for soils affected by metallurgical wastes. In addition, Li levels in the studied soils are major than many of those present in the literature as normal ones (Shahzad *et al.* 2016)

These levels could be the origin of several problems that affect citrus and rice crops from years ago, in quality and quantity. Al and Fe have an active role in the degradative effects on plant roots, particularly in rice, usually at acid pH. However, according Orvig (1993), at pH above 7.5, Al(OH)_4^- is formed and resolubilization of Al occurs, which could be happen in these soils. Al, Tl can contribute to the decreasing of rice production (Huang, 2016). These rice farming soils are periodically flooded producing an alternation of aerobic/anaerobic periods that favors the presence of oxides and amorphous hydroxides of Fe and Al that can also affect the roots development (Liu *et al.* 2017). Citrus crops are also affected in same way by these elements, but the levels of Li in their soils could cause damages in trees and fruits (Shahzad *et al.* 2016)

It has been observed that the northern part of the study area, including the lagoon, presents the major values of the majority of metals. It can be due to the influence of Valencia city (900.000 inhabitants), mainly through its two main WWTPs, and the belt of towns and industrial parks that limit the area by northwest.

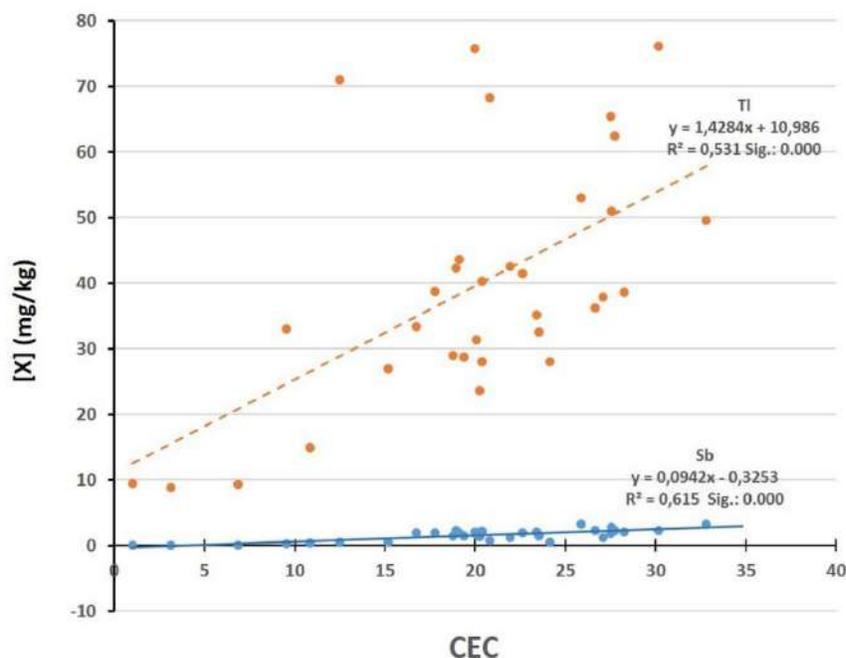


Figure 3. Statistical relationships between Sb and Tl with the cation exchange capacity (CEC) of soil.

Conclusions

In this work soils and water chemical degradation, through the study of 15 heavy metals, has been assessed. Both media showed very high values in toxic elements (Al, Li, Tl, etc.) mainly concentrated in the northern part of the study area. This zone support the major part of the population and a increasing industry. To better understand the different characteristics of the studied area, a geostatistical analysis based on land uses, water sources and human pressure was made, resulting in 9 Landscape Functional Sectors.

In waters Al, As, Fe, Li, Pb, Sb and Tl showed values that surpassed those marked by legal regulations. Li and Tl presented high significant relationships with the salts contents, which can be due in some zones to marine intrusion due to the overexploitation of aquifers. Nitrites content showed an inverse relationship with Cu, Ni and Rb, in the same way that dissolved oxygen with Al and Fe.

In soils, Al and Fe presented the highest values of the study area, reaching 45.64 and 28.99 g/kg, respectively. This fact together with the important values of Li and Tl determined in soils could be the cause of one of the most important problems of the area, which is the gradual decreasing on quantity and quality of the agricultural production that is more critical in the case of rice plants. Citrus crops are also affected by this phenomenon.

Cation exchange capacity is the most influencing soil characteristic regarding the dynamics of the studied metals.

A deeper study is needed to determine the sources and hot spots of pollution by these metals, mainly in the case of the most toxic ones. It is a necessary way to prevent the possible input of these elements through the soils in the different crops and their effect in the food chain, preventing its impact on population health.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.8. Mapping heavy metal pollution of agriculture soil in Orontes basin with semiarid mediterranean climate

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Abstract

Orontes River region is considered to be one of the most polluted areas in eastern Mediterranean due intense urban occupation and large numbers of different industries as well as using untreated sewage in agriculture irrigation. In order to assess the heavy metal soil pollution and provide the base maps for contents and fractions of four heavy metals (Cd, Cu, Pb and Zn), were determined using geostatistical techniques on a pilot area of Orontes basin surrounding Hama city. The resulting prediction mappings identify the locations of high concentrations of this heavy metals in topsoils of the study area, and the total concentrations exceeded the Syrian Normalize standard for soil, especially for Cd. Moreover, Cd, rated as being at high risk, had a high mobility as its great contents of exchangeable and carbonates fractions in spite of its relatively low content. The maps show that areas of high pollution of Cu are located in the northeast, where there is a predominance of industrial and agricultural activities; Pb and Zn also occur in high concentrations in the northeast, but the maps also show significant concentrations of Pb and Zn in other areas, mainly near central and southeastern parts, where there are industrial activities. Regression analysis revealed clay could well explain the regression equation for Cd, Cu and Zn while pH and sand could significantly interpret the regression equation for Pb.

Keywords: Pollution, Soil, Heavy metal, Orontes basin.

Introduction

Soil contamination poses an increasing threat to human health and environmental quality (Lourenço and Landim 2005), particularly Heavy Metals HM which are relatively high density with an atomic number greater than 20 (Raskin, 1994) naturally exist in soil and have received considerable attention over the last few decades (Franssen *et al.* 1977). Their concentration increased by geological and anthropogenic activates, such as the excess use of agrochemicals (Groom *et al.*, 1995), sewage sludge and municipal waste disposal (Alloway, 1990), (Shen *et al.*, 1994), to the extent that causes reduction in plant growth and yield. Some heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V, and Zn are required in minute quantities by organisms. However, excessive amounts of these elements can be accumulated in the food chain, giving a potential risk to human health, other heavy metals such as Pb, Cd, Hg, and As are very harmful, compromising the safety of the food consumed by both humans and animals (Tóth *et al.*, 2016). Although soil often acts as a filter, purifying and immobilizing many of the impurities deposited in it, its capacity is limited, so the soil can be negatively affected by the cumulative effects of atmospheric

pollutants, agrochemicals and fertilizers, industrial and domestic solid residues, and toxic and radioactive materials (Moreira-Nodermann 1987). Some Soil properties affected metal availability such soil pH (Harter, 1983), moisture content and water holding capacity (Rakesh Sharma, 2013). Soil contamination with heavy metals may also cause changes in the composition of soil microbial community, adversely affecting soil characteristics (Giller *et al.*, 1998; Kozdrój and van Elsas, 2001; Kurek and Bollag, 2004; Friedlová, 2010). On the other hand, the mobility of heavy metals is slow in clayey alkaline soils with a high content of calcium carbonate and their utility is limited due to immobilization (Müller *et al.*, 2005). Prediction mappings of samples are often based on geostatistical methods since soil properties present a continuum in their spatial variations, it is difficult to categorize soil samples without introducing errors or oversimplifications. This approach is increasingly used to characterize the spatial variability of soil properties because it can calculate unbiased estimates at un-sampled locations (Van Meirvenne and Goovaerts 2001; Webster and Oliver 2001; Lin *et al.* 2001; Romić and Romić 2003; McGraph *et al.* 2004). Therefore, class boundaries are usually chosen and values close to class boundaries can fall into different classes, the problems resulting from misclassification of soil units may be amplified (Dobermann and Oberthür 1997).

The aim of this work is to present the spatial distributions of heavy metal mapping of pilot area of Orontes basin soil, In order to provide an insight into possible heavy metal contamination that may be occurring in the study area, for that, data were interpolated using ordinary kriging and prediction mappings of polluted areas were generated.

Methodology

Study area

The Orontes basin is an important agricultural area of irrigated land in Midwest of Syria, submitted to semiarid Mediterranean climate with a total area of 23967 km², extended from NE of Lebanon through Syria to the South of Turkey. Orontes basin plays an important role in the agriculture economy of Syria, whereas irrigated winter wheat, sugar beet and cotton are growing depending mainly on Orontes river water which is highly polluted by both domestic sewerage and sludge sewerages (Abed Rabouh, 2005). Agricultural practices used on these soils, such as the intensive use of agrochemical products and wastewater, for soil irrigation, result in contamination that requires in-depth investigation. In addition, the concentration of industrial areas near villages and the presence of small industries in the agricultural zones could increase the concentration of pollutants, which should be assessed. The Orontes basin is characterized by intensive agricultural and industrial activity, a high population density and urban expansion. These factors exert a high pressure on the soils and could result in contamination. This land use pattern is typical and representative of Mediterranean semiarid areas with 19.3 °C annual temperature and 403 mm annual precipitation, where, in recent decades, agricultural intensification has occurred in parallel with industrial and urban expansion.

Water, Soil sampling and chemical analysis

The pilot area extended from 35.05-35.20 N to 36.85-36.67 E, in which, 5 water samples from Orontes river and 93 bulk soil samples were collected from 30 cm of plough layer at 0.5 km intervals along grid net of (60 grid SE, 60 grid NW), (Fig. 1).

The samples were air-dried and ground to pass through 2 mm sieve prior to analysis. Particle-size distribution of bulk soil (<2 mm) was determined by the sieve-hydrometer method (PKiN 1998). The organic carbon content in fine earth was determined by dichromate oxidation (Nelson and Sommers 1982). The soil pH was determined in 1:2 soil/water solution. Cd, Pb, Zn, Cu, the

samples were placed in Teflon tubes and digested with HNO_3 , HF , and HClO_4 . Then the solutions were diluted with 2% (v/v) HNO_3 to a final volume of 50 mL and analyzed by an atomic absorption spectrophotometer.

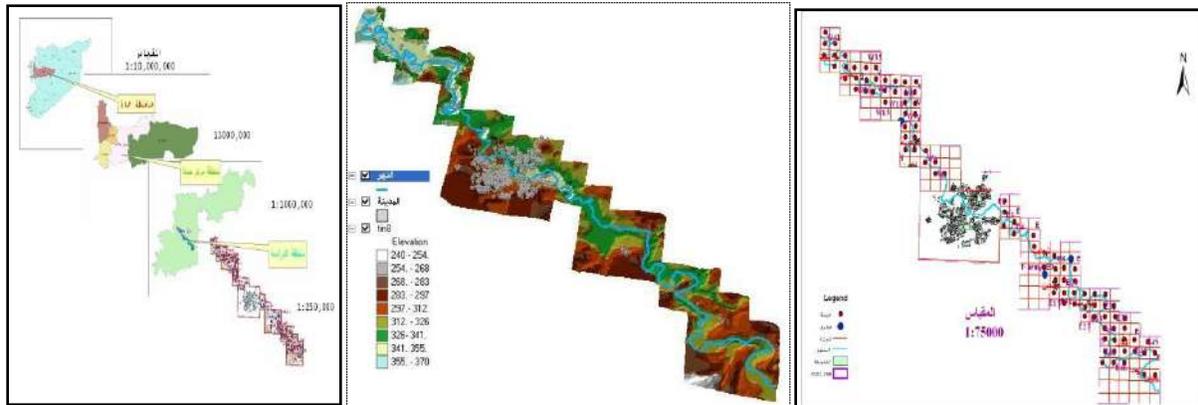


Figure 1. Location of study area and grid net of soil sampling.

Pollution Assessment

By applying Geo-accumulation Index (I_{geo}), (Müller, 1979)

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right)$$

Where C_n is the measured content of an element, and B_n is the background or pristine value of the element. The constant factor 1.5 is the background matrix correction factor due to lithogenic effects.

Geostatistical analyses were applied through the analysis of semivariograms of the selected individual variables. Experimental semivariograms were obtained from the omnidirectional semivariances, $\gamma(h)$, as a set of spatial observations, $Z(x_i)$, which were calculated as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2$$

where: $z(x_i)$ and $z(x_i + h)$ are experimental measures of any two points separated by the vector h , and $N(h)$ is the number of experimental pairs separated by h . In practice, a semivariogram simply enumerates the relationship between the degree of similarity between two measurements of some variable $Z(x_i)$ separated by distance h , which is termed the lag.

Results

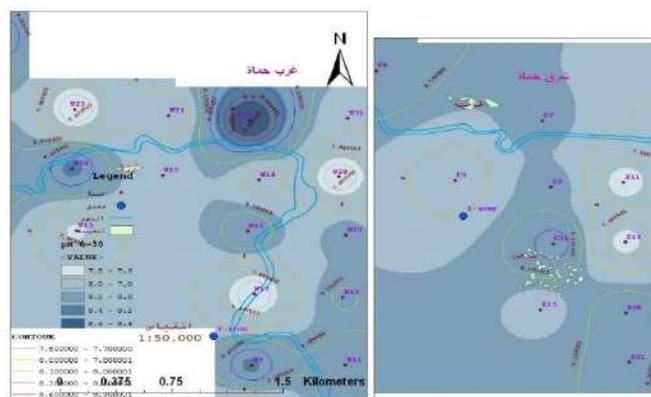
The Physicochemical parameters and heavy metal concentrations of Orontes river water were showed in table 1.

Table 1. Chemical analysis of Orontes River Water

Observation point	pH	EC ms.cm ⁻¹	NH ₄ ⁺ mg.kg ⁻¹	PO ₄ ⁻³ mg.kg ⁻¹	Pb mg.kg ⁻¹	Cd mg.kg ⁻¹	Cu mg.kg ⁻¹
Al Gassalat	7.9	0.82	0.58	6	0.35	0.091	0.55
Al Genan	7.8	0.86	0.7	7.37	0	0.079	0.22
Al araba nawaeer	7.5	0.79	0.38	3.5	0	0.084	0.15
Al Dahreah	7.6	0.87	0.7	5.5	0.08	0.086	0.35
Arza	7.22	0.87	1.8	6.8	0.14	0.103	0.73

In water samples, the pH range between 7.22–7.9, indicating the moderately alkaline nature. Electrical Conductivity (EC) ranges from 0.79 to 0.87 ms.cm⁻¹, Ammonium NH₄⁺ ranges from 0.38 to 1.8, Phosphate PO₄⁻³ ranges from 3.5 to 7.37, the concentration of Cu varied from 0.15 to 0.73, while the other metals were found to be in the range of Cd 0.079–0.103 which is higher of (IPCC, 1986) recommendation, Pb 0.00–0.35 and finally Cu 0.15–0.73, all on mg.kg⁻¹unit.

The Physicochemical parameters and heavy metal concentrations of Orontes basin were measured to get the general physicochemical characteristics of soils. Salinity refers by Electrical Coactivity (EC) is normal which value are between 0.1 to 0.84 ms.cm⁻¹. Soil pH is alkalescency, value ranges from 7.5 to 8.6, and this might be explained by the calcareous origin of parent material, (Fig. 2).

**Figure 2.** Soil pH.

The Organic matter (OM) content in soil showed high value comparing to soil existing in the area, ranges from less than 1% to 9.8%, the higher content near sewage stations support the idea of higher content due to direct irrigation with sewage sludge water, (Fig. 3).

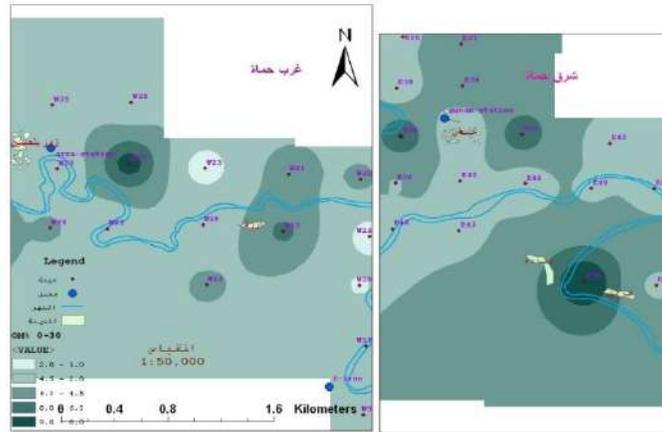


Figure 3. Organic matter (OM) content in soil.

Clay content is high, and the soil has clay loam texture and absence of clay migration process due to continuous soil cultivating and extensive agriculture rotation. In addition, oxidation and terraces of redox-morphic features observed, this are related to irrigation method applying by local farmers (flood irrigation), clay ranges from 12% to more than 40%, this may be the result of continuous deposition of alluvium on the riverbed in Orontes River, (Fig. 4).

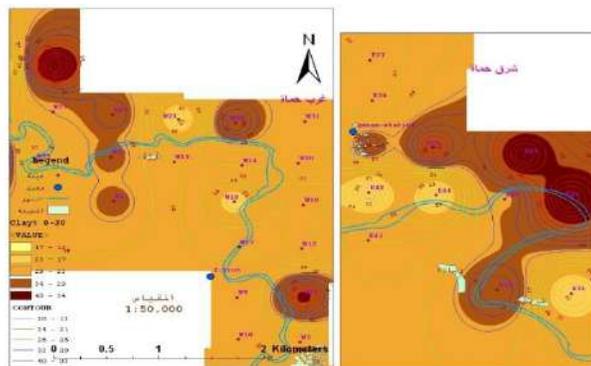


Figure 4. Clay content in soil.

Soil calcium carbonate content range from 23% to up 44%, the amount is normal for soil derived from calcareous material, (Fig. 5).

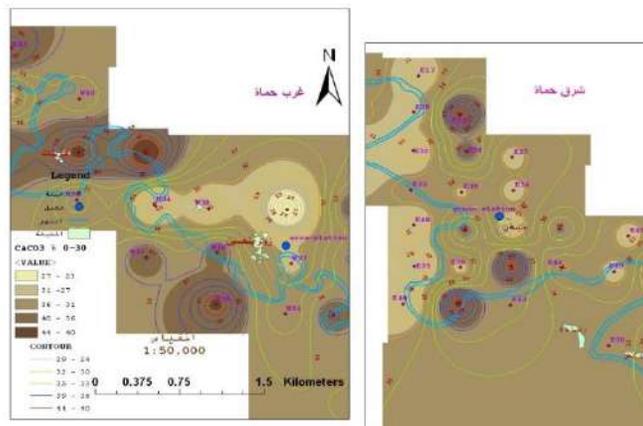


Figure 5. Soil calcium carbonates content.

The Cd concentrations was high near Zourblehasen (9.8) mg.kg⁻¹ and near Srehen, (Fig. 6).

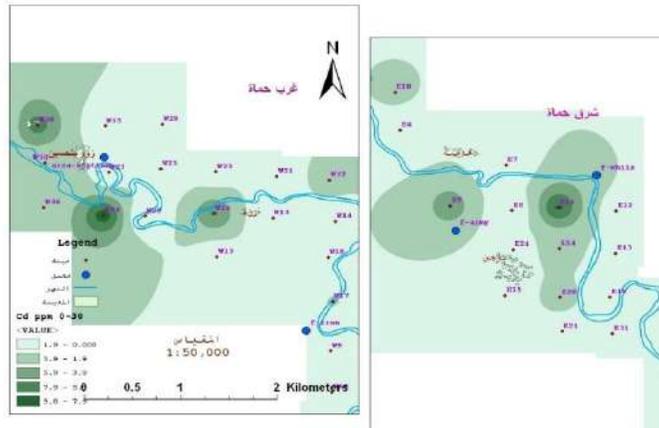


Figure 6. Cd content in soil.

Pb total concentration in general was low, Higher concertation were as in Al Dahrieh, Sraheen, and Kattab (95) mg.kg⁻¹, (Fig. 7).

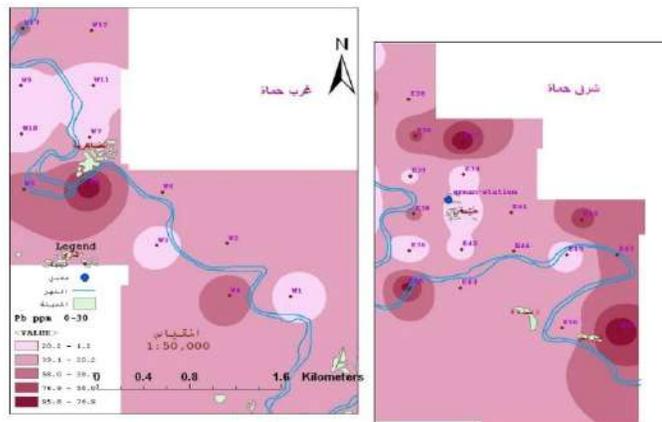


Figure 7. Pb content in soil.

Total (Cu) concentrations was high in some area and rich 127 mg.kg⁻¹, (Fig. 8).

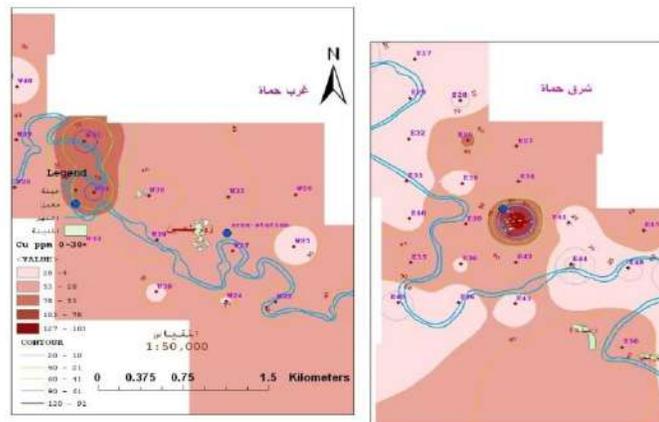


Figure 8. Cu content in soil.

Total (Zn) concentration was higher variability and values ranged from 13 to 760 mg.kg⁻¹, its environment risk will be more serious, (Fig. 9).

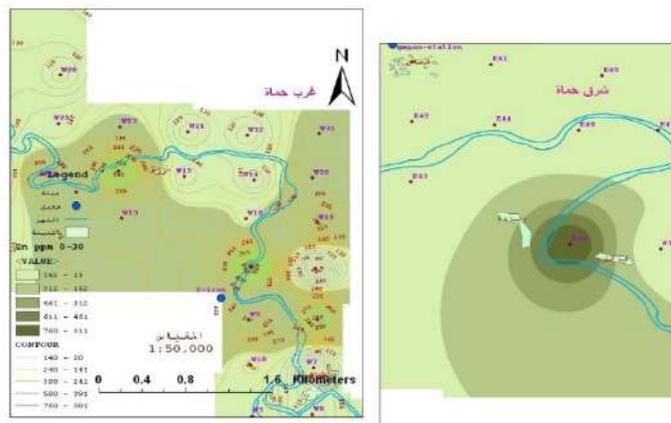


Figure 9. Zn content in soil.

Discussion

The contamination of heavy metals to the environment, i.e., soil, water, the plant is of great concern due to its potential impact on human and animal health. Clayey soil and high calcium carbonate, giving it a high potential for adsorption of heavy elements. The spatial variations of the concentrations of Cd, Cu, Pb and Zn in Orontes basin soils were more significant than that in Orontes river water. Geostatistical analysis showed that data did not well distributed because the high variation between the studied elements data. The spatial distributions of Cu and Pb concentrations in soil were unregularly, it may be that the movement of water washed out the top sediments which resulted in a higher concentration in soils than in sediments, also a high concentration of Cu was significantly associated with organic matter content. However, as Cu is considered more readily soluble. When some parameters change (soil pH) it would be released from associations with organic matter. The concentration of total (Cd) in near Steel and Wheel factories ranged between (0.01-9.8) mg.kg⁻¹. There were high concentrations of Zn at Jinan and Arza sites, due to the location of these samples near the sewage stations, while a significant increase in values was found even to the depth of 60 cm in Al Dahreah, near the sewage station. The concentration of Pb was within the limits, whereas Cu was higher in Al Dahreah, near the steel factory and Al Genan. Regression analysis revealed that clay was the main contribution and could well explain the regression equation for Cd, Cu and Zn, while pH and sand also significantly interpret the regression equation for Pb. The results of correlation analysis showed the four metals maybe had similar pollution sources such as human activities, especially industrial inputs.

Conclusions

Mapping of four heavy metals (Cd, Cu, Pb and Zn) in Orontes basin gave a comprehensive view and was saving time, labour and money consuming, and showed a significant accumulation both in water and soil. The concentration of four heavy metals was higher in soil samples nearby centre area than that in selvedges samples. Meanwhile, the speciation data of metals suggested that Cd had a high availability in exchangeable and carbonate bound fractions. Cu was preferentially found in the organic and residual fraction, this requires constant monitoring and identification of these pollutants accurately so that they can be disposed of. Analyzed correlations between heavy metal variables, the correlations for these heavy metals are related to the

geographical distributions in the study area, indicating a trend of spatial concentrations increasing from southeast to northwest. There was significant correlation between (Zn, Cu), as well as between (OC, Cd, Zn).

Acknowledgements

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3.1.9. Multi-isotope fingerprints to identify on-site and of-site impacts of agricultural contaminants from soil to water bodies

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Abstract

The expansion and intensification of agricultural systems in response to pressures to produce sufficient food to feed a growing human population often leads to overuse and misuse of agrochemicals (organic and inorganic fertilizers, pesticides, salts from irrigation practices, sediments, and drug residues from livestock) and irrigation water. This overuse has a worldwide impact on soil and water quality, due to the transfer of agricultural pollutants from soil to water bodies, and consequently also on food security and human health. When contamination of an agro-ecosystem occurs from multiple sources, it is difficult for traditional techniques to evaluate the relative contribution of each of the various sources. Complementary to conventional monitoring and mass balance approaches, stable isotopes of major elements (such as H, C, N, O and S) can be used to characterize and quantify sources and transport of solutes in agro-ecosystems. The Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture is currently developing protocols and guidelines on the use of stable multi-isotope fingerprinting to trace sources of agro-pollutants from soil to water bodies, and hence to develop soil and water management practices to reduce agro-pollutants in the environment.

Keywords: agricultural pollutants, agro-ecosystems, multi-isotope fingerprints, soil quality, water quality

Introduction, scope and main objectives

Soil and water pollution by contaminants from agricultural fields have direct negative impacts on food security, human health, biodiversity and fisheries (FAO and IWMI, 2017). The expansion and intensification of agricultural systems in response to the ever-increasing demand for food often lead to overuse and misuse of agrochemicals (organic and inorganic fertilizers and pesticides). A major knowledge gap regarding pollution in agro-ecosystems is source identification and apportionment, an area that requires extensive data, research and integration of approaches. When pollution occurs to an agro-ecosystem through multiple sources, conventional techniques, such as quantification of the polluting element and mass balance, are not effective in evaluating the relative contribution of the different sources. Complementary approaches are needed to address these gaps. Such approaches, using stable isotopes of the major chemical elements, are key to characterizing and quantifying sources and the transport of solutes through soil and water bodies in agro-ecosystems. A five-year coordinated research project (CRP), starting in 2018, aims to develop standardised protocols and guidelines for the tracing of sources of agro-pollutants using stable multi-isotopes of the chemical elements nitrogen, carbon, oxygen, sulphur and hydrogen to identify and apportion sources and transport of agro-contaminants from soil to water bodies in agro-ecosystems. The integrated use of stable multi-isotope fingerprinting with conventional analytical approach will result in more accurate environmental assessments with unambiguous identification of pollution sources, thus contributing to more efficient agro-ecosystem management practices and the adoption of appropriate remediation tools.

Methodology

Standard Operating Procedures that provide step-by step instructions on how to collect, prepare and preserve soil and water samples from intensive agricultural watersheds for stable multi-isotope analysis will be developed. This includes (1) nitrogen and oxygen composition of nitrates in water, (2) hydrogen and oxygen composition of water, (3) sulphur and oxygen composition of sulphates in water, (4) nitrogen and carbon composition of dissolved and particulate organic matter. Similarly, the application of oxygen-18 isotope signatures in inorganic phosphate and of compound specific isotope analysis (CSIA) to monitor pesticides in soil and water will be fine-tuned. The protocols will be tested and validated on three major agricultural watersheds in at least four countries.

Results and discussions

The results generated from this CRP will lead to (1) the establishment of an integrated approach to apportion and evaluate sources of agro-ecosystem contaminants; (2) the development and assembly of an analytical stable multi-isotope toolbox for use by member countries in their efforts towards sustainable soil and water management, and (3) Validated standard operating procedures for the use of this toolbox, including guidelines for the adaption of this toolbox to different agro-ecosystems. Together, this will help to provide the necessary data and confirmatory evidence to support actions and decisions to prevent and reduce soil and water pollution in national endeavours towards sustainable food security and ecosystem services.

Conclusions

Many pollutants originate from agricultural practices, including inorganic and organic fertilizers, pesticides, salt from irrigation practices, sediments and drugs residues from livestock. These pollutants spread in dynamic ways, including through rainfall and snowmelt runoff and sediments, and move into the ground through the soil and water bodies where they impact negatively on food security and ecosystem services. The use of integrated stable multi-isotopes of N, C H, O and S will provide information on the origins and pathways of such pollutants and hence facilitate more accurate and appropriate mitigation actions.

Acknowledgements

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3.1.10. Soil quality assessment, risk assessment and remediation strategy for a former pesticide distribution center, practical experiences from Tajikistan

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Abstract

The Oykamar site in Southern Tajikistan is a former pesticide distribution center that was operational till 2004. After closure of the center the area was resettled and currently 35 families are living on the site. An investigation of the soil at the site was executed in 2017. Out of the 32 kitchen gardens investigated 17 gardens contained POPs-pesticide concentrations in the topsoil above the US EPA residential limit values. The quantity of contaminated soil at the site is estimated at 8,000 tons. The remediation strategy for the site is focused on the sustainable use of the area in the future. This includes site specific risk based, removal of the most contaminated soil and concentration and isolation of the remaining contaminated soil. Awareness raising of the local population should lead to long term safe use of the site.

Keywords: POPs, DDT, contaminated land, environmental site assessment, Tajikistan

Introduction, scope and main objectives

This paper discusses the case of Oykamar as a practical example for investigation and risk assessment of the soil contamination status of former pesticide distribution centers. In brief the site investigation and contamination situation of the Oykamar site is discussed followed by an overview of the generic risk assessment of the contamination status of the site. International generic risk based screening levels (screening levels) are used to reflect on the contamination status of the soil and their implications for the use of the site. Based on the international screening levels insight is provided in the practical implications for the sustainable remediation of these types of POPs⁵ pesticide contaminated sites. The article is completed with suggestions for the set-up of the remediation of these types of sites.

Background on the site

The Oykamar site is located some 65 km south of the capital Dushanbe, in a primarily agricultural area on the outskirts of the village of Oykamar. East of the site is the main road from Dushanbe towards Qugontepa and the Afghan border. The site itself was a regional distribution center for pesticides and fertilizers measuring approximately 6 hectares. The distribution center housed three main covered pesticide stores, at least two outdoor storage areas and was enclosed by a concrete wall (“the compound”). From its opening around 1968 till its closure in 2004 large quantities of pesticides and associated products passed through. Used products included cotton dust (DDT), Lindane and HCH isomers, Sulphur and Butylphos. During the period of operation at least two and possibly three fires occurred on the site. One fire destroyed pesticide store 2 in the early eighties and

⁵ POPs-pesticides are those pesticides that are included the annexes of the Stockholm convention

the other fire took place in the outdoor storage area. Residual pesticides from the fire in store 2 were buried in a shallow pit just west of the store itself. In the period 2009 – 2010 the World Bank study ‘Obsolete pesticides technical study in Kyrgyz Republic, Republic of Tajikistan and Republic of Uzbekistan identified this site as high priority site. In the years after closure of the pesticide distribution center the area further developed and as of 2017 some 35 families are living within the former compound.

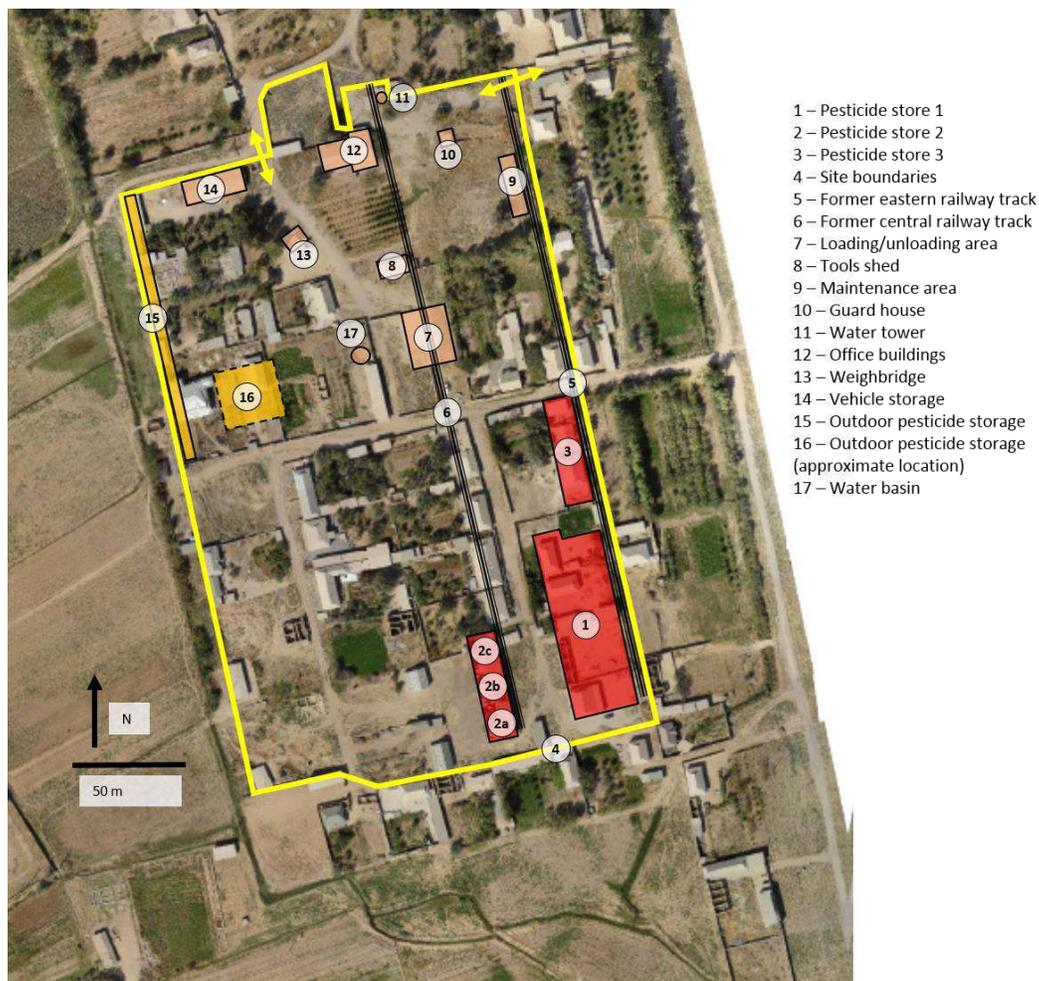


Figure 1. Aerial photograph of the Oykamar site including the main identified features from the pesticide distribution compound.

Methodology for soil investigation

In 2017, a soil investigation for the site was executed following the principles of the draft FAO EMTK 5 (FAO Pesticide Disposal Series, 2017). For the soil investigation, a twofold strategy was used:

- Individual sampling for areas suspected for contamination with pesticides and associated products in the soil. Individual sampling was done using a small back-hoe. At suspect locations trenches were dug to establish if pesticides were visible in the soil. Samples were taken from both the suspect soil layers as well as of the material underneath to establish to what extent the underlying soil was affected.

- Incremental sampling (US Army corps of engineers, 2009) was used for all non-suspect parts of the site. With the incremental sampling the designated Sampling Units were set at garden level. For each individual garden, soil was collected using either a freshly cleaned shovel or riverside auger and mixing in a clean bag an equal amount of topsoil (0 – 0.3 m bgl) from 5 individual points spatially distributed in the gardens. Areas where the owners of the gardens indicated the presence of pesticides or strong odor were not included. From each garden one sample of the mixed materials was sent for analysis.

Samples were shipped to the ISO 14001:2004 accredited laboratory of Eurofins Analytico B.V. in the Netherlands. Based on the historical information available, the main pesticide of concern was DDT. All samples were analyzed for organochlorine pesticides⁶. Several common pesticides, used fairly extensively in agriculture and horticulture in the past, contain substantial concentrations of metals (Wuana & Okieimen, 2011) as such a number of soil samples were further tested for their metal concentrations⁷. It should be noted that pure pesticides or obviously contaminated soil were not analyzed to protect the laboratory equipment from damaging.

Results of the soil investigation

The following suspect areas for the presence of pesticides were identified

- I. Pit with buried pesticides west of former pesticide store 2
- II. Pit with buried pesticides at former pond
- III. Pure pesticides in the topsoil west of pesticide store 2
- IV. Yellow coloration in the topsoil underneath the road centrally at the site
- VII. Plot with pungent smell of pesticides
- VIII. Road surfaces

In addition, 32 gardens were sampled. Not all gardens were accessible as some of the households were not at home during the site visits.

Except for the yellow coloration in the topsoil underneath the road centrally at the site, all suspect areas for the presence of pesticides contained high concentrations of POPs-pesticides (above US EPA RSL⁸ for industrial soil). Highest concentrations of pesticides were encountered in the topsoil (0 – 0.3 m –gl) of the public areas west of pesticide store 2 (DDX 910 mg/kg dry matter, β -HCH 230 mg/kg dry matter). The soil in this area also contained copper concentrations of 40,000 mg/kg indicating that metal-based pesticides (not further identified as part of this study) are present in the topsoil.

In the gardens the average concentration of DDX was 15.8 mg/kg d.m.. In the gardens directly adjacent to the former pesticide stores DDX concentrations averaged 53.4 mg/kg d.m.. Highest concentration recorded in the topsoil of a garden was 260 mg/kg d.m..

⁶ Analytical package including Hexachlorocyclohexane and metabolites, DDT, DDE, DDD, Hexachlorobenzene, Heptachlor, Endrin, Dieldrin, Aldrin, Chlordane

⁷ As, Sb, Ba, Be, Cd, Cr, Co, Cu, Hg, Pb, Mo, Ni, Se, Sn, V, Zn

⁸ RSL = Regional screening levels (<https://www.epa.gov/risk/regional-screening-levels-rsls>)

Results of Generic Risk Assessment

To assess human health risks from the soil contamination present at the Oykarar site, the gathered data on soil quality was evaluated according to two widely accepted soil contamination frameworks with risk based screening levels (screening levels):

- United States EPA Regional screening levels for superfund sites³
- Dutch Circular on Soil Remediation (bodemsanering, 2013) and Decree on Soil Quality (Bodemkwaliteit, 2016)

In the following table the screening levels for the two most common contaminants DDT and its most common breakdown products and Lindane (γ -HCH) and other HCH isomers is presented.

Table 1. Screening levels (mg/kg dry matter) for selected DDT and metabolites and Lindane and other HCH isomers in the soil

Description	US-EPA (RSL)		Dutch Framework			
	Residential	Industrial	Background values ¹ (AW)	Residential ¹	Industrial ¹	Intervention values ¹ (I)
DDT	1.9	8.5	0.2	0.2	1	1.7
DDE	2.0	9.3	0.1	0.13	1.3	2.3
DDD	1.9	9.6	0.02	0.84	34	34
α -HCH	0.086	0.36	0.0010	0.0010	0.5	17
β -HCH	0.3	1.3	0.0020	0.0020	0.5	1.6
γ -HCH	0.57	2.5	0.0030	0.04	0.5	1.2

¹Normalized values for Dutch standard soil (10% organic matter, 25% lutum). Measured concentrations are normalized to standard soil based on measured organic matter and lutum (clay) content

In the following figures the spatial distribution of contaminated soil following to the two frameworks is presented.



Figure 2. Topsoil (0 – 0.3 m-gl) quality for Oyukamar site and areas classified according to US EPA screening levels (RSL values)

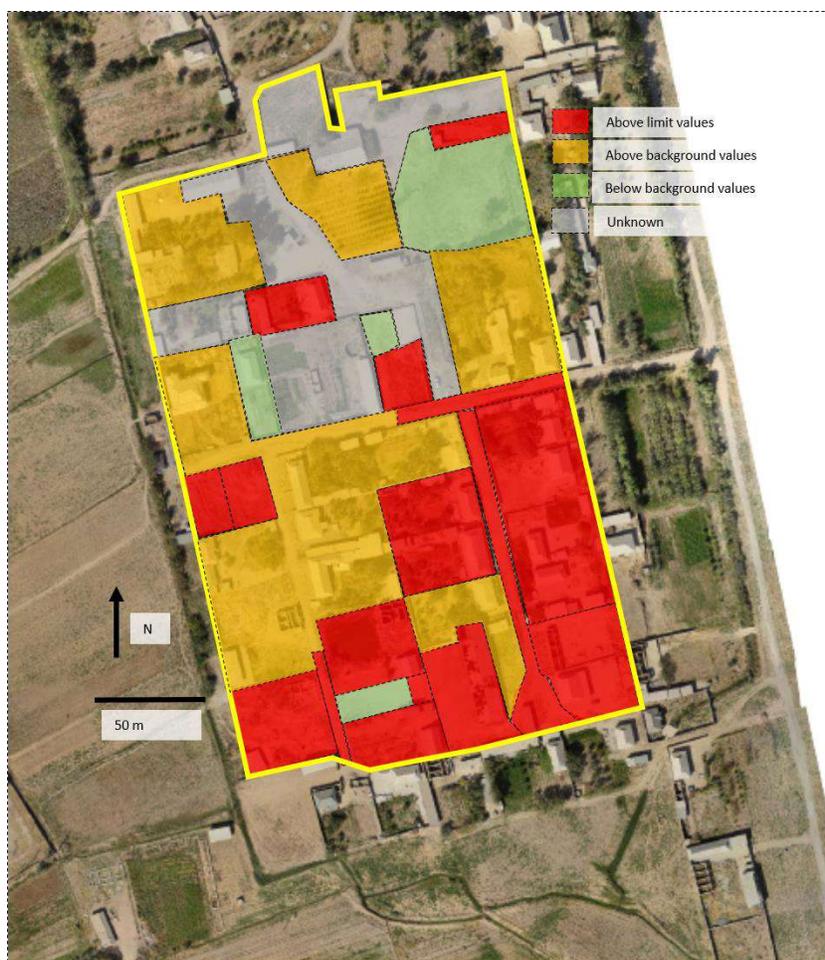


Figure 3. Topsoil (0 – 0.3 m-gl) Oykamar site and areas classified according to Dutch screening values (I-value)

According to the US EPA RSL values approximately 10% of the former compound is contaminated above the industrial soil use levels (red planes in figure 2). Another 30% of the site is contaminated above the residential soil use values (orange planes in figure 2). Out of the 32 gardens sampled 17 gardens contained concentrations above the residential limit values.

According to the Dutch framework approximately 20% of the former compound is contaminated above the intervention values (red planes in figure 3) with another 25% contaminated above the background levels (orange planes in figure 3). Out of the 32 gardens sampled 14 gardens were above screening values. The investigation of the Oykamar site shows that, for former pesticide distribution centers, the average soil quality is poor even in those areas where visibly no pure pesticides are found. Contamination levels in the gardens of the Oykamar site are above US EPA Residential soil and Dutch intervention values for approximately half of all gardens. Considering the very intensive use of these gardens as well as the consumption of animal products (eggs, milk and meat) from domestic animals roaming freely at these sites, the screening values as established by the US EPA and Dutch government are likely an underestimate. In fact the exposure of the local population to pesticides at a site like Oykamar is probably greater than at those locations where stockpiles remain, as these stockpiles are visibly present and discourage people from settling in their direct vicinity.

The estimated total quantity of pure pesticides and contaminated soil that has been identified during the 2017 investigations is presented in the following tables:

Table 2. Estimated quantities of pesticides and contaminated soil at the Oykamar site according to US EPA framework

Source area	Description	Area (m ²)	Quantity (m ³)	Quantity (tons)
Public spaces	Pure pesticides or soil containing visible pesticide residues	1100	500	700
Public spaces	Contaminated soil above industrial limit values (US EPA)	2090	1300	1820
Gardens	Contaminated above residential limit values (US EPA)	13000	3900	5460
Total		16190	5700	7980

Table 3. Estimated quantities of pesticides and contaminated soil at the Oykamar site according to Dutch framework

Source area	Description	Area (m ²)	Quantity (m ³)	Quantity (tons)
Public spaces	Pure pesticides or soil containing visible pesticide residues	1100	500	700
Public spaces	Contaminated soil above Limit values (Dutch)	2850	1500	2100
Gardens	Contaminated above limit values (Dutch)	13600	4080	5712
Total		17550	6080	8512

Remediation strategy

Known POPs-pesticide destruction techniques can roughly be divided between combustion and non-combustion techniques (Li, 2009). Although potentially suitable cement kilns for the co-processing of POPs contaminated soil are available in Tajikistan, these facilities need further investment to be able to process the materials (Global Environment Facility, 2016). As such the options for the short term remediation of the Oykamar site are limited to non-combustion techniques or export of the contaminated soil to surrounding countries with the appropriate facilities. The option of export, however, does currently not seem to be a realistic option, as surrounding countries do not have the appropriate facilities and or do not allow transportation of contaminated materials across their territory. From the non-combustion techniques bioremediation is known to reduce POPs concentrations in contaminated soil up to 60-80% (Li, 2009). In the case of Oykamar this would be, in the most optimistic scenario, still insufficient for the average contaminated garden to achieve minimum residential soil quality according to the US EPA RSLs for residential soil; a reduction of 80% of the average contamination level of 15.8 mg/kg d.m. would still yield concentrations above the US EPA RSL for residential soil as provided in table 1. What remains are either on-site but ex-situ processing methods for the contaminated soil with techniques such as:

- vitrification, pyrolysis, ball milling or similar or
- sanitary landfilling and containment of the contaminated materials.

In recent years, interest has been shown in including sustainability as a decision-making criterion. Sustainability concerns include the environmental, social, and economic consequences of risk management activities themselves, and also the opportunities for wider benefit beyond achievement of human health risk-reduction goals alone (Bardos, 2014). For the Oykamar site including the concept of sustainability in the remediation process is paramount to the success of the project. Only

when the remediation comprises a sustainable long term solution for the site can it be successful. The main concept is that the local population remains on their plots but that exposure to the contamination is reduced to acceptable levels. In the absence of sufficient funds for the complete removal and/or treatment of the contaminated soil the remediation solution is based on three principles:

1. Detailed risk assessment using existing exposure models adapted for the local situation
2. Soil remediation by removal of the contaminated soil where necessary
3. On site containment of residual contamination
4. Awareness raising for the local residents how to deal with the residual contamination at the site

The people living on the Oykamar site use their gardens as a major supplement to their diet. As such the importance of fruits and vegetables grown on the contaminated soil and poultry products from their own gardens is much bigger in the case of Oykamar than what is commonplace in the developed countries that have created the most widely used soil contamination risk assessment tools. On the other hand, the specific clayey soil characteristics and climatological conditions of the Oykamar area can positively influence the (bio)availability of the contaminants. It is therefore that a remediation strategy for a site like Oykamar should first establish local risk based target values (RBTL) before proceeding to the factual remediation itself.

Where the soil is contaminated above the local RBTL levels, it should be excavated. In this case, soil with visible pesticides or soil that is contaminated to such an extent that vegetation cannot or insufficiently sprout on the material, should be transported off-site to a designated pesticide storage facility for future processing or destruction. In the case of Oykamar this is about 10 – 20% of the severely contaminated materials.

All other materials that have pesticide contamination levels above the local RBTL levels should be concentrated in the empty plots within the compound and isolated from their surroundings. Main point of attention in this is that the isolated areas are immediately given a suitable long-term, public function. From our experience, areas that have not been given a suitable function tend to, especially when a strong enforcement of environmental laws is absent, relapse in the old ways where renewed exposure to the contaminated soil takes place.

The final, and in our opinion most crucial step, in the remediation is awareness raising of the people living on the site on the presence of residual contamination. Only if the families are aware of the risk associated with the contamination and knows how to deal with the contaminated soil the former pesticide distribution compound can be used sustainably in the future.

Conclusions

The Oykamar pesticide distribution center was investigated in detail to assess the contamination status of the soil due to the historical use of the site as a pesticide distribution center. Out of the 32 gardens investigated 17 gardens were contaminated above the US EPA screening levels (RSL) for residential soil. In addition large parts of the public space of the site contained high concentrations of pesticides in the topsoil. Total quantity of soil contaminated above the US EPA screening levels (RSL) for residential soil at the site is estimated at approximately 8000 tons.

The situation at the Oykamar site is exemplary for the situation in many closed former pesticide distribution centers. Even though the main stockpiles have been removed, the resettlement of these sites in effect creates a greater exposure of the local population to the POPs-pesticides left in the soil. For the Oykamar site a remediation strategy has been proposed that has four main components. Essential in this strategy is giving a suitable long-term function to areas with residual contamination and awareness raising among the people living on the site how to deal with the contaminated soil left behind.

Acknowledgements

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3.1.11. Application of GIS to characterize garden soil contamination in New York City

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Abstract

Heavy metals, in particular lead (Pb), are prevalent in urban soils and it is one of the main hurdles for urban agriculture. Increased gardening activities in urban areas could mean increased public health risk. Soil heavy metals data used in this study have been collected by the Brooklyn College Soil Research Lab and New York City Urban Soil Institute (USA) since 2009. In this project the spatial distribution of Pb levels in NYC gardens was analyzed and visualized with GIS tools. Gardens and areas at risk from historical and current contaminants sources were identified. Pollution and ecological risk of the 126 garden ecosystems were evaluated with different indexes. The degree of the contaminant factors was as follows: Pb > Cd > Cu > Zn > Cr > As > Ni. Single ecological risk index indicated that Pb and Cd had high to significantly high risk to the local ecosystem. According to the potential ecological risk index, the ecological risk comes mainly from the soil pollution with Cd. Based on the pollution load index, the gardens were characterized as having polluted soil quality. Geostatistical, geoprocessing, and spatial tools were applied to create color-coded maps to help residents and policy makers to make informed decisions related to gardening and to estimate potential human health risks from gardening, living, and/or working in the contaminated areas. These findings have important implications for the development of pollution prevention and mitigation strategies to reduce heavy metal contamination for cities undergoing fast industrialization and urbanization.

Keywords: heavy metals, GIS map, soil quality, index

Introduction

While water and air pollution have been widely recognized and subsequently protected by federal and state legislation, soil contamination in urban environments has only received attention over the past few decades (Mielke, 1999). Soil contamination may pose significant health risks to urban residents and particularly to gardeners, who may regularly interact with contaminated soil and consume garden produce. Urban gardening is on the rise; therefore, the inherent risks of gardening in contaminated soil will become a focus of urban health as more humans become affected by soil contamination.

Urban soil is a sink for anthropogenic lead (Pb) and other contaminants. The majority of soil contaminants are the result of historical deposition. According to an EPA report (U.S. EPA 1998), three sources responsible for the elevated soil-lead levels have been identified: (1) lead-based paint; (2) point source emitters; and (3) leaded gasoline emissions. Many studies cite more than one source as commonly responsible for elevated soil-lead levels at a given location.

Starting in 1973, the U.S. federal government initiated a gradual phase-out of Pb in gasoline, and by 1996, banned the sale completely (Smith, 1976). Homes near busy streets may have higher levels of Pb in the soil. Today, Pb is still emitted from some manufacturing sites such as metal

smelting, battery manufacturing, and other factories that use Pb in industrial processes. Flakes of lead-based paint on the outside of the old buildings can also get into the soil close to the foundation of buildings. Contaminated soil dust can be re-suspended by wind, and mobilized into homes and yards.

Although soil Pb distribution in many large cities have been conducted (Levin *et al.* 2008), including New York City (Cheng *et al.* 2015; Li *et al.* 2017). Previous studies have called for further detailed spatial analysis of the data using large-scale Geographic Information Systems (GIS) for a better health-based assessment in NYC (Datko-Williams *et al.* 2014), as well as the evaluation of soil contamination in the context of risk to human health and threat to ecological systems. Thus, the aims of this project are: 1) to examine the spatial distribution of Pb levels in NYC gardens using GIS; 2) to assess pollution and ecological risk indices; and 3) to identify gardens at risk from historical and current contaminants sources. Based on the data collected, this project includes color-coded maps to help residents and policy makers to make informed decisions related to gardening and to estimate potential human health risks from gardening, living, and/or working in the contaminated areas.

Methodology

Data collection and data management

The data on soil heavy metal concentrations have been collected by Brooklyn College Soil Lab and NYC Urban Soil Institute since 2009. This is part of a soil screening and testing service provided by the Soil Lab to the public. The soil samples were collected by gardeners and send to the lab for analysis. Soils are mostly screened by a pXRF (portable X-ray fluorescence) analyzer and ICP-MS (Inductively coupled plasma mass spectrometry). Each sample is recoded with a unique identification number, location, type of garden, soil heavy metal concentration and other soil characteristics. The first map of Pb for garden soils was published in 2015 based on collected data for 2009-2014 (Cheng *et al.* 2015). Li *et al.* (2017) added data from other land uses and published a second Pb map. New data have been continuously organized, georeferenced and added to the existing 2014 database. In total, there are 2079 garden soil samples in this study (Fig. 3 **Figure 3.** NYC Soil Garden Lead map shows predicted soil Pb distribution using the Kriging tool).

Data sources and analysis

Data for this study were obtained from the following sources: Brooklyn College Soil Research Lab, NYC Open data, US EPA website, the ToxiCity Mapping Project, Sanborn maps, BetaNYC's Community Data Portal, NYC Department of Health and Mental Hygiene Environment & Health Data Portal. ESRI ArcGIS 10.5 was used for geospatial analysis and visualization of the results. Shapefiles of Green Thumb Gardens, parks, schoolyards and playgrounds were downloaded from NYC Open data and combined as a one layer titled 'green spaces'. The NYC zip code boundaries were downloaded from NYC Open data.

Figure 3. NYC Soil Garden Lead map shows predicted soil Pb distribution using the Kriging tool. Kriging allowed predicting the value in unmeasured points based on the known data in neighboring points and spatial relationships between the points. Ordinary Kriging uses dimensionless points to estimate other dimensionless points, e.g. Pb contour plots.

Past manufacturing/industrial areas with potential Pb-containing products were mapped in relation to soil contamination. Locations of historical contaminant sources were found on the EPA website, the ToxiCity Mapping Project in Greenpoint and Williamsburg and Sanborn maps available in Digital Collections of Atlases of New York City in the New York Public Library.

Twenty-six sources were identified as coal yards, smelters, factories, refineries, lead companies existed between 1768 and 2004 that could be considered as potential lead sources. These sources were overlaid with soil contamination map (Fig. 4).

Distance of 1.6 km (buffer radius) from the industrial and current sites was used as a risk zone. Mielke and Reagan (1998) stated that living less than 1 mile (1.6 km) from the smelter is a health risk. Buffer and intersect tools were used in Model Builder to estimate risk zones of green spaces around the industrial sites that are considered as contaminant sources (Fig. 4).

To assess soil quality, pollution and ecological risk of the garden ecosystems the following indices were used: the potential ecological risk index ($PERI = \sum(E_i)$) posed by multiple element pollutions, the single ecological risk index ($E_i = T_i * CF_i$, where T_i is the toxic-response factor for a given metal (Hakanson, 1980); CF_i is the contamination factor for the same metal ($CF_i = C_m / B_m$, C_m is the measured concentration of the examined metals in the soil samples, B_m is the background concentration in unpolluted soils)), pollution load index introduced by Tomlinson et al. (1980) ($PLI = (CF_1 * CF_2 * \dots * CF_n)^{1/n}$, where n is the number of metals studied), which gives simple comparative means for assessing a site quality.

Results

Assessment of pollution

To assess quality of soils and their contamination levels different indices were used. Using the contaminant factors (CF) showed in Table 1, it was possible to determine the following degree of contaminant factors for 126 samples: $Pb > Cd > Cu > Zn > Cr > As > Ni$. This shows that Pb, Cd, Cu, and Zn have the highest CF. The contaminant factors are classified as: low ($CF < 1$); moderate ($1 < CF < 3$); considerable ($3 < CF < 6$); and very high ($CF > 6$).

Table 1. Summary statistics of the contaminant factors (CF)

Contaminant factors (CF)							
	Pb	As	Cd	Ni	Cr	Cu	Zn
Mean	35.86	4.43	9.28	1.24	5.32	7.76	7.28
Min	0.77	0	0	0	0.45	0.29	0.86
Max	180.53	119.87	96	4.35	72.13	64.26	30.77
Std Dev	37.36	11.50	19.29	0.70	7.36	9.52	5.56

The calculated E_i - Single ecological risk index of the individual contaminants are represented on the logarithmic scale in Fig. 1. E_i indicated that Pb and Cd had high to significantly high risk to the local ecosystem, while Zn, Cr and Ni indicated low risks and other elements (As and Cu) showed moderate risk.

Contributions of individual heavy metals to the mean potential ecological risk of the soil are represented on Fig. 2. The ecological risk comes mainly from the soil pollution with Cd (49%) and Pb (32%). When the overall potential ecological risk (PERI) to the local ecosystems is considered, 52% of the studied samples had very high PERI (> 600), 32% had considerable PERI (300-600), 21% had moderate PERI (150-300), and only 26% of the samples had low PERI (< 150).

The pollution load index gives simple comparative means for assessing a site quality. All 126 samples (which were also analyzed for all other metals in addition to Pb) were found to be polluted based on Pb, Ni, Zn, and Cu with $PLI > 1$ (polluted soil quality). PLI ranged from 1.1 to 64 with mean of 9.1.

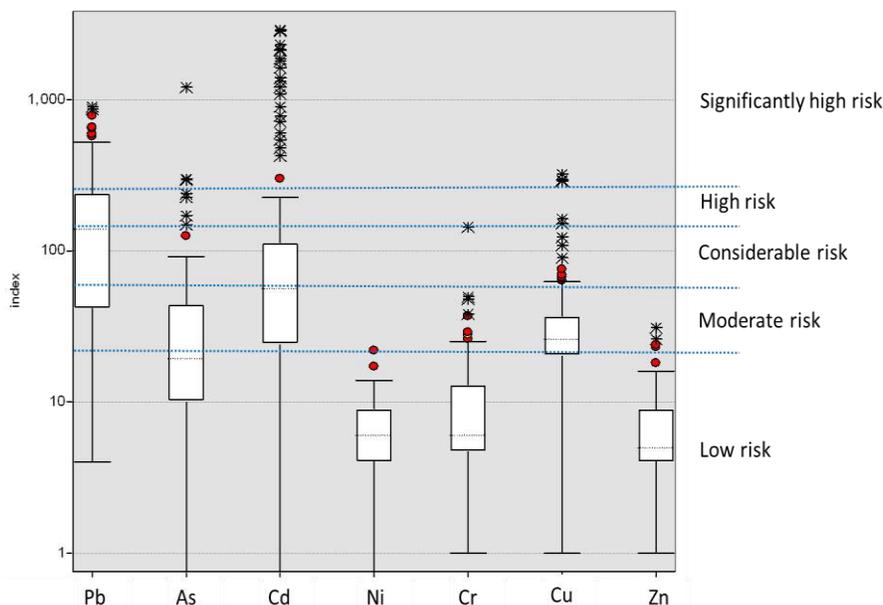


Figure 1. Single ecological risk indices of the individual contaminants represented on the logarithmic scale

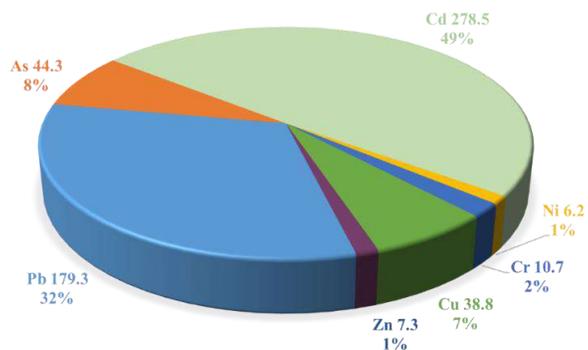


Figure 2. Makeup of the mean potential ecological risk index (565)

Distribution of soil Pb contamination in NYC gardens

Shown in Fig. 3 is the spatial distribution of soil Pb from the compiled database. Each point on the map is a garden and may represent multiple samples that are from the same address. Total Pb concentrations ranged from 3 to 45,000 ppm (mean 638 ppm and median 344 ppm). Overall, soil Pb contamination is mostly concentrated in Brooklyn and Manhattan. The highest range of 850 ppm and above is present in various parts of northern and central Brooklyn. Three samples were over 11,500 ppm. Two samples (14,502 and 45,076 ppm of Pb, respectively) were in the 11205 zip code (Downtown-Heights-Park Slope) and another one (15,911 ppm of Pb) was in the 11211 zip code (Greenpoint). It should be noted that there were not enough samples collected in eastern Queens, the Bronx and throughout Staten Island to confidently map and predict Pb distributions in those areas. The largest number of samples (219) was collected from the zip code 11238 (Prospect Heights). If neighborhood is considered, the most number of samples (421) was collected from the Downtown-Heights-Park Slope area. The highest mean Pb level among all zip codes (584 ppm) was found in the 11211 zip code in Greenpoint.

Historical and current contamination in NYC

Fig. 4 shows locations of industrial sites such as smelters, coal yards, factories, refineries, lead companies that existed between 1768 and 2004. The locations of current industrial sites (smelters, factories, superfund sites, waste transfer stations) and major roads were overlaid on the contemporary soil contamination map. Forty-six gardens were identified to be at risk from the current contaminant sources and 28 gardens are at risk from both historical and current contaminant sources. Thirty-three gardens were identified to be at risk from known historical contaminant sources.

Discussion

Soil quality evaluation

The average value of the potential ecological risk indices (PERI) for the studied soils, calculated as the sum of the mean factors of the heavy metals, is 565, indicating a considerable ecological risk posed by the heavy metals. The calculated E_i indicated that Ni, Cr, and Zn pose low risk to the local ecosystem, while Cd and Pb had the highest E_i . The overall potential ecological risk varies greatly for different gardens, highlighting the extreme heterogeneities of soil contamination in urban areas. The PLI values for all samples were >1 . According to Elnazer *et al.* (2015), it indicates external discrete sources of soil pollution, such as vehicle exhaust and agricultural activities.

Historically, leaded gasoline, lead-based paint, and many other lead-based products were widely used until around 1980's -1990's when the Pb was banished from gasoline (U.S. EPA 1996). The use of leaded gasoline and lead-based paint contributed to the widespread, non-point source Pb deposition into the soil. Manufacturing activities involving lead-bearing products, as point sources, also have contaminated soil with large quantities of Pb within the industrial site and neighboring areas. Total Pb concentrations found in this study ranged from 3 to 45,000 ppm with mean concentration of 640 ppm. The Pb distribution map shows that, in general, soil Pb content decreases from the inner city towards outskirts, which is commonly seen for cities with an industrial history (Mielke 1999). Li *et al.* (2018) found a correlation between Pb levels and historical land use, where highly elevated levels of soil Pb corresponded with industrialized areas. Specific hotspots of Pb were identified in such neighborhoods as Red Hook, Brooklyn Heights, Gowanus, Park Slope, Boerum Hill, Fort Greene, Williamsburg, and Bedford-Stuyvesant. These observations are consistent with findings from this study that the highest soil Pb is found in these neighborhoods. Moreover, solid waste incineration (during the 20th century) could be another source of Pb causing it is excessive deposition on soil (Walsh *et al.* 2001). Deposition of 34 million tons of refuse incineration throughout NYC landfills caused the release of 1 million tons of air pollutants, which eventually settled onto the topsoil.

The U.S. EPA has established 400 ppm as the human health SSL for Pb based on the direct soil ingestion exposure pathway, assuming a default relative bioavailability (RBA) of 60% (U.S. EPA 1998, 2014). Residential areas with soil Pb concentrations below 400 ppm may require no additional action. However, some actions may be needed in gardens containing soil Pb concentrations below 400 ppm to reduce the potential for increased Pb exposure (U.S. EPA 2014). According to recommended guidelines regarding gardening, soil Pb levels under 100 ppm are considered low risk, with no additional action needed (U.S. EPA 2014). Based on the results of this study, 73 out of the 142 gardens (at high and medium risks) are required to adopt remediation or best management practices to mitigate the exposure (e.g. mulch or straw cover, maintaining a moist soil, adding organic compost for aggregation stability, etc.).

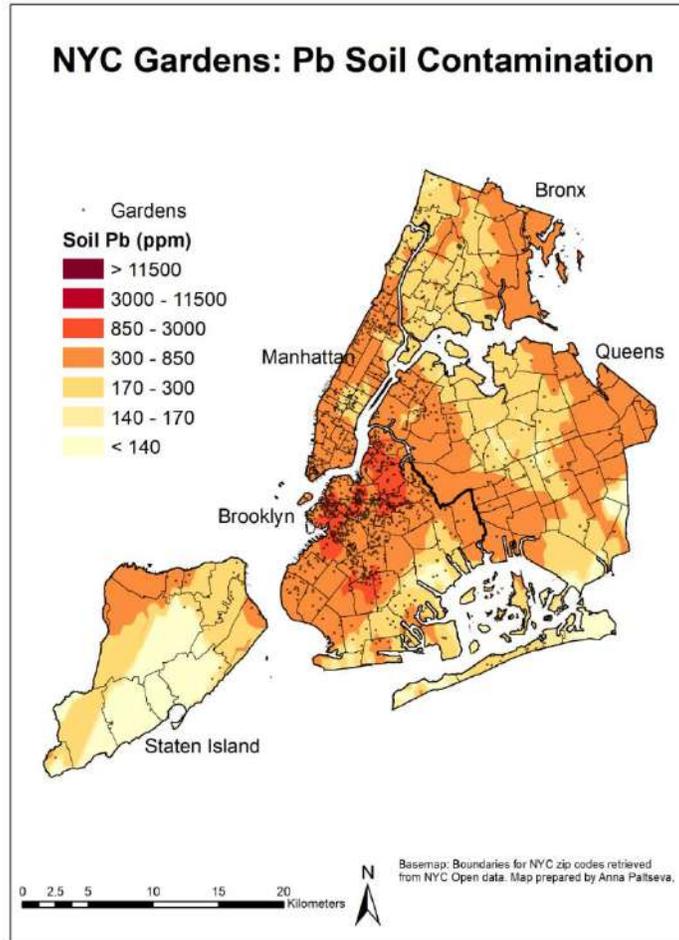


Figure 3. NYC Soil Garden Lead map shows predicted soil Pb distribution using the Kriging tool. (Note, there were not enough samples collected in eastern Queens, the Bronx and throughout Staten Island to confidently map and predict Pb distributions in those areas)

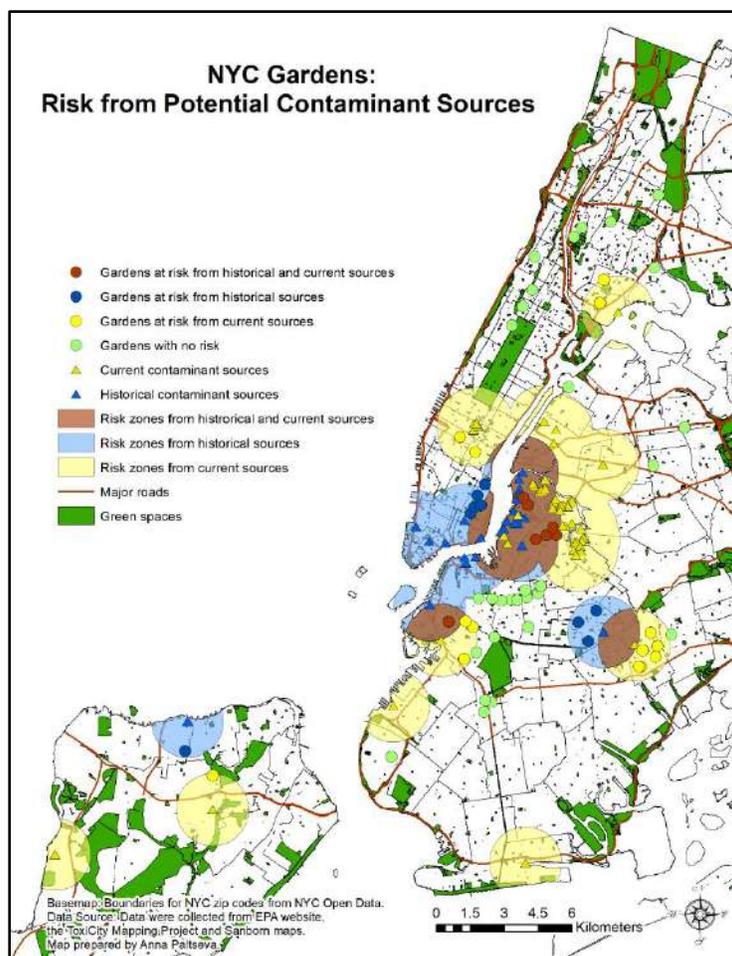


Figure 4. Potential sources of soil contamination. Data collected from EPA website, the ToxiCity Mapping Project and Sanborn maps. Buffers represent 1.6 km potentially contaminated areas from the sites

Conclusions

In this project, soil quality assessment indices were calculated based on individual metals (Pb, Zn, Cd, As, Cu, Cr, Ni) for 126 garden samples. The majority of soils is contaminated and poses significant risks to human health and ecological systems, particularly by Pb and Cd. A consolidated garden soil Pb database was compiled (total of 2079 garden samples), from which a series of color-coded maps were created to estimate potential health risk from living or working in contaminated areas. The highest Pb levels were found in northern and central Brooklyn. Generally, Pb levels became lower toward the suburban areas. The Pb contamination map would be valuable not only to guide remediation efforts but also for urban planning such as developing gardens and green spaces or sitting of new parks. A number of gardens were identified to be at risk due to historical and/or current contaminant sources.

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3.1.12. Comparative analysis of leaf litter and biochar for the onsite remediation of Hexachlorocyclohexane polluted soils

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Abstract

There is a growing priority for remediation of hexachlorocyclohexane (HCH) contaminated soil as it belongs to the category of persistent organic pollutants (POPs) listed under the Stockholm convention for global elimination. In this study we tried to evaluate the effectiveness of low cost substrates for remediation of HCH contaminated soil. To this, leaf litter, vermicompost and biochar were used for amendment in HCH contaminated soil (with pollutant level of α -HCH = 119 mg kg⁻¹, β -HCH = 97 mg kg⁻¹, γ -HCH = 14 mg kg⁻¹ and δ -HCH = 7 mg kg⁻¹). The vermicompost showed best response followed by leaf litter and biochar. After 90 days of leaf litter amendment there was 33.47, 39.85, 85.06 and 96.86% dissipation of α , β , γ and δ -HCH isomers. The leaf litter amendment also increased the microbial biomass carbon (MBC from 45.27 to 93.91 mg kg⁻¹) and soil dehydrogenase enzyme activity (30.55–63.17 μ g TPF g⁻¹h⁻¹). Similarly, the vermicompost amendment also helped in the dissipation of α -HCH 51.68%, β -HCH 59.69%, γ -HCH 76.30% and δ -HCH 96.79%. There was increase in microbial biomass from initial value of 57.17 to 92.17 mg kg⁻¹. However, soil dehydrogenase activity increased from 40.17 to 62.23 μ g TPF g⁻¹h⁻¹ after 60

days and then decreased to 53.14 $\mu\text{g TPF g}^{-1}\text{h}^{-1}$ after 90 days. Moreover the vermicompost amendment showed more rapid and enhanced increase in microbial activity in comparison to the leaf litter and biochar. This might be due to the more organic complexity of biochar and leaf litter in comparison to vermicompost. Our results clearly indicates that vermicompost rapidly increases the microbial activity and HCH dissipation in comparison to the leaf litter.

Keywords: Remediation, Hexachlorocyclohexane, Persistent Organic Pollutants (POPs), Leaf Litter, Vermicompost, Microbial Biomass, Soil Enzymes.

Introduction, scope and main objectives

Remediation and management of POPs contaminated soil has become a global priority due to nonspecific toxicity, lipid bioaccumulation properties, highly persistent nature and their ability to undergo long range atmospheric transport (Pariatamby and Kee 2016; Abhilash *et al.*, 2013). Hexachlorocyclohexane ($\Sigma \alpha, \beta, \gamma, \delta$, HCH) is an organochlorine pesticide (OCP) with its isomers α, β and γ listed under the category of persistent organic pollutants (POPs) for global elimination under the Stockholm convention (Tripathi *et al.*, 2014). Among the isomers only γ isomer, has insecticidal property which led to its enhanced production and application under the name lindane however, the technical composition consisting of all the isomers also continued for application in developing part of the world due to its cost efficiency. Production of lindane is a very inefficient process as 8-12 tonnes of waste isomers are generated for producing a ton of lindane, creating a huge pile of waste isomers that accumulate in landfills (Muñiz *et al.*, 2017). Though production and use of HCH and lindane has been banned globally its large scale application during the past 50 years has led to widespread contamination of the environment and a large number of dumpsites and abandoned plants are posing serious threat to the environment (Aresta *et al.*, 2015). Moreover, few Asian countries like India (Tripathi *et al.*, 2015) and China (Sun *et al.*, 2015) are still using lindane (γ -isomer) for control of Malaria. Soil act as a sink to the pollutants released in the environment thus a large number of HCH contaminated soil sites have been reported globally, requiring immediate action for their remediation and management to stop the further contamination of the environment (Vijgen *et al.*, 2011).

Organic amendments are one of the most commonly followed approaches for remediation and management of pesticide contaminated soil due to their cost effectiveness, *in-situ* application approach thus reducing the need for storage and treatment of contaminated soil and their ability to enhance soil quality and fertility (Tripathi *et al.*, 2017). The pesticides like HCH strongly absorb on soil particles becoming recalcitrant to degradation and persist in soil for longer duration. Organic amendments not only increases the microbial activity in soil leading to degradation of the pollutants but also affect the accessibility of the pollutants to microorganisms (Centofanti *et al.*, 2016). Due to all these properties the organic amendments are mostly preferred over physical and chemical treatments methods. Among the diverse substrates used for soil bioremediation compost addition, surfactant application, agricultural waste application and other organic amendments are the commonly applied for the bioremediation of organic pollutant contaminated soil (Meghraj and Naidu 2017; Centofanti *et al.*, 2016). Despite the beneficial application of organic amendment very limited substrates have been analysed for remediation of HCH contaminated soil. To this, we tried to study the bioremediation potential of three low cost substrates vermicompost leaf litter and biochar for restoration of HCH contaminated soil. The major objective of the study were (i) to evaluate the comparative bioremediation potential of vermicompost, leaf litter and biochar for remediation of HCH contaminated soil and (ii) to analyse the impact of vermicompost, leaf litter and biochar on microbial activity and fertility in HCH contaminated soil.

Methodology

Sample Collection and Soil amendment

Soil with previous history of HCH contamination was collected from earlier dump site of lindane producing factory, India Pesticide Limited near Chinhat area of Lucknow, Uttar Pradesh located between 27°59 North latitude and 89°39 East longitude. Subsurface soil sample were randomly collected from 10-35 cm depth and sieved and mixed together to form a composite sample. Leaf litter for amendment was collected from field of Banaras Hindu University, Varanasi, Uttar Pradesh, India and was kept in pits for partial degradation. Good quality Vermicompost and biochar was purchased from local market. One kg of contaminated soil was spiked with leaf litter and Vermicompost respectively in a weight by weight ratio (3:1 ratio).

HCH dissipation and soil microbiological analysis

Analysis of α , β , γ , and δ HCH isomers dissipation from soil samples was performed through soxhlet extraction followed by GC-ECD as mentioned in our previous studies (Abhilash and Singh, 2008). The method development, preparation of sample, instrumental calibration, quality assurance and quality control procedure for extraction and analysis of HCH isomers from soil are detailed in our earlier publications (Abhilash *et al.*, 2011; Abhilash and Singh, 2008a, b). Enumeration of fungal and bacterial colony forming units were analysed through earlier published standard procedures (Abhilash *et al.*, 2011; Sahu *et al.*, 1995; Waksman, 1922). Soil dehydrogenase activity was analysed by monitoring the rate of reduction of 2,3,5-triphenyltetrazoliumchloride (TTC) to the red, water insoluble triphenylformazan (TPF) (Fan *et al.*, 2008). Microbial biomass carbon (MBC) was analysed according to the soil fumigation method of Vance *et al.* (1987).

Results

Effect of amendments on HCH dissipation

We evaluated the dissipation of α , β , γ , and δ HCH isomers from soil amended with vermicompost leaf litter and biochar. The results are presented in Fig. 1. For leaf litter we found that dissipation of α isomer decreased from initial concentration of 120.29 to 116.72, 64.85, and 58.12 mg/kg after 30, 60, and 90 days respectively. The initial concentration of β isomer decreased from 98.82 to 72.70, 51.70, and 39.13, mg/kg after 30, 60, and 90 days respectively. Similarly the concentration γ isomer decreased from initial value of 14.94, to 9.27, 4.87, and 3.53 mg/kg after 30, 60, and 90 days respectively. Moreover the δ isomer we reported that its initial concentration decreased from initial value of 8.11 to 5.27, 3.65 and 0.26 mg/kg after 30, 60, and 90 days respectively. The corresponding values for vermicompost amendment were also analysed in a similar fashion. To this we found that dissipation of α isomer decreased from initial concentration of 120.57 to 116.86, 107.73 and 88.19 mg/kg after 30, 60, and 90 days respectively. The initial concentration of β isomer decreased from 98.83 to 95.08, 88.25, and 59.45 mg/kg after 30, 60 and 90 days respectively. Similarly the concentration γ isomer decreased from initial value of 15.07, to 11.97, 8.28, and 2.25 mg/kg after 30, 60, and 90 days respectively. Moreover the δ isomer we reported that its initial concentration decreased from initial value of 8.30 to 6.11, 2.40 and 0.26 mg/kg after 30, 60 and 90 days. Moreover for biochar amendment in case of α isomer the residual concentration decreased from 120.64 to 115.32, 96.30 and 81.35 mg/kg, for β isomer it decreased from 99.50 to 96.50, 93.39 and 72.30 mg/kg and for δ the decrease in residual concentration was from 8.31 mg/kg to 5.30, 3.84, and 2.75 mg/kg respectively after period of 0, 30, 60, and 90 days. The corresponding control values can be found in Fig.1 of the paper.

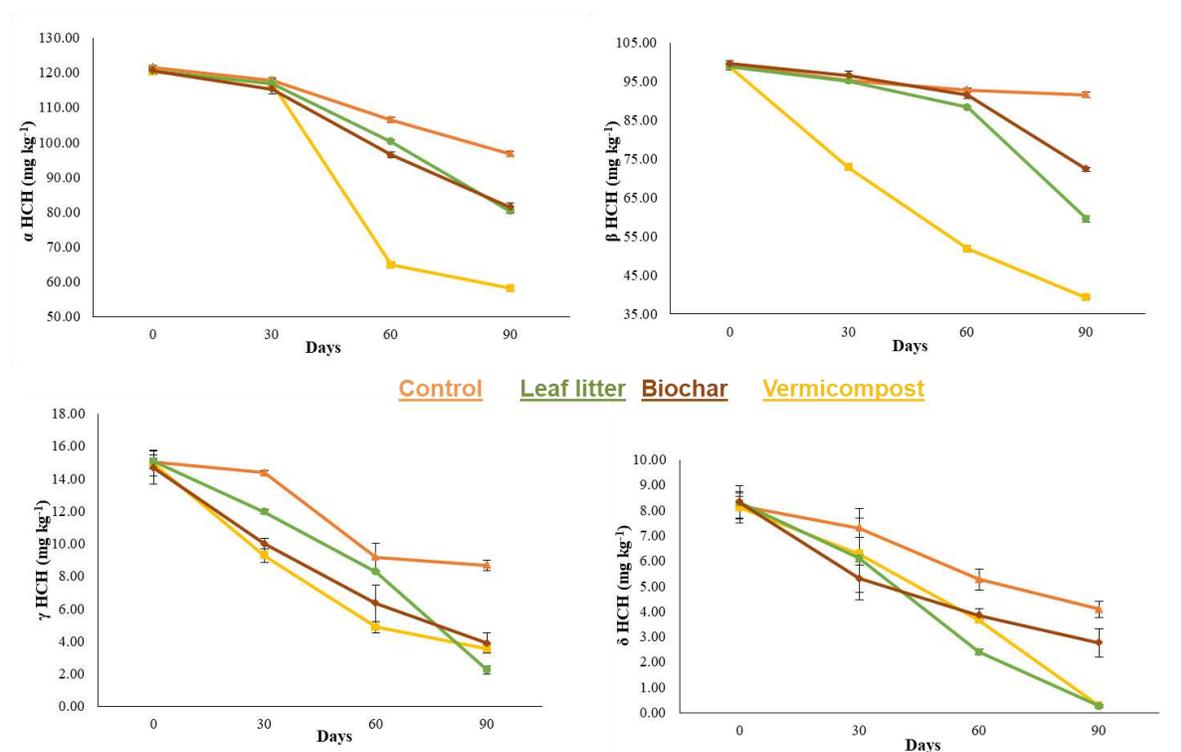


Figure 1. Effect of leaf litter, biochar and vermicompost on dissipation α, β, γ and δ-HCH isomers after 0, 30, 60 and 90 days.

Effects of amendments on soil microbiology

For evaluating the effect of different amendments on microbiological properties of HCH contaminated soil we analyzed bacterial and fungal colony forming units (CFU), microbial biomass carbon and soil dehydrogenase enzyme in leaf litter and vermicompost amended HCH contaminated soil. The results are represented in Table.1. In leaf litter amendment the bacterial CFU counts increased from 2.5×10^4 at zero days to 3.2 , 3.5 and 4.0×10^4 CFU after 30,60 and 90 days respectively. Similarly, the fungal CFU unit was initially reported to be 2.0×10^6 which later increased to 2.5×10^6 , 3.6×10^6 and 4.6×10^6 respectively after 30, 60 and 90 days of treatment. For MBC we found that leaf litter amendment enhanced the MBC value from initial value 45.27 to 58.61 , 72.71 and 93.91 mg kg⁻¹ after 30,60 and 90 days of treatment. In soil enzyme assessment for dehydrogenase activity, we reported that it increased from 30.55 μg TPF g⁻¹h⁻¹ at zero days to 39.36 , 47.12 and 63.17 μg TPF g⁻¹h⁻¹ after 30,60 and 90 days of treatment respectively.

In case of biochar bacterial CFU increased from 2.3×10^4 to 2.7×10^4 , 2.7×10^4 , 3.1×10^4 and finally 3.0×10^4 after 0, 30,60, and 90 days respectively. Similarly fungal CFU increased from 1.5×10^6 to 2.0×10^6 , 2.8×10^6 and 3.7×10^6 . For MBC we found that leaf litter amendment enhanced the MBC value from initial value 41.53 to 49.71 , 78.00 and 87.34 mg kg⁻¹ after 30,60 and 90 days of treatment. In soil enzyme assessment for dehydrogenase activity, we reported that it increased from 26.19 μg TPF g⁻¹h⁻¹ at zero days to 31.77 , 39.00 and 49.10 μg TPF g⁻¹h⁻¹ after 30,60 and 90 days of treatment respectively.

Likewise, for the vermicompost amendment the bacterial CFU count increased from initial value of 2.39×10^4 to 3.31×10^4 after 30 days of treatment and then showed a decreasing trend with values of 2.85×10^4 and 2.57×10^4 after 60 and 90 days respectively. Though the fungal CFU showed a continuously increasing trend with the initial value of 3.43×10^6 , to 3.80×10^6 , $4.37 \times$

10^6 and 4.87×10^6 after 30, 60 and 90 days of vermicompost treatment. In the same treatment, MBC also showed an increasing trend with 57.17 mg kg^{-1} at zero days and 67.51 , 85.36 and 92.17 mg kg^{-1} after 30, 60, 90 days. However, the soil dehydrogenase enzyme increased from the initial value of 40.17 to 51.31 , $62.23 \text{ } \mu\text{g TPF g}^{-1}\text{h}^{-1}$ after 30 and 60 days of vermicompost amendment and then decreased to $53.14 \text{ } \mu\text{g TPF g}^{-1}\text{h}^{-1}$ after 90 days of amendment. The corresponding control values can be found Table.1 of the paper.

Table 1. Changes in microbiological properties of soil after different amendments in comparison to control

	Control				Leaf Litter			
	0 Days	30 Days	60 Days	90 Days	0 Days	30 Days	60 Days	90 Days
Fungal CFU	1.8×10^6	1.6×10^6	1.7×10^6	1.4×10^6	2.0×10^6	2.5×10^6	3.6×10^6	4.6×10^6
Bacterial CFU	2.3×10^4	1.5×10^4	2.8×10^4	1.2×10^4	2.5×10^4	3.2×10^4	3.5×10^4	4.0×10^4
MBC (mg/kg^{-1})	38.73 ± 2.2	30.31 ± 1.3	35.14 ± 1.8	28.67 ± 2.1	45.27 ± 1.3	58.61 ± 2.2	72.71 ± 2.1	93.91 ± 1.1
Soil Dehydrogenase Activity ($\mu\text{g TPF g}^{-1}\text{h}^{-1}$)	21.23 ± 0.7	17.82 ± 1.0	19.33 ± 2.2	18.34 ± 1.6	30.55 ± 1.6	39.36 ± 1.0	47.12 ± 1.2	63.17 ± 1.8
	Vermicompost				Biochar			
	0 Days	30 Days	60 Days	90 Days	0 Days	30 Days	60 Days	90 Days
Fungal CFU	3.43×10^6	3.80×10^6	4.37×10^6	4.87×10^6	1.5×10^6	2.0×10^6	2.8×10^6	3.7×10^6
Bacterial CFU	2.4×10^4	3.3×10^4	2.9×10^4	2.6×10^4	2.3×10^4	2.7×10^4	3.1×10^4	3.0×10^4
MBC (mg/kg^{-1})	57.17 ± 1.0	67.51 ± 0.6	85.36 ± 1.9	92.17 ± 1.5	41.53 ± 1.9	49.71 ± 2.1	78.00 ± 0.95	87.34 ± 1.7
Soil Dehydrogenase Activity ($\mu\text{g TPF g}^{-1}\text{h}^{-1}$)	40.17 ± 2.1	51.31 ± 1.8	62.23 ± 0.8	53.14 ± 1.4	26.19 ± 0.89	31.77 ± 1.7	39.00 ± 1.3	49.1 ± 1.1

Discussion

Organic amendments are known to enhance the microbial activity and thus increases the degradation of pollutants in contaminated soil. In our study we found that both the amendments showed efficient remediation properties for clean-up of HCH contaminated soils. The leaf litter amendment showed 33.47, 39.85, 85.06 and 96.86% removal of α , β , γ and δ HCH respectively after 90 days of treatment. During the same time period the vermicompost amendment showed 51.68% α HCH, 60.40% β HCH, 76.30% γ HCH and 96.79% δ HCH removal. The removal of α , β was less pronounced than γ and δ HCH due to the higher recalcitrant nature of α and β isomers (Vijgen *et al.*, 2011; Abhilash and Singh 2008a). Also the δ isomer is reportedly very less stable thus its concentration decreases rapidly with passage of time (Lal *et al.* 2010). Thus the vermicompost treatment showed a better response for removal of HCH isomers from soil than leaf litter. This might be attributed due to the higher microbial activity in vermicompost treatment as evident from our results. Though in our result we have reported that there was decrease in bacterial CFU, MBC and soil dehydrogenase activity after 90 days of vermicompost treatment however, the trend during the first 60 days of the study is just opposite and vermicompost shows better response in

comparison to leaf litter. The higher microbial activity in vermicompost during that period is due its relative simplicity, being end-product of the breakdown of organic matter, in comparison to the partially degraded leaf litter (Diaz *et al.*, 2017). This is also the reason that the vermicompost amendment shows less microbial activity after 90 days in comparison to vermicompost treatment as it is easily and rapidly utilized by the microorganisms and its depletion leads to reduction in microbial activity after 90 days of the study. The increase in fungal CFU in leaf litter treatment is due to lignin and cellulose content of the leaf which is preferentially utilized by the lignocellulosic fungi (Dubey *et al.*, 2016). We reported that biochar has less pronounced results in comparison to vermicompost and leaf litter which is probably due to the recalcitrant nature of the carbon in biochar which is not readily available to the microorganisms to feast upon and increase the microbial activity in the contaminated soil system. However, the recalcitrant carbon rich nature of the biochar makes it an excellent resource for soil carbon sequestration and reducing the HCH bioavailability in the contaminated soil system (Zhang *et al.*, 2013). Thus our results indicates that vermicompost amendment is comparatively better for remediation of HCH contaminated soils as it leads to rapid degradation of HCH isomers and increases the soil fertility in comparison to leaf litter.

Conclusions

Our study clearly indicates that vermicompost performs better than leaf litter for remediation of HCH contaminated soil. However, cost efficiency of vermicompost to leaf litter might be a factor promoting preferential use of leaf litter especially in developing countries. Further investigation is needed to constitute the organic amendments used here in developing a promising tool for improving the HCH removal in contaminated soil systems.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.13. Assessment of ecological state of the halogenic technosoils in the former well drilling site using biological indicators

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Abstract

The subject of the study was the soil microbial communities condition and biological activity of soil territory around the borehole number 6 of the Svyrydivske gas condensate field Poltava region (Ukraine) at the points located at different distances from the place where the emergency flood of produced waters occurred, according to the number of main ecologically functional groups of microorganisms and enzymatic activity. Highly mineralized contaminated produced waters contain the complex of pollutants. The parameters of microbiological indices of the background dark grey soil and technosoils in different points near the borehole number 6 were determined. The comparative state assessment of the microbial community in the selected points of the technosoils and background soils on the parameters of the number, structure and functioning of microbial communities is given. Deviations of the number of microorganisms of certain groups at points 6-03, 6-04 and 6-08 technosoils territory drilling well number 6 in the unfavourable direction, decrease in the activity of soil enzymes have been detected.

Keywords: microbiological and biochemistry indicators, soil microbial community, soil enzymatic activity.

Introduction, scope and main objectives

Microbiological monitoring should be an integral part of environmental and soil monitoring oil and gas fields. Soil microorganisms are the first ones to react to pollution and associated changes in the chemical, physico-chemical and physical properties of soils and adequately reflect their stage. Microbiological indicators are sensitive indicators of changes in soil properties which have undergone man-made pollution, in particular, oil, heavy metals, components of drilling mud, adjacent reservoir waters, etc. Soil fertility largely depends on the state of their microbial community and biological activity. There are quite a significant number of biological indicators that characterize a huge variety of biological properties of the soil. As the problem of assessing the impact of oil and gas companies' activities in the context of environmental problems becomes extremely relevant, recently a number of scientific publications were dedicated to the solution of this problem. All scientists came to the same conclusion: for the assessment of the state of oil-contaminated, and contaminated with drilling fluid or mud components, and reclaimed soils, the most sensitive and universal indicators are the number of main ecological and trophic and taxonomic groups of microorganisms, certain functional groups, enzymatic activity of the soil and indicators of soil phytotoxicity.

The purpose of this work was to identify changes in microbial community condition of dark grey soil under their pollution with saline produced waters, and to determine the direction and

estimate the degree of change in biological properties of halogenic technozems under influence of salinization and pollution with saline waters.

Methodology

Microbiological research was carried out at the Soil Microbiology Laboratory in the NSC 'Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky' in soil samples taken in September 2017 from a layer of 0-25 cm at eight points on the territory of the explored borehole number 6 and two points of the background soil. The locations of the sampling points are shown in Fig. 1. In 2016, an emergency occurred near the borehole, a pipeline flood. The picture shows the salt spot formed as a result of the leakage of adjacent formation water.



Figure 1. The points of sampling at the site of the well number 6

We determined number of soil microorganisms belonging to basic ecological-trophic, taxonomical and physiological groups by methods, generally accepted in soil microbiology (Zvyahintsev *et al.*, 1980; ISO 7847: 2015, 2016).), namely by sowing dilutions of soil suspensions on dense nutrient media. The number of organic nitrogen assimilating bacteria was counted on the meat-peptone agar (MPA), mineral nitrogen utilizing bacteria and actinomycetes were grown on starch-ammonia agar (SAA), fungi on Rihter's medium, oligotrophic microorganisms were cultured on starvation agar (SA). Sowing of the suspension was plated in fourfold replication from dilution 1:10⁴. Summary biological index (SBI) and biological degradation index (BDI) were calculated by the method of relative values by Azzi (1959). Soil invertases activity was determined on air-dry soil by the method outlined by Zvyagintsev *et al.* (1980), dehydrogenase by the Galstyan's method (Chaziyeu, 1976), and polyphenol oxidase by Karyagina's and Mikhailovskaya's method (1986). An assessment of the negative changes in the biological properties of the soil was carried out according to the scale (Table 1).

Table 1. Assessment of the level of degradation of soil by biological indicators (Snakin *et al.*, 1992)

Degree of soil degradation	Deviation of biological indices from the background soil to unfavourable side
0 – non-degradated soil	< 10 %
1 – low	10 – 25 %
2 – moderate	26 – 50 %
3 – high	51 – 75 %

4 – extreme	>75 %
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The reliability of data obtained in the course of research was evaluated using ANOVA.

Results

Number of microorganisms belonging to different eco-functional groups

Microbiological studies have shown that the number of organic nitrogen assimilating bacteria in the halogenic technosoils of all investigated points territory borehole number 6 was lower than their number in the background soil, on average, by 46 % (Table 2). The greatest suppression of the microorganisms of this group was observed in the soil at the point 6-08, where the number of bacteria was lower by 88 % compared with the background soil (or 8.5 times lower than in the background soil). The picture (see Figure 1) shows that the point 6-08 is located in the zone of salt spot formed on the surface of the soil as a result of the draining of the produced water due to the lowering of the relief.

Table 2. The number of microorganisms of the main ecological-functional, trophic and taxonomic in the soil territory hole number 6 and background soil

Sampling points	Nitrogen assimilating microorganisms, mln. CFU/g		Actinomyces, mln. CFU/g	Fungi, th. CFU/g	Oligotrophs, mln. CFU/g	Eutrophs, mln. CFU/g	Indices	
	organic	mineral					SBI, %	BDI, %
6-03	21.40	5.65	2.43	32.88	6.82	32.51	39	-52
6-04	19.87	2.54	1.68	44.20	6.22	24.13	32	-62
6-05	21.44	17.81	7.02	128.50	24.41	46.43	78	-13
6-06	27.46	14.12	6.42	347.16	27.89	48.35	82	0
6-07	12.58	7.32	5.34	83.95	25.78	25.32	54	-27
6-08	3.69	5.03	2.36	29.64	7.70	11.11	21	-71
6-09	11.29	14.49	10.15	88.26	34.72	36.02	77	0
6-10	17.20	20.08	5.10	80.30	31.16	42.46	81	0
Average	16.87	10.88	5.06	104.36	20.59	33.29	58	-22
Background 1	32.99	9.26	5.65	180.53	25.44	46.66	77	0
Background 2	29.81	11.13	6.12	29.65	25.75	47.09	78	0
Average	31.40	10.20	5.89	105.09	25.60	46.88	78	0
LSD _{0,05}	2.04	2.10	1,06	7,96	4.22	32.51	–	–

Note to the table: CFU – Colony forming unit

In average, the number of mineral nitrogen utilizing bacteria did not differ significantly from those observed in the background soil. But there are clearly three points in which the number of mineral nitrogen utilizing bacteria is significantly lower than in the background soil points. These are points 6-03, 6-04 and 6-08. The number of these microorganisms was less than the average number in background soil points by 45, 76 and 51 %, respectively, points. In addition, at the points indicated above, the content of actinomycetes was considerably lower – by 59, 76 and 51 % compared to background soil. According to many experts, actinomycetes are sensitive indicators of negative soil changes when contaminated by heavy metals, alcalinization and salinization due to irrigation of saline waters, etc. (Andreyuk *et al.*, 2001).

The differences between the average number of microscopic fungi in the samples of the technosoils and average number in the background soil were not detected. However, at some points territory near borehole they were very significant.

In the samples of halogenic technosoil, the average number of oligotrophic bacteria was lower by 20 % than the average value of their number in the background. But at the points where there was a decrease in the number of mineral nitrogen assimilating bacteria and actinomycetes, the number of oligotrophs was also significantly lower than the background indicators: in the soil point 6-03 – by 73 %, in the point 6-04 – by 76 %, and in the point 6-08 – by 70 %.

The total number of eutrophic microorganisms in the technosoil was on average less by 31 % than their average number in the background soil samples. At points 6-05, 6-06 and 6-10, it did not differ significantly from the values in the background. At points 6-04 and 6-07 it was lower by 49 and 46 %, at points 6-03 and 6-09 by 31 and 23 %, respectively, while the smallest number of eutrophs was observed on the ground at the point 6-08, where it was lower than the average value in the background points by 76 %.

The assessment of the soil microbial communities' condition, taking into account the number of microorganisms of the main ecological functional groups, which was carried out using SBI, showed the following. The minimum values of the SBI are calculated for the technosoil points 6-03, 6-04 and 6-08: 39, 32 and 21, respectively. SBI for soil at point 6-07 was slightly higher. The rest of the technosoil points SBI did not deviating for the worse from the values in the points background soil.

According to BDI values a strong degree of biological degradation of the soil is determined at points 6-03, 6-04 and 6-08 (BDI are respectively -52, -62 and -71 %). At the point number 6-05 a weak degree was detected (BDI = -13), and at the point 6-07 - the average (BDI = -27) degree of degradation of the soil. Soils at points 6-06, 6-09 and 6-10 can be considered non-degraded (with respect to the background of the background points). But, it is likely and possible that the background in the background was also affected by pollution.

Soil enzymatic activity

The level of activity of all three investigated enzymes in the soil around the well number 6 was on average higher than the similar background soil (Table 3). However, the level of dehydrogenase and polyphenol oxidase activity in the soil samples of points numbers 6-03 and 6-04 was significantly lower than the average values in the background soil (by 9 and 15 and by 27 and 22 % respectively), and the invertase activity was lower at three points: numbers 6-03 and 6-04 and 6-05 (by 5, 12 and 14 %).

Table 3. Enzymatic activity of polluted soil of territory well number 6 and background soil

Sampling points	Dehydrogenase mg TPF/100 g per 24 hours	Invertase mg glucose/g per 24 hours	Polyphenol oxidase mg 1,4-n- benzoquinone/10 g per 1 hours
6-03	88.00	5.75	594.00
6-04	82.50	5.33	638.00
6-05	118.25	5.24	902.00
6-06	129.25	7.34	1122.00
6-07	140.25	7.07	1100.00

6-08	116.80	7.30	1166.00
6-09	107.25	7.21	1012.00
6-10	96.25	6.61	902.00
Average	109.82	6.46	929.50
Background 1	97.60	5.97	858.00
Background 2	96.25	6.15	770.00
Average	96.93	6.06	814.00
LSD _{0.05}	6.90	0.18	32.00

Note to the table: LSD – smallest significant difference

The soil at the point number 6-04 is moderately degraded, and soil at the point number 6-03 is weakly degraded with a decrease in the activity of dehydrogenase. The soil at the point number 6-05 is weakly degraded by the decrease in invertase activity.

Discussion

The results of researches showed that the microbial communities' condition of investigated soils depends on the distance of the selected points from the source of the emergency leakage. According to the numbers of microorganisms, severe degradation was observed at the points 6-03, 6-04 and 6-08, which are closer to the source of leakage of toxic salts.

In the background points, the number of fungi differed by six times. It should be noted that for chernozem there is no inherent large number of fungal microflora, on the contrary, they are characterized by considerable numerical superiority of bacterial flora and high fungistatic potential. Therefore, the number of fungi colony-forming units, such as 180.53 (point background-1), 128.50 (point 6-05) and more than 347.16 (point number 6-06), without a doubt, is a consequence of the influence of substances in concentrations that cause a stimulating effect. This may be acidification of the soil, because reducing the pH of the medium contributes to the development of fungi.

An important indicator of the biological activity of the soil is its enzymatic activity, which closely correlates with its fertility. Soil enzymes are catalysts of various biochemical reactions occurring in the soil.

The generalization of data on the enzymatic activity of soils showed that the technosoil at the points 6-03 and 6-04 on the parameters of enzymatic activity is degraded. A decrease in the summary index of enzymatic activity relative to the averaged value of the summary index of enzymatic activity of the background soil is 14 and 16 %.

Regarding enzymatic activity, this is a more stable indicator. On the other hand, as is known from numerous literary sources, the enzymatic activity of the soil may be increased in the presence of small doses of heavy metals, and, on the other hand, it weakens the larger ones. At points 6-03 and 6-04, which are close to the center of the source of pollution, there is a weak degree of degradation.

The worst parameters of microbiological and biochemical indicators are identified in soil samples taken at points 6-03 and 6-04, which are located closest to the point of gust, and at the point 6-08, which is located in the zone of the produced water runoff, which was formed as a result of the relief lowering. As the distance from saltines stains, the parameters of the biological indicators are approaching the background. Taking into account that some indicators characterizing the functional state of microbial communities showed a violation of the optimal ratio of individual groups of microbial cenosis, as a result of the leak, there was an imbalance of equilibrium, a shift in the structure of the microbial complex, a violation of homeostasis, which is maintained in the soils of microorganisms.

Conclusions

High informativeness of microbiological indicators determines the necessity of their application for assessing the state of soils contaminated with related pollutants and the effectiveness of conducting of soil reclamation after the completion of drilling operations.

The biological indicators used by us it is expedient to plug in the system of indices of the ecological monitoring of soils in oil and gas mining areas.

In order to improve the microbiological and biochemical properties of the technosoils, it is necessary to carry out reclamation measures, as well as the continuation of the biological stage of remediation with the selection of crops that promote the soil desalinization.

When assessing the impact of pollution on soil quality, it is necessary to take into account not only the content of pollutants, but also the response of soil microbial communities.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.14. Managing nutrients to mitigate soil pollution

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Abstract

The health of soils is key not only to agricultural productivity, but to all the ecosystem services provided in terms of maintaining the quality of water, air, and food. Nutrient inputs to agricultural soils produce large benefits to human health, including the provisioning of calories and protein supporting at least half the human population, enhancing micronutrient bioavailability in food, improving crop quality, and strengthening tolerance to plant disease. With appropriate nutrient stewardship, such inputs contribute to soil health and prevent soil degradation. When mismanaged and applied inappropriately, either mineral or organic sources of nutrients can become pollutants both in soils and in water and air. The solution being embraced by industry and governments around the world is the implementation of principles of 4R Nutrient Stewardship, ensuring that the right source of nutrient is applied at the right time, in the right place and at the right rate.

Keywords: 4R Nutrient Stewardship, soil health

Introduction

The definition of soil pollution refers to a degradation process caused by presence in soils of substances detrimental to the health of humans, animals and plants (FAO 2018). Soil pollution can thus be considered the converse of soil health, defined as the continued capacity of soil to function as a vital living ecosystem that sustains plants, animals, and humans (USDA-NRCS 2018). Soil health is crucial to ecosystem services, not only in the provisioning component with the production of food, fibre and fuel, but also in the regulating, cultural and supporting components. Nutrient cycling is an important supporting service, and nutrient inputs are important to replenishing nutrients removed by the provisioning component. Soil health is commonly considered to comprise physical, chemical and biological components. Thus soil and nutrient management impacts that improve the chemical component of soil health are important contributors to mitigation of soil pollution.

Human dependence on nutrient inputs to soil

Global food production depends heavily on the use of mineral fertilizer, with nitrogen playing a dominant role. During the century following 1908, the proportion of the global human population fed by the yield increase produced by nitrogen fertilizer increased to 48% (Erisman et al. 2008). The precise contribution of mineral fertilizer to global food production—while difficult to determine owing to variation in inherent soil fertility, climatic conditions, cropping systems, plant genetic changes, and agronomic management—has been estimated at 40 to 60 % (Stewart and Dobb 2005).

Soil fertility and soil organic matter

The dependence on fertilizers has led to concerns about its long term impacts on soil health. A review of 114 long term experiments around the world noted a general decline over time in soil organic matter, a key indicator of the chemical component of soil health. When comparing treatments at these site for the influence of mineral nitrogen fertilizer, however, the rate of decline

was slower when nitrogen was applied than when it was not (Ladha et al. 2011). The analysis concluded that “in addition to its role in improving crop productivity, synthetic fertilizer N significantly reduces the rate at which soil organic matter is declining in agricultural soils, worldwide.”

Vast areas of global soils have low pH, restricting the uptake of calcium and magnesium, two macronutrients very important to human health. Simple additions of dolomitic limestone can increase the concentration of these two mineral elements, particularly in vegetables, and thus prevent diseases like rickets. Work supported by Cornell University in Bangladesh has demonstrated yield increases (10 to 50%) and quality improvements in more than 40 crops including: groundnuts, radishes, garlic, cabbage, cauliflower, eggplant, and turmeric, resulting in adoption of liming on over 86,000 ha by over 280,000 farmers (Duxbury et al. 2015).

In sub-Saharan agriculture, low fertilizer use, inappropriate fertilizer recommendations and lack of access to information on good crop nutrient management practices are key factors limiting crop productivity (Vanlauwe et al. 2015). The low crop productivity situation is associated with reduced quality of life, especially among rural households who rely on agriculture as their livelihood source (Sanchez 2010). About 65% of the agricultural land is degraded, mainly due to low nutrient application, soil erosion and soil acidification. Increased fertilizer use, from both organic and mineral sources and balanced nutrient management in combination with various organic matter inputs offer the best prospects to reverse soil degradation. In some of these degraded soils, yields can be readily increased by balanced application of base cations (potassium, magnesium and calcium) and micronutrients. In so doing, higher levels of soil organic carbon can be maintained (Zingore et al. 2015). Integrated soil fertility management provides a framework where both organic and inorganic fertilizers can be provided to the soils to improve soil fertility and boost soil organic carbon. Judicious application of nutrients, along with lime to correct soil pH, is included within the concept of 4R Nutrient Stewardship (IPNI 2012).

Soil microbial biomass

Mineral fertilizers produce impacts on soil microorganisms that differ depending on whether the short or long term is considered. While specific forms of fertilizer such as urea and ammonia can temporarily increase pH, osmotic potential and ammonia concentrations to levels inhibitory to microbial communities, the long term effects in agricultural cropping systems are beneficial. A meta-analysis based on 107 datasets from 64 long-term trials from around the world revealed that mineral fertilizer application led to a 15% increase in the microbial biomass above levels in unfertilized control treatments (Geisseler and Scow 2014). The results suggested that the long term increase in soil organic carbon in fertilized as compared to unfertilized treatments was the major contributing factor. Benefit to soil microbes increased with soil pH, pointing to the importance of balanced management of soil fertility, liming to address soil pH as well as nutrient needs of crops.

Managing risks of accumulation of associated elements

Fertilizers, manures, soils, and soil amendments may be naturally rich in trace elements, or contaminated. Processes in the soil-plant system that alleviate risks associated with these trace elements need to be considered in the management and regulation of such risks (Chaney 2012). A very thorough review of the use of organic amendments and the risk to human health noted that risks including the presence of heavy metals, pathogens, antibiotics, pharmaceuticals, and hormones can be managed by treatment before land application, and by ensuring they are applied at the rate, time and place most appropriate to the crops and soils. (Goss et al. 2013). To be sustainable, agricultural crop production needs inputs. Ensuring risks are mitigated in a manner

balancing the material priorities of stakeholder requires systematic application of science-based risk assessment, rather than haphazard application of the precautionary principle, to the management of nutrient inputs.

Managing risks of nutrient losses from soils

Implementation of 4R Nutrient Stewardship has been a large component of the agricultural community's response to recent issues with harmful algal blooms in Lake Erie, linked to phosphorus losses (Vollmer-Sanders et al. 2016; IJC 2014). The 4R certification program was launched in March 2014 by the Ohio agriculture community. In its first two years, 30 retailers were certified. Through their producer customers, the reach of the certified retailers extends to over one million hectares of cropland, including almost 40% of the agricultural land in the watershed. Early reviews indicate actual and potential benefits to the participating stakeholders.

The importance of 4R nitrogen practices to mitigate nitrous oxide emissions has also been recognized by the Field to Market sustainability organization (Field to Market 2017) and by the province of Alberta (Alberta Government 2014). By emphasizing the application of nutrients needed by crops in a manner that maximizes their uptake, the 4R approach is the rational first step in addressing issues of nutrient pollution.

Principles of 4R Nutrient Stewardship

The principles of 4R Nutrient Stewardship were developed by consensus among the scientists of the International Plant Nutrition Institute, with input from their collaborators in industry and in public research institutions. Those principles, elaborated in full detail in IPNI (2012), connect management of crop nutrition to sustainable crop production. They are briefly reviewed in the following.

Principles for sustainability

Consider stakeholder priorities. Agriculture is connected to supply chains whose stakeholders include the whole human family. Stakeholders need to have a say, choosing sustainability goals and sustainability performance metrics that reflect outcomes of management that matter to them.

Choose practices that move sustainability performance metrics forward. Producers choose practices through adaptive management to meet the goals and make progress toward achieving targets on key performance metrics.

Use adaptive management. Adaptive management is an ongoing process of developing improved practices for efficient production and resource conservation. This is accomplished by participatory learning and continuous systematic assessment. Adaptive management for crop nutrition evaluates outcomes of choices of source, rate, time and place combinations applied in site-specific contexts in terms of stakeholder-centric performance metrics.

Fit the 4Rs into cropping systems. Management of crops, soils, and pests, including soil conservation practices, interacts with 4R management choices and influences 4R outcomes.

Principles for accountability

Consider economic, environmental and social impacts. Managing plant nutrition according to principles of 4R Nutrient Stewardship includes accountability for all three dimensions of sustainability.

Keep records. A 4R Nutrient Stewardship Plan tracks and records all crop management practices, including details on the source, rate, time and place of every nutrient application. This information is for the benefit of the manager.

Report performance. A 4R Nutrient Stewardship plan also tracks performance, the outcome of implementing a set of practices, on all metrics of material interest to stakeholders. Sharing data with trusted aggregators can improve public trust. Reporting performance information on economic, environmental, and social priorities established by stakeholders distinguishes a 4R Nutrient Stewardship plan from other nutrient management plans.

Principles for right source

Consider rate, time, and place of application. The 4Rs are interlinked.

Supply nutrients in available forms. The form applied may be either immediately or slowly releasing plant-available nutrients.

Suit soil physical and chemical properties. For example, nitrate is too easily lost from flooded soils, and urea on the surface of alkaline soils is too easily lost in the form of ammonia.

Recognize synergisms among nutrient elements and sources. For instance, nitrogen can increase availability of applied phosphorus. Applied phosphorus can reduce availability of zinc. Fertilizers complement manures.

Recognize blend compatibility. Avoid combinations that attract moisture when mixed. Match up granule sizes when blending.

Recognize benefits and sensitivities to associated elements. For example, the chloride in muriate of potash can benefit maize, but also increases salt risk and may be detrimental to tobacco and some fruits.

Control effects of non-nutritive elements. For example, natural deposits of some phosphate rock contain non-nutritive trace elements. The level of addition of these elements should be kept within acceptable thresholds.

Principles for right rate

Consider source, time, and place of application. The 4Rs are interlinked.

Assess plant nutrient demand. The crop takes up nutrients in proportion to its yield. Realistic yield goals are established from measured past performance.

Assess soil nutrient supply. Soil testing is one method. Other options include plant analysis, on-farm omission plot trials, and crop canopy sensors.

Assess all available nutrient sources. These may include manure, composts, biosolids, crop residues, atmospheric deposition, and irrigation water, as well as commercial fertilizers.

Predict fertilizer use efficiency. Some losses are unavoidable.

Consider soil resource impacts. If outputs exceed inputs, soil fertility declines. Whether this matters depends on current soil fertility levels.

Consider economics. The law of diminishing returns applies. For mobile nutrients like nitrogen, aim for the maximum return in the current crop, in the context of variability and uncertainty of the most economic rate.

For nutrients like phosphorus and potassium, which the soil can retain, maintain an optimum soil test level.

Principles for right time

Consider source, rate, and place of application. The 4Rs are interlinked.

Assess timing of plant uptake. Crops take up nutrients at different rates through the growing season. Crops also have specific sensitivities to specific nutrient shortages at different times.

Assess dynamics of soil nutrient supply. As soil warms up through the growing season, available nutrients mineralized from organic matter can accumulate.

Recognize dynamics of soil nutrient loss. Rains exceed soil water storage capacity most often in late fall and early spring, so runoff risks can be higher.

Evaluate logistics of field operations. Nutrient applications that delay timely planting are counter-productive, and the soil compaction effects of applications at different times need to be considered.

Principles for right place

Consider source, rate, and time of application. The 4Rs are interlinked.

Consider where plant roots are growing. Nutrients need to be placed where they can be taken up by growing roots when needed.

Consider soil chemical reactions. Concentrating soil-retained nutrients like phosphorus in bands or smaller soil volumes can improve availability.

Suit the goals of the tillage system. Subsurface placement techniques that maintain crop residue cover on the soil can help conserve nutrients and water.

Manage spatial variability. Assess differences within and among fields in crop productivity, soil nutrient supply capacity, and vulnerability to nutrient loss.

Relevance

The importance of these principles of 4R Nutrient Stewardship is that they have been carefully selected for consistency with the sciences of soil fertility and plant nutrition, and with global standards for sustainability verification. This consistency is important for the extensive collaboration that is essential to improving sustainability and to communicating those improvements to the wide range of stakeholders involved. The 4R path is the one most likely to harmonize profitable agronomics at the field scale with improved sustainability of the agricultural system as a whole. The 4R principles make a difference to the fertilizer industry's ability to participate with sustainability organizations like Field to Market®.

Conclusion

Adoption and promotion of 4R Nutrient Stewardship is a global strategy that can be expected to contribute toward the mitigation soil pollution.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.15. Management of contaminated groundwater in the Netherlands. Criteria for contamination, the management and restoration of groundwater.

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Abstract

In the soil-sediment-water system groundwater is the connecting medium. So groundwater quality is part of the soil legislation and of the water legislation. Groundwater pollution due to contaminated land is addressed in the Soil Protection Act. “Pump and treat” of contaminated groundwater for a long period is very costly. In the last decade changes have been made in dealing with risks of groundwater contamination. Upscaling from a site by site approach towards an area approach has proven to be a sustainable alternative. Transfer of liability of contaminated groundwater is the key.

The unacceptable risks of migration of contaminated groundwater are defined according to a set of criteria. Given these criteria approximately 1400 sites have been selected as urgent because of unacceptable risks for migration of contaminated groundwater. These sites are mainly located in urban areas. Due to the fact that these are all historical contaminations (originated before 1987), a lot of these locations are situated in the vicinity of each other and plumes of contaminants have mixed in the saturated zone. Therefore the liability is unclear. Who is liable for what?

The following concept is introduced: the source of the contamination should be remediated by the owners of the sites; the contaminated groundwater “plumes” must be managed together with other mixed plumes in an area approach. Upscaling towards an area based and integrated approach demands transfer of liability of the “plumes”. In return for the transfer of liability the owners of the sites have to pay redemption money for potential risks or future remediation costs.

Keywords: [Criteria, risks assessment, redemption money, area approach, liability, source, mixed plumes.]

Introduction, scope and main objectives

Industrial areas often have to deal with historical contamination of land and groundwater. Over time the contamination has spread over sometimes considerable areas. “Plumes” of different polluters have become mixed, the polluters cannot always be identified and are sometimes not even alive. Consequently the liability of the “polluter pays principle” cannot be executed. Also when the responsibility has been transferred to the “new” site owner the problem of mixed plumes makes it hard to define the liability.

The main objective of the presentation is to solve the dilemma of the liability (and prevent court cases) and to find a sustainable alternatives by upscaling towards an area approach and management. For example the inner city of Utrecht or Rotterdam harbour work with this approach. The Rotterdam project and some preliminary conclusions will be presented.

Instead of “Pump and treat”, a remediation technique which is often used but which is not very sustainable, area management is chosen as a solution to cope with the contaminated groundwater. An area plan is drawn up with several stakeholders, the site owners, local authorities and other stakeholders such as the Harbour Authorities. An inventory of the baseline is made: contamination sources, “plumes” and pathways, vulnerable objects and system boundaries are defined. A time line is set. Risks are determined as well as costs and benefits and a monitoring plan. The unacceptable risks of migration of contaminated groundwater are defined according to a set of criteria:

- The quality of the groundwater exceeds the intervention values for groundwater.
- The volume of affected groundwater is over 6.000 m³ and the annual increase in volume is over 1000 m³
- There is a layer of contaminants on top or below the aquifer
- Relation to vulnerable objects, defined according to the source-path-receptor model , for example within a protected area for water supply for human consumption, process water for industry or a protected area in accordance with the EU Water Framework Directory

Based on this inventory the redemption costs are determined. Management of contaminated groundwater on an area basis is a good alternative, especially in combination with in situ techniques.

Participation in this area approach is voluntary. When the site owner chooses not to participate, remediation on site level is obligated, this to avoid “free riders”. Costs of a site approach is much higher than the participation in an area approach with transfer of liability. This turns out to be an important trigger for participation. The liability is transferred to an existing public authority such as a municipality. This is important because they have the instruments to extract and manage

groundwater quality and groundwater quantity and the duty to register and publish the monitoring results to the public and other parties working in the area.

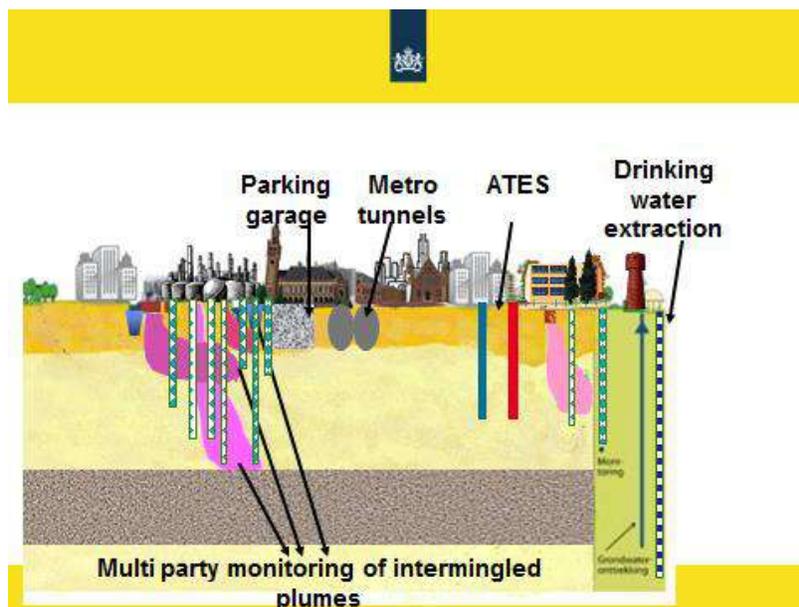


Figure 1. Liability problems by mixed plumes of contaminated groundwater in inner cities.

Results

Solving the dilemma of liability by mixed “plumes” when the “polluter pays principle” cannot be held. Compliance with the Water Framework Directive obligation of trend reversal is obtained by the remediation of the contamination source and management of the “plumes”.

Discussion

Governance is important to solve the problem of mixed plumes of contaminated groundwater. Public authorities should take the lead. Instead of going to court and sticking to the “polluter pays principle” a practical solution for historical contamination helps further spreading of contamination to vulnerable objects.

Conclusions

The concept has proven to have an added value and is formalized as part of the Dutch Soil Protection Act. The dilemma of mixed plumes cause by historical contamination and as a consequence the liability has been solved. Spreading of contamination is monitored, registered and under control. The obligations of the Water Framework Directive are met. The groundwater management plans for the Centre of Utrecht and harbor of Rotterdam are good examples.

Acknowledgements

Formulating soil and groundwater policy depends on all kind of studies. Pilot studies have been done in Rotterdam, Utrecht, ‘t Gooi, Zwolle etc. Without this studies it wouldn’t be possible to put this policy in legislation. All stakeholders are involved to make a vision of the to develop area.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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The Dutch Soil Protection Act

City chlor project, Interreg EU; partners from Flanders, Germany, France and the Netherlands.
<https://rwsenvironment.eu/subjects/soil/projects/citychlor/>

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3.1.16. Geostatistical mapping of metal elements distribution across conterminous USA

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Abstract

Assessment and proper management of sites contaminated with metal elements requires a precise information on the spatial distribution of these metals. This study aims to model and map the spatial distribution of Cd, Cu, Ni, Pb and Zn across the conterminous USA using point observations and geostatistics. About 4,400 surface soil observations of Cd, Cu, Ni, Pb and Zn concentrations (mg kg⁻¹) were compiled from the USDA-NRCS database in this study. Spatial autocorrelation of these elements was quantified with a variogram, and the continuous maps were generated using ordinary kriging. Prediction uncertainty was assessed through prediction standard error map and by cross-validation. Average Cd and Zn in the study area were 0.37 mg kg⁻¹ and 68.6 mg kg⁻¹, respectively; whereas, Cu, Ni, and Pb ranged between 29 to 31 mg kg⁻¹. A stable variogram was found to be the best model to quantify spatial autocorrelation of these elements. Based on cross-validation, Cd had the highest prediction performance and Ni the lowest. In general, the southeastern USA had lower concentrations of most metal elements compared to the rest of the USA. Cu was higher along the north eastern and west coast; whereas, a toxic concentration of Pb was predicted towards the northeast and a small area in the northwest. Results presented in this study provide general trends based on spatially available data. Nevertheless, results from this study give some general information on the spatial behaviours and general distribution pattern of metal elements across the

conterminous USA. In the future, mapping with advanced digital techniques will be adopted in which several soil-environmental variables can be used as predictors of these metals.

Keywords: heavy metals, toxic elements, kriging, cross-validation, soil

Introduction, scope and main objectives

Accumulation of excessive concentration of metal elements such as Cadmium (Cd), Cobalt (Co), Copper (Cu), Lead (Pb), Zinc (Zn), Mercury (Hg) etc. in soils can cause potential health hazards to humans and animals when the concentration exceeds toxic thresholds (Dudka *et al.* 1994; Otte *et al.* 1993; Wardrope and Graham 1982). The main source of metal contamination in soils include the use of synthetic products such as pesticides, paints, industrial waste or land application of municipal sludge, as well as metals from mining, manufacturing industries, road transport and combustion of fossil fuels (Colgan *et al.* 2003; Lin 2002; Nicholson *et al.* 2003; Palumbo *et al.* 2000). Cleaning soils contaminated with toxic metals is extremely expensive and difficult, so identifying and preventing such pollution is critically important. Therefore, understanding the concentrations of heavy metals in soils allows decision makers to assess the risk and provide information for the health of humans, animals and ecosystems and thereby develop appropriate plans and programs for proper soil and environmental management.

Geostatistics has been extensively used in modeling and mapping the spatial variation of soil and environmental variables (Goovaerts 1997; Webster and Oliver 2007) including metal concentrations in soil (Adhikari *et al.* 2009; Lado *et al.* 2008; McGrath *et al.* 2004; Rodríguez Martín *et al.* 2006). The main objectives of this study were to map the distribution of Cd, Cu, Ni, Pb, and Zn across the conterminous USA using geostatistics and to assess prediction performance using cross-validation.

Methodology

Point observation and laboratory analysis

The study is based on two major point data sources on metals sampled across conterminous USA—Soil Geochemistry Spatial Database (SGSD), and Holmgren Dataset (HD)—available from the USDA-NRCS. Metal data in SGSD consists of pedon data from over 1,150 sites sampled and analysed by soil horizons representing both contaminated and non-contaminated sites. Summary and analysis of these data used in this study are documented in Burt *et al.* (2003), and Wilson *et al.* (2008). The HD was compiled by the Soil Survey Laboratory during 1970's and 1980's and consisted of point observations on selected trace elements in agricultural soils from 3,400 sites. More detail on this database can be found in Holmgren *et al.* (1993).

About 4,400 observations on Cd, Cu, Ni, Pb, and Zn from the soil surface horizon were extracted from both databases and were considered for mapping. Laboratory analysis of the elements consisted of acid digestion of 0.5 g of milled (<150 µm) soil samples in a covered vessel with 9 ml HNO₃ + 3 ml HCL (aqua regia) at 180°C for about 7 minutes. The extracts were analysed by inductively coupled plasma atomic emission spectroscopy and the elemental concentration was expressed as mg kg⁻¹ (Burt *et al.*, 2003). Figure 1 shows the point geographical distribution of lead (Pb) observations across conterminous USA.

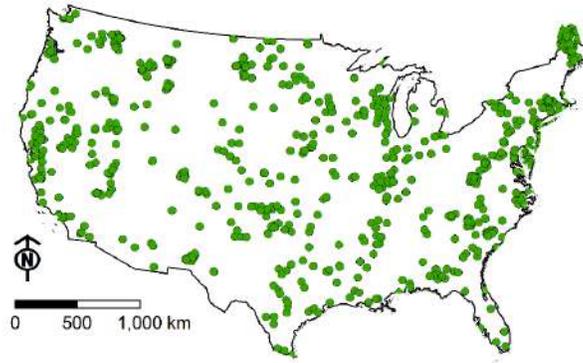


Figure 1. Georeferenced points illustrating the distribution of metal element (Pb; $n = 4,276$) across conterminous USA

Spatial prediction and mapping

A geostatistical method (Ordinary kriging) was employed to generate continuous maps of metal elements using discrete point observations. The spatial autocorrelation of the elemental distribution was estimated with a variogram that quantifies semivariance between the observation points for a given lag distance or sampling intervals (Goovaerts 1997), and provides the input parameters for spatial mapping using kriging (Krige 1951). An experimental variogram can be calculated as described in Eq. (1).

$$\gamma(h) = \frac{1}{2N(h)} \sum_{a=1}^{N(h)} \{z(x_a + h) - z(x_a)\}^2 \quad \text{Eq. (1)}$$

Here, $\gamma(h)$ represents the variogram for a distance (lag) h between observations $z(x_a)$ and $z(x_a + h)$ with $N(h)$ the number of pairs separated by h .

For all elements, an omnidirectional experimental variogram was calculated, to which the theoretical variogram models were fitted and variogram parameters were used to interpolate the metals values at un-sampled locations by means of ordinary kriging (OK). The OK is an exact interpolation technique that considers a local stationary of the mean which is unknown, and uses a linear combination of observations within a predefined neighborhood around observation locations (Goovaerts 1997). A mathematical function of the OK estimator and associated variance are calculated using Eq. (2), and Eq. (3), respectively, and the square root of the variance gives a prediction standard error.

$$Z_{OK}^*(x_0) = \sum_{a=1}^{n(x_0)} \lambda_a \cdot z(x_a) \quad \text{Eq. (2)}$$

$$\sigma_{OK}^2(x_0) = \sum_{a=1}^{n(x_0)} \{\lambda_a \cdot \gamma(x_a - x_0)\} + \psi \quad \text{Eq. (3)}$$

Where $Z_{OK}^*(x_0)$ is the OK estimated metal concentration z at location (x_0) , λ_a is the weight assigned to the n observations $z(x_a)$, γ is the modelled variogram, $\sigma_{OK}^2(x_0)$ the estimated OK variance, and ψ is the Lagrange multiplier.

The experiment variogram was calculated considering 12 lags with corresponding lag distance depending on the element in question. Among spherical, exponential, and stable variogram models

tested, the stable model performed the best estimator and it was selected for subsequent modeling and analysis. Together with an OK prediction map, a map showing the prediction standard error was derived as a measure of uncertainty in prediction. The error map suggests that 95 % of the time, the true value lies within the predicted value plus or minus two times the prediction standard error for normally distributed data.

The prediction model was also evaluated with common validation indices like R^2 , mean error (ME), and root mean square error (RMSE) using leave-one-out cross validation technique. Variogram modeling and ordinary kriging was done in ArcGIS (ESRI 2014) following Geostatistical Analyst tool.

Results

General statistics

Table 1 summarizes the descriptive statistics of metal elements used in this study. The number of observations (count) varied as not all elements were reported for each sample location. For example, data on Cu were recorded in 4,361 sites whereas Pb and Zn were reported from 4,276 sites. Average and standard deviation for Cd and Zn in the study area were 0.37 mg kg^{-1} (± 1.3), and 68.6 mg kg^{-1} (± 154), respectively. Cu, Ni, and Pb shared a comparable mean value of about 29 to 31 mg kg^{-1} . The distribution of all elemental data was highly positively skewed, consequently, data were log transformed to restrict to its normal distribution for modeling (Table 1). Data were presented in their original units for spatial distribution maps.

Table 1. Descriptive statistics of measured metal elements

Parameter	Cd	Cu	Ni	Pb	Zn
	mg kg^{-1} $\log(\text{mg kg}^{-1})$	mg kg^{-1} $\log(\text{mg kg}^{-1})$	mg kg^{-1} $\log(\text{mg kg}^{-1})$	mgkg^{-1} $\log(\text{mg kg}^{-1})$	mg kg^{-1} $\log(\text{mgkg}^{-1})$
Count	4259	4361	4269	4276	4276
Minimum	0.01 [-4.6]	0.08 [-2.5]	0.01 [-4.6]	0.05 [2.99]	0.86 [-0.15]
Maximum	36.3 [3.6]	735 [6.6]	3701 [8.2]	4,445 [8.4]	4873 [8.4]
Mean	0.37 [-1.6]	30.3 [2.9]	29.4 [2.8]	31.3 [2.5]	68.6 [3.8]
Std. dev.	1.3 [1.0]	44.0 [1.0]	120.6 [0.9]	208.8 [0.84]	154.2 [0.88]
Skewness	20.8 [-0.1]	5.6 [-0.09]	19.9 [0.03]	16.7 [1.5]	21.7 [-0.7]
Kurtosis	451.8 [4.3]	55.7 [3.9]	453.8 [6.9]	303.3 [12.5]	558.7 [4.8]
1 st quartile	0.11 [2.2]	10.4 [2.3]	9.81 [2.2]	8.0 [2.0]	31.9 [3.4]
Median	0.21 [-1.5]	18.6 [2.9]	18.1 [2.8]	12.0 [2.5]	57.5 [4.0]
3 rd quartile	0.38 [-0.96]	30.9 [3.4]	27.1 [3.3]	17.0 [2.8]	81.8 [4.4]

Predicted maps

Ordinary kriging was employed to predict concentrations of Cd, Cu, Ni, Pb, and Zn at un-sampled locations considering the autocorrelation of the distribution of these elements. Continuous maps of these elements with associated prediction standard errors are displayed in Figure 2. In general, southeastern parts of the USA had lower concentration of metals compared to the rest of the area. Distribution of Cu was minimum along central south and southeastern parts, whereas the remaining areas had moderate-to-high concentrations. A higher concentration of Cu was predicted along the northeastern and western coast. Zn was $<70 \text{ mg kg}^{-1}$ throughout the area except for northeast, and northwest of the USA. Conversely, Pb was found higher in the east compared to west and midsouth.

A toxic concentration of Pb greater than 400 mg kg^{-1} (in areas where children play) was predicted towards the northeast and a specific area in the northwest, which was predicted with $\text{Pb} >1200 \text{ mg kg}^{-1}$ has been reported to be toxic in bare soils. The distribution of higher values of Ni was mostly along the west coast, Midwest and Northwest Territories. For almost all elements except Ni, a specific area in the northwest and along the northeastern coast had higher concentrations of these elements. Areas that were predicted to have higher elemental concentration had a higher prediction error associated with the estimate (Figure 2). In general, predictions were better across the southeast for most elements, and for Pb predictions were greatest in the southcentral and central west.

Results for cross-validation are listed in Table 2. Overall, Cd was best predicted with a higher R^2 (0.61), and minimum ME (0.01) and RMSE (0.29). Pb had the highest R^2 of prediction but with a maximum ME of 6.8 and a RMSE of 48.1. Therefore, it was poorly predicted. The lowest performance was associated with the prediction of Ni where the RMSE was higher (17.5) and it showed the lowest R^2 (0.30) of prediction.

Table 2. Prediction model performance based on leave-one-out cross validation

Metal elements	R^2	ME	RMSE
Cd	0.61	0.01	0.29
Cu	0.40	-0.08	15.1
Ni	0.30	3.7	17.5
Pb	0.65	6.8	48.1
Zn	0.35	-1.0	23.1

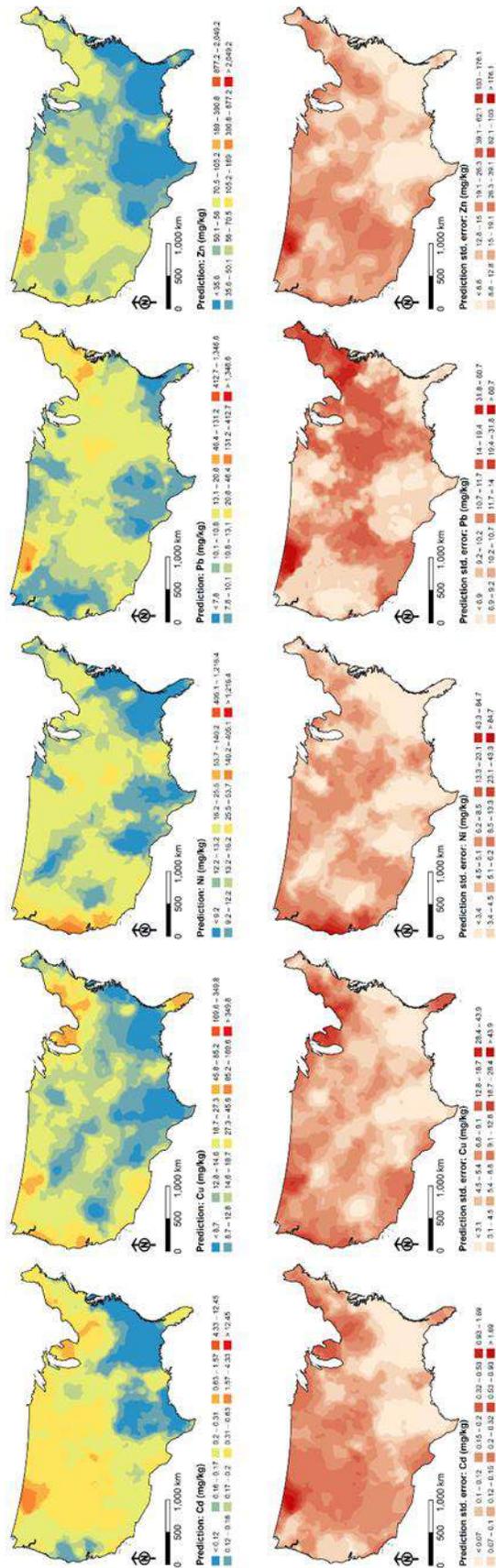


Figure 2. Predicted maps of metal elements (top) and associated prediction standard error (bottom) across the conterminous USA.

Discussion

This study employed geostatistical techniques to map spatial distribution of metals across the conterminous USA. Use of geostatistical techniques has been common to map metal elemental distribution across varying scales (Franco *et al.* 2006; Lado *et al.* 2008; Lark *et al.* 2006; McGrath *et al.* 2004). The availability of metal element across the USA made it possible to apply OK to mapping metal distribution. The results were promising with a good prediction performance, which was also reported by Lado *et al.* (2008) as higher performance using OK to map metal elements across Europe. Generally speaking, as reported in (Holmgren *et al.* 1993), we found a lower concentration of most metal elements towards the south-eastern USA. The highest concentration of Cd was found along the northeast and northwest parts, indicating Cd contaminations as the concentration exceeded 3 mg kg^{-1} (Cala Rivero *et al.* 1985). Much of the northern and western USA may have anthropogenic influences which elevated Cd in soils as its concentration was higher than 0.5 mg kg^{-1} (Errecalde *et al.* 1991). The higher concentration of Cd, and Zn from a small area in the northwest could possibly be linked to the use of phosphate fertilizer rich in Cd impurities (Holmgren *et al.* 1993; Mortvedt *et al.* 1981). The high concentration of Pb ($>70 \text{ mg kg}^{-1}$) could be attributed to fossil fuel combustion (Davies 1997), and industrial sources which are common in most areas in the central and eastern USA (Holmgren *et al.* 1993). The concentration of Zn and Cu was higher in western portions in the US and could be linked to bedrock types and the use of Cu fertilizers and fungicidal sprays in agricultural soils (Holmgren *et al.* 1993), which was also reported by Mantovi *et al.* (2003). Similarly, high concentrations of Ni along the west could be explained by parent material (serpentine) (Holmgren *et al.* 1993; Peng *et al.* 2016). As reported in Palumbo *et al.* (2000), concentration and distribution of metal elements in soils are greatly influenced by parent materials and pedogenesis. Our results indicate that distribution of metal elements across conterminous USA could be influenced by several environmental variables including parent material and soil types. Therefore, future research is necessary to integrate several soil and environmental variables as predictors of metal elements and map the distribution using advanced digital soil mapping techniques such as data-mining or classification and regression (Peng *et al.* 2016).

Conclusions

This study mapped the spatial distribution of metal elements (Cd, Cu, Ni, Pb, and Zn) across the conterminous US using point observation and geostatistics. Autocorrelation of the elements was modelled using a variogram and the values at un-sampled locations were estimated and mapped with ordinary kriging. Prediction error maps were generated, and cross-validation analysis were performed to assess uncertainty and to evaluate prediction model performance. Based on the results, the following were concluded:

- Spatial autocorrelation of Cd, Cu, Ni, Pb, and Zn was best quantified with a stable variogram model.
- The southeastern parts of the USA had lower concentration of most metal elements compared to the rest of the US.
- The distribution of Cu was higher along the northeastern and western coast. A toxic concentration of Pb was predicted towards the northeast and a specific area in the northwest.
- Areas with higher elemental concentrations had a higher prediction error.
- Cd was best predicted, whereas Ni had the lowest prediction performance.
- Further research is needed to map these elements using environmental variables as predicting covariates.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.17. Optimization of hydrocarbons biodegradation by bacterial strains isolated from wastewaters in Ouagadougou, Burkina Faso: Case study of SAE 40/50 used oils and diesel

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Abstract

Environmental pollution with petroleum and petrochemical products such as diesel and used oils has been recognized as one of the most serious current problem in the world, especially in developing countries. These petrochemical products devastate the soil, surface and underground waters and alter the microbial population at the polluted sites. Thus, the present work aims to optimize the biodegradation of diesel and two used oils (SAE 40 and SAE 50) by bacterial strains namely *Acinetobacter* S2 and *Pseudomonas* S7 using either nutrient factors (yeast extract, peptone or trace elements) or surfactants (tween 80 or Sodium Dodecyl Sulfate: SDS). The strains are incubated alone or together with the used oils or diesel supplemented or not with nutrient factors or surfactants for 14, 28, 42 and 56 days, respectively. For all the incubation period, the hydrocarbons degradation rates are determined by gravimetric assay. The results obtained show that nutrient factors increase significantly SAE 50 used oil biodegradation ($p = 0.009$). Similarly, tween 80 increases SAE 50 and SAE 40 used oils biodegradation but not diesel one. The results also show a significant difference between biodegradation rates at 14, 28, 42 and 56 days for all the hydrocarbons tested ($p < 0.0001$). For all the hydrocarbons, the association of strains *Acinetobacter* S2 and *Pseudomonas* S7 increases the degradation over the one of the strains alone.

Keywords: Biodegradation, Hydrocarbon, Nutrient Factor, Surfactant, Bacterial Strain

Introduction, scope and main objectives

Lubricant oil is a complex mixture of hydrocarbons and other organic compounds, including some organometallic constituents that are used to lubricate the parts of an automobile engine, in order to keep everything running smoothly (Butler and Mason 1997). The utilization of lubricant leads to the production of used oils commonly in the whole world. These used oils devastate the soil, surface and underground water and alter the microbial population at the polluted sites (Ainon *et al.* 2010). Spillage of used motor oils also contaminates our natural environment with polycyclic aromatic hydrocarbons (PAHs) which attract public attention because many PAHs are toxic, mutagenic and carcinogenic (Bumpus 1989). Similarly, diesel oil is one of the major products of crude oil that constitutes the main source of pollution in the environment (Adesodun and Mbagwu 2008). In addition, soil contamination by hydrocarbons, as well as underground and surface water, seriously affects the ecosystem, especially through the accumulation within animals and plants resulting in death and mutation (Ilyina *et al.* 2003). Environmental pollution with petroleum and petrochemical products (complex mixtures of hydrocarbons) has been recognized as one of the most serious current problem (Plohl and Leskovsek 2002). Fortunately, bioremediation of petrochemical products in the environment is possible and exploits the

metabolic properties of microorganisms (bacteria, yeast or fungi) to degrade these contaminating agents.

The application of bacterial isolates in degrading oil involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate (Vidali 2001). The intensity of oils biodegradation is influenced by several factors, such as nutrients, oxygen, pH, composition, concentration and bioavailability of the contaminants, chemical and physical characteristics and the pollution history of the contaminated environment (Al-Darbi *et al.* 2005). Particularly, lack of essential nutrients such as nitrogen and phosphorus is one of the major factors affecting biodegradation of hydrocarbon by microorganisms in soil and water environment (Abioye *et al.* 2012). In addition, studies report the use of surfactants to enhance hydrocarbons biodegradation (Mulligan *et al.* 2001). According to Chrzanowski *et al.* (2006), surface-active compounds may generally influence hydrocarbons biodegradation by increasing their solubility or they may interfere with the cell walls of microorganisms.

In our previous works, two bacterial strains able to degrade hydrocarbons were isolated (Sawadogo *et al.* 2014). The optimization of Total Quartz SEA 40 used oil and diesel oil biodegradation by these strains in presence of nutrient factors was also performed (Sawadogo *et al.* 2015). However, the effects of nutrient factors on SAE 50 used oil (oil commonly used in our country because of its low cost) degradation, as well as the effects of surfactants on both hydrocarbons degradation by these strains were not documented. Thus, the present work focused on the optimization of these hydrocarbons biodegradation using nutrient factors (yeast extract, peptone or trace elements) and surfactants (Tween 80 or SDS), respectively.

Methodology

Bacterial strains

Two bacterial strains, namely S2 and S7 used in this study were isolated during our previous work from wastewaters in Ouagadougou, Burkina Faso and partially characterized (Sawadogo *et al.* 2014).

Hydrocarbons used in this study

The diesel oil used in this experiment was purchased from a local oil filling station and stored in the dark at ambient temperature throughout the study. The used oils (SEA 40 and SAE 50) were collected from a local garage and stored in the same conditions as for diesel oil. Before use, the oils were sterilized using 0.2 µm pore size membrane filter.

Culture media and incubation condition

Bushnell-Haas Broth consisting of: K₂HPO₄ 1.0 g/L, KH₂PO₄ 1.0 g/L, NH₄NO₃ 1.0 g/L, MgSO₄ 0.2 g/L, CaCl₂ 0.02 g/L and FeCl₃ 0.005 g/L was used for incubation. Flasks (120 ml) containing 35.6 ml of the nutrient broth supplemented with 3% (v/v) of 0.22 µm pore size filter-sterilized hydrocarbon substrate were inoculated in triplicate with 4 ml exponential phase culture inoculum of *Acinetobacter* S2 and *Pseudomonas* S7 strains or their mixture (*Acinetobacter* S2 + *Pseudomonas* S7), respectively and then incubated at 37°C for 14, 28, 42 and 56 days (2 ml of the suspension of each strain culture was added in the case of the mix culture S2 + S7). Controls without bacterial inoculation were prepared similarly for all incubations to evaluate the abiotic loss of hydrocarbons.

The pH was adjusted to 8.00, 7.50 and 7.75 for cultures containing bacterial strains S2, S7 and their mixture (S2 + S7), respectively. To test the effects of nutrient factors, the above cultures were supplemented with 0.5% (w/v) yeast extract or peptone and 1% (v/v) trace elements of Widdel and Pfennig (1984), respectively.

The Widdel and Pfennig trace elements consists of : HCl (25%: v/v) 6.5 ml, FeCl₂·4H₂O 1.5 g, H₃BO₃ 60 mg, MnCl₂·4H₂O 100 mg, CoCl₂·6H₂O 120 mg, ZnCl₂ 70 mg, NiCl₂·H₂O 25 mg, CuCl₂·2H₂O 15 mg, Na₂MoO₄·2H₂O 25 mg, distilled water 1000 ml final volume. To evaluate the effects of surfactants on the biodegradation process, 0.5% (v/v) Tween 80 or 0.5% (w/v) SDS was added to the Bushnell-Haas Broth cultures described above.

Biodegradation study

Hydrocarbon degradation was studied by gravimetric analysis according to Panda *et al.* (2013). After different incubation periods at 37°C, the flasks (120 ml) were taken out and bacterial activities were stopped by adding 1% (v/v) 1N-HCL. For extraction of residual oil, 40 ml of culture broth was mixed with 40 ml petroleum ether/acetone (1:1) in a separating funnel and then shaken vigorously to get a single emulsified layer. Acetone was then added and shaken gently to break the emulsification, which resulted in three layers.

The top layer was a mixture of petroleum ether, diesel oil and acetone; clumping cells make a middle layer and the bottom aqueous layer contains acetone, water and biosurfactant in soluble form. The lower two layers were spread out while the top layer containing petroleum ether mixed with diesel oil or used oils and acetone was taken in a preweighed clean beaker. The extracted oil was passed through anhydrous sodium sulphate to remove moisture. The petroleum ether and acetone layer was evaporated on a water bath. The gravimetric estimation of residual oil left after biodegradation was made by weighing the quantity of oil in a tarred beaker. The percentage of biodegraded oil was then evaluated in comparison to the initial hydrocarbon amount in the control funnel according to Fusey and Oudot (1976), as described by Sawadogo *et al.* (2014).

Statistical analysis

The data collected were subjected to analysis of variance (ANOVA) with regards to the hydrocarbon used, nutrient factor, surfactant, incubation period and bacterial strain using XLSTAT-Pro 7.5 software. Mean variables were compared using the Newman Keuls test at probability level $p = 0.05$.

Results

Effects of nutrient factors on SAE 50 used oil biodegradation

After 14 days incubation period at 37°C, the biodegradation rates obtained on SEA 50 supplemented with nutrient factors are presented in figure 1.

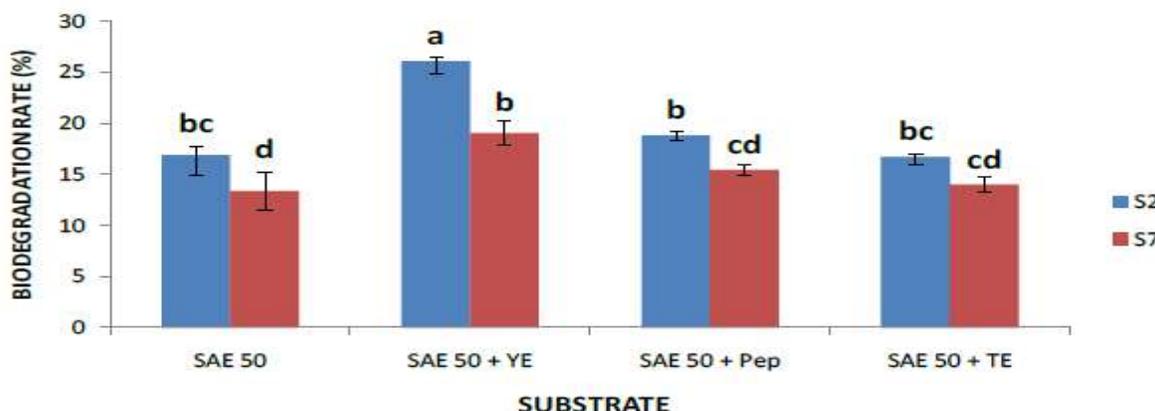


Figure 1. Biodegradation rates of *Acinetobacter* S2 and *Pseudomonas* S7 strains on SAE 50 used oil supplemented or not with nutrient factors after 14 days incubation period. For all strains and for all the substrates experienced, values sharing the same letter are not significantly different according to the Newman-Keuls' test at $p = 0.05$. YE: Yeast Extract; Pep: Peptone; TE: Trace Elements.

Effects of SDS and tween 80 on diesel oil, SAE 40 and SAE 50 used oils case of diesel oil

Case of diesel oil

After 14 days incubation period at 37°C, the biodegradation rates obtained on diesel oil, SAE 40 and SAE 50 used oils supplemented with surfactants are presented in Table 1, table 2 and table 3 respectively.

Table 1. Biodegradation rates of diesel oil supplemented or not with surfactant (tween 80 or SDS) after 14 days incubation period with regards to *Acinetobacter* S2 and *Pseudomonas* S7 strains.

Substrate	Bacterial strain	Biodegradation rate (%)
Diesel oil	<i>Acinetobacter</i> S2	30.57 ^a ± 1.09
	<i>Pseudomonas</i> S7	18.25 ^b ± 1.30
Diesel oil + Tween 80	<i>Acinetobacter</i> S2	30.81 ^a ± 0.63
	<i>Pseudomonas</i> S7	18.32 ^b ± 0.38
Diesel oil + SDS	<i>Acinetobacter</i> S2	30.25 ^a ± 0.53
	<i>Pseudomonas</i> S7	18.14 ^b ± 0.30

Means with a same letter within a column are not significantly different according to the Newman-Keuls' test at $p = 0.05$.

Case of SAE 40 used oil

Table 2. Biodegradation rates of SAE 40 used oil supplemented or not with surfactant (tween 80 or SDS) after 14 days incubation period, with regards to *Acinetobacter* S2 and *Pseudomonas* S7 strains.

Substrate	Bacterial strain	Biodegradation rate (%)
SAE 40 used oil	<i>Acinetobacter</i> S2	15.46 ^{bc} ± 1.24
	<i>Pseudomonas</i> S7	13.73 ^c ± 1.51
SAE 40 used oil + Tween 80	<i>Acinetobacter</i> S2	18.15 ^a ± 0.46
	<i>Pseudomonas</i> S7	16.76 ^{ab} ± 0.55
SAE 40 used oil + SDS	<i>Acinetobacter</i> S2	16.86 ^{ab} ± 0.69
	<i>Pseudomonas</i> S7	13.81 ^c ± 0.21

Means with a same letter within a column are not significantly different according to the Newman-Keuls' test at $p = 0.05$.

Case of SAE 40 used oil

Table 3. Biodegradation of SAE 50 used oil supplemented or not with surfactants (tween 80 and SDS) after 14 days incubation period, with regards to *Acinetobacter* S2 and *Pseudomonas* S7 strains.

Substrate	Bacterial strain	Biodegradation rate (%)
SAE 50 used oil	<i>Acinetobacter</i> S2	16.88 ^b ± 0.85
	<i>Pseudomonas</i> S7	13.41 ^c ± 1.90
SAE 50 used oil + Tween 80	<i>Acinetobacter</i> S2	18.83 ^a ± 0.32
	<i>Pseudomonas</i> S7	16.01 ^b ± 0.67
SAE 50 used oil + SDS	<i>Acinetobacter</i> S2	16.99 ^b ± 0.18
	<i>Pseudomonas</i> S7	13.63 ^c ± 0.32

Means with a same letter within a column are not significantly different according to the Newman-Keuls' test at $p = 0.05$.

Effect of incubation period on diesel oil, SEA 40 and SAE 50 used oils biodegradation

Case of diesel Oil

After 14, 28, 42 and 56 days incubation periods in diesel oil, SAE 40 and SAE 50 supplemented or not with yeast extract, the biodegradation rate obtained are presented in figure 2, 3 and 4.

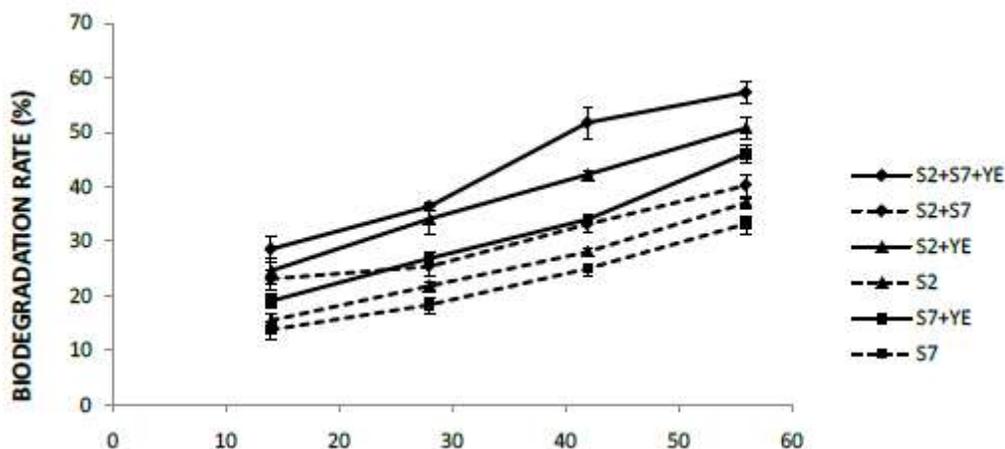


Figure 2. Biodegradation of diesel oil (supplemented or not with yeast extract) by *Acinetobacter* S2 and *Pseudomonas* S7 strains, with regards to incubation period. YE: Yeast Extract.

Case of SEA 40 used Oil

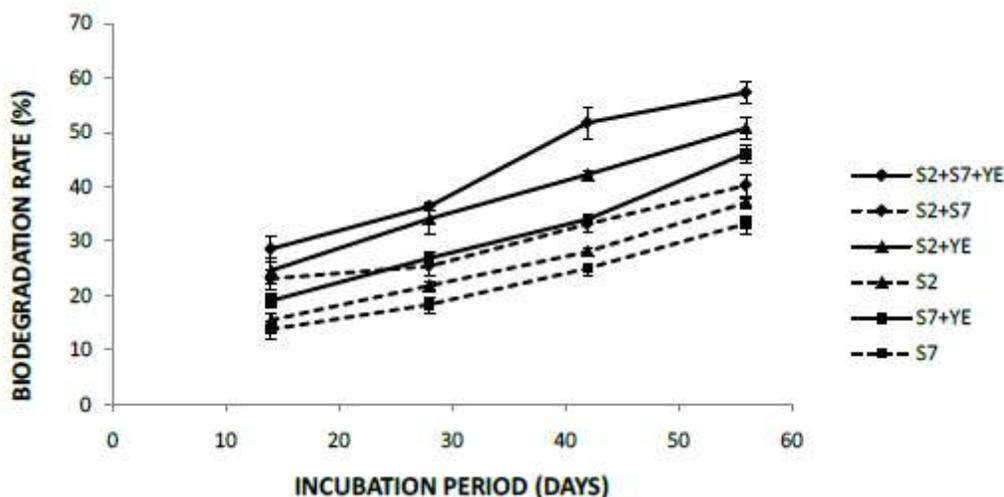


Figure 3. Biodegradation of SAE 40 used oil (supplemented or not with yeast extract) by *Acinetobacter* S2 and *Pseudomonas* S7 strains, with regards to incubation period. YE: Yeast Extract.

Case of SEA 50 used Oil

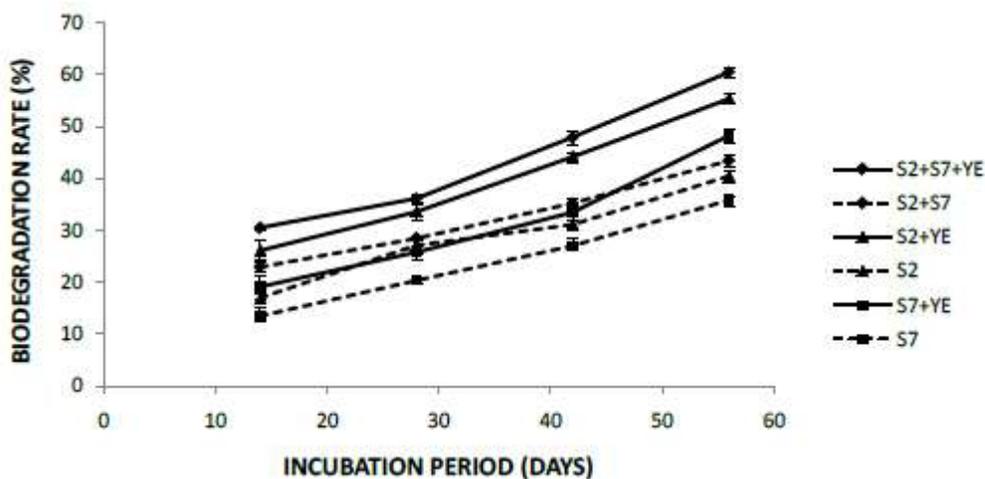


Figure 4. Biodegradation of SAE 50 used oil (supplemented or not with yeast extract) by *Acinetobacter* S2 and *Pseudomonas* S7 strains, with regards to incubation period. YE: Yeast Extract.

Discussion

All the organic nutrient factors (yeast extract and peptone) increased the SAE 50 used oil biodegradation. For all the bacterial strains and substrates, the biodegradation rates recorded in presence of yeast extract are significantly higher compared to those recorded in presence of peptone.

The increase of biodegradation rates in presence of nutrient factors could be explained by the presence of phosphorus and nitrogen in these nutrient factors.

For all the hydrocarbons used in this study, the results obtained after 14 days incubation period showed that tween 80 increases the biodegradation rates of the two used oils (SAE 40 and SAE 50) but not the of diesel oil. According to some authors, surfactant can increase the solubility of certain compounds such as hydrocarbons and by then, can facilitate the access of these compounds to microbial cell. This increase of microbial access to hydrocarbon could explain the increase of biodegradation rates.

According to Chrzanowski *et al.* (2018), surfactant can facilitate hydrocarbons entry in cell walls of microorganisms and then can increase their biodegradation.

The presence of SDS did not increase the hydrocarbons biodegradation because, according to Tiehm (1994), SDS can be used as growth substrate for microorganisms during hydrocarbons biodegradation and then, can lead to reduced hydrocarbons utilization.

The results obtained after different incubation periods showed that the biodegradation rates of the three hydrocarbons used in this study increase regularly with regards to incubation period. This increase of hydrocarbons biodegradation with incubation period is also reported by some authors (Panda *et al.* 2013; Nikhil *et al.* 2013).

For all the strains, the biodegradation rates were higher in presence of yeast extract as compared to those recorded in absence of yeast extract.

In this study, the results also showed that the biodegradation rates obtained with the strains mixture (S2 + S7) are higher than the biodegradation rates recorded with the strains S2 or S7 alone after 14, 28, 42 and 56 days incubation period. This synergy between bacterial strains leading to an increase of hydrocarbons biodegradation could be explained by an additional effect of enzymes present in each bacterial strain (Leahy and Colwell 1990).

Conclusions

This study show that *Acinetobacter* S2 and *Pseudomonas* S7 strains and their association are able to degrade SAE 40/50 used oils and diesel oil after 14 days incubation period, and more efficiently for an extend incubation period. Organic nutrient factors such as yeast extract and peptone are appeared to increase the biodegradation of these hydrocarbons. Moreover, surfactant like tween 80 reveals the capability to enhance the hydrocarbons biodegradation.

Therefore, nutrient factors (yeast extract and peptone) and surfactant (tween 80) can be utilized effectively to reclaim water contaminated with diesel and used oils.

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3.1.18. Geostatistical analyzes of heavy metals in soil of Zaida mine (Hight Moulouya, Morocco).

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Abstract

Geostatistical approach was used to investigate the spatial distribution of heavy metals in the soils around the abandoned mine of Zaida, located at about 30 km NW of Midelt in the Upper Moulouya (Morocco). A total of 51 soil samples were collected at various distances and directions from tailings and analyzed for Cu, Zn, Cd and Pb using Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). Results show that heavy metal contents in investigated soils are significantly higher than those in uncontaminated soils reported by many other authors. The average abundance order of heavy metal levels are Pb>Zn>Cu>Cd. Kriged maps of all studied heavy metals showed that the degree of contamination decreases when the distance from the tailings pounds increases. In addition, soils located in the prevailing wind directions from the mine tailings were enriched in heavy metals.

Keywords: Zaida mine, Heavy metals, Soils, contamination, Kriging

Introduction, scope and main objectives

Soil contamination by heavy metal due to the disposal of industrial and urban wastes is one of the most pressing environmental issues. Mining and associated activities are the main source of heavy metals and can be responsible for significant negative impacts on the surrounding environments. The mining activity in Zaida was abandoned several decades ago. However, those tailing ponds with high levels of heavy metals still remain in the area, which may create environmental risks of geochemical pollution, negatively affecting all components of the environment. As most of these ponds are not covered by vegetation or any other material, wind erode their surface and high amount of material is transported long distances, especially fine particles. The aim of this study is to assess the spatial distribution of lead and Zinc in the soils surroundings the abandoned tailings piles.

Methodology

A total of 51 soil samples were collected around the mine tailings, from a depth of about 0-20 cm (Figure 1). The soils were sampled using a plastic shovel and placed in clean plastic bags and stored at room temperature. Analysis of physico-chemical parameters (pH, electrical conductivity, total calcium, phosphorus, potassium and organic matter) were conducted at the National Institute for

Agricultural Research in Rabat. Total heavy metal concentration (Pb, Zn, Cu and Cd) was determined by ICP-AES (Inductive Coupled Plasma - Atomic Emission Spectroscopy). Samples were analysed at the National Centre for scientific and technical studies of nuclear energy (CNESTEN). The determination of heavy metals spatial distribution was carried out using ordinary Kriging interpolation.

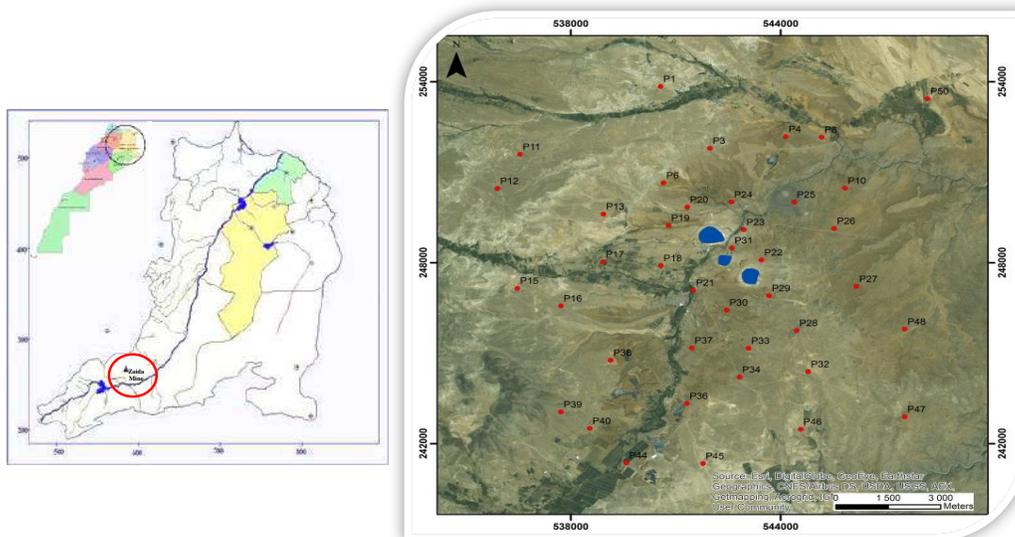


Figure 1. Location of the Zaida mine and distribution of soil samples

Results and discussion

Physico-chemical parameters

Table 1 presents some physico-chemical properties of studied soil samples. The pH value ranged between 7 and 8.6. This alkalinity can be attributed to the presence of carbonates. The electrical conductivity values ranged from 0.10 to 1.43 $\mu\text{S}/\text{cm}$. All the soil samples presented a low organic matter content ranging from 0.3 to 2.66%. The obtained results showed that soils in the mining area of Zaida are calcareous, with values ranging from 0.55 to 77.95%. These calcium concentrations are attributed to the formation lithology of the studied area.

Table 1. Physico-chemical characteristics of soils in Zaida mine

	pH	EC $\mu\text{S}/\text{cm}$.	CaCO ₃ total%	OM %	P mg/kg	K mg/kg
Min	7.00	0.10	0.55	0.30	2.14	146.00
Mean	8.16	0.31	39.04	1.26	19.37	299.62
Max	8.60	1.43	77.95	2.66	197.10	732.04

Heavy metal contents in soil

Levels of heavy metals in soil are shown in table 2. The mean concentrations were 0.99 (mg / kg) for Cd, 14.93 (mg / kg) for Cu, 47.60 (mg / kg) for Zn and 89.81 (mg / kg) for Pb. These contents are relatively high compared to uncontaminated soil standards carried by other authors Baize

(1997), Kabata-Pendias and Pendias (1999), World Health Organisation (WHO) cited by par Parizanganeh *et al.* (2012).

Table 2. Average, minimum and maximum contents (mg / kg) of heavy metals in soil samples

Variable	Mean	Min	Max	Median	SD	Reference values		
						1	2	3
Cd	0.99	0.03	3.0	0.4	1.01	0.05-0.45	-	0.3
Cu	14.93	0.11	77.2	8.98	20.04	2-20	14	4
Zn	47.60	0.13	206.0	49.97	45.76	10-100	62	50
Pb	89.81	0.36	830.95	17.82	162.87	9-50	25	0.2 - 2

- [1] Ordinary soils (Baize, 1997)
- [2] Kabata-Pendias and Pendias, 1999
- [3] OMS (cited by Parizanganeh *et al.*, 2012)

Spatial distribution of heavy metals

- The heavy metal distribution is influenced by two factors: the distance from the tailings dam and the wind dispersion of sand particles;

- The kriged maps showed that the heavy metal contents decrease with increasing distance between the sampled points and tailings residue;

- High levels of heavy metals were founded in the North East, north West and South West direction, which correspond to the prevailing wind directions.

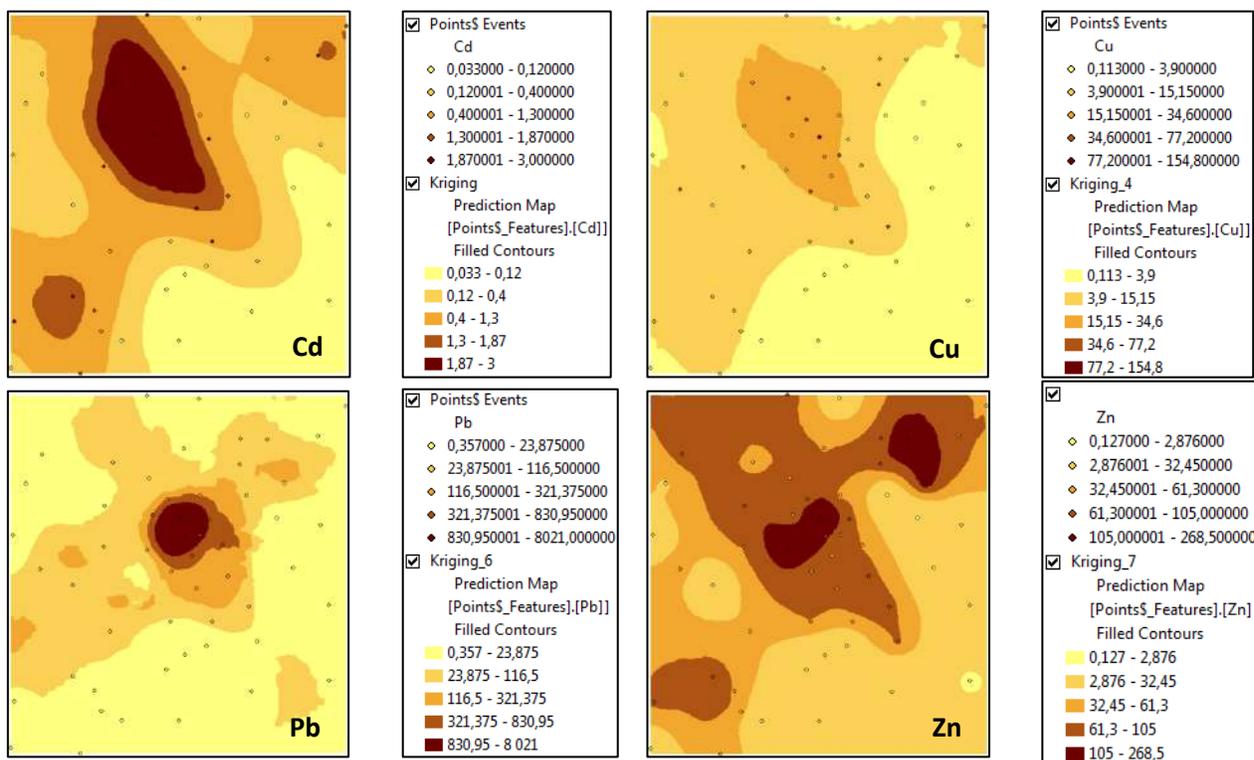


Figure 2. Distribution maps of heavy metals in soils surrounding the tailings piles in Zaida mine

Conclusions

The tailings of Zaida Mine, which were abandoned without any rehabilitation plan, constitute a major source of soil contamination by ETM. The assessment of soil contamination by heavy metals (Cu, Zn, Cd and Pb) shown that soils are affected by polymetallic pollution. Indeed, the soils located near the tailings dam and those in the two main prevailing wind directions in the studied area have relatively high levels compared to the values of uncontaminated soil from the literature. This enrichment by heavy metals can be mainly attributed to the action of the wind on the sand particles.

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3.1.19. State of the art techniques of mapping, monitoring and modeling soil pollution: a case study of German soils

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Abstract

A major threat to ecosystems and human health is the inadequate use of pesticides as part of the agricultural practice. In addition, in many cases agricultural areas are polluted by external influences such as industrial use of chemicals, waste dumps, emissions from traffic or residential areas. At present, the data basis is insufficient to give a concise picture on the global distribution and pathways of pesticides in soils.

A global screening strategy including a database could allow a holistic assessment of previous and preset pesticide applications as the major source of soil pollution (GSP, 2015). From an operational point of view harmonized experimental strategies could allow to compare results or use data of different studies for regional or global models.

In this paper a case study of German soils will be presented to outline the key concepts of POPs monitoring including sampling techniques and evaluation strategies. Some results will be presented spatial distribution patterns of POPs, assessment of fate and also methods to estimate legacy pollution. Finally, some guiding questions - and indications of its relevance - will be

addressed to be considered before any practical start of a soil inventory study. Also a reference will be made to the relevant standardized test guidelines such as the ISO / TC 190 soil quality – sampling procedures and analytical test procedures.

Keywords: monitoring, mapping, standardized methods, global models, pollution

Introduction, scope and main objectives

The issue of the global pesticide use in agriculture and its impact on human rights and its adverse effects on human health, the environment and society has been addressed recently by the report of the special rapporteur on the right to food transmitted to the Human Rights Council of the UN (UN, 2017).

Since more than two decades, POPs are monitored in environmental media and specifically in soils. Whereas harmonized methods for ambient air monitoring such as active and passive samplers or accumulation monitors such as spruce needles, kale, or bulk deposition samplers are used to give an image of the pollution on a short time scale, due to their heterogeneity, their accumulation and long-term storage potential soils ask for more specific and dedicated sampling and analytical methods.

Also, compared to water and air, soil processes act on a long-term scale and therefore accumulation and fate of POPs is less sensitive to environmental influences such as UV-light, temperature variance, and others. On the other hand, accumulation and fate of POPs in soils are largely influenced by the vegetation cover and the land use of (e.g. natural, agricultural, silvicultural soils, housing or industrial area).

POPs have been extensively studied in the atmosphere and atmospheric depositions specifically in urban areas in conjunction with the impact on agricultural or forest soils (Aichner *et al.* 2007, Aichner *et al.* 2013, Desaulles *et al.* 2008, Hafner *et al.* 2005, Holoubek *et al.* 2009, Kraus *et al.* 2000, Maliszewska-Kordybach 2008, Manz *et al.* 2001, Navarro-Ortega *et al.* 2012, Weiss *et al.* 2000). Some of these studies suggest a dependency between POP concentrations and environmental/local parameters, such as altitude, latitude, population density, or soil total organic carbon (TOC). However, in most cases it is difficult to make the proof as the areas studied are relatively small or the data basis is in a statistical sense limited. In addition, direct comparison of published data is often complicated by varying sampling strategies, such as sampled horizons and soil depths, as well as varying target compounds.

Considering this, the question arises if we need a best practice guidance for generating representative, reliable and comparable data from soil monitoring projects. Further, how can these data can be used for verifying past and present releases (inventories), do these data match with other monitoring results or can critical loads be evaluated to secure the health of soils in the future.

Methodology

In a recent inventory in Germany (second forest soil inventory) about 2000 forest sites have been sampled within three years by about 20 different sampling teams following the same standardized operating procedure (SOP) (Wellbrock *et al.* 2006). Each sampling plot is characterized inter alia by soil physics data such as bulk densities, TOC, and pH, types of soil horizons and their thicknesses, and also the soil and humus type, and the type of forest stand (deciduous, coniferous). In a subset of about 450 forest stands the Of/Oh-horizons and mineral soils at two depths (0-5 cm, 5-10 cm) were evaluated for concentrations and spatial distribution of selected

polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs). Sample preparation and combined multiresidue analysis of POPs are described in detail by Lehnik-Habrink *et al.* (2010). Additionally, in a sub-pollution of 76 samples emerging pollutants such as Endosulfan, BFRs, dl-PCBs, Dioxins/Furans were evaluated (Bussian *et al.* 2015, Pandelova *et al.* 2018).

In a complementary survey agricultural soils of about 500 locations were tested on POPs. The main difference is that the sampling was performed for the first mineral soil layers only, namely the upper Ap horizon (0-30 cm plough horizon of arable land), and upper Ah horizon (0-10 cm grassland) (Umweltbundesamt 2015).

Results

The highest abundance for all compounds investigated are found in the humic layers of forest soils followed by the top mineral soil layer of forest stands and the top mineral soil horizons of arable land or grassland (Aichner *et al.* 2013, Aichner *et al.* 2015, Umweltbundesamt 2015). The basic statistics for the humic layers of forest stands are given in Table 1. The concentrations decrease by about a third from the humic layer to the first mineral layer (0-5 cm) and by another third to the subsequent layer (5-10 cm).

The mean concentrations between the top mineral soils at the forest stands and the top plough layers (Ap horizon) of arable land show a ratio of about 3 : 1.

Table 1. Basic statistical parameters (ng/g of dry weight) of measured POP-contents in 447 samples at the forest stands. Σ 16-PAH: PAHs with 2 or 3 aromatic rings (Naph, Ace, Acy, Flou, Phe, Ant). Σ hmPAHs: PAHs, with 4, 5 and 6 aromatic rings without Fla and Pyr (BaA, Chry, BbF, BkF, BaP, IcdP, DahA, BghiP).

	Σ 16-PAH	Σ 16-PAH	Σ Fla+Pyr	Σ hmPAH	Σ 6-PCB	Σ DDx	Dieldrin	HCB
Min	104.6	22.2	22.1	44.4	0.5	0.8	0.0	0.0
50%	1447.9	171.8	361.2	803.2	13.6	31.3	2.7	3.0
Mean	2098.1	353.1	534.2	1210.8	18.2	146.3	2.7	3.7
Max	14889.0	4 424.1	5053.9	8613.4	106.3	4382.7	12.0	23.5

Additional data on Dioxins, Furans, Endosulfan, flame retardants were evaluated and can be found in literature (Bussian 2015 *et al.*, Pandelova *et al.* 2018).

Discussion

In general, POP concentrations in soils show a large inter- but also intra-site variation (Desaules *et al.* 2008, Holoubek *et al.* 2009, Aichner *et al.* 2013, Aichner *et al.* 2015). This makes it difficult to compare data from different sites without knowing the data characterizing these sites.

Average concentrations of POPs in soils are decreasing with depth (Aichner *et al.* 2015), which can be explained by decreasing organic carbon contents. However, in specific situations, this might not be true. Also, some plots show higher concentrations in the lower mineral soil layer compared to the upper organic layer. This can be explained by specific humus types, namely mor, moder, and mull and is expressed by enrichment factors (EF) according Krauss *et al.* 2000.

The spatial pattern of POP concentrations reflects the distribution of major emission sources such as highly industrialized and urbanized areas (e.g. Rhine-Ruhr Metropolitan Region and parts of

eastern Germany in the vicinity to industrial areas and brown coal strip mining with related brown coal fired power plants).

In a case study on Endosulfan (Bussian *et al.* 2015) it could be shown that in German forests the main metabolite Endosulfan sulfate (ESS) is found with up to 100 times higher abundance than the deposited technical product, while the ratio between the isomers α - and β -Endosulfan of the technical product is opposite from the ratio found in soils and shows a clear dependence on the type of forest stands (coniferous vs. deciduous) and humus type.

Conclusions

The organic carbon concentration in soils triggers the abundances of lipophilic organic pollutants while the humus type is an important variable influencing pollutants distribution among depth. In general, the higher the biological activity in the humic topsoil layer the more POPs are metabolized. To assess the pollution concentrations and stocks should be evaluated, which in turn needs a sampling campaign considering the physical properties of soils (thicknesses and densities, TOC) allowing comparison of different areas of soil morphology and different vegetation.

Before starting the experimental work of a soil inventory some guiding questions - and indications of its relevance - should be addressed, e.g.:

- identify the purpose of the study, e.g. (to derive background values or identify hotspots or levels of contamination; accidental or long-term monitoring,
- identify the group of POPs, their chemical properties
- sampling strategies, composite samples versus single samples, sampling by depth and/or by horizons
 - which data on soils physics are needed
 - sampling time, sampling frequency
 - sample pretreatment: drying, sieving, grinding
 - Extraction and separation of analytes, extraction solvent
 - QA/QC

On the other hand, when combining or merging data from different studies it should be severely checked, whether sampling strategies and analytical procedures are comparable. Our results show the need of information about the horizons and / or layers and soil physics data. In addition, it becomes increasingly difficult to compare results of different studies if they apply different sampling strategies or do not report the relevant information. There is no general procedure how to combine data from different sources.

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3.1.20. The development and preliminary assessment of using the biological indicators to evaluate the soil quality under *Miscanthus x giganteus* production at the contaminated abandoned sites

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Abstract

The soil –inhabiting nematode community was analyzed during the first year of vegetation season at the contaminated and control (not contaminated) plots established at former military location at the Eastern parts of Ukraine. The soil was chernozem stretch with thickness of the humus. Site was contaminated by heavy metals: Zn, As, Cd, Pb, Mn, Fe and Sr. Nematodes were recovered from the soil rhizosphere and morphological identified to genus and species by microscope analysis. Results showed that first year of growing *M.x giganteus* at polluted and control sites at the did not impact significantly the density and taxonomic diversity of the organisms; same time the taxonomic diversity of nematodes identified at the polluted sites tended to be reduced. The population density of all trophic groups at the contaminated plot was significantly lower compared to control. Results showed that having nematodes rather sensitive to soil pollution that groups of soil organisms sound perspective for evaluation the soil quality change in long- term cultivation of *M. x giganteus* at the slightly contaminated military sites.

Keywords: heavy metals, M.x giganteus, soil health, nematodes biological indicators, community structure

Introduction, scope and main objectives

Soils in Ukraine are very diverse. However, two-third of agricultural soils are chernozems that occupy 10,5 mln. ha. In the country representing bread basket of the former Soviet Union, a large portion of agricultural land was poorly managed and resulted in soil erosion which is considered as a biggest contributing to soil degradation factors. There are 13 forms of Soil degradation types in the country. Humus and nutrition level loss share the highest (43%) degradation level of the total area. Ukrainian soil is characterized by preferably medium (2-3%) and high (3-4%) humus content. The process of losing humus is continuing for the last 130 years. The highest ratio 22% of humus lost compared to original concentration observed in Forest-Steppe zone followed by 19.5% in the Steppe zone and 19% in the Forest Zone in Ukraine. Humus and correspondently soil organic matter (SOM) in major soil types are in range of 100-700 t/ha. According to preliminary estimation, the SOC stock in agricultural soil is about 7 Mt. Soil organic matter (SOM) is the key indicator of soil quality and health. Numerous researches indicated that the long-term use of tillage practices strongly effected the amount and quality of SOM. (Rise& Owensby, 2001; Pendel at al.). Over the last 120 years the key patterns in land use is land abandonment and cultivation of energy crops for using its biomass to produce first generation biofuels for the export. Currently, there is an emerging commercial production of energy crops for second generation biofuels. Soil natural carbon (SOC) changes related the increasing of second generation energy crops energy crops are fundamental to the open deliberation on bioenergy and their potential carbon storage. The main second generation energy crop's area currently occupy 1000 ha. (Fig.1). However, taking in account that percentage of bioenergy use in total energy consumption increase by 35 % annually, the main area under energy crops, including marginal/unutilized land will be significantly extending. Results of long- term researches provided in Europe indicated that development and distribution of energy crops, particularly perennial grasses improved soil quality, increased carbon sequestration and benefit biodiversity. In Ukraine the majority of studies were focused at agronomic aspects and feasibility of growing energy crops: perennial grasses and short rotation predominately at the Forestry-Steppe zone. No reliable data exist on the affect of energy crops biomass production to soil quality enchantment and consequences for the carbon budget from land change associated with this.

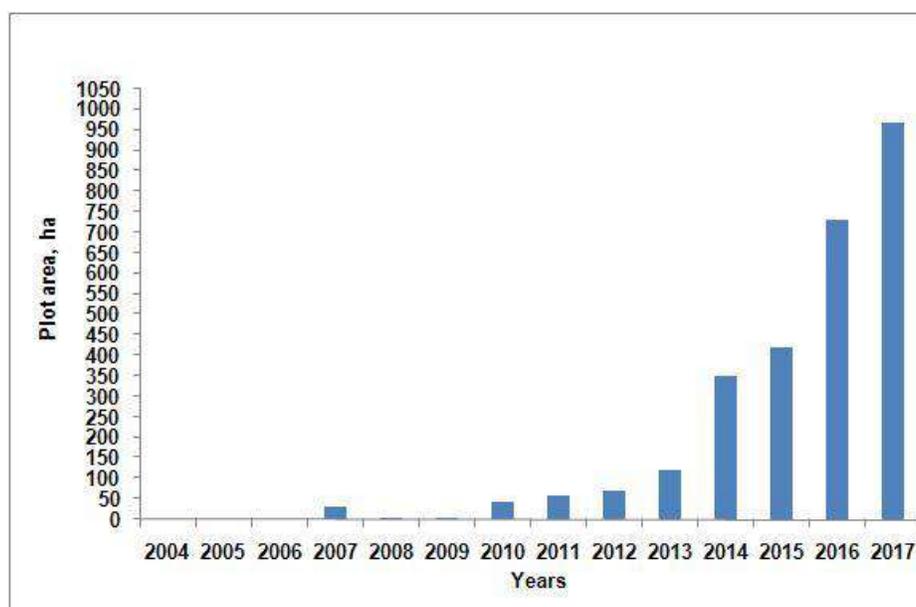


Figure 1. Main area under *M. x gignateus* cultivation in Ukraine.

The long-term study of biomass production of energy crop *M. x giganteus* at military contaminated site in Ukraine, Czech Republic and USA in the frame of supported by NATO SPS project has been conducting since 2016 year. Our preliminary results indicated that *M. x giganteus* is a suitable for the phytostabilization energy crop and has a high potential as biomass feedstock for bio-based products production at abandoned :marginal/unutilized, slightly contaminated by heavy metals land. Removing of heavy metals by phytoremediation do not always guaranty restoring soil capacity to function according to its potential. The success of soil restoration is very much depending on phytoremediation agent. Using *M. x giganteus* perennial, C-4 carbon fixation, high productive grass as remediation agent may help to improve contaminated by heavy metals soil quality and stability. Sustainable management of soil and quality improvement requires soil health monitoring. To evaluate soil quality using analysis of food web is technically infeasible. Alternatively, is possible to use biological soil quality indicators. The reliable soil quality indicators should match the following criteria (Wang&Hooks, 2011):

- Sensitivity to variations in disturbing activity
- Correlation with soil functions
- Usefulness for explaining environmental processes
- Comprehensibility and usefulness for land management tactics
- Cost- effectiveness

To monitor changing of soil quality at polluted by heavy metals sites the several indicators may be used, including: plant cover diversity, availability of nitrogen, abundance, diversity, community structure and activity of microbes, collembolan and mites' richness and soil nematodes trophic groups structure /colonizer- persistence classes. The nematode representing the group of soil micro-fauna which assemblage and trophic structure response rapidly to any soil broadly define disturbance (Sanchez-Moreno at al, 2009). They have several characteristics that settle on them the reliable and cost- effective and most promising biological indicators ([Achazi, 2002](#)). Analysis of the nematode community (assemblage and feeding groups) over time assess the impact of land use and management practices, biotic an abiotic stress and soil quality (Fig.2.)

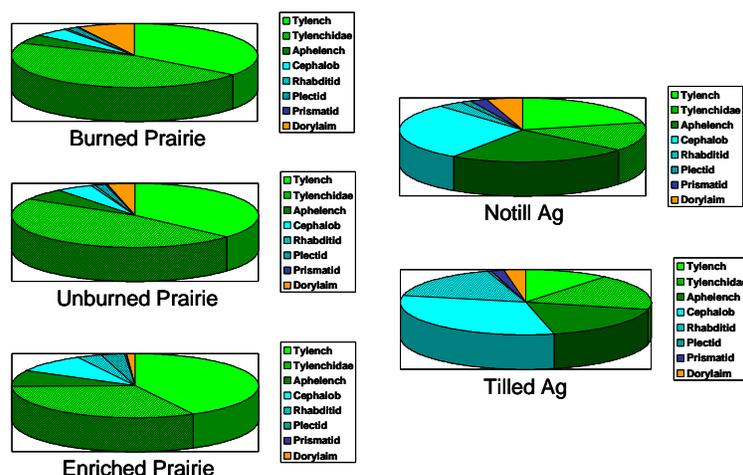


Figure 2. Impact of the land change to nematode community

Nematodes showed sensitivity and usefulness as bioindicators and of ecosystem recovery following traffic disturbance (Althoff et al., 2009). Several studies were done to show the sensitivity of nematode community structure to heavy metals appeared from industry, waste management, traffic or other sources on nematode and trophic structure in disturbed agricultural and natural ecosystems and urban ecosystems (Georgieva, 2002; Shukarov et al., 2006; Li Qi et al., 2006; Zing, 2007; Suschuk et al., 2008; Mcgrath, 2002; Šalamún, 2012). The researches of Park et al., 2016 confirmed the reliability of soil nematodes as indicators of soil ecosystem health in contaminated by heavy metals mining sites. Only a few studies are available about the success of using soil nematodes as indicator soil recovering using plants as remediation agents. Sevin et al., 2015 showed the change of the nematode community structure in response to the ecosystem rehabilitation during phytotechnology with Bermuda grass and rye-grass 69 months. No data is available on using nematode community response while growing with *Miscanthus x giganteus* for recovering of polluted soil although there has been an increasing interest to use this energy crop for remediation with biomass production for biofuels and biobased products. (Pidlisnyuk et al., 2014)

In 2016- 2017 the study was performed to assess the response of the nematode community while growing *M. x giganteus* at the Kurakhovo (Longitude:47.96786; Latitude:37.26700), (North-Easter part of Ukraine) military site at chernozem stretch with thickness of the humus. This study was design as long term and it is continuing.

Methodology

Research soils were tested for content of metals using Rentgen-fluorescence analyzer Expert 3L.EN 15309:2007.

The total contamination index Z_c was calculated using the following formula:

$$Z_c = \sum_{i=1}^n K_c - (n-1)$$

where: K_c a-ratio indicating the correlation of chemical element concentration in the soil to its maximum permitted level; n -number of elements considered in the analysis.

Nematodes were sampled from soil rhizosphere at a depth of 40 cm at contaminated/non-contaminated soil. Each sampling was done in four replications Nematodes were recovered using Biermann's funnel, sieving techniques. The isolated nematodes were morphological identified to genus and species by microscope analysis. Some species were identified with PCR to conform the correctness of morphometrical identification.

Results

Site was contaminated by heavy metals: Zn, As, Cd, Pb, Mn, Fe and Sr. The contaminated was very patchy. The contamination was distributed not uniformly. In some localities its total concentration exceed MPL.

Overall 40 nematode genera of soil inhabiting nematodes were identified. (Skwierch et al., 2017). Nematodes isolated from the contaminated/control plots were assigned to five ecological groups. It was observed that the nematodes from all trophic groups were more abundant at the control in comparison with the contaminated site. Taxa appeared less frequently in the contaminated site than in the control site (Table 1). The dominated taxa at the level of genera and species was Plant

parasitic nematodes in control/contaminated plots. This is in agreement with results obtained by Suschuk *et al.* (2008) who illustrated that plant parasitic nematodes were a dominated trophic group for industrially contaminated soil, polluted by heavy metals. The results of the current research concerning bacterivores showed the lower taxonomic diversity at the contaminated site.. However, the most abundant group was Fungivores followed by Bacteriovores and Plant parasitic. It indicated that bacterivores were sensitive to total heavy metals contamination The less represented was Omnivores and Predators. Interpretation of nematode community analysis allowed us to conclude that food web in studied military site is dominated by fungivores and we may expect slow nutrient cycle. Domination of fungivores and bactaeriovores is commonly observed in disturbed environments. The low population of omnivores and predators those occupy the highest position in a food web and very sensitive to disturbance indicates that the soil have a very low capacity to suppress soil-born pathogens and nematodes plant feeders.

Results showed that growing of *M. x giganteus* during the six month of first year vegetation at contaminated and control plots did not impact significantly the abundance and taxonomic diversity of nematodes. At the same time taxonomic diversity of nematodes from the contaminated plot tends to be reduced. 19 genera were found at the polluted site versus 40 units found at the control one. In respect of richness, the plant parasitic nematodes appeared to be the dominant group of nematodes at both: polluted and unpolluted sites.

The research is continuing and it will be focused at calculation of nematode diversity indexes, selecting the most sensitive to soil pollution nematode taxa, influence of the duration of miscanthus growing to nematode community structure.

Table 1. Soil nematode trophic structure, Kurakhove research site, 2017

Trophic groups		Contaminated		Control			Contaminated		Control	
		Sp.	Genus	Sp.	Genus		Sp.	Genus	Sp.	Genus
Plant Parasitic	With planting of <i>Miscanthus x giganteus</i>	10	Bitylenchus Trichodorus Paratrichodoru s Paratylenchus Pratilenchus Merlinus Rptylenchus	16	Trichodorus Paratrihodoru s Longiddorus Paralongidoru s Xiphinema Pratylenchus Paratylenchus Rotylenchus Criconemoides Mezocricinem a Bitylenchus Saurtylenchus	Without planting of <i>Miscanthus x giganteus</i>	9	Bitylenchus Trichodorus Paratrichodor us Paratylenchus Pratilenchus Merlinus Rptylenchus	18	Trichodorus Paratrihodoru s Longiddorus Paralongidoru s Xiphinema Pratylenchus Paratylenchus Rotylenchus Criconemoides Mezocricinem a Bitylenchus Saurtylenchus
Bacterivores		3	Rabditis Cephalobus Anaplectus	5	Cilyndrolaime s Cephalobus Anaplectus Plectus		3	Cilyndrolaime s Cephalobus Anaplectus	5	Cilyndrolaime s Cephalobus Anaplectus Plectus
Fungivores		8	Aphelenchus Aphelenhoides Dytilenchus Coslenchus	8	Aphelenchus Aphelenhoides Dytilenchus Felenchus Tylenchus Tylencholaimu s		9	Aphelenchus Aphelenhoides Dytilenchus Coslenchus		Aphelenchus Aphelenhoide s Dytilenchus Felenchus Tylenchus Tylencholaim us

Predators	3	Anatohous Momomchus Mylonchulus	8	Anatohous Clarcus Mylonchulus Pyonchulus	3	Anatohous Momomchus Mylonchulus	8	Anatohous Clarcus Mylonchulus Pyonchulus
Omnivores	3	Dyscolaimus Allodorylaimus	2	Discolaimus Allodorylaimu s	2	Discolaimus Allodorylaimu s	4	Discolaimus Allodorylaimu s

Conclusions

Nematodes in polluted plot is characterized by high total nematode density, low taxonomic richness, dominant of certain taxa in trophic group composition. Having nematodes community rather sensitive to soil pollution that groups of soil organisms sound perspective for evaluation the soil quality change in long-term cultivation of *M. x giganteus* at the slightly contaminated military sites.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.21. Identification of soils pollution points based on set of surface curvature

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Abstract

The organization of monitoring in most countries involves the activities of a number of organizations, and therefore minimizing the costs of its implementation by introducing the latest methods of sampling in contaminated zones or soils or other natural formations due to man-made substances is an urgent and necessary task. Soils are the interface of interaction between all the geospheres and flows of matter and energy and are constantly under anthropogenic pressure. Soils, at the same time, are one of the most critical and irreplaceable natural resources, therefore, permanently observing in the conditions of technogenic impacts is vitally necessary. That is what determined the choice of the object of research. Knowing the location of points of concentrated accumulation, one can establish approximate schemes for the distribution of solid particles and salts, in order to predict the trajectories of all types of pollutants movement. This will allow more accurate and reliable sampling. Particularly relevant is the use of such an approach in sites with a weakly defined relief, where the site of pollutants is not visually determined. We have proposed a method for determining the sampling points based on set of surface curvature. This technique includes calculating the plan and vertical curvature of the topographic surface, normalizing their values to a scale of 0-100 score; the separation of accumulation zones from the dissipation area and the final calculation of accumulative curvature. The main result of our proposed method is a cartographic model that clearly indicates the all sites of the pollution. Local accumulative zones, where it is expedient to sample set, are well detects in areas with relatively poorly defined relief.

Keywords: monitoring, control point, GRASS GIS, geomorphological analysis, curvature, DEM.

Introduction, scope and main objectives

The ecological safety of the countries is an integral part of their national security. Therefore, the existing or projected ecological situation in the state should ensure the health of the population, the solution of social and economic issues without degradation of the environmental components. Among the latter, special attention is required to the soil, the pollution of which directly determines the quality of water, air and human health. Modern technologies provide a number of opportunities for the creation of synthetic cards and their implementation in automated monitoring programs. Accordingly, the prediction of the effects of human activities and the use of

such forecasts are playing an important role in the state policy of environment monitoring in general and the soil cover in particular. Modern monitoring, especially ground-based, can be established on a number of models of motion of water streams and sediment, or on the use of the notion of surface curvature. The use of GIS for their calculation and further adaptation for monitoring purposes greatly increases its efficiency.

Proceeding from the importance of the correct choice of monitoring parameters, periodicity of environmental observations, the selection of relevant with respect to the accumulation of pollutant points for spatial monitoring is one of the most important moments during its implementation. The objective existence of areas of environmental tension, in particular in the areas of accidents, as well as in areas of dangerous natural phenomena, require crisis eco-monitoring, that is, intensive observation of natural objects, first of all soils, and sources of pollution.

Organization of monitoring in most countries involves the actions of a number of actors, and therefore need minimizing the costs of conducting it, either by introducing the latest methods of sampling in contaminated zones or in the soil, or other natural formations due to man-made substances, that is an urgent and necessary task. Soils are the interface of interaction between all the geospheres and flows of matter and energy between them, resulting they are constantly under anthropogenic pressure. Soils, at the same time, are one of the most important limited and irreplaceable natural resources, the observation of which, in the conditions of man-made impacts, is vital. That is what determined the choice of the research object.

Knowing the location of concentrated accumulation points, one can establish approximate schemes for the distribution of solid particles and salts, in order to predict the trajectories of all types of pollutants movement. This will allow more accurate and reliable sampling. Particularly relevant is the use of such an approach on sites with a weakly defined relief, where the site of pollutants localization is not visually determined.

This is especially important in modern Europe, where identified contaminated areas consist around 342 thousand sites, of which Municipal and industrial wastes contribute 38% most to soil contamination, followed by the industrial/commercial sector approximately 34%. Very significant share in soil contamination (around 60%) make a contribution Mineral oil and heavy metals, which are the main contaminants contributing (Panagos *et al.*, 2013). At the same time, we did not mention a large number of soil contamination by agrochemicals during intensive agricultural production.

In the organization of soil monitoring, apart the frequency of sampling data, using of standard analytical techniques has a certain consistency. However, the general problem of thorough monitoring, regardless of its type, is the choice of the minimum number of control points that will be sample for analytical procedures. Due to the uneven distribution of environmental pollution, the creation of a grid of sampling points depend on innovative methods (as opposed to the classical way by roses of the winds, regular grid or sector-segment sampling schemes) and gaining importance. Thus, the main objective of the article is the development and testing of a method for the specific identification of possible concentrations of pollutants based on the analysis of the digital elevation model.

In modern time some geomorphologists studied field-specific forms of relief Earth from point of view features of system "land surface + gravitational field" (Krcho, 1990; Evans and Minár, 2011). From four classes of morphometric variables and concepts greatest interest are those that determine the two main accumulation mechanisms: plan and profile curvatures. The first accumulation mechanism reflects surface flows convergence (Shary *et al.*, 2002). It was proven

(Shary, 1995) that divergence of flow lines equals the plan curvature of a surface (kp). This is the basis for quantitative description of the first accumulation mechanism. The second accumulation mechanism, as was proven by Shary (1995) is the derivative of gradient factor by flow line length and is the vertical (or profile) curvature kv . So, the second accumulation mechanism acts on profile-concave slopes, where $kv < 0$, and can be described by a map of kv (similarly kp). Hence, flow lines converge where $kp < 0$ (convergence areas) and diverge where $kv > 0$ (divergence areas). Unlike the first type of accumulation, the second type shows that flow decelerates where $kv < 0$ (relative deceleration areas) and accelerates where $kv > 0$ (relative acceleration areas). How does summarize the two main types of accumulation? Shary (1995) proposes to use accumulation curvature (Ka). Ka is a product of vertical and horizontal curvatures and equal $Ka = kp \cdot kv$. The classical theory states that the accumulation curvature is a nonnegative variable and the unit of Ka is m^{-2} . As we will show below, when calculating monitoring points, this calculation algorithm needs to be modified somewhat.

Methodology

Data processing has carried out by us using one of the most powerful and accessible software tools available to a wide range of scientists – GIS GRASS (GRASS Development Team, 2017). This software is distributed under the terms of the General Public License and allows the `r.mapcalc` module to calculate the entire spectrum of bitmaps in accordance with Shapiro and Westervelt (1992), including various types of curvature.

As part of the project, was selected a fragment of the territory of Ukraine (Fig.1a) within the limits of the Glybotsky district of the Chernivtsi region (Fig. 1b), confined to the Prut-Siret interflux (Cross-Border region) with contrasting geomorphological conditions (Fig. 1c). This area (4200x4200 m) has different administrative subordination and economic use, and at its choice were solved typical problems that often occur in Ukraine in works of this nature (Cherlinka and Dmytruk, 2014; Cherlinka, 2015; Cherlinka, 2017). The project coordinate system was set to SC 1963 (zone X2), scanned sheet of topographic map M 1:10000 – M-35-136-G-b-2 (Fig. 1d) was georectified using the created vector mathematical framework in GIS Quantum (QGIS Development Team, 2015) and digitized using Easy Trace (EasyTrace group, 2015). Digital elevation model was build using regularized spline with tension (Mitášová and Mitáš, 1993) with a spatial resolution of 10 m/pixel (Fig. 1d). The analysis of digital elevation model in GIS GRASS (GRASS Development Team, 2017) has identified a number of such local morphometric variables, as plan (or horizontal) (Fig. 2a) and vertical (or profile) (Fig. 2d) curvatures.

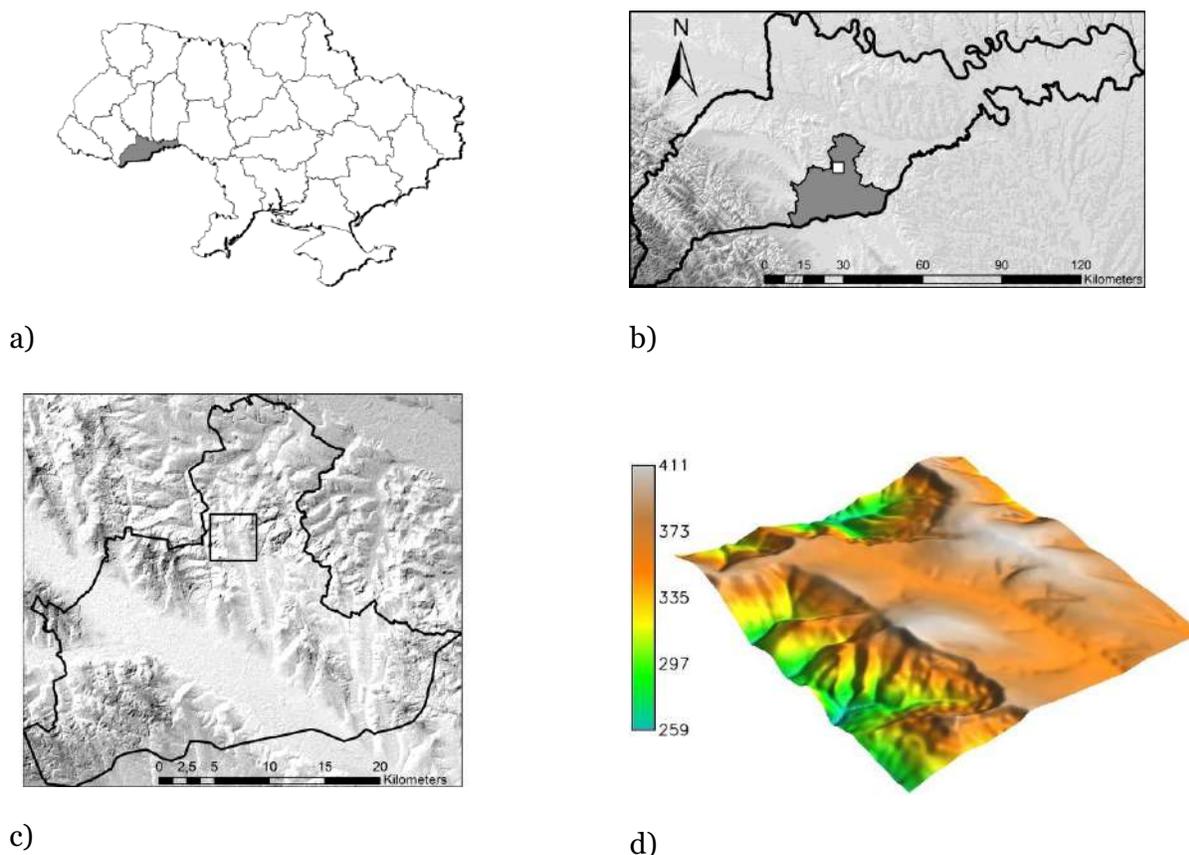
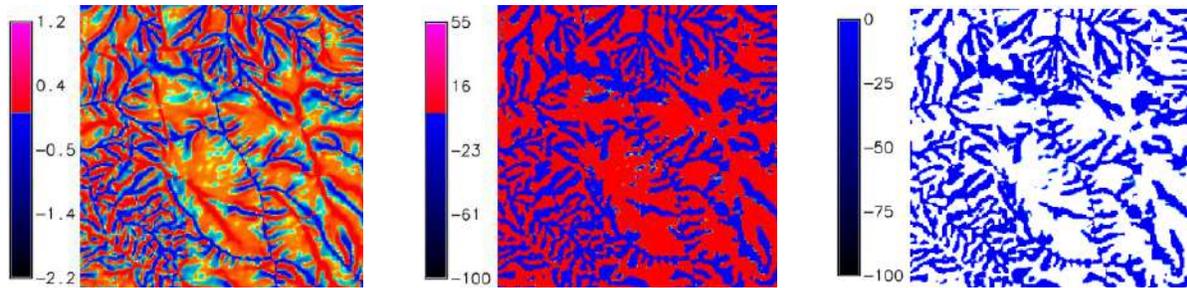


Figure 1. The geographical location of the region studies in Ukraine (a), Chernivtsi region (b), Glybotsky district (c) and digital elevation models (d) * SRTM data is used for the background – NASA’s Shuttle Radar Topography Mission

However, the variation between these plan and vertical curvatures is very large. For example, for plan curvature, the values vary from 1.2 to -2.2, and for profile curvature from 0.0014 to -0.017. Since we tried to take into account both types of accumulation to the same extent, we carried out the normalization of their values to a scale of 0-100 scores. This only applies to their negative values. Aligned results show that the accumulation zones clearly stand out on the map of the plan (Fig. 2b) and vertical curvature (Fig. 2e).

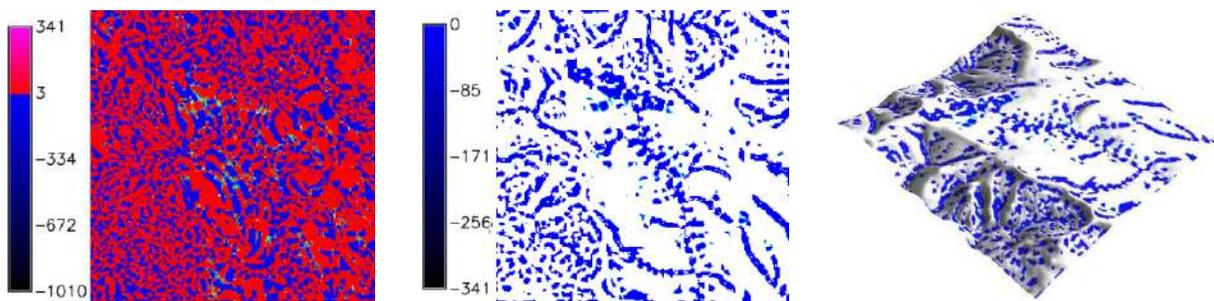
As noted above, we used accumulative curvature of the surface for a more accurate selection of monitoring sites. However, its classical definition by Shary (1995) has led to results that we rate as negative (Fig. 3a). Why is this so? The point is that when multiplying the positive and negative values of both curvatures, they become negative. When we get the product of negative values, its positive value coincides with the product of the areas where scattering takes place. This we can visualize in the form of a small matrix:

$$\begin{array}{rcccc}
 \mathbf{kp} & \cdot & \mathbf{kv} & = & \mathbf{ka} \\
 +1 & \cdot & +1 & = & +1 \\
 +1 & \cdot & -1 & = & -1 \\
 -1 & \cdot & +1 & = & -1 \\
 -1 & \cdot & -1 & = & +1
 \end{array}$$



a) b) c) d) e) f)

Figure 2. Distribution horizontal and vertical curvature of test area: *kh* original (a), *kh* normalized (b), *kh* cleaned (c); *kv* original (d), *kv* normalized (e), *kv* cleaned (f)



a) b) c)

Figure 3. Cumulative curvature: with an error in the formula (a), according to our calculations option (b) and three-dimensional representations *ka* on terrain (c)

As we see, a direct computation of this formula for yields results that do not allow separating the accumulation zones from divergence zones and only confusing. Therefore, we only separated the

accumulation zone for both curvatures (Fig. 2c, f) using *r.mapcalc* (Shapiro and Westervelt, 1992) and only then received the expected results, that is, the accumulation zones that coincide for both curvatures (Fig. 3b). It is combination of type's accumulation that allows us to choose the most characteristic spatial localization of pollutants (Fig. 3c).

Results

The main result of our proposed method is a cartographic model that clearly indicates the sites of the pollutant concentration. Locally accumulative zones, where it is advisable to sample (Fig. 3c), are well detected in areas with relatively poorly defined relief. Consequently, the map was created to clearly depict the confinement of pollution zones and accumulation of toxic substances in the research area to specific relief sites. This solution is well scalable and can be using for any territory.

Discussion

Based on the analysis, we believe that there is still some potential for improving the quality of the allocation of control pollution points, in particular using a full set of local morphometric variables. Considering that soils are a global biospheric filter and differ in their qualitative characteristics, among the directions of future investigations will be the study of the interconnections between all types of surface curvature and types of soils that are distributed on this surface.

Taking into account the fact that the quarter of Ukraine's territory are not covered by soil surveys, the filling of gaps with forecast data (Cherlinka, 2017) with attraction as predictors of various curvatures has interesting prospects.

The positive effect of the simulation is the possibility of establishing monitoring points depend on the analysis of the digital model of the relief. Of course, this does not rule out the possibility of using other ways to build a sampling scheme. The proposed method allows adapting it for many applications of monitoring in soil science, agronomy, land management and land tenure, etc.

Conclusions

We have proposed a method for determining the sampling points based on accumulative curvature. This technique includes calculating the plan and vertical curvature of the topographic surface, normalizing their values to a scale of 0-100 scores; the separation of accumulation zones from the zones of dissipation and the final calculation of accumulative curvature. Obtained models with the detected maximum concentration of pollutants expand the possibilities of environmental monitoring, assist in determining the rate of distribution of pollutants and identify the natural barriers that may accumulate toxicants. Our proposed models contribute to the correct determination of points for control in the development of appropriate monitoring programs. Our studies also confirm the effectiveness of using GRASS GIS in similar procedures, especially for the needs of geomorphological analysis.

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3.1.22. Embedding sustainability in contaminated site management. Practical experiences and case studies

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Abstract

This paper describes a practical approach for embedding sustainability into contaminated site management that draws on UK (SuRF UK), European (NICOLE) and international (ISO) guidance. In this approach sustainability is integrated with existing site practice and begins by assessing and developing a robust conceptual site model, evaluating whether remediation is needed or whether the scope of the remediation can be mitigated through land use changes or additional site specific risk assessment. Where remediation is required then the objectives are to ensure that the optimal solution is selected through consideration of relevant environmental, social and economic indicators and that the remediation is procured, implemented and managed in a way to ensure that the benefits are fully realised through the lifecycle of the project.

Our experience to date suggests the early incorporation of sustainability has a significant positive benefit in the context of the overall project life cycle. Examples of how sustainable remediation principles have been incorporated into contaminated site management at a number of sites in the UK are presented and identify the key drivers in implementation. A critical interpretation of the benefits of the approach and the potential conflicts and tensions that may exist between the selection of the most sustainable approach and traditional technology selection is made.

Keywords: [Up to eight keywords can be added here.]

Introduction, scope and main objectives

In common with other countries the UK has seen significant interest in the subject of sustainable remediation. It is seen as complementary to existing legislation for the management of contaminated land (DEFRA, 2012) and consideration of sustainability is embedded in soils policy (DEFRA, 2009) and practical guidance for determining the nature of remedial options (Environment Agency, 2012). Guidance on the implementation of sustainable remediation has been developed both by SuRF UK (CL:AIRE, 2010), for Europe as a whole by NICOLE (NICOLE, 2010) and more recently an international standard has been published (ISO, 2017). The latter defines sustainable remediation as “elimination and/or control of unacceptable risks in a safe and timely manner whilst optimising the environmental, social and economic value of the work”(ISO,2017). Common to each of these documents is an emphasis on establishing principles and overarching frameworks for applying sustainable remediation in projects. The SuRF UK document emphasises that sustainability should be considered at the planning stage or land use stage before remedial objectives have been finalised (Stage A) as well as at the time of remedial options appraisal when the remedial objectives have been set (Stage B). A summary of this approach is illustrated in Figure 1.

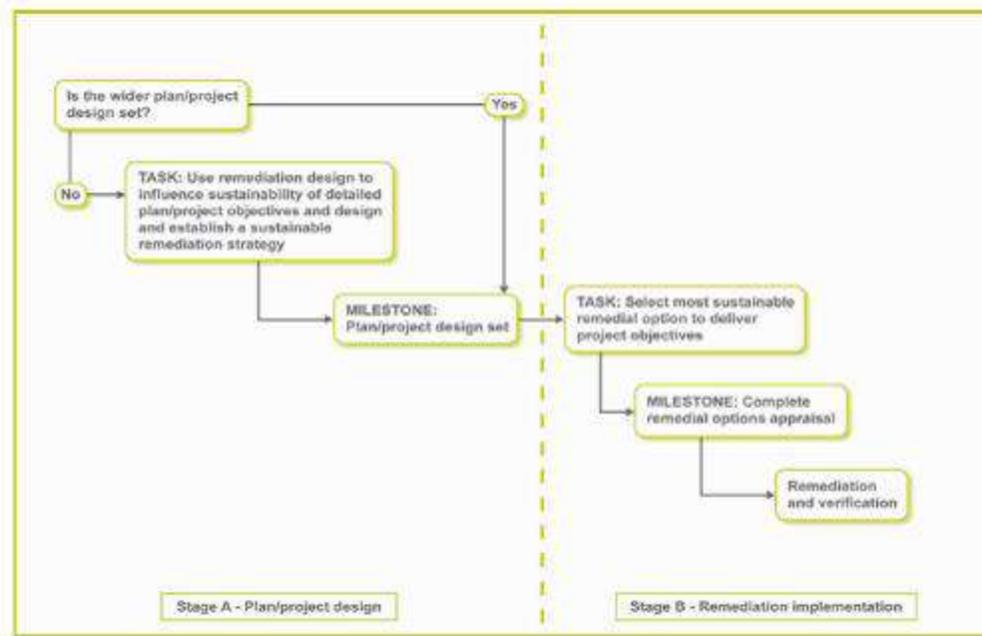


Figure 1. SuRF UK framework two stage approach (SuRF UK 2010)

The underlying rationale for this is that greater sustainability benefits can be gained by considering sustainability early in the project lifecycle before the final project design is set.

Using these principles and reflecting available guidance we have developed practical framework that integrates these stages and objectives with our own commitment to embed sustainability in our practice. The resulting framework that integrates sustainability through the typical stages and lifecycle of a project is illustrated in Figure 2.

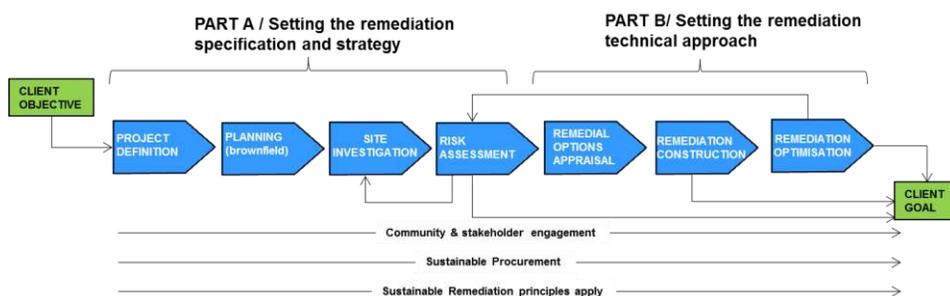


Figure 2. Integrated sustainable site investigation and remediation

Key Features

As indicated above this approach seeks to integrate the SuRF UK and NICOLE guidance with key stages in the lifecycle of a project in a similar way to the SURF US framework (Holland *et al.*, 2012) and so embed sustainability through our practice. The key features of this approach are:

- Sustainability is seen as central to and integral to the meeting the client objective and is not an “add on”;

- In the “Stage A” equivalent as well as including problem definition and planning it emphasises the importance of project definition, site investigation and risk assessment as key stages in underpinning a sustainable solution. A robust conceptual site model and a detailed site specific assessment of risks being central to defining the need for and objectives of any subsequent remediation;

- When remediation is to be undertaken then emphasis is not on remedial options appraisal alone, but consideration of sustainability is carried through construction and optimisation of the selected alternative; and

- In common with published frameworks it is flexible, iterative and tiered and efforts can be tailored to given site, scale and complexity of project. For existing sites or projects then the framework can be retrospectively applied to any stage in particular to operational systems.

Results

For the purposes of this paper three practical examples of the application of the framework at different stages in the life cycle are illustrated in Table 1. The three examples have been chosen to illustrate “non-typical” considerations of sustainability at the site investigation stage (Case study A), at the risk assessment stage (Case study B) and in optimisation of an existing system (Case study C) rather than at the remedial options appraisal stage. In each case the focus was on definition of the underlying problem such that the need and scope for remediation could be more accurately defined (and from a stakeholder perspective be better communicated), whilst at the same time a contribution to the overall sustainability of the project was made through the adoption of appropriate Sustainable Management Practices (SMPs). In one case (Case study A) the sustainability metrics were quantified using Life Cycle Analysis (with a focus on environmental metrics including green house gas emissions (GHG) emissions, water usage and waste) but in the other two case studies financial metrics were quantified but broader environmental and social benefits were qualitatively described consistent with the tiered application of the framework.

Table 1. Example Case Studies

Site	Problem	Approach	Outcome	Sustainability Benefits		
				Environmental	Social	Economic
Case Study A Manufacturing Site, Halifax, UK	Former 8ha manufacturing site contaminated with chlorinated solvents in fractured bedrock, previous consultant incurred investigation costs of £1m and had estimated remedial costs of £10m	ERM used a variety High Resolution Site Characterisation (HRSC) techniques to characterise the site, develop a revised understanding of the conceptual site model and refine the risk assessment	The focus on ensuring that the remediation was based on a sound understanding of the site conceptual model and site specific risks changed the nature and objectives of the remedial strategy, enabling consideration of alternative more appropriate solutions	Investigation generated a smaller environmental footprint compared to undertaking the same scope of works using conventional approaches. The resulting conceptual site model significantly refined the volumes of soil and groundwater to be treated and so had a significant influence on the scope of the full scale works.	There was no local community or stakeholders other than the site and regulatory authorities. Fewer mobilisations and less time was spent on site reduced health and safety risks .	The additional investigation and remedial solution were delivered for <£2.5m a significant saving over that anticipated at outset.
Case Study B Former Petrochemical Works, Wales, UK	Former Petrochemical works with a number of known areas of significant hydrocarbon impacts. The objective was to undertake source removal to demonstrate that natural attenuation could occur within a strict timeframe of one year for agreement of this objective with regulators	Innovative approach coupling risk evaluation and assessment of geochemistry with molecular biological techniques including: analysis and enumeration of hydrocarbon degrading genes at the site; and use of 13C benzene labelled bio-traps in subsurface.	Natural attenuation was proven and regulatory agreement was obtained to required schedule.	Smaller environmental footprint compared to undertaking the same scope of works using conventional long term monitoring. The amount of active source reduction required was minimised from an anticipated 40,000m ³ to 25,000m ³ .	Excavation, handling and treatment of contaminated soils was a significant challenge given the proximity of neighbours down gradient. The requirement for less active remediation resulted in a significant reduction in the duration of the works and in potential for short term noise and odour impacts	The reduced volume of soil requiring treatment resulted in a significant economic saving to the project.
Case Study C Engineering Site, Portsmouth, UK	Aero-engineering site located in an industrial area. Site only 100m from an estuary site of ecological interest and located on 4-6m of clay and silt drift confining the Chalk Aquifer. Pump & Treat system in place to protect receptor but no clear end point and operations and maintenance costs increasing.	ERM was appointed to develop a closure strategy for the site. The strategy included regulatory liaison, fractured bedrock investigation, production of detailed conceptual site model and risk assessment.	The additional works updated the conceptual site model and proved no linkage between the source and receptor. As a result it was agreed with the regulators that pump & treat operations should cease and the plant was decommissioned.	Cessation of pump & treat operations and associated environmental footprint was a significant result that had a significant effect on the environmental footprint both from energy use and associated travel for operation and maintenance	No significant social benefits as site was operational and stakeholder involvement limited to regulators. Health and safety risks associated with travel to site and maintenance operations eliminated.	Achieved both considerable cost reductions for the Client and agreed a site closure strategy with the regulators.

Discussion

Overall in our experience the application of the framework and incorporation of sustainability in projects has resulted in a number of benefits and has also raised a number of issues:

- There is more explicit recognition of sustainability in the overall process and the clear definition of sustainability goals at the outset of the project gives a clear focus and rationale. This has generally been welcomed by both clients and other stakeholders;
- The process is consistent with the UK regulatory framework and has facilitated discussions with stakeholders. In some cases however regulator acknowledgement of the role of sustainability in decision making remains variable, with a perception in some cases that sustainability is another argument to do nothing;
- The focus on the overall cycle of the project has resulted in greater sustainability benefits than focussing at the remedial options appraisal stage alone and has encouraged increased focus on high quality site investigation and risk assessment activities and this is our view underpins a sustainable approach. Nevertheless the development of a robust conceptual site model and detailed assessment of risks can involve a significant investment and it remains difficult to sell this in context of typical practice despite proven overall economic benefits;
- In some instances even where site specific risk assessment indicates the absence of significant risks other drivers such as reputational risks or potential long term liabilities can still mean that active remediation is warranted. The emphasis then is on selecting and optimising the remedial system with the greatest net benefit. This is a site specific evaluation and in our experience short term high energy approaches can compare favourably to those that are more often perceived as being 'green';
- Qualitative appraisal is a feature of the SuRF UK approach and does have a significant role to play in sustainability assessment. However caution is required as site specific factors can mean that qualitative judgements based on experience are not always representative of site circumstances and quantitative appraisal that is transparent with respect to the assumptions made may be more defensible.
- Overall the process has resulted in benefits to the business (lower cost/ quicker remediation close out) as well as contributing to broader sustainability goals.

Conclusions

The introduction of sustainable remediation is in many respects the natural evolution of risk based contaminated land management where the requirement to manage unacceptable risks is now considered holistically such that the remediation itself delivers an overall net benefit and these principles have been embraced in the UK. In addition by incorporating sustainability principles in a framework that encompasses the whole life cycle of a project the benefits may be broader with an increased emphasis on defining the need for remediation through high quality robust site investigation and risk assessment that ultimately may eliminate or more clearly focus the requirement for remediation. Our experience to date is that this can be a valuable process both in terms of business and sustainability gains particularly at complex sites. Further case studies, and examples are required to encourage the development and integration of sustainable remediation in normal practice.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.1.23. Soil pollution in Iran. Current situation and potential biomonitoring and bioremediation solutions

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Abstract

Soil is the habitat of huge number of organisms and provides the basic resource which our food production is relied on. However, this issue is not considered appropriately and while there is huge concern on air and water pollution, soil contamination is a topic that is not even considered on the international soil day. According to the statistics, a small percentage of industrial and municipal wastewater is treated in Iran, and most of the domestic and industrial wastewater is discharged into the environment without treatment. This results in soil and groundwater contamination, including the increase of nitrate concentration in the wells, and soil salinization. Landfills are another dilemma, and the lack of proper sanitary landfills and proper methods of waste disposal is one of the major causes of soil pollution. The mine and industrial activities are other sources of pollution in Iran. Setting up and submitting a soil bill to the parliament by the Environmental Protection

Agency (EPA) is one step which has been taken in order to overwhelm the current status of soil contamination. In this paper several investigations conducted in the University of Tehran to determine metal concentrations of soils, and its living organisms are summarized. The purpose was to identify the situation of metal pollution in soils, and subsequently discover appropriate compartments of the ecosystem for biomonitoring and bioremediation purposes.

Keywords: soil pollution, Iran, metal

Introduction, scope and main objectives

Soil pollution by chemicals has been one of the major environmental concerns, especially with its role in feeding people. Among the pollutants, heavy metals are known to be of high concern even in low concentrations due to their non-degradability and physiological effects on living organisms. Metals are introduced into the soil in a variety of ways, such as precipitation, the use of chemical and animal fertilizers, compost, sewage sludge and pesticides.

In contrast, absorption by plants and other types of bioremediation and self-purification determine the extent of their extinction from the system. Regardless of atmospheric precipitation, the amount of inputs of elements to agricultural lands depends on agricultural management, while the extraction of elements from the ecosystem is further controlled by soil properties. Unlike the differences in the behavior of heavy metals in terms of mobility and their absorption capacity in soil, the input is usually higher than the output.

The process of accumulation of heavy elements in soil is very slow and its effects can be detected after decades. In addition to natural processes, soils can be contaminated by elements that are released from human resources in the environment (anthropogenic activities). These elements can be accumulated in plants and animals (bioconcentration and biomagnification) and eventually transmitted to the human body through food chain (biomagnification). Swallowing, breathing and skin contact are the most important ways in which humans are exposed to heavy elements. By definition (Hamidian, 2014), Bioconcentration is defined as an increase of the pollutant concentrations from the environment to the organisms (measured as BC Factor), and bioaccumulation is an increase in the concentration of pollutant during the growth, and by increasing the age of the organisms (showed by BAF); while an increase of the pollutant concentration through higher levels of a food chain is defined as biomagnification (calculated as BMF).

The anthropogenic effects of the activities such as mining, landfilling, waste, excessive use of chemical fertilizers, pesticides, soil erosion, forestry, and land-use change include serious risks to health and well-being of human being and the environment. Therefore, it is necessary to increase the level of knowledge and recognition of such threats caused by the disruption of earth and soil systems in order to reduce destructive effects and improve human health.

Methodology

The study areas were selected based upon expert judgment and observation by considering the geography and topography of various areas. Soil samples were collected from the surface parts of the soil, i.e. rhizosphere (around roots) at an approximate depth of 5-30 cm. Plant samples were collected as a whole sample (with roots and shoots). Samples were then transferred to the laboratory and air-dried. Fig. 1 displays the provinces, where the samples have been collected. Some physico-chemical properties of the soils were also measured including soil texture, calcium carbonate concentration, pH and EC.

To determine the total concentration of elements in soil and plant samples, the samples were dried, weighed, and then ashed. Soil samples were air-dried and passed through a 2 mm sieve. ISO 11466 method was used as the source for sample preparation. A volume of 3.5 ml of nitric acid and 10.5 ml of hydrochloric acid (aqua regia method; ratio 1:3) were added to 1 g of each sample and kept in laboratory temperature for 16 hours. Afterwards, the liquid was placed for 2 hours in an oven at 130°C and passed through whatman filter paper grade 42. The volume was increased to 50 ml with nitric acid 1% (Solá *et al.*, 2004). The blank samples were prepared for the batch of each 25 samples. The concentrations of elements were measured using ICP-OES (VARIAN, 725-ES) device. In order to determine the absorbable concentration of the elements in soil samples, 40 ml of DTPA (diethylenetriaminepentaacetic acid) was poured into 20 gr of air-dried soil. The liquid was shaken for 2 hours at 170 rpm, and the resulting liquid was passed through whatman filter paper grade 42 (Lindsay and Norvell, 1978). The chemical experiments were conducted at the pollution laboratory of the University of Tehran.

Results and discussion

Yazd province

Pollution of agricultural lands is a widespread problem in mine regions. The transport of the pollutants through the food chain, causes their accumulation in tissues of plants and animals which endangers their health. In a study the concentrations of heavy metals (lead, copper, zinc and manganese) in soil and plant samples of different rural and natural areas around a copper mine were measured. The concentrations of metals in the Persian Jird of this area were also measured, which is published elsewhere (Khazaei *et al.*, 2015). As the study area is located in copper deposit and as in the previous studies zinc sulfide was found in the area (National Iranian Copper Industries Company 2011), the high concentration of Cu and Zn in the area is justified. The road from Yazd to Shiraz can justify part of the Cu concentration of the samples as the road passes by near the villages. Another reason for the uptake of Pb by the environment is the vehicles and transportation activities (Bech *et al.*, 2012).

Two important factors in transferring the pollutants are the prevailing winds (north to south) and the watershed slope, which makes the transfer of pollution from the mining area to other villages. In a study by Rodríguez *et al.* (2009), wind is the most important factor in transfer of the pollutants.

Given that Darreh Zereshk village is located in the major parts of the mining area and due to the critical amounts of Cu, Pb, and Zn, farming is not recommended in this area. Since the Pb mine is being established in the region and concentration of Cu, Pb, and Zn is also critical, it is necessary that, besides exploitation of these deposits, all terms and activities to be also considered to better improve environmental standards. Given that the current soil pH in the area is alkaline, by controlling the pH and by preventing its loss, the risk of dissolution of elements can be decreased. Because Darreh Zereshk will become a major mining area, the preservation of the surrounding environment with an emphasis on pollution control and prevention is necessary. Table 1 presents the concentrations of metals in soils of the study area, while the average absorbable concentration of elements in the villages is illustrated in Figure 1.

The concentration of heavy metals in soil, wheat and alfalfa of the region were significantly different. The highest concentrations of Cu, Pb and Zn were 71.2, 434.1 and 332.9 mg kg⁻¹ dw, respectively; and their lowest soil concentrations were 17.4, 36.1 and 72.4 mg kg⁻¹ dw, respectively. The highest concentrations of metals were found in roots of the plants, with roots of wheat having 58.6, 156.7 and 125.4 mg kg⁻¹ dw of Cu, Pb and Zn, respectively. The highest concentrations of Cu, Pb and Zn in the roots of alfalfa were 36.6, 30.3 and 57.1 mg kg⁻¹ dw, respectively (Chitsaz *et al.*, 2016; 2013 1,2).

Table 1. Mean of total concentration of elements in soil samples and their normal limit and critical concentration in soil mg kg⁻¹dw

	Cu	Pb	Zn	Mn	Fe	As	Ni	Cr	N
Study area	71.2 ±6.59 ^a	434.1 ±48.36 ^a	332.9 ±54.99 ^a	448.1 ±8.17 ^a	18639.6 ±759.52 ^a	107.8 ±17.23 ^a	28.1 ±1.55 ^b	26.1 ±1.26 ^b	6
* Normal range	2-250	2-300	1-900	20-10000	-	0.1-40	2-750	5-1500	-
*Critical concentration	60-125	100-400	70-400	1500-3000	-	20-50	100	75-100	-

*Alloway (1995)

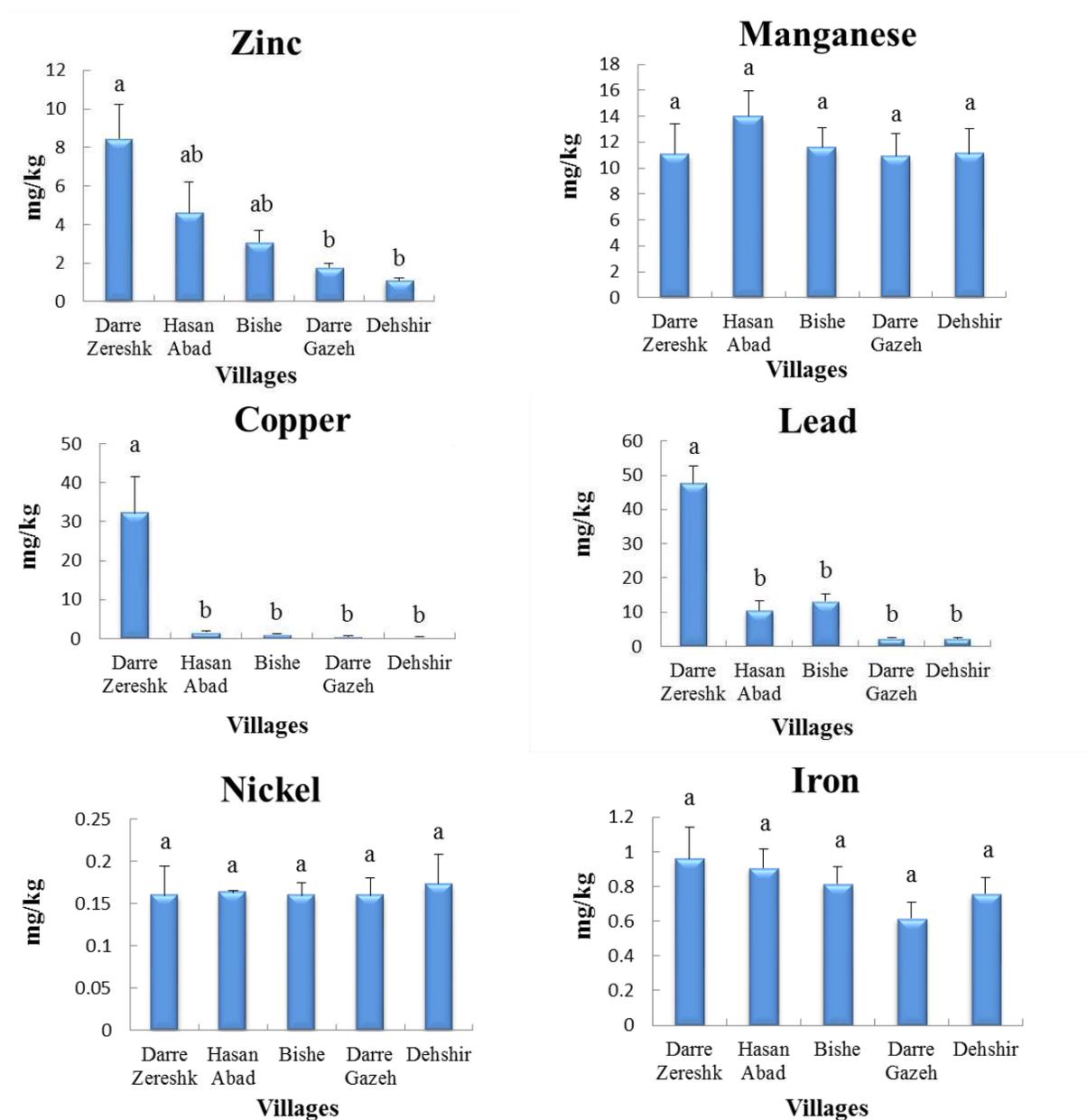


Figure 1. Mean of absorbable concentration of elements in the villages

The other objective of this study was to determine concentration of heavy metals including Cu, Pb, Zn, As, Mn, Cr, Ni, V, Mo, Fe, Al and Si in natural soil and plant species *Artemisia sp.* and *Astragalus sp.* in the surrounding rangelands of Darreh Zereshk copper mine. Therefore, the study area was divided into 10 sections based on factors such as distance and orientation relative to mine, prevailing wind direction and etc. 10 samples of each species were taken from each region using random sampling method. In addition, six soil samples of surface horizon and rhizosphere area were taken in each region. Based on the results, there were significance differences between metal concentrations in all regions. According to the results of Factor analysis, Cu, Pb, Zn, As and Mn were in a same group. Changes in concentrations of this metals relative to other elements in the region was perceptible and was higher in the mine and parallel and adjacent areas to it. Perhaps the most important reason for such result is the location of mine region on the principal deposit of copper mine. In addition, part of the concentration could be due to the ongoing initial activities in the mine and adjacent areas.

Much lower concentrations of metals were observed in the native rangeland plants of the area. The concentrations of Cu, Pb, Zn, As and Mn in the roots of *Artemisia sp.* were 9.20, 1.65, 22.30, 6.50 and 43.63 and in the roots of *Astragalus sp.* were 4.35, 1.35, 12.94, 3.45 and 32.82 mg kg⁻¹ dw, respectively. The soils of the rangelands contained much lower concentrations of metals comparing to the agricultural soils, with concentrations of 38.17, 46.44, 113.76, 25.13 and 631.61 mg kg⁻¹ dw of Cu, Pb, Zn, As and Mn, respectively (Dalvand *et al.*, 2016 1,2; 2015; 2014)).

Zanjan Province

A number of 46 industrial units are active in the zinc industrial zone of Zanjan city. Due to toxic and hazardous waste, these industries are the main source of heavy metal release in the environment. The concentrations of Pb, Cd and Zn in the soils samples collected from the areas around the industrial town were 163, 5.4 and 1710 mg kg⁻¹, respectively. Comparing to the average concentrations of these metals in the global soil, the average concentrations of Pb and Cd were 8 and 18 times higher than the global average. The absorbable concentrations of Pb, Cd and Zn were 15, 0.89 and 15 mg kg⁻¹, respectively. The calculations showed these concentrations are due to anthropogenic activities rather than having natural reasons. The high absorbable concentrations of these elements in the region is also alarming.

We also studied the potential of natural compartments of the surrounding ecosystems for monitoring and purification of these pollutants. One method of removing heavy metals from the environment is biosorption. One aim was to identify the fungi which are adapted with zinc industries wastes and have a high potential for lead and cadmium removal. Samples of sediment which contaminated by zinc industries wastes were collected during spring and fall seasons, then by using the MIC, minimum inhibitory concentration, tolerance of fungi for lead and cadmium were determined. Two isolated funguses, *Aspergillus fumigatus* PZ and *A. fumigatus* BZ with the maximum growth and metals resistance were selected. Isolates sorption capacity against the concentration of lead and cadmium ions, pH, contact time and the presence of surfactants were investigated, the obtained solutions were measured by Atomic Absorption system and the data obtained from experimental results were matched with kinetic and isotherm models. By using commercial toolbox Prism 6.1 and Minitab 17.1 the figures were developed. Average absorption capacity of samples and obtained data from kinetic and isotherm adsorption models, were performed with the Excel software and linear regression analysis. The fungal strain which was compatible with zinc wastes was identified as *A.fumigatus*. The sorption capacity by live biomasses shows 53.75 mg g⁻¹ for lead and 7.02 mg g⁻¹ for cadmium and the optimum pH for high sorption capacity was 6. The use of polymeric surfactant at a concentration of 2% volume and pH 5 can increase the sorption removal efficiency up to 21.4%. The autumn isolated fungi showed perfect compatibility with the pseudo-second kinetic model of lead ion adsorption with 0.999 correlation

coefficient and also comply with the Langmuir isotherm absorption model with correlation coefficient of 0.997. Adsorption mechanism of Pb^{2+} and Cd^{2+} on *Aspergillus fumigatus* showed a FTIR results that functional groups CH_2 , $C=O$, CH , (OH^-) , $N-H$ in biomass of this fungus is an important factor for binding of lead and cadmium ions. Therefore, it is suggested that fungus could be used both for monitoring and the removal of metals from the polluted soils (Khamesi *et al.*, 2016 1,2,3).

In another effort in order to investigate responses of oribatid mite's communities to metal (Zn, Cu and Cd) contamination of grasslands nearby a Pb and Zn smelting plant in Zanjan soil samples were collected from different sites in different distances from the industrial plant. The industrial Zanjan plant was recognized as the major source of Zn and Cd contamination in the region. The mean bioavailable concentrations of metals were decreased with the increasing distance from the plant. No relationship could be found between metal pollution and total density of oribatids. However, the species richness, the Shannon diversity index and Pielou's evenness were lowest in the sites polluted by Zn and Cd. Species diversity was significantly negatively correlated with Zn and Cd, but not with Cu concentrations. *Oribatula (Zygoribatula) connexa connexa* Berlese 1904, was a dominant species at all sites and its dominance was the highest (38%) at the most polluted sites located very close to the smelting plant. Overall, the results showed that oribatid mite's communities display a great variety of responses to metals, depending on the species. Therefore, the presence of certain species could be used as an indicator of metal pollution in soils. As an example Figure 2 shows the relationship between bioavailable concentrations of Zn ($mg\ kg^{-1}$) and Shannon species diversity index of oribatid mites in stations around the Zanjan smelting plant.

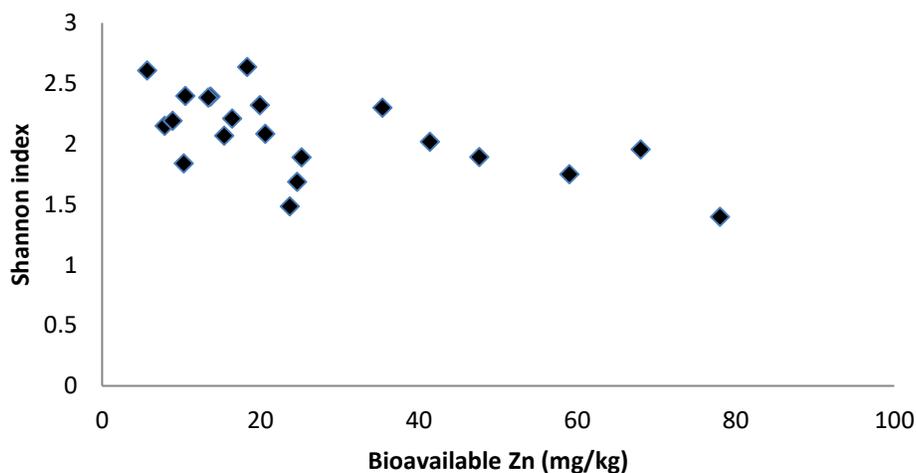


Figure 2. The relationship between bioavailable concentrations of Zn ($mg\ kg^{-1}$) and Shannon species diversity index of oribatid mites

The concentrations of the metals were also measured in the textures of *Oribatula (Zygoribatula) connexa connexa*. In order to do so, because of very low mass of the samples 50 individuals of the species were specified, separated and mixed in order to prepare one single sample. While the highest Zn concentration was related to the most polluted site (153 comparing to the lowest $29.3\ \mu g\ g^{-1}$), the highest Cu concentration was related to the lowest polluted site (35.3 comparing to the lowest concentration of $14.7\ \mu g\ g^{-1}$). This needs to be further investigated through the ecotoxicological studies (Keshavarz Jamshidian, 2015).

Alborz Province

A source of soil pollution in this province is Halgheh Darreh landfill. We conducted a research in order to determine the concentrations of two metals Ni and Pb in soils and three plant species *Artemisia sieberi*, *Salsola orientalis* and *Halimocnemis pilifera*. Three 50*50 m plots in the direction of the prevailing wind were selected. First plot was close to the leachate ponds and the next two plots were located at 500 and 1000 m from the first plot, respectively. Ten random samples from root and shoot of the plants and also from the soil were collected. The results revealed that the soil of the different plots do not have a significant difference in Ni and Pb concentrations. No significant difference was observed between the metal concentrations in roots and shoots of *Artemisia sieberi* and *Salsola orientalis*, however there was a significant difference observed in Ni in *H. pilifera*. The plants in the second and third plots showed to have the highest concentration of Pb and Ni, respectively. Bioconcentration and transmission factors for Ni and Pb, suggested that *H. pilifera* and *A. sieberi* are appropriate plants to remove Pb from soil. The concentrations of Ni and Pb in soils of different plots are presented in Table 2.

Table 2. The concentrations of metals (Ni and Pb) in soils around Halgheh Darreh Landfill (mg kg⁻¹dw)

Plot No.	Ni				Pb			
	SD	Average	min	Max	SD	Average	min	Max
1	0.46	14.4	13.8	15.2	2.31	6.53	2.58	9.70
2	2.13	16.3	13.1	19.5	2.49	6.25	2.46	10.4
3	4.19	17.6	12.7	24.9	2.20	4.86	0.89	8.79

According to the results, *H. pilifera* had the highest concentrations for Pb in its roots and shoots, comparing to the other two species. The concentrations of Ni did not show any significant difference between the three species. Calculated BCF values showed that except *S. orientalis*, the concentration of metals in underground (root) tissues was higher than that of the soil (BCF>1). Thus, for the two species *H. pilifera* and *A. sieberi*, this factor is greater than 1, which might be a good indicator to suggest these species for soil phytoremediation. Transmission Factor (TF) is used to determine the transfer of accumulated metal to the aerial part of the plant (shoots). The species other than *H. pilifera* had a minimum accumulation of Pb and Ni in their shoots, but in the *H. pilifera* species, the TF value for Pb was higher than 1. This TF shows how to manage the species after accumulating the contaminants from the soil (Panahi *et al.*, 2016; 2013).

In another attempts in Alborz Province, we studied the concentration of Pb (an indicator of metal pollution in air) along one of the most crowded highways of Iran. Tehran-Karaj highway connects two states (Tehran and Al-Borz). The purpose of the current study was to assess the impacts of this highway on the surrounding environment by using analytical methods. The sampling stations are distributed along the highway. The assessment procedure was based on measuring lead concentrations in soils and plants of these stations. The samples were collected from different distances from the highway (0-10-20-50-100-200 and 300 m), which was also covered by different land-uses. By increasing the distance from the highway the mean of Pb concentration was significantly decreased. The average, and Max Pb concentration along the highway were 115.22 and 302 mg kg⁻¹, respectively. The Pb concentrations in plant species varied between 1.53 to 11.3 mg Kg⁻¹. The concentrations were significantly higher in stations closer to Tehran, rather than in those close to Karaj in Alborz Province. The mathematical models showed the Pb levels in soils and plants is a good indicator of metal pollution and subsequently air pollution in this area (Nur Istanbuly, 2017).

Tehran Province

As mentioned in the previous section, the metal concentrations in Tehran is much higher than those of Alborz Province (Nur Istanbuly, 2017). All soils around Tehran are contaminated. Even if the best water used for the irrigation of agricultural lands around the city, the people's food will be still unhealthy due to excessive use of pesticides, excessive amount of fertilizers and soil pollutants. Pollution caused by oil spill from oil pipelines in southern Tehran has been reported as a major cause of soil pollution in Tehran. The use of agricultural pesticides in the province of Tehran is mentioned as another source of soil pollution. Acid rain, due to the heavy air pollution in Tehran, is another factor contaminating the soil. At least seven major sources of soil contamination in Tehran are involved: small and large polluting industries dispersed around Tehran, the existence of old oil and gas arches and their storage tanks, very old fuel supply sites, two oil refineries in Tehran, Kahrizak landfill, the agricultural lands in southern Tehran and the acid rain. The two oil refineries in Tehran have contaminated an area of 4-5 thousand hectares of southern Tehran lands with oil. The refinery has not only polluted the soil, but also the wells of this area with petroleum and its derivatives. The Kahrizak landfill covering an area of 800 hectares has contaminated the soil to a depth of 100 meters, and caused the most severe case of soil pollution in Tehran. This landfill has also contaminated the wells of the area to a radius of 4 kilometers. Agricultural lands of southern Tehran are land plots with an area of 2 to 4 thousand hectares that are irrigated with the creek of Firoozabad. The high concentrations of metals in this creek and the irrigation of agricultural products with this water causes the accumulation of metals in agricultural products of the southern Tehran and their entry into the food of citizens.

The concentrations of lead and nickel in this area, where the agricultural products are harvested, is up to 8 and 4 times of the limit, respectively.

Mazandaran Province

Concentration of Pb, V and Cd were measured in 4 soil samples and 20 plant samples of two species: *Alopecurus myosuroides* and *Rumex crispus*. This is a region which is polluted with high levels of radioactive contaminants including radon and radium and currently we are investigating the effects of radioactivity on gene destruction in two native snake and worm species. Our former studies showed that the concentrations of both Cd and V were high but still below the critical concentrations for plant species. There were no significant correlation between the concentrations of rhizosphere soils and the plant tissues (Figures 3 and 4). The average concentrations of Cd in *Alopecurus myosuroides* and *Rumex crispus* were 1.48 and 1.34 $\mu\text{g g}^{-1}\text{dw}$, respectively, which is much lower than the critical concentrations for plants (5-30 $\mu\text{g g}^{-1}\text{dw}$) and comparable with the natural concentrations of this element in soil (0.1-2.4 $\mu\text{g g}^{-1}\text{dw}$). It was similar to the concentrations of V, which was lower than the critical concentrations (AliTaleshi *et al.*, 2012).

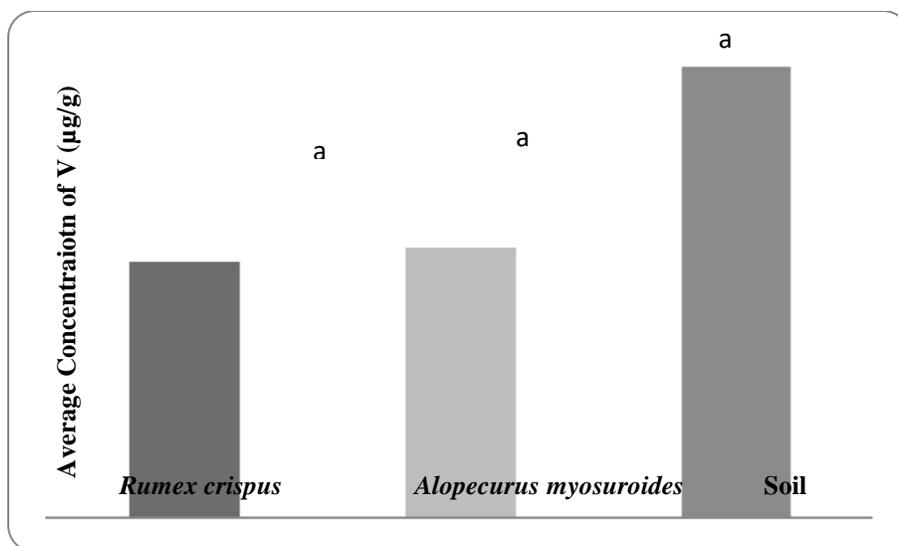


Figure 3. Average concentrations of V for soil and plant species, the similar “a” for each column shows there is no significant difference between the compartments based on Duncan test

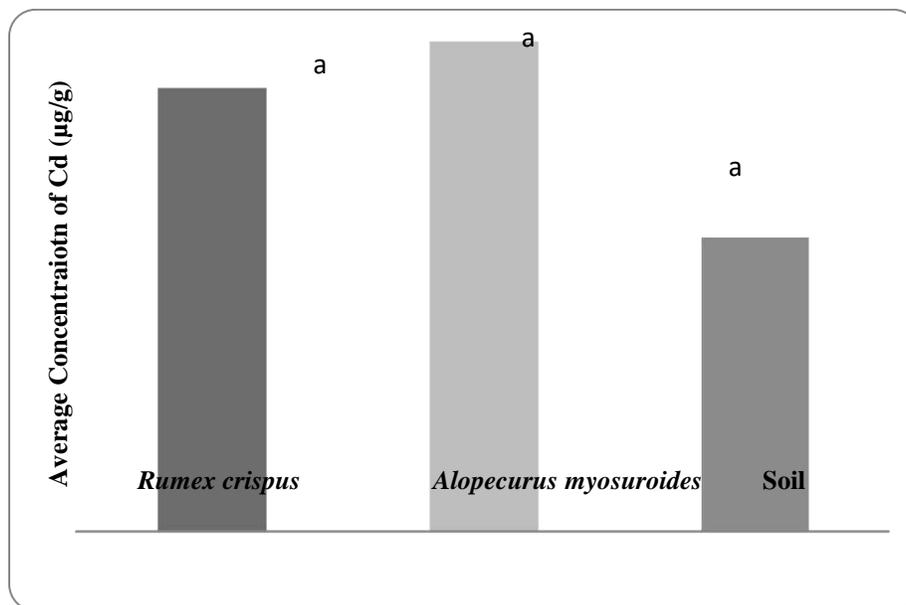


Figure 4. Average concentrations of Cd for soil and plant species, the similar “a” for each column shows there is no significant difference between the compartments based on Duncan test

Conclusions

Significant variances in soil pollution in Iran were observed in different provinces, soil types and soil organisms. There is a great potential to use the natural compartments of soil ecosystem to monitor its metal pollution and more importantly use them as a bioremediation technique, which is part of the soil self-purification mechanism.

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3.1.24. Applying nuclear techniques to assess the sources and transport of antibiotics from intensive agricultural areas to the environment through soil and water

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Abstract

Antimicrobials play a critical role in the treatment of diseases of farm animals (aquatic and terrestrial) and plants. Their use is essential to food security, human well-being, and animal welfare. However, the misuse of these drugs, associated with the emergence and spread of antimicrobial-resistant micro-organisms, places everyone at significant risk. Substantial amounts of antibiotic-resistant bacteria are present in agricultural soil which may spread into the food chain. However, little is known about how AMR is moving from agricultural areas to the environment through two major vectors: soil and water, and the diagnostic tools required to monitor its movements. Existing conventional monitoring and mass balance approaches are not sufficient to identify and apportioning AMR movement in soil and water. The Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture of the International Atomic Energy Agency and the Land and Water Division (CBL) of the Food and Agriculture Organization is currently working to develop protocols and guidelines using nuclear and isotopic techniques to assess the sources and transport of antibiotic-resistant bacteria in agricultural soils which may spread into the food chain and further to develop mitigation tools to manage the risk posed by AMR in the environment.

Keywords: antibiotics, antimicrobial resistance (AMR), nuclear techniques, soil, water

Introduction, scope and main objectives

The release into the environment of antimicrobial compounds in effluents (households, hospitals and pharmaceutical facilities and in agricultural run-off), combined with direct contact between natural bacterial communities and discharged resistant bacteria, is driving bacterial evolution and the emergence of more resistant strains. Increasing global antimicrobial resistance (AMR) is a major threat to human and animal health, and biodiversity. Studies on the sources and transport of antibiotics from intensive agricultural areas to the environment through soil and water and the potential impact on the food chain has received less attention. This paper focusses on the role of soil and water as the two major vectors where AMR moves from agroecosystems to the environment, and explores the state-of-the-art tools (nuclear and multi-isotopic techniques) for more efficient and accurate assessments of the sources and transport of antibiotics in the environment, that will assist FAO (and WHO) to develop mitigation tools to manage the risks posed by AMR.

Methodology

Standard Operating Procedure (SOP) guidelines that provide step-by-step instructions on how to collect and prepare soil and water samples from intensive agricultural areas and preserve for stable isotopes analysis will be developed. This includes the (1) the delta carbon ($\delta^{13}\text{C}$ and delta chloride ($\delta^{37}\text{Cl}$) during microbial oxidation, (2) the application of compound specific isotope analysis (CSIA) to detect microbial degradation pathways, and (3) the sulphur and oxygen composition of sulphates in water $\delta^{34}\text{-SO}_4$ and $\delta^{18}\text{O-SO}_4$.

Results and discussions

The overall results expected from the presentation are to (1) create awareness of the two important vectors of AMR, the soil and water that we need to know more about, (2) develop and test a set of

an isotopic analytical toolbox that provide information on the sources and transport of antibiotics through the soil and water, and (3) develop guidelines and mitigation tools to manage the risks posed by AMR through soil.

Conclusions

Existing conventional monitoring and mass balance approaches are not sufficient to identifying and apportioning AMR movement in soil and water. However, multi-isotopes fingerprinting has the potential to assess sources and transport of antimicrobial resistance from intensive cropping-livestock systems through the soil to water bodies.

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3.1.25. The status of heavy metals (Cd, Pb) in the agricultural soils of Iran

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Abstract

The production of safe and healthy crops requires healthy basic resources (soil, water and atmosphere), properly managed using safe and healthy inputs. Therefore, it is necessary to understand their conditions. One of the most important value to look at is the pollution by heavy metals in soil, which is originated from geogenic or anthropogenic sources. To study the status of heavy metals in agricultural soils of Iran, 265 soil samples were collected from different agricultural lands. Site selection for sampling was based on both the cultivating area and expert opinions in different regions of the country. The heavy metals were measured using the methodology of Chen and Ma (2001) and the ICP. The results indicated that the mean, min and max amounts of soils Cd were 0.29, 0.11 and 0.72mg.kg⁻¹, respectively. Based on the Iranian soil contamination standard, the max permitted amount of soil total Cd is 5mg.kg⁻¹. So, soil Cd pollution was not observed in our samples. Also, the max, min and mean amounts of Pb in agricultural soils were 93.9, 18.5 and 41.1mg.kg⁻¹, respectively, and so, according to Iranian standard, only 3 soil samples had Pb amounts higher than permitted level (75mg.kg⁻¹). According to the results of the research and to other studies conducted in the country, soil contamination seems not to be a widespread issue, but only a local

issue mainly due to anthropogenic sources. However, the actual scale of the study is not wide enough to accurately analyze the contamination status of agricultural soils in Iran. The identification of high risk contaminated areas and their mapping is considered a top priority in the country.

Keywords: Heavy metals, Agricultural soils, Cadmium, Lead, pollutant

Introduction, scope and main objectives

The term 'heavy metal' has been used for many years and generally refers to the metals and metalloids especially the transition metals, such as Pb and Cd, that have relatively high atomic mass ($>5 \text{ gcm}^{-3}$) and can cause toxic problems (Alloway 2013).

Cd and Pb at high concentrations cause important damages to the environment and human health (Rezaei *et al.* 2015). The high concentrations of heavy metals in soil, in addition to those that have geological origins, can be the result of the addition of fertilizers, pesticides, or have urban origins (landfill, sewage sludge, organic pollutants, combustion of fossil fuels, sewage), industrial (mines, heavy metal smelting, metallurgy, chemical industries and electronics), atmospheric (airborne pollutants, dust and acid deposits) and incidental (Explosions, warfare and industrial accidents) (Misral, 2004). In 2016, about 11.7 and 2.7 million ha of soils were cultivated with agronomic crops and horticultural crops, respectively (regardless of fallow lands) (Ministry of Agriculture-Jahad 2017).

The first step in preventing the extension of contaminated soils is to know about the extent and distribution of contamination (Abdolahi *et al.* 2012). Considering the extent of soils under cultivation of agricultural products, various studies have been conducted on heavy metals contaminations. The standard of pollutant levels in agricultural soils with pH higher than 7 is designated at 5 and 75 mg.kg^{-1} for Cd and Pb (Iranian Department of Environment, 2014).

There are various reports about the impact of human activities on the amount of heavy metals in the soils of Iran. Abdolahi *et al.* (2012) reported that heavy metal contamination in the regions around the zinc processing factories in Zanjan province is mainly due to these factories. Also, in the industrial town of Semnan and its surrounding areas, high concentrations of Lead and Cadmium have been reported in surface soils (Nikrvavesh *et al.* 2017).

The use of waste water in agriculture and its contamination with heavy metals has been studied in some areas. Bagheri (2014) studied the heavy metals in the south of Tehran. He reported the average of 0.27 mg.kg^{-1} for Cd in the studied soils. The highest amount of Cd in these soils was 0.82 mg.kg^{-1} . Also, an increase in Pb, Cd and Ni concentrations was reported (Mostashari and Baghori 2002).

Several studies were also conducted in Isfahan and saffron-cultivated land in South Khorasan Province. The results showed that there was not high concentrations of heavy metals (Cd, Cr and Co) in soils (Jorkesh *et al.* 2014, Behdani *et al.* 2015).

To conclude, there is a potential for contamination of plant products when there are pollutant sources such as mines and metal processing factories (such as Zanjan and Isfahan provinces) and also fields irrigated with industrial and urban wastewaters.

Methodology

This study was carried out to study the status of heavy metals in the agricultural soils of Iran by 265 samples which distributed in all of country. Samples was chosen based on cropping area and local expert opinion. Soil samples have been taken at depth of 0-30cm and the geographic position was

recorded by GPS. Samples at each point, include at least 5 sub-samples were taken from a circle of 25 m radius to the center of the point, and then a composite sample was prepared. The map of sampling areas is shown in Fig. 2 (a, b). The content of Cd and Pb were measured after passing the samples through 2mm sieve, by the method of Chen and Ma (2001) and using the ICP device.

Results

The condition and location of pb and Cd of all sampled soils in the different regions is illustrated in Fig. 2 (a, b). The amount of total soil Cd in different regions showed that the concentration of Cd was not superior to the standard one in Iran (5 mg.Kg⁻¹). The mean, min and max amount of total soil Cd were 0.29, 0.11 and 0.72 mg.kg⁻¹, respectively, which implied the risk of Cd pollution, was not observed in the studied soils (Table 1). The histogram of total Cd concentration is presented in Fig. 1 (a, b). Correlation between Cd and calcium carbonate and clay percent appeared to be significant (Table 2).

The total Pb in studied soils was inferior to the standard (75mg.Kg⁻¹) amounting at 41.4 mg.Kg⁻¹ (Table 1). Also, in only 3 out of 265 samples the amount of Pb was more than 75 mg.Kg⁻¹ (Fig. 2b). Investigations on the correlation between Pb and CaCO₃, OC, pH and clay percent showed that only soil pH had significant correlation (Table 2).

Table 1: Descriptive Statistical analysis of Pb and Cd contents in soil samples.

Element	N	mean	median	Std.deviation	variance	skewness	kurtosis	min	max
Cd	265	0.29	0.28	0.088	0.008	1.21	2.98	0.11	0.72
Pb	265	41.36	39.76	11.1	122.37	0.72	1.58	18.50	93.92

Table 2: Pearson correlation between Cd and Pb and the other soil characteristics.

Element	CaCO ₃	OC	pH	Clay
Cd	0.209**	0.277**	-0.276**	0.281**
Pb	-0.486**	-0.020	0.008	-0.160**

** . Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

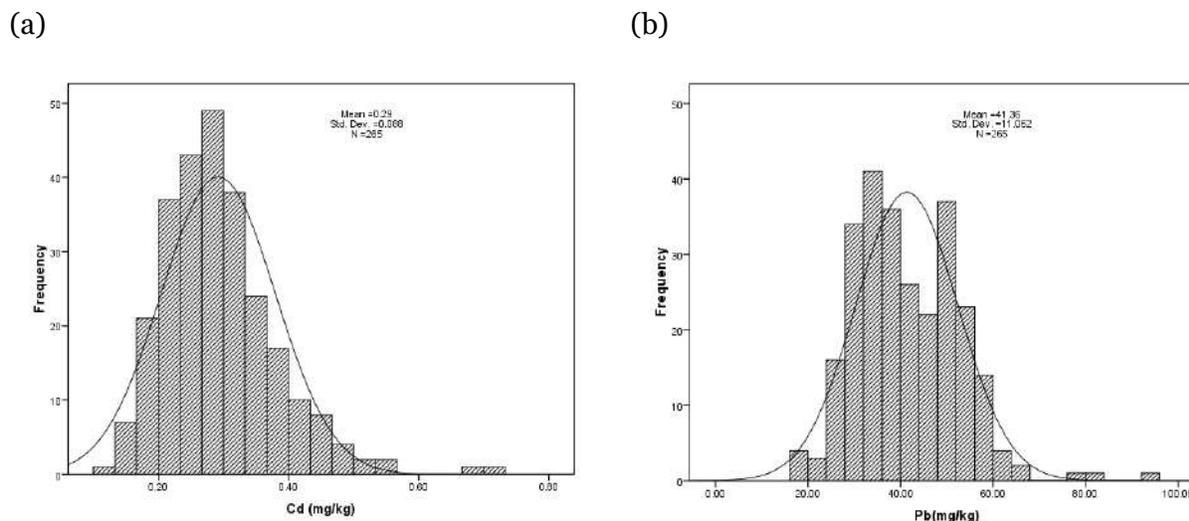


Figure 1. Histograms of Cd (a) and Pb (b) amount in soil samples

Discussion

Iran is located in a arid and semi arid region and most of its soils are carbonated soils. The existence of high amounts of CaCO_3 in soils has an important role in the fixation and reduction of metals such as Cd and Pb bioavailability. The results of this study demonstrated that pollution of Cd and Pb was not significant in the studied soils. These results are not representative of the condition of soil pollution in all regions of Iran. Then, more extensive studies shall be carried out to determine the amount of polluted lands in Iran.

Conclusions

Pollution of soil resources in Iran is not widespread and often is spotted and localized. By performing small scale surveys, the probability and possibility of identifying polluted areas is very weak. For this reason the works should be performed at a larger scale. But this requires a lot of time and money. The best way to do this, is identifying high risk areas and determine their boundary, and then conduct more precise studies in each area.

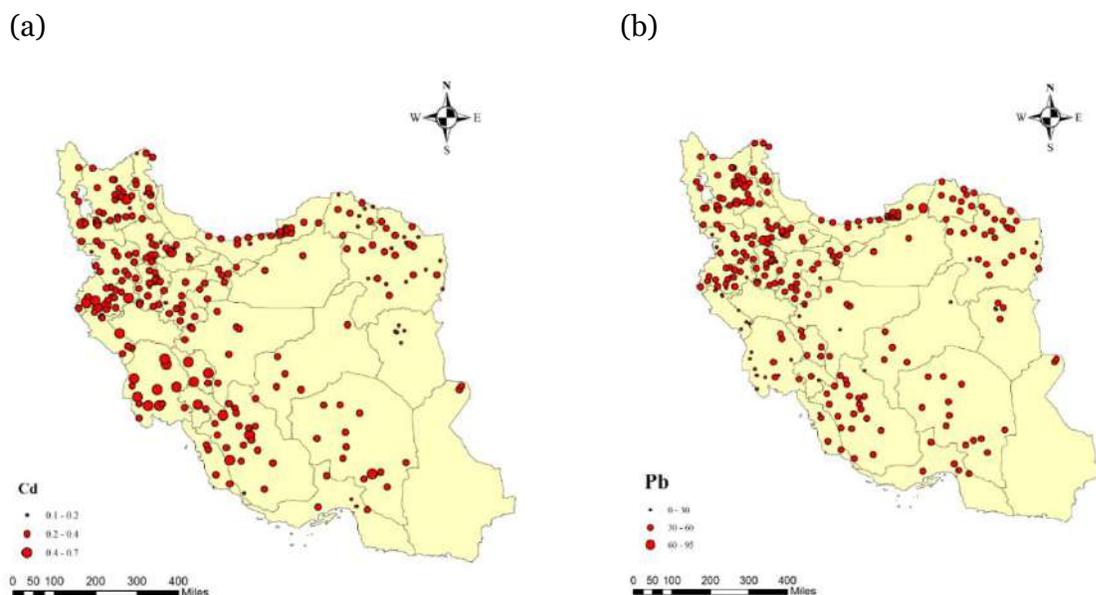


Figure 2. Distribution of samples and total Cd (a) and Pb (b) in soils

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3.1.26. Relationships between a mixture of trace elements and enzyme activities are better explained by potentially available fraction

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Abstract

The conventional management of agricultural soils can increase the (bio)availability of some contaminants. Trace elements (TE) are deposited in these soils by the use of fertilizers, fungicides, leachates from landfills and/or by aerial deposition of particles from industrial or high traffic. These TE appear as a mixture of trace elements (MTE), which can induce greater effects, by synergistic/antagonistic, than separately. In this context, to carry out reliable environmental risk analysis with MTE it is necessary quantify the effect in targeted and endogenous organisms presents in soil. The enzyme activities (EAs) are able to show harmful effects produce by TE. The aim of this study was to evaluate the impact of a MTE on key EAs of different agricultural land uses under conventional management (olive grove, rainfed and forest).

In the Southeast of Madrid (Spain), soils of the three adjacent land uses considered were sampled at twenty selected points. Forest use was considered as control. EAs related to main biogeochemical cycles of nutrients in soils were determined: alpha-glucosidase (AG), beta-glucosidase (BG), beta-galactosidase (BGA), phenoloxidase (PHE), arylamidase (ARYLN), N-acetyl-glucosaminidase (NAG), urease (URE), phosphatase (PHOS), acid phosphatase (ACP),

phosphatase alkaline (PAK), arylsulfatase (ARYLS) and dehydrogenase (DH). In each sample, total and potentially available fraction of sixteen metals (As, Sb, Ba, Be, Cd, Cr, Co, Cu, Hg, Pb, Mo, Ni, Se, Sn, V and Zn, these groups of TE is considered as the MTE in this study) were determined in order to know the effect of a MTE, and if this effect is better explained by total or potentially available concentration.

The EAs were higher in forest soils which was attributable to a greater amount of plants and animals induces higher microbial population. Only PHE was higher for rainfed, possibly reflecting a greater need for nutrients that are scarce or less available being forced to degrade lignin sans other phenolic recalcitrant compounds. Two hybrid redundancy analysis (hRDA) were performed: one with EAs, as response dataset, and total contents of the TE in the MTE, as environmental dataset, and another with the EAs, as response dataset, and the potentially available contents of the TE in the MTE, as environmental dataset. In both cases, land use was considered as covariable. The results showed differences in the total concentrations of ET among soil uses: Cu, Se and Sn are higher for rainfed and Pb and Mo for forest, while in partially available concentrations: Cu for rainfed and Co, Ni, Pb, Zn and Mo for forest soils. The concentrations of olive grove are always intermediate or lower than the other uses. In the hRDA between the EAs and the total TE concentrations, only four variables had a p-value <0.1 Pb (0.002), Ni (0.04), As (0.062) and Co (0.086), explaining a 10.1 % of the variance of the AEs for the first axis and 4.9 % for the second axis. For the hRDA between the AEs and the potentially available TE concentrations six variables had a p-value <0.1: As (0.002), Ni (0.008), Cd (0.008), Cu (0.032), Co (0.038) and Zn (0.092), explaining 24 % for the first axis and 10.8 % for the second. It was noted that the total concentration of MT explains a lower variance of the EA and hides the effect of other TE. In both hRDA there was a positive relationship between EA and TE concentration, this may be due to the role played of some of these TE as enzymatic cofactor. However, this positive relationship may hide a gap between the biogeochemical cycles. The worse explanation in the variability of the EAs of the total concentration shows that is need to determine the partially available concentration in order to carry out reliable environmental risk analysis.

Keywords: Enzyme activity, mixture of trace elements, trace element availability, risk analysis

Introduction, scope and main objectives

The conventional management of agricultural soils can generate a loss of soil quality by influencing several factors, such as: organic matter amount, C mineralization, biological activity, microbial community structure, and soil texture among others (Jackson *et al.* 2003, Madejón *et al.* 2007). In this context, the (bio)availability of some contaminants in soils could be increased (Frische *et al.* 2003; de Santiago-Martín *et al.* 2016). In agricultural soils trace elements (TE) are deposited by the use of fertilizers (Chen *et al.* 2009), fungicides (Micó *et al.* 2006), leachates from landfills (Slack *et al.* 2005), and/or by aerial deposition of particles from industrial zones or high traffic (Luo *et al.* 2012; Peña-Fernández *et al.* 2015). These TE are not isolated, but as mixtures of TE (MTE). In the MTE, synergistic effects can be produced, with the presence of certain TE affecting the behavior of others TE as well as their toxicity on soil microorganisms. Currently, most risk analysis does not take these processes and potential interactions into account (Cipullo *et al.* 2018). Nevertheless, to carry out reliable environmental risk analysis with MTE, in a more global and systematic way, it is necessary to quantify the effect produced in both target organisms and endogenous organisms presents in the soil. In this sense, enzyme activities (EAs) of soils have shown their ability to quickly identify harmful effects of TE (Paz-Ferreiro and Fu 2003). The aim of this study was to evaluate the impact of MTE on key EAs of agricultural soils of different land uses under conventional management (olive grove, rainfed, and forest) in order to determine if environmental risk analysis are more reliable taking into account total or potentially available concentrations of TE.

Methodology

The study area is located in the southeast of Madrid (Spain). Based on previous studies, 20 sampling points were selected. In these points differences have been observed in the spatial distribution between total and available TE content. At each point, three plots with different soil uses were selected (olive grove, rainfed, and forest uses) with the aim to reduce the abiotic variables between uses. Forest use was considered as control. Soil samples were taken at 0-30 cm depth in order to display all the tilling depth. Refrigerated samples were taken to the laboratory where they were sieved within 2 mm mesh and again cooling until the subsequent determination of a range of EA related to the main biogeochemical cycles of nutrients in soils: i) related to C cycle: alpha-glucosidase (AG), beta-glucosidase (BG), beta-galactosidase (BGA), phenoloxidase (PHE), ii) related to N cycle: arylamidase (ARYLN), N-acetyl-glucosaminidase (NAG) and urease (URE), iii) related to P cycle: phosphatase (PHOS), acid phosphatase (ACP) and phosphatase alkaline (PAK), iv) related to S cycle: arylsulfatase (ARYLS) and v) dehydrogenase (DH) to reflect the total amount of living microorganisms. For AG, BG, BGA, ARYLN, NAG, URE, PHOS, ACP, PAK and ARYLS activities, the ISO / TC 190 / SC 4N 422 standard was followed; PHE activity was obtained following DeForest (2009) and Schaefer (1963) was followed for DH.

To determine the potentially available fraction of TE, the DTPA method was followed in which extractions with a solution of triamine pentaacetic acid (DTPA), triethanolamide (TEA) and CaCl_2 were performed. Sixteen metals (As, Sb, Ba, Be, Cd, Cr, Co, Cu, Hg, Pb, Mo, Ni, Se, Sn, V and Zn) were considered as MTE in this study and were analyzed in the total and the potentially available fraction by a certified laboratory (Eurofins Analytic, The Netherlands) in ICP-MS following the NEN-EN-ISO 17294-2.

As a first approximation to the results, the means and standard errors of the EAs and the TEs were obtained. All variables were logarithmized and after removing the outliers, two hybrid redundancy analyzes (hRDA) were carried out, one with EAs, as response dataset, and total contents of the TE in the MTE, as environmental dataset, and another with the EAs, as response dataset, and the potentially available contents of the TE in the MTE, as environmental dataset. In both cases, land use was considered as covariable. Subsequently a Monte Carlo simulation (499) was carried out to show the minimum number of variables that explained the greater variance of the EAs, those with a p-value < 0.1 were selected. The software used was SPSS v.22.0 and Canoco 4.5.

Results

Overall, the EAs (Table 1) were higher in forest soils, olives grove soils always showed the lowest values. The only exception was the PHE activity, which was higher in rainfed soils.

Table 1. Summary of enzymatic activities

EA (mU.g ⁻¹)	All samples	Rainfed	Forestal	Olive grove
	Mean ± Std. Error			
AG	0.0402 ± 0.0022	0.0382 ± 0.0027	0.0534 ± 0.0039	0.0290 ± 0.0026
ARYLN	0.0280 ± 0.0015	0.0268 ± 0.0022	0.0358 ± 0.0023	0.0215 ± 0.0022
ARYLS	0.0212 ± 0.0028	0.0134 ± 0.0013	0.0413 ± 0.0061	0.0088 ± 0.0016
BGA	0.0143 ± 0.0025	0.0113 ± 0.0034	0.0229 ± 0.0056	0.0085 ± 0.0026
BG	0.1893 ± 0.0154	0.1468 ± 0.0115	0.2936 ± 0.0317	0.1275 ± 0.0140
NAG	0.0163 ± 0.0021	0.0133 ± 0.0020	0.0286 ± 0.0048	0.0070 ± 0.0010
PHOS	0.6934 ± 0.0873	0.6236 ± 0.1355	10.1329 ± 0.1628	0.3237 ± 0.0918
ACP	0.2450 ± 0.0403	0.1135 ± 0.0128	0.5270 ± 0.0903	0.0945 ± 0.0223
PAK	0.5047 ± 0.0557	0.3677 ± 0.0560	0.8907 ± 0.1074	0.2558 ± 0.0466
URE	0.0102 ± 0.0007	0.0103 ± 0.0012	0.0115 ± 0.0012	0.0087 ± 0.0012
DH	0.1124 ± 0.0107	0.0969 ± 0.0156	0.1784 ± 0.0194	0.0620 ± 0.0088
PHE (U.g ⁻¹)	0.1509 ± 0.0082	0.1601 ± 0.0132	0.1460 ± 0.0144	0.1467 ± 0.0152

The concentrations of total As, Ba, Be, Cd, Co, Cr, Hg, Ni, Sb and V (Table 2) were similar among different uses. However, the concentrations of Cu, Se and Sn showed higher values in rainfed soils, and the forest use presenting higher values of Mo and Pb concentrations. The olive grove soils always had intermediate or lower values.

The potentially available amounts (Table 3) of As, Ba, Be, Cd, Cr, Hg, Sb, Sn, Se and V were very similar between soil uses. The potentially available amounts of Cu were higher in dry land use. The forest use shows higher levels of potentially available Co, Ni, Pb, Zn and Mo.

In the hRDA between the EAs and the total TE concentrations (Fig. 1.a) the variables with a p-value <0.1 in the MTE were: Pb (p 0.002), Ni (p 0.040), As (p 0.062) and Co (p 0.086), explaining a 10.1 % of the variance of the AEs for the first axis and 4.9 % for the second axis. For the hRDA between the AEs and the potentially available TE concentrations (Fig1.b), the variables with a p-value <0.1 in the MTE were: As (p 0.002), Ni (p 0.008), Cd (p 0.008), Cu (p 0.032), Co (p 0.038) and Zn (p 0.092), explaining 24 % for the first axis and 10.8 % for the second. In both hRDA there was a positive relationship between EA and ET concentration, this relationship was more significant for DTPA extraction.

Table 2. Summary of total concentrations of trace elements

TE (mg/kg)	All samples	Rainfed	Forestal	Olive grove
	Mean ± Std. Error			
As	11.1133 ± 0.5230	11.3050 ± 0.5068	10.8200 ± 1.3688	11.2150 ± 0.6408
Ba	110.8833 ± 5.3108	107.5500 ± 5.4572	113.5500 ± 11.8935	111.5500 ± 9.5147
Be	1.1838 ± 0.0702	1.1185 ± 0.0999	1.1845 ± 0.1422	1.2483 ± 0.1235
Cd	0.1156 ± 0.0074	0.1106 ± 0.0095	0.1277 ± 0.0157	0.1084 ± 0.0127
Co	6.9433 ± 0.2544	7.0500 ± 0.3729	6.6750 ± 0.4805	7.1050 ± 0.4766
Cr	20.2590 ± 0.8121	20.4516 ± 1.0333	20.5949 ± 1.8126	19.7307 ± 1.3295
Cu	11.0700 ± 0.6825	12.8350 ± 1.7972	9.6400 ± 0.6412	10.7350 ± 0.6485
Hg	0.0405 ± 0.0054	0.0456 ± 0.0081	0.0499 ± 0.0132	0.0261 ± 0.0040
Mo	0.4018 ± 0.1078	0.2882 ± 0.0352	0.5980 ± 0.3171	0.3192 ± 0.0578
Ni	13.3550 ± 0.4718	13.9500 ± 0.6782	12.7800 ± 0.9373	13.3350 ± 0.8362
Pb	18.0271 ± 1.0530	16.2094 ± 0.8164	21.6341 ± 2.6696	16.2380 ± 1.2280
Sb	0.4645 ± 0.0186	0.4534 ± 0.0222	0.4908 ± 0.0432	0.4492 ± 0.0286
Se	1.1251 ± 0.2020	1.5085 ± 0.3958	0.9266 ± 0.3167	0.9403 ± 0.3341
Sn	1.3385 ± 0.1125	1.4838 ± 0.2058	1.1634 ± 0.2059	1.3682 ± 0.1742
V	25.7500 ± 1.0438	25.5500 ± 1.4281	25.4000 ± 2.2342	26.3000 ± 1.7593
Zn	41.4619 ± 1.5938	43.0500 ± 2.1132	41.9301 ± 3.2859	39.4057 ± 2.8347

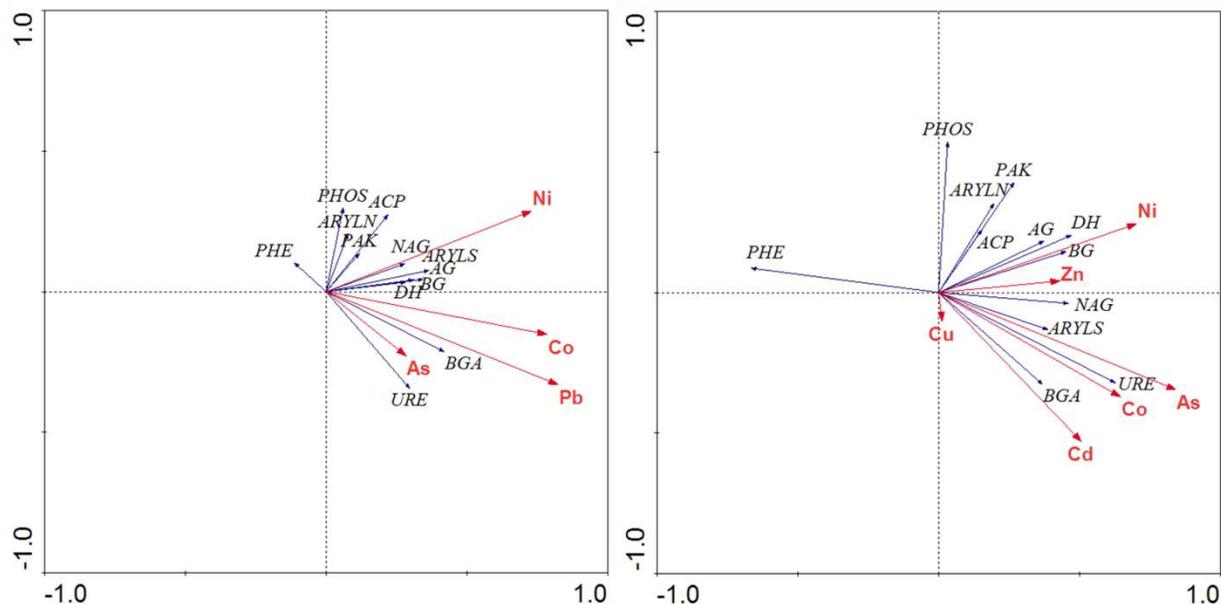


Figure 1. hrDA ordination between EAs (response dataset) and total (a) and potentially available (b) fraction

Table 3. Summary of potentially available trace elements

TE (mg/kg)	All samples	Rainfed	Forestal	Olive grove
	Mean ± Std. Error			
As	0.0426 ± 0.0037	0.0416 ± 0.0056	0.0490 ± 0.0073	0.0373 ± 0.0064
Ba	0.4793 ± 0.0322	0.4602 ± 0.0248	0.5047 ± 0.0713	0.4731 ± 0.0625
Be	0.0009 ± 0.0002	0.0007 ± 0.0002	0.0011 ± 0.0006	0.0008 ± 0.0003
Cd	0.0179 ± 0.0015	0.0168 ± 0.0018	0.0239 ± 0.0032	0.0130 ± 0.0018
Co	0.0549 ± 0.0048	0.0538 ± 0.0067	0.0714 ± 0.0106	0.0395 ± 0.0053
Cr	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0001 ± 0.0001	0.0000 ± 0.0000
Cu	0.4750 ± 0.0219	0.5270 ± 0.0450	0.3981 ± 0.0288	0.4999 ± 0.0337
Hg	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000
Mo	0.0010 ± 0.0003	0.0010 ± 0.0006	0.0012 ± 0.0005	0.0008 ± 0.0003
Ni	0.1318 ± 0.0067	0.1404 ± 0.0095	0.1433 ± 0.0133	0.1118 ± 0.0107
Pb	0.8568 ± 0.0410	0.7824 ± 0.0339	10.0530 ± 0.1007	0.7350 ± 0.0359
Sb	0.0009 ± 0.0001	0.0008 ± 0.0001	0.0011 ± 0.0003	0.0009 ± 0.0001
Se	0.0011 ± 0.0002	0.0009 ± 0.0002	0.0013 ± 0.0002	0.0012 ± 0.0004
Sn	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0000 ± 0.0000	0.0001 ± 0.0001
V	0.0045 ± 0.0007	0.0048 ± 0.0014	0.0043 ± 0.0012	0.0043 ± 0.0011
Zn	0.5397 ± 0.0481	0.5281 ± 0.0862	0.7831 ± 0.0842	0.3078 ± 0.0323

Discussion

The higher EA in forest soils may correspond to a bigger microbial population, as DH activity showed. A greater amount of plants and animals induces a greater microbial activity, explaining this result. The PHE activity possibly reflects a greater need for microorganisms in rainfed use for nutrients (such as C, N or P) that are scarce or less available, being forced to degrade lignins and other phenolic recalcitrant compounds.

A common lithogenic origin can be attributed to the TEs with similar total concentrations, while the differences observed in rainfed use are more likely attributable to the use of fungicides in crops. The greater amount of organic matter in forest soils would contribute to the stabilization of certain TE by organo-mineral complexes.

A positive relationship was found between most of the EAs and TE. This may be due to the role played by some of these elements as enzymatic cofactors. Ekenler and Tabatabai (2002) recorded an activation of NAG activity at low concentrations of Co (II) and As (V) among other TE. Kouchou *et al.* (2017) found positive correlations between different EAs and Cu, Zn and Cr and negative with aromaticity, which in our study would be represented by PHE activity. Haggmann *et al.* (2015) also observed positive correlations among EAs and some TE. In these studies, the authors concluded that the increase in EAs is due to the continued presence of TE in soils, which would cause the adaptation of soil biological communities. The positive relationship may hide a gap between the biogeochemical cycles of the main nutrients, assuming an effect on the soil functions (Kouchou *et al.* 2017), so it is necessary to continue with the corresponding studies. The potentially available TE

fraction can better explain the variations observed in the EAs since this fraction is more related to TE (bio)availability in soils (de Santiago-Martín *et al.* 2014). If only the total concentration had been taken into account, less EA variance was explaining and the effect of some TE had been obviated, this shows the need of using potentially available concentrations in risk analysis.

Conclusions

- Different total concentrations of Cu, Se, Sn, Mo and Pb and potentially available concentrations of Co, Cu, Ni, Pb, Zn and Mo were found in soils under olive, rainfed and forest uses.
- There are differences between the EAs for different agricultural land uses under consideration.
- The total concentrations of TE in the MTE considered explain the variability in the EAs worse and obviated some TE than the potentially available concentrations, highlighting the need to consider the potentially available fraction in the risk analysis.

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3.1.27. Simulation of silver nanoparticles transport with runoff water and related erosion processes using LISEM and PestPost models

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Abstract

The fate of nanoparticles (NPs) in soil has attracted attention in recent years because of the growing amounts of NPs used in many applications. It is expected the pollution of the environment with NPs will grow exponentially with time. Thus, many studies have investigated pathways, impact, and transport of NPs. During and after rainfall, silver nanoparticles (AgNPs) can be transported through the soil profile and over the soil surface.

In the present study, we combined a hydrological soil erosion model (LISEM) with a recently developed particle-transport model (PestPost) to simulate the transport of AgNPs due to runoff and erosion processes. The models were calibrated with the results of laboratory experiments. AgNPs were applied to the upper one of 5 segments in 2 soil flumes of size 0.5 m². The flumes were placed with 10% (F1) and 20% (F2) inclination. The initial AgNPs content in segment 1 was 16 µg/segment. Measurements showed that 7.5% of AgNP was transported with runoff water in F2 compared to 8.6 % in F1. For sediments, after the experiment, the AgNPs content in F2 was 7.7% compared to only 2.6 % in F1 of the initial AgNPs content.

The two models were calibrated separately using measured data from the rainfall experiments. The calibration of LISEM showed high model efficiency (MEF) for both sediment =0.81 and runoff =0.79.

For the PestPost model, a simple optimisation procedure was used to find the simulated results were closest to the measured ones. AgNPs simulation in runoff water was better than that in the eroded sediment for both flumes (Δ_{pi} for runoff <0.01 and for sediment =0.061 in F1 and 0.022 in F2). This is related to the increase of AgNPs content in the sediment after subsequent rainfall events due to the increase of AgNPs adsorption on soil particles. It is shown that the processes affecting the transport of AgNPs transport on the soil surface, mainly runoff and erosion due to rainwater can be predicted using the combination of LISEM and PestPost.

Keywords: AgNPs, transport, runoff, erosion, modelling

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Sub-theme 3.2: State of the art of remediation techniques of polluted sites

3.2.1. Environmental electrokinetics for a sustainable subsurface

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Abstract

Soil and groundwater are key components in the sustainable management of the subsurface environment. Source contamination is one of its main threats and is commonly addressed using established remediation techniques such as in-situ chemical oxidation (ISCO), in-situ chemical reduction (ISCR; most notably using zero-valent iron [ZVI]), enhanced in-situ bioremediation (EISB), phytoremediation, soil-washing, pump-and-treat, soil vapour extraction (SVE), thermal treatment, and excavation and disposal. Decades of field applications have shown that these techniques can successfully treat or control contaminants in higher permeability subsurface materials such as sands, but achieve only limited success at sites where low permeability soils, such as silts and clays, prevail. Electrokinetics (EK), a soil remediation technique mostly recognized for in-situ treatment of low permeability soils, has, for the last decade, been combined with more conventional techniques and can significantly enhance the performance of several of these remediation technologies, including ISCO, ISCR, EISB and phytoremediation. Herein, we discuss the use of emerging EK techniques in tandem with conventional remediation techniques, to achieve improved remediation performance. Furthermore, we highlight new EK applications that may come to play a role in the sustainable treatment of the contaminated subsurface.

Keywords: electrokinetics, remediation, subsurface contamination, phyto-remediation, bioremediation, ISCO, nano zero valent iron (nZVI), landfill

Introduction, scope and main objectives

Contamination in low permeability materials remains a significant and unresolved remediation challenge. A large contaminant source has the potential to generate a significant plume in groundwater, and presents a risk to potential down gradient receptors (A in Figure 1). A unique form of contaminant transport occurs with dense non-aqueous phase liquids (DNAPLs), including chlorinated solvents, polychlorinated biphenyls (PCBs), coal tars etc. since they tend to sink to the bottom of aquifers due to their density (Macdonald *et al.*, 2000). Contaminants in the context of

groundwater exposure pathways are varied, and can consist of organic molecular compounds, nano-substances, pharmaceuticals, immiscible liquids, and are often toxic at very low (part per billion) concentrations. New ingenious approaches are needed for in-situ (and ex-situ) remediation of soils, sediments and aquifers, particularly when they are comprised of low permeability materials.

Recent successes in electrokinetic (EK) or EK assisted remediation programs have demonstrated that the technique may be a viable and versatile remediation tool for low permeability soils and sediments. EK approaches generally consist of the application of a direct current (DC) electric field to the subsurface through electrodes to move porewater or migrate contaminants or remediation amendments. EK approaches have wide applicability, from soil dewatering (Lockhart and Stickland, 1984; Yang *et al.*, 2005) to desalination of built environments (Ottosen and Rorig-Dalgaard, 2009), removal of soil metal contaminants (Jensen *et al.*, 2007; Ottosen *et al.*, 1997; Pamukcu *et al.*, 1997; Pamukcu and Wittle, 1992) or degrading/removing soil organic contaminants (Lima *et al.*, 2012a; Lima *et al.*, 2011; Pamukcu, 1994; Reddy *et al.*, 2011; Saichek and Reddy, 2004, 2003), including immiscible oil constituents (Ghazanfari and Pamukcu, 2014; Pamukcu *et al.*, 2016). First used at the beginning of the last century for dewatering and stabilizing clays (Casagrande, 1949; Reuss, 1809), EK was intensively studied in the 1990s for removing metals from soils (Acar and Alshwabkeh, 1993; Lageman, 1993; Ottosen *et al.*, 1997; Ottosen and Hansen, 1992; Schultz, 1997), as well as radionuclides and other inorganic species (Acar *et al.*, 1995). More recently EK has been used in various formulations for the removal of organic contaminants (Lima *et al.*, 2011; Pamukcu, 1994; Ribeiro *et al.*, 2005). The approach has been highly successful at the laboratory scale for both inorganic and organic contaminants and in recent field trials for organic contaminants. Field-scale in-situ applications are becoming more common, and have demonstrated the potential of the approach. In spite of promising early results at a variety of scales, the technology has not yet advanced to a commonly-accepted commercial status.

EK is an approach with the capacity of overcoming traditional problems in soil remediation practices. The technique can be applied in-situ in a manner that avoids soil excavation and minimizes the disturbance of soil texture, porosity and biodiversity (Saichek and Reddy, 2005; Virkutyte and Sillanpaa, 2002). Treatment costs are variable depending on the contaminant, approach, and other site-specific factors, but are in line with other intrusive in-situ approaches (Virkutyte and Sillanpaa, 2002). Due to low soil disturbance, low water and energy usage, EK is often less expensive than other remedial techniques (Alshwabkeh and Acar, 1992; Gomes *et al.*, 2015; Higgins *et al.*, 2008; Wittle *et al.*, 2011; Yang *et al.*, 2011). Herein, we discuss the strength of EK as a complement to traditional soil and groundwater remediation techniques and explore future avenues for EK as a sustainable subsurface remediation approach.

Conventional soil remediation techniques for source control and their limitations

Commonly practiced technologies for soil and groundwater remediation include permeable reactive barriers (PRBs) (Benner *et al.*, 2002), bioremediation (Guerin, 1999; Tromp *et al.*, 2012), i.e. the use of either plants (phytoremediation) or microorganisms (bioremediation) to degrade, accumulate or reduce/oxidize chemical contaminants, soil-washing (Meuser, 2012), pump-and-treat (Meuser, 2012), in-situ chemical oxidation (ISCO) and in-situ chemical reduction (ISCR), the use of chemicals to oxidize or reduce redox sensitive contaminants in high porosity soils and sediments, vapour-technologies to volatilize organic contaminants, thermal approaches to vapourize organic contaminants and remove them through vacuum extraction, and “dig-and-dump”. The majority of these approaches (with the exception of thermal and dig-and-dump) have significant limitations when contaminants to be treated reside in low permeability regions. Table 1 summarizes the main characteristics and main challenges of bioremediation, phytoremediation,

nano-particles, ISCO, thermal, and landfilling (dig-and-dump). As mentioned previously, a number of these techniques can be combined with EK to increase their suitability for treatment of contaminants in low permeability regions. A summary of the techniques that can be enhanced using EK, and a brief synthesis of the target contaminants and major limitations is presented in the next sections.

Table 1. Summary of the main defining characteristics of soil remediation techniques, main challenges and how EK can overcome them *in* (Lima *et al.* 2017)

	In-Situ Bioremediation	Phytoremediation	Nano-scale Zero Valent Iron (nZVI)	ISCO	Landfilling	Thermal (Lebrón <i>et al.</i> 2013; McGuire <i>et al.</i> 2016)
Target pollutants	Organic contaminants (chlorinated solvents, BTEX and other aromatic compounds, pesticides); some metals(Vidali 2001)	Metals, metalloids (Ali <i>et al.</i> 2013) and organic contaminants (Seeger <i>et al.</i> 2013)	Organochlorines, nitroaromatics, dyes, phenols, heavy metals, pesticides, and anions (e.g., NO ₃ ⁻¹)	All oxidizable pollutants like organic pollutants and redox sensitive metals (Nieto Castillo <i>et al.</i> 2012)	Metals, hazardous contaminants unamenable to in-situ remediation	Volatile organic compounds
Energy requirements	Low; depends on contaminant, bacteria, and technique. Laboratory scale experiments and treatability studies prior to field applications are often required	Low. Plants are placed in-situ and some maintenance is required. Harvesting and replacement of plants	Low to moderate. It requires pumping and delivery of nano-particles to pollutant	Moderate to high; higher than other in-situ (non-thermal) remediation technologies (Yan <i>et al.</i> ; USEPA 2006)	Moderate to high. Mainly for excavation and transportation	High. The approach requires heating of impacted soil and groundwater to (at a minimum) the boiling point of water)
Water usage	Low to moderate; depends on nutrient requirements	Low to moderate; depends on vegetative cover. Continued irrigation is required	Moderate. ZVI needs to be diluted in water (e.g. 68 m ³ of water with a concentration of 2 g/L of nZVI(US EPA and USEPA 2000)). Intensive at the	Moderate. Oxidant needs to be diluted in water (e.g. 8 – 14.5 m ³ of water for persulfate dilution(Yan <i>et al.</i>)). Intensive at the beginning stages	Low. Landfill leachate needs to be treated, but does not add to water requirements	Low. Water may be used to increase contact with the soil to be treated or to cool electrodes.

				beginning stages			
Maintenance requirements	Low to moderate (nutrient additions); pH, oxygen content, nutrient regulation(Vidali 2001)	Low to moderate. Maintenance requirements	Low	Low to moderate depending on oxidant choice, soil/site conditions	Moderate; landfill maintenance and leachate management	Moderate.	
Duration	Long (can last years); depends on microorganisms, contaminant availability (US EPA and USEPA 2000), and soil heterogeneity	Long (up to 30 years or more(Kamath <i>et al.</i> 2004))	Short (depends on transport of ZVI to target area). However recent studies suggest that nZVI can stimulate bioremediation (Kocur <i>et al.</i> 2015)	Short to moderate. Variable depending on nature of contaminant (sorbed, free phase, solubility, etc.)	Long. Waste is deposited in landfill, contamination transference	Short. Remediation programs are often on the order of weeks to months.	
Disturbance of the subsurface	Mechanical	Low	Low	Low	Low	High	Moderate. Potential for changes to soil structure.
	Biological/chemical	Moderate	Low	Moderate. Change of geochemical conditions	Moderate. Change of geochemical conditions	High	Moderate. Biological polishing following thermal treatment necessary
Cost (all values in USD)	Wide range of low to high. From USD30 – 100/m ³ (aerobic degradation field demonstration); USD323,000 for a specific site of	Low. USD15 -25/m ³ (calculated based on the treatment of upper 1 m layer)(McCutcheon and Schnoor 2004)	High. USD255,000 to USD1,400,000 for 2987 ha (numbers based on a specific site)(Gavaskar <i>et al.</i> 2005).	Moderate. Median cost of USD123/ m ³ based on 33 case studies (Krembs <i>et al.</i> 2010) but can amount to	Low to moderate. Landfill disposal costs between USD250 – 350/m ³ (US EPA 2014),	High.	

	480 m ² (based on project costs) (US EPA and USEPA 2000)		Nano-particles cost is USD50/kg of nZVI	USD527/m ³ (Innocenti <i>et al.</i> 2014)	and with possible total costs (excavation, transport, disposal, labour) amounting to USD650/m ³ (personal communication, Geosyntec)	
Main challenge	Limited to biodegradable compounds, where degradation products may be more persistent or toxic than parent compounds. Long remediation times for some compounds (Singh and Ward 2004)	Long remediation times. Address contaminant mainly at the relatively shallow subsurface (root zone)	nZVI particles need to be delivered to contaminant zone. Limited reactive lifetime of nZVI	Slow mass transfer, transport, and less control over oxidant due to limiting hydrogeological settings (USEPA 2006). Rapid oxidant reaction rates (esp. H ₂ O ₂ , Fe ²⁺ , and O ₃)	Contamination transference: environmental issues concerning soil are merely leachate transferred to landfill site	High energy costs and potential difficulties due to surface infrastructure requirements. Not suitable for inorganic contaminants
How EK can help	Electromigration and/or electro-osmosis can deliver nutrients, microorganisms to target zone	Electromigration can bring pollutants to roots for easier phytostabilisation, rhizofiltration or rhizodegradation (Aboughalma <i>et al.</i> 2008; Cameselle <i>et al.</i> 2013)	Electrophoresis (if sandy soil) and/or electro-osmosis (if clayey soil) can enhance nanoparticle delivery to contaminated regions; faster nanoparticle	Oxidant delivery to contaminated regions; faster oxidant delivery than natural hydraulic conductivity	Electro-osmosis can be used to dewater soil and reduce total residue weight/volume for landfilling; metals or organic contaminants	Not amenable to improvement through EK approaches

			transport than natural hydraulic conductivity		can be extracted ex-situ through the electro-dialytic method and avoid landfill all-together	
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Discussion

Sustainability principals are being increasingly recognized as important considerations in the remedy selection process (Hadley and Ellis, 2009). SURF (Sustainable Remediation Forum) defines sustainable remediation as those practices that reduce global impacts at the same time as minimizing local atmospheric effects, potential impacts on worker and community safety, and/or the consumption of natural and energy resources that might be attributable to remediation activities (Hadley and Ellis, 2009; ITRC (Interstate Technology Regulatory Council), 2011). As presented in Table 1, even the most promising techniques present limitations.

Bioremediation presents a number of limitations, including the need to control abiotic conditions, mass transfer challenges, bioavailability, bioaugmentation and potentially high operation or long-term re-application costs (Vidali, 2001) (Table 1). EK has been used to surpass some of these challenges, such as control of physico-chemical conditions of soil (Niqui-Arroyo *et al.*, 2006), decrease mass transfer limitations through nutrient transfer and stimulating bioactivity and controlling bacterial population (Mao *et al.*, 2012; Tyagi *et al.*, 2011). Different EK principles have been used: electro-osmosis or electrophoresis to mobilize bacteria (Figure 2) (DeFlaun and Condee, 1997; Wick *et al.*, 2004) and electromigration to drive nutrients in low porous materials (Gill *et al.*, 2014; Mao *et al.*, 2012). After successful lab trials, the patented EK-BIO has been applied in-situ (Luo *et al.*, 2006) with considerable success (Riis *et al.*, 2012). Some bioremediation drawbacks (primarily challenges with nutrient distribution in low permeability soils) may thus be addressed remarkably with EK, but evidently target contaminants still need to be biodegradable.

Phytoremediation has shown positive results for the in-situ remediation of both metals and organics. This feature can be further enhanced using EK (Aboughalma *et al.*, 2008; Cameselle *et al.*, 2013a). EK can be used to mobilize and redistribute metals in situ, and therefore enhance their transport to the plant roots (Aboughalma *et al.*, 2008); EK can help stimulate plant growth by mobilizing (micro)nutrients in/to the root zone. Cameselle *et al.* (Cameselle *et al.*, 2013a); and electromigration can be used to transfer ions and metals to the root zone while the development of heat (AC electric field) may create ideal assimilation conditions for the plant.

Nano-ZVI shows potential to treat redox sensitive contaminants (i.e. organic contaminants in general, or redox sensitive metals) but also stable metal ions, such as divalent Cd²⁺ (Boparai *et al.*, 2011). EK has the potential to enhance nZVI in-situ transport by electrophoresis. Studies have reported the enhancement of nZVI delivery through coarse and medium grained soils (Chowdhury *et al.*, 2012) while others found that electro-osmosis can enhance nZVI delivery through clayey soil (Figure 2) (Gomes *et al.*, 2013; Krishna R. Reddy, 2007).

ISCO performance in low permeability or highly heterogeneous soils is often a significant unresolved challenge. Commonly used chemical oxidants (permanganate, persulfate) are negatively charged, and highly mobile through electromigration in low permeability soils (Figure 2) (Alshawabkeh, 2009; Nieto Castillo *et al.*, 2012). Electroosmosis or electromigration may also help mobilize specific contaminants (non-charged hydrophobic organics or metals, respectively) by encouraging desorption or transport to different phases (Isosaari *et al.*, 2007; ITRC, 2001).

Remediation of fine grained soils contaminated with metals has historically been performed through landfilling (Reddy, 2010). Landfilling costs are generally higher and less sustainable in the long-term than any in-situ soil remediation (Table 1), in addition to the environmental costs and sustainability considerations addressed elsewhere in this review. When there is no in-situ solution in sight, an alternative to soil landfilling is off-site treatment of soil. This occurs often where brownfields are considered, either for metal (Merckx *et al.*, 2013) or organic pollutants (Gomes *et*

al., 2015; Lima *et al.*, 2012a; Pamukcu, 1994). The electro-dialytic remediation (EDR) method has been proposed as a fast and continuous in-situ or off-site alternative to landfilling for excavated soil. Promising results through the application of EDR for heavy metal polluted harbour sediment (Nystroem *et al.*, 2005) have been obtained by treating a stirred suspension instead of a stationary matrix. The stirred system for EDR was adapted for the soil remediation, and the soil was suspended in water during the remediation (Gomes *et al.*, 2013; Jensen *et al.*, 2007; Lima *et al.*, 2012b; Ottosen *et al.*, 2012; Sun *et al.*, 2012). Advantages of off-site EDR treatment involve (i) transient and nonlinear changes during remediation that are overcome by the continuous mixing; (ii) the removal rate of heavy metals is faster, as stirring enables mixing and desorption; (iii) easy handling for adding chemical desorbing solutions; and (iv) stirred EDR can be combined with soil washing for minimizing the volume to be treated. In this case the clean coarser fraction and the highly polluted fine fraction are separated during the soil washing and only the fine fraction is treated by EDR. Successful removal rates have been obtained for both metals (Jensen *et al.*, 2007; Ottosen *et al.*, 2012; Sun *et al.*, 2012) and organics (Gomes *et al.*, 2013; Lima *et al.*, 2012b).

Conclusions

Because EK acts as a transport tool for dissolved and colloidal particles, as well as solvent through porous media, the possibilities for future applications are varied and only limited by inventiveness and possibly limited research funds. Therefore, we highlight how EK can act as a versatile and manifold tool for the sustainable treatment of contaminated soil. Some new developments emerged that brink between laboratory and pilot scale research:

- In-situ manipulation of redox-state via EK for redox sensitive metals (e.g. Cr, As, Cu) (Brosky and Pamukcu, 2013; Pamukcu *et al.*, 2004; Sun *et al.*, 2015)
- Application of EK in the field of oil extraction and oil transport in water wet porous media (Amba *et al.*, 1964; Chilingar *et al.*, 1968; Ghazanfari *et al.*, 2014, 2012; Ghazanfari and Pamukcu, 2014; Haroun *et al.*, 2013; Pamukcu *et al.*, 2016; Shalabi *et al.*, 2012; Wittle *et al.*, 2011)
- Remediation of oil contaminated soils and sediments where spills have occurred (i.e., coastal sediments, coal gasification sites, abandoned oil production or refinery sites);
- Change in physical properties can be triggered via electrokinetic methods as the classic soil consolidation (Adamson *et al.*, 1966) with the aid of calcium carbonate producing bacteria (Keykha *et al.*, 2014);
- Product extraction, with special interest for mobilization of crude oil in enhanced oil recovery (EOR) processes (Al Shalabi *et al.*, 2012; Amba *et al.*, 1964; Haroun *et al.*, 2013; Shalabi *et al.*, 2012; Wittle *et al.*, 2011) from formations where other extraction methods (i.e., drilling) may not be feasible or environmentally viable.
- Permeable Reactive Barrier (PRB) previous combination with EK has proven advantageous in terms of treatment, PRB material longevity and cost reduction (Ramírez *et al.*, 2015).

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3.2.2. Restoration strategies in soils of Guadiamar area (South Spain). Evaluation of the success after twenty years since the Aznalcóllar mine accident

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Abstract

The Aznalcóllar accident (1998, Sevilla) was considered as one of the worst environmental catastrophes in Europe. We summarize here 20 years of soil monitoring to evaluate the success of remediation measures in the affected area. In an experimental plot different soil amendments were tested. Positive effect of the amendments on soil pH and organic carbon content were detected. A large-scale monitoring of the soils along the whole area showed a general stabilisation of trace elements in the Guadiamar Green Corridor, although in some spots like river banks and channels are still acidic and contaminated. Phytoremediation can be a feasible alternative to achieve soil remediation in trace element contaminated soils.

Keywords: Phytoremediation, trace elements, soil amendments, pH, Organic matter, plant cover.

Introduction, scope and main objectives

During the night between 25th and 26th of April 1998, a failure of the tailing dam wall occurred at “Los Frailes” mine and 4-5 million m³ of toxic tailings (slurry and acid water) flowed down through the courses of the Guadiamar and Agrio river (Madejón *et al.*, 2018). The spill completely ruined the area for any agricultural and cattle raising activities. Besides the economic disaster, the proximity to Doñana National park made more dangerous the accident. The Andalucía Regional

Government supported by experts' opinion, decided to create an ecological corridor giving priority to the immobilization of the contaminants into the soil. Soils can naturally reduce mobility of trace elements (TE) by sorption, precipitation and complexation reactions. These processes can be accelerated by the addition of amendments. The objective of this work was to evaluate the success of amendment application and the development of a plant cover (phytoremediation) in the restoration of these contaminated soils.

Methodology

Along the contaminated area three types of amendments were used: calcic (sugar-beet lime (SL)), iron oxide-rich red soil and different organic matter-rich composts (Madejón *et al.* 2018). To investigate more precisely the effect of the amendments on soil restoration, our research team designed experiments under semi-controlled field conditions. One of these experiments was carried out in a plot in which the only remediation activity was the removal of the sludge and top soil layer (about 20 cm). Three treatments were established, using two types of amendments (biosolid compost (BC) and SL), and a control without amendment (Madejón *et al.*, 2010). The soils were sampled and analyzed periodically. Apart from these designed and located experiments, the concentration of TE has been monitored in plants and soil along the Guadiamar area (e.g., Domínguez *et al.* 2016).

Results

Soil pH mean values in BC and especially in SL treatment were significantly higher than in control during all the experimentation period (Figure 1). TE availability (represented here by the Cd evolution) decreased over time being this decrease more efficient in amended soils (Figure 1). The durability was noticeable more than 12 years after application. Organic matter and fertility increased in amended soils. In comparison to non-amended soils, total organic carbon increased 47% and 67% in soils treated with SL and BC respectively, 14 years after the first amendment application. Nutrient content increased noticeably in amended soils.

Analysis of soils sampled along the river basin showed that soil pollution, 16 years after the accident, depended on the capacity of the soil to buffer against changes in soil pH and the topographical location. River channels and banks remained more contaminated due to the limited accessibility for cleaning-up operations and amendment application. Cd and Zn were easily redistributed downstream due to their high solubility, while As and Pb remained at shorter distances from the pollution source (Domínguez *et al.* 2016).

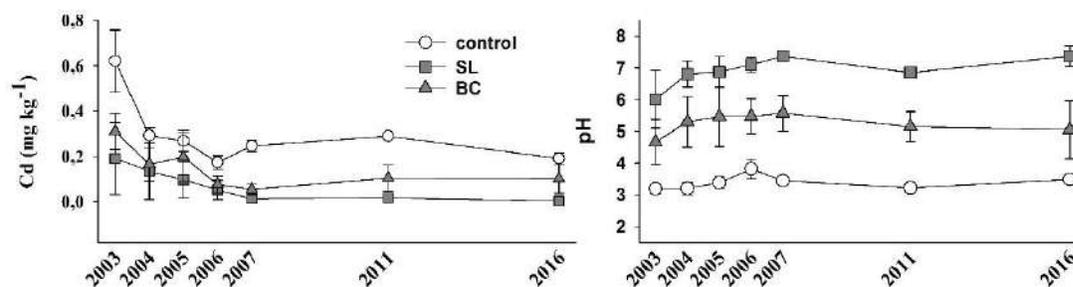


Figure 16. Evolution of Cd availability and pH in soils treated with the amendments. (adapted from Madejón *et al.*, 2018)

Discussion

Raising soil pH is a common practice to remediate acid soils affected by TE pollution, as most elements are less soluble at alkaline conditions. Amendments produced a rapid decrease in soil acidity mainly due to the buffering effect of the BC and the CaCO₃ content of the SL (Madejón *et al.* 2010). Moreover, improvement of the soil chemical properties is especially interesting in this case, where the soil was highly degraded, devoid of its surface litter and upper soil horizon. The amendments increased the organic matter content and enhanced fertility, structure and water retention. The improvement of soil condition affected positively plant cover enhancing plant colonization and plant development (Madejón *et al.* 2018).

Conclusions

The Aznalcóllar mine spill and subsequent large-scale contamination was a challenge for researchers and managers. The results obtained under semi-controlled field conditions and by large-scale soil sampling showed that the phytoremediation can be a feasible alternative to achieve soil remediation goals, but the continuous evaluation and monitoring of the soils is crucial at adjusting the amendment doses maintaining neutral pH conditions over time in order to immobilize TE and to preserve or increase soil fertility.

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3.2.3. Remediation by enhanced natural attenuation of polluted sites in UN field missions: a case study on Onuci, Ivory Coast

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Abstract

The General Assembly (GA) Resolution requests the United Nations (UN) Secretary-General to continue his efforts to reduce the overall environmental footprint of each peacekeeping mission (A/RES/70/286). In November 2016 the Department of Field Supports (DFS) promulgated the department's Environmental Strategy and in July 2017 established the Environmental Technical Support Unit (ETSU) in the UN Global Service Centre (GSC) with the aim to provide technical support solutions that are rapid, effective, efficient and responsible to all field missions.

The consumption of Petroleum Oil and Lubricants (POL) in field missions is inevitable due to their use in generating electricity and operating mechanical equipment to support peacekeeping operations. Through these processes, having a major environmental footprint, a potential soil contamination arises. This paper presents a case study of remediation work conducted by GSC/ETSU on POL polluted sites during the liquidation of a UN field mission in Ivory Coast (ONUCI).

The goal of the project was to reduce the level of Total Petroleum Hydrocarbon (TPH) in polluted soil (36,000 to 75,000 ppm) to a background TPH level of 400-1000 ppm, providing an enabling environment for revegetation of plants. The project entailed the removal of over 1,200 tons of POL contaminated soil from sites and replacing it with fresh soil. The excavated contaminated soil was treated using natural occurring materials derived locally.

Contaminated soil was deposited in a large concrete mixer to tumble and aerate to promote microbe growth, breaking down POL. Two ingredients [chicken extract and Naturally Occurring Surface Active Materials (NOSAM) or palm ash soap (also known as black soap)] were added to the mix to improve the soil condition and accelerate the microbial remediation.

The result showed an over 95% reduction in TPH levels immediately after remediation work, with natural microbial activities ensuring more reduction in TPH within a 14 day period. Native grasses were planted in the restored areas. The case study highlights the importance of implementing low cost remediation techniques in mitigating POL polluted sites within the UN field missions.

Keywords: Natural attenuation, POL, TPH, NOSAM, Chicken extracts, Liquidation

Introduction, scope and objectives

The General Assembly (GA) resolution requests the United Nations (UN) Secretary-General to continue his efforts to reduce the overall environmental footprint of each peacekeeping mission (A/RES/70/286). In November 2016 the Department of Field Supports (DFS) promulgated the department's Environmental Strategy and in July 2017 established the Environmental Technical Support Unit (ETSU) in the UN Global Service Centre (GSC) with the aim to provide technical support solutions that are rapid, effective, efficient and responsible to all field missions.

The consumption of Petroleum Oil and Lubricants (POL) in field missions is inevitable due to their use in generating electricity and operating mechanical equipment to support peacekeeping operations. POL contains a complex mixture of compounds, mainly hydrocarbons which are Non Aqueous Phase Liquid (NAPL). The major constituents of POLs are grouped into four; the saturated compounds, the aromatics, the resins, and the asphaltenes and their main environmental concern if not handled carefully, may pose significant hazards to human health and the earth's ecosystem during all stages of production, processing and consumption. The major causes of environmental damage have been noted to be due to accidental spillages and sometimes-intentional discharge of POL or oily waste to water or land, through regular use (Tonero and Hanke 2016).

USEPA (2018) proposed various technological approaches (chemical, physical, biological and thermal) for treating land contaminated by POL. Most of these treatment technologies are termed innovative due to their limited full-scale applications with respect to POL contaminated soils. In field-scale applications, some of these treatment methods (such as bioremediation, incineration and phytoremediation) destroy the contaminants, are time-consuming and may not be cost effective when handling large volumes of the contaminated material, while others (such as the natural attenuation) reduce the contaminants from soil without chemically modifying them.

Natural Attenuation (NA) relies on natural processes to clean up or attenuate pollution in soil and groundwater (CLU-IN 2018) and works best where the source of pollution has been removed. Thus, buried waste must be dug up and removed using other available clean-up methods and natural processes get rid of the small amount of pollution that remains in the soil (CLU-IN 2018). The soil is then monitored regularly to make sure it is cleaned up.

To enhance the process of NA during remediation of POL polluted sites, Naturally Occurring Surface Active Materials (NOSAM) (surfactant) and chicken extract could be used. The use of surfactant in oil-contaminated soil has been used extensively in research work. Their use in subsurface systems dates back to 1963 when petroleum sulphonates were patented for widespread use in the enhanced oil recovery process (Pope and Wade 1995). Nevertheless, their applications in environmental remediation have gradually been increasingly explored. Surfactants are amphiphilic molecules that consist of a hydrophilic head and a hydrophobic tail, they are the active ingredients found in soaps and detergents with ability to concentrate at the air–water interface and are commonly used to separate oily materials from a particular media (Urum and Pekdemir 2003).

Surfactants increase the aqueous solubility of NAPL by reducing their surface/interfacial tension at air–water and water–oil interfaces. As the interfacial tension is reduced and the aqueous surfactant concentration increased, the monomers aggregate to form micelles (Urum and Pekdemir 2004). This concentration corresponds to the point where the surfactant first shows the lowest surface tension. Many physical properties used to characterize surfactants depend on the CMC such as; emulsion formation, oil solubilization, foaming and detergency, interfacial and surface tensions.

The physical characteristics of POL, such as density, temperature, surface and interfacial tension of oil-surfactant-soil system, will give an idea of the mechanisms behind the reduction of POL from soil, without chemically destroying or modifying them. This will be possible because of the interfacial tension lowering ability of surfactant in oil–water systems.

The aim of the project is to reduce the level of total petroleum hydrocarbon (TPH) in 1200 tons polluted soil from (36,000 to 75,000ppm) to a background TPH level of 400-1000ppm. Therefore, the project objectives include:

- to demonstrate the effectiveness of using NOSAM and chicken extract in the reduction of TPH in polluted soil;
- to establish the initial contamination levels in soil (to enable a risk based remediation approach);
- to reduce TPH level immediately after treatment (testing technical capabilities and assumptions) to an appropriate level;
- to re-vegetate and re-grass the area using native species (to confirm physical/visual remediation).

Material and methods

The following materials were used in this project and the methods adopted were discussed below. Among them, include contaminated soil, chicken extract, Remscan handheld device and a surfactant.

Contaminated Soil

The contaminated soil was readily available at the project site, the soil was recorded to have between 36000 to 75000ppm TPH levels. Contaminated soils were excavated from different locations and stockpile at the treatment center.

Chicken extract

Chicken extract was sourced locally from nearby farmers. The quality of the chicken extract was noted by observing their texture, in terms of mixture with sawdust. Chicken extract is a natural fertilizer that improves soil conditions, because it contains most of the essential plant nutrients that are used by plants such as; nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg). Plant nutrients originate from the feed, supplements, medications, and water consumed by the animals (John, *et al.* 2018).

Surfactant

Natural occurring surface active material (NOSAM), black soap, sourced locally was used as surfactant. The NA process was developed using NOSAM as the surfactant. The black soap has both micro/macronutrients for plants, the ability to reduce the interfacial forces between soil and POL and thus increase the effectiveness of the microbial breakdown of the oil. The concentration of NOSAM solution used throughout the project was 0.5% in the concrete mixer.

RemScan handheld instrument

In order to determine the amount of POL in soil, Total Petroleum Hydrocarbon (TPH), a field handheld tool (RemScan) was used and no further laboratory test was conducted. The RemScan instrument was procured from Ziltek, Australia. The instrument is used for rapid measurement of TPH, utilizes infrared technology, for real-time measurement of petroleum contamination in soil. RemScan allows for simple handheld operation where the extent of TPH contamination across a site can be more comprehensively assessed than would ordinarily be feasible through standard sampling and laboratory testing. Although RemScan is not intended to replace

laboratory analysis, validation testing has shown that the accuracy of the equipment provides sufficient confidence in results (Ziltek 2018).

XRF handheld Analyzer

The analysis of soil for contaminant metals is the most common environmental application of handheld X-ray fluorescence spectrometry. It screens for toxic metals by placing the analyzer directly on the soil, in-situ (Olympus 2018). During this project, it was used in detecting metals for site characterization, contamination tracking and remediation monitoring.

Concrete mixer

A concrete mixer is a device that homogeneously combines concrete, aggregate such as sand or gravel, and water to form concrete (Stretdirectory, 2018). For the purpose of this project, the concrete mixer was used to mix the contaminated soil, Chicken extract, Water and surfactant. It also provided an opportunity for the aeration of the mixture.

Method

A simple and cost effective approach was adopted for the treatment of POL contaminated soils as presented below.

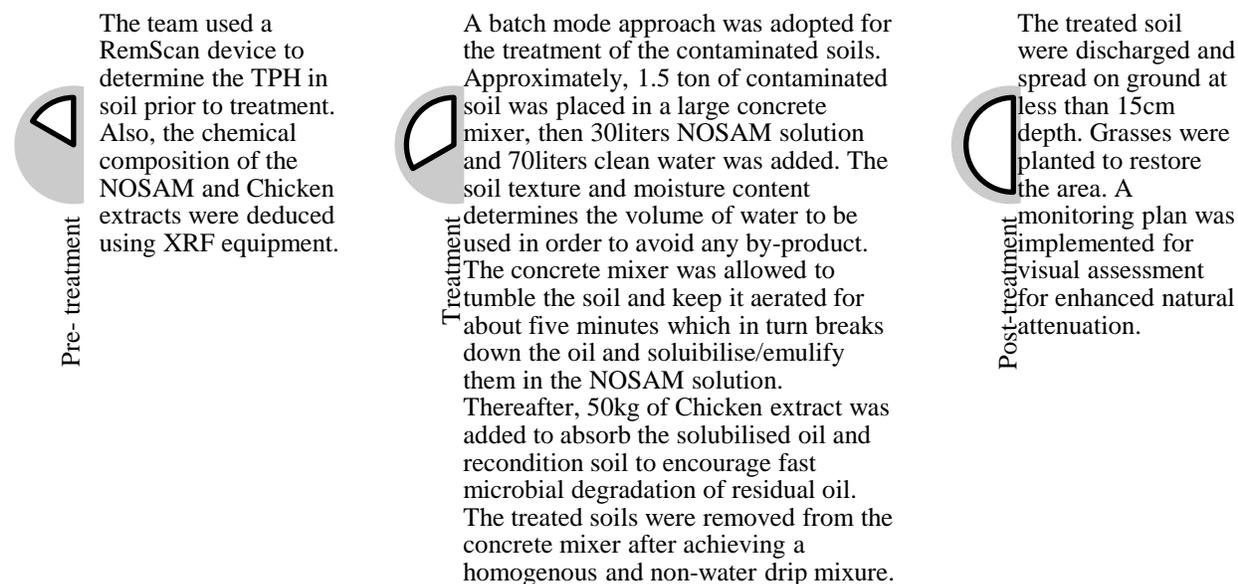


Figure 1. Steps adopted in remediating contaminated soil

Even though the process and treatment method appears simple, the equipment, measurements and adjustments made in amount of materials to mix into the contaminated soil and how long to mix to add oxygen is all calculated. This is further summarized in Table 1.

Table 1. Detailed steps and timeline adopted during the project

Steps		Description	Typical time per site
Pre-treatment	Soil characterization	Soil characterization and calibration of REMSCAN equipment (for measuring TPH and organic/inorganic materials), to ensure on site treatment and regulatory targets are achieved.	5days
	Site screening	Screening of soils for other contaminants, nutrients and inhibitors. Assessing sites conditions (vegetation, weather and climatic issues) to optimized remediation targets.	0.5 day
	Installation of remediation equipment	Installation of remediation equipment, provision of site specific utilities (e.g. water, fuel) and other relevant resources to enable remediation.	0.5 day
Treatment	Evaluation of interactions	Evaluation of chemical interaction between soil and the various contaminants: that is, assessment of oil-soil-water chemistry, degradation potentials, etc. Also, appraisal of potential mechanisms (for soil-NOSAM interaction and soil-NOSAM-Chicken extract interaction) and optimize the process that leads to oil degradation and TPH reduction.	2 days
	NOSAM	Addition of natural occurring surface active materials (NOSAM) derived locally around the remediation area, having the potential to reduce Van-der-Waals force at oil-soil interface.	Part of remediation time
	Remediation (batch process)	Full remediation of contaminated soils using the most appropriate options available on site to achieve remediation by enhanced natural attenuation. This includes a systematic rearrangement of the oil-soil-water geometry in either a vertical or horizontal orientation: to homogenize contaminated soils and reduce localized contaminants; and to enhance aerobic process and microbial activities.	Time for a 1.5tons batch operation is approximately 10 minutes including loading/discharging of soil
Post-treatment	Phytoremediation (revegetation and re-grassing)	The final disposal site for the treated soil is restored and revegetated. The concept of phytoremediation was implemented with plants (trees and grasses) of native species, where practicable. The intention is to speed up degradation of residual contaminants, improve soil conditions and dissolved oxygen levels, and increase ecological rehabilitation.	2 days and as required.
	Monitoring	Scientific equipment to detect the amount of TPH and other contaminants (before/after) treatment. Also, visual assessment was used to determine plant growth and revegetation process. If necessary, samples were planned to be sent to an approved laboratory.	As required

Results and discussion

The real-time concentration of contaminated soils (before and after treatment), chemical composition of Chicken extract and NOSAM were measured during the remediation work and results are presented in Table 2.

Table 2. Results of real time analysis of contaminated soil before and after treatment

Samples		Oil concentration (mg/kg) Analytical Method: Infrared	Key Elements (mg/kg) Analytical Method: XRF					
Date	Description		TPH	P	S	Cl	K	Ca
8/12/2016	Clean soil	400 to 1,400	3,058	ND	ND	ND	ND	37,517
8/12/2016	Highly contaminated soil	97,000	2,250	7,120	ND	1,887	3,744	15,568
8/12/2016	Mixed contaminated soil	22,000 to 65,000	7,828	1,149	590	6,873	1,980	26,685
8/12/2016	NOSAM	17,000 (high concentration)	ND	4,01	841	340,504	ND	690
8/12/2016	Chicken extract	11,000 (with leaves)	40,810	85,33	4,662	377,98	38,24 1	1,425
9/12/2016	Treated soil	6,000	5,643	1,936	468	8,014	264	36,997
10/12/2016	Treated soil	2,560	ND	838	ND	3,961	138	26,362
11/12/2016	Treated soil	4,000	2,659	786	ND	2,975	ND	24,435
12/12/2016	Treated soil	500	3,169	958	322	4,600	996	24,092
13/12/2016	Treated soil	6,000	2,659	786	ND	2,975	ND	24,435
14/12/2016	Treated soil	2,400	3,169	958	322	4,600	996	24,092
15/12/2016	Treated soil	1,890	1,036	578	223	3,670	456	24,018
16/12/2016	Treated soil	3,400						

In order to enhance the remediation process, a dissolved oxygen level of above 9 mg/L should be achieved and maintained, so that natural biodegradation of materials will commence. The chart below schematically describes dissolved oxygen and TPH reduction (an indication only). A combination of other physical parameters such as electrical conductivity, pH, cation exchange capacity, have been monitored for biodegradation effectiveness (Allen *et al.* 2011).

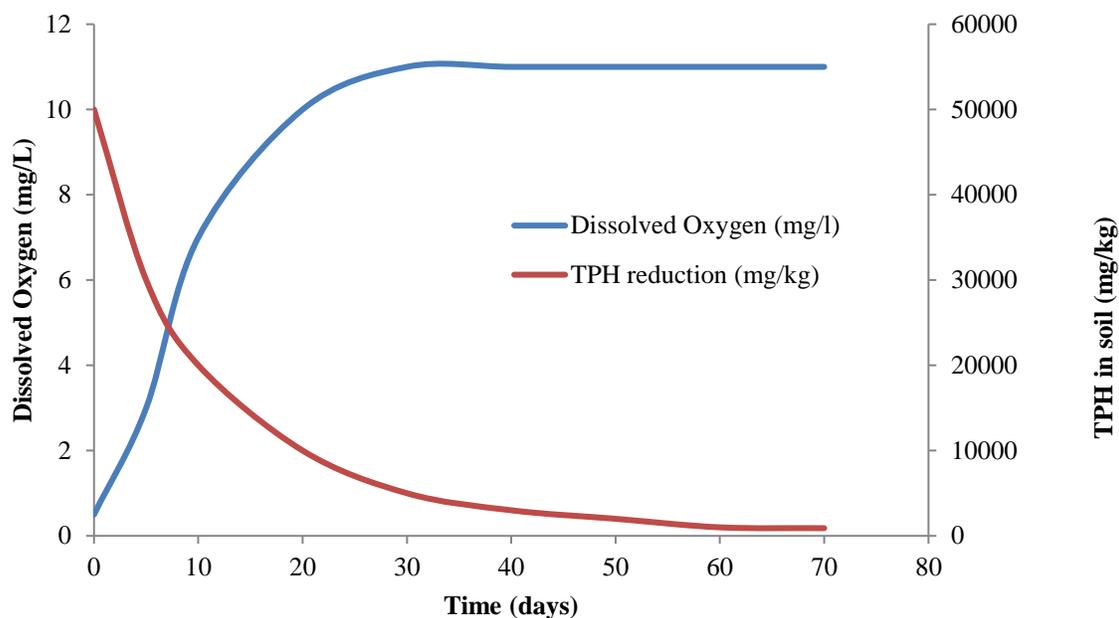


Figure 2. Graph of dissolved oxygen against time and TPH in soil

Using the chicken extract and NOSAM in combination with oxygenation is an effective and low cost way to naturally remediate POL contaminated soils. A high level of oxygen in the soil is desirable for promoting microbe growth. This is a great example of using a scientific approach to treat a problem in a natural and simple way to get good results.

Conclusions

Based on the results, the following conclusions and recommendation were derived.

- Provision of appropriate containment bunds with oil/water separator systems for generators, diesel and oil storage facilities should be mandatory and implemented before storing materials. This is the first step to reduce negative environmental impact through spillage.
- There is a need to increase remediation awareness and its impact in the field missions, as well as capacity building on contaminated soils remediation with low cost and self-sustaining options.
- The preparation of tender packages should be enabled for engaging vendors to carry out remediation activities, with actual work to be done and monitoring of remediation progress.
- There is a need for GSC Environmental Technical Support Team to commence soil characterizations in field missions, especially where containment bunds are not provided for generators, fuels, etc.

- The use of chicken extract and NOSAM will improve the social economic aspects of the local population.

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3.2.4. Reversing soil degradation via phytoremediation techniques in an ex-tin mine and gold mine in Peninsular Malaysia

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Abstract

Soil degradation is a major global concern due to the increasing demand for food production, waste disposals and climate change. In ex-tin mines or gold mines, major challenges include soil erosion, soil organic matter depletion and toxic heavy metal pollutants. This paper addresses the utilization of selected tropical forest species for phytoremediation of an ex-tin mine and a gold mine. Small roots and wood discs of *Acacia mangium* were able to absorb aluminium and iron in higher quantities in an ex-tin mine. Both arsenic and lead were lower in an area planted with *Shorea roxburghii* and *Hopea odorata* compared to a new gold mine dump. Selected forest species assisted in removing toxic heavy metals which paves way for the establishment of new forests as a long term solution for a sustainable environment.

Keywords: soil restoration, mining, heavy metals pollution, afforestation, tropical

Introduction

Sustainable management of natural resources involves “using, improving, and restoring” the productive capacity and life-support processes of soils. This involves minimizing soil degradation and reversing soil degradation via restorative methods (Lal and Stewart, 2010). Soil degradation is caused by adverse changes in soil properties, may it be physical, chemical or biological processes. According to Global Assessment of Soil Degradation (GLASOD), about 1965 Mha of the Earth’s soil has been degraded (Lal and Stewart, 2010). Soil degradation and soil pollution go hand-in-hand especially in areas which have been opened up for mining. Mining dictates one of the oldest industries in Malaysia, which enjoyed a boom in the 1930’s. Although most mining operations have slowed down with the start of the 21st century, some mines are still operative. In the pursuit of obtaining tin ores, gold and iron ores, the landscape suffered a massive transformation that has taxed the soil and natural resources. An estimated 35,650 hectares of ex-mining lands existed in

1995 in Peninsular Malaysia compared to 158, 968 hectares in 1970 (Lim, 1995). Mining creates serious environmental consequences such as erosion, formation of sinkholes, biodiversity loss and soil contamination leading to ground and surface water pollution due to the chemicals used in the mining processes. Soils here are characterized by low levels of macronutrients, high levels of heavy metals, acidic conditions and altered soil texture and moisture properties. Due to the adverse effects, the Operational Mining Scheme, Plans and Record Books Regulations 2007 states the requirements to delineate environmental protection measures and a check and progress of a rehabilitation plan. Thus, an ecological approach of afforestation was suggested. Afforestation is an artificial establishment of forest land on areas which were not forest previously (IPCC, 2006). Before afforestation measures were implemented, care and knowledge on the habitat, soil suitability, and suitable forest tree species and silvicultural techniques were designed to suit the heterogeneous sites. The suitable forest species are chosen based on their ability to phytoremediate the soil and reduce the leakage of harmful elements into waterways. Phytoremediation is a process that utilizes plants to filter and remove contaminants through biological, physical and chemical activities initiated by the plant. The aim of this paper was mainly to highlight if phytoremediation with tropical forest species were viable options for soil restoration.

Methodology

The study was carried out in two different mining areas. The first was an ex-tin mining situated in Hulu Perak (GPS coordinate : 05°25'N, 101°8' E) of 4 hectares. *Acacia mangium* trees were planted in early December 2011 in order to remediate the soils which have been heavily polluted after mining activities (Figure 1). Soil samples were collected in February 2016 up to 100 cm (0-65; 65-80; 80-100 cm) depth. The soils were tested for heavy metal concentration such as aluminium (Al), iron (Fe), nickel (Ni) and copper (Cu). Three trees from the afforested area were felled after 4 years of planting in order to determine the heavy metal concentration in plant tissue samples. Samples were further sub divided into leaves, big roots (from stump to middle point) and small roots (from middle point to root edges) and wood discs. Similarly, soil and plant tissue samples were extracted from a research plot planted with similarly aged *A. mangium* trees in Bukit Hari, FRIM Selangor as a control plot.

The second area was in Central Pahang in a gold mining area (GPS coordinate: 04°07'N, 101°59' E). This gold mine was reported to produce 3.1 million grammes of gold /annum. *Hopea odorata* and *Shorea roxburghii*, two indigenous timber species were selected for afforestation in 2014. Both are categorized as vulnerable and endangered, respectively in the International Union for Conservation of Nature (IUCN) Red list species. In 2017, soil samples were collected from the afforested area (0-30; 30-60 cm) and another control which was a fresh mine dump with similar depths. Soils were tested for arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg). Soil samples from both areas were digested using *Aqua-regia* method (EPA-ROC 1994) for extraction of heavy metals. Heavy metals in plant tissues (ex-tin mine) were extracted using nitric acid and hydrogen peroxide by the microwave digestion method. The concentrations of heavy metals in the plant and soil extracts were then analysed using the Varian 725 Inductive Couple Plasma Optical Emission Spectrometer (ICP-OES).



Figure 1. The ex-tin mine area in Hulu Perak; Left: Before afforestation (2011); Right: After afforestation (2014); From Ahmad Zuhaidi et al., 2018.

Results

From the soil analysis (Table 1), we discovered that the levels of heavy metals such as Ni and Cu were relatively higher in the ex-tin mine. Copper was 34 – 150 folds higher across the soil depths in the ex-tin mine compared to control. Nickel was the highest at 65- 100 cm, where values soared 78- 165% in an ex-tin mine compared to control. The results in Table 2, generally shows that leaves and big roots in the control plot were able to have higher concentrations of Al and Fe. Small roots and wood discs were able to absorb Al, Fe, Ni and Cu in higher quantities in the ex-tin mine. This was prominent especially in the wood discs, where Al and Fe were 2 and 6 folds higher in wood discs samples of the ex-tin mine compared to control, respectively.

Table 1. Soil analysis results from Bukit Hari (control) and Hulu Perak (ex-tin mine)

Total heavy metal concentration	Soil depth (cm)					
	0-65		65-80		80-100	
	Control	Ex- tin mine	Control	Ex- tin mine	Control	Ex- tin mine
Al (%)	9.51	6.14	9.93	1.64	9.96	0.86
Fe (%)	2.22	5.12	2.81	2.11	2.98	1.26
Ni (mg/kg)	6.11	7.5	7.5	21.14	8.27	21.89
Cu (mg/kg)	1.45	50.35	0.9	79.41	0.53	79.1

Table 2. Plant tissue analysis results from Bukit Hari (control) and Hulu Perak (ex-tin mine)

Total heavy metal concentration	Plant tissue samples							
	Leaves		Big roots		Small roots		Wood discs	
	Control	Ex- tin mine	Control	Ex- tin mine	Control	Ex- tin mine	Control	Ex- tin mine
Al(mg/kg)	120.62	0.02	265.34	0.26	trace	0.48	26.46	53.14
Fe (%)	197.9	0.02	114.13	0.15		0.28	22.4	132.79
Ni (mg/kg)	1.55	1.47	1.03	2.58		5.12	0.59	0.77
Cu (mg/kg)	9.09	9.75	1.88	3.16		4.86	0.2	1.88

Results from the gold mine showed that the range values for As were markedly lower in an afforested area compared to a fresh mine dump (Table 3). Lead (Pb) was also relatively lesser (77%) in an area planted with *Hopea odorata* and *Shorea roxburghii* compared to the control. We were unable to retrieve tissue samples for analysis due to mine restrictions but the preliminary soil data was promising for further investigations.

Table 3. Soil analysis results from Central Pahang goldmine

Total heavy metal concentration in soil (mg/kg)	Mine dump	Afforested
As	910.98–1042.56	11.72–17.93
Cd	3.62–4.26	6.42–6.46
Pb	14.63–21.68	8.81–18.31
Hg	trace	trace

Discussion

Our results indicate that the metals of concern in this ex-tin mine were Ni and Cu, as the soil results showed high amounts, especially at the deeper region of soils (Table 1). Both Ni and Cu values were relatively lower than the maximum value for Malaysian soils (114 and 73.5 mg/kg) as reported by Fauziah *et al.* (2001).

The excessive amounts of Al and Fe observed in the leaves and big roots in the control plots are owed to the inherent properties of the soils at the site (Table 2). Since the soil pH values in the ex-tin mine was acidic (2.4–3.3, data not shown), it was common that metal solubility increased with lower soil pH (Alloway, 2013), and displayed higher quantities in this location. Since Al and Fe were quite notable in wood discs, these plant parts were more efficient in storing heavy metals in the ex-tin mine during the initial period. Juvenile trees tend to translocate heavy metals slowly to plant upper parts (Ma *et al.* 1997). Thus, the amount of heavy metals were detected in lesser quantities in leaf samples.

Arsenic values more than 12 mg/kg is considered hazardous to human health (Canadian Council of Ministers of the Environment, 2001) and our data in the afforested area shows that afforestation was able to reduce As values up to 11.72 mg/kg (Table 3). Arsenic in the gold mine dump was comparable to a gold mine in Ghana which reported values up to 1700 mg/kg (Bempah *et al.* 2013). Soil Pb values was within permissible levels (Fauziah *et al.* 2001) for Malaysian soils, and the decreasing trend of heavy metals in afforested areas show the importance of phytoremediation using forestry species.

Phytoremediation methods, particularly phytoextraction, have been used on a variety of metal contaminants. Since soil rehabilitation is a requirement for degraded soils; phytoremediation using forestry species assist in various ways. Acacias have the potential to rehabilitate the soil through absorption and storage of heavy metals such as zinc, lead, copper, cadmium and chromium (Nik *et al.* 2012) in its leaves, shoots and roots (Veronica *et al.* 2011). Acacia trees can yield 550 kg/m³ wood density with moderate strength for paper and pulp industries and furniture production (Ahmad Zuhaidi *et al.* 2015). Indigenous timber species such as *Hopea odorata* and

Shorea roxburghii are not well known for timber production due to lack of research but they have been used for landscaping and medicinal purposes. Current efforts show these IUCN Red List species being introduced to ex-tin mines (Ho *et al.* 2017; Ahmad Zuhaidi *et al.* 2018) as a germplasm depository, greening strategy and for conservation purposes as they tend to withstand drought and poor soil conditions.

Conclusions

Small roots and wood discs of *Acacia mangium* were able to absorb Al and Fe in higher quantities in the ex-tin mine compared to control. Both As and Pb concentrations were lesser in areas afforested with *Shorea roxburghi* and *Hopea odorata*. In order to sustain soil 'health' and to combat soil pollution of heavy metals, soil quality needs to be restored. This can be done by selecting suitable forestry species that not only serve as phytoremediators but can create a conducive environment for successful establishment of other flora and fauna that enhances soil quality via litterfall, microbial decomposition, improvement of soil structure and soil moisture content.

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3.2.5. Remediation of contaminated soils using innovative methods

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Abstract

The complex of methods for technogenic contaminated soils remediation was elaborated as a result of long-term investigations on contaminated soils and areas in Ukraine. List of methods for remediation of contaminated soils includes: 1) method of heavy metals detoxication in the soil-plant system; 2) method for predicting the ecological condition of soil in the technogenic pollution zones; 3) method for technogenic polluted with heavy metals soil remediation; 4) method for ecological rehabilitation of technogenic soil contaminated primarily with cadmium, lead, zinc and chromium; 5) method for ecological rehabilitation of technogenic soil contaminated primarily with cadmium, zinc and copper; 6) method for phytoremediation of technogenic heavy metal contaminated soils for effective use; 7) method for soil system - soil biota - plant bioremediation if contaminated with heavy metals as a factor of chemical and biological degradation; 8) method for determining total content of oil and oil products in soils for monitoring contamination and effectiveness of remediation. Elaborations are protected by patents for utility models documents and invention document.

Keywords: soil, contamination, remediation, innovative methods

Introduction, scope and main objectives

Increasing environmental pollution has resulted in contamination of all its components and migration of pollutants in trophic chains, which is reflected in the decrease especially of soils quality and increase degradation of soil cover [1-2].

The elaboration of new and improvement of existing methods for the remediation of chemically degraded soils, restoration of their structure, function and properties is an actual problem in the conditions of increasing anthropogenic loads on the soil cover, the deterioration of the ecological state of different genesis soils. The bases for solving this problem are the new methodological approaches for chemical, physical and biological remediation of contaminated soils [3]. Elaboration of methods, as a result of innovative activities in the field of rehabilitation and protection of soils from pollution, should include a requirement for patent information research trends of investigation in the chosen direction.

Restoring the quality of heavy metals (HM) technogenic contaminated soils for using of different methods of remediation is a modern trend that is developing in the world and in Ukraine. Prospects for effective ecological management of soil resources are based on the basic concept of resource management - management through innovation, taking into account that the methods of contaminated soils remediation should provide ecologically safe soil condition improvement without cardinal interference with natural processes, minimal influence to the physical and chemical composition of soils; the use of methods should be safe, their widespread introduction will reduce the cost of remediation works carrying out.

The purpose of the research is to elaborate a complex of remediation methods for the restoration of the technogenic contaminated soils quality. Research objectives: to elaborate chemical, physico-chemical and biological methods of effective remediation of contaminated soils for optimization and restoration of the soils ecological state in areas with intensive influence of atmospheric pollution, while increasing the bioenergy potential and buffering capacity of soils, activating self-purification of soils from the HM for accelerating microbiological processes, physico-chemical adsorption of HM various classes of danger by the complementary introduction of organic and inorganic type of structure improvers; expansion of the spectrum of HM migration incapable in contiguous to the soil environment.

Methodology

Methods elaboration included the stages:

- 1) The patent investigations stage according to DSTU 3574 and DSTU 3575. The object of research – methods of soil remediation; separate operations (stages) of the method are independent patentable subject matter; methods for their preparation and application; the equipment used in the methods; methodological approaches for the remediation of contaminated soils of different genesis. Research methods – expert evaluation, analyzing and comparison.
- 2) The field stage – soil-geochemical surveys in conditions of constant exposure of atmospheric emissions sources of HM pollution (Zmijivska TPP of PJSC "Tsentrenergo" NAC "Energy company of Ukraine"; PAO "Baltsem" Eurocement-Ukraine in Kharkov region; JSC "Ukrzinc" and JSC "Avdiivka coke plant", Mironovskaya TPP and Starobeshevskaya TPP of PJSC "Centrenergo" in the Donetsk region); series of microfield researches in zones of technogenic pollution, laboratory and vegetation experiments. Research methods – universal scientific methods, the theoretical analysis methods, system and ecosystem approaches, and landscape-geochemical methods. Samples from the arable (0-20 cm) soil layer in accordance with DSTU 4287.
- 3) The analytical stage, using laboratory-analytical methods of research to determine the levels of Cd, Pb, Ni, Cr, Zn, Co, Cu, Fe, Mn mobile forms content in soils using atomic absorption method and extractants of acetate-ammonium buffer solution with pH 4.8 (DSTU 4770.1 – DSTU 4770.9) and 1N HCl according to MVV 31-497058-016, DSTU 7607, DSTU 7831, DSTU 7832, DSTU 7851, DSTU 7852, DSTU 7853. 4) The desk stage – the assessment of HM content and of soils micronutrient status conducted in accordance with applicable regulatory and methodological base for expert assessment of the current normative documentation, using established HM background levels for soils of different natural-climatic zones of Ukraine [4]. The obtained analytical data were statistically treated with the modules correlation, variance analyses as part of the *Statistica 10.0* package.

Results

The complex of methods for technogenic contaminated soils remediation was elaborated as a result of long-term investigations in contaminated areas in Ukraine. Elaborations are protected by patents for utility models documents. List of innovative methods includes:

1. Elaborated method for HM detoxification in the soil-plant system (*patent for utility model № 20299 UA, 2007* [5]). *The essence of the method:* the process of geochemical and biochemical antagonism, leads to active detoxification of the HM, significant reduction in the pollution of plant products. The method includes the introduction of reclamation and mineral fertilizers, differs in

that the contaminated soils additionally introduce a mixture inactivates of organic and inorganic nature, and the solution of metal antagonists is introduced into the soil and sprayed to plants in the active growth phase, and this solution is used in the following ratios: Cd-Fe - 2: 1, Ni-Zn - 3: 5, Pb-Zn - 3: 5, Cr-Fe - 2: 1. *The advantages of the method:* reduction of HM toxicity in high-buffer soil-plant system on the basis of activation of adsorption and ion exchange processes in the soil system due to the using of ameliorants of organic and inorganic nature, the principle of antagonism in the soil-plant system. *The technical result:* the introduction of a mixture of inactivates of organic and inorganic nature, and of solution of antagonists of metals directly into the soil and spraying plants in the active growth phase with this solution, taken in a certain ratio, amplifies and accelerates the mechanisms of self-purification, optimizes the microelement content of plants, localizes the cell of toxic pollution not only by area, but also vertically, which provides a delay in the possible migration of HM in contiguous environments.

2. Elaborated method for forecasting the ecological state of the soil in the zone of technogenic pollution (*Ukrainian patent for invention № 83563 UA, 2008 [6]*). *The essence of the method:* sampling, analysis, mathematical treatment of the obtained results are carried out not only in the soil, but also in plants, and, based on the results of the data obtained, for each type of soil, plot the crop dependence on the level of pollution for each of its elements and use them for soils and pollutants for the determination of the soils ecological state and prediction of the impact of pollution on yield and its quality and the necessity of attracting soil remediation methods. *The advantages of the method:* universality, method is suitable for all types of technogenically contaminated soils with different buffering properties, self-cleaning ability and levels of different nature pollutants content; efficiency for a comprehensive study of the state of the soil-plant system under pollution conditions, prediction of its recovery, expressiveness for the determination of the limiting levels of soil pollutants toxicity, the ranges of critical, admissible and optimal values of the pollutants, the objective assessment of the safe and dangerous levels of contamination, the determination of the optimum for the toxicity in the soil-plant system, the initiation of the need for detoxification measures. *Technical result:* increase of accuracy of pollution levels determination by expanding sources of information on the degree of the soil-plant system contamination, in which it is necessary to carry out remediation measures, creating an express method for determining these levels in the soil-plant system, while reducing the complexity and determining the zones of expected yield.

3. Elaborated method of HM polluted soils remediation (*patent for useful model № 85002 UA, 2013 [7]*). *The essence of the method:* by using a mixture of sodium humate with the addition of superphosphate, lime or organic substances depending on the nature and type of soil contamination, provides the effective remediation of polluted soils, increases plant resistance to pollution, restores their productivity. *The advantages of the method:* allows to reduce the toxicity of the HM in the soil-plant system due to the acceleration of biochemical and physicochemical processes in soils, that ensures the activation of self-purification of soils different buffer properties to HM under the different levels of polyelemental contamination of Cd, Pb, Ni, Cr, and Zn in the areas of intensive impact of permanent sources of anthropogenic emissions; provides the efficiency of application in different soil and climatic conditions by the reduction of resource costs to conduct remediation with facilitating of the restoration of the soil natural properties, improving plant tolerance to pollution and to restore their productivity. *The technical results:* by expanding the spectrum of soils improves by introducing the additional detoxicants mixture of organic and inorganic nature and their combinations, accelerating of the soil biochemical and physical-chemical processes, allows a significant acceleration of the recovery of the natural properties of degraded soil, improvement of the ecological state of the environment are provided.

4. Elaborated method for ecological remediation of technogenic soil contaminated primarily with cadmium, lead, zinc and chromium (*patent for useful model N° 85544 UA, 2013 [8]*). *The essence of the method:* in the proposed method by the using of ferrous sulphate with application of vermicompost as an activator of soil self-purification and soils improver of prolonged action in soil polyelemental contamination mainly Cd, Pb, Zn, Cr according to the level of pollution; restoring of the soil natural properties, creating a reserve of soil nutrients which ensures restoring of plant productivity are provided.

The advantages of using the method: allows to reduce the HM toxicity in the soil-plant system by the acceleration of soils microbiological, physical and chemical processes, what ensures the activation of their self-purification with different levels of HM pollution in the areas of intensive impact of permanent sources of anthropogenic emissions; method provides the opportunity to obtain objective assessment of the polluted soils remediation effectiveness under the HM influence of different classes of hazards and levels of technogenic pollution. *The technical results:* by the acceleration of microbial processes, physical and chemical adsorption of HM of the different classes of hazards by complementary introduction of organic and inorganic type soil structure improvers, an effective remediation of industrially polluted soils optimization and restoration of the soil humus, expands the HM range that unable to migrate into the adjacent soil environment is provided.

5. Elaborated method for ecological remediation of technogenic soil contaminated primarily with cadmium, zinc and copper (*patent for useful model N° 92170 UA, 2014 [9]*). *The essence of the method:* a one-time of nitrogen fertilizer application with a sorbent- ameliorants in the soil, as a sorbent-ameliorants compounds of ferrous sulfate (II) and phosphate mineral fertilizers are used in accordance with reasonable and dangerous levels of soil pollution. By the using of ferrous sulfate (II) and phosphate fertilizer compounds in a ratio of gradation of soil pollution as a sorbent-ameliorants, enhances the effectiveness of their environmental rehabilitation and restoration of their natural buffer properties by influence on the migration processes of HM various hazard classes and trophic mode in soils and plant productivity with higher rates of environmental safety. *The advantages of the method using:* the increasing ability for HM physical and chemical adsorption and a significant reduction of their toxicity in soil-plant system with different levels of pollution primarily by Cd, Zn and Cu in the areas of intensive impact of permanent sources of anthropogenic emissions, what contributes the effective environmental rehabilitation of contaminated HM soils and restoration of the natural soil properties and plant productivity with the best indicators of environmental security; decrease the resource cost and the complexity of implementation procedures for environmental rehabilitation of HM contaminated soils by precision in determining the ratio of the doses soil structure improvers of inorganic type and fertilizer, and simultaneously reduce the cost of material resources as a result of effective influence of the proposed composition from the first year of application and the prolongation of up to 5 years; ensuring the improvement of the trophic regime HM polluted soil.

6. Elaborated method for HM contaminated soils phytoremediation for their effectively use (*patent for utility model N°96936 UA, 2015 [10]*). *The essence of the method:* the extension of the spectrum of use as phytoremediators dominant herbaceous wild species of competing plants of the families *Asteraceae*, *Fabaceae* and *Poaceae* with their necessary alternation every 2 years, then biological remediation process intensification, increasing its effectiveness while minimizing the necessary costs for soil clean up over the full rotation. By expanding the application spectrum of plants different competitive families with properties remediation directed action in accordance with the nature of soil contamination, which ensures the reduction prices of soil clean, optimizes its use by shortening the period of biological remediation and restoring the quality of contaminated soils while avoiding unnecessary processing load on the soil. *The advantages of the*

method: providing of necessary costs minimization for soil remediation by cost savings, lubricants seed and fuel materials for the simultaneous implementation of ecologically safe way of using the competitive families, characterized by different levels of phytoremediation activity, which ensures the effective impact of the proposed competitive combinations of plants certain families already from the 1st year of continuous use and remediation of contaminated soils with increasing cleaning depth directly in the area of HM pollution (*in situ*). *The technical results*: by expanding the range of using the phytoremediators of different competitive families with remediation properties directed action in accordance with the level of soil contamination, provides a cheaper cleanup of soil, optimizing its use by reducing the period of contaminated soils biological remediation and simultaneously avoiding unnecessary processing loads on the soils.

7. Elaborated method for bioremediation of soil - soil biota - plant system, polluted by HM as a factor of chemical and biological degradation (*patent for utility model N^o 100982 UA, 2015* [11]). *The essence of the method*: through the use of the fungus preparation *Trichodermin BT* new property intensified bioremediation processes and reclamation of HM technogenic contaminated soils, increased immune status and productivity of plants and improving their quality, which ensures bioremediation effect, the decrease of fungus preparation use while increasing biological effectiveness. *The advantages of the method*: promotion of the implementation of ecologically safe way soil bioremediation by using fungus preparation *Trichodermin BT*, which provided the environmental stabilization of contaminated soil-plant-microbiocenosis system with simultaneous neutralization of pollution negative processes and improvement of the soil ecological status by enhancing natural soil biological potential, plant productivity; preserving of the soil natural biological properties by creating optimal conditions for the formation of soil micro - and fungal organisms with higher levels of biological activity for effective bioremediation of HM-contaminated soils and restore of their quality. *The technical results*: improvement of bioremediation method of HM technogenic contaminated soil by the expansion of the fungus preparation bank as natural remedies with the fertilizers effect, contributing to the bioremediations effect, ecological stabilization of environment with simultaneous activation of the soil biological potential, plant productivity, and resource efficiency.

8. Elaborated method for oil and oil products total content determines in soils for contamination monitoring and effectiveness of remediation (*patent for useful model N^o 103978 UA, 2016* [12]). *The essence of the method*: by the using of established thermogravimetric curves of optimum temperature and time intervals of the thermal decomposition of contaminated soil sample, determination of the total losses of its mass with the applicable formula, quantitative determination of total content of petroleum hydrocarbons and petroleum products in the soil with increased accuracy and quick testing were the method of diagnosis and effectiveness of contaminated soil remediation. *The advantages of using the method*: the algorithm of the method is possible to implement in the absence of unpolluted counterpart (a survey on the route of the pipeline, or in terms of the soil cover diversity), on samples contaminated by oil and oil products of the soil when their mass fraction is less than 1% and with different humus content and granulometric composition; the ability to identify quantitative values of light fractions of oil and residual hydrocarbons that are characterized by low mobility; software diagnostics effectiveness of polluted soil remediation. *The technical results*: improvement of method of determining total content of oil and oil products in soils by a combination of individual components of the known methods of thermogravimetry and gas chromatography, the distribution patterns of mass change of the sample under the action of thermal effects in a new class of objects with the simultaneous production of a rapid method for the determination of petroleum hydrocarbons total content in the soil, improving its accuracy and selectivity, simplicity of soil samples algorithm analysis to determine pollution and obtaining of savings in resources using.

Conclusions

New methods are an integral part of the environmental rehabilitation of technogenic contaminated soils methodology. Elaborated methods should be used in the ecological management of soils, environmental monitoring of their technogenic contamination, various purposes and soils use; for reduce man-made and processing loads on soils of different genesis, the intensity of the degradation processes and recovery soils properties with improving of the fertility and soils quality; in research practice - for the elaboration of innovative remediation measures of contaminated soils and areas.

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3.2.6. Copper phytoremediation potential of wild plant species growing in the mine polluted areas of Armenia

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Abstract

Nowadays the pollution by heavy metals from mining industry is one of the biggest threats to ecosystems and human health. The detection of phytoremediation potential of wild plant species in areas polluted by heavy metals will enable the use of eco-friendly remediation methods in these territories.

In this study, sixteen native wild plant species grown in Cu contaminated soils of mining region in Armenia were investigated to reveal their phytoremediation potential. During the investigation soil main characteristics affecting Cu accumulation capability of plants were also determined. In roots (dry weight) of dominant plant species growing in Cu contaminated areas the content of copper varied between 55 mg/kg (*Hypericum perforatum*) and 775 mg/kg (*Thymus kotschyanus*), and in shoots of plants - in the range from 33 mg/kg (*Teucrium orientale*) to 243 mg/kg (*Phleum pratense*). Since the Cu accumulation capability of plants depends not only on physiological peculiarities of plants but also on the content of Cu_{bioavailable} in the soil, the studies were carried out in this direction and it was found that the high contents of humus and clay in the soil facilitated the decrease of ratio Cu_{bioavailable}/Cu_{total} and as a result - the decrease of Cu accumulation capability of plants.

Thymus kotschyanus, *Phleum pratense* and *Achillea millefolium* had the highest phytostabilization potential from all studied plant species so long as high BCF_{root} and low TF values were registered in these plants, and further field and laboratory experiments are planned to confirm this useful ability for remediation of copper contaminated soils.

Keywords: Mine pollution, Copper accumulation, Native wild plants, Phytoremediation, Bioconcentration factor of root, Armenia

Introduction, scope and main objectives

Considering the pace of economy development, particularly of mining industry, toxic metals contamination had gradually become a major problem not only worldwide (Chopin and Alloway 2007; Moreno *et al.* 2007; Farmaki and Thomaidis 2008; Peng *et al.* 2009), but also in Armenia. Areas near mining activities can become polluted by the transfer of heavy metals that have strong toxic impacts both on ecosystems (Bech *et al.* 2012) and on human health (Sing and Sing 2010). With swift mining industry development without enough attention paid to ecological problems, the soils of risky regions in developing countries such as Armenia were polluted with heavy metals including copper and posed different ecological problems in last years.

In view of previously mentioned the remediation of soils contaminated by heavy metals is an actual environmental and social problem in Armenia. Traditional remediation methods, such as soil excavation, burial, replacement, dilution, organic fertilizing, use of absorbents, washing with chelators and strong acids (Garcia-Sanchez *et al.* 2002; Fernández-Caliani and Barba-Brioso

2010; Cheng *et al.* 2015), cannot remediate heavy metals fully from the soil, moreover in certain cases they can be environmentally destructive and degrade the biodiversity, structure and fertility of soil (Chen *et al.* 2000; Barančíková *et al.* 2004; Muddarisna *et al.* 2013).

Therefore, the traditional methods of soil remediation must be replaced by alternative eco-friendly (green) and sustainable methods such as phytoremediation (Lasat 2002; Ghosh and Singh 2005; Abreu *et al.* 2008). Phytoremediation that uses the ability of plants to concentrate and metabolize different heavy metals from the soil in their tissues appears to be very useful for the remediation of contaminated soils (Alkorta and Gurbisu 2001; Zhi-xin *et al.* 2007). This method is acceptable by the society, does not require heavy expenses and at the same time can have a positive impact on the stability of ecosystem.

Therefore, the objectives of present study were as follows: (1) to identify the Cu accumulation capability of native wild plant species grown in contaminated soils of mining region, (2) to determine the characteristics of soil appreciably affecting Cu accumulation capability of plants, (3) to ascertain the plant species that are more acceptable for phytostabilization and that are more suitable for phytoextraction purposes depending on the kind of tissue where they accumulate Cu.

Methodology

Site description

The study area is situated in the south part of Armenia, near Kajaran town in the surroundings of Zangezur Copper and Molybdenum Combine. The soils of study region belong to mountain cambisol. The combine delivered its first production in 1951. It is operated by open-cut method. Currently approximately 22 million tons of ore is being processed annually. The combine extracts and processes the copper and molybdenum ore.

Soil and plant sampling and analysis

Based on our previous studies the most risky three sites (Q-F-01 with coordinates N 39° 09,369' and E 46° 08,43'; Q-OM-03 with coordinates N 39° 09,135' and E 46° 07,879'; Q-F-11 with coordinates N 39° 09,241' and E 46° 08,52') and one checking (unpolluted) site (Q-CONT with coordinates N 39° 13,018' and E 46° 13,96') were chosen for investigation. Soil sampling was performed from the topsoil (0–25 cm depth) directly nearby the plants. For determination of copper total content the soil samples were digested with mixture HNO₃+HClO₄+HF (5:1:1, v:v:v) (Baker and Amacher 1982). Cu content was measured by AAS. For determination of bioavailable copper in the soil the acetic acid was used (He *et al.* 2013).

Plant sampling was done in vigorous growth stage (in June). Three replicates were done for each plant species within the sampling area. The plants were separated into root and shoot parts. Hereupon the underground and aboveground tissues of plants were dried at 70°C to reach the constant weight. The samples were digested by mixture of HNO₃ and HClO₄ (4:1, v:v) (Zemberyová *et al.* 2006; Qu *et al.* 2008). In the resulting solution the content of total copper was determined by AAS.

Phytoremediation potential of plants

Two indices, the bioconcentration factor of root (BCF_{root}) and translocation factor (TF), were determined to assess phytoremediation potential of plants (Mertens *et al.* 2005; Wang *et al.* 2007).

BCF_{root} may be used to assess the copper accumulation capacity of root. BCF of root was calculated by following equation (Marchiol *et al.* 2013):

$$BCF_{root} = Cu_{root}/Cu_{soil} \quad (1),$$

where Cu_{root} is the copper concentration in harvested plant roots and Cu_{soil} is the bioavailable copper concentration in soils.

The TF was calculated using the following equation:

$$TF = Cu_{shoot}/Cu_{root} \quad (2),$$

where Cu_{shoot} is the copper concentration in harvested plant shoots and Cu_{root} is the copper concentration in harvested plant roots.

Results

Soil characteristics of study areas

Findings of investigation of soil samples from four study areas revealed that pH of soils fluctuated in the range 7.6-8.2 that was sufficient for normal growth and development of vegetation (Tab. 1). Humus content in studied territories was fluctuating in the range 1.8-6.48%. As far as the deposit in study area is a copper-molybdenic mine and copper is the main pollutant of soils in this territory, the contents of total and bioavailable copper in soil samples were also determined. In the studied three risky areas the highest contents of total as well as bioavailable copper were registered in the site Q-F-11 that is situated at a distance of approximately 300 meters from ore mills of processing plant (the ore dust spread to surrounding territories) and is subjected to negative influence of mining industry the most.

Table 1. Characteristics of plant root zone soils in three risky and one checking study sites (mean \pm SE)

Soil characteristics	Q-F-01	Q-OM-03	Q-F-11	Q-CONT
pH	8.2 \pm 0.2	7.6 \pm 0.2	7.9 \pm 0.3	7.8 \pm 0.1
Humus content, %	1.80 \pm 0.22	4.34 \pm 0.34	3.61 \pm 0.40	6.48 \pm 0.38
Sand, %	45 \pm 4	16 \pm 2	40 \pm 4	31 \pm 4
Silt, %	35 \pm 3	45 \pm 5	39 \pm 3	39 \pm 4
Clay, %	20 \pm 2	39 \pm 4	21 \pm 1	30 \pm 3
Cu_{total} , mg/kg	1951.25 \pm 184.7	888.8 \pm 71.4	3480.3 \pm 209.8	71.6 \pm 11.0
$Cu_{bioavailable}$, mg/kg	148.4 \pm 10.8	82.4 \pm 8.9	494.4 \pm 24.1	3.2 \pm 0.5

Copper accumulation by dominant plants in three risky and one checking sites in surroundings of Zangezur Copper and Molybdenum Combine

Copper concentrations in dominant plant shoots and roots collected from three risky and one checking sites in surroundings of Zangezur Copper and Molybdenum Combine are shown in Figure 1. The common eight species of plants per area were gathered in three risky study areas: golden locoweed (*Astragalus aureus*), lacustrine locoweed (*Astragalus uraniolimneus*), oriental germander (*Teucrium orientale*), common yarrow (*Achillea millefolium*), mugwort (*Artemisia vulgaris*), timothy-grass (*Phleum pratense*), thyme (*Thymus kotschyanus*) and small tumbleweed mustard (*Sisymbrium loeselii*) in area Q-F-01, *Artemisia vulgaris*, red clover

(*Trifolium pratense*), *Achillea millefolium*, yellow sweet clover (*Melilotus officinalis*), dog rose (*Rosa canina*), coltsfoot (*Tussilago farfara*), *Sisymbrium loeselii* and St John's wort (*Hypericum perforatum*) in area Q-OM-03, *Phleum pratense*, *Thymus kotschyanus*, *Astragalus aureus*, *Astragalus uraniolimneus*, feverfew (*Tanacetum parthenium*), *Achillea millefolium*, Caucasian stoncrop (*Sedum caucasicum*) and oriental chervil (*Astrodaucus orientalis*) in area Q-F-11. Areas Q-F-01 and Q-F-11 resemble by vegetation that is conditioned by similar soil characteristics as well as by their natural-climatic peculiarities. Only one common plant species (*Achillea millefolium*) was found in all three risky areas. Among the plant species sampled in the area Q-F-01 the highest concentration of copper in root was found in *Thymus kotschyanus* (718 mg/kg), while the highest concentration of copper in shoot was found in *Phleum pratense* (243 mg/kg). In the area Q-OM-03 the highest concentration of copper in roots of plants was revealed in *Achillea millefolium* (325 mg/kg) and in shoots – in *Trifolium pratense* (100 mg/kg). In the area Q-F-11 the highest concentrations of copper were found in roots of *Thymus kotschyanus* (775 mg/kg) and in shoots of *Tanacetum parthenium* (127 mg/kg), respectively.

Ten plant species (in total) found at least in one from studied risky areas were sampled in the area Q-CONT for comparative analysis and collation of this unpolluted territory with three risky areas. Only *Achillea millefolium* was found in all study areas (Figure 2).

In roots and shoots of all plants sampled in unpolluted area the content of copper was lower than in the same plant species growing in any of risky areas. This difference is conditioned not only by high contents of copper in the soils of risky areas but also by other properties of soil as well as by physiological peculiarities of plants indeed. The appreciable exceeding of copper content in shoots as compared with control was registered in *Tanacetum parthenium* (3 times, area Q-F-11), in *Achillea millefolium* (2.85 times, area Q-F-11) and in *Sisymbrium loeselii* (2.53 times, area Q-F-01). This difference became more evident in roots of plants, particularly in *Thymus kotschyanus* (18.55 times in area Q-F-01 and 20.03 times in area Q-F-11).

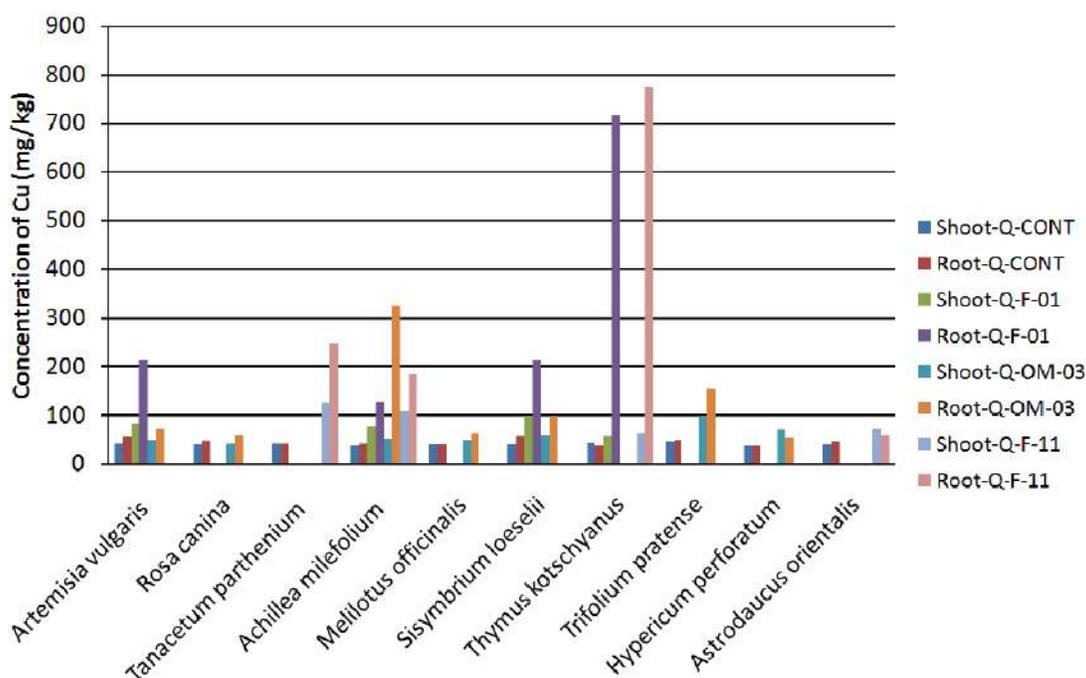


Figure 2. Copper concentrations in shoots and roots of some plant species growing in the three risky and one checking sites

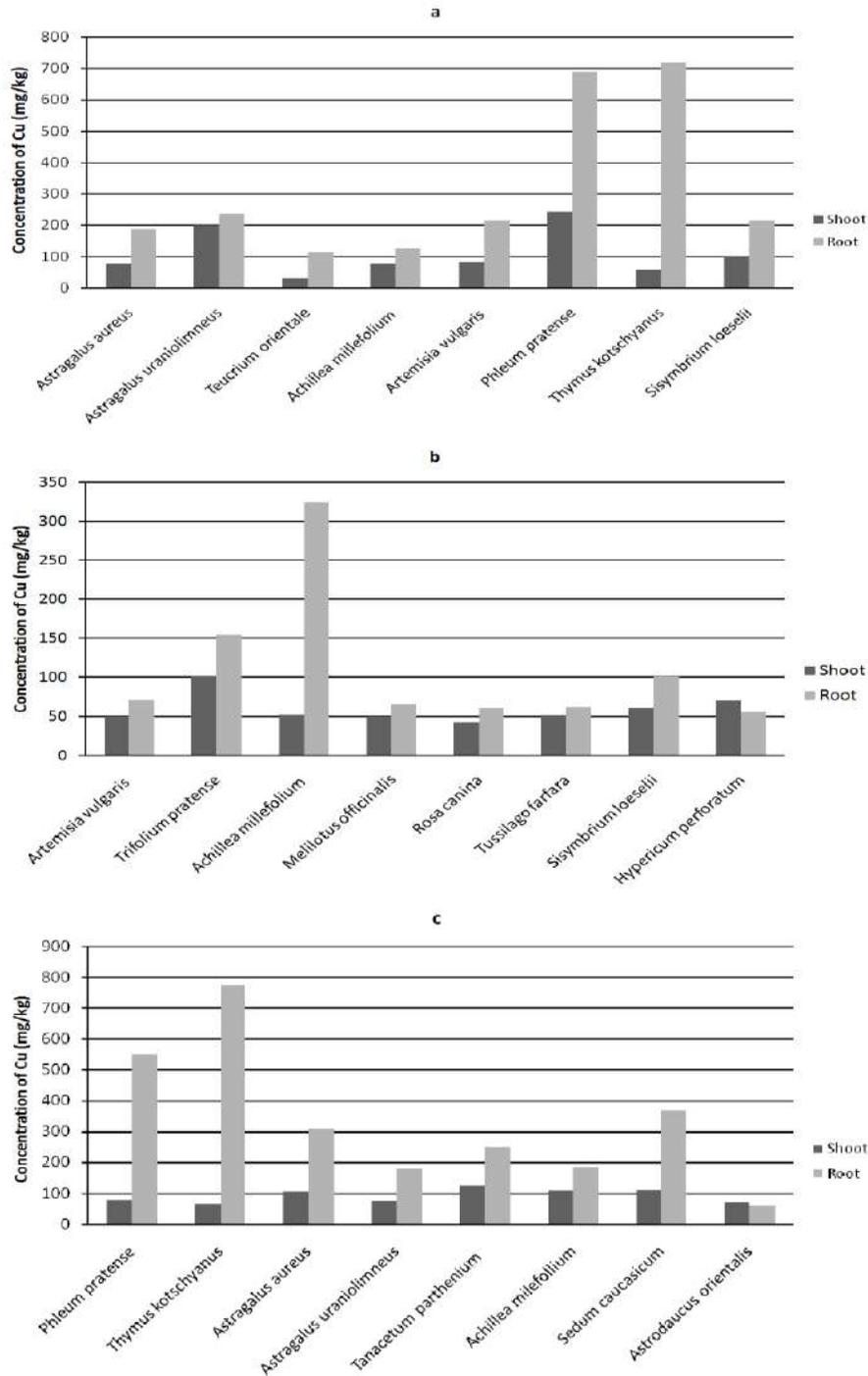


Figure 1. Copper concentrations in shoots and roots (dry matter) of dominant plants collected from three risky sites of Zangezur Copper and Molybdenum Combine surroundings (**a** - Q-F-01; **b** - Q-OM-03; **c** - Q-F-11)

Discussion

Dependence of copper bioavailability on some soil characteristics

The strong toxic impact of heavy metals, particularly of copper, on ecosystems and human health is caused primarily by content of their bioavailable forms and not by their total contents. To identify factors affecting the alteration of the content of copper bioavailable form the correlation analysis was performed. Results of the analysis are shown in Figure 3. It was revealed that the content of copper bioavailable form was in strong positive correlation ($r=0.983$) with the copper total content consisted both of copper bioavailable form (exchangeable, water and acid soluble) and its form bounded to iron and manganese oxides, organic matter and soil matrix (residual fraction). It is logical because the bioavailable form of copper is the constituent of total copper. The lowest ratio was registered in area Q-CONT and made up to 4.5 % of the total copper content, while the highest ratio was observed in area Q-F-11 constituting 14.2 % of the total content.

But then the bioavailable copper generally is formed from the other components of total copper since they can turn into bioavailable form due to various biological and chemical processes in the soil.

The increase of the portion of copper bioavailable form in the total content of copper in the soil or the transition of biologically not accessible form of copper to its bioavailable form depend on the variety of soil characteristics (Tab. 2). From the correlation analysis with these characteristics it was found out that the change of the portion of bioavailable copper content in the total content of copper ($Cu_{\text{bioavailable}}/Cu_{\text{total}}$) was in average negative correlation ($r=-0.564$) with humus content in the soil. This negative correlation can be explained by the fact that the high content of humus leads to the binding of heavy metals, in this case to formation of the compounds of copper with organic matter and hereupon to decrease of its biological availability. The high content of humus also promotes the development of soil biota which in turn absorbing the bioavailable copper causes a decrease of its content in the soil.

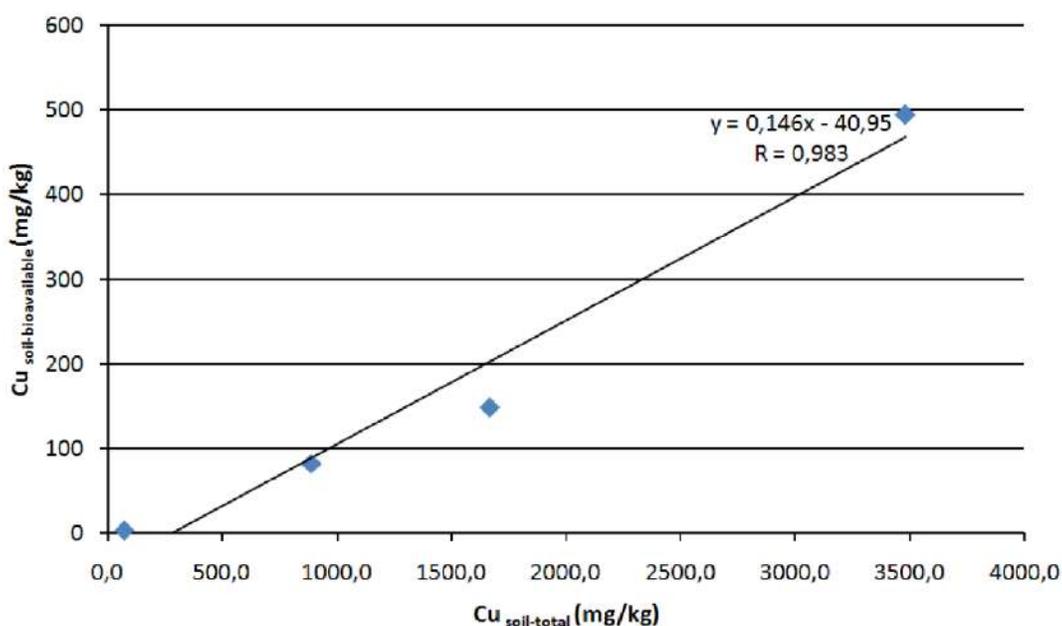


Figure 3. Correlation between concentrations of bioavailable and total soil Cu

Table 2. Correlation analysis of some characteristics of plant root zone soils in three risky and one checking sites

	$Cu_{bioavailable}/Cu_{total}$	pH	Humus content, %	Sand, %	Silt, %	Clay, %
$Cu_{bioavailable}/Cu_{total}$	1					
pH	0,123	1				
Humus content, %	-0,564	-0,692	1			
Sand, %	0,262	0,932	-0,539	1		
Silt, %	0,031	-0,954	0,448	-0,953	1	
Clay, %	-0,390	-0,893	0,565	-0,990	0,900	1

The identification of phytoremediation potential of wild plant species

Phytoremediation is considered a harmless approach for removal of pollutants, especially heavy metals, from the ambient environment or for their conversion into forms that are unavailable for other organisms (Cunningham and Berti 1993). And depending on the ability of plant to accumulate heavy metals in its underground or aerial parts the phytoextraction and phytostabilization capacity of a given plant could be revealed. BCF_{root} and TF are the important indices for revelation of phytoremediation potential. High bioconcentration factor of root is a significant characteristic of plant species for phytostabilization suitability. BCF_{root} values for 16 dominant plant species from three risky areas are shown in Tab. 3. The highest BCF_{root} values were registered in *Thymus kotschyanus* ($BCF_{root}=4.84$) and *Phleum pratense* ($BCF_{root}=4.64$) growing in area Q-F-01 as well as in *Achillea millefolium* ($BCF_{root}=3.94$) growing in area Q-OM-03.

These plant species are quite developed in mentioned areas and can be used for phytostabilisation purposes. As a result the content of bioavailable copper in soil will decrease which in turn will reduce the pollution of ground and surface waters as well as will limit the transfer of copper to food chains in toxic quantities.

It should be noted the BCF_{root} indices for the same plant species had variant values in different areas. For example, in *Achillea millefolium* in area Q-OM-03 a high value of BCF_{root} was registered while in area Q-F-11 it was low. This fact can be explained by significant differences in soil characteristics of these two areas that had a direct impact on plant growth and development while BCF_{root} different values in *Thymus kotschyanus* growing in areas Q-F-01 and Q-F-11 with similar characteristics of soil can be explained by physiological peculiarities of the particular plant species. In particular, the copper contents in the given plant species in both Q-F-01 and Q-F-11 areas were 718 mg/kg and 775 mg/kg, respectively, but in the area Q-CONT where the content of bioavailable copper in soil was low the copper content in the plant amounted barely to 38.7 mg/kg (Figure 4).

High translocation factor is a significant characteristic of plant species for phytoextraction suitability, but for phytostabilization suitability a low translocation factor is required. The highest TF values (>1) were observed in *Hypericum perforatum* (TF=1.27) and in *Astrodaucus orientalis* (TF=1.19). This fact indicates that mentioned plants by active mechanisms transfer the copper to their aboveground parts and it can be removed from the soil through harvesting. However in *Astrodaucus orientalis* very low value of BCF_{root} (0.12) was observed which limits the use of this plant species for phytoextraction purposes. But in *Hypericum perforatum* BCF_{root} is 0.65 and for the identification of potential for its use in phytoextraction purposes further laboratory studies are required to reveal the factors that may contribute to increase of BCF_{root} and TF values. In this

way it is possible to remove bioavailable copper from the soil and prevent its transfer to food chain and further toxic effects on human health and other living organisms.

Table 3. BCF_{root} and TF of 16 plant species growing in three risky study sites

Plant species	Q-F-01		Q-OM-03		Q-F-11	
	BCF _{root}	TF	BCF _{root}	TF	BCF _{root}	TF
<i>Artemisia vulgaris</i>	1.45	0.39	0.87	0.70	-	-
<i>Rosa canina</i>	-	-	0.73	0.71	-	-
<i>Tanacetum parthenium</i>	-	-	-	-	0.51	0.51
<i>Achillea millefolium</i>	0.86	0.61	3.94	0.16	0.37	0.59
<i>Melilotus officinalis</i>	-	-	0.79	0.77	-	-
<i>Sisymbrium loeselii</i>	1.44	0.47	1.21	0.60	-	-
<i>Thymus kotschyanus</i>	4.84	0.08	-	-	1.57	0.08
<i>Trifolium pratense</i>	-	-	1.87	0.65	-	-
<i>Hypericum perforatum</i>	-	-	0.67	1.27	-	-
<i>Tussilago farfara</i>	-	-	0.75	0.84	-	-
<i>Astragalus aureus</i>	1.28	0.42	-	-	0.63	0.34
<i>Astragalus uraniolimneus</i>	1.60	0.84	-	-	0.36	0.42
<i>Teucrium orientale</i>	0.77	0.29	-	-	-	-
<i>Phleum pratense</i>	4.64	0.35	-	-	1.11	0.15
<i>Sedum caucasicum</i>	-	-	-	-	0.75	0.31
<i>Astrodaucus orientalis</i>	-	-	-	-	0.12	1.19

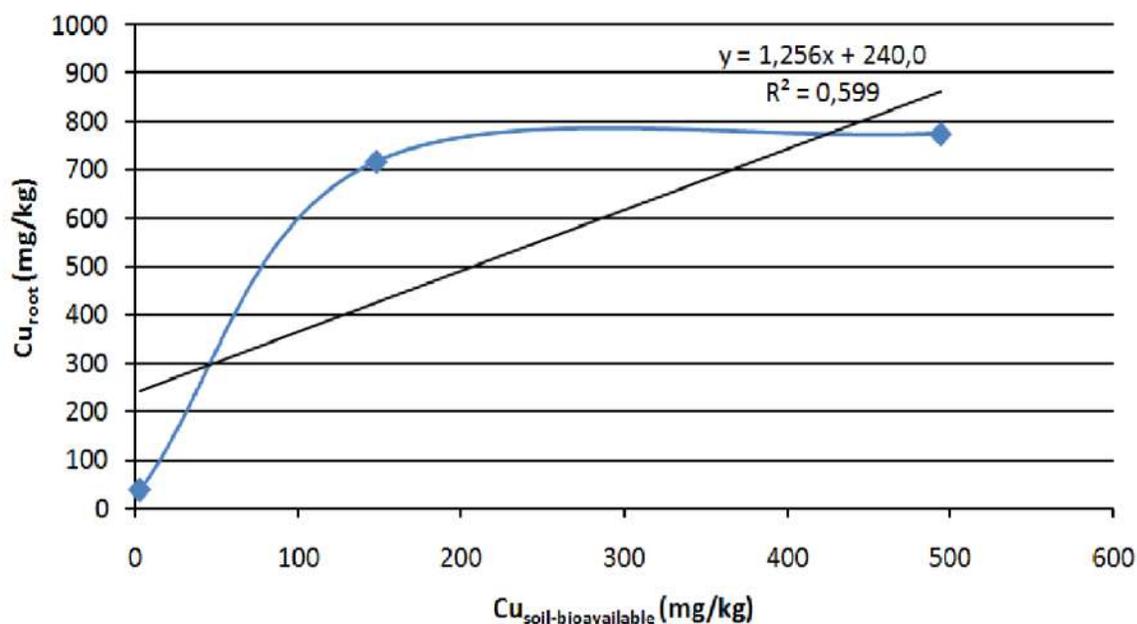


Figure 4. *Thymus kotschyanus* root copper concentrations as a function of bioavailable copper concentration in soils

Conclusion

Studies were conducted to determine the phytoremediation potential of wild plant species growing in areas contaminated with copper as well as the dependence of such ability on certain characteristics of soil. Studies have shown that the content of bioavailable copper in the soil primarily depends on copper total soil content and the dependence of the ratio $Cu_{\text{bioavailable}}/Cu_{\text{total}}$ on different characteristics of soil made the following descending series: humus content > clay > sand > pH > silt. In some cases this dependence was negative (humus content, clay), and in other cases - positive (sand, pH, silt).

Studies of copper content in underground and aboveground tissues of 16 dominant plant species from three risky areas revealed that investigated plant species very differed in their capability to accumulate copper.

Aerial tissues of 14 plant species accumulate less copper than their roots which shows plant ability to absorb the copper by roots but then to limit the mobility of this heavy metal in its interior (binding of copper with metallothioneins, phytochelatins, organic acids or accumulation in vacuoles). That indicates the capability of plants to quite balanced uptake and translocation of copper under strong polluted conditions.

Thymus kotschyanus, *Phleum pratense* and *Achillea millefolium* demonstrated higher copper accumulation in their root tissues (depending on soil characteristics this feature was displayed in *Achillea millefolium* in different ways) than the other 13 plant species, all of which well grew in copper contaminated areas.

In these plant species low values of TF has also been observed that improved their phytostabilization abilities. Phytostabilization potential is greater in *Thymus kotschyanus* and *Phleum pratense* as far as they are perennial plants and develop a strong root system. Study results have led us to the conclusion that *Thymus kotschyanus*, *Phleum pratense* and *Achillea millefolium* are suitable for use in remediation of copper contaminated soils due to their good phytostabilization potential, and further field and laboratory experiments are planned to confirm this useful ability.

Acknowledgements

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3.2.7. Implications of phosphorus recycling from sewage sludge ash for Austria's heavy metal balance in arable soils

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Abstract

This work determines the relevance of altered heavy metal inputs in soils if P-recycling from SSA were to be implemented on a nationwide scale in Austria. Substance flow analysis (SFA) is used to contrast current mean heavy metal in- and outputs to arable soil, and different scenarios of P-recycling from SSA are applied to investigate impacts on the heavy metal balance. Results show that an adapted P management can contribute to an improvement of Austria's mean heavy metal balance in soils on a short-term basis. On a long-term basis, adequate decontamination or source-control strategies for heavy metals in SSA are recommended.

Keywords: Phosphorus; Sewage Sludge Ash; Recycling

Introduction, scope and main objectives

Recovery of phosphorus (P) from sewage sludge ash (SSA) is a promising approach to recycle P from municipal wastewater and to significantly decrease the dependency on phosphate rock (PR) resources (Egle *et al.*, 2014). Legislation to enable fertiliser production from SSA and related quality criteria to ensure their safe use in agriculture are currently discussed widely across the European Union (EC, 2015). One remaining concern is posed by the heavy metal concentrations present in SSA, which are not or only partly removed through P recovery, depending on the applied technology (Kraus & Seis, 2015; Egle *et al.*, 2016).

In Austrian national law, fertiliser heavy metal concentrations are primarily limited on a dry mass basis (DMVO, 2014). Even if not decontaminated, SSA-based fertilisers could comply with these limits if they were mixed with other P-containing raw materials during the production process of mineral fertilisers. This implies that dry mass based limits are inadequate to evaluate the potential threat of recycling SSA-based fertilisers to agricultural soils.

Methodology

Therefore, this work takes on an alternative approach based on heavy metal/nutrient ratios in fertilisers to determine the relevance of altered heavy metal inputs in soils if P-recycling from SSA were put into action on a nationwide scale. By using substance flow analysis (SFA; Brunner & Rechberger, 2016), current mean heavy metal inputs to Austrian arable soils through fertilisers and atmospheric deposition are contrasted to mean outputs through plant uptake, leaching and erosion.

Impacts of P recycling on this heavy metal balance are then simulated through a set of scenarios, which assume the replacement of ~30% of PR-derived fertiliser by SSA from wastewater treatment plants above sizes of 50.000 people equivalent (PE). **S.1** covers the direct use of SSA without proper decontamination. **S.2** considers an intermediate step of phosphoric acid production (with significant heavy metal reduction) via the EcoPhos® process, which then is used as an input material for fertiliser production.

Lastly, changes to the status quo are evaluated: (i) in terms of relative changes of total heavy metal inputs and (ii) by contrasting yearly concentration net-increases with current and critical heavy metal concentrations in arable soils.

Results and discussion

Relative changes of total heavy metal inputs

Results reveal that by substituting 30% of PR with non-decontaminated SSA (S1), Austrian soil heavy metal inputs are reduced for Cd, V and U (see Table 1). As, Cu, Pb, Ni and Zn inputs are expected to increase by more than +10% with the highest impact on Pb inputs (+36%), mainly due to the fact that PR contains hardly any Pb whereas concentrations in sludge are considerably higher. Cr and Hg inputs are only slightly increased. With an intermediate heavy metal decontamination step (S.2), inputs are reduced compared to the status quo for all analysed heavy metal except As and Pb.

Table 1. Relative change of heavy metal inputs in relation to the status quo

	As	Cd	Cr	Hg	Ni	Pb	V	Cu	Zn	U
S.1	+13.9%	-14.2%	+9.9%	+0.7%	+13.3%	+36.1%	-11.3%	+28.9%	+24.3%	-26.8%
S.2	+4.3%	-18.5%	-9.8%	-1.2%	-2.8%	+1.7%	-15.7%	-1.2%	-1.9%	-29.8%

As an example, varying inputs in the different scenarios are given for Cd in Figure 1.

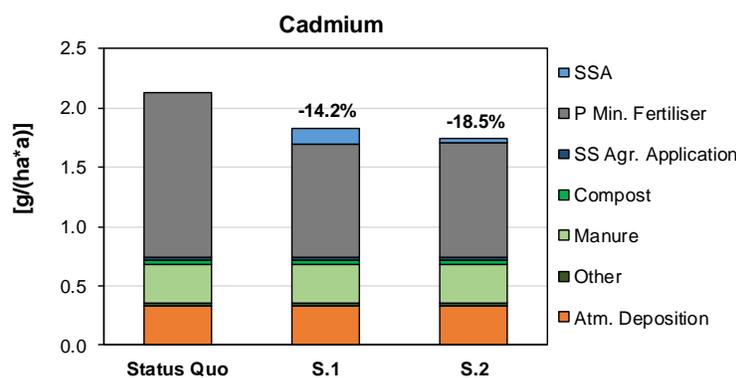


Figure 1. Exemplary illustration of mean Cd inputs in arable soil

Exceedance of critical heavy metal concentrations in arable soil

Table 2 shows the mean number of years until critical heavy metal concentrations in soil are exceeded in the given scenarios. Values are not expected to irrefutably depict reality but are rather used as a means to compare the criticality of the different heavy metals in soil. It is shown that those heavy metals for which inputs are expected to decrease through a recycling of SSA (Cd, V and U) are highly critical in comparison to others (low number of years), resulting mainly from the currently high inputs through mineral P-fertiliser application. In contrast, mean vulnerability of arable land to the heightened inputs of Pb and Ni through SSA recycling is lower (high number of years). Of potential concern are the increases in Cu and Zn as other inputs, mainly through manure, are high. Considering their diverse role both as micronutrients and as pollutants, the need for proper management strategies for these two metals is evident. Cr is of less concern, as the potential for a critical enrichment in soil is shown to be lower than for other metals. In the case of Hg, criticality in soil is simulated to be low, however largely owing to the fact that outputs

through plant uptake and leaching are high. Considering that Hg is listed as a priority hazardous substance in rivers in European legislation (EC, 2013), and that river monitoring showed an EU-wide exceedance of the current environmental quality standard for biota (Nguetseng *et al.*, 2015), additional inputs from SSA should be minimised nonetheless.

Table 2. Mean number of years until critical heavy metal limits in soil are exceeded in the different scenarios

	As	Cd	Cr	Hg	Ni	Pb	V	Cu	Zn	U
Status Quo	no increase	811	15,482	63,259	6,796	15,410	1,345	786	1,110	1,763
S.1	no comparison possible	1,176 (+45%)	11,467 (-26%)	57,273 (-9%)	5,286 (-22%)	8,856 (-43%)	1,519 (+13%)	519 (-34%)	698 (-37%)	2,439 (+38%)
S.2	no comparison possible	1,364 (+68%)	23,646 (+53%)	77,522 (+23%)	7,232 (+6%)	14,905 (-3%)	1,599 (+19%)	804 (+2%)	1,164 (+5%)	2,548 (+44%)

Conclusions

In conclusion, an adapted P management, through recycling of P from SSA, can contribute to an improvement of the Austrian mean heavy metal balance in soils on a short-term basis, even if SSA no heavy metal removal is applied. However, taking the precautionary approach, adequate decontamination or source-control strategies need to be implemented to reduce the risk for individual arable soil plots and ensure a safe recycling of nutrients from SSA to agriculture.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.2.8. Potentially toxic element hyperaccumulator plants: preliminary evaluation of the phytoextraction duration to remediate a contaminated agricultural soil by *Brassica juncea* successive croppings

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Abstract

Phytoextraction by hyperaccumulator plants is an in situ eco-friendly and cost-effective method to remediate soil by potentially toxic elements (PTEs). The plants uptake the bioavailable forms of PTEs and progressively reduce the soil bioavailable pools till safety levels that could be addressed as remediation objectives. However, during the phytoextraction some changes may occur in the repartition of the PTEs among the soil geochemical fractions and in their equilibriums with the soil solution, and these changes can influence the phytoextraction duration. We report the preliminary results of an ongoing pot experiment of PTEs phytoextraction by consecutive croppings of *Brassica juncea* L from agricultural soil samples contaminated by Cr, Zn, Pb and Cd (up to: 550 mg/kg for Cr, 617 mg/kg for Zn, 161 mg/kg for Pb, 14 mg/kg for Cd), as result of past industrial waste dumping. The aim is to estimate the time-span of soil remediation and the changes in the PTEs repartition between total, potentially bioavailable and readily bioavailable pools that may occur in soil during the phytoextraction cycles. After the first cycle of *B. juncea*, a general depletion of the potentially bioavailable and an increase of the readily bioavailable pool was observed. These changes were particularly evident for Cd and Zn in the soils where these elements occurred in highest amounts. The increase in soil bioavailability enhanced accumulation of Cd and Zn in the leaves of Rocket salad grown right after *B. juncea*; an opposite behavior was observed for the less mobile Cr and Pb. According to the amounts of PTEs removed by *B. juncea*, the number of crop cycles needed to remove the amounts of potentially bioavailable Cd, Cr and Zn at pot scale ranged from 15 and 112; the time-span was much higher for lead (981-2416 cycles).

Keywords: contaminated soil, potentially toxic elements, bioavailability, hyperaccumulator plants, phytoextraction

Introduction and main objectives

Soil contamination by potentially toxic elements (PTEs) is a subject of great concern due to their harmfulness for the biota at certain concentration, and to their persistence in the environment (Cristaldi *et al.* 2017). Various soil remediation techniques exist, but many of them are complex and expensive. In recent years much research has been done on soil phytoremediation because it is an in situ eco-friendly and cost-effective method respect to the others (Mir *et al.* 2017). The main phytoremediation mechanisms are phytostabilization, that reduces contaminant mobility toward other environmental compartments and the phytoextraction that exploits the ability of some plants to uptake potentially toxic elements from the contaminated soil. The best suitable plants for phytoextraction are the hyperaccumulator of some elements, which have among their main peculiarities that of tolerate high concentration of these elements in soil and to uptake and accumulate them in the shoot tissue (Guerra *et al.* 2011). In any case, the contaminant, to be absorbed by the plants, must be in a bioavailable form in the soil (Cristaldi *et al.* 2017). PTEs in the soil from anthropogenic sources tend to be more mobile and bioavailable than the geogenic ones (Mir *et al.* 2017), and this is also the reason for their dangerousness for the transfer to other environmental compartments and to the food chain. Therefore a realistic remediation objective through phytoextraction can be the progressive reduction of the bioavailable portion of the contaminant until safety levels, rather than of the total content (Keller and Hammer 2004). However the bioavailability of a PTEs is closely linked to the nature of the elements, on the chemical form in which they occur in soil and on the chemical-physical characteristics of the soil that determined the repartition of the element between the various soil geochemical fraction and the soil solution (in which the element are readily bioavailable) (Agrelli *et al.* 2017). This repartition is a dynamic equilibrium and this aspect must be considered in strategy of phytoremediation, because after short-term phytoextraction (or only few cycles of phytoextraction) the decreased element in the readily bioavailable fraction may be replenished through soil element re-equilibration, and the kinetics of replenished can change over time (Keller and Hammer 2004).

In this work we report the preliminary results of an ongoing pot experiment of PTEs phytoextraction from an agricultural soil polluted by illegal dumping of industrial wastes by consecutive croppings of *Brassica juncea* L, with the aim to estimate the time-span of soil remediation and the changes in the PTEs repartition between the total, potentially bioavailable and readily bioavailable pool in soil, that may occur during the phytoextraction cycles. The pot experiment was set up in parallel to a similar field application in order to have a clearer evaluation of the results, obtained in a controlled condition, because the high spatial variability of field contamination made comparison between data obtained at different times very difficult.

Methodology

The polluted site

The study site is an agricultural area of 6 ha, currently under sequestration, located in the province of Naples (Campania, south Italy), interested by past illegal dumping of industrial wastes, mainly from tanneries. The soil of the area is widely polluted by Cr and Zn (up to: 4500 mg/kg for Cr, 1850 mg/kg for Zn). Only in certain sub-areas it was found a contamination by lead and cadmium (up to 420 mg/kg for Pb, 280 mg/kg for Cd). For all elements a high spatial variability, both horizontal and vertical, was observed. In the area, the ECOREMED protocol (LIFE11/ENV/IT/275) of phytoremediation based on the use of poplar trees and grass species was applied to securing the site. In the sites where PTEs hot-spots were detected, an intensification of the phytoextraction process with consecutive *Brassica juncea* L croppings was realized. The soil

of the area is sandy and sub-alkaline, with chemical characteristics showing a great variability as a function of the contamination level (Table 1). The extractions in NH_4NO_3 1 M (indicative of the amount of readily bioavailable elements; DIN 19730, 2008) and in EDTA 0.05 M pH 7 (indicative of the amount of potentially available elements to the plants; Rauret *et al.* 2001) (Figure 1), as well as the distribution of the elements among the soil geochemical fractions (Rauret *et al.* 1999) (Figure 2), indicate a very low mobility and bioavailability of chromium (despite the high total content); the bioavailability of the other PTEs of interest are higher, in particular for zinc and cadmium. The amounts of bioavailable PTEs are positively correlated to the soil total contents (not shown), and the PTE amounts extracted in NH_4NO_3 in the most contaminated field soil samples exceed the limit values adopted by some European countries for agricultural soil.

The pot experiment

Soil excavation of 1.5 m² x 0.3 m has been carried out in three field sub-area, two identified as Cd and Pb hot-spots (F4 and C13) and one identified as control (A7) on the basis of PTEs total contents data; for each excavation the soils were mixed, homogenized and transported in a greenhouse; total and bioavailable content of PTEs were determined for each of the three soil samples as described above. Four pots of 7 kg for each soil sample were prepared and 15 seed of *Brassica juncea* were sowed, few week later the five more robust and better distributed plants per pot were selected and the others uprooted. At the end of cycle (end of flowering and beginning seed maturation), the 5 plants/pot were uprooted and divided in roots, stems and leaves, washed with tap water for removing soil particles and successively with deionized water, and analyzed for the concentration of PTEs after drying and acid digestion. For each pot a sample of soil was taken and analyzed for the PTEs bioavailable content as described above. Furthermore, after *Brassica juncea* crop, in each pot Rocket salad (*Eruca vesicaria*) was sowed as food-plant bioindicator for verifying the PTEs accumulation in the edible part after a cycle of phytoremediation with *Brassica juncea*; the Rokat salad was sowed in quadruplicate also in the each of the three original soil samples for comparison the PTEs accumulation with and without *Brassica juncea* precession. The Rokat salad was harvested for four time in each pot when commercial maturity is reached, and was analyzed for PTEs concentration in the edible part.

Table 1. Ranges of the main soil characteristics.

Texture	sandy
pH – H ₂ O	7.4 – 8.0
C.E 1:5 (ds/m)	0.1 – 2.3
C.O. (g/kg)	8.0 – 29
N (g/kg)	1.5 – 7.1
Carbonates (g/kg)	0 – 79

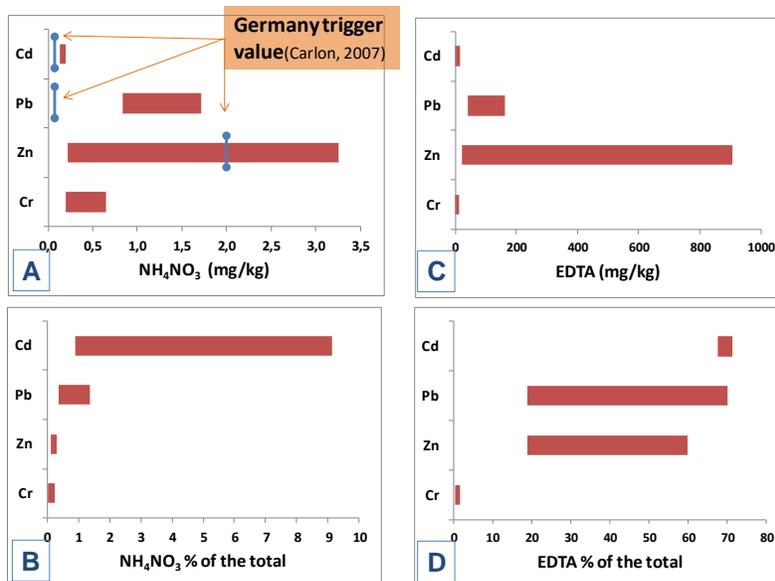


Figure 1. Range of PTEs concentration extracted in NH_4NO_3 (readily bioavailable; A in mg/kg, B in % of the total) and in EDTA (potentially bioavailable; C in mg/kg, D in % of the total) from selected soil samples of the study site.

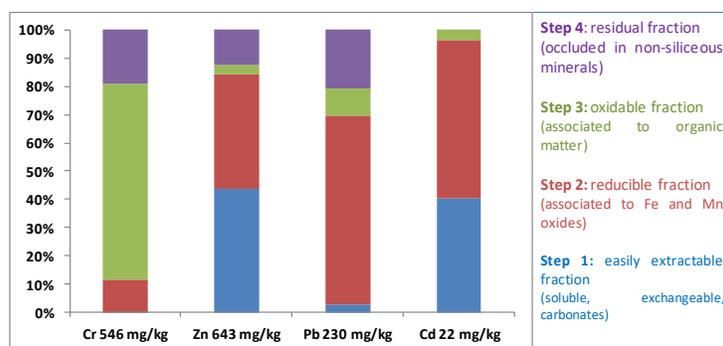


Figure 2. Examples PTEs distribution in the soil geochemical fractions by EU-BCR sequential fractionation of same soil samples.

Results

Brassica juncea plants grown in pot on the soils from A7, F4 and C13 field plots, removed amount of PTEs positively related to the total content of the soils (Table 2, Figure 3). An accumulation plateau seems to be reached for Zn and Pb. Chromium and lead accumulated principally in the roots, zinc and cadmium in the leaves (Figure 3). The comparison between the amounts of potentially and readily bioavailable PTEs extracted before and after the first cycle of *B. juncea* (Table 3), in general show a depletion of the potentially bioavailable PTEs pool and an increase of the readily bioavailable pool, suggesting that the latter is replenished during the phytoextraction, and likely the plant roots enhanced the release of the PTEs from the potentially bioavailable pool. Indeed, the accumulation of Cd and Zn (the two most mobile contaminants of the studied soil) in the first cut leaves of the Rocket salad grown after *B. juncea* seems higher than in the salad grown without *B. juncea* precession (Figure 4). This accumulation was likely promoted by an higher readily bioavailable pool in soil. The contrary was observed for Cr and Pb, less mobile contaminants and with a less marked increase in the readily bioavailable pool after *B. juncea*

growth. Also at the IV cut of the Rocket salad grown without and with *B. juncea* in precession, the trend of PTEs accumulation in leaves seems the contrary of the I cut, except for lead.

Considering the amounts of PTEs removed by *B. juncea*, the number of crop cycle needed to remove the amounts of potentially bioavailable PTEs extracted from A7, F4 and C13 soils, is reported in Table 4.

Table 2. PTEs total concentration (mg/kg) in the three soil samples collected for pot experiment.

	Cr	Zn	Pb	Cd
A7	123	147	68.0	0.23
F4	549	305	79.8	14
C13	555	617	161	0.50

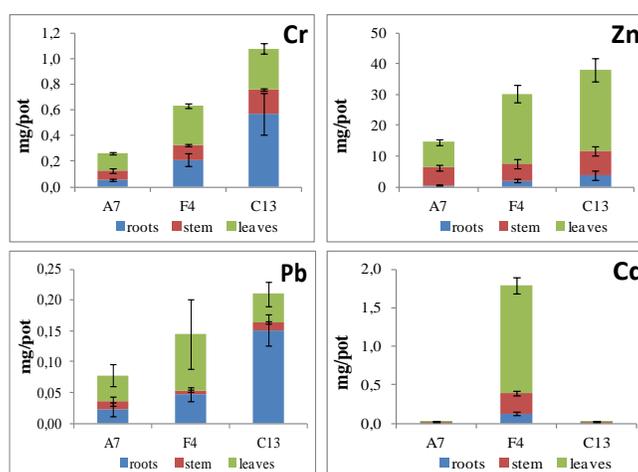


Figure 3. Amount (mg/pot) of PTEs removed from the three collected soil by *Brassica juncea*.

Table 3. % of variation of the PTEs amount extracted in EDTA and NH_4NO_3 from the studied soils after *Brassica juncea* cycle, respect to the initial amount.

		A7 %	F4 %	C13 %
Cr	EDTA	- 8	+ 1	+ 5
	NH_4NO_3	+ 6	+ 6	+ 5
Zn	EDTA	- 26	- 2	- 8
	NH_4NO_3	+ 141	+ 118	+ 15
Pb	EDTA	- 9	- 8	- 20
	NH_4NO_3	nd	nd	nd
Cd	EDTA	- 2	+ 4	- 2
	NH_4NO_3	- 9	+ 48	- 8

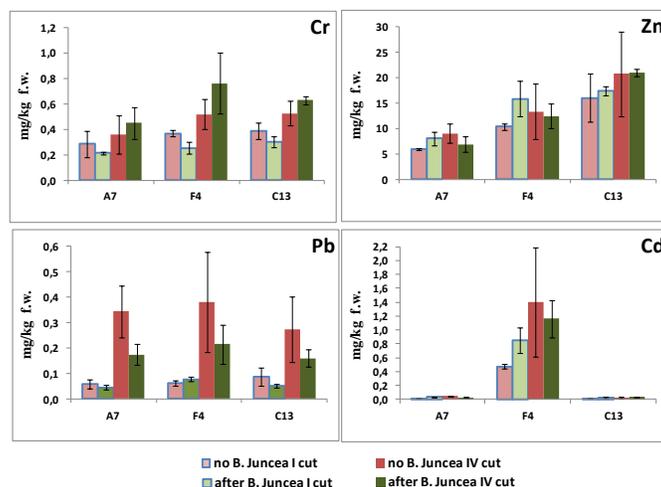


Figure 4. Concentration of PTEs in the leaves at I and IV cut of Rocket salad grown in the three collected soil without and with *Brassica juncea* in precession.

Table 4. Estimation of the number of *Brassica juncea* cycles needed to remove the potentially bioavailable PTEs according to the data of PTEs extracted in EDTA and the PTEs removed by *B. juncea*.

		Cr	Zn	Pb	Cd
Amount of PTEs extracted in EDTA before <i>B. Juncea</i> (mg/pot)	A7	10.1	220	76.1	1.60
	F4	18.3	917	147	61.1
	C13	42.6	2401	508	3.56
Amount of PTEs removed by <i>B. Juncea</i> (mg/pot)	A7	0.266	14.7	0.0776	0.0371
	F4	0.632	30.2	0.146	1.79
	C13	1.08	37.9	0.210	0.0317
n° of <i>B. juncea</i> cycles needed to remove the potentially bioavailable PTEs in pots	A7	38	15	981	43
	F4	29	30	1011	34
	C13	40	63	2416	112

Discussion

According to the pot experiment results, the estimated duration of PTEs phytoextraction by *Brassica juncea* is acceptable for all elements, except for lead. Extrapolation of this result to field scale has to be evaluated. Nevertheless, it must be taken into account that it could not be necessary to eliminate all the PTEs bioavailable amounts, but it could be sufficient to reach safety levels of bioavailable amounts as they are in A7 soil. At the same time, it is worth to note that the phytoextraction times might be underestimated because, as clearly appears from the data of PTEs removed (Figure 3, Table 4), the plant uptake decreases with the total amount in soil, and consequently the bioavailable amounts also go down. Also the kinetics of the readily bioavailable fraction reintegration may decrease during the phytoextraction. Furthermore, the changes in the equilibrium between the PTEs soil pools should be deeply investigated, because during the phytoextraction it is possible that occurs elements movement in favor of a reclamation objective, or unfavorable to a successive food-plant cultivation. In our case, the decrement of the PTEs potentially bioavailable amounts after *B. juncea* cycle is higher than the amount removed by plants (not shown), and it is possible that a certain elements amount has moved to soil fractions that exert a greater retention; at the same time the accumulation of PTEs in Rocket salad in some cases was enhanced after *B. juncea* grow.

Conclusions

For the evaluation of the phytoremediation duration in a specific soil with specific contaminants, it is crucial to monitor multiple successive phytoextraction cycles to become aware of the changes in the repartition of the elements in the soil induced over time by the plant and the element uptake itself. These changes can modify the pollutant amounts extracted over time both by the plants used for reclamation, but also by the plants of food interest in a scenario of possible return of the site to agricultural use.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.2.9. Remediation of soil contaminated with persistent organic pollutants in Sumgait, Azerbaijan

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Abstract

The Sumgait remediation project was implemented in 2015 as a partnership between Blacksmith Institute and the site owner Azerikimya Joint Stock Company (Azerikimya) in Sumgait City, Azerbaijan Republic, about 30 km northwest of Baku. The project was financed by European Commission and supported by the Ministry of Ecology and Natural Resources (MENR) and Sumgait Municipality. The site is a place on the Caspian Sea coast that was formerly an industrial area highly contaminated with various pollutants and particularly benzo(a)pyrene, benzene, and polychlorinated biphenyls (PCBs). As part of initial environmental assessment the project team took soil samples at 19 locations at the surface and at the depth of 0.5 m. The maximum topsoil benzo(a)pyrene concentration was 76.21 mg/kg, benzene – 121.5 mg/kg, and PCBs – 121.02 mg/kg. The remediation project involved the removal of 804 m³ of contaminated soil, and disposal of the contaminated soil at the MENR Hazardous Waste Polyqon (landfill). A comparison of pre- and post-excavation sampling shows that average contaminant levels in soils in the upper 0.5 m were reduced by an average of 97 percent. These actions were followed by bioremediation activities. More than 13,000 m³ of clean soil and organic fertilizer were placed and leveled over an area of two hectares. Approximately 1,200 locally grown native tree species were planted, and a drip-irrigation system was installed. The area is now a park close to the beach.

Keywords: remediation, chemical contamination, Sumgait, Azerbaijan

Introduction, scope and main objectives

Sumgait is the third largest city of Azerbaijan with a population over 300,000 people. During the Soviet era, Sumgait was a major industrial center with more than 40 factories that produced various metals and chemicals. Over the last decade, the municipal, national government, and local industries have taken important steps to reduce the impacts of the city's industrial legacy, including closing polluting factories, upgrading facilities, treating contaminated wastewater and transferring contaminated materials to a secure facility (Eminov 2012). Despite this progress, regional soil test results show that large areas are still highly contaminated with heavy metals and other pollutants known to impact human health. If old obsolete industrial facilities are removed and pollution cleaned up that would allow using the land for other purposes, for instance creating new park areas for recreation (Ismailov 2009, Mamedov 2011, Kahramanova 2012).

For the pilot soil cleanup project a highly contaminated area was selected in Sumgait. The site is a small piece of the larger Sumgait industrial area, northwest of the main part of the city. The area is dry and the vegetation is sparse, with sandy soil. The closest residential areas are about 1.5 km away. The site was a high priority for remediation because it is located on the Caspian Sea, where the public used this highly contaminated area as a beach.

The site used to be a disposal area for wastewater residue from the state-owned Organic Synthesis Plant and Ethylene-Propylene Plant. Organic wastes containing benzene, benzo(a)pyrene, and

polychlorinated biphenyls (PCBs) originated primarily from the former Organic Synthesis Plant and the Ethylene-Propylene Plant. Wastewater discharge from the Ethylene Propylene Plant was completely stopped before remediation began, and the Organic Synthesis Plant was decommissioned in recent years. The closed Organic Synthesis Plant used to produce propylene oxide, propylene glycol, and polyester resins.

The site was used to settle and evaporate liquid chemical wastes from the Organic Synthesis Plant and as a wastewater pumping station for the plant. The liquid waste entered the site through a pipe. There was a settling/evaporation pond, and some of the waste was pumped from the pond to another site for treatment. After settling and evaporation, the sludge was periodically cleaned out of the pond and placed on the ground. The pond sometimes overflowed, and wastes spread to the north and south.

The goal of the project was to eliminate health risks to people from the site.

The project objectives included:

1. Environmental assessment to determine the levels and extent of contamination;
2. Soil cleanup;
3. Post-cleanup assessment of soil residual contamination;
4. Revegetation of the area.

The project was implemented by the Blacksmith Institute/Pure Earth and Azerikimya Company, supported by Sumgait Municipality, Ministry of Ecology and Natural Resources (MENR) of Azerbaijan, and co-financed by European Commission.

Methodology

The environmental assessment of the area was conducted in order to determine the concentrations of main contaminants: benzene, polychlorinated biphenyls (PCBs), and benzo(a)pyrene. The site was mapped and targeted soil samples were collected. Soils samples were taken near the settling pond as the assumed main source of contamination, along the perimeter of contaminated area and between the settling pond and borders of the site. Geographic coordinates of all samples were recorded. At each location samples were collected at the surface and at the depth of 0.5 m. Soil samples were analyzed in Environmental Laboratory of State Oil Company of Azerbaijan Republic (SOCAR).

The results were mapped using ArcGIS 10.2. The spatial data was organized in shapefiles. Background georeferenced images for mapping were obtained through SAS.Planet software.

The main cleanup method was to remove the most contaminated soil and place it to the special Hazardous Waste Storage (Polygon) of MENR. The removal was conducted using heavy machinery: excavator and trucks. Transportation of contaminated soil followed safety regulations of Azerbaijan. The results of the soil contamination assessment were used to determine where the most contaminated soil is located at the site. After the contamination was removed new clean fertile soil was brought in for the purposes of revegetation and also to exclude contact of people with remaining contaminants.

Results

In July 2015 the project team collected samples at 19 locations. The maximum concentration of benzo(a)pyrene in topsoil was 76.21 mg/kg, at the depth of 0.5 m – 51.45 mg/kg, the lowest concentration was below level of detection (LoD). The maximum concentrations of benzo(a)pyrene exceeded United States Environmental Protection Agency (USEPA) standard of 2.1 mg/kg for industrial soils more than 38 times. The maximum concentration of PCBs in topsoil was 121.02 mg/kg, minimum – 0.15 mg/kg. At the depth of 0.5 m the maximum concentration of PCBs – 73.29 mg/kg, minimum – below LoD. The maximum concentration of PCBs at the site exceeded USEPA standard of 0.94 mg/kg for industrial soils more than 120 times. The maximum concentration of benzene in was 109.5 mg/kg, minimum – 0.73 mg/kg. The maximum concentration of benzene in soil at the depth of 0.5 m was 121.5 mg/kg, minimum – below LoD. The maximum concentration of PCBs at the site exceeded USEPA standard of 5.1 mg/kg for industrial soils more than 24 times. Most concentrations of contaminants at the site exceed both industrial and residential USEPA standards for soil. This is a former industrial area, but now it is a public area, so the residential soil standards should apply. The concentrations tend to be lower at the depth of 0.5 m. The results are presented in Table 1.

Table 1. Concentrations of benz[a]pyrene, PCB, and benzene in soil before remediation

№	Concentrations, mg/kg					
	Benzo(a)pyrene		PCB		Benzene	
	Surface	Depth 0.5 m	Surface	Depth 0.5 m	Surface	Depth 0.5 m
1	0.033	0.000	0.65	0.21	1.21	0.92
2	0.087	0.119	2.44	1.17	1.78	0.35
3	76.210	51.450	33.08	12.89	4.32	2.65
4	32.930	21.310	64.02	21.32	1.95	0.45
5	0.008	0.000	2.87	1.91	1.11	0.98
6	0.009	0.005	1.28	1.31	0.83	1.03
7	0.000	0.000	0.15	0.06	1.14	0.65
8	5.120	3.920	2.21	3.29	0.73	3.87
9	12.430	3.110	42.91	31.41	2.11	2.82
10	28.900	11.620	121.02	73.29	8.41	2.22
11	64.200	23.090	84.32	45.39	6.81	2.89
12	0.060	0.000	1.09	0.76	1.04	0.55
13	3.310	1.760	34.30	6.11	4.43	4.01
14	0.005	0.000	0.63	0.67	1.01	0.43
15	11.900	12.100	1.34	2.56	109.50	92.10
16	9.600	8.400	1.21	0.98	88.40	121.50
17	21.900	11.900	2.43	3.71	66.10	72.30
18	19.200	6.100	3.19	1.23	23.30	56.40
19	12.500	0.000	7.10	0	64.10	0
Mean	15.7	8.2	21.4	11.0	20.4	19.3
Rec level for residential soils	0.11		0.23		1.2	
Rec level for industrial soils	2.1		0.94		5.1	

The next stage of the project was removal of 804 m³ of contaminated soil, and disposal of the contaminated soil at the MENR Hazardous Waste Storage (Polyqon). This was done in February 2016. The volume and location of contaminated soil was determined by the previous soil sampling and mapping. After the removal of contaminated soil the area was sampled again to determine the levels of remaining contamination at the site.

The maximum concentration of benzo(a)pyrene in topsoil was 0.41 mg/kg, at the depth of 0.5 m – 1.56 mg/kg. The maximum concentration of PSBs in topsoil was 0.98 mg/kg, at the depth of 0.5 m – 1.07 mg/kg. The maximum concentration of benzene in topsoil was 0.02 mg/kg, at the depth of 0.5 m – 0.07 mg/kg. The minimum concentrations of contaminants were below LoD. The results are presented in Table 2.

Table 2. Concentrations of benz[a]pyrene, PCB, and benzene in soil after remediation

No	Concentrations, mg/kg					
	Benzo(a)pyrene		PCB		Benzene	
	Surface	Depth 0.5 m	Surface	Depth 0.5 m	Surface	Depth 0.5 m
1	0.00	1.29	0.29	1.01	0.00	0.01
2	0.23	1.01	0.00	0.31	0.02	0.02
3	0.00	0.75	0.04	0.33	0.00	0.04
4	0.00	0.44	0.00	1.07	0.00	0.00
5	0.00	1.15	0.98	1.01	0.00	0.00
6	0.04	0.91	0.45	1.03	0.00	0.00
7	0.09	1.19	0.06	0.14	0.02	0.07
8	0.41	1.56	0.00	0.71	0.00	0.01
9	0.02	1.54	0.00	0.94	0.00	0.00
10	0.00	0.02	0.00	0.02	0.00	0.01
11	0.00	0.00	0.00	0.76	0.00	0.00
12	0.00	0.01	0.00	0.91	0.00	0.00
Mean	0.07	0.82	0.15	0.69	0.00	0.01
Rec level for residential soils	0.11		0.23		1.2	
Rec level for industrial soils	2.1		0.94		5.1	

Figures 1-3 show comparisons of concentrations of main contaminants before and after remediation and soil standards of USEPA.

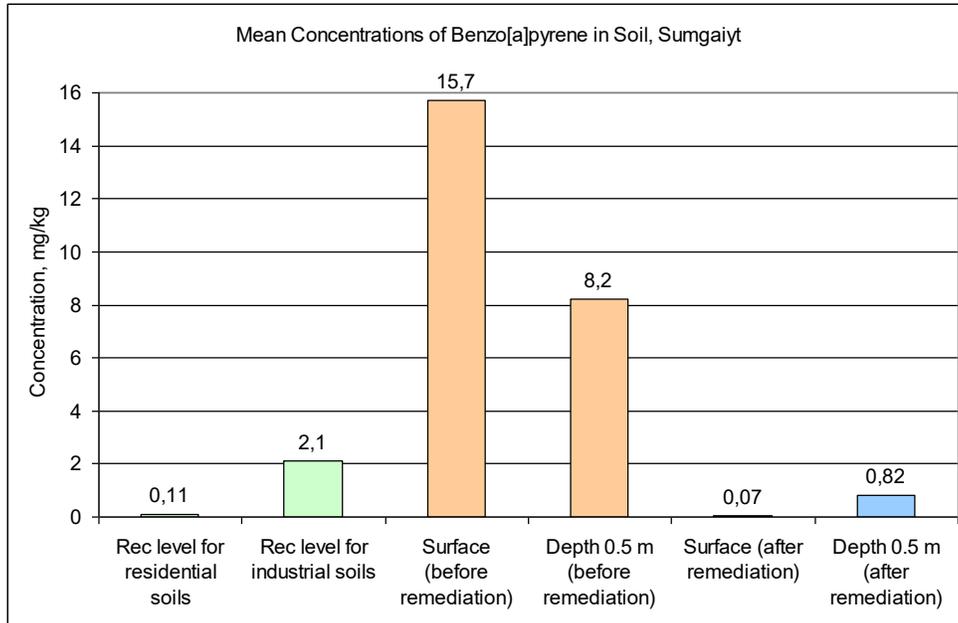


Figure 1. Mean concentrations of benzo[a]pyrene in topsoil and on the depth of 0.5 m before and after remediation

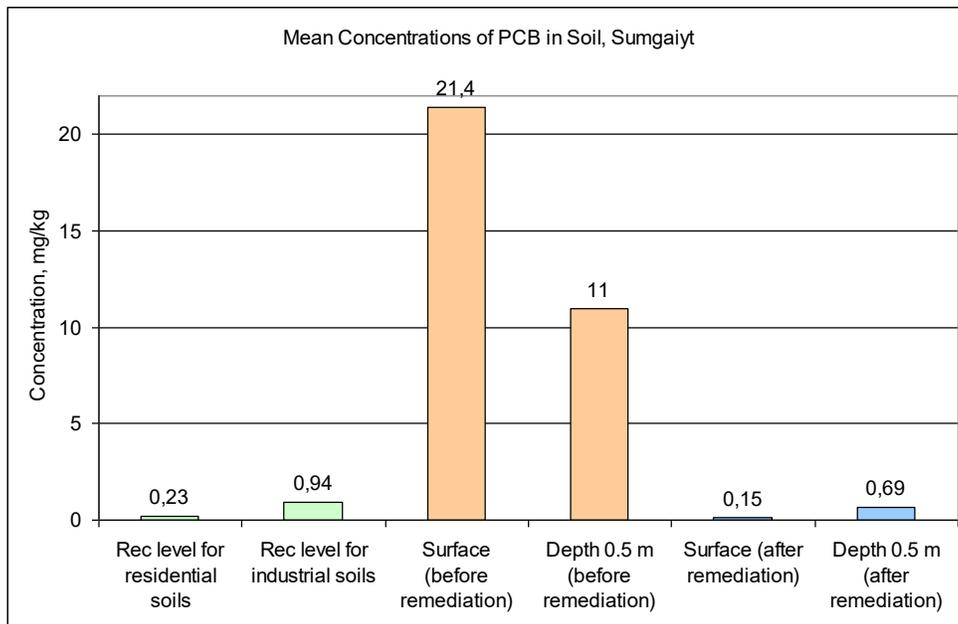


Figure 2. Mean concentrations of PCB in topsoil and on the depth of 0.5 m before and after remediation

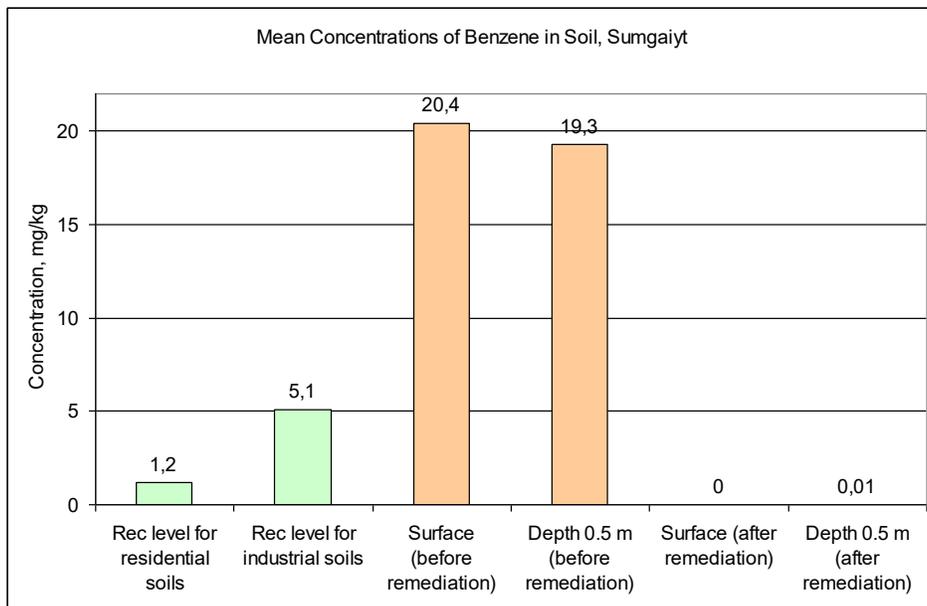


Figure 3. Mean concentrations of benzene in topsoil and on the depth of 0.5 m before and after remediation

Figures 4-6 show sampling locations and results of analyses for topsoil. These maps were used for planning removal of contaminated soil.

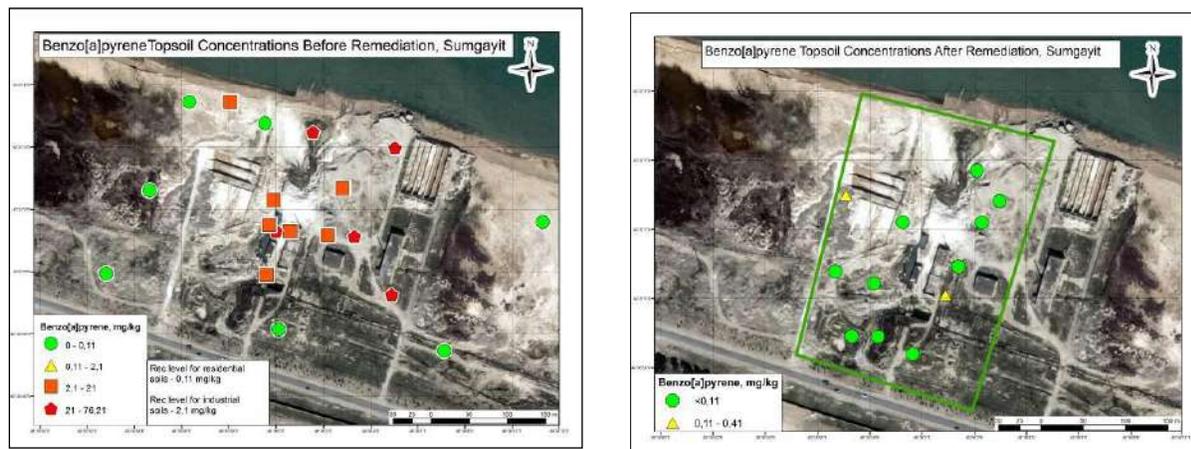


Figure 4. Concentrations of benzo[a]pyrene in topsoil before and after remediation



Figure 5. Concentrations of PCB in topsoil before and after remediation

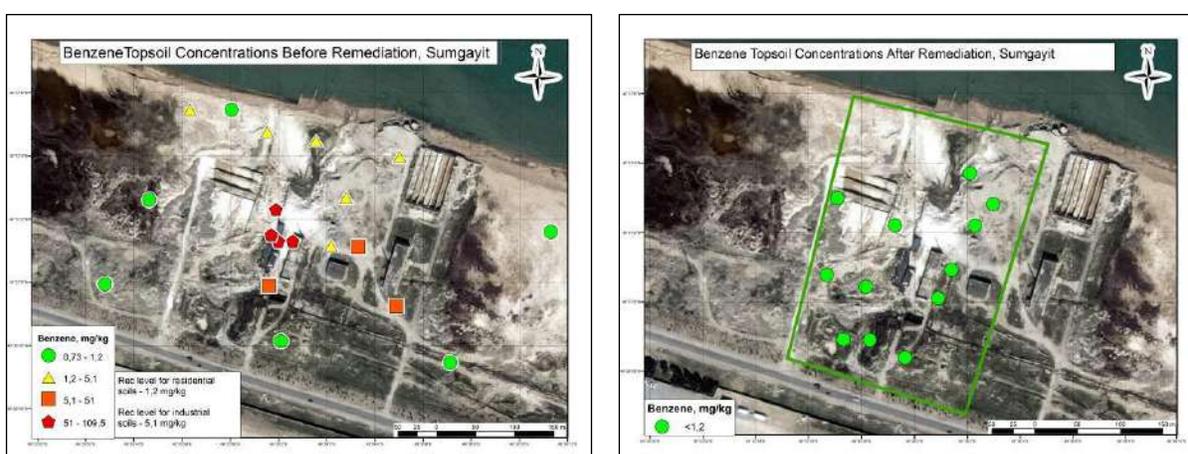


Figure 6. Concentrations of benzene in topsoil before and after remediation

At the next stage of the project in spring 2016 the area was graded and over 13,000 m³ of clean soil and 125 m³ of organic fertilizers were brought in. In June 2016 a drip irrigation system was installed and trees were planted. The revegetation plan was developed by Azerkimya and coordinated with Sumgayit Municipality. Azerkimya used its nursery to provide seedlings. Over 2 hectares were revegetated with 1200 trees and bushes native to Absheron Peninsula: Olive (*Olea europaea*), Willow (*Salix*), Caspian Elaeagnus (*Elaeagnus caspica*), Eldar Pine or Pinus brutia (*Pinus eldarica*), Oriental Plane (*Platanus Orientalis*), Poplar (*Populus*), Flowering ash (*Fraxinus ornus*), White acacia (*Robinia pseudoacacia*). The drip-irrigation system is employed to help the trees to grow in their first years. It is anticipated that in several years the plants would survive without additional watering. The growth of trees is expected to contribute to further degradation of remaining contaminants at the site.

Discussion

The choice of methods for soil remediation in a contaminated area depends mainly on the type of contaminant, its concentrations and feasibility. The main methods include: chemically treating soil to degrade the contaminants or make them less bioavailable, capping the contamination with a layer of clean soil to prevent contact of people with toxic agents, using bioremediation, or removing contaminated materials.

Chemical treatment of soil is often an expensive and labor intensive process because you would need to buy chemicals and mix it in large volumes of soil. And the list of contaminants that could be dealt with this way is limited. Therefore this option was not considered for the site in Sumgait.

Some organic contaminants may be degraded by plants and bacteria. Such methods work best when it is necessary to preserve the soil, the contamination levels are relatively low and there is enough time for the process. Bioremediation usually takes long time. Depending on the contamination levels and type of contaminants may take several years. In Sumgait there was no need to preserve original soil because it was mostly infertile sand. Also the concentrations of contaminants were very high and it was important to make the place for people safe fast. Therefore the bioremediation was not chosen as the primary method of clean up.

Capping the contaminated area with a layer of clean soil is usually used when the volume of contaminated materials is too big and contamination goes deep so it becomes impractical to extract it. The main disadvantage of capping is the necessity to maintain the barrier of clean soil for as long as the underlying contaminants remain toxic. In Sumgait the volume of contaminated soil was calculated and it was determined feasible to remove the most contaminated soil.

Mechanical removal of contaminated soil is most practical when the contamination levels are very high and there is a hazardous waste storage facility available (Rogozina and Morgunov 2016). This was the case in Sumgait. Therefore after careful consideration it was decided to dig out and remove most contaminated soil. Then the less contaminated soil was capped with a layer of clean soil. Then vegetation cover was established to prevent erosion of the layer of clean soil and contribute to biological remediation of the less contaminated soil beneath. So Sumgait project is an example of three methods combined.

The remaining contamination levels were measured before capping. The levels were much lower compared to those before remediation. But still some contamination remained. Further research would be necessary to study the effect of plants on degradation of the remaining contaminants.

Conclusions

The project was successful in turning the highly hazardous former industrial area into a small park absolutely safe for recreational activities. The project included standard stages: environmental assessment, selection of remediation methods, cleanup, post-cleanup environmental assessment, revegetation and making the area suitable for intended use. Soil sampling conducted by the project team indicated that before remediation the site was highly contaminated with such persistent toxic organic pollutants as benzo(a)pyrene, benzene, and PCBs. After the remediation the contamination levels dropped and the possibility of human contact with contamination excluded. The goal of the project achieved. The project also makes an example of productive cooperation of international non-governmental organization, commercial company, and government agencies.

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3.2.10. Initial approach for phytoremediation of petroleum hydrocarbons-mixed soil at oil industry in Skopje region

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Abstract

Phytoremediation has long been applied as a treatment technology that is cost-effective, ecologically friendly and efficient for the decontamination of hydrocarbon pollution (Saadawi *et al.* 2015). Rye (*Secale cereale* L.), barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.) were selected in order to identify plants that can enhance the remediation of soil mixed with petroleum hydrocarbons. Field trials were established at oil refinery near Skopje, in randomized block system with three replications, in eighteen trial microplots. Soil was mixed with petroleum hydrocarbons in concrete basins with three layers providing high hydrophobic protection. Laboratory experiment was designed in four variants with two replications (control, 3% of soil/oil sludge, 5% of soil/ oil sludge, soil from the prepared basin). Laboratory analysis were performed to identify petroleum hydrocarbons content, some chemical and physical properties. The effect of the plant growth of on the hydrocarbons content and chemical properties of soil

mixed with petroleum hydrocarbons and possibilities of production of crops with high yield and good quality was investigated in this study.

Keywords: phytoremediation, petroleum hydrocarbons, soil, wheat, rye, barley

Introduction, scope and main objectives

Phytoremediation, defined as the use of plants to assimilate, transform, metabolize, detoxify and degrade various toxic inorganic and organic compounds found in soil, water, groundwater, and air is generally considered as an environmentally friendly, cost effective, and socially accepted remediation approach (Salt *et al.*, 1995, 1998; Alkorta and Garbisu, 2001; Pilon-Smits, 2005; Sandhu *et al.*, 2007; Reichenauer and Germida, 2008; Wenzel, 2009; Prasad *et al.*, 2010). There are six basic ways plants can clean up a contamination: rhizodegradation, phytoextraction, phytovolatilization, phytodegradation, rhizofiltration, and rhizostabilization (Pilon-Smits, 2005).

In order to survive and thrive in PHC contaminated environments, plants must exhibit: (i) a tolerance to one or more components of petroleum mixtures, (ii) high competitiveness, (iii) fast growth, and (iv) the ability to produce and secrete hydrocarbon degrading enzymes (Wenzel, 2009). The initial physiological response of plants to PHCs in soil includes PHC uptake, translocation, and accumulation in organs such as roots and shoots and the rates of these processes are generally related to PHC concentration (Wild *et al.*, 2005; Lu *et al.*, 2010). The specific physiology and biochemistry of plant roots along with the activity of rhizosphere microorganisms make plant metabolic systems able to remediate toxic xenobiotics (Yavari *et al.*, 2015). Numerous studies focusing on plant species suitable for phytoremediation of PHC-contaminated soils have recognized that among others, Italian ryegrass (*Lolium perenne*), sorghum (*Sorghum bicolor*), maize (*Zea mays*), tall fescue (*Festuca arundinacea*), alfalfa (*Medicago sativa* var. *Harpe*), elephant grass (*Pennisetum purpureum*), bermuda grass (*Cynodon dactylon*), birdsfoot trefoil (*Lotus corniculatus* var. *Leo*), sunflower (*Helianthus annuus*), southern crabgrass (*Digitaria sanguinalis*), red clover (*Trifolium pratense*), beggar ticks (*Bidens cernua*), and sedge species (*Cyperus rotundus*) may be effective (Radwan *et al.*, 1995; Wiltse *et al.*, 1998; Chaineau *et al.*, 2000; Huang *et al.*, 2004; Parrish *et al.*, 2004; Rutherford *et al.*, 2005; Kaimi *et al.*, 2007; Muratova *et al.*, 2008; Shirdam *et al.*, 2008; Ayotamuno *et al.*, 2010; Tang *et al.*, 2010; Yousaf *et al.*, 2010; Hall *et al.*, 2011; Basumatary *et al.*, 2012, 2013).

Phytoremediation of soils with heavy metals near Veles was pioneer research in Macedonia (Mitkova *et al.* 2015). In the Republic of Macedonia, 16 sites with soil contamination have been identified, characterized as hotspots (Environmental statistic, 2007). One of the hotspots is OKTA refinery located in a vicinity of Skopje and for a period of five years, refinery closed crude oil processing. During the period 30 years of crude oil processing and within its operations, oily sludges were generated as a waste product. Presence of hazardous materials in oil sludges and their disposal presents a huge problem for the petroleum refineries, taking into consideration all aspects, especially environmental, social and economic ones. OKTA refinery required know-how and accept the proposal from the scientists at the Faculty of Agricultural Sciences and Food in Skopje to use phytoremediation as technique of treating refinery sludge, which both meets environmental regulations and it's cost-effective.

Main objective was selection of plants with best potential for phytoremediation of soil mixed with petroleum hydrocarbons and determination of reduction of hydrocarbons presence in soil.

Methodology

Preparation of soil mixed with hydrocarbons

Oily sludge was generated during 30 years of operations, as a waste product in OKTA refinery, and they contained water (50%), oil (30%), and solids (20%). Those sludge were initially treated by using three phases: mechanical treatment, physic-chemical treatment, final recovery/ disposal of generated waste. The water was as a result of the use of water for process cooling, cleaning, or the like. The oil component was typically one or more liquid hydrocarbon fraction of petroleum ranging from gasoline components to heavy oils. The solids component may comprise high boiling organic materials, or carbonaceous solids, and contain metallic and various inorganic materials. The solid materials were divided and disposed. Product from initial treatment was oily emulsion with the following composition 69% water, 15 % oil materials and 16% oil sludge. The generated emulsion was separated by gravity in three phases and it was possible to direct the water phase into the waste water treatment plant (WWTP) for further mechanical, physic-chemical and biological treatment. The biological degradation system was upgraded with proper nutrition and new cultures of microorganisms. The concrete basins were prepared with three layers providing high hydrophobic protection and surface around the basin was prepared with a film of geomembrane and geo-textile. The semi-solid oily phase was directed to the basins and mixed with clay loam soil. Presence of heavy metals were not detected in preliminary investigations. Prepared petroleum hydrocarbons-mixed soil for phytoremediation was isolated in the basin and has no influence on the environment.

Plant material

Various plants have been identified for their potential to facilitate the phytoremediation of sites contaminated with petroleum hydrocarbons and the majority of studies singled out grasses and legumes for higher potentialities (Ismaila *et al.* 2014). Selection of plants suitable for phytoremediation of mixed soil with petroleum hydrocarbons for autumn planting, was conducted on the basis of literature references (Ndimele, 2010). From the list of plants with high potential to phytoremediate mixed soil with petroleum hydrocarbons, rye (*Secale cereale* L.) was selected and from the list of plants with demonstrated potential to tolerate mixed soil with petroleum hydrocarbons barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.) were selected. Higher planting density was applied in order to eliminate the chance of a reduced sprout due to the contaminated soil, as well as to secure a maximum biomass production.

Field trials

Experiment was establish in basin at OKTA-AD Skopje. Field trials were prepared in randomized block system with three replications, in eighteen trial microplots with basic size of 6m². Mineral N:P:K (Mg)=8:16:24 (2) and organic fertilizers were applied. Soil samples were taken from the field area before the trials, average soil samples in a disturbed condition and soil samples in a natural undisturbed condition with Kopecki rings (only before the start of vegetation) were taken at 0-30 cm for determination of petroleum hydrocarbons. Field survey included collection of soil samples for laboratory analysis (ISO 10381-1:2002 and ISO 11464:2006).

Laboratory trials

Laboratory trial was established at Faculty of Agricultural Sciences and Food, with all selected crops that have high potential to phytoremediate and with demonstrated potential to tolerate soils mixed with petroleum hydrocarbons. Experiment was designed in four variants with two

replications: 1. Control, 2. 3% of soil/oil sludge, 3. 5% of soil/ oil sludge, 4. Soil from the prepared basin. The selected plant species were planted separately in the contaminated soil pots.

Laboratory Analysis

Analysis of petroleum hydrocarbons was according BS EN 14039:2004 Characterisation - Determining of hydrocarbon content (in the range of C₁₀ to C₄₀) in solid material by gas chromatography. Using this standard all hydrocarbons with a boiling range of approximately 175 °C to 525 °C, e.g. n-alkanes from C₁₀H₂₂ to C₄₀H₈₂, isoalkanes, cycloalkanes, alkyl benzenes, alkyl naphthalenes and polycyclic aromatic compounds are determined as hydrocarbons, provided they do not adsorb on the Florisil column during clean-up (Laboratory for soil and agroecology, Institute of Field and Vegetable Crops, Novi Sad, Serbia).

Laboratory analysis of the soil (some chemical and physical properties) are in according ISO standards.

Table 1. Soil samples analysis and methods

Type of analysis	Method	ISO Standard
Determination of pH	Electrometric	ISO 10390:2005
Humus content in %	Tjurin method	by Kozman
Total nitrogen (N%)	Kjedahl method	ISO 11261:2004
Available P ₂ O ₅ and K ₂ O mg/100g	AL method by Egner, Riehm, Domingo	
Carbonate content (CaCO ₃)	Volumetric	ISO 10639:2004
Total form of Cd, Pb	Aqua Regia, EDTA, AAS	ISO 11466:2004
Soluble form of Cd, Pb		ISO 14870:2001 ISO 11047:2004
Mechanical content (particle size distribution)	Method by sieving and sedimentation	ISO 11277:2004
Particle and Bulk density	Pycnometer and Kopecki rings	ISO 11508:2004 ISO 11272:2004
Sampling	Soil sample	MKC ISO 11464:2015

During the vegetation, biological, morphological and productive parameters are observed, as germination rate, plant's phenophases development, plant height, and number of plants per m², yield and yield components.

Results

The fixation/mobilization potential of the soil with respect to petroleum hydrocarbons depends on pH, organic matters and clay content of the soil. Table 2 and 3 show the mechanical composition and chemical properties of the soil used in a laboratory experiment. Table 3 and 4 show the mechanical composition and chemical properties of the petroleum hydrocarbons-mixed soil used for field trial.

Before starting with phytoremediation process analysis of soil mixed with petroleum hydrocarbons in the basin was performed. Analysis detected 65,973.3 mg/kg total hydrocarbon content in dry soil sample. The given value far exceeds soil remediation value of 5,000 mg/kg, as given in Dutch Target and Intervention Values, 2000 (the New Dutch List).



Figure 1. Preparation of petroleum hydrocarbons-mixed soil



Figure 2. Field trial planting



Figure 3. Field trial design



Figure 4. Crops germination at the field trial



Figure 5. Initial germination in lab pot



Figure 6. Rye germination



Figure 7. Barley germination



Figure 8. Wheat germination

Table 2. Texture of the soil used for the laboratory experiment

Fine soil separates in %												
Coarse sand 0.2-2mm		Fine sand 0.02-0.2mm		Total sand 0.02-2mm		Silt 0.002-0.02mm		Clay <0.002mm		Silt+clay <0.02mm		Texture
\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	
20,21	2,35	47,9	3,49	68,11	3,56	18,85	0,92	13,2	0	32,05	1,13	Sandy loam

\bar{x} % - average; SD - standard deviation

Table 3. Chemical properties of tested soil used for laboratory experiment

Chemical properties											
Humus (%)		N in %		pH in H ₂ O		CaCO ₃ in %		P ₂ O ₅ (mg/100g)		K ₂ O (mg/100g)	
\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD
3,1	0,06	0,14	0	7,57	0,01	4,79	3,01	41,95	0,21	24,03	1,1

\bar{x} % - average; SD - standard deviation

Table 4. Texture of the petroleum hydrocarbons-mixed soil used for the field trial

Fine soil separates in %												
Coarse sand 0.2-2mm		Fine sand 0.02-0.2mm		Total sand 0.02-2mm		Silt 0.002-0.02mm		Clay <0.002mm		Silt+clay <0.02mm		Texture
\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	\bar{x} %	SD	
5,01	0,08	30,95	5,51	35,96	5,39	29,59	5,61	34,46	0,08	64,05	5,59	Clay loam

\bar{x} % - average; SD - standard deviation

Table 5. Chemical properties of petroleum hydrocarbons-mixed soil used for field trial

Chemical properties											
Humus (%)		N in %		pH in H ₂ O		CaCO ₃ in %		P ₂ O ₅ (mg/100g)		K ₂ O (mg/100g)	
\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD
2,4	0,05	0,12	0	7,3	0,04	0	0	22,94	0,28	30,38	0,03
5											

\bar{x} % - average; SD – standard deviation

Current status

Faculty of Agricultural Sciences and Food (FASF) in Skopje in cooperation with oil company OKTA-AD Skopje, jointly work on treatment of oil sludge. This project aims to use plants and new technologies for soil cleaning and purification. The application of phytoremediation processes could save the ecosystem from further deterioration and can be considered as first steps in the restoration programs of endangered habitats. The main objective of any future project is to recognize plants and the associated microbes which have the ability to absorb and degrade the contaminants.

Expected results for this immense research are: quantification of the effect of phytoremediation with different crops on soil mixed with petroleum hydrocarbons, classification of crops according their phytoremediation effect, selection of crops with best potential for phytoremediation of soil mixed with petroleum hydrocarbons for further research activities, determination of reduction of hydrocarbons presence in soil, addressing the impact of phytoremediation, possibilities of production of crops with high yield and good quality on soil mixed with petroleum hydrocarbons. Proposed design had a few weaknesses as unidentified ratio soil/oil sledge in the lagoon, water/air pores in soil, formed oil film around seed coat and even flood and sinking. Nevertheless, the research has a enormous opportunities and strengths, as educated research team with scientific knowledge of field trials and laboratory methods, knowledge of crop biology, physiology and productivity, knowledge of soil science, accredited laboratory for soil and fertilizers analysis at FASF (MKC EN ISO/IEC 17025:2006), extension of research activities and long-term monitoring with best crops for phytoremediation and addition of other plant species and knowledge transfer of results and conclusions to students at FASF.

Conclusions

Selected plants with high potential and plants with demonstrated potential to tolerate petroleum hydrocarbons-mixed soil were planted on prepared soil mixed with petroleum hydrocarbons. Preliminary result were obtained of chemical properties and texture of soil used for field trial and laboratory experiment. Analysis of total hydrocarbon in soil mixed with oil sludge indicated higher value than proposed in legislation. Lab experiment purpose was intended to study the best ratio of soil and oil sludge for planting various crops. Monitoring plant growth and productivity, will enable recommendation of prospective combination for future preparation of the basins.

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3.2.11. The Effectiveness of using bioremediation measures to podzolized chernozem, which is contaminated by heavy metals.

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Abstract

It is substantiated the effectiveness of using soil, which is artificially enriched by agronomic useful *Bacillus* bacteria strains, as a means of bioremediation of podzolized chernozem, which is contaminated by heavy metals Cd, Pb, Ni, Zn on the level of 5 clarks. It is estimated the level of support and renewal of biological activity of contaminated soil upon the biological indications of bacterial complexes. It is indicated positive trends where the microbiological activity of podzolized chernozem increases because of preplant bacterization of spring barley seeds.

Keywords: heavy metals, bacterial cenosis, microbiological soil activity, bacteria strains, podzolized chernozem, bacterization

Introduction, scope and main objectives

In modern conditions a technogenic soil pollution is a global problem. In Ukraine more than 4,5 millions ha of farmlands predominantly are polluted with industrial waste - heavy metals, petrochemicals, radionuclides etc. The degradation of soils caused by ongoing intensive anthropogenic influence [0, 14].

Biological degradation of soils, which were polluted by anthropogenic factors, is defined as a process of steady changes of soil biological characteristics and manifests in quantity adjustment of microorganisms, decreasing of various species and dysfunction of balance among various species of soil's meso- and microfauna, the increasing of pathogenic microflora and changing the intensity of biochemical processes [0, 0]. Depending on soil contamination level the ecological pre-crisis situation occurs, where negative changes in soil biological characteristics take place.

It is known that bacterial cenosis have a potential facility to autoregulation and adapting to environmental changes [2, 15]. Resistibility (tolerance) of microorganisms to heavy metals manifests in its ability to grow at high boundary concentrations of pollutants. In certain concentration of heavy metals may be an adaptation of microorganisms. In bacterial cenosis, which comes under influence of one of the metals, the resistibility to this definite metal increases, herewith it must be taken into account the nature of the metal. Thus, soil bacterial cenosis are capable of resisting environmental factors or come back to normality after deviations.

Whereas, the support and activation of soil microbocenosis may be implemented by its artificial enrichment with high-value selected *Bacillus* bacterial cultures. Its various biological activity, high resistibility to adverse environmental conditions have a high profile in circulation of elements in nature, forming stability and activity in soil biological processes [5, 6, 0, 0, 0, 0]. Consequently, there is an opportunity to develop bioremediation method of anthropogenic load reduction on soil and support of its biological activity using *Bacillus* bacterial cultures, which have a complex of useful agronomic capabilities.

Methodology

Microbiological and biochemical researches were performed with samples, which were selected from rhizosphere of spring barley, which was growing in polluted with heavy metals podzolized chernozem on the level of 5 clarks Cd (5 mg/kg), Pb (10 mg/kg), Ni (250 mg/kg), Zn (250 mg/kg) on condition of introduction of active strains of microorganisms.

The researches were performed on microfield dummy experiment relating to soil conservation Department State Enterprise Experimental Farm "Grakivske" experimental field NSC "Institute for soil science and research named after O.N. Sokolovsky". There was examined the influence of introduction selected *Bacillus* bacterial strain cultures (*Bacillus* strains N^oN^o123, 531) in rhizosphere of spring barley for the purpose of define biological soil activity parameters and plant productivity. Bacilli strains *Bacillus* sp. were taken from the collection of soil microbiology sector of NSC "Institute for soil science and research named after O.N. Sokolovsky".

Experimental design with spring barley: 1. Control (unpolluted soil); 2. Background N₆₀P₆₀K₆₀; 3. Background + Cd₅; 4. Background + Pb₅; 5. Background + Ni₅; 6. Background + Zn₅; 7. Control (unpolluted soil) + bacterization strain 123; 8. Background + bacterization strain 123; 9. Background + Cd₅+bacterization strain 123; 10. Background + Pb₅ + bacterization strain 123; 11. Background + Ni₅+bacterization strain 123; 12. Background + Zn₅+bacterization strain 123; 13. Control (unpolluted soil) + bacterization strain 531; 14. Background + bacterization strain 531; 15. Background + Cd₅+bacterization strain 531; 16. Background + Pb₅ + bacterization strain 531; 17. Background + Ni₅+bacterization strain 531; 18. Background + Zn₅+bacterization strain 531.

The research of soil microbiota was performed at sections inclusive of mineral backgrounds, which are used in Ukrainian agriculture.

In soil samples, which were selected from rhizosphere of plants, the quantity of main microbiotic groups were defined, such as: organotrophic bacteria, microorganisms, which adopting nitrogen mineral compounds and actinomycetes, microscopic fungi and oligotrophic microorganisms. The integrated indexes of biogenesis (IIB), biological activity (IBA), and biological condition (IBC), were calculated by relative magnitude method according to Azzi Dj [1, 16].

The biochemical characteristics of soil were defined by indexes of fermentation activity of invertase with photo colorimetric method [3, 6], dehydrogenase according [0] and polyphenol oxidase according to Karyagina and Mikhailovskaya [4].

The established information of the research were statistically analyzed by analysis of variance. Provide sufficient detail to allow the work to be reproduced.

Results and discussion

On the basis of structural and functional characteristics of podzolized chernozem microbiocenosis it is defined, that under the influence of heavy metals (the pollution is on the level of 5 clarks) the rebuilding of microbial cenosis takes place. Herewith the influence of every heavy metal on microbiota has its specify according to its aggression level. The main oppression happens under the influence of cadmium and lead, where microbial cenosis decreasing a population of eutrophic groups on 7-18% appropriately, which are capable to adopt an organic nitrogen, on 23-40% - the population of oligotrophic microorganisms, on 5-16% - micromycetes comparatively with the control (without pollution) (Figure 1).

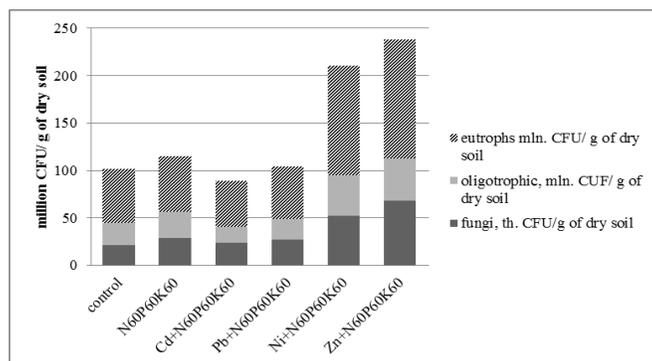


Figure 1. Structural changes of microbial cenosis in spring barley rhizosphere, which was grown in podzolized chernozem, under the influence of heavy metals

A little bit different tendency of changes detected in microbiocenosis structure under influence of nickel and zinc. It was explored by other scientists, that microbial cenosis has a multistage (4 stages) reaction on pollutant's concentration and its nature: homeostasis, stress, period of resistibility and repression [15]. On the first and the second stages we can see the stimulation effect of less aggressive heavy metal, on the other hand - the appropriate reaction on external agent, which is followed by significant changes of quantitative correlation of microbial populations.

In such a manner, biogenesis was increased on 52-97% according to the main eco-trophic groups of microorganisms concerning variants, where there was Ni integrated, while Zn variants - biogenesis was increased almost in 1,6-4,5 times comparatively with control. Here there is a key distinction comparing with repressive cadmium and zinc activity, which substantively depress a growth and development of soil microorganisms.

At the same time, the artificial soil enrichment with active bacilli cultures profoundly change the orientation of the rebuilding processes of microbial cenosis in contaminated soil (Figure 2).

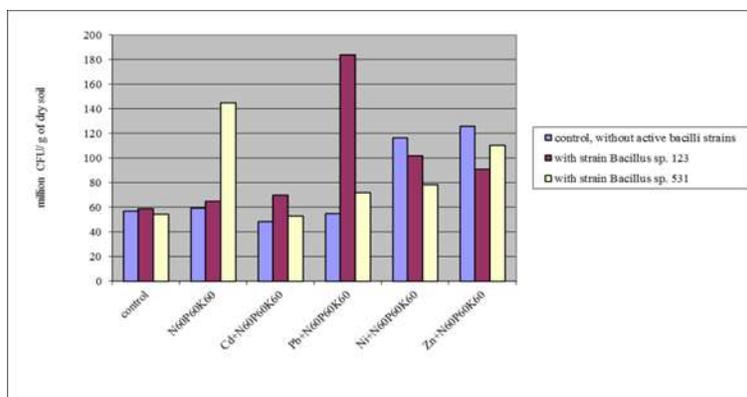


Figure 2. The influence of active bacilli strains introduction on biogenesis of podzolized chernozem, which is contaminated with heavy metals

The quantity of eutrophs was increased min on 4%, max – on 145% in control variants (agricultural background N60P60K60 without contamination). But the considerable increase of microorganisms (in average on 80% eutrophs and on 54% oligotrophs) was detected in the soil, which was contaminated by more toxic Cd and Pb. At first sight, such a contradiction could be explained, that natural microbial cenosis become less stable under the influence of heavy metals, the groups of non-resistant bacteria are depressed, which facilitate an active fungi development, what is more pathogenic fungi development, which occupy free ecological niche. But on condition of artificial enrichment with highly-active pure bacilli culture, which proper for adaptation to severe environment, processes of fungi development slow down and microbial cenosis resumes it's useful agronomic properties, in some variants even to the level of uncontaminated soil, where the calculated integrated index of soil biogenesis (IIB) indicates on it (Figure 2). Some other tendency of changes in microbial cenosis structure was detected under the influence of nickel and zinc. It is known, that less toxic metals in fractional amount play a good part as microelements in development of soil microflora, that is why regarding variants without introduction of selected bacilli strains, the soil biogenesis was on higher level relatively to control variants because of natural groups of microorganisms and artificial soil enrichment didn't has such an effect. That's why using bioremediation facilities of soil, which was contaminated with heavy metals, we must take into account the specificity of acting and toxicity level of every heavy metal on soil biota.

It is detected some intensity changes of biochemical processes in soil under certain conditions. All things considered, indexes of fermentation activity of podzolized chernozem were increased under the influence of strains introduction, but an appreciable difference had been determined between dehydrogenase and invertase soil activity. The most sensitive to heavy metals was dehydrogenase ferment, which characterize the activity of microbial cenosis. Its activity was cum down in polluted soil: under the influence of Cd – in 1,2 times, Pb – in 4,2 times, Ni – in 3,5 times, and Zn – almost in 13 times. Entering of active bacilli strains appreciably improved dehydrogenase activity in the majority of variants: background with Cd it is detected the increasing on 17 %, background with Ni – already on 40 %, especially against the background with Pb – in 2,7-2,9 times comparatively with soil indexes without introduction. Only under the influence of Zn the effectiveness of artificial enrichment with bacterial cultures didn't reflected, and even was decreased in some measure, but comparably with other variants – not fundamentally.

Fixed indexes of fermentation activity of soil confirm the specificity of BM effect on biochemical activity of podzolized chernozem. The calculated integrated index of biological activity (IIBA) of podzolized chernozem point out on yet more sensibility of fermentative soil activity till negative

influence of heavy metals comparatively with quality and quantity indicators of microbial community structure (Figure 3).

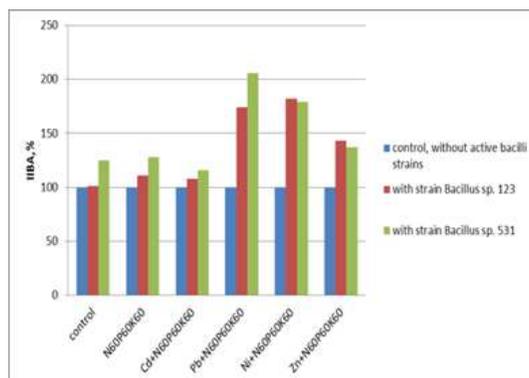


Figure 3. The influence of active bacilli strains introduction on biogenesis of podzolized chernozem, which is contaminated with heavy metals

The analysis of spring barley and corn harvest productivity (which was undertaken during follow-up researches) has allowed to confirm positive changes in structure and functioning of microbial cenosis for contaminated soil under the influence of enrichment with selected cultures of microorganisms.

The character of changes in microbial communities depends on definite property package, which is related to introduce bacteria. The biggest resistance to heavy metals was found out by bacilli strain *Bacillus sp. 531* with nitrogen-fixing and growth parameters; a little lower effectiveness was found out by the strain *Bacillus sp. 123* with antagonistic and growth parameters (Figure 4).

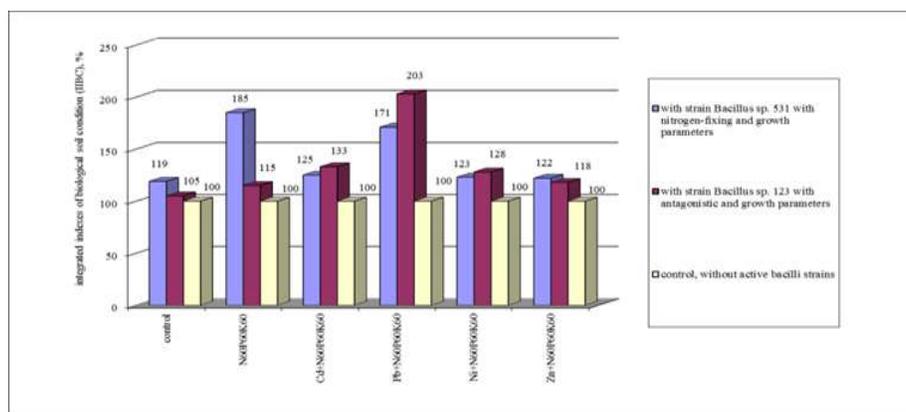


Figure 4. Changes of integrated index of biological condition (IIBC) of podzolized chernozem, which is contaminated with heavy metals, under the influence of selected microorganisms introduction

There was taken an assessment of changes of podzolized chernozem biological properties, with calculated integrated indexes of biological soil condition (IIBC) (Figure 4), which happen during the artificial soil enrichment with active bacterial cultures, make possible to define terms of soil support in biologically active condition and resuming a plant productivity level, which are growing in podzolized chernozem, contaminated with heavy metals.

In order to use in practice this microbiologic agro-method for its effectiveness it is necessary to take into account the specificity of negative influence on soil microbiota of every metal and physiological

peculiarity of integrated bacterial cultures. In general, the results of researches tell us about the improvement of ecological state of podzolized chernozem in conditions of contamination with heavy metals on the level of 5 clarks using the activation of microflora.

Conclusions

- On the basis of the complex of biological parameters it is proved, that heavy metals (Cd, Pb, Ni, Zn) on the level of 5 clarks have a negative influence on biological properties of podzolized chernozem: cause a rebuilding of microbial cenosis of podzolized chernozem and decrease a biological activity of soil. The most toxic in soil are cadmium and lead.
- The introduction of bacilli strains, with complex and useful agronomical properties, activates microbial communities in rhizosphere of spring barley, which was grown in podzolized chernozem and was contaminated with heavy metals, that is point out to fixity of *Bacillus* bacteria for toxic effect of Cd, Pb, Ni, Zn.
- It was taken an assessment of changes of biological properties of podzolized chernozem according to calculated integrated indexes of biological soil condition (IIBC). Due to the assessment there were improvement of ecological condition of podzolized chernozem, which was contaminated with heavy metals on the level of 5 clarks, in conditions of artificial soil enrichment with active bacterial cultures, which give a boost to microflora. IIBA has increased on 52 % in average.
- In order to use in practice this microbiologic agro-method for its effectiveness it is necessary to take into account the specificity of negative influence on soil microbiota of every metal and physiological peculiarity of integrated bacterial cultures. The highest resistibility to heavy metals was defined by bacilli strain *Bacillus sp.* 531 with nitrogen-fixing and growth parameters.

• The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.2.12. Biochar an efficient tool to decrease Pb and As in metal(loid)s contaminated soils and to allow assisted phytoremediation of multicontaminated technosols using tree species.

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Abstract

Soil contamination by metal(loid)s is one of the most important environmental problem. It leads to loss of environment biodiversity and soil functions and can have harmful effects on human health. Therefore, contaminated soils could be remediated, using phytoremediation. Indeed, plant growth will improve soil conditions while accumulating metal(loid)s and modifying their mobility. However, due to the poor fertility and high metal(loid)s levels of these soils, amendments, like biochar, has to be applied to promote phytoremediation and to stabilize pollutants in soil. We demonstrated that biochar according to feedstock and particle size was efficient in improving soil physico-chemical properties and reducing Pb and As soil pore water concentrations. These ameliorations allowed plant growth and increased dry weight production of tested tree species.

Keywords: Metal(loid)s, Pb, As, Phytoremediation, biochar, trees, remediation, contaminated soils

Introduction, scope and main objectives

Soil contamination presents multiple risks for the environment: it reduces soil fertility and ecosystemic functions as well as biodiversity. In addition, contaminated soils often lack of vegetation and therefore are subjected to wind erosion and water leaching, endangering surrounding non-contaminated environments. Moreover, contaminants can pass into the food chain and cause harmful effects to human health (Jarup, 2003; Purdy and Smart, 2008). Consequently, those contaminated areas need to be remediate and one of the possible techniques is phytoremediation and mainly phytostabilization which consists to stabilize soil contaminants by the combined effect of root exudates and associated microflora, which neutralize the potential metal(loid)s uptake by plants in upper parts (Mahar *et al.*, 2016; Gomes *et al.*, 2016). Such positive effects can be increased by using amendments such as biochar. Biochar is a stable, carbon rich material with a porous structure, obtained by biomass pyrolysis under low oxygen conditions (Sohi *et al.*, 2010; Jeffery *et al.*, 2011; Beesley *et al.*, 2013; Paz-Ferreiro *et al.*, 2014). It is characterized by an alkaline pH (Cantrell *et al.*, 2012), a high cation exchange capacity (Paz-Ferreiro *et al.*, 2014), an elevated water holding capacity (Molnar *et al.*, 2016), a low density (Mary *et al.*, 2016) and a large surface area (Beesley *et al.*, 2013; Paz-Ferreiro *et al.*, 2014). Therefore applying biochar to soil can have beneficial effects on both soil physico-chemical properties and plant growth. Indeed, several studies showed that biochar amendment to soil, contaminated or not, improved soil agronomic properties (Biederman and Harpole, 2013; Hua *et al.*, 2014; Laghari *et al.*, 2015; Rees *et al.*, 2015). Moreover, biochar reduced soil pollutants extractability (Houben *et al.*, 2013; Bian *et al.*, 2014) and soil pore water concentration (Beesley *et al.*, 2014). However, biochar effects on soil and plants will depend on soil characteristics, plant species but also on the feedstock pyrolyzed and on biochar particle size (Sun *et al.* 2014).

Phytoremediation success will depend on several parameters but one of the most important is the plant species used. Ideally, the species chosen will have to present a tolerance to the soil contaminants, be able to grow in poor soils, have a fast growth and a high biomass production associated to a deep and important root system (Gerhardt *et al.*, 2017). Since no plants meet all the previous required criteria, plant selection programs must be undertaken based on remediation objectives. Among woody species, *Salicaceae* have a good potential for being used in phytoremediation. Firstly, they present a high and rapid biomass production (Justin *et al.*, 2010; Chen *et al.* (2013). In addition, their deep and wide root system allows a higher soil colonization (Marmioli *et al.*, 2011) and thus stabilization. They are also characterized by a high transpiration rate associated with a high soil water uptake, which can reduce percolating water and leaching of the contamination to the groundwater. Secondly, some *Salicaceae* are adapted to metal(loid)s stress (Justin *et al.*, 2010) and present a good growth in such conditions (Laidlaw *et al.*, 2012). Thirdly, *Salicaceae* can accumulate substantial amounts of metal(loid)s (Migeon *et al.*, 2009; Mleczek *et al.*, 2010) and have been shown as metal(loid)s stabilizers (Lebrun *et al.*, 2017; Touceda-Gonzalez *et al.*, 2017). Finally, *Salicaceae* represent an economic gain. Indeed, in addition of being used to remediate contaminated soils, their biomass obtained in short rotation coppice allows bioenergy production (Greger and Landberg, 1999). In addition to *Salicaceae* we have been also interested in nitrogen fixing woody species such as *Alnus* or *Ailanthus*.

The aim of our work was to evaluate the combination of biochar amendment and tree species in order to stabilize a post-industrial area and an acidic former mine technosol, highly contaminated by Pb, and presenting a poor organic content. In this study, different size fractions of wood feedstock biochar were used to evaluate their effect on soil characteristics and plant growth. The main goal was to evaluate the ability of tree to grow on these amended technosol in order to limit metal(loid)s dispersion through wind erosion and leaching. The specific objectives were to assess

the biochar particle size and dose effects on (i) the main physicochemical soil properties, (ii) plant development, and (iii) metal(loid)s concentrations and distributions in plants. The ultimate goal was to determine which biochar feedstock, particle size and rate combination allowed a good root development and a minimal metal(loid)s translocation.

Methodology

Site description

A former silver-lead extraction mine, located in Pontgibaud district, Massif Central, France, was investigated. This site, which has been disused since 1897, covers 15 ha and is composed of four areas and the two main contaminants are Pb ($11,453.63 \pm 0.18 \text{ mg kg}^{-1}$) and As ($539.06 \pm 0.01 \text{ mg kg}^{-1}$). The technosol was sampled between 0 and 20 cm depth at the second settling pond (GPS coordinates $45^{\circ} 47' 27''$ Nord and $2^{\circ} 49' 38''$ East), located at Roure-les-rosiers (St Pierre le Chastel).

Experimental design and soil preparation

A mesocosm experiment was performed in greenhouse using Pontgibaud contaminated technosol and three different biochar feedstocks (lightwood, hardwood or pinewood) presenting 4 different particle size (inferior to 0.1 mm; 0.2 to 0.4 mm; 0.5 to 1 mm; 1 to 2.5 mm) at two rates (2% and 5%) (w/w). Three hundred grams of the different mixtures were placed in plastic pots (0.4 L). The pots were allowed to equilibrate 5 days at field capacity before starting experiments. One non-rooted cutting of *Salicaceae* or a two months old *Alnus* or *Ailanthus* tree obtained from seeds germination were introduced in pots whereas three pots per treatment were left un-vegetated. Trees were grown for at least 45 days in a greenhouse.

Biochar analysis

pH and electrical conductivity (EC) were measured with a combo pH and EC (HI 98130, Hanna Instrument) according to the following protocol: 3 g of biochar were suspended in 21 mL distilled water. The solutions were shaken (150 rpm, ambient temperature) during 4 h, then left to settle for 15 min before measurements were made. Three replicates per biochar were done. Water holding capacity (WHC) were measured by saturating samples with distilled water. BET measurements, to assess specific surface area, pore diameter, and pore volume, were realized using a BelSorp Mini II (MicroTrac Bel) (LMI, Villeurbanne, France).

Soil pore water analysis

Before planting the cuttings, as well as before harvesting the plants, the SPW of each pot was sampled using soil moisture samplers (Rhizon™) (Modele MOM, Rhizosphere Research Products, Wageningen, The Netherlands). Rhizon were placed close to the root system in the middle of the pot at an angle of 40° . Pots were watered and let to equilibrate for 4 h before sampling. SPW samples (20 mL) were used directly to measure pH and EC with a combo pH and EC. Metal(loid)s concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (ULTIMA 2, HORIBA, Labcompare, San Francisco, USA) after sample acidification (HNO_3 , 0.15 M final), according to Bart *et al.* (2016)

Plant Analysis

At the end of the experiments, all the plants were individually harvested and newly formed organs (leaves, stem, and roots) were separated. Roots were rinsed twice in tap water and three times in

distilled water to remove soil particles. Samples were dried during 72 h at 60 °C and dry weight (DW) was measured. As and Pb organ concentrations were determined by ICP-AES according to Bart *et al.* (2016).

Results

Biochar characterization

The biochar particle size had a significant effect on the physicochemical biochar properties measured. All the four biochar size fractions were significantly different ($p < 0.01$) with respect to pH, EC, and WHC; however, all presented an alkaline pH and a high WHC. In general, when particle size decreased, an increase in pH and EC was observed, whereas the WHC decreased. In detail, the pH of hardwood biochar which was the most efficient to ameliorate the agronomic characteristics of the soil was between 9.53 and 8.81. Inferior to 0.1mm particle size biochar presented a twofold higher EC than 1-2.5mm particle size biochar (669 and 348 $\mu\text{S cm}^{-1}$, respectively). Regarding WHC, the adverse effect was observed. For instance, the smallest particle size biochar was able to retain 160% of its mass in water while the biggest was able to retain 200% of its mass. The biochar specific surface area and total pore volume decreased with increasing particle size. Finally, the mean pore diameter values showed the opposite trend: indeed, biochar pore diameter increased when particle size increased.

Soil water holding capacity (WHC)

The non-amended Pontgibaud technosol presented a low WHC (34.94%). When amended with biochar its WHC increased. Thus the particle size had a significant effect ($p < 0.01$) on WHC: when particle size increased, WHC increased.

Soil pore water physico-chemical properties

Pontgibaud SPW presented an acidic pH (4.98), and no pH variation was observed at the end of the experiment, either with or without tree growth. At the beginning of the experiment, a SPW pH increase was observed after biochar addition, at 2 and 5%. The hardwood biochar amendments presenting a particle size < 0.1 mm led to a higher SPW pH increase when they were added at 5% than at 2% and reached the value of 7.4. At the end of the experiment time course, no significant difference was observed between the vegetated and the non-vegetated soils. In general, when the biochar particle size was smaller, there was a significantly ($p < 0.001$) higher EC increase compared to the larger particle size; and a 5% amendment resulted in a higher EC than a 2% amendment ($p < 0.001$). Concerning the Pb SPW concentration, biochar induced almost a 90% decrease whereas for As the effect was less significant.

Plant growth

For all plant tested, biochar amendments induced an important growth. Whereas no growth was obtained on contaminated soil not amended. Only *Alnus* trees demonstrated a growth on non-amended polluted soil.

Metal(oids) concentration in plants

For all the tested conditions, the highest metal(loid)s concentrations were observed in the roots. The plants grown on contaminated soil presented the highest As stem concentrations, with 17.98 mg kg^{-1} and very low As leaf concentrations (0.17 mg kg^{-1}). When the contaminated technosol was amended, at 2 or 5%, by hardwood biochar, no As was detectable in the leaves, while stem As

concentrations decreased. The greatest decrease, 96%, was observed for the low particle size biochar applied at 2%. In general, for the Pb content of the three organs (roots, stems and leaves), even if there was an increase of Pb content there was no particle size effect, and no significant difference between 2 and 5% biochar addition.

Discussion

For all plant tested a better dry matter production was found in the biochar-amended conditions. This growth improvement can be the combined effect of biochar properties. Indeed, as found in other studies and in our own work, biochar (i) improves agronomic soil qualities by increasing pH and EC (Chintala *et al.* 2013), (ii) increases water content and nutrient availability (Houben *et al.* 2013, Molnár *et al.* 2016), and (iii) decreases PTE bioavailability. It has to be noted that although biochar significantly reduced SPW Pb concentrations, high Pb concentrations were found in roots and at a lower level in aerial parts. Several hypotheses can be formed in order to explain this: (i) a weak sorption strength of Pb onto the biochar, and (ii) a higher bioavailability of Pb. This requires further investigations. Also, it has to be noted that we do not differentiate Pb absorbed in the roots from Pb adsorbed onto the root surface. The majority of metal(loid)s accumulated by the plants was found in the root system, and very little As and Pb translocation towards upper parts was observed. The high accumulation of As and Pb in roots and low upper parts translocation show the “excluder” nature of tested trees towards As and Pb.

The biochar dose application had an effect on soil pore water pH and EC, with a higher increase with increasing dose, while it had no effect on most of the plant growth parameters measured. It was observed that hardwood biochar was the most effective to stabilize Pb in soil and to allow plant growth.

Conclusions

A phytostabilization study was performed in mesocosm in order to evaluate the effect of biochar addition presenting different feedstock origins and particle size on (i) mine technosol physico-chemical properties and (ii) plant growth parameters. Biochar addition to Pontgibaud technosol modified the technosol physico-chemical properties. We observed a pH, EC, and WHC increase as well as a SPW Pb concentration decrease. These improvements allow a better tree growth development with a Metal(loid)s accumulation preferentially in the roots. The association plant–biochar seems to be an efficient combination for metal(loid)s soil stabilization, especially Pb. According to our results, the use of the biochar size fraction 0.2–0.4 mm, which is easy to produce and applied at 2%, appears to be the best candidate for a long-term field experiment, since it combines three advantages: a pH increase, a Pb immobilization, and a high plant growth, which will prevent wind erosion and contaminant leaching. However, even though biochar reduced Pb concentration in soil pore water, high Pb concentrations and quantities have been found in the aerial parts, which, in the long term, could present a problem for plant growth but also in terms of return of the pollution to the soil after leaves fall.

Finally, it can be concluded that particle size fraction is an important factor when using biochar as a soil amendment, while no difference between 2 and 5% application rates was observed on most of the parameters measured and hardwood biochar is the most effective to allow the growth of *Salicaceae*, *Alnus* and *Ailanthus* trees which are good candidates for phytoremediation.

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3.2.13. Agronomic feasibility of bioenergy crop cultivation on polluted soils: Insights and opportunities for land use design and environmental suitability

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Abstract

The FORBIO consortium applied integrated evaluation to assess the agronomic and techno-economic potential of the selected advanced bioenergy value chains in the identified sites of the target countries not used for supply food and feed. In the Italian study area (Sulcis district), a detailed database on bioenergy crops suitable for the region based on literature was created. The agronomic potentials and yield potentials were compared, with the aim of further developing a landscape design based on GIS multi-criteria evaluation for land environmental suitability and production potential. The study provides a quantitative comprehensive assessment for providing biomass and raw materials in the supply chain for a biorefinery in one of the most polluted industrial areas in Italy, framing the basis for realistic industry's feedstock demand and sustainable land use actions for reducing heavy metal accumulation on polluted soils

Keywords: Polluted land, agronomic feasibility, bioenergy production, sustainability

Introduction, scope and main objectives

Anthropogenic soil diffuse pollution with heavy metals is of increasing question because of its potential effects on environment and ecosystem, as well as human health and safety. Heavy metal accumulation in agricultural and productive soils can be transferred to the food and feed or dispersed and lixiviated on freshwater, ground water, and rivers. The cultivation of dedicated energy crops across unavailable soils for food production could be a possible pathway for restoring contaminated and polluted soils, fostering land amelioration and rural development, responding to the European Union (EU) 20-20-20 targets and the EU's Renewable Energy Directive. A recent

study suggests that in EU at least 50,000 hectares are eligible as suitable sites for growing energy crops on contaminated soils (Allen *et al.*, 2014).

This work reports the results of the agronomic feasibility of bioenergy crop cultivation on polluted land in the Sulcis area (Sardinia, Italy) (Figure 1) within the framework of the EU project FORBIO (Fostering Sustainable feedstock Production for Advanced Biofuels on underutilized land in Europe). The FORBIO consortium applied integrated evaluation to assess the agronomic and techno-economic potential of the selected advanced bioenergy value chains in the identified sites of the target countries not used for supply food and feed.

In the Italian study area (Sulcis district) we develop three major steps: (1) development of a detailed database on bioenergy crops suitable for the region based on literature search and field results; (2) comparison of agronomic aspects and yield potentials; (3) landscape design based on GIS multi-criteria evaluation for land environmental suitability and production potential. The results of the study will provide a useful reference for the overall feasibility of sustainable biomass cultivation on polluted soils in this region.

Methodology

The study area is located in the largest Site of National Interest (SIN) in Italy (about 22.000 ha), contaminated with heavy metals (Pb, Cu, Zn, Co, As) from industrial plants located in the municipality of Portoscuso (Figure 1). Today operates a coal power generation plant, while in the past industrial pollution derives from bauxite and aluminum production, as well as by old previous mining activities. The most polluted area is annually checked by ARPAS (Agenzia Regionale per la Protezione dell'Ambiente della Sardegna) with a monitoring network of soils, water, air, and vegetation.

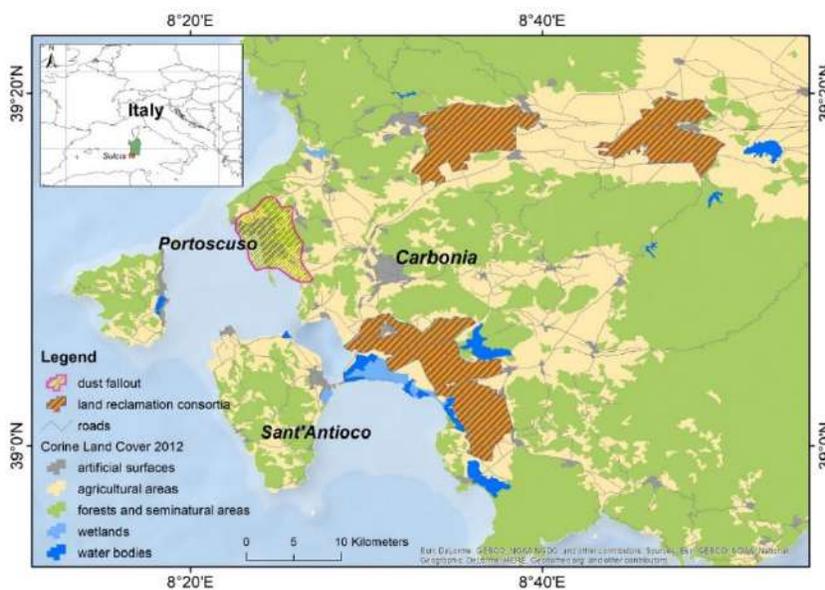


Figure 1. Overview of the study area.

In the first phase, in order to establish the most suitable bioenergy crops, relevant results from scientific studies and field trials regarding bioenergy crops conducted in Sardinia were collected. We identified and analyzed in detail the main agronomic traits of these crops: yield, dry matter, cultivar, fermentable sugars, irrigation, fertilization, soil texture and pH, elevation, growing

seasons. All relevant information was implemented in a relational database implemented in MySQL. The database includes 451 observations, for a total of 19 sites for 17 different crops. In the second phase, we develop a comparison of agronomic aspects and yield potentials of the agronomic traits, with a final short list of suitable energy crops that could be cultivated on polluted soils. In the final phase, we implement a multi-criteria decision making approach based on GIS procedure to accurately spatialize and identify the most suitable areas for the cultivation of bioenergy crops. The dataset used comprises land use map, digital elevation model, soil map, meteorological data, and ancillary data. A conservative landscape management approach was chosen, excluding from the model the most vulnerable and fragile areas such as rivers, lakes, meadows, and forests.

Results

According to the data analyzed, the most suitable annual crops for bioenergy cultivation on polluted soils are milk thistle (*Silybum marianum* L. Gaertn.), sorghum (*Sorghum bicolor* L.) and maize (*Zea mais* L.) (Table 1). Among perennial crops, the most productive and interesting are smilo grass (*Piptatherum miliaceum* (L.) Coss.), giant reed (*Arundo donax* L.), cocksfoots (*Dactylis glomerata* L.) and cardoon (*Cynara cardunculus* L. *var. altilis*).

Table 1. Biomass yield for the most suitable crops for bioenergy production in the Sulcis area.

Typology	Herbaceous plants		
	Annual	Perennial	
Lignocellulosic crops	Globe-artichoke Milk thistle	Giant reed Miscanthus Switchgrass Smilo grass Tall fescue Ryegrass Cocksfoot Cardoon	Eucalyptus
Oleaginous crops	Rapeseed		
Sugar crops	Sweet-sorghum		
Starch crops	Maize Durum-wheat Triticale		

According to the GIS-based suitability model (Figure 2), the available surface for biomass cultivation is approximately 1000 ha with regard to the most polluted soils (unequipped area for irrigation), 5700 ha in the surrounding area equipped for irrigation within the Land Reclamation and Irrigation Consortium (Figure 1), while the total suitable area amounted to 51.000 ha, hypothesizing a supply radius of 70 km from the biorefinery located on Portovesme.

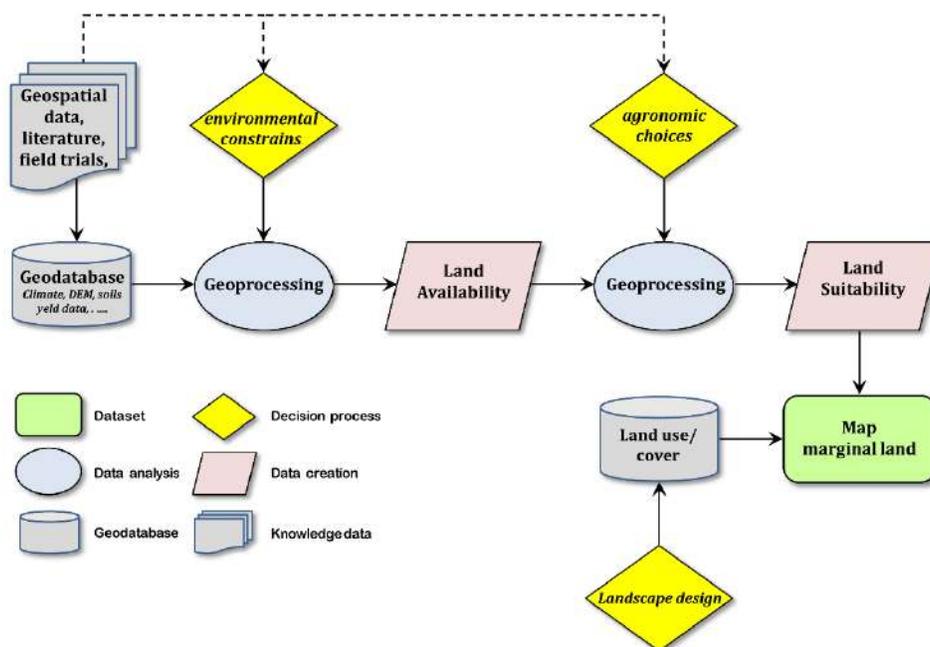


Figure 2. Flowchart of the suitability analysis

Discussion

Based on the findings gathered in this study, annual bioenergy crops most suitable for grown on polluted soils in the Sulcis area are milk thistle and sorghum thanks their phenotypic plasticity in terms of drought tolerance, water demand and evapotranspiration rate, especially. Recent results are accord with our findings that indicate that *Cardueae* species are versatile and promising crops for long-term cropping systems thanks to the attributable stable productions under low input (nitrogen application and minimum tillage) and water use efficiency (Deligios *et al.*, 2017; Gominho *et al.*, 2018; Ledda *et al.*, 2013). Among perennial crops, giant reed and native germoplasm of perennial grasses are the most suitable considering their stable biomass yields, low input, fermentable sugars, and adaptability in the Mediterranean environment (Cosentino *et al.*, 2014; Sulas *et al.*, 2015). In addition, a number of studies suggest that giant reed as great adaptability and phytoremediation capacity on polluted soils, with phytoextraction and accumulation in the hypogeal part (Barbosa *et al.*, 2015; Fiorentino *et al.*, 2013). These results have encouraging implications for soil restoration and remediation, coupling of phytoremediation with sustainable bioenergy production. In fact, considering the outcome of the GIS-based suitability approach can be produced 15.000 tons dry biomass in the most polluted area, assuming a mean biomass productivity of 15 dry tons/ha. Moreover, can be produced about 142.000 tons dry biomass in the surrounding area equipped for irrigation (biomass productivity 25 dry tons/ha), in accordance with agronomic inputs and crop management.

Conclusions

The aim of the present research was to examine the agronomic feasibility for the cultivation of bioenergy crops on polluted and underutilized soils located in the Sulcis area (Italy), and evaluate the land suitability and production potential with a GIS-based methodology. Based on the findings gathered in this study, the following conclusions can be drawn:

- Dedicated bioenergy crops such as giant reed and *Cardueae* species can be potentially grown on polluted soil for providing biomass and raw materials in the supply chain for a biorefinery;
- According to our GIS-based multi criteria approach, the most contaminated area, unequipped for irrigation, is suitable only for rainfed crops.

The present study provides a quantitative comprehensive assessment for providing biomass and raw materials in the supply chain for a biorefinery in one of the most polluted industrial areas in Italy, framing the basis for realistic industry's feedstock demand and sustainable land use actions for reducing heavy metal accumulation on polluted soils.

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3.2.14. Bioremediation of crude oil contaminated soil

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Abstract

This study aims to develop certain perspectives based on the principle of on-site remediation of the soil through biological means which is known as "bioremediation" against soil pollution issues resulting from fuel contamination in our country and to reveal the fatty acid profile in the final soils. The fatty acid profile of the soils was pointed out by testing the activity of three basic bioremediation applications (biological multiplication, biological excitation and the combined application of these two approaches) established in the laboratory environment for this aim. Under biological multiplication applications, 6 strains of bacteria were selected which exhibit the highest growth in crude oil environment isolated from oil-contaminated soils of Adana, Batman and Adiyaman and which have the highest levels of crude oil degradation. (*Pseudomonas aeruginosa*, *Pseudomonas putida* biotype A, *Citrobacter amalonaticus*-GC subgroup A, *Acinetobacter genomospecies*). Under biological excitation applications, the organic materials being humic-fulvic acid and, in combined applications, different combinations of bacteria mixture and organic materials were examined as to the amount of crude oil they degrade in an incubation period of 120 days by qualitative hydrocarbon-type analyses. The highest level of oil degradation, being %56, occurred under biological multiplication applications where the bacteria mixture was applied. Under biological excitation conditions where various organic materials were applied to the contaminated soil, degradation to %18 was observed. In combined applications, oil degradation was achieved to %30.

Keywords: Soil, crude oil, bacteria, bioremediation

Introduction, scope and main objectives

Several researchers explained that in soil, number and types of existing microorganisms are affected by biological and physicochemical events including soil properties such as suitable conditions for microbial decomposition (oxygen, food substance, temperature and pH), microbial decomposition of hydrocarbons, quantity and quality of contaminants and its biological usefulness and particle distribution. (Atlas 1981, Atlas and Bartha 1992, Steffan *et al.* 1997; Morgan and Watkinson 1989; Margesin and Schinner 1997a).

Although there are many studies made on microorganisms which head for individual hydrocarbons or hydrocarbon groups forming structure of petroleum and petroleum products

(PPP) and remove them in a short time. Our knowledge is limited on hydrocarbon decomposition in soil could be effectively eliminated by using soil microorganisms.

In addition, such microorganisms and its mixtures were investigated in different soil ecosystems. In Turkey, separate laboratory and field experiments need to be made on eliminating PPP-related contamination in different soil from other countries similar as Turkey's environmental conditions. In this regard, main purpose of the study is to develop a method and a material which can be utilized for elimination of petroleum and similar organic contaminants. For this, basically, economical and environment-friendly "biological improvement (bioremediation)" approach shall be taken as a model in the elimination of petroleum and similar organic contaminants. This study aimed to elimination of crude oil-based contamination by testing the efficiency of three basic bioremediation treatments (bio-augmentation, bio-stimulation and the combined application of these two approaches) which established in the laboratory environment.

Materials

Soil material from trial lands of AUZF Research and Application Farm (approximately 40 kg, taken from 0-20 cm depth) were brought to laboratory after sieved through a sieve of 2 mm. Crude oil was procured from Kırıkkale Refinery Premises of Turkish Petroleum Corporation (TPAO). The bio-augmentation material (Bacteria-Bac) were procured from; i) Batman Refinery waste accumulating field, samples taken form 0-20 cm depth: waste 1 and samples taken form 20-40 cm depth: waste 2, ii) Samples taken from Adiyaman TPAO petroleum wells inner station petroleum water accumulating area, iii) From "BTC (Bakü - Tiflis - Ceyhan) crude oil loading terminal area in Adana.

Samples were kept at +4°C until analyses were made. As bio-stimulation material, soil regulator sold in the market, coded as HFA (Humic-Fulvic- Acid) (K- Humate) was used.

Methods

The soil taken to be used in this study (about 40 kg), was taken one week before the setting of last trial after all preliminary trails and preparations related to biological improvement applications and was kept in room temperature. The reason of this is to make the research when the soil properties are as near as possible to its original conditions.

Isolation of bacteria from petroleum-contaminated soils

The following procedures were followed with isolation purposes on the samples; 10 gr soil sample, 1 g KNO₃, 0,2 g MgSO₄, 0,1 g NaCl, 0,1 g CaCl₂ g, 1% crude oil into 1L broth medium including 1 g K₂HPO₄ : left for incubation at 180 cyc/min at 28°C for 3 days adding Triton-X-100 emulsifier (1:1). At the end of the 3rd day, 10 ml was taken out from this broth medium and was put in a fresh environment again which has the same components (Erdoğan *et al.* 2011, Rojas-Avelizapa *et al.* 1999).

MIS (Microbial Identification System) identification of isolated bacteria

PLFA analysis made on pure bioremediation bacteria cultures was carried out using Microbial Identification System (MIS) as stated by Miller and Berger (1985). This system is based on the fact that number, variety and quantity as % (fatty acid profile) of fatty acids in the cells of microorganisms with same genetics and that they do not change as long as environment conditions keep same (Şahin 1997, Şahin *et al.* 1999, Erdoğan *et al.* 2011).

Bioremediation Applications

Preparation of Experimental Contamination Conditions

Soil sample weighed into plastic pots of 1000 gr and moisturized by 50% of its water holding capacity under oven dry conditions was taken in pre-incubation at 25°C for ten days. After three days of pre-incubation, soil sample was contaminated by applying crude oil of 1% on weight basis (w/w) homogeneously. Incubated at 25°C for 3-4 days for microbial activity in the sample to adapt itself to new conditions after addition of petroleum. Clean soil material was left in room conditions for the same duration

Preparation of bioremediation bacteria mixture cultures

6 bacterial strains, their petroleum decomposition abilities in liquid culture having been determined, were applied homogeneously to clean and contaminated soils by spraying, after obtaining a bacteria density of 10^{10} CFU/ml. (Erdoğan 2010; Erdoğan *et al.* 2011).

Experimental Design

Table 1. Experimental Design

Treatment Number	Treatment	Treatment of Content
1	*BAC + *N	Biological Multiplication
2	*HFA + *N	Biological Excitation
3	*BAC + *HFA + *N	Combined Application (1+2)
4	C + *N	Control (basic fertilization)

*BAC: Bacteria Mixture *N: Nutrient *HFA: Humic Fulvic Acid

Trial was set in 5 kg plastic mouth capped cups. Samplings were made on 1, 30, 60, 90 and 120 day. Determinations of “indicator-fatty acid methyl ester” were made with respect to only bioremediation bacteria which is to be used, by making TPH analyses and cultural count (on 1, 30, 60, 90 and 120 day) for monitoring Crude Oil decomposition and PLFA-FAME analysis (on 1, 30, 60, 90 and 120 day), with direct extraction method, for investigating soil community structure in each sampling (Erdogan 2010).

Determination of Efficiency of Bioremediation Applications

In soil samplings taken on the on 1, 30, 60, 90 and 120 day of the trial, petroleum analyses, chromatographic analysis results (Total Petroleum Hydrocarbons), how much of the crude oil was decomposed was calculated as mgkg^{-1} . These analyses were conducted with ASE device (Dionex ASE 300) in TPAO-Research Central Geochemistry Laboratory (EPA method 3545).

Statistical Analyses

Results were evaluated with repeated measures variance analysis with respect to features focused on. Repeated measures were made at the levels of time factor and conducted in three repetitions. “SPSS 12.0”, MSTAT software packages were used for calculations. In addition, correlations between investigated parameters were evaluated using Pearson Correlation Test. In evaluations, Winer *et al.* 1991, Gürbüz *et al.* 2003 were utilized.

Results

As a result of MIS identification of isolation of bacteria from contaminated soil, the following species-genus-order-families were found; (See Table 3.1)

Table 2. Genus-species-order-families of isolated bacteria

Bacteria (Genus-species)	Order - Family
<i>Pseudomonas putida</i>	Pseudomonadales - Pseudomonadaceae
<i>Pseudomonas aeruginosa</i>	Pseudomonadales - Pseudomonadaceae
<i>Pseudomonas mucidolens</i>	Pseudomonadales- Pseudomonadaceae
<i>Acinetobacter genomospecies</i>	Pseudomonadales - Moraxellaceae
<i>Stenotrophomonas maltophilia</i>	Xanthomonadales - Xanthomonadaceae
<i>Enterobacter hormaechei</i>	Enterobacteriales - Enterobacteriaceae
<i>Enterobacter sakazakii</i>	Enterobacteriales - Enterobacteriaceae
<i>Citrobacter amalonaticus</i>	Enterobacteriales - Enterobacteriaceae
<i>Escherichia coli</i>	Enterobacteriales - Enterobacteriaceae
<i>Sphingobacterium multivorum</i>	Sphingobacteriales - Sphingobacteriaceae
<i>Aeromonas caviae</i>	Aeromonadales - Aeromonadaceae
<i>Paucimonas-lemoignei</i>	Burkholderiales - Burkholderiaceae

Regarding with changes in Total Petroleum Hydrocarbons (TPH), the values of Pet+BAC+N, Pet+HFA+N and Pet+BAC+HFA+N treatment applied on petroleum-contaminated (Pet.) soils for 120-day incubation period are given in Figure 1. When variance analysis table relating to TPH in petroleum-contaminated soils was examined, time-bacteria-HFA triple interaction was found statistically significant ($P < 0,05$). When we compare petroleum-contaminated soils in respect of their TPH values, time-dependent reduction is observed in all applications except control. While the biggest reduction was observed in Pet+BAC+N soils, the smallest reduction was observed in Control soils. If we are to compare application types with each other, the highest TPH value (7998 mg.kg⁻¹) was determined in soil Pet+BAC+N on the 1st day and the lowest one (4500 mg.kg⁻¹) was determined in soil Pet+BAC+N on the 120th day; the difference between applications was found to be significant statistically at level of $P < 0,05$.

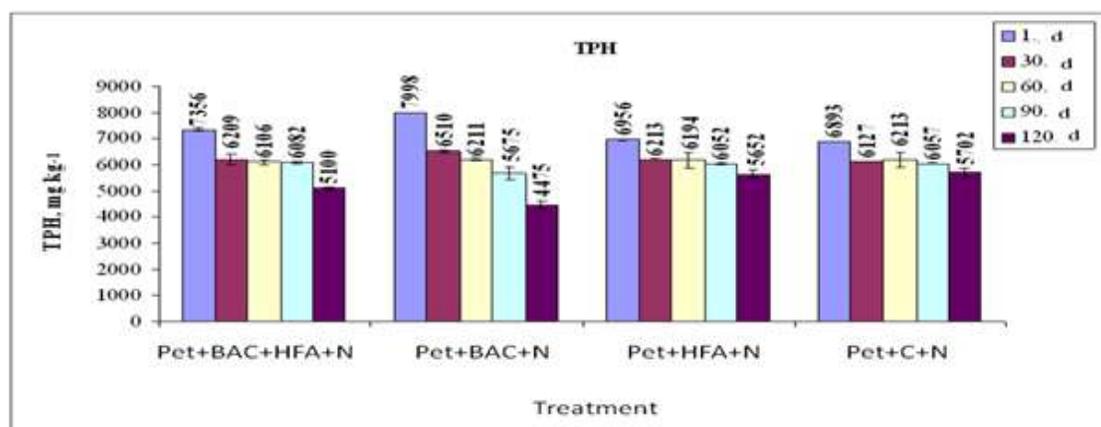


Figure 1. TPH values relating to applications Pet+BAC+N, Pet+HFA+N and Pet+BAC+HFA+N applied on petroleum-contaminated soils.

Discussion

One of the basic intentions of this study is to determine those microorganisms which can eliminate contamination in soil stemming from petroleum and that kind of materials and to evaluate their efficiency in laboratory conditions. Applications known as bioremediation, which are explained in different aspects at the beginning part, are based on use of microorganisms, which have different levels of hydrocarbon decomposing capability, in petroleum-contaminated environments. The most important measure that is taken as basis in revealing bioremediation potential of applications used (bio-augmentation, bio-stimulation, bio-augmentation + bio-stimulation) is soil TPH analysis results based on total hydrocarbons in soil. The highest decrease in total petroleum hydrocarbon rate over time among treatments was found in bacteria (Pet+BAC+N) application, which is followed by bacteria + humic fulvic acid (Pet+BAC+HFA+N) application and the lowest decrease was found in the control application. When we look at the 1st and 120th days of the study with respect to TPH, bioremediation process proceeded fastest in bacteria (Pet+BAC+N) application by 56%, which is followed by bacteria + humic acid (Pet+BAC+HFA+N) application by 30%, only humic fulvic acid (Pet+HFA+N) application by 18% and control application by 17%. And this shows that mixture bacteria culture (*Pseudomonas aeruginosa*, *Pseudomonas putida* biotype A, *Citrobacter-amalonaticus-GC subgroup A*, *Acinetobacter-genomospecies*) gave the best result. When we look at levels of decrease in TPH values in bacteria (Pet+BAC+N) application, the fastest degradation is measured between 1-30 days and 90-120 days. It is seen that between 30-90 days of incubation, there is a very little change. This shows that petroleum decomposition is not continuous but has some inactive periods. We see that other applications also have the same inactive phase.

Conclusion

Turkey becomes one of the centers of energy transport. In this regard, many pipelines project has been completed and is still being carried out. These developments are brought the soil pollution risk. On the other hand, bioremediation gains popularity because there is no arrangement for the elimination of soil pollution caused by crude-oil in Turkey. In this sense, our research institutions despite their scientific endeavors, do not have a clear answer in which remediation treatments should be implemented.

This study is important to shed light on the solution of a potential problem in Turkey. In this context, in medium- calcaric, slightly alkaline and 1% (w / w) petroleum contaminated soil; the highest petroleum distillation occurs under the application of a mixture of bacteria with bioaugmentation at 56%, and the situation that must be kept in mind is that the applied multiplication material is indigenous bacteria.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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3.2.15. Organic soil amendments ineffective for Pb mobilization in mine-scarred soil

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Abstract

Phosphorus (P) amendments are often recommended for lead (Pb) contaminated soil because lead phosphates are among the least soluble Pb compounds. Synthetic P amendments for Pb immobilization have been studied extensively, but wariness of chemical amendments and preference for “natural” inputs have made recycled materials common. Additional data that evaluates the ability of common organic soil amendments to immobilize Pb as compared to highly effective P sources (e.g. H₃PO₄ and TSP) is needed to determine whether these materials are viable alternatives to chemical P sources. A randomized complete block design with two blocks, five treatments, and four replications was established in a farm field containing lead and zinc mine waste materials. The treatments consisted of composted yard waste, fishbone meal with added elemental sulfur, triple super phosphate, H₃PO₄, and a non-amended control. This study suggests that disturbing soil during in situ Pb remediation interventions may actually exacerbate soil Pb bioavailability in soils due to oxidation of Pb species into more soluble forms. However, in cases where land will be tilled or aerated for other purposes (e.g. planting), applying compost or fishbone meal may counteract increased bioavailability from oxidation resulting in a negligible net change.

Keywords: lead, fish bone meal, mine-scarred land, bioaccessibility

Introduction, scope and main objectives

Lead (Pb) is toxic to many systems in the human body and is associated with permanent cognitive and behavioral deficits even below the U.S. Center for Disease Control threshold for elevated

blood Pb (5 µg/dL) (NTP, 2012). Pb minerals that are readily absorbed by the body (i.e. bioavailable) present a greater risk to human health. Direct measurement of soil Pb bioavailability is a complicated, timely, and resource intensive process involving *in vivo* feeding trials. However, plant available phosphorus tests such as the Mehlich 3 are promising candidates to determine soil Pb bioaccessibility because they are designed to dissolve labile P but extract only small amounts of strongly adsorbed P and recalcitrant P compounds (Havlin *et al.*, 2005).

In rural areas, pesticide applications, ammunition remnants, and mine tailings commonly contribute to soil Pb contamination. Urban expansion and high commodity crop prices often encourage development and/or cultivation of available land, despite the presence of soil contaminants. Development of Pb contaminated land may expose people who live and work near the soil to Pb, as well as impact adjacent communities via atmospheric suspension and deposition of contaminated dust.

Soil removal, and physical and chemical immobilization of soil Pb are primary strategies for reducing soil Pb hazard. Soil removal is costly and shifts hazards to a new location. Physical immobilization creates barriers via planting, asphalt capping, and other landscaping interventions that impede human contact with contaminated soil. However, these restrict land uses to those compatible with the physical barriers and do not alter the contaminant itself. A barrier breach (e.g. unsuccessful cover crops) therefore threatens re-exposure. Chemical immobilization alters Pb mineralogy to form more recalcitrant Pb species, thereby potentially allowing continued use of the land with reduced hazard and at lower cost.

Organic matter and phosphorus (P) are common soil amendments used to reduce Pb bioavailability. P sources including phosphoric acid (H₃PO₄) and triple superphosphate (Ca(H₂PO₄)₂) have been studied extensively for their ability to immobilize soil Pb (Zia *et al.*, 2011). While effective, some communities are reluctant to use chemical soil amendments and prefer materials perceived as natural or organic, such as fishbone meal common recovered from fish processing waste streams and compost (Barringer, 2011; USEPA, 2012).

Enthusiasm for natural amendments currently exceeds the available scientific data to support their use. For example, reports of compost effectiveness as a soil amendment for Pb immobilization range from 5% to 67% reductions in Pb bioaccessibility (Brown *et al.*, 2004; Farfel *et al.*, 2005; Udovic and McBride, 2012). Although fishbone meal is routinely used for Pb remediation, at present only one study has quantified changes in soil Pb bioaccessibility following bone meal amendment (Obrycki *et al.*, 2016). This study found bone meal ineffective for Pb immobilization with 10.5% reductions in Pb bioaccessibility using bovine bone meal at P:Pb ratios as high as 30:1 and 0% reductions in all soils using fishbone meal amendments as high as 17:1 P:Pb.

The objective of this study is to evaluate the ability of fishbone meal and compost to reduce Pb bioaccessibility compared to TSP and H₃PO₄ in a mine-contaminated soil.

Methodology

Field plots were established on a farm field contaminated with mine tailings. The field was located in southwest Wisconsin, U.S.A. within the Upper Mississippi River Lead and Zinc Mining Region that had active mining from 1820-1950. Throughout this time period, waste rock was haphazardly deposited on surface soils near mines and ore processing sites.

Due to heterogeneous soil Pb content, the experiment was designed as a randomized complete block design with two blocks, five treatments, and four replications. Test plots measured 2.3 m² with 0.9

m borders separating the plots. Immediately prior to amendment, plots were rototilled to a depth of approximately 10 cm and pre-treatment samples collected.

The treatments consisted of composted yard waste (covered to 7.6 cm depth, 200 g compost kg⁻¹; Purple Cow Organics Classic compost), fishbone meal (1500 mg P kg⁻¹; Down to Earth Fish Bone Meal) with added elemental sulfur (1184 mg S kg⁻¹), triple super phosphate (TSP) (1500 mg P kg⁻¹), H₃PO₄ (3.7 M H₃PO₄, 1500 kg P kg⁻¹), and a non-amended control. Amendment rates were calculated assuming a soil bulk density of 1.3 Mg m⁻³. Amendments were incorporated to a 10 cm depth using a three-point PTO driven rototiller. Each plot was seeded with 30.6 g m⁻² tall fescue (*Festuca arundinacea*) to mitigate erosion.

The plots were resampled after 91 days. Five soil cores (10 cm depth) were collected from each plot and homogenized. Samples were air dried at 66°C, ground and sieved to 2 mm. Vegetative cover was determined visually on a scale from 1 (very sparse vegetation, maximum of two plants) to 5 (vigorous vegetative cover).

Soil was analyzed for texture, organic matter, pH, total Pb, and Mehlich 3 extractable Pb. Total Pb was determined according x-ray fluorescence (USEPA Method 6200). Mehlich 3 extractable Pb was determined according to the procedure outlines by Mehlich (1984) and analyzed for total Pb content using ICP-OES. Blanks and soil 2711 Montana I from the National Institute of Standards and Technology were also analyzed for quality assurance. Analysis of variance with a student T test was performed using JMP software.

Results

Results for total Pb, Mehlich 3 extractable Pb, pH, and vegetative cover are presented in Figure 1

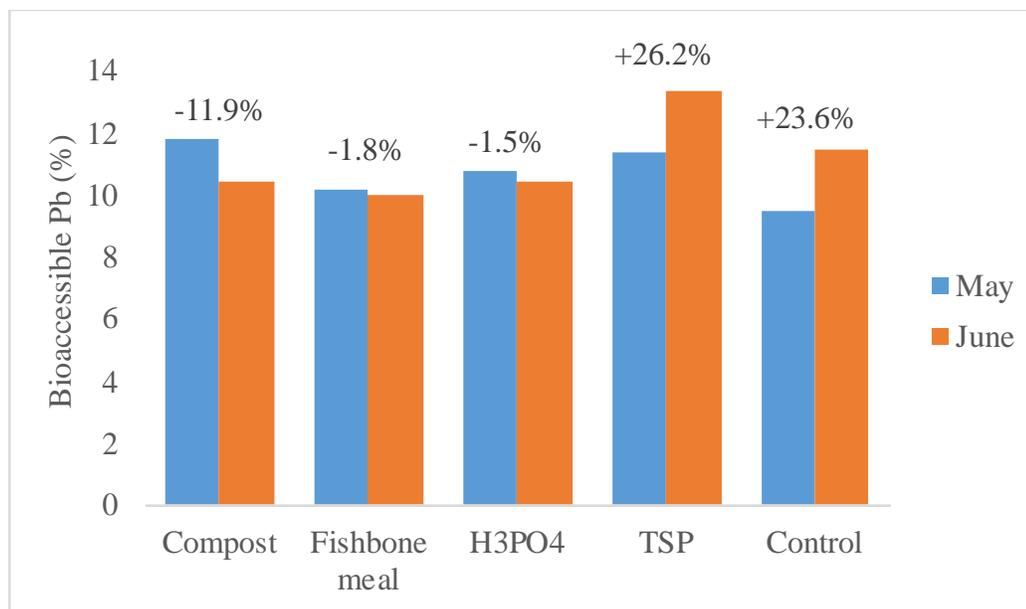


Figure 1. Bioaccessible Pb (Mehlich 3 extractable Pb divided by total Pb) before and after treatment.

Bioaccessible Pb increased by 23.6% in the control soil after three months. This result is likely due to soil aeration from tillage leading to oxidation of galena (PbS) ($K_{sp} = -27.51$) to anglesite (PbSO₄) ($K_{sp} = -7.79$) (Lindsay, 1979).

Compost, fishbone meal, and H₃PO₄ treatments showed minimal reductions in Pb bioaccessibility after three months. However, assuming that tillage alone increased Pb bioaccessibility similarly in all plots (i.e. 24% as in control treatments), actual reductions in Pb bioaccessibility attributable to compost, fishbone meal, and H₃PO₄ may be closer to 36, 26, and 25%, respectively. While this increase was statistically significant, this absolute difference in Pb bioaccessibility (from 9.5 to 11.4% bioaccessible Pb) is unlikely to translate to meaningfully different health impacts

The TSP amendment yielded results comparable to the control. Previous research on smelter contaminated soil showed 52 and 21% reductions in bioaccessible Pb with TSP rates of 9.6:1 and 2.5:1 P:Pb (Brown *et al.*, 2004). P:Pb rates in the present study were six times lower than those employed by Brown *et al.* (2004) which likely contributed to the discrepancy.

There was virtually no establishment of tall fescue grass in the plots. Instead, ragweed (*Ambrosia artemisiifolia*) provided nearly all of the vegetative cover. Poor establishment of tall fescue is likely attributable to toxic Zn soil concentrations (40,000-100,000 ppm Zn). There was no significant relationship between vegetative cover and treatment.

Conclusions

This study suggests that disturbing soil during in situ Pb remediation interventions may actually exacerbate soil Pb bioavailability in soils due to oxidation of Pb species into more soluble forms. *In situ* remediation should therefore only be conducted in soil systems where the lead mineralogy is well understood. In this case, the increase in Pb bioaccessibility after tillage appeared to negate the potential benefits of compost, fishbone meal, and H₃PO₄ to immobilize Pb as illustrated by minimal overall changes in Pb bioaccessibility. It is possible that the muted impact of H₃PO₄, fishbone meal, and compost on Pb bioaccessibility may also be due in part to the low initial Pb bioaccessibility and limited capacity for reductions. A superior strategy for landowners hoping to mitigate Pb risk from minerals susceptible to oxidation may be to establish vegetative cover of the soil to stabilize the soil to prevent translocation and contamination other areas.

For farmers with Pb contaminated soil, maintaining perennial ground cover is unlikely to be an option as it likely reduces the area available to grow crops. In cases where landowners plan to till or otherwise aerate soils containing reduced Pb compounds applying fishbone meal or compost may counteract increased bioavailability from oxidation resulting in a negligible net change in Pb bioavailability.

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3.2.16. Is aided phytostabilization a suitable technique for tailings remediation? A field case study in SE Spain

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Abstract

Mining activity in Cartagena-La Union mining district (SE Spain) dates back to more than 2500 years. As a result, high amounts of sterile materials with high metal(loid) contents (mostly Zn/Pb) have been accumulated in tailings ponds. A reclamation strategy based on aided phytostabilization was performed to reclaim one tailings pond in order to reduce environmental and public health hazards. The main goal of this study was to determine the effectiveness of the aided phytostabilization strategy after 30 months from of implementation to enhance soil quality and fertility and reduce metals mobility. Marble waste, raw pig slurry and its solid phase after physical separation were applied as amendments, and thirteen plant Mediterranean native species were planted/sown. Various soil physicochemical and biochemical properties, together with the total and bioavailable fraction of metal(loid)s (As, Cd, Pb and Zn) were monitored for 30 months. Results showed that aggregates stability, pH, total organic carbon (TOC), total nitrogen (TN), cation exchange capacity (CEC), available phosphorus (P), exchangeable potassium (K) increased with the application of the amendments and development of vegetation. In addition, the available fraction of metals drastically decreased (90-99%). Most plant species present in the area did not transfer high amounts of trace elements to the aerial tissues. The roots of *Lygeum spartum* and *Piptatherum miliaceum* accumulated the highest As, Pb and Zn contents. Thus, the application of marble waste to increase pH and immobilize metal(loid)s, and pig slurry as a source of organic matter and nutrients, together with the development of vegetation to immobilize metal(loid)s in roots and rhizosphere, have contributed to decrease the availability of metal(loid)s trace elements, improving soil quality and fertility. Once the soil quality of mine tailings was improved, the development of vegetation was favoured, promoting the integral reclamation of the area. Therefore, aided phytostabilization was a suitable technique for remediation of this tailings pond.

Keywords: amendments, contamination, phytostabilization, reclamation, tailings pond, metal(loid)s, vegetation.

Introduction, scope and main objectives

Soil pollution is one of the major environmental problems on a global scale. Mining has been present in Sierra Minera de Cartagena – La Unión (Murcia, Spain) for more than 2500 years. This activity has generated large amounts of tailings from the exploitation of mineral sulfides (mainly ZnS and PbS). Tailings ponds have been abandoned after the cessation of the activity in 1991. Such tailings are of great concern due to the risk associated to the high content of toxic metal(loid)s. Moreover, these tailings have low fertility, low organic matter content and high acidity. Therefore, the establishment of native vegetation is very difficult unless organic and/or inorganic amendments are applied (García and Lobo 2007). Phytoremediation is considered an economic and environmentally-conscious method to remediate polluted soils (Wan *et al.* 2016). Among phytoremediation techniques, aided phytostabilization can be a solution to reduce the risk of pollutant dispersion (Yang *et al.* 2016). Several amendments have been proposed to stabilize

metal(loid)s in soils (Kumpiene *et al.* 2008). Organic amendments and materials rich in carbonates have been successfully used to reduce the bioavailability of metals and restore the ecological function of contaminated soils (Park *et al.* 2011).

The main goal of this study was to determine the effectiveness of aided phytostabilization applied to a tailings pond from Zn/Pb mining 30 months after its reclamation. The effectiveness was evaluated by monitoring physicochemical and biochemical properties and bioavailable metal(loid) (As, Cd, Pb and Zn) contents in the tailings. In addition, we also evaluated metal(loid)s translocation to plant species (root, stem and leaf) and evolution of plant communities. Our initial hypothesis was that the implementation of phytostabilization with native plant species aided with inorganic and organic amendments would contribute to decrease metal(loid)s mobility, and so risks for environment and public health, and increase soil quality and fertility and vegetation cover. Plants should accumulate high contents of metal(loid)s in their roots with low translocation to shoots.

Methodology

Study area

This study was performed in Santa Antonieta tailings pond (37° 35' 38" N, 0° 53' 11" W), located in Cartagena-La Unión Mining district (Figure 1). The pond has a surface of 1.4 ha. The climate is Mediterranean semiarid with an annual average temperature of 18 °C, precipitation of 275 mm and potential evapotranspiration of 900 mm (Zornoza *et al.* 2013). The dry season is long and most of the precipitation is concentrated in spring and autumn.

Tailings can be classified as Espodic Technosol (IUSS 2014). The characteristics of the tailings are: sandy-loam texture, weak cohesion and stability, low organic matter and nutrient content, extreme acidity and high content of metal(loid)s: 1246-2048 mg kg⁻¹ of Pb, 829-5899 mg kg⁻¹ of Zn, 0.73-6.65 mg kg⁻¹ of Cd and 187-606 mg kg⁻¹ of As (Martínez-Martínez *et al.* 2013).

Experimental design and soil/plant sampling

The surface of the tailings pond was divided using a square grid of 35 m x 35 m where samples were taken in the nodes of these squares giving a total of 11 sampling points (Figure 2). This sampling grid was used to carry out an initial characterization of the tailings pond before application of amendments (sampling 1 (S1)) (October 2011) and to monitor the evolution of soil properties after 6 (January 2012 (S2)), 12 (July 2012 (S3)), 18 (January 2013 (S4)), 24 (July 2013 (S5)) and 30 (January 2014 (S6)) months of the application of the amendments. Samples were collected from surface (0-15 cm) and subsurface (15-30 cm). Samples were air-dried, passed through a 2-mm sieve and stored at room temperature prior to laboratory analyses. The species were planted between March and April 2012: *Atriplex halimus* L., *Cistus albidus* L., *Helichrysum stoechas* (L.) Moench., *Hyparrhenia hirta* (L.) Stapf., *Lavandula dentata* L., *Lygeum spartum* (L.) Kunth., *Rosmarinus officinalis* L., *Phagnalon saxatile* (L.) Cass.. Since the hydrological year 2011-2012 was extremely dry, seeding of several species (*Piptatherum miliaceum*, *Cynodon dactylon*, *Limonium caesium*, *Sonchus tenerrimus*, *Atriplex halimus*) was postponed to October 2012, in order to be successful with the plant germination and growth. The evolution of the vegetation was assessed in July 2012, January 2013, July 2013 and January 2014 by collecting different parts of the plants as roots, stems and leaves. The harvested species were selected because of their higher survival, growth and abundance for the study time.

Marble waste was used as a source of carbonates to neutralize acidity, immobilize metals and develop soil structure. Pig slurry and its solid phase (manure) after physical separation was used as a source of organic matter and nutrients for soil development and vegetation establishment. The

characterization and the amounts applied of the amendments in the phytostabilization of the tailing pond are shown in study carried out by Zornoza *et al.* (2017).

Analytical methods

Soil samples

Soil analyses used in this study are shown in Zornoza *et al.* (2017). The methodology for total metal(loid)s concentration was referenced using the Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany).

Plant samples

Vegetation cover was estimated as the percentage of total surface that was covered by vegetation.

Five plants were randomly uprooted from each species, and separated into root, stem and leaf for analyses. Samples were washed with deionized water and dried in the oven at 60°C for 48 h, then ground. Metal(loid)s bioaccumulation was determined after calcination at 480°C for 12 h. Metal(loid)s in the ashes were extracted by HNO₃ 0.6N and quantified by ICP-MS (Agilent 7500 CE). The bioaccumulation factor (BCF) and the translocation factor (TF) were calculated.

Statistical analyses

The fitting of the data to a normal distribution for all properties and metal(loid)s concentrations was evaluated by the Kolmogorov-Smirnov test. Data were submitted to one-way ANOVA to assess the differences among samplings and between depths. Differences between means were assessed by Tukey's test at $P < 0.05$. These analyses were performed with the software IBM SPSS for Windows, Version 22.

Results

Evolution of soil properties

The mean values of physicochemical and biochemical properties are shown in Table 1, respectively.

Evolution of metal(loid)s

Bioavailable Cd in surface samples significantly decreased from 225 $\mu\text{g kg}^{-1}$ before application of amendments to $< 39 \mu\text{g kg}^{-1}$ after the application. Differences were not significant among the values obtained for the last five samplings, with no effect of the development of vegetation. For subsurface samples, bioavailable Cd significantly decreased from 570 $\mu\text{g kg}^{-1}$ (S1) to 425 $\mu\text{g kg}^{-1}$ (S2). This decrease pattern continued in S3 (32 $\mu\text{g kg}^{-1}$), and the concentration remained without significant differences among samplings S3, S4, S5 and S6. As a general pattern, no significant differences were found between surface and subsurface values for the last five samplings. Bioavailable Pb significantly decreased in surface samples after amendments application (670 $\mu\text{g kg}^{-1}$ in S1 to 40 $\mu\text{g kg}^{-1}$ in S2; 94%). Bioavailable Pb was stabilized at this level until the end of the experiment, without significant differences among samplings. Subsurface samples followed a similar pattern, with no significant differences between depths. Concentration of bioavailable Zn significantly decreased from 1320 $\mu\text{g kg}^{-1}$ (S1) to 40 $\mu\text{g kg}^{-1}$ (S6).

Bioavailable Zn concentrations significantly decreased from 82.02 mg kg^{-1} (S1) to $< 0.43 \text{mg kg}^{-1}$ (S2) (99% of decrease). No significant differences were found over the sampling period. In

subsurface samples, available Zn significantly decreased from 129.3 mg kg⁻¹ (S1) to 96.76 mg kg⁻¹ (S2). This decrease pattern continued over the sampling period with concentrations < 5 mg kg⁻¹ at the end of the experiment. If the total metal content is taken into account, the percentage of the bioavailable Zn content was 2.5% and 5.3% for the surface and subsurface samples in S1, respectively. With the addition of the amendments, bioavailability dropped up to 0.02% in all samples. Bioavailable As content was below 0.04 mg kg⁻¹ over the experimental period with the exception of S2 where values were 3.5 and 5.1 mg kg⁻¹ for surface and subsurface samples, respectively.

Table 1. Evolution of soil physicochemical properties in Santa Antonieta tailings pond at two different depths (values are mean (standard deviation)).

Sampling	Depth (cm)	TOC (g kg ⁻¹)		CaCO ₃ (%)		TN (g kg ⁻¹)		pH (dS m ⁻¹)		EC (cmol+kg ⁻¹)		CEC (cmol+ kg ⁻¹)		P (mg kg ⁻¹)		K (cmol+ kg ⁻¹)	
S1	0-15	1.40	(0.58)a	0.0	(0.0)a	0.35	(0.09)ab	2.9	(0.5)a	3.6	(0.9)d	5.8	(2.5)a	6.03	(1.61)c	0.07	(0.01)bc
	15-30	1.48	(0.65)ab	0.0	(0.0)a	0.36	(0.11)abc	2.9	(0.5)a	3.6	(0.8)d	6.6	(3.2)ab	0.42	(0.51)a	0.08	(0.01)bc
S2	0-15	4.53	(2.61)c	4.4	(3.2)bc	0.70	(0.13)ef	6.9	(0.4)c	2.7	(0.2)abc	10.7	(3.1)c	12.06	(3.22)d	0.34	(0.10)d
	15-30	1.68	(1.06)ab	2.1	(3.5)bc	0.52	(0.26)bcde	5.4	(1.5)b	3.1	(0.5)cd	9.5	(2.3)bc	3.99	(3.83)bc	0.09	(0.08)ab
S3	0-15	4.98	(1.64)c	3.9	(2.3)bc	0.80	(0.17)f	7.2	(0.3)c	3.1	(0.3)cd	8.1	(1.9)abc	1.26	(0.76)ab	0.15	(0.06)c
	15-30	3.65	(1.51)bc	1.9	(2.3)b	0.53	(0.11)bcde	7.1	(0.4)c	2.9	(0.2)bc	7.8	(2.3)abc	0.78	(1.00)ab	0.10	(0.04)bc
S4	0-15	3.76	(2.44)abc	4.5	(3.3)bc	0.59	(0.13)def	7.0	(0.4)c	2.6	(0.2)abc	8.3	(1.4)abc	0.37	(0.269)a	0.10	(0.04)bc
	15-30	2.33	(2.08)abc	3.4	(2.3)bc	0.45	(0.15)abcd	6.8	(0.4)c	2.9	(0.3)abc	8.5	(1.1)abc	0.17	(0.20)a	0.05	(0.03)ab
S5	0-15	5.14	(2.82)c	3.9	(1.9)c	0.57	(0.16)cde	6.8	(0.4)c	2.6	(0.3)abc	10.4	(2.3)c	0.80	(0.46)ab	0.11	(0.04)bc
	15-30	3.65	(2.46)abc	2.8	(1.9)bc	0.39	(0.14)abcd	6.8	(0.4)c	2.9	(0.3)abc	11.3	(2.8)c	0.32	(0.50)a	0.05	(0.03)ab
S6	0-15	5.85	(3.18)c	2.2	(1.8)bc	0.39	(0.11)abcd	7.1	(0.4)c	2.3	(0.1)a	21.0	(7.5)d	5.78	(5.10)c	0.07	(0.03)abc
	15-30	6.00	(3.88)c	2.1	(2.0)bc	0.30	(0.07)a	6.9	(0.5)	2.4	(0.1)ab	20.8	(10.5)d	6.68	(4.39)c	0.04	(0.02)a
F value			7.3*		114.1*		11.5**		82.7*		9.3**		12.4*		26.8**		13.1**

Within each column, values followed by the same letter are not significantly different, $P < 0.05$.
Significant at * $P < 0.001$, ** $P < 0.01$, *** $P < 0.05$.

In Table 2 are shown the metal concentrations in plants.

Table 2. Metal concentrations in roots, stems and leaves of harvested plants growing in the tailings pond.

		<i>R. officinalis</i>	<i>L. dentata</i>	<i>C. albidus</i>	<i>P. saxatile</i>	<i>A. halimus</i>	^a <i>L. spartum</i>	^a <i>H. hirta</i>	<i>H. decumbens</i>	^a <i>P. miliaceum</i>
Cd (mg kg ⁻¹)	root-1 ^b	0.62	0.39	0.59	2.78	1.29	0.72	1.25	1.12	*
	stem-1 ^b	0.51	0.25	1.22	2.36	1.01	0.73	0.45	1.70	*
	leaf-1 ^b	0.29	0.22	1.56	6.25	1.52			1.17	
	root-2 ^c	*	0.98	0.56	4.31	1.19	1.07	1.34	1.43	0.85
	stem-2 ^c	*	0.50	1.23	7.44	0.91	0.47	0.53	1.47	0.27
	leaf-2 ^c	*	0.38	1.66	9.53	1.24			1.91	
	root-3 ^d	*	0.95	1.12	2.26	1.63	3.02	1.08	0.77	1.81
	stem-3 ^d	*	0.73	1.86	2.94	2.14	0.58	0.47	1.52	0.24
	leaf-3 ^d	*	0.77	2.09	7.46	5.66			2.45	
As (mg kg ⁻¹)	root-1	5.24	4.49	1.22	3.84	2.72	27.84	18.22	2.23	*
	stem-1	4.90	6.47	4.56	5.60	4.14	12.04	11.02	5.32	*
	leaf-1	8.90	33.97	23.50	13.76	9.90			26.99	
	root-2	*	2.81	0.75	3.26	5.20	23.43	6.34	1.76	10.90
	stem-2	*	5.44	2.41	4.20	1.05	3.10	3.25	6.33	1.62
	leaf-2	*	13.56	2.83	5.42	1.61			18.33	
	root-3	*	3.06	1.45	2.81	1.97	34.63	2.50	1.83	19.70
	stem-3	*	5.07	2.32	8.20	1.68	1.52	2.25	6.06	1.68
	leaf-3	*	13.95	2.70	10.71	2.22			11.11	
Pb (mg kg ⁻¹)	root-1	39.37	30.11	4.30	27.57	14.06	131.82	109.09	9.23	*
	stem-1	29.48	30.82	21.49	36.88	20.47	35.65	29.04	24.68	*
	leaf-1	344.86	140.52	82.50	73.46	29.30			81.14	
	root-2	*	27.16	7.59	22.11	35.96	146.36	57.14	12.36	52.80
	stem-2	*	36.99	18.23	28.42	13.20	8.64	12.81	31.39	2.32
	leaf-2	*	84.24	16.95	51.26	21.59			142.12	
	root-3	*	22.26	10.14	20.45	18.85	244.59	26.05	8.13	158.06
	stem-3	*	39.39	20.61	40.20	8.73	7.35	8.34	26.96	6.37
	leaf-3	*	95.22	19.65	44.48	9.08			58.84	
Zn (mg kg ⁻¹)	root-1	80.10	57.30	62.40	92.52	183.20	134.14	148.37	7.63	*
	stem-1	140.61	62.56	100.57	103.01	139.99	62.19	59.11	13.63	*
	leaf-1	104.77	184.73	250.01	441.65	308.35			42.90	
	root-2	*	71.66	41.60	124.41	148.06	289.80	137.31	66.77	264.25
	stem-2	*	104.48	86.21	224.31	146.30	55.25	89.98	90.93	116.14
	leaf-2	*	175.65	106.80	911.89	235.07			247.24	
	root-3	*	123.70	82.84	144.99	153.14	999.28	101.88	47.28	403.60
	stem-3	*	149.62	133.10	208.54	213.78	69.08	115.61	103.18	104.49
	leaf-3	*	266.85	192.51	738.50	594.51			354.93	

Note. ^a: In grasses such as *L. spartum*, *H. hirta* and *P. miliaceum* only two parts were differentiated (root and stem); ^b: Root, stem, leaf-1.- samples collected in January 2013; ^c: root, stem, leaf.- samples collected in July 2013 and ^d: root, stem, leaf-3.- samples collected in January 2014. *: the plants were not collected because they were dried in that sampling. **Metal(loid) concentrations in roots are marked in bold.**

Discussion

Influence of amendment application and aided phytostabilization on soil properties

The application of phytostabilization technique aided with marble waste, pig manure and pig slurry in Santa Antonieta tailings pond allowed a significant increase in pH, TOC, CaCO₃, stable

aggregates, TN and CEC, while decreased the values EC. Some of these properties such as pH, TOC, EC and CaCO_3 show a considerable influence on the bioavailability and mobility of metals in soil (Minnikova *et al.* 2017). The pH increase is due to the presence of carbonates from marble waste, which neutralizes the acidity. The Ca^{2+} and Mg^{2+} ions from carbonates replace Al^{3+} ions present in the exchange complex of the acid tailings and also contributes to increase the pH (Brady and Weil 2002). TOC content increased after organic amendments application and it remained stable over time. This was somewhat not expected, since TOC tends to decrease over time under semiarid conditions due to mineralization (Zornoza *et al.* 2012), due to the labile carbon present in the pig manure and pig slurry (Kabas *et al.* 2012). The maintenance of TOC levels could be related to the development of a vegetation cover, which resulted in root exudates and litter accumulation (Bouwman and Vangronsveld 2004) and the increase of microbial biomass and activity; in fact, the vegetation cover at the end of the study was 69% of the total surface.

The increase in stable aggregates could be explained by the increase in TOC content, root development and higher microbial activity (Porta *et al.* 2003). The addition of the organic amendments favored the increase of N, P and K in the tailings pond, which are essential nutrients for plant growth. Pig manure and slurry are rich in nutrients, mainly N, and have been recommended by many authors for use in soil rehabilitation projects through aided phytostabilization (Jin *et al.* 2016). The increase of available P in the last sampling may be due to the increase of organic acids in the soil that have the capacity to solubilize the phosphates by the complexation with Cd, Al and Fe, thus leaving the phosphate ion in the soluble state (Munera and Meza 2013). The main source of organic acids in the soil is the decomposition of organic matter and root exudates. It is hypothesized that the important increase of the vegetation cover in January 2014 (69%) favored a greater activity of decomposition of the litter, enhancing available P content.

Exposure of sulfides to oxidizing conditions results in the release of sulfate anions and metal cations that increase the EC of tailing ponds (Martínez and Pérez 2007). The addition of marble waste led to a significant reduction of soil EC. This could be explained by the reaction of Ca^{2+} from CaCO_3 with sulfates forming stable precipitates, thus decreasing the concentration of sulfates in soil solution (Fernández-Caliani and Barba-Brioso 2010). Increases in pH may have also contributed to precipitation of ions present in the soil solution (Brallier *et al.* 1996), thus decreasing EC. The CEC increased due to the addition of organic matter from pig manure and pig slurry. Kabas *et al.* (2014) observed a clear positive correlation between soil CEC and the TOC content provided by pig slurry in tailings ponds.

Effect of aided phytostabilization on metal(loid)s availability

Total metal(loid) concentrations did not significantly change over the experimental period (data not shown). This was expected since the aided phytostabilization technique is not intended to reduce metal(loid)s contents, but to immobilize them to become less available to living organisms and minimize their dispersion by erosion and leaching (Parra *et al.* 2014).

The values of CaCl_2 -exchangeable metals concentrations found in this study were lower than those reported by other authors in mining areas contaminated by metals under similar climatic conditions (De la Fuente 2014). The addition of amendments caused important decreases of metal availability due to, mainly, a direct effect of the pH. Soil pH increase favors the processes of adsorption, precipitation and co-precipitation with oxihydroxides, the formation of chelates, metallic carbonates and metallic phosphates (Khalid *et al.* 2017). The increase of the available As concentration after amendment applications may be likely due to the fact that carbonates from marble waste increased soil pH and so favored its mobility and availability.

Plant development

Aided phytostabilization allowed an adequate colonization of plant species which were able to grow in the reclaimed tailings pond. In the last sampling, a vegetation cover of 69 % was observed, which evidenced that liming material and organic amendments were effective in reducing the phytotoxicity of metals, providing an environment suitable for germination and growth of plants.

Piptatherum miliaceum and *Lygeum spartum* were the species with the highest Zn, Pb and As concentrations in roots. Therefore, both species would be good candidates for phytostabilization of tailings ponds, since were characterized in the experiment by a bioaccumulation coefficient (BCF) > 1 and translocation factor (TF) < 1 (Méndez and Maier 2008). Studies previously carried out in tailings ponds have demonstrated the effectiveness of both species for aided phytostabilization (Zornoza *et al.* 2012). However, *Phagnalon saxatile* and *Atriplex halimus* growth should be thoroughly monitor since Zn concentrations in the leaves exceeded 500 mg kg⁻¹, which is the toxicity level for herbivores proposed by Méndez and Maier (2008). Thus, the development of these species should be controlled to avoid risks to the value chain.

Conclusions

The combination of marble waste, pig slurry and manure was efficient for the reclamation of an acidic tailings pond by aided phytostabilization. The technique allowed to increase soil pH, CEC, TOC and nutrients content, improve soil structure and reduce the mobility of metals, mainly Cd, Pb and Zn up to 90-99 %. Our results show that a second application of organic amendments rich in N, P and K would be advisable due to nutrient depletion after 30 months. This would ensure that plant growth is not limited in the long term. Another possibility would be the use of a complementary organic amendments characterized by having more recalcitrant forms of carbon such as biochar, with lower degradation rates. It could be also tested the introduction of plant species that fix atmospheric N such as legumes to contribute to enhance soil fertility.

Lygeum spartum and *Piptatherum miliaceum* were effective in phytostabilization of Pb, Zn and As, since they accumulated high metal concentrations in roots, with low aerial translocation. *Atriplex halimus* and *Phagnalon saxatile* presented phytotoxic concentrations of Zn in leaves. Therefore, the use of these species should be avoided in soils contaminated with high concentrations of Zn.

Monitoring the soil following aided phytostabilisation is still necessary to assess the long-term evolution of soil properties, the ecological succession and evolution of metal(loid)s concentrations. This will allow a deeper understanding of the ecotoxicological results.

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3.2.17. Detoxifying ability of humic substances in relation to heavy metals

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Abstract

The structural complexity of humic substances (HS) creates opportunities for a broad range of chemical interactions with heavy metals and other pollutants in the environment. Despite the diverse protective functions of humic substances in the polluted environment, application of natural organic substances and humic-based products for remediation remains limited. The effect of HS and their different fractions (humic acids (HA) and hmatomelanic acids (HMA)) on the toxicity of zinc and lead to different strains of bacteria was studied. Tested bacteria demonstrated a lower resistance to zinc than lead showing minimum inhibitory concentrations of 0.1 - 0.3 mM and 0.3-0.5 mM, respectively. The highest resistance to lead was characteristic of *Pseudomonas chlororaphis* PCL1391 and *Rhodococcus* RS67, while *Pseudomonas chlororaphis* PCL1391 showed the greatest resistance to zinc. The combined fractions of HS and HA alone reduced zinc toxicity at all added concentrations of the organic substances (50 – 200 mg L⁻¹) to all microorganisms, while HMA reduced zinc toxicity to *Pseudomonas chlororaphis* PCL1391 at 200 mg L⁻¹ organic concentration only. The HS fractions imparted similar effects on lead toxicity also. This study demonstrated that heavy metal toxicity to bacteria could be reduced through complexation with HS and their fractions.

Keywords: heavy metals, humic substances, remediation

Introduction, scope and main objectives

An introduction of heavy metals in the environment can produce toxic effect on soil biota and plants. At polluted sites, the response of microbial communities to heavy metals depends on the concentration and bioavailability of the elements. Numerous studies have shown that humic substances (HS) are capable of altering both the chemical and physical speciation of trace elements and affecting their bioavailability and toxicity (Tipping 2004, Violante *et al.*, 2010, Boguta and Sokolowska 2016). The structural complexity of HS creates opportunities for a broad range of chemical interactions with heavy metals and other pollutants. The high molecular weight fractions of HS could get readily adsorbed onto the plant cell wall, but do not enter the cell. On the other hand, low molecular weight fractions of HS were shown to reach the plasmalemma of root cells, and in parts were translocated into the shoots (Perminova *et al.* 2006). Irrespective of their molecular sizes HS hold a great potential to function as amendments for mitigating adverse impacts of pollutants and as active agents in environmental remediation (Perminova and Hatfield 2005).

In the present study we investigated the effect of humic substances and their different fractions (humic acids (HA) and hmatomelanic acids (HMA)) on the toxic properties of lead and zinc to different strains of environmentally important bacteria.

Methodology

Humic substances extraction

HS from the local mesotrophic sphagnum peat were isolated using alkaline extraction procedure as described by Stevenson (1994). The yield of HS in the employed procedure was 12.4%.

For the preparation of the humic acid fraction, concentrated HCl was added to the solution of HS to adjust the pH to 1 following the alkaline extraction. The humatomelanic acid fraction of the HS was obtained by ethanol extraction.

IR characterization of humic substances

Infrared (IR) spectra of the extracted HA and HMA were collected on a Nicolet-380 FTIR spectrometer (Thermo Scientific, USA). IR spectra were obtained using potassium bromide pellets technique, in which 2 mg of dried humic material was mixed with 200 mg of dried FTIR grade KBr. The instrument was set up with a resolution of 8 cm⁻¹ and 64 scans per analysis. Scans covering the 4000-500 cm⁻¹ range were recorded and averaged.

Determination of minimum inhibitory concentrations of different HS

Three non-pathogenic, easily cultivable and environmentally important bacterial strains were used in this study. The first bacterial candidate was a Gram negative natural rhizobacterium *Pseudomonas chlororaphis* PCL1391. It was isolated from plant roots grown in unpolluted areas. This bacterial strain is able to produce the antibiotic phenazine-1-carboxamide, have active colonizing ability and poses high antagonistic activity against phytopathogenic fungi, in particular, *Fusarium oxysporum*. The second bacterial strain was *Pseudomonas fluorescens* 142NF (pNF142) which is also a natural strain of Gram negative bacterium. It was isolated from oil contaminated soils. It has plasmid responsible for the degradation of petroleum hydrocarbon contaminants in the environment (Filonov *et al.* 2005). The third test strain was *Rhodococcus* RS67 which is a Gram positive soil bacterium able to degrade petroleum hydrocarbon contaminants. It was isolated from oil polluted soils. All the bacterial strains were initially cultivated in LB medium with an initial neutral pH. Minimum inhibitory concentrations (MIC) (levels of bacterial resistance) of Zn and Pb nitrates and MIC in the presence of HS fractions were determined in a modified mineral Duxbury medium by a method described previously (Podolskaya *et al.* 2002).

Microorganisms were first grown for 18 h in LB medium until achieving their stationary phase which corresponded to optical density (OD) values 0.6-0.7 and colony forming unit (CFU) counts 5 x 10¹¹ mL⁻¹. Then bacterial strains in LB medium (50 µL) were inoculated into experimental test tubes with 10 mL of the mineral Duxbury medium (OD of initial experimental medium was 0.025-0.03 and CFU counts 1-2 x 10⁸ mL⁻¹) with corresponding additions of the trace elements and HS. The heavy metal concentrations in the media ranged from 0.1 to 1.5 mM in steps of 0.1 mM. Test tubes without the metal addition served as the control treatments. The test tubes following bacterial inoculations were incubated on a horizontal shaker with 150 rpm at 24°C for 24 h in the cases of *Pseudomonas chlororaphis* PCL1391 and *Phodococcus* RS67, and 30 h in the case of *Pseudomonas fluorescens* 142NF (pNF142). The incubation durations were decided from some preliminary growth tests on the selected microorganisms. The MIC was evaluated from the growth of the bacterial strains (OD of culture) in the above treatment media. All experiments were performed in triplicate, and the OD values were collected on a Shimadzu spectrophotometer at a wavelength of 600 nm.

To study the detoxifying effect of HS, series of solutions comprising Zn or Pb and corresponding dissolved fractions of HS were prepared in deionized water and simultaneously added to the Duxbury medium. Final concentrations of heavy metals in the experimental test tubes were 0.1 - 1.5 mM, and the concentrations of HS were 50, 100 and 200 mg L⁻¹. After inoculation, the strains were cultured in test tubes with constant shaking as stated previously, and the growth of microorganisms was evaluated by measuring corresponding OD values as described above. A control with corresponding bacterial strains in uncontaminated HS was used as the zero point of OD determination.

Results and discussion

IR characterization of humic substances

The FTIR spectra of the isolated HA exhibited similar absorption bands as reported elsewhere (Kar *et al.* 2011). The signals centered at ν 3260 (HA) and 3240 (HMA) cm⁻¹ were assigned to the N-H/O-H stretching vibrations, confirming the presence of free and intermolecular bonded alcohols/phenols, amines/amides and possible carboxylic acids. A couple of bands at 2920 and 2860 cm⁻¹ was attributed to aliphatic asymmetric and symmetric C-H stretching, respectively. A weak signal near 2620 cm⁻¹ could be attributed to thiol groups. A peak at 1710 cm⁻¹ in HMA spectra was due to the C=O stretching of ketonic and carboxylic groups. This peak was diffused in the HA spectra. Peaks at ν 1640, 1605 and 1505 cm⁻¹ could be assigned to aromatic C=C stretching. A couple of peaks at 1450 cm⁻¹ and 1370 cm⁻¹ were due to C-H stretching; they were more expressed for HMA than HA. Spectral bands at 1220 and 1025 cm⁻¹ were attributed to the stretching vibration of the C-O bond in ethers (Kar *et al.* 2011). The presence of different functional groups gives the HA and HMA the ability to form complexes with cations. Many acids have two or more of these groups arranged so as to enable the formation of chelate complexes that are important aspect of the biological role of soil organic matter.

Minimum inhibitory concentration determination

The MICs (levels of bacterial resistance) of Zn and Pb (as their nitrate salts) in the Duxbury medium for the selected bacterial strains are shown in Table 1. Results showed that all the three strains had a low resistance to Zn (0.1 - 0.3 mM) and a slightly higher resistance to Pb (0.3 - 0.5 mM) (Table 1). In the current study, the highest resistance to Pb was the characteristic of the strains *Pseudomonas chlororaphis* and *Rhodococcus* RS67 (MIC = 0.5 mM). The strain *Pseudomonas chlororaphis* showed the greatest resistance to Zn also (MIC = 0.3 mM).

Table 1. Minimum inhibitory concentrations of zinc and lead for the tested bacterial strains grown in Duxbury medium (modal values)

Bacterial strain	Zn (mM)	Pb (mM)
<i>Pseudomonas chlororaphis</i> PCL1391	0.3	0.5
<i>Pseudomonas fluorescens</i> 142NF (pNF142)	0.1	0.3
<i>Rhodococcus</i> RS67	0.2	0.5

In spite of limitations, the technique of MIC measurement remains a valid approach to evaluate the microbial toxicity of heavy metals in polluted habitats such as agricultural soils (Hassen *et al.* 1998). Mechanisms of bacterial tolerance to heavy metals could vary and might include: binding of the metal by proteins, extracellular polymers or to the cell wall, compartmentation inside cells, formation of insoluble metal sulphides, decreased uptake, enhanced export from cells and volatilization (Giller *et al.* 2009). In our work we used MIC determination as a baseline approach to assess the bacterial resistance to heavy metals in the presence of HS.

Zn detoxifying ability of HS

The HS and their fractions reduced Zn and Pb toxicity and increased bacterial resistance to these toxicants in different degrees. The combined fractions of HS (humic acid plus humatmelanic acid) reduced the Zn toxicity at all studied concentrations of the organic substances in case of all the microbial strains (Figure 1a). The MIC at the highest organic matter (HS) concentration (200 mg L⁻¹) was increased by 5 times for *Pseudomonas fluorescens* strain, by > 3 times for *Pseudomonas chlororaphis* strain and by 4 times for the *Rhodococcus* strain.

The HS are known to form stable complexes with trace elements, mediate redox reactions and influence the interphase distribution of the contaminants (Perminova *et al.* 2006). The HS could have an impact on heavy metal toxicity to microorganisms in the soil solution, converting them into less-toxic complexed forms. Perdue (1984) found that the carboxyl groups of HS played a decisive role in making up the two main types of binding sites: salicylate and phthalate. Ephraim (1991) also pointed out the significant contribution of catechol-type functional groups of HS in binding of heavy metals. It was reported that HS from natural waters were prevalent in their carbon skeleton aliphatic fragments and the interaction with heavy metals was mainly determined by carboxylate ions, ester groups, and various combinations of functional groups (Orlov 1990). Moreover, HS could strengthen the resistance of microorganisms against non-specific stress factors as analogues of biologically active substances (Perminova and Hatfield 2005).

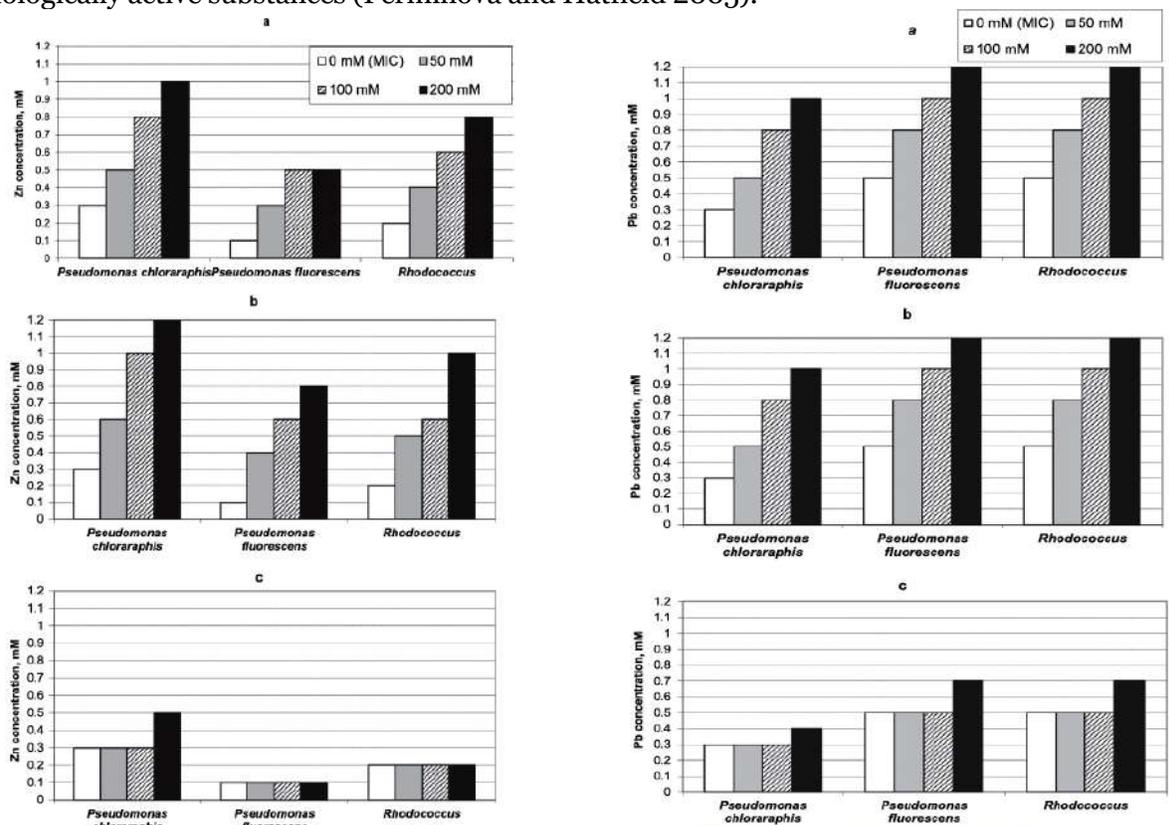


Figure 1. Minimum inhibitory concentrations of zinc (modal values) obtained for 3 strains of bacteria in the absence or presence of 50, 100 or 200 mg L⁻¹ of (a) humic substances, (b) humic acids, and (c) humatmelanic acids.

Figure 2. Minimum inhibitory concentrations of lead (modal values) obtained for 3 strains of bacteria in the absence or presence of 50, 100 or 200 mg L⁻¹ of (a) humic substances, (b) humic acids, and (c) humatmelanic acids.

The chemical properties of HS are diverse and determined by their fractions with different compositions, molecular weights and chemical structures (e.g., humic, fulvic and humatomelanic acids). Fulvic acid (FA) has a lower molecular weight, a higher functional group density and higher acidity than HA. The molecular weights for FA are in the range of 0.5-2 kDa, while they extend from 2 to 1300 kDa for HA. The oxygen content is reported as 32.8-38.3% for HA, and 39.7-49.8% for FA (Steelink 1985). Heavy metals complexed by FA presumably are more available to plant roots and soil biota than those complexed by HA which can form both water-soluble and water insoluble complexes with metal ions (Kabata-Pendias 2010). Thus, our experiments indicated that the HS extracted from peat formed stable complexes with Zn that were inaccessible to the microorganisms. This was the reason for the significant shift of MIC and increased resistance of microorganisms to Zn in the mineral medium.

The HA fraction reduced Zn toxicity maximally to the bacteria in the growth medium for all the tested strains (Figure 1b). The MIC for *Pseudomonas fluorescens* at the highest organic matter (HA) concentration (200 mg L⁻¹) was increased by 8 times, while the same for *Pseudomonas chlororaphis* and *Rhodococcus* increased by 4 and 5 times, respectively. Such toxicity reduction by HA was higher than the combined HS. Thus, at increasing concentrations of HA and HS in the growth medium, there was reduction of Zn toxicity to microorganisms, which was also demonstrated by their increasing MICs. The reported molecular mass of HA generally vary between 2 – 1300 kDa. The interaction of HA with Cu²⁺, Fe²⁺, Co²⁺, Zn²⁺, Pb²⁺, and Ni²⁺ was reported extensively, and is based on the formation of metal-humate compounds through both covalent bonds and electrostatic interactions (Senesi and Loffredo 2005). All these mechanisms explain the greatest resistance of the tested microorganisms to Zn in the presence of HA.

The humatomelanic acid fraction of HS had the least effect on Zn toxicity in this study (Figure 1c). At all the added concentrations of humatomelanic acids, no effect on the Zn toxicity to *Pseudomonas fluorescens* and *Rhodococcus* was observed. Similarly, no effect was also observed in the case of *Pseudomonas chlororaphis* when humatomelanic acid was added to the media at a concentration of 50 and 100 mg L⁻¹. However, the addition of humatomelanic acid at the concentration of 200 mg L⁻¹ showed a significant increase in the microbial resistance to Zn.

Humatomelanic acids hold an average molecular mass between 5 and 10 kDa (Ziechmann 1993). They contain methoxyl, carboxyl and hydroxyl functional groups, and have characteristically high carbon content (more than 60%) (Kononova 1966). Grimalt and Saiz-Jimenez (1989) showed that fatty acids constituted the predominant components of all humatomelanic acids encompassing distributions in the C₁₂-C₃₄ range where microbial and higher plant contributions could be recognized. Despite a wide diversity of soil samples was analyzed, no major qualitative differences were found in the humatomelanic acid extracts.

Clearly, at low concentrations of humatomelanic acids, the processes of the formation of unstable or stable Zn-complexes were possibly dominated. The formation of complexes that are inaccessible to microorganisms apparently took place at the highest concentration of humatomelanic acids only. Overall, the strain *Pseudomonas chlororaphis* was the most responsive to HS additions in the media in terms of Zn toxicity. The resistance of all the strains increased with the introduction of combined HS, or HA and humatomelanic acid alone.

Pb detoxifying ability of HS

It was interesting to note that the combined HS caused an increase in Pb MICs absolutely similar to the HA fraction (Figure 2a, Figure 2b). Christl (2000) reported significant differences in Pb²⁺ binding behavior of HA and FA at pH 4 only, but not at pH 6 and 8 (i.e., conditions of the growth

medium). This suggested that the Pb binding to HS was almost unaffected by the difference in the chemical composition of HS.

The HA fraction decreased the toxicity of the heavy metals (both Pb and Zn) at all concentrations of HA and for all the bacterial strains. However, the shift (increase) in MICs was slightly lower for Pb than Zn (Figure 1b, Figure 2b). The stability constant of Pb-humate complexes was reported to be greater than that of Zn-humate complexes (Kostic *et al.* 2013). Thus, Pb might form more stable complexes with organic components than Zn in the growth media. This was evidenced in this study from the high MICs for Pb, but not essentially for Zn.

The HMA fraction showed a Pb detoxifying effect on all the studied bacterial strains, but only at the maximum concentration of the organic substances (200 mg L⁻¹) (Figure 2c). So, their effect on the binding of Pb was significantly lower than the HA fraction, and was shown only at the highest concentration. There are many contradictory data on the elemental composition and chemical structure of HMA. However, there is no doubt about their differences in the molecular weights as compared to HA and FA. Hymatomelanic acids are regarded as the intermediates between HA and FA with molecular weights in the order of 5-10 kDa. Zdanova (2011) reported that the metal-hymatomelanic acid complexes might partly penetrate to the cytoplasm of microorganisms and cause a toxic effect.

All the strains of microorganisms increased the resistance to Pb with application of HS in this study. The increase of resistance was different depending on the strain of microorganisms and organic substances used. The results demonstrated that the mechanisms of increasing resistance of microorganisms to heavy metals possibly involved the formation of stable complexes as well as biological availability of these complexes.

Conclusions

The strains of microorganisms used in this work demonstrated a lower resistance to Zn than Pb showing The strains of microorganisms used in this work (*Pseudomonas chlororaphis* PCL1391, *Pseudomonas fluorescens* 142NF (pNF142) and *Rhodococcus* RS67) demonstrated a lower resistance to Zn than Pb showing minimum inhibitory concentrations (MIC) of 0.1 - 0.3 mM and 0.3-0.5 mM, respectively. The humic substances and humic acids reduced the Zn and Pb toxicity at all the added organic matter concentrations irrespective of all the microbial strains. On the other hand, the addition of hymatomelanic acid only at the maximum concentration (200 mg L⁻¹) showed a significant increase in the resistance of *Pseudomonas chlororaphis* PCL1391 to Zn and all the three studied microorganisms to Pb. Thus, under certain conditions, metal ion toxicity might be reduced through complexation with humic substances and their fractions. This is particularly true when the metal-organic complexes hold high stability and low solubility and bioavailability.

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3.2.18. Use of polyamine compounds for the detection of metals such as cadmium, mercury and lead in waters

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Abstract

The study of the affinity of two types of polyamine ligands in sequestering heavy metals from water has been carried out. Cadmium, mercury and lead have been used as examples of water contaminants.

The acid-base properties of the polyamines in aqueous solution have been characterized, the interaction of these receptors with the different cationic species by means of potentiometric, fluorometric, NMR techniques for their later application. The receptor Pytren-F is more selective for this metal than Tren-F.

Keywords: polyamine ligands, water contaminants

Introduction

The pollution due to human activity agriculture, industry, land uses, has as a consequence that deep waters cannot be used directly for human consumption since it is not purely biologically or chemically.

The study of the affinity of two types of polyamine ligands in sequestering heavy metals from water has been carried out. Cadmium, mercury and lead have been used as examples of water contaminants.

The acid-base properties of the polyamines in aqueous solution have been characterized, the interaction of these receptors with the different cationic species by means of potentiometric, fluorometric, NMR techniques for their later application

Methodology

The receptors used derive from the polyamine tris-2-aminoethylamine commonly known as TREN. This is joined by an aromatic group, fluorene, which is called TREN-F (tripodal ligand). If the TREN-F is cycled with an aromatic spacer, a scorpion-type ligand, PYTREN, is obtained, which is linked to the Fluorene aromatic unit form the PYTREN-F.

Nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra were carried out at a controlled temperature with Avance DRX Bruker 300MHz and Avance DRX Bruker 400MHz spectrometers. The ¹H-NMR spectra are recorded at 299.95 and 399.95 MHz and those of ¹³C-NMR at 75.43 and 100.58 MHz, respectively.

The solvents used were D₂O and CHCl₃. The ¹H-NMR spectra are referenced to the corresponding solvent signal, while for ¹³C-NMR, dioxane (67.4 ppm) is used as external reference.

Fluorescence. Emission spectra were performed on a modular PTI fluorimeter with Xenon lamp. The geometry used was always at right angles. Transparent Hellma quartz cells were used on all 4 faces and thermostated at $25 \pm 0.1^\circ\text{C}$. The data were corrected with the volume dilution necessary to adjust the pH (solutions of HCl and NaOH in water at different concentrations). Finally the data was normalized for a maximum emission of 1. Sabatini *et al.*, (1992); Czarnik, *et al.*, (1993), Bruno, *et al.*, (2002).

Results

Logarithms of the protonation and global basicity constants for PYTREN-F and TREN-F, determined at $298.1 \pm 0.1 \text{ K}$ in NaNO_3 $0.15 \text{ mol} \cdot \text{dm}^{-3}$ and NaNO_3 $0.15 \text{ mol} \cdot \text{dm}^{-3}$ Ethanol: water (30:70) respectively (Pina, *et al.*, 2002).

By fluorimetry A) Variation of fluorescence intensity as a function of the pH of PYTREN-F-Pb (1:1) (pH values: 2.08, 2.11, 2.51, 3.22, 3.70, 4.12, 4.66, 5.21, 5.72, 6.23, 6.79, 7.21, 7.95, 8.57, 9.10, 9.62, 10.23, 10.95). B) Representation of the distribution diagram of species next to the maximum emission of the free ligand (●) and the ligand with Pb (II) (●).

Representation of the distribution diagram of species next to the maximum emission of the free ligand (●) and the ligand with Pb (II) (●).

Representation of the distribution diagram of species next to the maximum emission of the free ligand (●) and the ligand with Cd (II) (■).

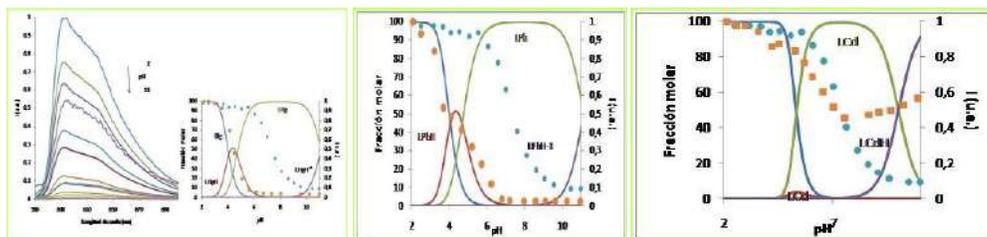


Figure 1. A) Complexity VARIATION of the fluorescence emission spectra of PYTREN-F as a function of pH (pH values: 2.16, 2.51, 3.18, 3.67, 4.09, 4.55, 5.06, 5.56, 6.06, 6.57, 6.99, 7.6, 8.1, 8.6, 9.05, 9.55, 10.45, 10.97). B) ● Maximum fluorescence emission at 613 nm for the PYTREN-F receptor (excitation length = 285 nm)

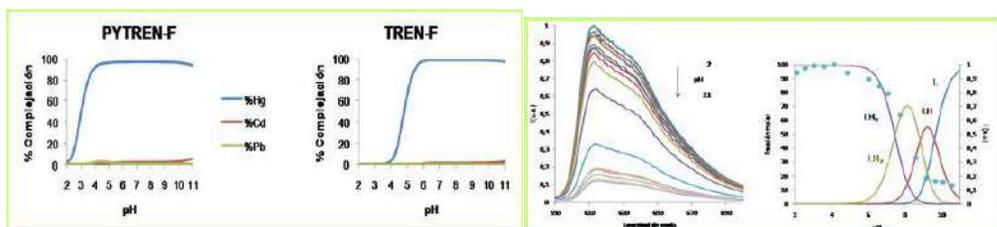


Figure 2. A) Variation of the fluorescence emission spectra of TREN-F as a function of pH (pH values: 2.11, 2.57, 3.04, 3.59, 4.14, 4.89, 6.03, 6.64, 7.09, 7.75, 8.6, 9.19, 9.67, 10.07, 10.57, 11.03). B) ● Maximum fluorescence emission at 613 nm for the TREN-F receiver (excitation length = 285 nm).

Conclusions

From the studies carried out with both receptors for the different metals, we can say that both the Pytren-f and the train -f interact with all the metals studied.

Both receptors have greater affinity for Hg (II). Comparing the two ligands with Hg (II), Pytren-F is more selective for this metal than Tren-F.

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3.2.19. Phytoremediation of contaminated soils in mining area using Ray Grass. Case study: Abandoned mine of Zaida and Mibladen (High Moulouya, Morocco)

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Abstract

Ray-grass Italy (*Lolium multiflorum L*) is characterized by its rapid growth and ease of implantation. The present study investigates the potential use of this plant in the phytoremediation of heavy metals contaminated soils. Growth performance of Ray-grass Italy was studied on various substrates collected around the abandoned mines of Zaida (waste treatment, waste of coverage) and Mibladen (mining waste), as well as a witness agricultural soil. The observation of the plant growth during 7 weeks shows that agricultural soil is more adapted for Ray-grass Italy followed by waste of coverage. The results of this study show that Ray-grass Italy can grow in contaminated soil and accumulate heavy metals into tissues which prove the ability to use this plant for phytoremediation of heavy metal contaminated soils.

Keywords: Contamination, Heavy metals, Phytoremediation, Ray-grass Italy

Introduction, scope and main objectives

The lead mining district of High Moulouya, comprising the mines of Zaida, Aouli and Mibladen, constituted the largest lead deposit in Morocco. These mines are considered as the main source of environment contamination by heavy metals because they are abandoned without any environmental rehabilitation plan. It today is therefore essential not only to a better understanding of the effects of these elements on the living organisms, but also to implement sustainable solutions, designed to restrict their risks. . In this context, we evaluated the ability of Ray-grass Italy to absorb heavy metals and its potential use in remediation of contaminated soil.

Methodology

The soil used in the present study was collected around the abandoned mines of Zaida and Mibladen (Figure 1). The characteristics of the different substrates are presented in table 1. The experimental set-up consists of plant development monitoring in the different collected substrate. Each of the 4 substrates used has undergone three treatments:

- Without fertilizer,
- Sheep manure,
- Fertilizer.

In total, 72 pots were used at a rate of 6 pots per treatment. In each pot, we planted 7 seeds. After 7 weeks, the whole plants were harvested individually. The different plant parts (roots, stems and leaves) were separated, washed with distilled water and then transferred to a paper bag where

their fresh weights were measured using a precision scale, then left to free air for 4 days finally dried in an oven at 70 ° C for 48 hours to evaluate their dry weight. Determination of heavy metals in substrates and plants has been performed by means of atomic absorption spectrometry Varian (AAS). Samples were analyzed at the chemical analysis laboratory at the National Institute for Agricultural Research (Rabat, Morocco).

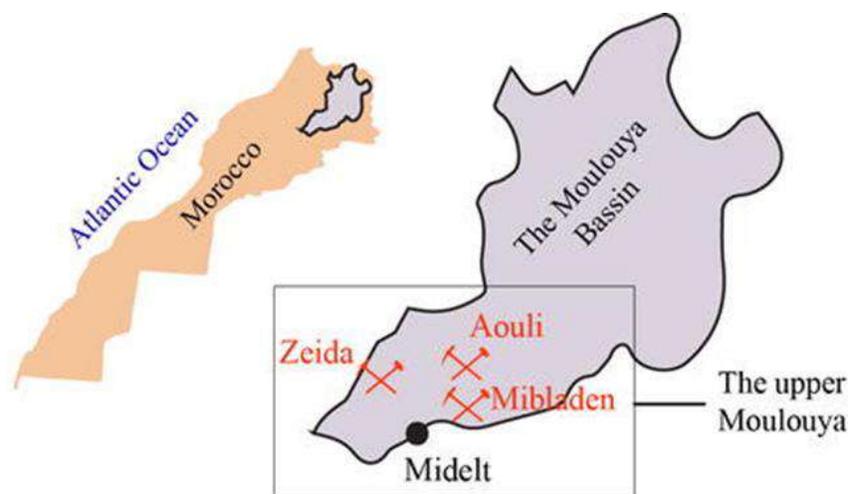


Figure 1. Location of the studied mines

Table 1. Characteristics of studied substrates

ubstrates	% Clay	% Silt	% Sand	Soil texture	pH
Mining waste Mibladen	10,2	12,7	77,1	Sandy	7,95
Waste of coverage Zaida	18,6	29,3	52,1	Loamy	7,83
Waste treatment Zaida	7,2	27,7	65,1	Loamy-sandy	8,09
Witness agricultural soil	10,6	2,6	86,8	Sandy	7,80

Results and discussion

Comparison of height growth of plants

After 7 weeks of culture, we noticed a difference in height growth of Ray-grass Italy in the different substrates (Figure 2). The lowest growth rate was observed in Mibladen substrates without fertilizer addition. However, under the effect of manure and fertilizers, plant growth stops after 20 days with an average of 46.5 cm. For waste treatment substrates, we recorded low growth in plants without fertilizer, which after 21 days begins to decline due to heat and lack of water. However, the plants, under fertilization effect, can resist and show a continuous development up to 30 cm on average. The growth of the plants in the waste of coverage is good; the height reaches 29 cm without fertilizer, and about 40 cm with manure and fertilizer.

The differences recorded between the substrates are due to their physicochemical properties. We notice that the growth in the witness soil is the highest, because the soil is well structured, with a more or less good concentration of organic matter compared to the other types of substrates. This is followed by waste of coverage as they have a loamy texture able to hold water.

The development of each plant was remarkable after adding inputs of manure and fertilizer to the substrates. The plants have grown to 40 cm, confirming the essential role of fertilizers by

increasing nutrients, such as N, P and K for fertilizers, and organic matter, essential element of manure, which plays a role in improving productivity and soil structure.

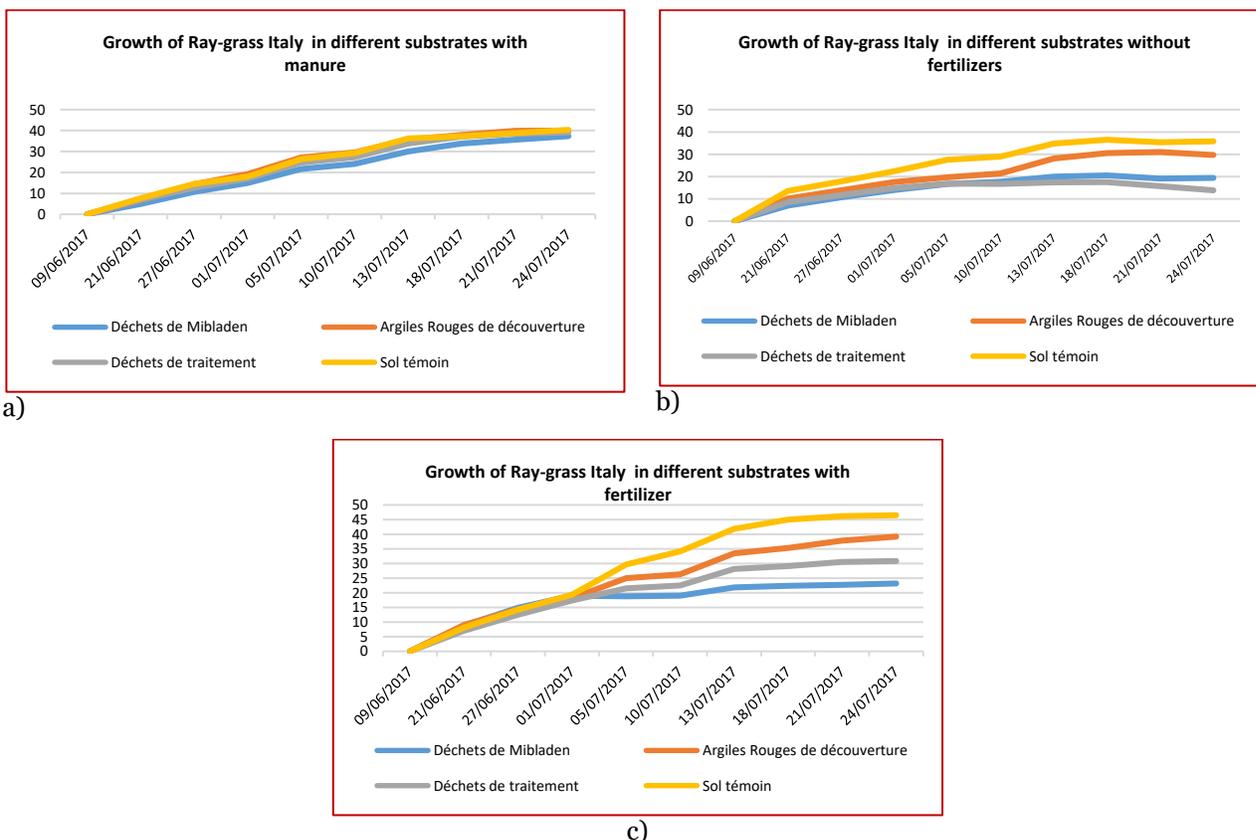


Figure 2. Growth of Ray-grass Italy in different substrates with different treatments

Effect on biomass

The root and foliar biomass of Ray-grass Italy increased with the different inputs (manure and fertilizer) whatever the type of substrate.

- *Root biomass*

Figure 3 shows a marked improvement in root biomass in manure and fertilizer treatment waste, which increases from 0.12 without fertilizer to 1.46 g with manure and 1.25 g with fertilizer addition. The lowest root biomasses were recorded in the mining waste of Mibladen, 0.25 g and 0.10 g respectively under manure and fertilizer treatment.

- *Leaf biomass*

Foliar biomasses in waste of coverage are well developed. They are of the order of 0.50 g without fertilizer, and increase significantly with the fertilizing effect of manure at a value of 1.50 and 1.79 for fertilizers (Figure 4).

In contrast, the mining waste of Mibladen did not record a great evolution with fertilizer. The values of foliar biomass without input are 0.10 g, and 0.56 g and 0.25 g respectively under the effect of manure and fertilizer.

Manure and fertilizer have increased the leaf and root biomasses of plants, especially for plants growing on treatment waste substrates of Zaida. However, the Mibladen soil has evolved poorly even with fertilizer input. This difference would be related to the amount of nutrients and organic matter available to the plants, and also to the structure and texture of each substrate.

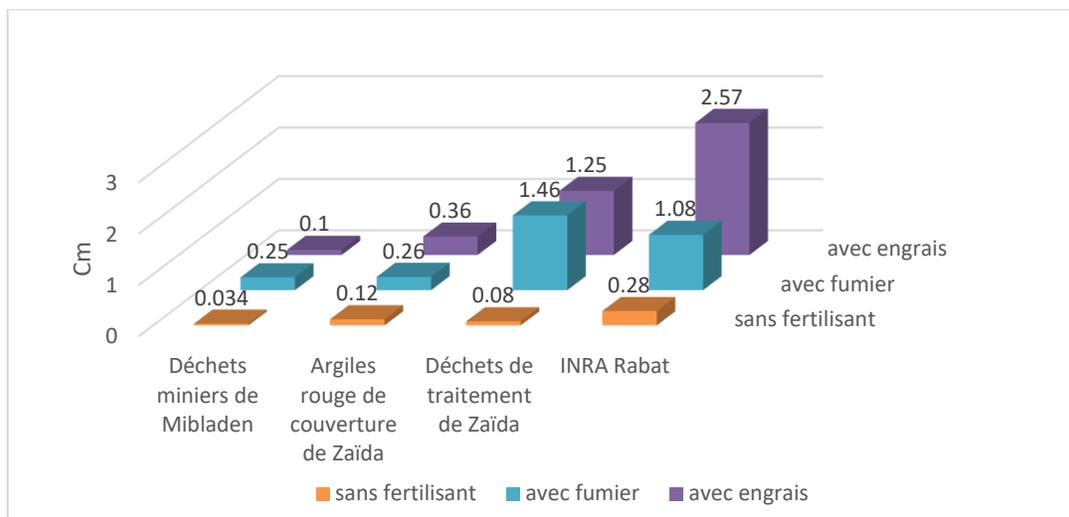


Figure 3. Root biomass in different types of substrates and different inputs

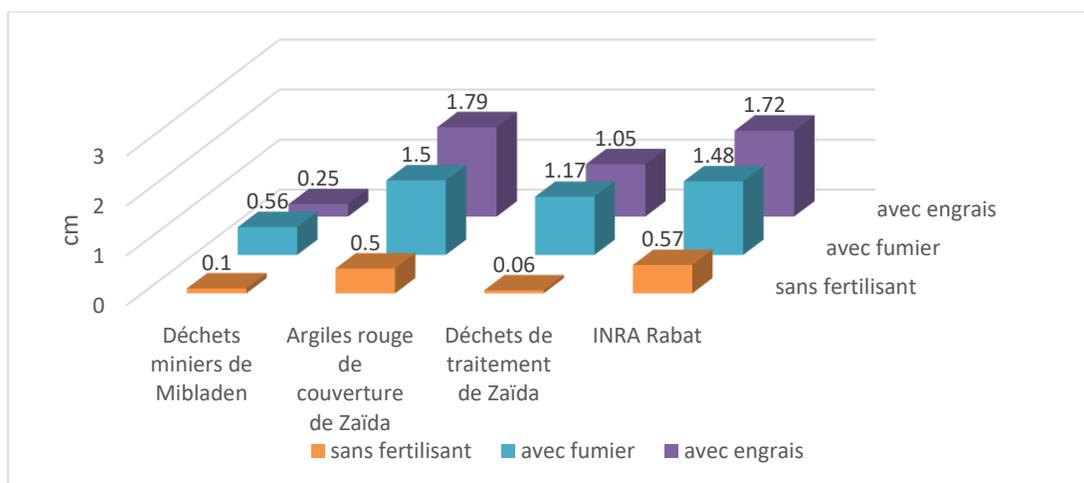


Figure 4. Leaf biomass in different types of substrates and different inputs

Phytoremediation of heavy metals using Ray-grass Italy

We note a non-significant decrease in Zinc concentration in rhizospheric soils compared to soils before culture regardless of the type of substrates. Decreases in Copper concentration were also recorded in the treatment waste and in the control soil. On the other hand, it stagnates in the soil of Mibladen and waste of coverage. For chromium, cadmium and lead, concentrations were generally lower in rhizospheric soils than in non-rhizospheric soils in most substrates.

We have noticed that heavy metal concentrations have varied irregularly between different substrates. The reduction in Zn content is important with the addition of fertilizer in the control soil and the treatment waste. The decrease in concentration of the contents of Cr, Cd and Pb can

be explained by the removal of heavy metals by plants. Such results are similar to those found by Luo *et al.* (2000). The decrease in the five heavy metal levels could be attributed to soil remediation (Kabata and Pendias, 1992).

Table 2. Concentration of heavy metals in different soil types before and after the test facility.

		Zn	Cu	Cr	Cd	Pb
Mining waste Mibladen	SAC	349,58	29,96	465,44	4,49	9997,99
	SRS	273,24	30,36	460,46	4,05	9917,60
	SRF	281,96	30,21	411,86	3,52	9566,50
	SRE	300,54	30,05	413,74	4,01	9917,82
Waste of coverage Zaida	SAC	100,01	20,00	175,02	2,00	350,04
	SRS	69,60	17,40	152,25	1,74	313,20
	SRF	87,23	17,45	131,81	1,45	329,53
	SRE	81,38	12,21	167,85	1,02	274,67
Waste treatment Zaida	SAC	191,90	30,30	145,44	4,04	2787,60
	SRS	181,35	30,23	122,92	3,53	2559,05
	SRF	149,61	29,92	150,61	2,49	2513,45
	SRE	131,77	20,27	150,20	2,53	2442,78
Witness agricultural soil	SAC	50,70	12,17	273,78	4,56	101,40
	SRS	39,82	9,96	219,01	2,99	99,55
	SRF	30,30	10,10	252,53	3,03	80,81
	SRE	40,36	10,09	225,99	3,03	100,89

SAC: Soil Before culture

SRS: Rhizospheric soil without fertilizer

SRF: Rhizospheric soil with manure

SRE: Rhizospheric soil with fertilizer

The results showed that Ray-grass Italy has a good ability to settle and grow on substrates contaminated with Zn, Cu, Cr, Cd and Pb. Tables 3 and 4 summarize heavy metal concentration in root and leaves.

Table 3. Heavy metal content in Ray-grass Italy roots.

		Zn	Cu	Cr	Cd	Pb
Mining waste Mibladen	RS	2,27	0,19	5,65	0,13	5,31
	RF	0,49	0,03	0,76	0,02	3,97
	RE	0,95	0,10	3,25	0,08	6,08
Waste coverage Zaida	RS	3,05	0,53	12,06	0,11	3,05
	RF	0,29	0,32	5,02	0,11	3,20
	RE	5,34	0,99	16,72	0,31	5,34
Waste treatment Zaida	RS	0,49	0,10	1,62	0,03	0,39
	RF	53,63	0,00	91,65	1,95	53,63
	RE	232,78	7,63	82,04	1,91	587,66
Witness agricultural soil	RS	0,67	0,56	4,94	0,10	0,56
	RF	54,64	0,19	28,72	0,62	9,37
	RE	389,17	1,26	250,33	4,73	157,77

RS : Root Without fertilizer

RF : Root With manure

RE : Root With fertilizer

Table 4. Heavy metal content in Ray-grass Italy leaves.

		Zn	Cu	Cr	Cd	Pb
Mining waste Mibladen	FS	3,70	0,46	3,15	0,30	4,17
	FF	14,24	2,85	18,65	1,00	12,82
	FE	1,36	0,23	2,89	0,15	2,71
Waste coverage Zaida	FS	9,00	2,00	8,30	0,05	13,00
	FF	11,60	4,64	35,50	0,93	4,64
	FE	23,56	5,89	4,71	1,03	76,57
Waste treatment Zaida	FS	2,08	0,52	5,04	0,31	0,52
	FF	18,00	1,00	10,40	0,70	12,00
	FE	29,43	1,09	17,33	0,55	8,72
Witness agricultural soil	FS	5,65	1,13	12,42	0,85	2,26
	FF	14,18	1,77	31,36	1,06	5,32
	FE	14,22	3,56	29,34	1,24	5,33

FS : Leaves Without fertilizer

FF : Leaves With manure

FE : Leaves With fertilizer

Analysis of the heavy metal content in the plant organs (leaves and stem) of Ray-grass Italy allowed determining the quantities of heavy metals accumulated after 7 weeks of plant cultivation. However, the quantities exported by each plant organ depend on its biomass, which also depends on the fertilizer provided. This result confirms those of Khan *et al.* (2000) who showed that the efficiency of the depollution depends on the quantity of aboveground biomass.

Also, Adhikari *et al.* (2010) observed that the different quantities of metals exported by plant organs could be explained by the biomasses produced but also by the ability of each plant to transfer the metal to its aerial parts and the time of cultivation.

The low Pb content exported could be explained by the low mobility of this metal even though Mibladen substrates and treatment wastes are very rich in lead.

The process of phytoextraction of metals depends on the bioavailability of the metal in the soil (Brown, 1995). However, this bioavailability can be influenced by multiple factors (abiotic and biotic) in the contaminated environment.

Conclusions

The addition of fertilizer and organic matter has significantly improved the substrates quality and this appears through the development of plant biomass and the growth of Ray-grass Italy. The effectiveness of the decontamination depends on the amount of biomass produced. The high plant biomass has had a very positive impact on the quantity of heavy metals exported. After comparing our results with those obtained in the literature, it appears that Ray-grass Ital can accumulate significant levels of heavy metals, which means that it is interesting for remediation of soil contaminated with heavy metal.

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3.2.20. Sustainable soil management of polluted military site by phytostabilization with biomass production using biofuel crop *Miscanthusxgiganteus*

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Abstract

Application of the phytotechnology with biomass production using the second generation biofuel crop *Miscanthusxgiganteus* was tested at the soil from the military site in Sliach, Slovakia polluted by different metals: Fe, Ti, As, Cu, Mn, and Sr. The peculiarities of metals uptake during two vegetation seasons in greenhouse conditions were investigated. The accumulation of metals by stems and leaves was much lower than by roots. As and Ti were almost not accumulated by stems and leaves during both seasons; accumulation of Cu, Fe, Mn, Sr was not essential. Data confirmed that biomass of *M.xgiganteus* produced at the military polluted soils might be processed for the energy purpose, which makes the proposed approach sustain.

Keywords: military polluted site; sustainable soil management, Miscanthusxgiganteus; metals uptake

Introduction, scope and main objectives

Former military sites are widely dispersed in the countries of Eastern and Central Europe and in the US (Pichtel, 2012). Those locations, often polluted by heavy metals, oil and degraded organic products as well as some unknowns, negatively affect soil and water resources, deteriorate the biodiversity and pose essential health risks. There is no general best practice approved for the remediation of contaminated soil at former military facilities. Current approaches rely on transporting the contaminated soil off site to be treated, which is a costly venture. For an on-site remediation method to be an effective practice, it must meet several criteria, including (1) be easily applied over a large area, (2) not require specialized equipment or operators, (3) be cost effective, and (4) be implemented as part of normal site operations (Craig *et al.*, 1995).

One of the innovative approach for sustainable management of slightly polluted military soil is a combination of phytostabilization technology with production of biofuel crops (Pidlisnyuk *et al.*, 2016; Pidlisnyuk *et al.*, 2018). This allows to restore polluted military land and to meet demand for biomass production as an alternative energy source and/or raw materials for proceeding to bioproducts. The approach is effective when military sites are located at relatively big areas and slightly or midium polluted.

The perennial grass *Miscanthus x giganteus*, second generation biofuel which is not in contraversity with the food security, is considered as promising plant for that approach (Pidlisnyuk *et al.*, 2014).The developing of phytotechnology for the sustainable management of military polluted soils has been based on confirmation the ability of the crop to be growth at the military slightly polluted soils; determination percularities of metals uptake during growth at such soils a number of vegetation seasons; elaboration conditions for limitation uptaken of

pollutants to the above part of the plan in order to receive a good quality biomass by treatment of soil by different amendments and providing planted materials actions by growth regulators and microfertilizers. The overall research military sites are diverse and include airports of the former Soviet Air Force in Mimon (Czech Republic) and Sliac (Slovakia), former training field at Ft. Riley (USA), former military storages in Kamenetz-Podilsky (Ukraine) and former tank training site in Dolyna (Ukraine). The recently appeared military site in Kurakhove, East of Ukraine, as result of Russian intervention in 2014, which was elaborated by Ukrainian army in 2015 is under consideration as well. Locations are classified as contaminated and damaged sites by the local environmental authorities of the corresponding countries and are need revitalization. The main contaminants at the sites are diverse and include spilled jet fuel and different metals (Pidlisnyuk *et al.*, 2016; Davis *et al.*, 2017; Pidlisnyuk *et al.*, 2018).

That study presents results of the application the proposed approach to the soil from the former military site located near village Sliac, Slovakia; control soil was taken near village Velká Luka. The military site was used as an airport of the former Soviet Union Air Force, and was classified as highly contaminated by the Slovakian Environmental Agency and Ministry of Defense of the Slovak Republic. Spilled jet fuel (kerosene) was the main contaminant (Andersen 2000). In addition, the area has relatively high arsenic levels due to its complex geology as the downstream region of a highly erosive river system descending from mountainous central Slovakia (Lindberg *et al.*, 2006). The aim of the study was to test in a greenhouse pot experiment the process of metals uptake from the contaminated military soil while growing the crop *M. x giganteus* during two growing seasons, to analyse peculiarities of the process, and to compare the metals uptake behavior in the plant during first and second vegetation seasons.

Methodology

The plant used at experiments was *M.xgiganteus*, a sterile inter-specific hybrid of *Miscanthus sinensis* and *Miscanthus sacchariflorus* (Clifton-Brown *et al.*, 2007; Nsanganwimana *et al.*, 2014). It belongs to perennial grass with woody stems of heights of 2-4 m. The stems senesce in autumn, but the plant is able to regenerate stems in the spring from its rhizomatous root system. Plant foliage dies at the end of the growing season and can be harvested at high dry matter content. The plant has a C-4 photosynthetic pathway, and has been demonstrated to achieve high light interception and conversion efficiency of C-4 plants, which exceeds that of C-3 crop plants by about two-fold (Beale *et al.*, 1995). The plant was already introduced in Europe and the US and exhibited good production properties while used for remediation of brownfield sites, former mining sites and contaminated agricultural lands (Brosse *et al.*, 2012). The crop has a C-4 photosynthetic pathway, a good environmental profile with the potential to increase soil carbon, soil fertility and biodiversity and to reduce nutrient run-off and leaching (Nsanganwimana *et al.*, 2015). Rhizomes exercised at the experiment were three years old and obtained from the agricultural experimental station in Bytča, Žilina region, Slovak Republic.

The location of the studied contaminated military site had the following coordinate: Latitude: 48°62'34; Longitude: 19°13'49 and was chosen as research one in accordance with the assessment of Sliac-South done by the Ministry of Defense of the Slovak Republic in 2013. The sampling of the control (relatively "clean") soil was withdrawn from the agricultural field at the nearby located village Velká Luka on the opposite bank of the Hron river which had the following coordinate: Latitude: 48°63'02; Longitude: 19°15'57. The soil sampling at contaminated site at Sliac and control site at Velká Luka was carried out using the standard approach (State Standard of Ukraine, 2001): one testing square was selected at the soil with the size: 5m x 5m; from the square five samples were taken from the deep: 0-0,3m using "envelope methods", mixed and used further in the experiment. The pot experiment was carried out in the greenhouse. Fourteen kg of soil in

each pot in duplicates (labeled as a and b) was used. Concentration series of five mixtures of control and contaminated soils was used: 100%, 75%, 50%, 25% and 0% of contaminated soil. In each pot two rhizomes of *M. x giganteus* were planted. The overall accumulation of metals into the roots, stems and leaves of *M. x giganteus* was determined at the end of the two growing seasons of 2014 and 2015. The height of the plants (in cm) were measured during vegetation seasons occasionally using ruler, produced by Koh-i-noor Hardtmuth Slovensko a.s (The Slovak Republic).

The agricultural characteristics of the military polluted soil from Sliac were measured in accordance with the standards (DSTU 4729-2007; DSTU 4289-2004; Mehlich, 1978).

The determination of concentrations of metals in the soil, roots, stems and leaves was provided by X-Ray fluorescence analysis using analyzer Expert-3L. The device was produced at the Institute for Analytical Methods of Control, Kyiv, Ukraine (<http://inam.kiev.us/contact-information>) in accordance with the requirements of EPA 6200 (US EPA, 2007). The accuracy of determination was in accordance with ISO/IEC 17025[39]. Three parallel measurements were taken for each sample. The level of metals in the soil was determined in mg/kg. For the roots, stems and leaves, levels were determined in mass units in the ash and then further recalculated to mg/kg based on ash content of plant material. For overall calculation the concentration was expressed in mg/kg dry weight. In case of soil analysis, sample (~2 g) were placed on ultra-thin (4 µm) polypropylene film (supplied with the device), which is transparent to X-rays, further accurately transferred to the device where measurement was performed. In case of plant parts, combusted samples (ash) of roots, stems and leaves were placed inside a glass ring with diameter of 1.25 cm, which was located on a similar thin polypropylene film and compacted using a glass rod. The resulting sample was transferred into a device for measurements.

Statistical evaluation of data received was carried out using Microsoft Excel. Since a majority of data did not pass the Jarque-Bera normality test (Pidlisnyuk *et al.*, 2018), non-parametric statistics (Spearman correlation, Friedman test,) were applied (Altman 1990). The non-parametric calculations were carried out using PAST 3.0 software at the significance level $\alpha=0.05$.

Results

The agricultural characteristic of the research soil from the military polluted site is presented at Table 1.

Table 1. Characteristics of military soil from the site in Sliac, Slovakia

Parameter	Value
pH*	7.06
C _{ox} (g/kg)**	14.60
Humus (g/kg)**	25.16
N _{tot} (g/kg)*	2.97
P (mg/g) extractable***	13.59
K (mg/kg) extractable***	156.96
Mg (mg/kg) extractable***	630.80

* according to DSTU 4729-2007

**according to DSTU 4289-2004

***according to Mehlich, 1978

The content of metals in soil samples is presented in Table 2. The soils contained dominantly Fe and Ti, and other metals (Mn, Cu, Zn, Zr) are presented at lower concentrations. With the exception of As, the soils contained all other elements within the range of elemental concentrations reported for uncontaminated soils collected from around the world (Hettiarachchi *et al.*, 2016).

Table 2. Concentrations of metals in mixtures of contaminated and control soils (average±standard deviation, n=2) taken from military polluted site at Sliac and control site at Velka Luka, the Slovak Republic

soil label	1	2	3	4	5
contaminated soil	0%	25%	50%	75%	100%
As [mg/kg]	290±40	515±15	430±79	465±15	425±45
Cu [mg/kg]	310±0	380±60	395±5	440±100	565±125
Fe [mg/kg]	174555±5395	194485±8645	205640±7540	209480±6830	215210±5720
Mn [mg/kg]	2995±185	3605±485	4110±340	4495±555	4660±500
Sr [mg/kg]	685±65	695±15	925±15	1185±75	1200±40
Ti [mg/kg]	20620±0	24410±260	25935±615	27940±2420	28170±530
Zn [mg/kg]	960±90	1025±45	1115±115	1205±335	1015±235
Zr [mg/kg]	1275±275	1455±75	1345±205	1500±60	1625±225

Discussion

Despite significant gradient of metal concentrations in the soils (variants 1 to 5), no correlation is observed between level of soil pollution and metals concentration in plant parts as well as plants height. That observation was detected for both growing seasons and illustrates that metals are uptake by *M. x giganteus* with no regard to contamination of researched military soil. This result enabled comparison of metals concentrations in plant parts jointly for all variants in order to obtain higher significance of comparisons based on higher number of values. Non-parametric Friedman test with post-hoc Wilcoxon test of metals concentrations are presented in Table 3.

Table 3. Concentrations of selected metals in *M. x giganteus* parts in two vegetation seasons (average±standard deviation, n=10). Letters denote comparable metal concentrations, bold-face indicate values significantly different form 0; both based on Wilcoxon test ($\alpha=0.05$), Pidlisnyuk *et al.*, 2018

	[mg/kg dwt] soil	Year 1			Year 2		
		roots	stems	leaves	roots	stems	leaves
As	425±86d	6±6bc	1±1ab	1±1a	25±10c	0±0a	0±0a
Cu	418±114e	58±24cd	23±11bc	26±4c	76±48d	8±3ab	8±3a
Fe	199874±15943e	1514±455c	119±34ab	213±33b	23779±10167d	101±36a	252±41b
Mn	3973±748d	85±52b	20±20a	181±54bc	488±266c	131±55bc	131±43b
Sr	938±230c	37±17ab	39±21ab	51±19b	135±78b	13±2a	24±10a
Ti	25415±2994d	225±72b	8±19a	2±3a	3114±1180c	40±30a	33±24a
Zn	1064±214e	63±19ac	117±33bd	40±4a	179±74cd	78±34ab	61±13a
Zr	1140±224d	13±7b	1±1a	0±0a	125±61c	0±1a	0±1a

The analysis of data presented at Table 3 show that, in accordance with expectation, the uptake of metals by *M. x giganteus* roots is the biggest in comparison with the above parts of the plant and the phenomena observed for all monitored metals. Also, the level of accumulation of metals in the roots is higher at the end of the second growing season for all metals which is in accordance with the previously reported results, when *Mxgiganteus* was used at the different phytoremediation processes (Pidlisnyuk *et al.*; 2014; Nsanganwimana *et al.*, 2015). The data illustrate the differences in metals' uptake between first and second growing seasons. The results show that metals' up taken by above part of the plant is very limited during both seasons referring to the

concentration of metals in the soils. Consequently, As and Zr are almost not accumulated by stems and leaves during both vegetation seasons and accumulation of Cu, Mn, Zn and Sr is not essential which confirmed that biomass may be processed for the energy. Moreover, data presented at Table 3 illustrate that for some metals accumulation by the above part of *M.xgiganteus* decreases at the second year in comparison with the first year: that is observed for Cu and Sr (stems and leaves); Fe (stems); Mn (leaves) and Zn (stems).

Our previous studies (Pidlisnyuk *et al.*, 2016) done with the military polluted soil from Kamenetz-Podilsky, Ukraine (former military storage) with critical concentration of such metals as Mn, Ti, Fe and Zr did not detected any growth inhibition of the plant, indeed, *M.xgiganteus* demonstrated a good growth at that soil with limited accumulation of metals in the aboveground parts. Results obtained in the current research with military soil from Sliac, Slovakia (former military airport) polluted by Fe, Ti, As, Cu, Mn, Sr, is supplemented to the previously received data; again, no obvious inhibition of growth and limited uptake of metals to the aboveground parts are observed. Such behavior is favorable for application of *M. x giganteus* as source of biomass for the direct burning, fermentation to biofuels and make the proposed phytotechnology with biomass production sustain.

Further research is needed regarding improving quality of *M. x giganteus* biomass growing at the polluted military sites. It is planned to accomplish by adding amendments to the polluted soils and treatment of the planted materials by plant growth regulators.

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3.2.21. Rock fines as amendment enhances crop yield and soil chemicals while decreasing soil acidity on a tropical soil in the northwest region of Cameroon, Africa.

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Abstract

Rocks made up of basalt and trachyte were crushed into smaller fragments and ground into fines after several 1x1 mm mesh sieve to obtain fines used as amendments and applied on a tropical soil to grow up *Solanum Tuberosum*, commonly known as irish potatoes in the northwest region of Cameroon. In addition, coal fines were applied as manure. The different treatments are made up of the control, basalt fines alone, trachyte fines alone, basalt + coal fines and trachyte + coal fines. At the end of the crop growth, the treatments with fines of trachyte alone gave the poorest yield of 11 111 Kg/ha. This yield was boosted to 13 333 kg/ha with the addition of coal fines as manure to this treatment. However, this is still lower than 14 815 Kg/ha portrayed by the control soil. The treatment with basalt fines alone yielded 16 296 Kg/ha. The addition of manure on this treatment enhances the yield to 20 741 Kg/ha while the treatment amended with conventional chemical fertilizers and manure yielded 23 704 kg/ha. Then, chemicals analyses were carried out to assess crop nutrients loaded in soils through rock fines. Rock fines added treatment with the highest yield is that with basaltic fines mixed with manure. This treatment also showed the highest CEC, N, Ca, Mg and Na with values of 24.16, 0.05 %, 10.24 meq/100g, 45.76 meq/100g and 0.005 meq/100g, respectively. However, the highest phosphorus (= 95.96 mg/Kg) was encountered on the treatment made up of trachyte fines. This treatment with basalt + manure also showed the lowest pH (= 5.2 as pH_{water} or = 4.8 as pH_{KCl}), then rendered the control more acidic. In fact, the amendment of thic local tropical soil with basalt fines + manure enhances significantly the yield while loading the soils with considerably amount of chemicals. However, this amendment renders this acid soil more acidic therefore susceptible to increase the bioavailability of toxic metals.

Keywords: rocks fines; enhance; decrease; chemicals; pH; amendment; yield; tropical soil; acid; toxic metals

Introduction, Scope and main objectives

The need to feed approximately 9 to 10 billion people during the middle of the 21st century has put increasing pressure on land resources. Then, to keep pace with rising food demands, it is obvious that the production of food will have to rise (van Straaten, 2006). Then, the quality of agricultural soil is crucial to increase food production. Sanchez (2002) stated the declining soil quality is an important root cause for the falling per capita food production, in particular in the Sub Sahara African countries. The restoration of soil fertility through nutrient replenishment which is commonly done using short term quick-fix chemical fertilizers (van Straaten, 2006) is one of the

best entry points to raise crops production. Although chemical fertilizers replenished the soil, its continuous use alongside herbicides and pesticides is causing an increasing collapse of soil nutrients through leaching. Then, an alternative to chemical fertilizers such as agro-geology is an option for sustainable agricultural production. This concept is the process of loading the soil with crushed rocks which restore lost minerals essential for plant growth. It aims at increasing the nutrient release rates from widely occurring nutrient rich minerals and rocks, as the solubility and release rates of these naturally occurring materials are generally very low, then keeping soil fertility for longer period.

There is also a need to assess the negative aspect of using rock fines as alternative to chemical fertilizers since they may possess harmful effects on soils as being a potential source of toxic metals that may negatively affect some important soil properties. The aim of this study is to assess crop yields, chemicals and pH variation on a soil treated with rock fines such as basalt and trachyte.

Methodology

Fresh rock samples, in order to avoid contamination, were locally collected from several rock exposures namely basalt and trachyte. Samples of coal were collected from the nearby sedimentary rocks. These rocks were crushed separately into powders and sieved using a 1 mm sieve to remove the larger grains that are crushed again into smaller sizes. A farm that meets all the conditions for the growth of *Solanum Tuberosum* was selected in the locality of Batibo, near Bamenda in the northwest region of Cameroon. The total surface area of the farm was 13.5 m by 5 m (67.5 m²). The ridges had equal length of 6.75 m and width of 20 cm and a total surface area per ridge of 1.35 m². The ridges had equal height of 25 cm with a distance between ridges of 70 cm. Each ridge had nine planting spots made in the middle of the ridges of equal spacing between plants (50 cm). The spacing is within the optimum planting for Irish potato according to the Technical Bulletin on the fertilization of potato in Cameroon. Beds were randomly selected for each treatment, making sure that the same treatments were not positioned side by side. Three replications of each treatment were done. For growth and yield comparison, bed T₅ was introduced with organic manure and chemical fertilization. The treatments are made up of the following: T₀ = control beds corresponding to the normal practice of farmers, T₁ = treatments with basalt fines, T₂ = treatments with basalt fines + coal fines, T₃ = treatments with trachyte fines, T₄ = treatments with trachyte fines + coal fines, T₅ = treatments with chemical fertilizers. Potatoes seedlings of almost the same size about 2-3 cm in diameter, were buried into the spots about 10 cm deep. After harvesting, soils from the control and from the treatments with best yields were sampled for chemical analyses and pH determination.

For the chemical analysis, soil samples were taken to the Laboratory of soils and Environment of the Faculty of Agronomy (FASA) of the University of Dschang, Cameroon. The soil samples were subjected to physiological analysis using a standard laboratory procedure for soil analyses (AFNOR). Soil reaction was determined in soil water suspension 1:2:5 using a glass electrode. Organic matter was determined by wet digestion according to Walkley and Black (1934). Total nitrogen was analyzed by the modified Kjeldahl method. Exchangeable cations and exchange capacity (CEC) were determined by percolation with 1 M ammonium acetate, pH and determination of Ca, Mg, K and Na using a flame photometer and Mg with an atomic absorption spectrophotometer.

Results

The main results of this work are crop yields, chemical analyses and pH as presented in Table 1 and Table 2.

Yields

Out of the 06 treatments used for this field trial, 02 were made up of rock fines alone. 02 treatments are composed of rock fines + manure. 01 treatment is the control and the other is made up of the conventional NPK + manure. Yields were determined after weighting the quantity of tubers harvested per treatment and per hectare (ha) and recorded on Table 1. The lowest yield (= 11 111 Kg/ha) was reported on treatment T3, made up of trachyte fines alone. Then followed by the yield from the treatment with trachyte fines + manure (T4) (= 13 333 Kg/ha). The control (T0) yielded 14 815 Kg/ha. The treatment with the basalt alone (T1) yielded 16 296 Kg/ha. The highest yield was obtained on the treatment with the chemical fertilizers (T5) with a value of 23 704 Kg/ha, next to 20 741 Kg/ha obtained on the treatment with basalt + manure (T2).

Table 1. Weight (g) and yields (Kg/ha) of potatoes harvested at the end of the crop growth

Treatments	Composition	Weight (g)	Area (m ²)	Yield (Kg/ha)
T0	Control (local soil)	2000	1.35 m ² (each ridge)	14815
T1	Fines of basalt alone	2200		16296
T2	Fines of basalt and coal	2800		20741
T3	Fines of trachyte alone	1500		11111
T4	Fines of trachyte and coal	1800		13333
T5	Conventional NPK + coal	3200		23704

Chemical analyses

Chemicals contents and the pH of the control and treatments with rock fines + manure were determined to assess the variability of chemicals after amendment (Table 2). The lowest effective Cations Exchange Capacity (CEC) was encountered on the control with values of 20.40 and the highest of 24.16 showed by the treatment with basalt fines + manure. An intermediate value of 21.20 for the CEC was found on the treatment with trachyte fines + manure. The contents of Organic carbon (OC) showed values of 7.22, 6.74 and 7.03 % for the control, the treatment with trachyte + manure and the treatment with basalt + manure, respectively. The contents of Organic matter (OM) vary from 12.4 to 11.62% for the control and the treatment with trachyte + manure, respectively. Then, the SOC which represents the sum of OC + OM is below 20 % for the all these treatments. The total Nitrogen (N) is very low for the treatment with basalt fines + manure with values of 0.05 %. The content of N increases to 0.16 % for the control and the treatment with trachyte fines+ manure. The calcium contents with values of 3.20 meq/100g are comparable for the control and that of the treatment with trachyte fines + manure.

Table 2. Soil chemical analyses and measured pH of treatments To, T2 and T4

Treatments		Control	Rock fines + manure	
		To	T4 (=trachyte+manure)	T2 (=Basalt+manure)
Chemicals Parameters	Effective CEC	20.40	21.20	24.16
	Organic carbon (%)	7.22	6.74	7.03
	Organic matter (%)	12.45	11.62	12.12
	Soil Organic Carbon (SOC) (%)	19.67	18.36	19.15
	Total nitrogen (%)	0.16	0.16	0.05
	Calcium (meq/100g)	3.20	3.20	10.24
	Magnesium (meq/100g)	3.20	24.00	45.76
	Potassium (meq/100g)	0.008	0.008	0.008
	Sodium (meq/100g)	0.0007	0.0007	0.005
	Phosphorus Bray II (mg/kg)	19.13	95.96	24.3
pH _{H2O}		5.8	6.1	5.2
pH _{HCl}		4.9	5.1	4.8

CEC: Cation Exchange Capacity. meq: milliequivalents/100g

The increase to 10.24 meq/100g for the treatment with basalt fines + manure suggests Ca-rich minerals in this rock. This treatment also showed highest magnesium content with value of 45.76 meq/100g. Values of magnesium of 24.00 and 3.20 meq/100g were observed on treatment with trachyte fines + coal and on the control, respectively. Potassium shows also similar contents with values of 0.008 meq/100g for all the treatments. Sodium showed comparable values of 0.0007 meq/100g for the control and the treatment with trachyte fines + manure. The content of this element increases more than 7 folds to a value of 0.005 meq/100g for the treatment with basalt fines + manure. This suggests the later treatment to encompass more Na-rich minerals than the formers. The lowest and highest phosphorus content (=19.13 and 95.96mg/Kg) was encountered on the control and the treatment with trachyte fines + coal. The treatment with basalt fines + manure showed a value of 24.3 meq/100g (Table 1). This may suggest the main host of phosphorus compounds such as apatite is much more abundant in trachyte than basalt. According to Newman (1995), Smeck (1973) and Walker and Syers (1976) parent materials are the only significant sources of P to natural systems other than the minimal amounts supplied in precipitation. The dissolution of apatite is enhanced at lower pH and in the presence of organic acids (Valsmai Jones *et al.*, 1998); in acid soils apatite weathers approximately 1000 times faster than silicate minerals such as feldspars and exposed apatite is largely weathered from the soil over a relatively short time period (Blum *et al.*, 2002; Walker and Syers, 1976; Yanai *et al.*, 2005).

The control exhibits a pH (= 5.8 as pH_{water} or = 4.9 as pH_{HCl}) (Table 2). This indicates the moderately acid to very strongly acid nature of the local soil in the experimental field. This soil treated with trachyte fines + manure increased the pH to 6.1 (pH_{water}) or 5.1 (pH_{HCl}). However, the control treated with basalt fines + manure decreased the pH at 5.2 as pH_{water} or 4.8 as pH_{HCl}, further to the strongly acid property (Figure 2).

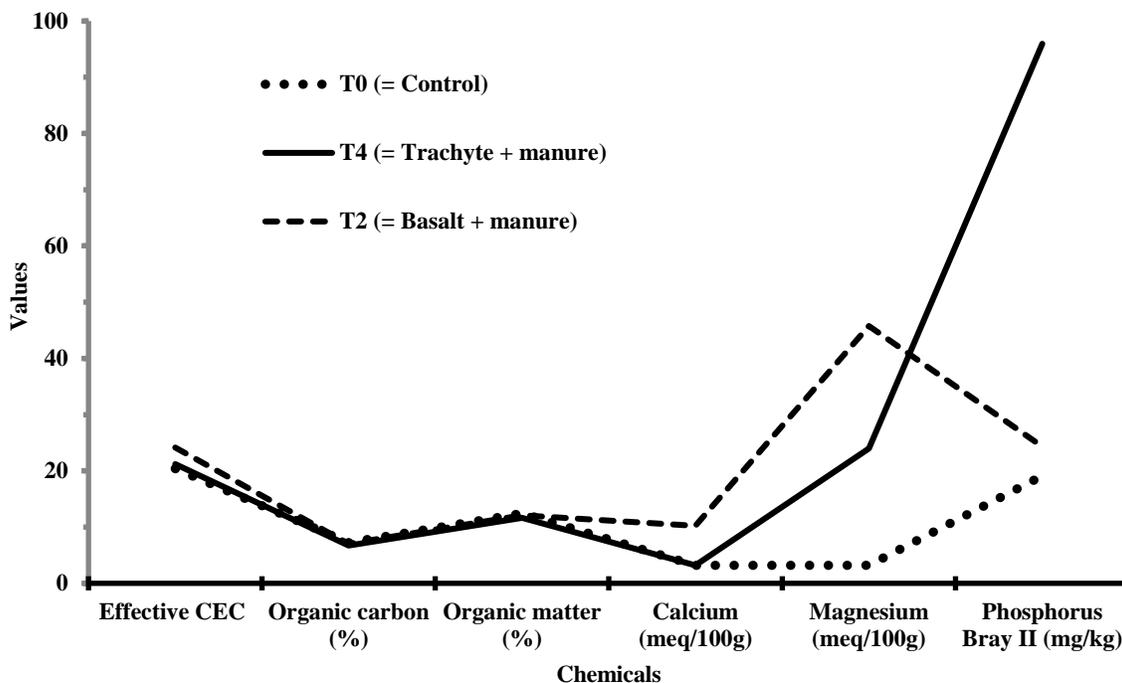


Figure 3. Chemicals contents of the Control and the treatments with rock fines + manure

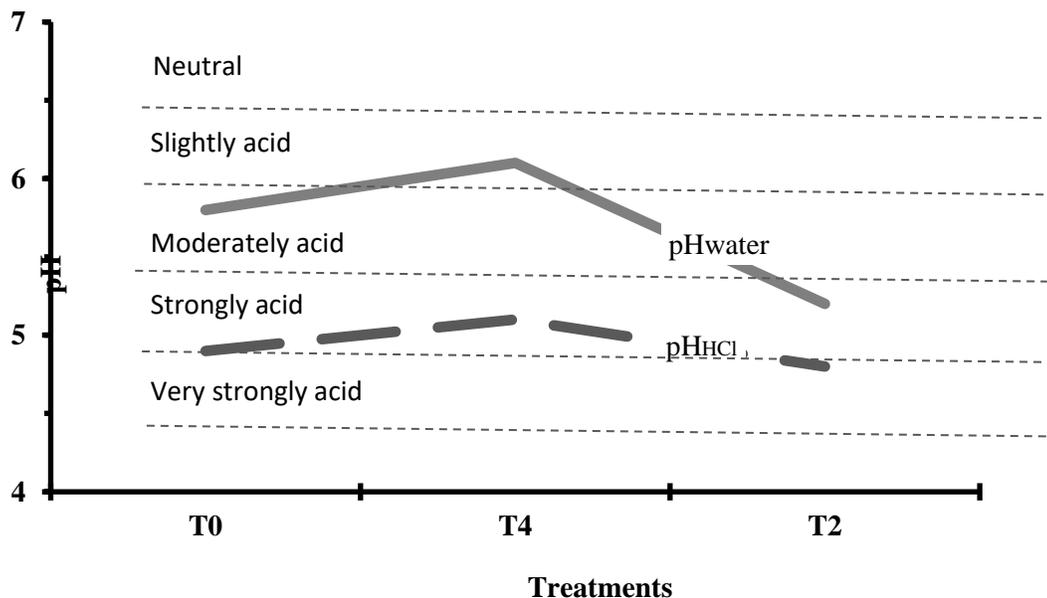


Figure 2. pH variations of the Control and the treatments with rock fines + manure

Discussions

The use of rock dust as a means of enhancing plant growth and crop quality through improving soils in which they grow has been proposed by a number of authors (Szmidt *et al.*, 2004). Finely ground, chemically unprocessed rocks of different types have been used in agriculture since the latter half of the 19th century (van Straaten, 2002). Then, rocks made up of basalt and trachyte

were crushed into smaller fragments and ground into fines after several 1x1 mm mesh sieve to obtain powders used as amendments and applied on a tropical soil with coal fines applied as manure to grow up potatoes in the northwest region of Cameroon. Treatments incorporated with manure portrayed better results in their yields than their counterparts without manure. For example, yields of 11 111 and 13 333 Kg/ha were obtained for the treatment with trachyte alone and the treatment with trachyte + manure, respectively. And yields of 16 296 and 20741 Kg/ha were obtained for the treatment with basalt alone and the treatment with basalt + manure, respectively. This suggests that some minerals in the presence of manure released much more necessary elements for plant growth. For example, basaltic rocks show crystals of olivine, pyroxene and amphibole that may have easily released elements like such as calcium, magnesium, sulphur, potassium necessary for plant growth. According to Goldich (1983), fine grained rocks containing high proportions of olivine, pyroxene and Ca-rich plagioclase feldspars as well as low concentration of quartz have the highest natural weathering rates. Therefore basalts will probably undergo weathering releasing mineral elements faster than trachyte since trachyte has a low concentration of olivine, pyroxene and feldspars but richer in quartz than basalt.

This fast release of cations such as Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , K^+ and Na^+ from some minerals in basalt may have also increased CEC (= 24.16) in the treatment with basalt + manure than in the treatment trachyte + manure (= 21.20). This latter CEC is also higher than that of the control (= 20.40) indicating that trachyte has also loaded cations into the soil. This is in line with the studies of Gillman (1980) and Gillman *et al.* (2000, 2002) in tropical Australia. These authors illustrated the positive effects of the application of large amounts of ground basaltic rocks on weathered and nutrient depleted soils with increased cations exchange capacities. Magnesium was released from both basalt (= 45.76 meq/100g) and trachyte (= 24.00 meq/100g) powders into the soil. However, the contents of calcium are similar for both the control and the treatment with trachyte + manure. This suggests that trachyte fines did not release calcium which is concordant with the absence of Ca-bearing minerals in this rock. The equal contents of K (= 0.008 meq/100g) in all treatments indicate that negligible quantity of this element was release from the rocks. The content of Na (= 0.005 meq/100g) for the treatment with basalt + manure which is more than seven folds higher than that of the control and that of the treatment with trachyte + manure (= 0.0007 meq/100g) indicates the occurrence of Na-bearing minerals such as plagioclase in basalt and absent in trachyte. There is a very high contents of phosphorus (= 95.96 mg/Kg) (Figure 1) suggesting the abundant occurrence of accessory minerals such as apatite, monazite and zircon which are sources of high-phosphorus in trachyte. In addition, one may expect to have higher yield in this treatment since it exhibits high-phosphorus content. But this is not the case. Then, the phosphorus content in this treatment may be considered to be in excess and has inhibited the intake of other elements and then negatively affected the crop growth and yield. Or high-phosphorus alone is not enough to get considerable yield productivity.

This work indicates that best agronomic performances were achieved with the application of basalt powders mixed with manure. However, the variation pH in this work (Figure 2) may affect the soil fertility and the toxicity of some elements. According to the studies of Gillman (1980) and Gillman *et al.* (2000, 2002), soil pH was raised after the application of large amounts of ground basaltic rocks on depleted soils in tropical Australia. In this work the pH decreased or increased according to the type of treatment for the soil amendment. The pH variation from the more acidic conditions has negative consequences on the soil toxicity with the increased bioavailability of toxic metals. In fact, aluminum becomes more available when pH is below 6 and especially below 4.75, and can be toxic to plants. So does manganese at pH below 5.

Conclusions

A field experiment for a duration of 03 months was carried out with the application of rocks fines made up of basalts and trachyte in addition to caol as manure to grow up *Solanum Tuberosum* locally known as Irish potatoes in the northwest region of Cameroon. After harvesting, the treatments with fines of trachyte alone gave the poorest yield of 11 111 Kg/ha. The addition of coal fines as manure to this treatment boosted the yield to 13 333 kg/ha. However, this is still lower than 14 815 Kg/ha portrayed by the control soil. The treatment with basalt fines alone yielded 16 296 Kg/ha, higher than that of the control. The addition of manure on this treatment enhances the yield to 20 741 Kg/ha. Rock fines added treatment with the highest yield is that with basaltic fines mixed with manure. This treatment also showed the highest CEC (= 24.16), N (= 0.05 %), Ca (= 10.24 meq/100g), Mg (= 45.76 meq/100g), Na (= 0.005 meq/100g) and lowest pH (= 5.2 as pH_{water} or = 4,8 as pH_{HCl}). However, the highest content of phosphorus was obtained on the treatment with trachyte fines + manure. This treatment also showed the highest pH_{water} (= 6.1). Despite the addition of rock fines on the control, the contents of K remains unchanged at 0.008 for all treatments. This may suggest a late dissolution of K. In fact, the amendment of the local tropical soil with basalt fines + manure enhances significantly the yield while loading the soils with considerably amount of chemicals. However, this amendment makes the soil to become strongly acid and susceptible to increase the bioavailability of toxic metals and rendering it more toxic.

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3.2.22. Recuperation of acid saline soil by application of organic amendments

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Abstract

Soil degradation due to salinization is one of the major environmental concerns, threatening the sustainability of world's agricultural production and threats to global food security. Moreover, acidic salinity limits the uptake of essential plant nutrients and negatively influence soil microbial activity as well as soil chemical and physical properties, thus causing a decline in soil productivity. The overall goal of this research was to assess the reclamation potential of *Gliricidia sepium* biochar (produced at 300, 500, & 700 °C), solid waste composts and municipal sewage sludge as organic amendments at 1.0, 2.5, 5.0% w/w application rate for acid saline soil and evaluate the most suitable amendment. Treated soils were subjected to laboratory incubation for 120 days at room temperature (26±1 °C). Electrical Conductivity (EC), pH, NO₃⁻, PO₄⁻³, Cation Exchange Capacity (CEC), Exchangeable Sodium Percentage (ESP), Total Organic Carbon (TOC), Acid phosphatase (Acidpht), Alkaline phosphatase (Alkpht) and Catalase activities (CA) were tested to characterized the amendments. Application of organic amendments to soil was successful in restoring both salinity and acidity levels simultaneously up to some extent. Findings indicated that the maximum EC reduction was 19% at the application of sludge, ESP by 17.6% (12 units) at 700 BC and pH increment by 54% (2 units) at compost. Maximum increment of PO₄⁻³ by 96% (5.2 mg/kg) at 500BC, NO₃⁻ by 5 times (1.5 mg/kg), CEC by 51% (14 cmol/kg), Acidpht: by 54% (86 units) at compost, Alkpht: by 50% (30 units) at 300 BC and CA by 158% (1.6 units) at 700BC, are evidences of the potential of organic amendment to enhance nutritional availability and microbial activity. Highest performance was observed at 5% amendment compared to 1 and 2.5%. Based on the outcome of this study, compost and 500BC respective amendments are the most suitable soil amendments for saline soils, since they improved soil chemical and biological properties.

Keywords: Salinity, Acidity, Biochar, Organic amendments, Soil quality

Introduction, scope and main objectives

Soil salinization is generally referred to as the accumulation of salts in the soil root zone to the extent that depresses plant growth (Rengasamy, 2006). Salt affected soils are characterized by having high concentration of dissolved mineral salts, primarily composed of chlorides, sulfates, carbonates and bicarbonates of sodium (Na), calcium (Ca) and magnesium (Mg) (Manchanda and Garg, 2008). The high salt concentration negatively affects soil microbial activity as well as soil chemical and physical properties, thus causing a decline in soil productivity. Declination of vegetation growth due to salt toxicity and detrimental osmotic potential, results in lower Carbon (C) inputs into these soils and further deterioration of their physical and chemical properties (Wong *et al.*, 2009).

Globally, salt affected soils are distributed across all continents and about 100 countries all over the world face this menace (Rengasamy, 2006). In addition, approximately 831 million hectares of land is estimated to be salt affected across different countries (Martinez-Beltran and Manzur, 2005). Both saline (high pH) and saline acid soils (low pH) are distinctive features of the coastal saline soils (Bandyapadhyay *et al.*, 2003). General management practices recommended for amelioration of

irrigation induced salt affected soils cannot be applied directly to these soils. For restoration of soil there are two types of amendments, namely organic and inorganic. The remediation of salt-affected soil using naturally occurring chemical agents that are either extracted, mined, or man-made chemicals that includes gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and few organic matters that arose from living materials, or their dead bodies (farmyard manure, green manure, organic amendment and municipal solid waste), which the latter has proven its effectiveness in these soils in terms of low costs and a simplicity in the process due to which it was successfully implemented worldwide (Mitchell *et al.*, 2000; Sharma and Minhas, 2005; Tejada *et al.*, 2006). These organic amendment is the most sustainable and persistent one to remediate both saline and acidic conditions under cost effective manner, comparing with other inorganic method.

Whereas only a few systematic studies exists on the soil salinization problem in Sri Lanka, especially about amelioration of salt- affected soil and there are no records of the actual extent of lands affected by salinity, or data that indicate its trend (Subasinghe 2004; Thiruchelvam and Pathmarajah 1999; Vivekananda 1989). In Sri Lanka, soil degradation due to salinization is a significant problem with an affected land area in Sri Lanka is about 223,000 hectares or about 3% of land area of the island that are mostly in the dry zone which receives an annual rainfall between 500 – 800 mm during the North-East monsoon (Oct. - Dec.) with a moisture deficit period (drought) of 6 to 8 months (Subasinghe 2004). Therefore, there is an important and urgent need to restore these lands for agricultural production. In this regard, identification of salt- affected lands and taking necessary steps to restore these lands seems to be a national priority. The main objective of this research was to compare and evaluate the effects of organic amendments (biochar, composts and sewage sludge onto the soils) as individual applications on the reclamation potential of a saline-acidic soil has been thoroughly studied in the Sri Lankan coastal dry zone.

Methodology

Acid saline soil samples were collected from the East coast of Sri Lanka, Kokkuvil, Batticaloa where samples were collected from first 20 cm. Air dried soil was sieved by 2 mm. Amendments were characterized and used as 16 incubation treatments with biochars manufactured at three different temperatures (300, 500, & 700 °C), compost and sludge application as 1.0, 2.5, 5.0% w/w and control as respectively. Treated soils were subjected to laboratory incubation for 120 days at room temperature (26 ± 1 °C). Electrical Conductivity (EC), pH, NO_3^- , PO_4^{3-} , Cation Exchange Capacity (CEC), Exchangeable Sodium Percentage (ESP), Total Organic Carbon (TOC), Acid phosphatase (Acidpht), Alkaline phosphatase (Alkpht) and Catalase activities (CA) were tested to characterized the amendments.

Results

Chemical and biological properties obtained for *Gliricidia sepium* biochars manufactured at different temperatures, solid waste compost and sewage sludge onto the soils are unique to each amendment. The characteristics of amendments are shown in Table 1.

Table 1. Biochemical properties of soil amendments

Amendment	EC Sat. (1:5) dS/cm ³	pH Sat. (1:5)	Avail. (NO ₃ ⁻) mg/kg	Avail. (PO ₄ ⁻³) mg/kg	CEC (cmol/kg)	SAR	ESP %	TOC %	Catalase activity ml (0.05mol/l KMnO ₄) g ⁻¹ h ⁻¹	Phosphatase activity (acidic) µg p-nitrophenol g ⁻¹ h ⁻¹	Phosphatase activity (alkali) µg p-nitrophenol g ⁻¹ h ⁻¹
Sludge	0.7	4.9	2.1	8.4	43.3	11.4	66.7	9.5	0.8	1895	1616
Compost	5.2	7.6	3.9	8.8	48.4	6.2	36.6	10.4	0.8	682	1587
700 BC	14.8	10.2	1.8	71.7	52.1	0.6	2.4	5.9	0.4	53	49
500 BC	9.2	10.8	2.1	80.9	52.2	0.92	2.3	6.6	1.7	96	54
300 BC	5.2	7.9	1.7	61.9	51.3	0.4	1.8	8.8	5.7	134	101

Five different types of amendments were compared for each parameter and ultimately amendments were ranked according to their overall performance from high reclamation potential to low reclamation potential (Figure 1). Results indicate that 300BC has shown highest decrement in EC and highest increment in Acid:pht and TOC whereas nitrate, phosphate and pH changes are relatively low. High temperature BC has shown highest pH increment and lowest EC reduction, whereby Acid:pht, Alk:pht and TOC increments. Overall, 300BC represents positive sign about enhanced soil biological activity and salinity reduction whereas 700BC exhibited highest reduction in soil acidity but caused to increase salinity. According to results 500BC is ideal among three types of biochars to reclaim this acid saline soil because their intermediate nature of properties and it can reclaim both salinity and acidity as simultaneously (Figure 1).

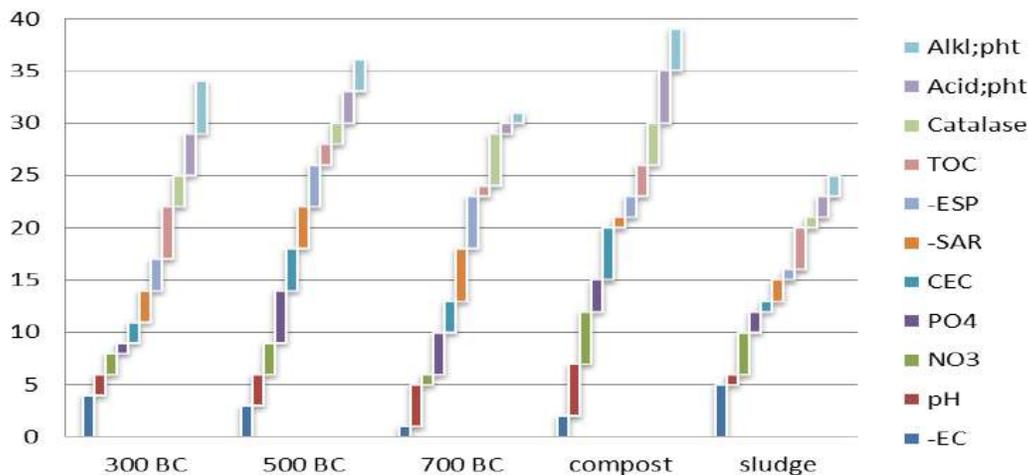


Figure 1. Overall comparison of amendments after 4 month incubation

Discussion

Application of organic amendment significantly ($P < 0.05$) increased soil pH but pH increment of sewage sludge amended soil is relatively lower than biochars and compost. Soil pH observed for various treatments after incubation was in the order; compost = 700BC > 500 > 300BC > sludge > control. Initial (NO_3^-) content of soil is 0.224 mg/kg before amendment application. Soil available nitrate content for different treatments follows the order; compost > sludge > BC = 500BC = 700BC > control after the amendment. Initial (PO_4^{3-}) content of soil is 5.440 mg/kg before amendment application. Available (PO_4^{3-}) contents were observed for different treatments after the amendment follows the order; 500 BC > 700 BC = compost > 300BC = sludge > control. The highest increment is observed in 700BC among all treatments.

Compost is the amendment that was shown highest increment 50.5% (16.50 cmol/kg) in CEC. Biochars 500BC, 700BC and 300BC increased soil CECs by an average of 44.2 (14.40 cmol/kg), 42.2 and (13.84 cmol/kg) 40.8% (13.4cmol/kg) while sludge and control are increased the same by 38.7% (12.7cmol/kg) and 21.0% (7.10 cmol/kg), respectively, relative to the initial. Relative to the control, 700BC lowered soil SAR maximum by 14.9% (1.6 units) compared to the control. With the increase in pyrolysis temperature the solid carbon condenses into dense aromatic rings structures and also increases with mineral ash content in biochars. As a consequence, Na^+ and Ca^{2+} exchange at the soil's cation exchange sites, leaches off the exchanged Na^+ in percolating water and thereby subsequently showing a reduction in soil sodicity (Qadir *et al.*, 2004). At the end of four month period TOC values are statistically following the order; 300BC = compost = sludge > 500BC = 700BC > control. However, there are no significant difference between 300BC, compost and sludge

compared to each other and also changes of 500BC and 700BC are statistically same. Increment of Acid:pht by an average of 54.4% (86.0 units), Alkpht: 49.5% (30.15 units) and CA by 158.0% (1.60 units) is another evidence for improvement of microbial activity and soil health. Changes of salinity, CEC and acidity may be suggested via (i) electrostatic outer- sphere complexation due to metal exchange with K⁺ and Na⁺ available in the organic matter, (ii) co-precipitation and inner-sphere complexation of metals with organic matter and (iii) surface complexation with active carboxyl and hydroxyl functional groups by the amendments.

Conclusions

Considering the amendment percentages of biochar, highest performance was observed at 5% amendment compared with to 1.0 and 2.5% w/w but their efficiencies and effectiveness are different in each parameter as an overall assessment. Amendments have shown gradual improvements in the biochemical properties of acid saline soil with period of incubation. Based upon the findings of this study, compost might be considered as a most suitable amendment for saline soils, since it greatly reduced the salinity and acidity. Moreover, amending of soil by compost is enhancing the nutrient availability as well. In terms of biochars, best reclamation is shown by 500 °C produced BC than 300 and 700 °C, because low temperature pyrolyzed biomass are efficient for inorganic contaminants due to the presence of more O-O- containing functional groups and the greater release of cations but alkaline effect is low. Further investigations are recommended to assess the reclamation capacity of compost with 500BC biochar as a hybrid in acid saline soils.

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3.2.23. Polycyclic aromatic hydrocarbon polluted soil remediation by using nano- fertilizers

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Abstract

Environmental pollution and its harmful effects on human and environmental health is a main concern, worldwide. Polycyclic aromatic hydrocarbons (PAHs) are counted as important pollutants due to their ubiquitous occurrence and carcinogenicity. The solubility of PAHs decreases in water with an increase in the number of their rings, which is why they are usually counted as the main pollutants of soil. Different biological, chemical, thermal and physical methods are introduced for the remediation of PAH-contaminated soils. In many cases, the typical treatment methods have been inefficient in reducing the concentration of pollutants or have been very costly which is not reasonable, especially for developing countries. Over the past years, the field of remediation has improved by introducing and developing new technologies. Nanotechnology is introduced as a novel technology which is defined as “research and technology development at the atomic, molecular, or macromolecular levels using a length scale of approximately one to one hundred nanometers in any dimension; the creation and use of structures, devices and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on an atomic scale” (US EPA 2007). Nanomaterial have brought promising future for remediation due to its effectiveness, low cost and suitability for in-situ remediation. Using nano-materials such as nano ZVI, bimetallic nanoparticles, and emulsified zero valent nanoparticle has shown remediation effects for both contaminated soil and groundwater. Nano-fertilizers are other products of nanotechnology which their suitability for crop yields has been under experiment.

This study will examine the capability of nano-fertilizers for PAH depletion in laboratory scale. This work reports the PAH concentration change over time in a laboratory scale. Astonishing results revealed the effectiveness of applying nano-fertilizers for PAHs degradation in contaminated soil.

Keywords: polycyclic aromatic hydrocarbons (PAHs), contaminated soil, removal of PAHs, nanoremediation

Introduction, scope and main objectives

Industrialization and increase in human population are main causes of environmental degradation. Due to introducing new industries new chemicals emit to the environment. Polycyclic Aromatic Hydrocarbons (PAHs) form one of the most important classes of persistent pollutants which are widely distributed in the environment and are considered as ubiquitous contaminants (Hussein I. Abdel Shafy & Mona S. M. Mansour 2016). PAHs were ranked as the ninth most threatening compounds to human health in 2001 (King *et al.* 2002). The US.EPA currently regulates 16 PAH compounds as priority pollutants in water and generally considers them as “total PAHs” in contaminated soils. The carcinogenicity and mutagenicity of several compounds in this category is proved (Armstrong *et al.* 2004; Li *et al.* 2006; Okuda *et al.* 2010). PAHs pose an important environmental and health threat.

PAHs have two main sources: Petrogenic sources include crude oil and petroleum products such as kerosene, gasoline, diesel, fuel, lubricating oil and asphalt and Pyrogenic sources which form by the incomplete combustion of organic matter (eg. coal, petroleum and wood) and in industrial operations and power plants that fossil fuels, smelting, garbage incinerators and vehicle engines powered by gasoline and diesel fuel and forest fires. Many PAHs in the environment are by-products in petroleum based manufacturing. Numerous countries consider this pollutant among priority pollutants and have defined standards for acceptance source such as soil, water or air. Due to low solubility of PAHs with higher rings PAHs are concerned to be soil contaminant, mostly. Recently, the soil pollution standards are defined for soil resources in Iran and PAHs concentration standards is defined for various land uses which reflects the soil function.

In general, the fate of aromatic hydrocarbons in the environment will be the evaporation of some of its compounds especially low molecular weight compounds, photo oxidation, chemical oxidation, adsorption and bioremediation. Conventional methods have been proposed for the polluted site treatment including incineration, thermal desorption, confinement/encapsulation, soil washing, solvent extraction wet oxidation, bioremediation, landfilling and land farming. Most of these technologies are not only economically justified, but also will mainly lead to the transmission of pollution from one environment to another. Therefore environmentalists are seeking for environmentally friendly and cost-effective options. In this regard, nanotechnology is introduced as neoteric technology. Nanotechnology as defined by nanotechnology Initiative in 2008 is “ the technology at the scale of one to one hundred nanometers (nm) in any dimensions; the creation and use of structures, devices, and systems with novel properties and functions due to their size in this range; and the ability to control or manipulate matter on an atomic scale. Nanomaterial are reactive agents due to their large surface areas which increase the capacity for chemical and biological responsiveness (Rickerby & Morrison 2007). They reveal novel properties which are not expected from the same material in macro size.

One of the main properties which is considered mostly by environmentalists is their potential for site polluted remediation in a cost- effective, less time consuming and more efficient manner. Application of this method for in situ remediation is another advantage (Mura *et al.* 2013). For this purpose, different types of nanoscale materials have been distinguished, such as nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals [mainly as

bimetallic nanoparticles (BNPs)], and titanium dioxide. Among those, nanoscale zero-valent iron (nZVI) is considered mostly for removal of organic and inorganic contaminants (Nowack 2008). Based on study by Li *et al.* in 2006, reaction rate of nanoscale zero-valent iron (nZI) is 25-30 times faster than granular iron in microscale. This could be related to the surface area per mass, of this component which is 30 times more than granular irons in larger scales which cause 10 to 10,000 times more reactivity (US Navy 2010). Iron nano powders are used also as an effective tool for cleaning contaminated water. Iron acts as a catalyst for the oxidation and cause to breaking organic pollutants which convert it to less toxic to carbon compounds (O'Carroll *et al.* 2012).

As mentioned before one of the treatment methods to remediate contaminated soil is land farming. The process treats the top 30 cm layer of the soil and by applying fertilizers and bulking agents. Periodic tilling and irrigation during the whole process which help microorganisms for better degradation of pollutants. Besides, one of the products derived from nanotechnology are nano-fertilizers. Nano-fertilizers are the products which are synthesized in order to regulate the release of nutrients upon the crops needs. The efficiency of nano-fertilizers in comparison to ordinary ones is also reported (Prasad R *et al.* 2014) which is due to their much more ratio of surface to volume, more chemically saving energy, much more density, better Electrical Control (EC), and more advanced efficiency such as targeted delivery. This study will combine the last two methods to examine the effects of nano-fertilizers as a product of nanotechnology and land farming as a successful practice for remediation purposes.

One of the main challenges is the fate of nanomaterial in the environment and its effects on human health. The selection of nano-fertilizers was due to its less harmful effects which contain nutrients which is needed for plants and microorganisms and will help them for better phytoremediation and bioremediation, respectively. In this regard, further investigations on effects of nano-fertilizers on bioremediation of PAHs is done by the authors.

Methodology

Chemicals

All chemicals except than PAHs were purchased from Merk (Darmstadt, Germany). PAHs were purchased in highest purity grade from Sigma Aldrich Chemicals. Nano particles are purchased from Khazra Company.

Collection of Soil Sample

Soil samples were collected from the least PAH pollution probability in Hesar District in Alborz Province in Iran to prepare spiked soil out of it.

Soil preparation

Soil was dried overnight and passed through 2mm sieve and homogenized. Non-contaminated soil sterilized in autoclave at 121°C and 15 psi for 20 minutes to eliminate the effects of microorganisms in bioremediation process. Sterilized soil spiked with 6 PAHs. The concentration of each is mentioned in Table 1.

Table 1. PAHs characteristics (E. Stogiannidis & R. Laane, 2015) and Initial Concentrations in spiked soil

PAHs	Ring numbers	Molecular weight	Aqueous solubility (mg/l in 25°C)	Vapor pressure (Pa)	Concentration (mg/kg)
Naphthalene	2	128	32	11	25.3
Acenaphthylene	3	152	3.9	9.0×10^{-1}	27.88
Phenanthrene	3	178	1.1	2.0×10^{-2}	25.3
Pyrene	4	202	0.13	6.0×10^{-4}	31.5
Chrysene	4	228	0.002	1.4×10^{-6}	28.3
B(a)P	5	252	0.009-0.014	7×10^{-7}	30

The experiments were performed in laboratory condition. Twelve 25ml sterile test tubes were filled with 6gr spiked soil and closed with sterile cotton which reduces evaporation of lighter PAHs. Afterwards the tubes were placed in incubator in 25°C to control the effect of temperature. The soils were moistened to approx.80% of the soil water holding capacity. Every week the soils in tubes were stirred and homogenized and the moisture content were checked. Each treatment was done in three replicates.

Nano-fertilizers which are applied for this study are: nano-Fe (contains 9% chelated Iron), nano-NPK (contains 20% Nitrogen, Phosphate and Phosphorus Nano chelates), nano Micro (contains 8% Iron, 1.5% Zinc, 1.5% Manganese, 0.5% Boron, 0.5% Molybdenum, and 0.5% Copper). Required nano-fertilizers were calculated to provide 33mg nano-Fe, 33mg nano-Micro and 200mg nano-NPK per kilogram soil which is recommended dosage from the Khazra Company, the producer of the nanofertilizers and were dissolved in amount of water which was needed to provide approximate 80% of the soil water holding capacity and added to the polluted soils.

Extraction and measurements of PAH

The standard solvent PAH in acetone solution at 500 mg/kg concentration was prepared. Surfactants or detergents can be used to extract PAHs from organic and inorganic soil levels. These factors increase the bioavailability of these compounds.

The concentration of selected PAHs including Naphthalene, Acenaphthene, Phenanthrene, Pyrene, Chrysene and Benzo (a) Pyrene were measured using a gas chromatography (GC, Agilent 7890N, Agilent Co.) with mass spectrometry (MS, Agilent 5975C, Agilent Co.). A 30 m × 0.25 μm × 0.5 μm fused silica (DB-5MS) capillary column (Agilent Co., USA) in selected ion monitoring (SIM) mode was used. The injection volume was 3.0 μL in the splitless mode at 290 °C, and helium with a purity of 99.99 % was used as a carrier gas at constant flow rate of 1 mL/min. The column temperature program was as follows: initial temperature of 60 °C, increased at a rate of 10 °C/min to 100 °C, then held for 1 min, raised to 285 °C at 4 °C/min, and held for 15 min.

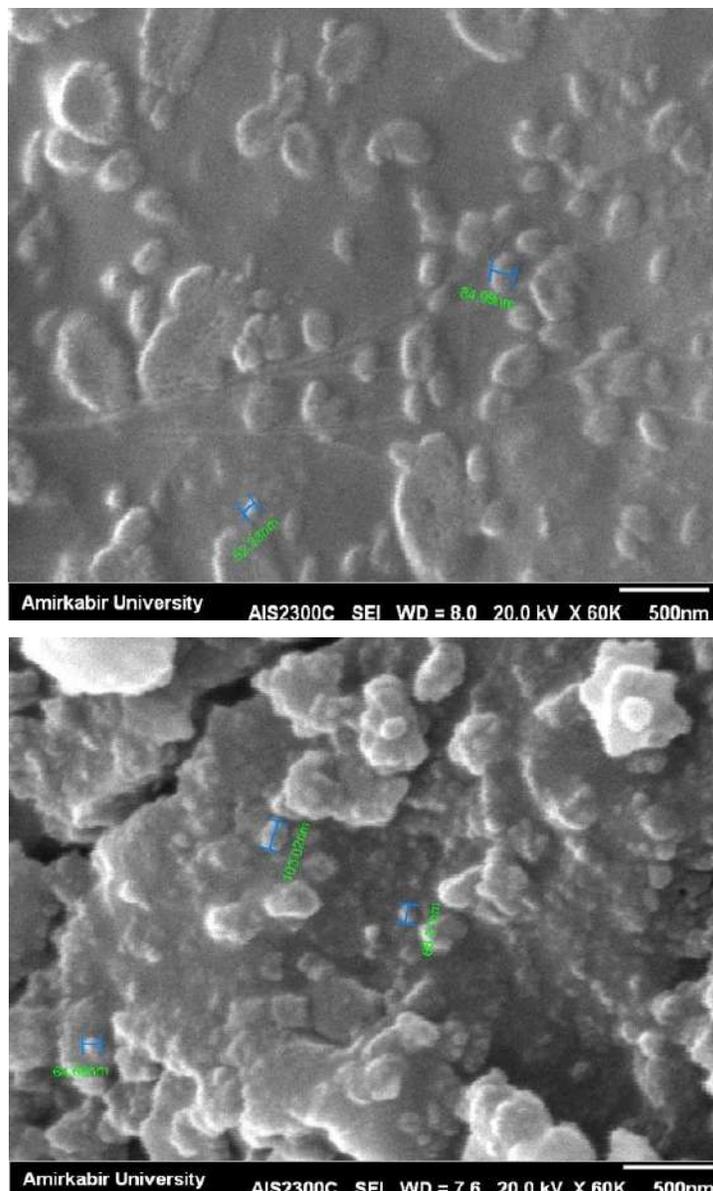


Figure 1. SEM image taken from one of Khazra chelated nano-fertilizers by Amirkabir University

Following formula was used to measure residual PAH concentration in vials after 21 and 50 days after adding nano-fertilizers to spiked soil:

$$\text{PAH depletion efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where, C_0 is initial concentration of PAHs and C_e is PAHs concentration in following measurements in experiment period of time.

Results

The capability of three selected nano-fertilizers to deplete PAHs in spiked soil with equal initial concentration is revealed in Table 2 and Figure 2.

The control experiments have shown no depletion and just for Naphthalene and Acenaphthene that as mentioned before is due to evaporation which could be ignored.

Table 2. PAHs degradation after 21 and 50 days of adding nano-fertilizers into the soil samples

PAHs Concentration (mg/kg dw)	Nano Fe			Nano NPK			Nano Micro		
	1 day	21 days	50 days	1 day	21 days	50 days	1 day	21 days	50 days
Naphthalene	25.3	2.7	1.9	25.3	2.7	1.5	25.3	2.8	2.5
Acenaphthene	27.9	13.4	11.8	27.9	13.2	11.1	27.9	26.5	17.3
Phenanthrene	25.3	24.4	22.9	25.3	24.8	22.0	25.3	22.5	15.8
Pyrene	31.5	27.8	26.1	31.5	27.3	25.3	31.5	28.8	23.7
Chrysene	28.3	20.3	18.5	28.3	22.2	20.3	28.3	22.6	21.8
B(a)P	30.0	24.4	23.5	30.0	26.5	24.8	30.0	28.6	23.3

The first thing to note is the high degradation of Naphthalene and Acenaphthene which is due to their low molecular weight and vapor pressure will cause evaporation of these compounds. As we expected, by increasing the ring numbers and therefore the mass weight the depletion trend decreased, substantially. This will make Benzo (a) Pyrene and PAHs with more molecular weight and less water solubility and less vapor pressure more challenges to remediation.

Naphthalene concentration is almost zero after 50 days. Acenaphthene with 3 rings depleted 60% in presence of nano-Fe and nano-NPK and 38% of nano-Micro.

The trend of depletion for nano-Fe and nano-NPK is almost the same. The best results were obtained with nano-Fe with up to 35% depletion of Chrysene and nano-micro up to 38% depletion of Phenanthrene after 50 days. However, the variable of time has not significant effect on the trend of depletion from the 21days to 50 days after adding Nanos and it may remain constant overtime. The slope of depletion of Chrysene is also constant and it shows 35% decrease by nano-Fe, 28% by nano-NPK and 23% by nano-micro after 50 days. Nano-micro has shown different behavior and it reduced Phenanthrene concentration for almost 38% in comparison to nano-Fe and nano-NPK which shows just 10 and 13% reduction by the end of the experiment. Although Chrysene has more rings than Phenanthrene, in existence of nano-Fe and nano-NPK it shows more degradation rate. More interesting results obtained from degradation of Benzo (a) Pyrene by more than 20% which is one of the most carcinogenic PAHs and is rather high in molecular weight.

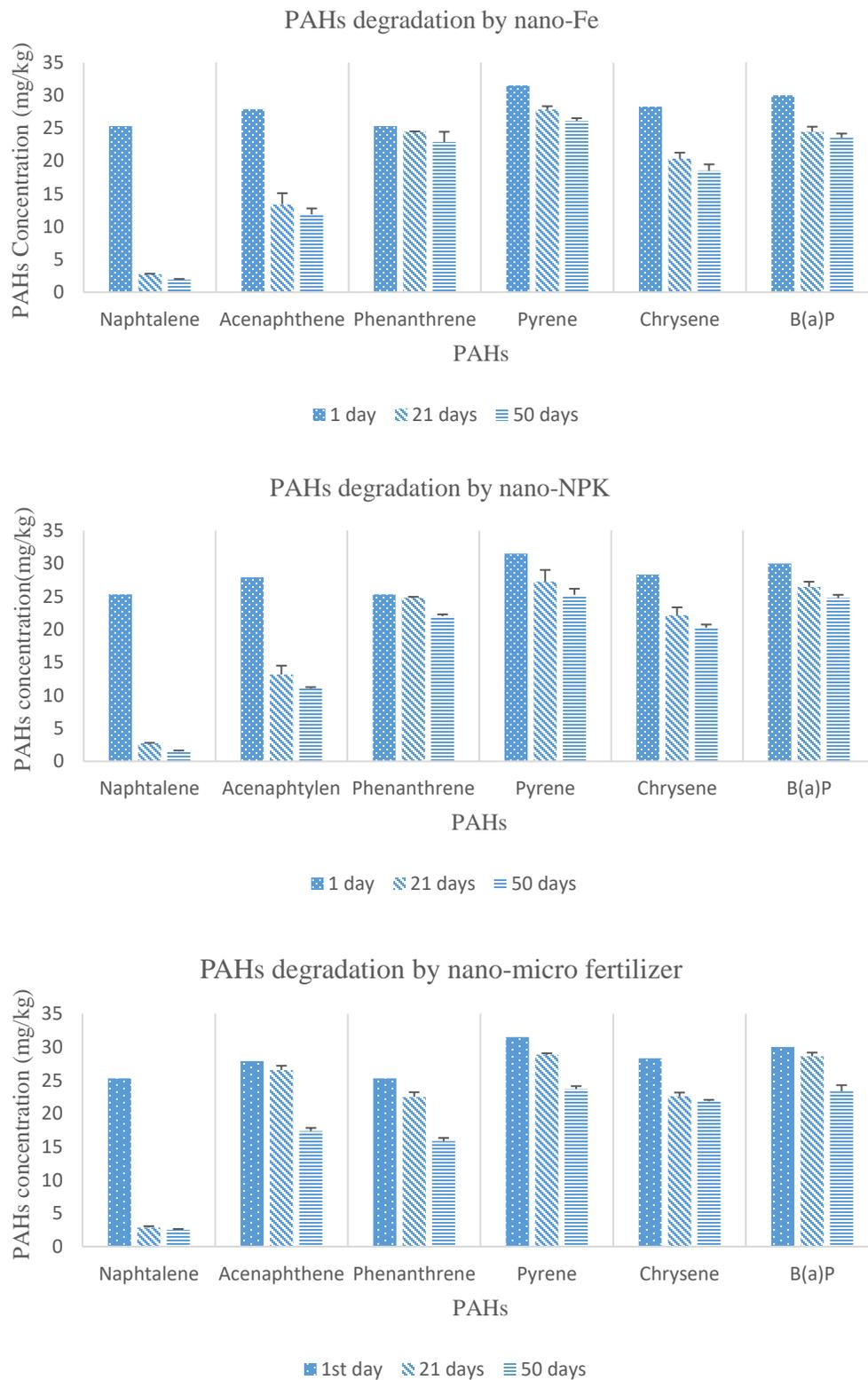


Figure 2. Nano-Fertilizers including nano-Fe, nano- NPK and nano-Micro involved in PAH degradation in soil laboratory experiment.

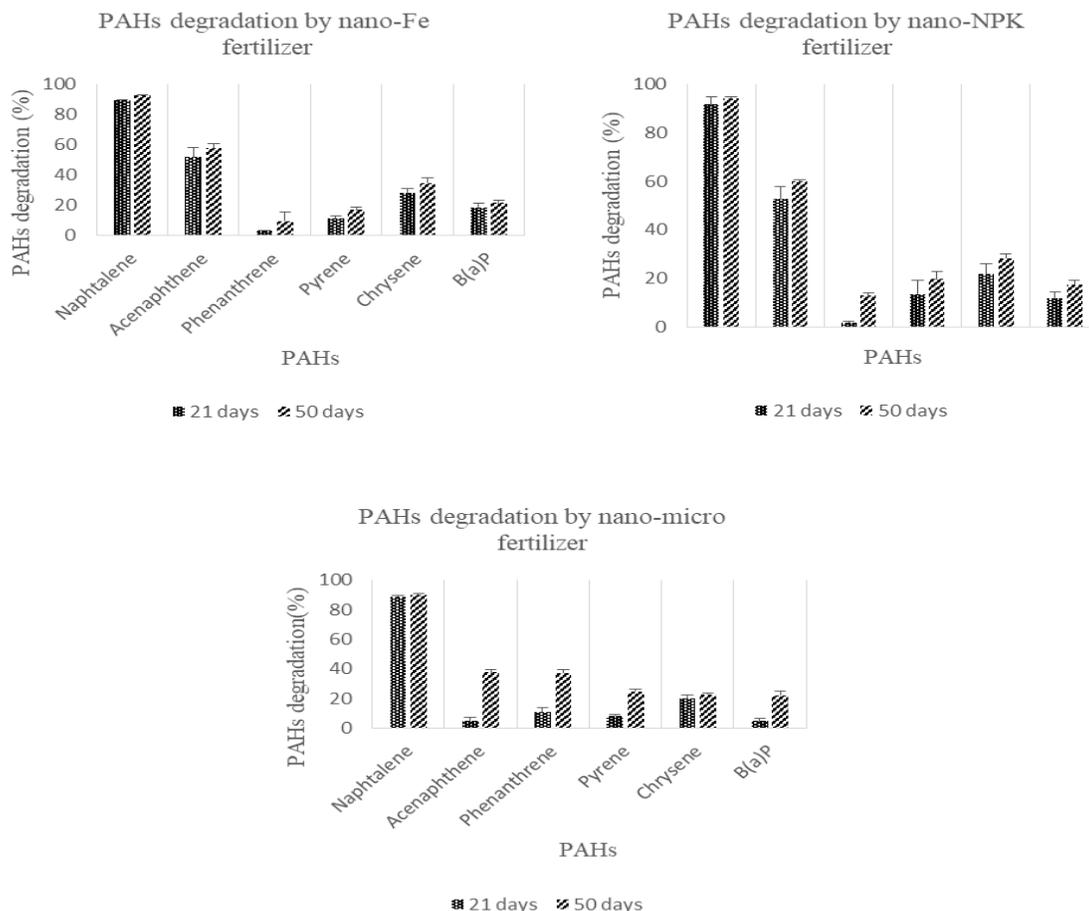


Figure 3. PAHs degradation (%) by using nano-fertilizers

Discussion

In evaluating the nano-fertilizers for potential use in remediation of contaminated soil with a defined concentration of PAHs, some nano-fertilizers including nano-Fe, nano-NPK and nano-Micro was introduced to soil samples. In the assays we preferred to use sterile soil to eliminate the effects of bioremediation on PAHs degradation process. The temperature was constant and kept at 25°C as the aqueous solubility and vapor pressure of PAHs were measured in this standard temperature (Lide, 2004, Haftka, 2009 and Stogiannidis .E & Laane R., 2015). In fact in a controlled condition give us the opportunities to find out the best solutions with less cost and time consuming since it reveals the effect of each variable explicitly.

The contribution of nano-fertilizers in PAHs depletion especially for lighter PAHs was obvious, although it did not show increase over time. Use of nanomaterial which have less dimensions and more surface area give them the ability to have contact with PAHs which are mostly not water soluble and absorbed to organic matter and therefore are less available.

Adding fertilizers in nano scale provide the condition to distinguish the effects of these nanomaterials on PAHs adsorption or degradation. In further studies which has been done by the authors the bioremediation of PAHs by applying nano-fertilizers is examined and this study

helped us to measure the effectiveness of distinguished microorganism's isolations in presence and absence of nano-fertilizers.

The level of PAHs degradation acquired by applying nano-fertilizers after 50 days was not expected. The most surprising result was degradation of 4 and 5 rings PAHs, since several previous investigations presented as PAH degradation potential decreases as the molecular weight of compounds increases (Eggen 1999, Potin *et al.*, 2004).

To our knowledge no research has addressed the capability of nano-fertilizers on organic contaminants' depletion and further studies are needed to gain details information on degradation procedure.

Conclusions

Although nanotechnology has high potential for application in various environmental fields, a wide study on any probable adverse impacts on human and environment health is needed. There are still too many uncertainties for use of nanomaterial in daily life and proper evaluation of their impacts is necessary before addressing this technique is mass scale. In addition, selection of nanomaterial and applying in safe range will reduce the possible risks could will be occurred.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Sub-theme 4.1: Developing policies and setting thresholds for addressing soil pollution

4.1.1. Setting the thresholds for heavy metals based on their background & soil resilience

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Abstract

Maximum permissible concentrations (MPC) of pollutants adopted in Ukraine should be updated as soon as possible because does not meet modern requirements and world best practices. Objective of these studies was preliminary dividing of soils based on their protective abilities against contamination of plants and groundwater.

The difference between incomes of Cd, Zn, Ni, Pb, Cu into eluate and plants was compared in 42 samples of different soil types of Ukraine. The leaching of Zn, Cd, and Ni from contaminated low-buffered soils increased in 39-45 times, and lead and copper – in 12-18 times more than from the high-buffered soils. The difference in the accumulation in plants was smaller and amounted to 2-3 times for lead and 5 times for nickel. Based on the experimental data all soils of Ukraine were divided on 4 groups according their properties using the value of pH 5.7 and clay content 40 %. Each of such soil groups ($pH_{KCl} \leq 5.7$; clay $\leq 40\%$; $pH_{KCl} \leq 5.7$; clay $\leq 40\%$; $pH_{KCl} > 5.7$; clay $\leq 40\%$, and $pH_{KCl} > 5.7$; clay $> 40\%$) unites several soils types and occupies the large area in Ukraine.

MPC for each soil group combines evaluation of soil resilience with information about background of heavy metals. MPC was calculated for total content of heavy metals due to their mobile forms do not well correlate to leaching into eluate and accumulation in plants. Depending to soil properties, the total content of zinc should be limited from 120 to 270 ppm, nickel - from 36 to 90 ppm, lead - from 36 to 76 ppm, copper - from 24 to 64 ppm.

Keywords: soils, contamination, heavy metals, maximum permissible concentrations, background, soil resilience

Introduction, scope and main objectives

The history of soil contamination in Ukraine has started since the middle of XIX century when coal mining and steelmaking began to develop intensively. At that time, Ukraine was providing more than half of cast iron and 70 % of steel rolling in Russian empire. However, no one even suspected of the long-term consequences of soil pollution in industrial areas. Since the beginning of XX century, due to further industrial growing technogenic factor began to change the ecologic state of soil appreciably. In the soviet period a lot of enterprisers did not provide necessary level of protection from industrial emissions to the atmosphere. The most changes occurred up to the 80th of the last century when key soviet experts Evgeny Goncharuk and Gennady Sidorenko (1986) had developed the system of maximum permissible concentrations (MPC) of pollutants. This system was based on the weak link principle. Conclusion about dangerous of certain chemical substance was making after comparing its negative effect on soil microbiology, translocation to plants and migration to groundwater. This approach did not take into account soil properties; so many scientists have criticized it (Yakovlev 2013, Vodyanitskii, 2016). Nevertheless, the system of MPC

stays constantly in Ukraine until now, although this cannot provide reliable protection of environment.

What is the best way to improve the legal thresholds for pollutants? Many nearby countries have already corrected abovementioned MPC. In 1995, Russia passed some indicative permissible concentrations of available heavy metals (HM) differed for three soil groups: sandy soils, loam soils with $\text{pH} < 5.5$, and loam soils with $\text{pH} > 5.5$. Government takes another criterion for dividing of thresholds. According to legislation of Belarus (2008), MPC of available Cr, Zn, Cd, Ni, Cu, add total Pb depend on land use. Ecologic regulation norms of many countries takes into account soil properties and land use to achieve flexibility and more correspond to the real danger of contamination. For instance, the Methodology of ecological investigation levels accepted by the Australian Environment Protection Council is used to derive soil quality guidelines for a variety of different land uses: urban residential, public open space, commercial, industrial, agricultural and national parks or areas with high ecological value (Heemsbergen *et al.* 2009). A similar dividing on 4 clusters was used in the Netherlands, namely, residential and intensively used parkland, extensively used parkland, buildings and paved areas, and agriculture or nature reserves (Crommentuijn, 1997), Canada (residential/parkland, commercial, industrial and agricultural) (a Protocol... 2006), and Germany (playgrounds, residential areas, parks and recreational facilities, industrial and commercial real properties) (BBodSchV 1999).

At the same time, usage of soil parameters in derivation of MPC or other numeric targets does not accept so widely due to diversity of soils. Instead this the approach to determine a toxic effect on the nominal “standard soil” was used in Australia (pH 6, 10 % Clay, 10 cmol/kg CEC, 1 % Organic Carbon) (Heemsbergen *et al.* 2009), the Netherland (25 % clay and 10 % organic matter) (Crommentuijn 1997). U.S. Environmental Protection Agency recommends to share Eco-SSLs only on the soils with pH is greater than or equal to 4.0 an (Guidance) % (EcoSSL 2003). Then, soil protective ability is estimated more precisely by a combination of three groups values of pH (4-5.5; 5.5-7; 7-8.5) and organic matter (<2 %; 2-6 %; 6-10 %).

Thus, MPC adopted in Ukraine should be updated as soon as possible because does not meet modern requirements and world best practices. Ukraine has a very diverse soil cover. Different perennial rocks, hydrothermal conditions, and biologic cenoses caused to forming a wide geochemical environment and more than 600 soil varieties. Therefore, it would be advisable to grouping soils of Ukraine according their distinctive features. Objective of these studies was preliminary dividing of soils based on their protective abilities against contamination of plants and groundwater.

Methodology

The set of soils for research contained 42 samples of different soil types of Ukraine taken from the 0-30 cm layer. Mountain soils did not include due to their very specific properties. When we were collecting this set, we sought to maximally cover all soil diversity and, simultaneously, reach to normal distribution on the organic carbon content.

Each sample was divided on two parts, the first one not contaminated and the second one was contaminated by standard pollution mixture. This mixture was prepared according to receipt contained Cd 3 mg/kg, Ni 100 mg/kg, Cu 100 mg/kg, Pb 150 mg/kg, Zn 300 mg/kg. All soil samples were moistened to 60 % of water capacity, and composted for one month under the temperature 20°C. The soil of both variants was placed in the vessels where plants of oats were growing during 30 days. After this plants were removed from the vessels, and soil has been washed with water in the regime of 100 ml per month. The cycle of growing-washing was repeated three times. Then, the

content of HM (Cd, Zn, Ni, Pb, Cu) were measured in eluates, plants and soils. The eluates were analyzed after drying and dissolving the precipitate in 1 n HCl. HM in the plants were determined after burning under the temperature 500 °C. Mobile forms of HM in soils was measured using extraction of buffered ammonium-acetate solution with pH 4.8 by atomic-absorption spectrophotometry. The content of organic carbon was measured according to ISO 10694:1995, texture – to ISO/TS 7892-4:2008, and pH – to ISO 10390:2006.

Results

The collected soil samples had a wide variability of the main parameters. pH of salt extract (1 n KCl) was in the range from 3.7 to 7.8, and pH in water extract – from 4.8 to 8.2. The value of organic carbon content varied from 0.08 % in sandy and eroded soils to 4.3 % in chernozems and meadow soils. The texture varied accordingly, and the content of clay was in the range from 17 % to 70 %. According to the concept of Galina Motuzova, soil resistance to contamination depends on two key processes (Motuzova 2001). The first process is associated with precipitation of hydroxides, carbonates or other sparingly soluble salts. The second process is related to the sorption capacity of the soil and can be characterized by an ECO or associated indicators, for example, silt, clay, or organic carbon.

These leaching of HM from contaminated soils correspond well with the aforementioned concept. The presence of two separate data clouds is clearly visible on the graph of the dependence of the zinc intake in the eluate (fig. 1). A similar pattern can also be observed for cadmium, nickel, lead and copper. This means that at least two criteria are needed to adequately divide the soils according to their resistance to contamination. The clay content and pH_{KCl} are the most suitable, since there are numerous data on them in Ukraine.

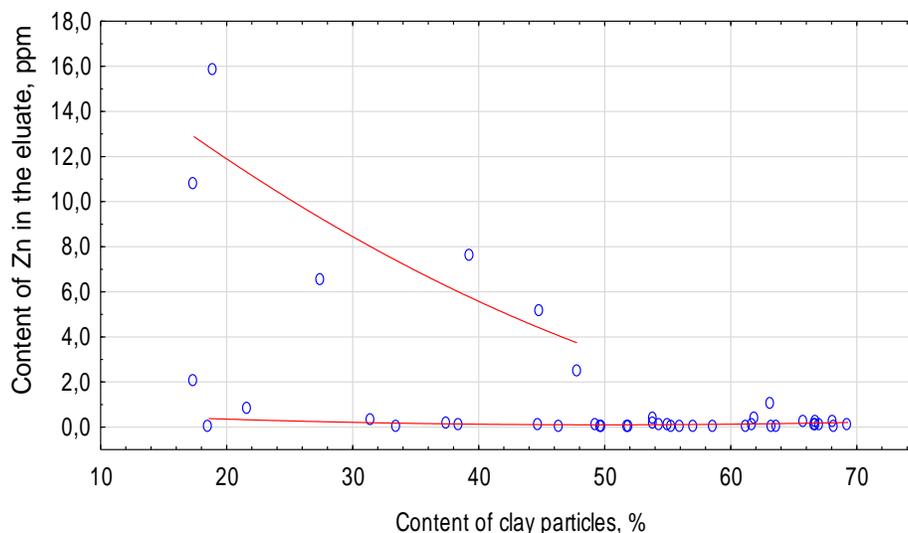


Figure 1. Two sets of leaching zinc values in different texture soils

Using the cluster analysis, we divided all the collected soils into two groups, very different in the content of Zn, Cd, Ni, Pb and Cu in the eluate and plants obtained from contaminated variants (fig. 2). The decrease in oat productivity was also used as an additional criterion for assessing the soil resilience. The first group includes acidic soils with a light texture ($\text{pH}_{\text{KCl}} \leq 5.7$; $\text{clay} \leq 40\%$), the second group has opposite values ($\text{pH}_{\text{KCl}} > 5.7$; $\text{clay} > 40\%$).

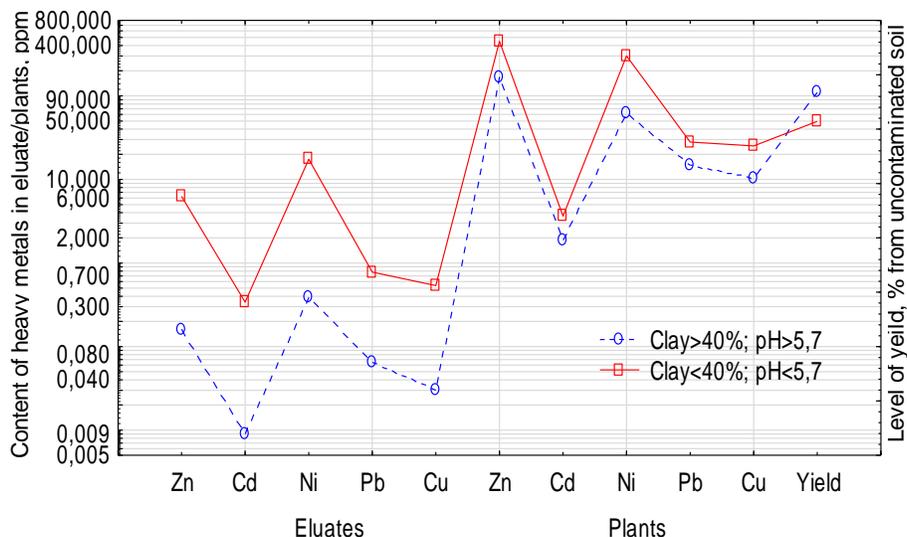


Figure 2. Average leaching of HM, their accumulation in plants and yield reduction on contaminated soils with different properties

The leaching of Zn, Cd, Ni from contaminated soils of the first group was on the average 39-45 times more intense, and lead and copper - 12-18 times more intense than from the soils of the second group. Due to the protective properties of the roots, the difference in the accumulation of HM in plants grown on the soils of the two groups was smaller and amounted to 2-3 times for lead and 5 times for nickel. However, this accumulation of HM was sufficient to halve the productivity of plants on the soils of the first group in comparison with the soils of the second group that did not suffer.

Taking into account that in addition to the above two groups of soils there are soils with $pH_{KCl} \leq 5.7$; $clay \leq 40\%$ and soils with $pH_{KCl} \leq 5.7$; $clay > 40\%$, we compared their resistance to contamination by criteria of leaching HM to the eluate, accumulation HM in the plants, and changing of plant productivity. To do this, we calculated the average values of all studied elements for each of the groups (table 1).

Table 1. Comparing the protective abilities of soils with different properties against leaching of HM and their affect to plants

Parameters of soil properties	Number of observations	Average ratio contaminated soils/uncontaminated soils		
		for leaching HM to the eluate	for accumulation HM in the plants	for changing of plant productivity
$pH_{KCl} \leq 5.7$; $clay \leq 40\%$	6	1600	17.4	12
$pH_{KCl} \leq 5.7$; $clay > 40\%$	6	600	12.1	35
$pH_{KCl} > 5.7$; $clay \leq 40\%$	5	36	5.3	125
$pH_{KCl} > 5.7$; $clay > 40\%$	25	30	4.1	114

As these calculated data show, the protective ability of soils with $pH > 5.7$ is very close, regardless of their texture. However, one must take into account the fact that soils with light texture have a much lower buffer capacity for acidification. In the case of acidification of soils with low buffering, leaching of HM and their entry into plants increases many times. Acidic soils with a clay content of more than 40% occupy an intermediate position between acidic light soils and soils with $pH > 5.7$. Thus,

the soil collection can be adequately divided into four groups, which provide a different level of protection from contamination by the HM of plants and groundwater.

The content of mobile forms of HM was determined in the soils after the completion of three washing cycles and two-fold growth of oats. The level of mobile Zn, Cd, Ni, Pb and Cu in the soils where pollutants were introduced exceeded the permissible standards or was very close to them (table 2). However, we did not find a clear pattern for the above-mentioned soil groups, although the difference between acidic light soils and heavy soils with pH was significant.

Table 2. The content of mobile forms of HM in the contaminated soils with different properties

Group Number	Parameters of soil properties	The content of mobile forms of HM, ppm				
		Zn	Cd	Ni	Pb	Cu
1	pH _{KCl} ≤5.7; clay≤40 %	130.0±57.5	1.9±0.3	48.0±11.6	70.1±8.7	23.3±3.7
2	pH _{KCl} ≤5.7; clay>40 %	17.0±3.1	2.1±0.1	67.0±13.2	58.3±7.4	21.5±8.0
3	pH _{KCl} >5.7; clay≤40 %	108.4±41.7	2.4±0.2	23.6±3.6	65.0±12.8	16.1±4.0
4	pH _{KCl} >5.7; clay>40 %	58.1±13.0	1.7±0.1	17.9±1.6	29.0±2.8	4.5±0.8
MPC for mobile HM		23.0	0.7*	4.0	6.0*	3.0

*Note. Not official, but mentioned in some sources (Technique, 2013)

Discussion

The obtained experimental data allow not only to justify the expediency of MPC differentiation but also to establish quantitative parameters for this. Dividing of the three groups of soils according to their resistance to contamination is well correlated with the geography of the soil cover of Ukraine. Acidic soils with a light texture (pH_{KCl}≤5.7; clay≤40 %) are represented by Eutric Podzoluvisols (according to FAO classification), Mollic Gleysols, most part of Haplic Greyzems, Umbric and Gleyic Cambisols, and occupy more than 9.2 mio hectares of agricultural land on the northern part of country. The second group of soils (pH_{KCl}≤5.7; clay>40 %) is represented by the rest part of Haplic Greyzems, Umbric and Gleyic Cambisols, Haplic and Luvic Chernozems which dominate in the northern Forest-Steppe. We assess the area of these soils in 2.5 mio ha. The third group does not large but very specific because located mainly in floodplains and on the coast of the sea where alluvial sands are a perennial rock (0.8 mio ha). The most widespread fourth group of soils (pH_{KCl}>5.7; clay>40 %) include the rest varieties of Chernozems and all Kastanozems in the southern Forest-Steppe and all Steppe zones on the area above 22 mio ha.

The principle of soil dividing is very close to what is used in Russia because it is based on the formation of soil resistance to contamination with HM. Nevertheless, we believe that it is necessary to separate the MPC for the total content of HM rather than their mobile forms. As the data in Table 2 show, mobile forms reflect differences only between very stable and very unstable soils. The reason for this lies in the technique for determining of mobile forms. The ammonium acetate buffer solution with pH 4.8, which is used in Ukraine maintains pH after interaction with the soil at almost the same level. Thus, using buffer solution with pH4,8 we eliminate the effect of pH on the mobility of metals that leads to a distortion of the real situation in the soil. For this reason, we intend to recommend MPC for the total amount of HM, dividing them into the four above-mentioned soil resilience groups.

Our concept of MPC based on the combining evaluation of soil resilience with information about HM background. For this, after dividing soils of Ukraine on four groups we calculated the average background values for each of them based on the data mentioned by Fateev and Paschenko (2003), Zhovinskyi and Kuraieva (2002), Dmytruk and Stepanchuk (2017) and others (table 3). According to the national standard, the background of HM is a median value for set of soil samples taken far

that 20 km from industrial sources of pollution. In most cases, there were an agricultural land but natural parks also were included. The real background values should be a zero point to further calculation of maximal permissible addition (MPA), i.e. quantity of element, which does not yet worsen the quality of groundwater or plants significantly.

Table 3. The background values of total HM contain in the uncontaminated soils with different properties

Group Number	Parameters of soil properties	The average background of HM and the variation range for different soil types, ppm				
		Zn	Cd*	Ni	Pb	Cu
1	pH _{KCl} ≤5.7; clay≤40 %	40 (25-55)	-	12 (10-14)	12 (9-15)	8 (5-11)
2	pH _{KCl} ≤5.7; clay>40 %	50 (44-60)	-	28 (21-35)	13 (10-16)	20 (14-26)
3	pH _{KCl} >5.7; clay≤40 %	45 (31-62)	-	12 (9-15)	12 (11-13)	8 (7-9)
4	pH _{KCl} >5.7; clay>40 %	70 (56-86)	-	30 (24-36)	16 (10-22)	24 (16-31)

*Note. Data on variation are incomplete.

Comparing the data of leaching HM in eluate and their accumulation in plants, the last criteria seems better for agricultural land because of its importance to the assessment of a real risk for crop production. Furthermore, full assess of risk for groundwater needs consider not only top soil layer but also lower horizons. It is possible that after flowing through these horizons the difference between concentration of HM in eluate in the soils of first and fourth groups will not be so big.

Based on the experimental data of accumulation HM in plants adjusted for low buffering of third soil group we calculated MPA for 1-4 soil groups by the proportion 16:12:8:4. It's mean the MPA for 2nd soil group should be higher 1st group in 1.25 times, for 3rd group – higher 2nd group in 1.33 times, and 4th group – higher 3rd group in 1.5 times. The final system of MPA/MPC levels is shown in the table 4.

Table 4. The content of mobile forms of HM in the contaminated soils with different properties

Group Number	Parameters of soil properties	The maximum permissible addition / the maximum permissible concentration of HM, ppm				
		Zn	Cd	Ni	Pb	Cu
1	pH _{KCl} ≤5.7; clay≤40 %	80/120	-	24/36	24/36	16/24
2	pH _{KCl} ≤5.7; clay>40 %	100/150	-	30/58	30/43	20/40
3	pH _{KCl} >5.7; clay≤40 %	135/180	-	40/52	40/52	26/34
4	pH _{KCl} >5.7; clay>40 %	200/270	-	60/90	60/76	40/64

We believe this system is fairly well correlated with the estimated levels of other countries and takes into account both soil resistance to contamination and the background content of HM in soils of Ukraine.

Conclusions

Due to the diversity of soils in Ukraine, it is proposed to set thresholds of HM for the large groups of soils with different resilience. The experimental comparison of soil resilience to contamination shows very big differences between acid soils with light texture and neutral and alkaline soils with high clay content. Therefore, it is advisable to divide soils on four group using pH_{KCl} and clay content 40 % as dividing values of soil properties. Each of such soil groups (pH_{KCl}≤5.7; clay≤40 %; pH_{KCl}≤5.7; clay>40 %; pH_{KCl}>5.7; clay≤40 %, and pH_{KCl}>5.7; clay>40 %) unites several soils types and occupies the large area in Ukraine.

Mobile forms of HM do not an optimal way for setting thresholds as much as they do not well correlate to leaching HM to eluate and accumulation in plants. The proposed method to setting thresholds based on the combining evaluation of soil resilience with information about HM background. Using this method, the maximum permissible additions and concentration were calculated for four elements. Depending to soil properties, the total content of zinc should be limited from 120 to 270 ppm, nickel - from 36 to 90 ppm, lead - from 36 to 76 ppm, copper - from 24 to 64 ppm.

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4.1.2. How do soil thresholds function in the policy on contaminated land in Flanders?

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Abstract

Soil thresholds differ according to their functioning in a legal or regulatory framework. However, they are interrelated. In order to obtain a consistent legal framework, these underlying relationships and the level of protection must be taken into account when deriving thresholds for a certain purpose. As an example, the soil thresholds of the Flemish legislation on soil, materials and wastes are discussed here.

Derivation of soil thresholds is based on many scientific data on toxicology, on contaminant characteristics, on transfer processes in soil and groundwater, etc. This knowledge is evolving continuously. Therefore regular updates of the scientific basis of soil thresholds is necessary, in order to guarantee adequate protection of the soil and, finally, safe food production.

This paper gives an overview of the different soil thresholds that are used in the legislation on soil contamination and waste in Flanders. The functioning in the legal framework, the protection targets, as well as the derivation method from scientific data is described. In Flanders, following soil thresholds exist: soil remediation standards, background values, target values, values of free use of excavated soil, values for the use of excavated soil for construction purposes, criteria for soil improving agents and fertilizers.

For a whole range of new substances, the so-called contaminants of emerging concern, no threshold values are available in the present regulations. Nevertheless, the legislation includes obligations regarding the investigation and remediation of soil contamination with these substances. This is a major challenge, for which intensified collaboration is needed on different levels: between scientists and policy makers; on regional, national and international level; and across different policy domains.

Keywords: soil policy, threshold values, soil remediation standards, background values, target values, contaminants of emerging concern

Introduction

Soil thresholds are important tools in regulatory frameworks dealing with soil protection and the management of soil pollution. Most commonly, they are expressed as a concentration of a pollutant in soil. Exceeding these values entails certain consequences, decisions or actions. Regulations to guarantee the quality and safety of food generally apply other thresholds, e.g. concentrations in plants; thresholds for soil concentrations are less frequently used.

However, there is a direct link between the quality of food and the level of pollutants in the soil. In order to outline guidelines for agricultural practices that take into account soil pollution, looking at approaches followed by the policy on soil pollution may be very useful.

Soil thresholds function in a decision-making process or legal framework, and are related to a target that needs protection (human health, ecology, groundwater, surface water, etc.), a level of

protection and a certain use. Legal frameworks differ in different countries, and therefore soil thresholds vary widely between countries. For the European countries, a comprehensive overview is given by Carlon (2007). Merrington and Schoeters (2010) described the science and methodology used to derive soil thresholds for trace elements.

Generally, soil thresholds are derived for different uses and different targets, leading to a whole framework of values, that are interrelated and that need to be adjusted to one another. For example, applying sewage sludge containing traces of pollution on arable land should not cause exceedance of soil remediation values in the long-term. Soil threshold used in a legal framework, and entailing certain action, such as further investigation or remediation, must be significantly higher than background values, in order to avoid legal uncertainty. Furthermore, guidelines about the method of analysis must be defined together with the soil threshold.

This paper gives an overview of the different soil thresholds that are used in the legislation on soil contamination and waste in Flanders. The functioning in the legal framework, the protection targets, as well as the derivation method from scientific data is described. In Flanders, following soil thresholds exist: soil remediation standards, background values, target values, values of free use of excavated soil, values for the use of excavated soil for construction purposes, criteria for soil improving agents and fertilizers. OVAM, the competent authority for the management of materials, waste and soil contamination in Flanders, is responsible for the derivation and implementation of these thresholds.

The aim here is to show possibilities of exchange of data and knowledge, and to indicate knowledge gaps and research needs.

Soil remediation standards

In Flanders, soil remediation standards are given in VLAREBO (2008), the implementation order of the Soil Decree (in force since 1995). Soil remediation standards reflect a level of contamination that, if exceeded, could cause significant harmful effects for human health or the environment. The remediation standards depend on land use, and take account of soil properties.

Soil remediation should take place if soil remediation standards are exceeded in the case of new pollution. New soil pollution is soil pollution that was caused after the Decree became into force (1995). Historical soil pollution is soil pollution that was caused before the decree became into force. In the case of historical pollution, soil remediation standards are an element in the decision on indications of serious threat. Remediation in the case of historical soil pollution is based on a site-specific risk assessment.

Soil remediation standards are derived for five land-use classes: nature, agriculture, residences, recreation and industry. These land-use classes are characterized by pre-defined exposure scenarios. Two values are calculated, namely based on protection of human health, and based on ecotoxicity. To derive human health based criteria, different exposure scenarios were defined for the different land use classes (Table 1). For the ecotoxicological criteria, different acceptable levels of protection were defined for the different land use classes. Both values are combined into one standard, opting for the lowest value.

Soil remediation standards based on human health are adjusted for legal criteria in other environmental compartments, e.g. in drinking water or ambient air. For agricultural land-use, remediation standards are adjusted for legal maximum levels in crops.

In Flanders, the model S-Risk (VITO 2017a; VITO 2017b) is used for site-specific human health risk assessment of soil contamination, and for the derivation of soil remediation standards based on human health. This model is a state-of-the-art model for assessing exposure and human health risks at contaminated sites. Fate and distribution of chemical pollutants in soils are calculated according to the principles of steady-state conservation of mass. It is a flexible model and easily to modify according to other purposes; it is available in English.

In VLAREBO (2008) soil remediation standards are given for all parameters that are frequently present in contaminated soils: heavy metals, monocyclic aromatic hydrocarbons, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, etc. For other parameters, e.g. dioxins, and some other new substances, no legal soil remediation standards are defined in VLAREBO, but similar soil criteria are provided in guidelines. In this way, it remains possible to follow a flexible and risk-based approach for soil contamination caused by these compounds of which scientific knowledge is evolving rapidly. However, recently the amount of new substances is increasing quickly, and it is no longer possible to provide soil criteria for all emerging contaminants in the guidelines.

Table 1. Fate, transfer and exposure pathways per land-use class

	nature agriculture	residences	recreation	industry
Fate and transfer				
leaching to groundwater	X			
volatilization to outdoor air	X	X	X	X
volatilization to indoor air	X	X	X	X
soil resuspension	X	X	X	X
transfer of soil to indoor dust	X	X	X	X
uptake by plants	X	X		
uptake by cattle	X			
transport through drinking water pipes		X	X	X
Exposure				
ingestion of soil/dust particles	X	X	X	X
dermal absorption from soil dust	X	X	X	X
inhalation of vapours	X	X	X	X
inhalation of particles	X	X	X	X
consumption of vegetables	X	X		
consumption of meat/dairy products	X			
intake of groundwater as drinking-water	X			
intake of drinking-water		X	X	X
dermal absorption from water	X	X	X	X

Background values

Background values as defined in VLAREBO (2008) reflect the normal values found in unpolluted soils. They can reflect the influence of soil properties on normal concentrations. For metals and metalloids, background values correspond with the 90-percentile of concentrations measured in Flemish top soils; a linear regression line allows recalculation for measured organic carbon and clay content. For most organic contaminants, the background level equals the limit of detection; except if they show diffuse enrichment. In that case, the 90-percentile of measured values is used.

Background values have a limited function in the legal framework; they are used as the lower limit for all other soil thresholds.

Target values

Target values serve as remediation goals in case of new soil pollution. These values correspond to negligible risk levels. BATNEEC considerations (best available techniques, not entailing excessive costs) can be used to deviate from this remediation goal.

Target values are defined as values between background values and soil remediation standards, and for which a sufficiently accurate analytical determination must be possible. For organic compounds, the target value equals the sum of the background value and soil remediation standard for agricultural land-use, divided by two. For inorganic compounds, the target value is derived as 60% of the soil remediation standard for agricultural land-use.

Values for free use of excavated soil

Excavated soil with contaminant concentrations below the values for free use, can be used everywhere without restrictions. The soil is considered clean, and suitable for multifunctional use. The values for free use of excavated soil are identical to the target values, i.e. the derivation of these values is the same. Target values and values for free use of excavated soil are defined in VLAREBO (2008).

Values for the use of excavated soil for construction purposes

Excavated soil can be used as building material for constructions or in products. Examples are the use in the core of dykes, the use of sandy soil in concrete, or the use of clay in ceramic products. Only soil with contaminant concentrations below the values for construction purposes can be used. In addition to these threshold values, leachability of metals determined by a shaking test should be below values stated as well in VLAREBO.

To derive the values for excavated soil for construction purposes, the environmental compartments that need protection are defined. These are the soil and groundwater beneath the construction or application of the product. Then, the criteria for protection of these compartments are defined, taking into account effects on human health and ecology. 'Safe' concentrations for the soil and groundwater are, for example, background values or negligible risk levels (target values), etc. Then standard scenarios for constructions and applications are defined, as well as the models used to calculate the transfer of contaminants into the compartments that need protection. Finally, the values are adjusted so that they are equal or below the soil remediation standards for industrial use.

The framework, as described above, is the same as used to derive regulatory values for the re-use of other materials in the context of the Flemish legislation on materials and wastes.

Criteria for soil improving agents and fertilizers

Some organic or inorganic wastes contain substantial amounts of nutrients or organic matter. They can be re-used as a soil-improving agent or as fertilizer, when they contain no or low levels of contamination. Maximum criteria for soil improving agents and fertilizers are defined in VLAREMA (2012), the implementation order of the Flemish legislation on sustainable management of materials and wastes. These criteria are maximum concentrations of contaminants in the residual products that will be applied to soils.

The criteria are derived allowing a limited enrichment in the soil, until the 'safe' concentrations in soils, as defined for the derivation of the values for excavated soil for construction purposes.

Relevant input/output processes are taken into account: atmospheric deposition, uptake by plants, leaching and degradation.

The issue of contaminants of emerging concern

In the common practice of soil remediation and management of contaminated soils, only a limited number of parameters are analyzed and evaluated. For these parameters, thresholds are set. This includes heavy metals, mineral oil, PAHs, chlorinated solvents, etc.

However, information from scientific research shows that there are whole ranges of new substances that have been used, are present in soil, groundwater and sediments, and can cause risks. E.g. perfluorinated compounds, brominated flame-retardants, pharmaceuticals, pesticides, crop protection products, including additives in these products, etc. In the common practice, they are usually not measured due to the lack of guidelines and threshold values.

Nevertheless, the present legislation provides rules on how to deal with these new substances. For example, in the Flemish regulation, the problem owner should propose remediation values for parameters for which no standards are set, when there is a suspicion that this substance may be present on the site. The obligation to investigate and remediate contamination as well as liability are the same as for contamination with more common parameters.

We are facing here a major challenge. The most urgent problems occur when dealing with excavated soils. To meet this challenge, we need an intensified collaboration on different levels: between scientist and policy makers, between different levels of authority (regional, national, international), and across different policy domains (agriculture, food safety, water and soil protection, etc.).

Conclusions

Soil thresholds differ according to their functioning in a legal or regulatory framework. However, they are interrelated. In order to obtain a consistent legal framework, these underlying relationships and the level of protection must be taken into account when deriving thresholds for a certain purpose. As an example, the soil thresholds of the Flemish legislation on soil, materials and wastes are discussed here.

Derivation of soil thresholds is based on many scientific data on toxicology, on contaminant characteristics, on transfer processes in soil and groundwater, etc. This knowledge is evolving continuously. Therefore regular updates of the scientific basis of soil thresholds is necessary, in order to guarantee adequate protection of the soil and, finally, safe food production.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.3. Policy on diffuse soil pollution in Flanders: human health issues and local food production

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Abstract

Until recently, the soil policy in Flanders was focussed on soil pollution related to known risk-entailing activities. However, it becomes increasingly evident that also diffuse soil pollution should be included as well in the policy and legal framework. The OVAM, the Flemish authority responsible for the management of materials, waste and soil contamination, is developing a general approach for the management of diffuse soil contamination. The aim is to eliminate risks and prevent more diffuse soil pollution.

In a first phase, the emphasis was on the avoidance of risks for human health resulting from diffuse soil contamination. Due to concerns about the presence of pollutants in homegrown food and eggs, combined with increased interest in gardening and local food production, targeted actions were needed. In collaboration with local authorities, an advice system based on soil analysis was set up, to provide suitable and case-specific information for citizens. The system is easily accessible, and operates at low cost.

In a next phase, OVAM will look at all available data on diffuse soil pollution, including those from agricultural inputs. The development of a legal framework on diffuse soil pollution is envisaged. The case of Flanders is presented as an example, and the need for (inter)national collaboration between policymakers and scientists is emphasized. Finally, the long-term objective is to make all relevant data on soil quality available to users, in order to guarantee safe food production globally.

Keywords: soil policy, diffuse soil pollution, human health, urban gardening, threshold values

Introduction: policy on soil pollution in Flanders

For more than 20 years, the Soil Decree is operative in Flanders, and proved to be a very successful legal instrument. Many contaminated sites are cleaned up, and a rigorous system of data collection

and processing on soil and groundwater quality is set up. Key principles are: (i) delivering of a soil certificate, legally required with every transfer of land, with the aim to inform new owners on soil and groundwater quality; (ii) obligation of soil investigation when risk-entailing activities took place on the site; (iii) remediation of polluted sites according to the 'polluter pays'-principle, with exoneration for owners who are not responsible and co-financing mechanisms; and (iv) a soil information register, containing geographical and cadastral data, as well as all available data on levels of contamination.

Two decades of experience learned us that even with a legally binding instrument, not all pollution can be removed. In many cases residual contamination is left behind, which needs to be managed. The base of this management is to provide information to (future) users of land. Data exchange will be crucial for future management of soil contamination.

Until recently, the focus has been on soil contamination related to known risk-entailing activities e.g. from industries, petrol stations, etc. However, more and more, it is clear that soil contamination, which cannot be directly linked to a known source, should be integrated as well in order to complete the information system.

Developing a policy on diffuse soil pollution in Flanders

In Flanders, with its long industrial history and high population density, diffuse soil contamination is widespread, especially in urban areas. In the Flemish soil policy, diffuse soil contamination is contamination which cannot be linked directly to a known point source. It can be due to all kinds of small-scale artisanal activities in the past, including waste burning and disposal, of which no record has been kept. However, it can also be caused by dispersed sources, and introduced in the soil by atmospheric deposition, agricultural inputs or flood events. In practice, these two kinds of diffuse soil pollution can often not be distinguished.

Concerns about diffuse soil pollution arose for different reasons: (1). Results of the Flemish human bio-monitoring program (2001-2006) showed higher levels of chlorinated components (e.g. dioxins, DDT en PCB's) in the blood of inhabitants living in rural areas compared to the general population. Further research on routes of exposure indicated that this was linked with the consumption of locally grown vegetables and eggs. (2) There is an increased interest for urban gardening and local food production. We need to ensure that people can do this without worrying about their health. (3) Contaminants of emerging concern such as dioxins, perfluorinated compounds, etc., including those from agricultural inputs (e.g. pesticides and antibiotics) are often present as diffuse soil contamination.

Furthermore, diffuse soil contamination can interfere when dealing with soil contamination caused by known sources, and can sometimes, for example, complicate liability issues.

The OVAM, the Flemish authority responsible for the management of materials, waste and soil contamination, is developing a general approach for the management of diffuse soil contamination. The present legal instrument, the Soil Decree, is not always well suited to deal with diffuse soil contamination. In a first step, the focus was on the avoidance of risks for human health resulting from diffuse soil contamination.

Human health issues and diffuse soil pollution with dioxins

Gardening and the production of homegrown food has gained a lot in popularity recently. To harvest and eat one's own vegetables, to raise chickens and to collect and eat their eggs, can be real pleasure. Local food production has many other advantages as well: it contributes to a

sustainable and healthy lifestyle, increases social cohesion, etc. However, in some cases, there are concerns about the presence of pollutants in homegrown food and eggs. Especially with regard to increased levels of dioxins in eggs of home-raised chickens, there are matters of concern. Several studies (Schoeters and Hoogbeem 2006; Van Overmeire *et al.* 2006) demonstrated increased levels of dioxins in eggs of free-range chickens as compared to barn or cage eggs, and attributed this to environmental pollution.

In order to solve the problem, more information was needed on the nature of the pollution: was it caused by atmospheric deposition, diffuse soil contamination or local soil contamination related to point sources? Therefore, in 2010 a measuring campaign was commissioned by OVAM. In 15 private gardens, soils, deposition, vegetables and eggs from free-range chickens were sampled and analyzed for polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls (PCDD/Fs and dl-PCBs). The results of this study (Cornelis *et al.* 'Dioxins in eggs and vegetables of private gardens' OVAM 2011) showed again elevated concentrations of dioxins in eggs from free-range chickens, as compared to eggs from barn or cage chickens (commercial circuits), and a significant correlation between the concentration of dioxins and dl-like PCB's in eggs and those in soils. On a weekly basis, the tolerable intake was not exceeded, except for one household, for whom consumption of eggs from their own chickens was discouraged from then on. The soil of this garden showed high concentrations of dioxins and dl-PCB's. The origin was difficult to trace, but there were some indications that in the past there might have been a joinery on the site.

The 15 private gardens were selected among the participants of the bio-monitoring program. The location in relation to possible sources of contamination was not taken into account for the selection. For several gardens, soil concentrations of dioxins/furans and dl-like PCB's were substantially higher than the background concentration in soil, i.e. higher than 2,43 ng TEQ/kg ds (WHO-TEF, 2005) (Cornelis *et al.* 'Background values – dioxins, furans and dioxin-like PCBs' OVAM 2011). These results indicate that occurrence of dioxins in soils in Flanders is heterogeneous. Derivation of general advices on avoidance of exposure risks is difficult, and probably not adequate. A case-specific approach was needed.

Safe gardening – an advice system based on soil analysis

How can we ensure that people can eat their home-grown vegetables and eggs from their own chickens without having to worry about their health? Together with the Service Health and Environment of the Department Environment, the OVAM has set up a system to provide suitable advice and information for citizens. The aim was not to discourage growing one's own food, but to reduce possible health risks by practical measures. A online platform was created with simple and easily accessible information (www.gezonduiteigengrond.be, in Dutch). This was done in collaboration with local authorities, who support their citizens when needed.

Practical guidelines are provided on how to grow vegetables and to raise chickens in allotments and private gardens in a safe way. For example, the guidelines include advices on the location of the garden in relation to heavy traffic, industry, historical contaminated sites, etc. When the quality of the soil is uncertain or questionable, the advice is given that one should test the soil for contamination, i.e. to take a soil sample and to get it analyzed.

However, the cost of soil analyses may be too high for private persons who are gardening for leisure. This is especially the case when one wants to raise chickens for egg production and soil testing for dioxins is needed. Therefore, the possibilities of organizing a system for soil analyses at reduced prices were investigated in a feasibility study. This study ('Feasibility study subsidy system for private gardeners' OVAM 2014) dealt with the organizational, financial and legal

aspects, and included also an online survey of gardeners about their concerns related to soil contamination, their willingness to pay, ... Two pilot studies, each in collaboration with a local authority, were done, and proved to be successful. In these communities, soil testing at a reduced price was offered for private gardeners during a certain period.

In support of previous actions, a framework for the interpretation of the results of the analyses was developed. Reference values were calculated for soil concentrations that allow growing food products without health risks (Cornelis *et al.* 'Reference values for soil quality in private gardens' OVAM 2014). This was done for a whole range of parameters (heavy metals, polycyclic aromatic hydrocarbons, pesticides, dioxins, etc.) and for different scenarios, e.g. for low and high consumption rates of local grown vegetables and eggs from home-raised chickens. In the online advice system based on soil analyses, only the most relevant parameters are implemented, namely heavy metals and benzo(a)pyrene for vegetable garden soils, and dioxins/furans and dl-PCBs for soils from chicken runs.

The model S-Risk was used to calculate the reference values (VITO 2017a; VITO 2017b). This model is a state-of-the art model for assessing exposure and human health risks at contaminated sites. Fate and distribution of chemical pollutants in soils are calculated according to the principles of steady-state conservation of mass. The model is used in Belgium to calculate soil remediation values, to assess site-specific risks and to calculate site-specific remediation objectives. It is flexible and easily to modify according to other purposes, and available in English. With this model, it was possible to calculate different exposure scenarios, and to take also into account the exposure route by consumption of eggs from home-raised chickens.

An additional advantage of the advice and subsidy system is that it provides (anonymous) data on diffuse soil contamination. How frequently are reference values exceeded? For which parameters? Are there differences between urban and rural areas? Such data allow authorities to plan targeted actions. However, it is important to note that in this case soil analyses are done on a voluntary basis, and that results do not enter the legal framework, which could involve obligations to remediate.

Future policy actions in Flanders

In a next phase of developing a policy on diffuse soil contamination, we will look at the legal framework and the competence of action. Is incorporation of data on diffuse soil contamination in the OVAM database possible and appropriate? A first preparatory step is the inventory and analysis of all available data on diffuse soil contamination in Flanders. For example, data from technical reports on excavated soil, or large scale monitoring studies on soil quality. The aim is to have an idea of the scale of the problem and of the characteristics of diffuse soil pollution. Data related to agricultural inputs in soils can be included as well, e.g. data on fertilizer use, use of crop protection products, etc.

A global risk analysis will be done, in order to be able to prioritize the different kinds of diffuse soil pollution. Gaps in information will be indicated, where monitoring may be appropriate. In addition, juridical consequences will be considered, such as the legal obligation to investigate and remediate. It may be necessary to adapt legislation in order to maintain justice and fairness.

Finally, the way forward is to make all relevant data on soil quality available to users, with the objective to ensure safe food production, whether from private gardens or from agricultural practices. This may seem very challenging to achieve. However, relative costs of laboratory analysis have decreased enormously the last few decades; and the expertise of data exchange and storage is evolving rapidly.

Conclusions

This paper describes, as an example, the policy on diffuse soil contamination in Flanders. Priority was given to the avoidance of risks to human health due to local food production. In a next phase, the development of a legal framework for diffuse soil pollution is envisaged. It is clear that the policy on soil contamination and the policy on agriculture will converge on this topic. Intense collaboration between policy makers and scientists on soil remediation from one side, and agriculture from the other side, will be essential, at a regional, national and international level.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.4. Policy questions addressing the management of contaminated sites in Europe

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Abstract

The 7th Environment Action Program of the European Union makes soil 'pollution' management a priority and calls for the design of sustainable development strategies. On this paper, the findings of the questionnaire commissioned by the European Commission Joint Research Centre for the revision of the Indicator "Progress in the management of contaminated site in Europe" in 2016 are presented. This indicator aims to answer the following policy-relevant questions: What is the estimated extent of soil contamination? How much progress has been achieved in the management and control of local soil contamination? Which sectors contribute most to soil contamination? What are the main contaminants affecting soil and groundwater in and around Contaminated Sites? How much is spent on cleaning up soil contamination? And how much of the public budget is used?

In the present decade, an overall improvement in the management of contaminated sites in Europe has been observed. For the 39 surveyed countries, 2,5 million sites have been estimated where polluting activities have taken place considering the artificial surface. Nowadays, there are more than 650 000 registered sites where polluting activities took/are taking place in national and regional inventories of replying countries; more than 235 000 sites have been remediated. Efforts are mainly focused on investigation and remediation of sites where polluting activities took/are taking place due to many countries already have an accurate inventory. Overall, the production sectors contribute more to local soil contamination than the service sectors (60 % compared to 32 %). The most frequent contaminants are mineral oils and heavy metals. The most commonly used remediation procedure seems to be the ex-situ technique "dig-and-dump", which implicates the excavation and off-site disposal of contaminated soil. With the available data provided by replying countries, the average overall expenditures to assess soil 'pollution' account for €4,3 billion where on average more than 32% of total expenses comes from public budget.

Keywords: indicators, priorities, management of contaminated sites, environment, human health

Introduction, scope and main objectives

European environmental policy is one of the policy areas mostly developed in the last decade. It is well recognized that environmental problems go beyond national and regional borders and can only be solved through collective actions at EU and international level. From an initial focus on chemical pollutants and impacts, environmental policy is moving into an integration phase, with the emphasis on understanding and addressing the pressures on the environment and examining the effects of different policies and behavior patterns. Priorities have been set for water, air, waste and chemicals, where several Directives and Regulations have been implemented in Europe. However, the existing legislation does not address all the soil threats in a comprehensive way and not all EU Member States have specific legislation on soil protection. Article 191(2) of the Treaty on the Functioning of the European Union (TFEU), "Union policy on the environment" aims at a high level of protection taking into account the diversity of situations in the various regions of the Union, and is based on the precautionary principle and on the principles that preventive action should be taken,

that environmental damage should, as a priority, be rectified at the source and that the polluter should pay.

In the area of contaminated sites, the Soil Thematic Strategy (EC STS, 2006) proposed that Member States must draw up a list of sites polluted by dangerous substances when concentration levels pose a significant risk to human health and the environment, and of sites where certain activities have been carried out (landfills, airports, ports, military sites, activities covered by the Industrial Emissions Directive (IED, 2010), etc.). The Soil Thematic Strategy contains a list of these potentially polluting activities. On 2012, the European Commission reports on the implementation of the Soil Thematic Strategy and ongoing activities and on the State of Soil in Europe (Jones, A. *et al.*, 2012) it is highlighted the continuous degradation of soils in Europe. The State of the Environment Report (SOER) (EEA, 2015) of the European Environment Agency underlines that "soil stores, filters and transforms a range of substances including nutrients, contaminants, and water. In parallel, this function in itself implies potential trade-offs: a high capacity to store contaminants may prevent groundwater contamination, but this retention of contaminants may be harmful for biota". The issue of pollution is crucial for the biota function thus affecting a soil's capacity to 'regenerate'.

In Europe a set of indicators contributes to the Core Set Land and Soil Indicator "Progress in the Management of Contaminated Sites" (LSIO03) of the European Environment Agency (Van Liedekerke M., 2014), which is used for reporting on the State of the Environment in Europe. The indicator identifies local soil 'pollution' as an important threat to human health and ecosystems. It aims to inform policy makers, professional practitioners, researchers, citizens and the media on the various Directives and projects related to soil protection. Data are collected from the National Reference Centres for Soil in 39 countries belonging to the European Environment Information and Observation Network (EIONET) during campaigns organised by the JRC European Soil Data Centre.

Six data collection exercises had been completed since 2001 to support reporting by the EEA of the indicator CSIO15 "Progress in the management of contaminated sites". This indicator aims to answer the following policy-relevant questions:

1. What is the estimated extent of soil contamination?
2. How much progress has been achieved in the management and control of local soil contamination?
3. Which sectors contribute most to soil contamination?
4. What are the main contaminants affecting soil and groundwater in and around Contaminated Sites?
5. How much is spent on cleaning up soil contamination?
6. How much of the public budget is used?

Methodology

On December 2016, the JRC sent a Questionnaire to the National Reference Centres (NRCs) for Soil of 39 European countries, with the request to reply with the status on the progress in the management of contaminated sites. The information sent back by countries representatives was analyzed and presented in the report "Status of Local Soil Contamination in Europe" by Payá Pérez and Rodriguez Eugenio (2018).

The objective of the indicator is to define the trends in the management of contaminated sites. In order to establish a trend it is necessary to compare the actual data with the one from previous years. However, as the concepts and methodologies for defining contaminated sites have been revised after each data collection exercise since year 2001 and a new classification is now used for sites status definition as presented in Fig. 1, comparison between countries and among the same country in different periods may be controversial.

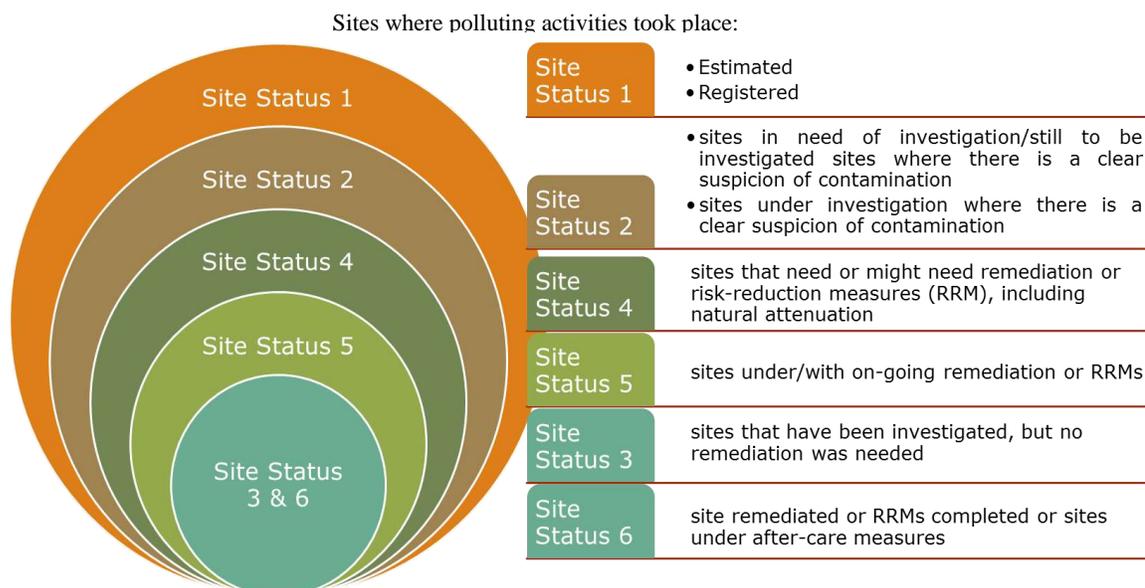


Figure 1. Representation of six site status, depending on its management steps. By Payá Pérez and Rodriguez Eugenio (2018), Status of Local Soil Remediation in Europe. JRC Technical report.

Results

Today, data on the extent of soil 'pollution' in Europe is available for 31 of the surveyed countries (39 countries: 33 European Economic Area countries and 6 cooperating countries in the West Balkans), data on the extent of the territory and population are presented in Table 1. In most countries, this compilation process starts with the establishment of a register of sites where potentially polluting activities have taken or might have taken place.

Table 1. Coverage of the survey in European countries By Payá Pérez and Rodriguez Eugenio (2018)

	Countries surveyed	Total
Countries	31	39
Population (Million inhabitants)	513,4	621,2
Total surface area (thousands of km ²)	4 869,6	5 994,9
Artificial surface (thousands of km ²)	217,9	239,3
Surveyed of total population	83 %	100 %
Surveyed of total artificial surface	91 %	100 %

An average of 4,6 sites are reported per 1 000 inhabitants in Europe. In the European Union (EU-28), the estimation of the extension of soil 'pollution' is of 2,8 million sites where polluting activities took/are taking place, considering the artificial surface. An attempt of extrapolation to all surveyed countries in Europe has given an estimate of 2,5 million sites where polluting activities took/are

taking place by km² of artificial surface. This difference is due to available data mainly comes from EU-28.

Nowadays, there are more than 650 000 registered sites where polluting activities took/are taking place in national and regional inventories of replying countries. The number of registered sites has been reduced 2.4 times since the baseline report “Progress in the management of contaminated sites in Europe, 2005”, considering data from those countries replying in both exercises. This reduction may be due to the changes in which polluting activities have been considered and the existence of dynamics inventories in some countries.

A significant effort is being made to remediate these contaminated sites with more than 14 000 sites under remediation or risk-reduction measures (Site status 5) across replying countries.

Nowadays, more than 235 000 sites have been already remediated or are under after-care measures. However, this number could be higher because in many countries these sites are removed from national inventories once it has been confirmed that pollutants level are under established screening values or they do not pose a risk for the environment and human health.

28 of the 39 surveyed countries maintain comprehensive inventories for contaminated sites at different levels. Among them, 68% of the inventories are managed at national level, frequently by environmental agencies.

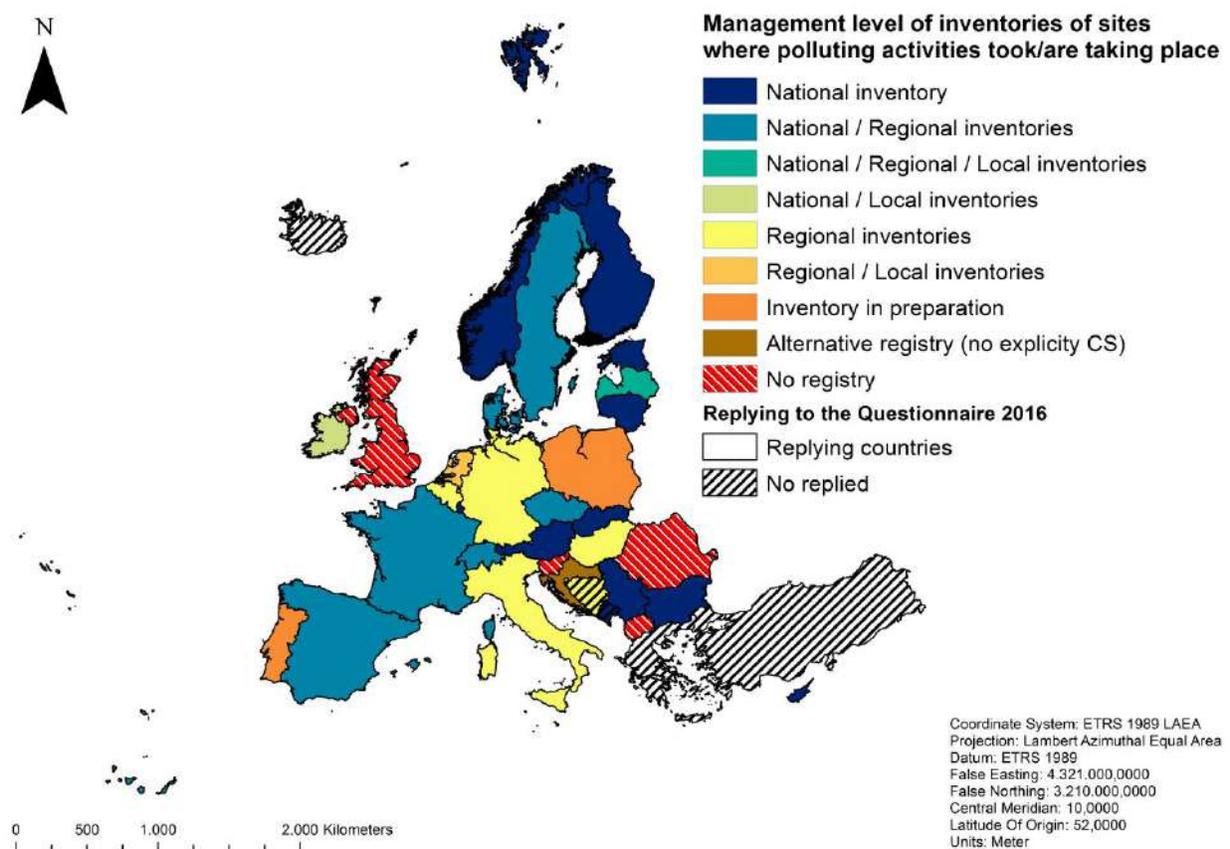


Figure 2. Management level of inventories of sites where polluting activities took/are taken place. By Payá Pérez and Rodríguez Eugenio (2018), Status of Local Soil Remediation in Europe. JRC Technical report.

Combined approaches to encourage staged assessment processes, considering screening values but allowing the flexibility to use comprehensive assessment tools for site-specific risk assessment are nowadays the most extended practice to deal with soil contamination across Europe. Due to the existence of a wide variety of soil types and 'pollutants' with different solubility and bioavailability, the use of screening values alone, seem not to be appropriated to assess the problem in an efficient and economically viable manner.

The average of the overall expenditures of the management of contaminated sites varies in a significant way among countries in Europe. The industrial past, the number of sites where polluting activities took/are taking place, the existence of a legal framework on soil 'pollution', the availability of technologies and techniques for remediation and the existence of well-defined procedures to investigate and remediate contaminated sites are aspect that determine the total amount countries would need for a complete risk management.

The polluter-pays principle is applied in every country in a systematic way for new 'pollution'; however, on average more than 32% of total expenses to deal with contaminated sites come from public budgets in replying countries. This is mostly linked to the fact that polluter-pays principle is rarely applicable to historical contamination. 86% of the replying countries have a national program to deal with orphan sites. The responsibility for identification and remediation of those sites that have been contaminated in the past and where it is not possible to identify the polluter varies among countries, as well as between states, as does the funding regime.

Discussion

There are many differences between the concepts, terminology and management efforts of the replying countries. Those that have been tackling the problem of soil 'pollution' since 3 decades, now are focusing their efforts into remediating those sites previously identified, where polluting activities took/are taking place. However, a clear relationship has been observed between the political support, understood as the existence of a legislation that addresses directly soil 'pollution' and remediation, and the completion of the registers of contaminated sites.

Conclusions

Many countries have reported that there is a lack of a common and legal framework to develop a national strategy on soil protection.

There is the lack of agreement on what are the triggers for starting an investigation in a site suspected of being contaminated. It is clear that differences in soil types among countries, with heterogeneous pedogenic processes as selective dissolution and weathering, volatilization, vertical and lateral transport, pedoturbation and soil accretion by dust and organic matter, make difficult to establish a unique procedure.

Due to the transboundary nature of soil contamination, there is a need of having agreed guidelines and common strategies to deal with contaminated sites, setting screening values for all the pollutants between all countries.

Developing a common language for discussing contaminated soil issues is of crucial interest. Furthermore, as many countries have reported, the lack of a common and binding framework is a neck-bottle for them to develop a national strategy due to the political difficulties to face soil protection.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO or the European Commission.

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4.1.5. Derivation and application of soil guideline values in contaminated land management – Case Finland

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Abstract

Soil guideline values are commonly used tools to regulate soil contamination. The excessive emphasis put on the derivation of soil guideline values, nevertheless, does not necessarily support justified decision-making and reasonable soil management practices if the appropriate application of the values in the regulatory frameworks is not highlighted clearly enough.

Keywords: Soil, contamination, guideline value, risk assessment, threshold

Introduction

Risk-based approach is one of the key principles in the management policy on soil contamination both in Finland and internationally. In contaminated land management, a tiered risk assessment procedure that relies on the ‘source–pathway–receptor’ pollutant linkage and the integration of health and environmental considerations is usually followed. Within such procedure, the application of soil guideline values as generic decision benchmarks is a common practice, having also resulted in the development of technical approaches for their derivation.

Soil guideline values (SGV) or soil thresholds are generic quality standards for contaminant concentrations in soil that are used to regulate soil contamination and simplify decision-making. The purpose and regulatory significance of SGVs vary from generic long-term soil quality objectives to investigation triggers and remedial action values (Carlon *et al.* 2007). Hence, SGVs may represent various protection targets and risk levels regarding both prevention and cleanup of soil contamination.

In order to support defensible decisions, the derivation basis of SGVs has to be scientifically justified, transparently documented, and fit for purpose. The derivation basis of SGVs, nevertheless, is irrelevant if the values are not applied in a proper manner (Reinikainen and Sorvari 2016). The same holds true for any other quality standard as well as site-specifically derived decision criteria.

In Finland, mandatory risk assessment is integrated into the regulatory framework by the Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007). In the Decree, three categories of SGVs - the threshold value and the lower and upper guideline value - for 52 substances or groups of substances are presented. The threshold value indicates a warning risk and is used as a mandatory trigger for site-specific risk assessment, alongside background concentrations. The lower and upper guideline values refer to potentially unacceptable risks to human health or the soil ecosystem in residential and industrial areas, respectively, and they can be used to assess the need for soil remediation. However, the guideline values are not legally binding benchmarks for remediation meaning that the actual site-specific assessment should be prioritized.

This paper discusses the derivation of SGVs as well as the challenges and inconsistencies of using them in contaminated land management, based on the Finnish experience.

Derivation of the Finnish guideline values

The Finnish SGVs are based on a generic risk assessment, in which various ‘reference values’ for contaminant concentrations in soil were derived representing different protection targets and risk levels, i.e. Predicted No-Effect Concentration (PNEC) and Potentially Significant Concentration (PSC) for setting the threshold values and guideline values, respectively (Reinikainen *et al.* 2007) (see Figure 1). The ecological reference values were mainly derived by applying the Dutch methodology (Traas 2001), which corresponds in outline the European Commission’s Technical Guidance Document on Risk Assessment (ECB 2003). The ecological risk assessment considered HC₅ and HC₅₀ values (Hazardous Concentration for 5/50% of the species or microbiological processes in the ecosystem) derived from the Species Sensitivity Distribution (SSD) curve. The SSDs were based on statistical interpretation of literature data, i.e. observed NOEC values (No Observed Effect Concentrations), using primarily the data presented by the Dutch RIVM (e.g. Verbruggen *et al.* 2001). When the toxicity data was not adequate for statistical inferences, assessment factors (AF) for individual species data (NOECs or L(E)C₅₀s, Lethal/Effect Concentration) were used. Equilibrium partitioning (EqP) method for aquatic data was used when the data on soil organisms was considered as insufficient. For metals, the ‘added risk approach’ was applied by taking national background concentrations into account (Strjuijs *et al.* 1997). In addition, for several compounds, reference values were derived based on secondary poisoning to birds and mammals.

In the health risk assessment, conceptual exposure scenarios for residential and industrial land use were first defined to describe standardized exposure conditions for human receptors. Theoretical exposure for the both land use scenarios was then calculated applying the Risc-Human software (version 3.1), the commercialized version of the Dutch CSOIL model (Brand *et al.* 2007), with modified input parameters representing Finnish conditions. In addition, a separate soil-plant uptake calculation for the ingestion pathway of homegrown vegetables was performed for lipophilic organic contaminants using more relevant equations (Trapp and Matthies 1995). Lifetime average daily dose (ADD) via all the exposure routes was next calculated and compared with the acceptable intake values (TDI/TCA, Tolerable Daily Intake/Concentration in Air or CR, Cancer Risk in oral/inhalation exposure 10⁻⁵) presented in Baars *et al.* (2001) or the IRIS database of the U.S.EPA. The health-based reference value was then set at concentration where the calculated exposure equaled the acceptable intake. In the generic health risk assessment three-exposure routes, i.e. soil ingestion, inhalation of indoor air and ingestion of homegrown vegetables, count for over 90 % of the total exposure and so determine the health-based reference values.

For setting the threshold value, conservative reference values for the protection of groundwater quality were also derived. On the other hand, potential migration of contaminants to groundwater or surface water was not considered in the setting of the guideline values in order to promote actual site-specific assessment in cases where migration needs to be evaluated.

In the final stage, the calculated reference values were integrated. The lower value representing the potentially unacceptable risk/effects (i.e., health risk value or HC₅₀-based ecological value) was used as a base for the guideline values along with some additional criteria and uncertainty estimates. As for the threshold values, the reference values representing insignificant risks/effects were considered alongside certain socio-economic factors, and integrated in a simple multi-criteria decision analysis (Reinikainen 2007).

As a result from the integration, most of the guideline values for metals, polyaromatic hydrocarbons (PAH) and pesticides are primarily based on the ecological reference values,

whereas for aromatic hydrocarbons (BTEX) and chlorinated compounds health risk is the determining factor.

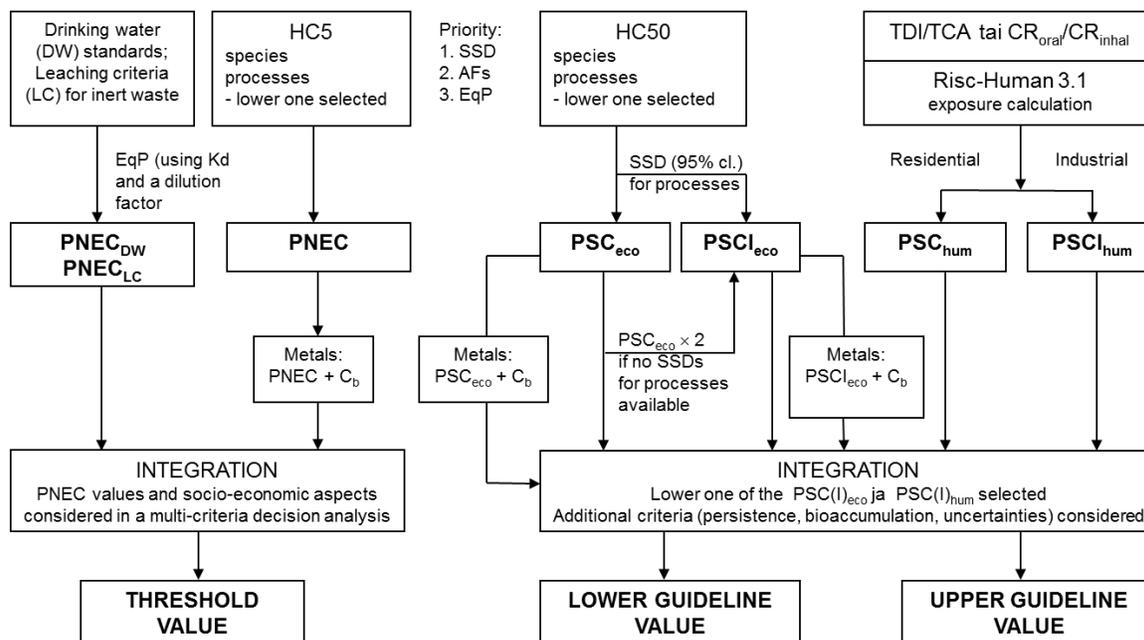


Figure 1. Derivation of the Finnish SGVs. PNEC = Predicted No-Effect Concentration, PSC(I) = Potentially Significant Concentration (I refers to industrial scenario).

Application of guideline values - prerequisites and challenges

The foundation of risk assessment relies on reliable site investigations, in which sampling is the most crucial step. Representative sampling and the development of a sound conceptual model are therefore prerequisites for any risk assessment, including the application of SGVs for both prevention and remediation of soil contamination. However, specific instructions on representative sampling for the different purposes of site assessment do not exist in many regulatory frameworks. Thus, the foundation of using SGVs in an appropriate manner – i.e. comparing them with valid sampling data – is compromised from the beginning of the decision making process.

In order to ensure that the results from sampling can be considered as representative for risk assessment, a systematic sampling approach has to be followed addressing both the theoretical and practical demands for representative sampling as well as the regulatory needs. The three main steps within a systematic sampling protocol are (e.g. Ramsey and Hewitt 2005; U.S. EPA 2000):

- Setting clear objectives;
- Defining proper 'decision units' (= 'assessment units' for the purpose of risk assessment); and
- Ensuring sufficient quality assurance.

By following such approach, representative concentrations for the defined assessment units, such as exposure routes or pathways for contaminant migration, can be derived. Representative concentration herein refers to a contaminant concentration in a single assessment unit that meets the requirements of risk assessment with adequate reliability. Hence, representative concentrations can be defined directly by representative sampling measurements or theoretical estimates (calculations) based on such data. When SGVs are applied in site assessment, sampling should in general provide reliable estimates of the average concentrations in the predefined assessment units for soil.

Many risk-based policy frameworks in different countries have adopted the traditional ‘tiered approach’ that proceeds stepwise from simple qualitative tier 1 assessment to more complex tier 2 and 3 quantitative assessments combined with using generic or land use-specific SGVs (e.g. Vegter *et al.* 2002). Although such approach has advantages, it can also be easily misused in which case it tends to provide information that is not the most relevant for defensible decision-making.

Firstly, the lower tier assessments with generic SGVs often result in very cautious risk estimates that do not necessarily reflect at all to reality. This is partly due to SGVs (e.g. when they are based on over-conservative assumptions and model parameters), but also to non-representative discrete sampling practices and using ‘maximum’ concentrations as a typical default to ensuring sufficient caution. Secondly, the very straightforward use of generic or land use-derived SGVs tends to ignore the actual, site-specific exposure setting and relevant protection targets with regard to the scenarios incorporated into SGVs. If the SGVs’ suitability to a specific site is not considered in detail, inconsistent and unjustified decisions are prone to be made.

In Finland, inconsistencies occur, for example, when the soil ecotoxicity-based SGVs are used as decision criteria for remediation even though the local soil ecosystem were not considered as a relevant protection target e.g. due to land use. In fact, according to a survey from 2014, protection of the terrestrial ecosystems was not mentioned as a driver for remediation in any single remediation case contrary to health risks and other environmental risks such as potential groundwater contamination. However, at the same time remediation need and its goals were determined based on the ecological SGVs in up to 95 % of the cases. From the perspective of risk-based decision-making, such practice is irrational. In addition, as the most typical remediation in such cases involves soil excavation and off-site disposal and refilling the excavation pits by virgin soil materials, it is reasonable to ask whether the soil ecosystem is truly being protected by such remediation. Applying SGVs to the whole soil matrix without defining representative assessment units has also been a common practice that does not promote sound risk-based decisions. Potential for significant exposure by soil ingestion, for example, covers only those contaminants that exist in the uppermost open topsoil (0-20 cm). Yet the SGVs, even for immobile compounds, are often applied also to subsoil and soils under pavements. SGVs that are mainly based on homegrown crops consumption or indoor air inhalation, on the other hand, do not correspond with the actual health risk when gardens or buildings do not exist on a specific site, but are still often used as such.

It should also be noted that if the derivation basis of the generic SGVs is not valid for describing the site-specific risks (e.g. due to excluded transport routes) even seemingly conservative tier 1 risk assessment that mostly relies on SGVs can provide a non-conservative risk estimate (Nathanail 2006). In addition, if the sampling strategy fails to meet the requirements of representative sampling, not even the use of ‘maximum’ concentrations necessarily ensures conservativeness, since the measured maximum never equals the true maximum, and can even underestimate the mean (e.g. ITRC 2012). Hence, the lower tier assessment approach with SGVs and unrepresentative sampling practice can also result in false perception of caution. Although such misuse of the SGVs is not intrinsically a deficiency of the tiered approach or the SGVs, based

on the Finnish experience these kinds of problems easily arise when the role of the SGVs and lower tier assessments in regulatory policy become too strong.

Discussion

It can be argued that the international debate and efforts with regard to improving SGVs have been concentrated a bit too much on their scientific background, whereas the proper application and implementation of the values into national regulatory frameworks have not drawn enough attention. In fact, the derivation basis of the SGVs is effectively irrelevant if the values are not applied in an appropriate manner. For example, where inclusion of bioavailability in human health risk assessment, a topic that has been extensively discussed in the literature, may allow for deriving a higher SGV roughly by a factor of two to ten, comparison of the same SGV to an unrepresentative sampling measurement may result in uncertainty that is several orders of magnitude higher. Parameters such as bioavailability are even less important when the derivation basis of SGVs does not correspond with the site-specific exposure setting or the relevant protection targets. In the Finnish case, the misuse of SGVs has actually turned out to be the greatest complication in the risk-based decision making as described in previous section. Based on the authors' experience, the same holds true for site assessments in many other countries.

Moreover, as risk assessment is an interdisciplinary procedure, combining e.g. science, policy, and regulations, also SGVs include elements that are not directly related to toxicological risks. The political factors, such as the acceptable risk levels, have actually been found to cause the greatest variation in SGVs based on several studies (e.g. Carlon *et al.* 2007; Provoost *et al.* 2006). Recognition of these different factors and understanding the rationale behind the numerical values are prerequisites for using them in a reasonable way. This should also be highlighted when new quality criteria are being developed or adapted from one purpose and regulatory context to another.

It is also evident that apart from environmental and health risks due to contamination, there are always a great number of other aspects and motives (i.e. regulatory, political, economic, social, operational etc.) that play an important role in decision making on a specific site (e.g. Ellis and Hadley 2009). Such factors often relate to land use and ownerships with potential long-term liabilities and uncertain cost estimates, and they have a direct influence on the risk management approach potentially favoring the use of generic SGVs. When decisions are being made from that premise, it is very important not to confuse these factors with the risk basis. Only by doing that can the actual risk-based decision-making on contaminated land be promoted. Hence, a decision that is based on SGVs because of common practice, avoiding future liabilities etc. is not a risk-based decision although it can be seen as being reasonable.

Conclusions

Justified risk-based decision making and sustainable management practice in the regulatory context of soil contamination is often compromised due to the very straightforward use of generic SGVs. Hence, contributing to the appropriate application of SGVs in addition to their scientifically sound derivation basis should be a common goal in all the regulatory frameworks worldwide.

To improve the situation in Finland, a new regulatory guidance on risk assessment and sustainable risk management has been introduced, highlighting realistic assessment approach as well as constraints of the SGVs and principles for their proper application (Reinikainen and Sorvari 2016). Sustainable risk-based decision making is also the starting point in the new national strategy for contaminated land management (Reinikainen *et al.* 2016). Moreover, the

Decree on risk assessment (214/2007) along with its SGVs is now under revision with the aim to advancing sustainable risk-based decision making even further.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.6. Development and implementation of health risk-based soil quality guidelines in Turkey

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Abstract

Soil Quality Standards (SQSs) are considered as an important tool for management of contaminated sites. In order to manage adverse effects associated with soil contamination, risk-based SQSs are used worldwide. However, developing health risk-based SQSs is a challenging work. It involves comprehensive assessment of nationwide site characteristics (e.g. soil, (hydro)geological, climatic properties), understanding of social behaviours that determine human exposure to soil contaminants (e.g. exposure scenarios and parameters), and making political decisions regarding economical concerns. To set these fixed level standards that apply for various cases and that is protective of human health, conservative assumptions should be made. While the level of conservativeness of the standards should not challenge the objectivity of the decision given and not force technical and financial resources. In regard of that challenge, a conceptual framework is developed for derivation of human health risk-based SQSs for Turkey. In this paper, the main elements of the established conceptual framework, the methods used for specification of the generic site characteristics, the information sources used for compilation of needed chemical and toxicological data, the political decisions taken, and the challenges encountered during implementation of the developed standards are discussed. It is believed that the developed framework and the shared experiences will assist other countries that are planning to develop health risk-based SQSs in a more efficient manner.

Keywords: soil contamination, risk assessment, risk-based soil quality standards, conceptual framework, site characteristics

Introduction, scope and main objectives

Together with air and water, soil constitutes the environment to sustain the life on earth. These three components are intimately related to each other through hydrologic cycle, which defines the occurrence, exchange and movement of water on the earth. In this respect, soil has two fundamental environmental functions; soil acts as (i) a receiving medium for disposal of wastes and (ii) a natural recharge zone for surface water and groundwater (Ünlü *et al.* 2009). Consequently, the quantity and the quality of surface water and groundwater are directly affected by soil, and because of its role in hydrologic cycle, soil appears as a key element in terms of environmental pollution problems. Since soil serves as an underlying material for various human activities, it became a receiving body for various contaminants. In many countries and also in Turkey, poor waste management practices, discharge of wastewater, application of herbicides and pesticides onto soil for agricultural purposes, spills, leaks and/or discharge of chemicals during handling, storage and transportation result in complex environmental problems threatening human health and ecology (Swartjes 2011). Because of the widespread occurrence of soil contamination events and its effects on human health and environment, soil quality has been an issue taken more seriously during the last three decades. During this period, significant improvements have been recorded related to identification, registration, assessment, and clean-up of contaminated sites in terms of frameworks and technological developments. Since the number of contaminated sites increased significantly, mostly due to industrial and agricultural

activities; many countries, environmental agencies and organizations configuring their framework by integrating efficient management systems for contaminated soils.

In this respect, most EU Member States and the North American Countries define risk-based approaches as the best available strategy for dealing with the problems posed by soil contamination, assessing the need for clean-up and planning remedial actions. Because of the success achieved, the risk-based site management approaches have been included in the environmental policy of many countries (NICOLE 2002), and risk-based SQSs are used in most European countries (e.g., Austria, Belgium, Germany, the Netherlands, United Kingdom, Norway, Sweden, Spain, etc.), Canada, and the USA, either to define target levels, to screen sites that do not need further investigation, to determine the urgency of remediation, or as clean-up levels.

As an important tool of contaminated site management, the intended purpose of use of the risk-based SQSs varies, and thus they have to be developed based on the specific needs of the country. Because derivation of risk-based SQSs, which indeed is a highly challenging process, requires a comprehensive assessment and understanding of the environmental, socio-cultural, and economical conditions of the country. While developing country-specific SQSs, the regulatory needs of the country in terms management of contaminated sites and priority pollutants based on the common potentially polluting activities taking place within the country should be identified, and the key elements for derivation of SQSs should be specified. As risk-based SQSs are based on the source-pathway-receptor analysis, these elements involve assessment of source characteristics (e.g., source type, size and depth, contaminants of concern and their fate and transport characteristics), site characteristics (e.g., soil, geology, hydrology, climatic conditions, etc.), receptor characteristics (e.g., exposure duration and frequency, body weight, etc.), and the potential exposure pathways (e.g., ingestion, dermal contact, inhalation, etc.), which connect the source to the receptors. In addition, it is needed the determination of generic figures that are reasonable to apply for various cases, conservative enough to protect human health, and objective not to force technical and financial resources.

In regard of these challenges, a conceptual framework that identifies the essential steps for derivation of human health risk-based SQSs is developed for Turkey. In this paper, the main elements of the established conceptual framework, the methods used for specification of generic characteristics, the information sources used for compilation of needed chemical and toxicological data, the political decisions taken, and the challenges encountered during these studies are discussed. It is believed that the developed framework and the shared experiences will assist and guide the countries that are to face with inevitably the huge stock of technical documents available in the literature.

Methodology

Although development of risk-based SQSs relies on the same principles, different countries end up with different generic standards depending on the scientific approaches they adopt, the use of different assumptions, toxicological data, generic site-characteristics, accepted risk level, etc. (Carlon *et al.* 2007). Therefore, it was essential to review the approaches used in different countries to attain a background and to establish a conceptual framework for development of SQSs.

The conceptual framework established for development of generic SQSs for Turkey consists of two main tasks. The first task was to attain a general overview of the approaches for derivation of health-risk-based SQSs, identification of the needs, while the second task was the derivation of the generic site characteristics for Turkey to be used in the development of risk-based SQSs. In

the first task, the approaches of European and North American Countries for development of health-risk-based SQSs were investigated thoroughly; the scientific approaches, the assumptions made, and the data used in derivation of standards were compared. The regulatory needs of Turkey in terms of contaminated site management were evaluated and the role of SQSs in the management system was specified. In order to determine the priority pollutants to be included in the regulation, potential soil polluting activities in Turkey and potential soil pollutants arising from these activities were identified. With the insight gained from other countries' approaches, the most appropriate approach to be utilized for development of Turkish SQSs and the necessary modifications to this approach were identified in consideration with the regulatory needs. The key elements for derivation of health-risk-based SQSs, such as acceptable (target) risk level, generic exposure (land use) scenario, relevant exposure pathways, generic values for the exposure parameters and contact rates, and chemical-specific data requirement were determined. Since risk-based SQSs are developed in conjunction with the national site-specific properties, generic site characteristics for Turkey were needed to be derived. In this respect, the second task was specification of the generic soil characteristics, derivation of air dispersion factors that represent the dispersion of soil contaminant (i.e., volatiles and fugitive dusts) emissions in air under regional meteorological conditions, and specification of the other site characteristics that control generation of fugitive dust emissions. Figure 1 schematically illustrates the conceptual framework of the study on derivation of health-risk-based SQSs for Turkey. In the end, human health risk based SQSs were calculated by using the values defined for the abovementioned parameters.

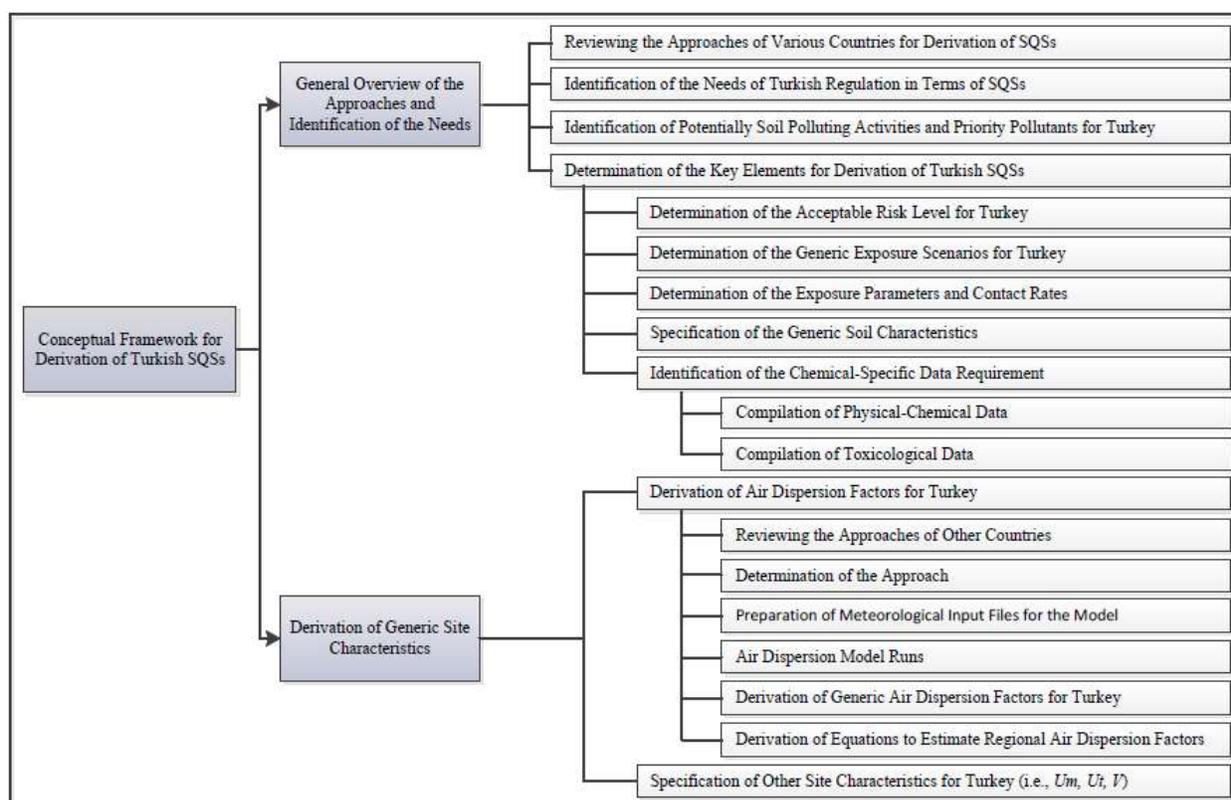


Figure 1. Framework of the study on developing health-risk-based SQSs for Turkey

Results

In this study, a two-phased approach was used for development of human health risk based SQSs for Turkey. In the first phase of the study, the conceptual framework for derivation of human health risk based SQSs was established.

Derivation of human health risk based SQSs involves use of a large amount of information and data, which are progressively subject to changes or upgrades. SQSs derivation process is very dynamic in nature, because SQSs are sensitive to changes in

- exposure parameters and contact rates that differ with respect to the exposure scenario and receptors of concern,
- generic site characteristics with respect to soil, hydrogeologic and climatic conditions,
- physical-chemical and toxicological properties of contaminants, which are periodically upgraded or newly produced through recent scientific research.

Therefore, to maintain the sustainability and currency of generic and site-specific SQSs, the improvements in the toxicological and other scientific research should be monitored continuously and SQSs should be upgraded with the use of latest information or data produced.

Consequently, the second phase of this study aimed developing the technical infrastructure for derivation of Turkish human health risk based SQSs that ensures the sustainability, maintenance and dynamism of the Turkish contaminated sites management system. One specific task to achieve this objective is development of a computational tool (called exposure model), which includes the physical-chemical and toxicological data libraries embedded in its structure, to facilitate calculation of generic and site-specific SQSs and to eliminate the potential calculation mistakes that may result due to various parameter values and chemical-specific data used in calculations.

On the other hand, generic and site-specific risk assessment entails a comprehensive understanding of the soil and hydrogeological (groundwater) conditions at contaminated sites (URL 1). These conditions are significant for determination of the generic site characteristics to be used in calculation of generic SQSs, calculation of site-specific SQSs, assessment of the dilution conditions as contaminants leach from soil to groundwater, development of pertinent conceptual site models (CSMs) during site assessment studies, characterization of site conditions and development of accurate sampling strategies.

In this regard, another task to strengthen the technical infrastructure is development of a Geographical Information Systems (GIS) based soil/hydrogeological database (S/HGDB) which includes the general soil and hydrogeologic characteristics of a site needed for human health risk assessment studies. The sub-tasks for development of the S/HGDB involves delineation of the basic hierarchic mapping and management units (i.e., groundwater regions, and groundwater bodies within each groundwater region) that enables collecting easily manageable soil/hydrogeological data at both regional and local scales in a systematic manner, and development of the descriptive infrastructure of the database specific to each groundwater body within a region.

Discussion

To maintain the sustainability and currency of SQSs, the improvements in the toxicological and other scientific research should be monitored continuously and SQSs should be upgraded with the use of latest information or data produced. Thus, conceptual framework should be enhanced

with the technical infrastructure for derivation of human health risk based SQSs that ensures the sustainability, maintenance and dynamism of the contaminated sites management system.

One specific task to achieve this objective is development of a computational tool (called exposure model), which includes the physical-chemical and toxicological data libraries embedded in its structure, to facilitate calculation of generic and site-specific SQSs and to eliminate the potential calculation mistakes that may result due to various parameter values and chemical-specific data used in calculations.

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Conclusions

The developed SQSs are subject to periodic upgrade and update. Thus, necessary efforts should be put in for upgrade of generic site characteristics with the recently obtained field data, development of scientifically based dilution factors (DFs) for Turkey, monitoring recent chemical-specific data and re-calculation of generic SQSs accordingly.

For Turkey, the human health risk based SQSs were developed for residential land use scenario by considering four generic exposure pathways (i.e., ingestion-dermal contact, inhalation of volatiles, inhalation of fugitive dusts and ingestion of contaminated groundwater). However, additional exposure scenarios (e.g. agricultural land use) and pathways (e.g., inhalation of volatiles in indoor air) may be considered for development of generic SQSs in the future depending on the requirements in this field. Besides, it is known that ecological risk based SQSs are vital for protection of the ecosystem. Thus, future studies should focus on this subject.

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4.1.7. Soil restoration and management of the UNESCO MAB Maya Biosphere Reserve and Trifinio Fraternidad forest ecosystems in Guatemala, Central America

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Abstract

Human and wildlife well-being are indispensably linked to forest ecosystems, soil and water resources management. Nevertheless, the impacts of anthropogenic activities and extreme weather events affect not only the global environmental sustainability but also the quality of life of most populations. In order to protect rare ecosystems, international strategies and frameworks have been established for both the public and private sector. Furthermore, the principles of environmental education and awareness have become global necessities, especially for the stakeholders and young generations, whereas, innovative approaches in the fields of agroforestry and soil and water protection are the key products for the conservation of ecosystems, local culture and uniqueness. This research tries to contribute in the crucial fields of soil restoration and management by emphasizing the importance of forests and their “smart” use without causing any impact to their characteristics or biodiversity. To further support its philosophy, this research investigates the UNESCO MAB areas of the Maya Biosphere Reserve and Trifinio Fraternidad, located in Guatemala.

Keywords: Environmental Sustainability, Forest Ecosystems, UNESCO MAB, Soil and Water Resources

Introduction, scope and main objectives

The “Strategy National Forest Landscape Restoration: Mechanism for Sustainable Rural Development of Guatemala, 2015 – 2045” was first launched on May 14th, 2015, in Guatemala City. It aims to restore forest ecosystems under the processes of recovery, conservation and optimization of biological diversity, flow of rural goods and services, as well as to protect soil and water resources against human overexploitation and natural hazards for the sustainable development of local communities and unique ecosystems. Forest restoration can be defined as “the process aimed at recovering ecological integrity and improving human welfare in deforested areas or degraded forest

landscapes" (IUCN, 2005); whereas, environmental services are all those benefits provided by forests and productive ecosystems to man. It is a mechanism of monetary compensation or flexible compensation and it is adaptable to different conditions, which points to a payment or direct compensation for the maintenance or provision of an environmental service, by the users of the service, which is destined to the suppliers" (Technical C, 2014 P. 54). However, soil pollution that is primarily caused by xenobiotic chemicals results in land degradation and other alteration in the natural soil environment besides the multiple health risks. Industrial and agricultural activities, including any improper disposal of wastes are the main factors of soil contamination. EPA, U. (1989). Risk assessment guidance for superfund—Human health evaluation manual (Part A) (Vol. I). Interim final.

Soil pollution is a spreading threat for global ecology; nevertheless, efforts are made to minimize its impact especially in protected areas. In Guatemala and other countries of Central America, forest restoration seeks to contribute to the construction of sustainable livelihoods in rural villages that depend on natural resources that are essential for the forestry sector, such as the issue of firewood for energy purposes. In this sense, it is necessary that any process focused on conserving ecosystems, to be sustainable and generate economic incomes without impairing the conservation of local environments. Considering this, it can be stated that agroforestry systems with species and forest products of high commercial value, such as coffee, cocoa, xate and cardamom under systems with shade trees as well are forests with high calorific value for energy purposes. Furthermore, it is necessary to establish an integral vision of the sectors that are intrinsic parts of sustainable ecosystems.

Any human activity should be the outcome of balanced environmental management and social governance; since the decisions can affect the prosperity of local populations. Therefore, territorial forest governance should promote inter-institutional coordination and integration of efforts to achieve agreements and consensus, which favours the consultation, implementation and evaluation of measures that produce concrete results in the territories. The contribution of science and technology is a starting point for evaluating the policies and strategies that emanate sectorally (government, private sector, academia and civil society), since they generate high expectations for compliance, even so; by several factors to mention: lack of budget, indicators not affordable to comply, lack of monitoring etc. or on the contrary, it turns out to be a mechanism applicable to different regions whose results can be combined with efforts to counteract the effects of climate change and other extremes.

All those mentioned previously are based on the Sustainable Development Goals (SDG) for the availability of raw material from productive chains, actions in the face of vulnerability to the effects of climate variability, which affects the region as well as the relationship of the forest ecosystem with other economic sectors in the country.

This research uses the Strategic Environmental Analysis (AEA) as a tool.

In the words of Herrera and Madriñán (2009), EAE is a support instrument for the incorporation of the environmental dimension into strategic decision making, which are usually identified with policies, plans or programs. It is a procedure to improve these planning instruments. "The fundamental purpose is to advance in the full development of environmental and sustainability policies from the first decision stages, those in which the basic intervention frameworks are defined and, therefore, those that in general have a greater ability to determine the final environmental effects in the environment and its sustainability in the medium and long term "(Herrera and Madriñán, 2009 p.13).

The contribution of the research has four major pillars:

- To evaluate the integration of public policies implemented in Guatemala on the issue of forest restoration and thereby measure the processes of effectiveness and efficiency, to meet the needs of citizens at the lowest possible cost.
- To integrate the evaluation of public policies, applying the instrument (AEA).
- To publicize how restoration projects prepare a road map and how they contribute to the conservation of ecosystems.
- To determine how the UNESCO MAB Maya Biosphere Reserve and Trifinio Fraternidad areas are part for the soil conservation.

The general objective is to evaluate the progress of the components of the National Forest Landscape Restoration Strategy. Three specific objectives have been defined:

- To determine the impacts of economic development from sources that generate income, employment, goods and services.
- To evaluate the livelihoods and biological diversity of the use of native species, provision of goods for subsistence (food, medicine and firewood) and the use of native species that contribute to the maintenance of ecosystem services.
- To determine territorial forest governance oriented to the development of technical, administrative and financial capacities of government institutions, non-governmental organizations, indigenous peoples, the private sector, local governments and academia.

Additionally, the research project is divided into five chapters as follows:

Chapter I: Background Referential Framework of the Forest Ecosystem at the international and national levels

That is the framework of the Sustainable Development Goals (SDG) specifically the objective No. 15 forests. Likewise, the REDD + strategy and how both are linked to the Public Investment System (SNIP) as part of the country's National priorities within the framework of the National Development Plan of the K'atun 2032 Plan.

It describes in a general way how the ENRPS was elaborated, who participated, the content, the budget; how the forestry incentives and Decree 2-2015 of the PROBOSQUE Law sustain the national restoration strategy.

Chapter II: Approach of the research problem and the approach

The chapter is divided into two phases: in the first, the approach to the research problem is presented, the importance and relevance of its study is explained, and the problematizing question, the general theme and the objectives of the research are presented. . In the second phase, the methodological guidelines are presented, highlighting the SEA, describing the type of research carried out and indicating the methods used to obtain the information.

Chapter III: Strategic Environmental Analysis in Forest Ecosystems

In this chapter, what is described is what the SEA consists of as a support instrument for the incorporation of the environmental dimension into strategic decision making, which are usually

identified with policies, strategies, plans or programs and; as such it is a procedure for improving these planning instruments.

The fundamental purpose is to advance in the full development of environmental and sustainability policies from the first decision stages, those in which the basic frameworks of intervention are defined and, therefore, those that in general have a greater capacity to determine the final environmental effects in the environment and its sustainability in the medium and long term.

The fundamental purpose of the SEA is to facilitate a support structure to develop a strategic environmental assessment of plans and programs that improve the integration of the environmental dimension and sustainability into plans and programs. (Herrera and Madriñan, 2009 p.13).

Linked to one of the justifications of the research, the evaluation of public policies, the EAE, focuses on the levels of hierarchy in decision-making. Policies are at the top of decision-making. Evaluation at the policy level tends to deal with more flexible proposals and a broader range of scenarios. The evaluation at the project level usually has well-defined and prescribed specifications "(OECD, 2007). In other words, the SEA is a useful tool for evaluating the ENRPS, since it meets the issue of public policies, as much as the scope of decision making as the natural environment.

Chapter IV: Maya and Trifinio Areas.

Boosting socio-economic development and environmental sustainability under smart disaster management strategies in the Maya Biosphere Reserve (MAB)

Human and wildlife well-being are indispensably linked to forest ecosystems, watercourses and bodies. Nevertheless, the impacts of anthropogenic activities (farming, deforestation, waste pollution) and extreme weather events (hurricanes, floods, torrents) affect the environmental sustainability worldwide. In order to protect rare ecosystems, international strategies and frameworks have been established for both the public and private sector. Furthermore, the principles of environmental education and awareness have become global necessities, especially for the stakeholders and young generations, whereas, ecotourism, as a key product of such awareness activities, has resulted not only in the conservation of ecosystems, local culture and uniqueness but also in economic benefits.

There is no doubt that a lot have been achieved in environmental protection and disaster resilience of vulnerable groups and natural sites; yet, strategies which solely focus on isolated concerns sound rather inefficient when ecosystems and their affected populations must cope with a plexus of survival problems, especially after the occurrence of natural and manmade disasters. Although relative innovations in science and technology have resulted in fascinating discoveries, the promising “marriage” of Ecosystem Conservation, Socio-economic Growth and Disaster Management is rather unexplored.

This research introduces a progressive scheme that aims to change the current thinking of dealing with extreme water-based threats in unique forest ecosystems by investing in “disaster-harvesting” for both increasing the survival rate of their habitants in cases of emergency and providing a mixture of alternative solutions for disaster resilience, socio-economic development and biodiversity protection.

Additionally, it explores ways of connecting autonomous ecosystems and their communities with each other in order to further promote ideal environmental globalization models under the principles of 2030 Agenda for Sustainable Development and the UNESCO Man and the Biosphere Programme (MAB).

The expected results will provide sufficient information in the following issues:

- How can illegal deforestation, farming and other human activities be stopped while the local populations can develop new skills that do not harm the environment (e.g. ecotourism activities)?
- How can the local government and the population secure environmental sustainability, turning the Maya Biosphere Reserve into a global model of successful ecosystem?
- How can science and technology, as well as the expertise of other ecosystems in Europe and Asia can provide disaster resilience and benefits (e.g. electric power) to populations of the Maya Biosphere Reserve without affecting its unique flora and fauna?

Evaluation in the System of Monitoring of Management of Protected Areas in the Trifinio Biosphere Reserve Guatemala (MAB).

Methodological proposal of evaluation in the System of Monitoring of Management of Protected Areas in the Trifinio Biosphere Reserve that cover Guatemala (MAB) has as objective: Strategic Environmental Analysis, Public Policies, Public Investment System, Forest Restoration and Governance among others as a fundamental mechanism in the fulfillment of Sustainable Development Goal (SDG) No. 15 (Territorial Ecosystem Life) and SDG No. 13 Climate Action.

The Trifinio Biosphere Reserve is a key function of this mountain area that guarantees the supply of water for local communities. It also plays an important role in regional development through the promotion of coffee activities, the extraction of coniferous forests and agro-tourism. This biosphere reserve has received strong support at high political levels (vice ministers of the three countries), as well as the participation of local communities in the promotion of sustainable development.

It should be noted that Trifinio MAB is an urgent measure of protection, so that the effects of climate change, which affects the Central American region, are mitigated.

Likewise, the contribution of the study is the link with the stakeholders of Guatemala, as an example of governance with a Sustainable Development approach aligned with the 2030 Agenda, as well as linking the Institution Rector of MAB in Guatemala Consejo del Áreas Protegidas (CONAP) and Secretaría de Planificación y Programación de la Presidencia (Segeplán) is the leading institution of public policies, public investment and focal point of the SDG.

The proposal has a multidisciplinary, intergovernmental and inter-institutional approach.

Multidisciplinary: Exact sciences are complemented with social sciences, complying with the MAB guidelines, combining the natural and social sciences, economics and education to improve human lives and the equitable sharing of benefits, and to safeguard natural and managed ecosystems, thus promoting innovative approaches to economic development that are socially and culturally appropriate, and environmentally sustainable.

It complies with the Intended Nationally Determined Contributions (INDCs), which is part of the Paris Agreements and the 2030 Agenda.

Inter-institutional: various institutions that link stakeholder and the natural environment

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Secretaría de Planificación y Programación de la Presidencia <http://www.segeplan.gob.gt/nportal/> both complement each other they are part of Guatemala Government.

American Association for the Advancement of Science <https://www.aaas.org/> and UNESCO CHAIR for the Conservation and Ecotourism of Riparian and Deltaic Ecosystem <http://unescochair.teiemt.gr/> [List any people to thank or funding sources]

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.8. Lessons learned after 20 years of soil remediation policy in Flanders

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Abstract

In 1996, Flemish soil remediation was boosted by the Soil Remediation Decree. In this decree, tactical choices were made leading to new legal instruments. In 2006, the Flemish government decided to adapt a new contaminated land decree. The novelty of this decree consisted in the fitting of soil remediation with the plans for land management by the individual owner. Prevent new contamination and remediate historical contamination are the main objectives of this Decree for soil remediation and soil protection.

After 20 years of soil remediation policy Flanders learned that most of the instruments were successful for the planned purpose, namely the remediation of the historical contaminated land in a period of 40 years. Some instruments needed an adjustment. Finally, new policies were installed in 2018 through an amendment to the decree.

Keywords: soil policy, soil investigation, land information register, soil certificate, obligation for remediation, transfer of land, risk-assessment

Introduction

In 1996, Flemish soil remediation started with the Soil Remediation Decree. In this decree, tactical choices were made leading to a number of new legal instruments:

- a difference between historical and new contamination was made: it gives a signal to pay attention to pollution prevention, on the other hand flexibility was guaranteed to treat the old problems;
- a difference was made between obligation to remediate and liability;
- an economical driving force is linked to soil remediation: land transfer. Soil quality becomes an element of real estate price;
- a duty for local authorities to develop an inventory of risk-sites was installed. A risk-site is a parcel of land where an activity has or had an elevated risk for soil contamination.

In 2006, the Flemish government decided to adapt a new contaminated land decree. Prevent new contamination and remediate historical contamination are the main objectives of the Decree for soil remediation and soil protection from 27th October 2006, ratified by the Flemish government. This decree came into force on June 1, 2008 by the VLAREBO (Order of the Flemish Government of 14 December 2007 regarding soil remediation and protection).

After 20 years of soil remediation policy Flanders learned that most of the instruments were successful for the planned purpose, namely the remediation of the historical contaminated land in a period of 40 years. Some instruments proved to be less effective while others needed an adjustment. Finally, new policies were installed in 2018.

Soil investigation

There is an obligation of investigation of soils at the moment of property transfer, on a periodical base or by closure of certain installations who can or could cause soil contamination. The authorities may also gather information as a result of its investigations into soil quality. The preliminary investigations include a limited investigation into the history of the soil, as well as restricted sampling operations.

If these investigations indicate the presence of contaminating substances, the need for further soil investigation depends on comparison of the concentrations with soil remediation values. During a descriptive soil investigation, the contamination will be characterized in detail and the risk for humans and ecosystems will be defined. The aim of this investigation is to give a description of the nature, quantity, concentration and origin of the contaminating substances, the possibility that these might spread, and the danger that human beings, plants and animals, as well as surface and groundwater, might be exposed to the contaminating substances.

After 20 years of experience, the OVAM has learned that good procedures for soil investigation are necessary to have a level playing field. The ordering party has to know what kind of efforts are demanded in his specific situation. Local situations can be very divers, so procedures have to describe clearly, what is required. A clear linkage of the different investigation steps is necessary to save costs.

Until 2018, each individual soil investigation was assessed by the OVAM. The OVAM stated the accordance with the guidelines or required additions to the soil investigation. By the amendment of the Soil Decree in 2018, the general assessment of soil investigations was abolished. After 20 years, soil remediation experts have developed sufficient maturity to work in accordance with government guidelines. To maintain the quality of the soil investigations, the decree provides for an audit of the experts.

Need for remedial operations

There is made a distinction in policy depending on the origin of the soil contamination. "Historical" soil contamination is contamination originated before the first Decree came into force; this is before 29 October 1995. "New" soil contamination originates after the Decree came into force.

The remediation of new pollution is, according to the Decree, required as soon as the soil remediation values are exceeded. With respect to historical contamination, the decision to remediate will depend on the actual danger to man and the environment (non-quantified general criteria). Therefore, a risk-assessment approach is followed in the descriptive soil investigation. The remediation actions are determined in a soil remediation project. The Public Flemish Waste Agency (OVAM) supervises the remediation operations.

Land information register (LIR)

The Land information register is an inventory of all the parcels of which data are known at the OVAM. The LIR serves as a database for policy decisions and functions as an instrument to protect and inform potential buyers of contaminated sites. The LIR is open to the public. The soil certificate, an extract of this register for a specified ground, gives all the information known by the OVAM. The maintenance of the register requires a lot of work but the retribution that is asked for the soil certificate brings the OVAM more than 12 million euro a year.

Obligation for remediation and liability

In the Flemish Soil Decree, a remediation obligation rests on the operator, the user or the owner of the land where the pollution entered the soil. This means also that the obligation does not rest on the owner of the land contaminated by migration of contaminating substances from another property. If new contamination is concerned, the obligation exists automatically. In the case of historical contamination, the obligation only arises after the remediation order by the government.

The Flemish Soil Decree introduced a non-retroactive strict liability rule and channeled the liability for the new contamination to those that caused the contamination. Recourse against other responsible parties is however possible. With respect to historical contamination, liability is determined by the rules in effect before the decree came into force.

The user or operator of the land where the pollution entered the soil is not obliged to carry out the remediation if he can prove that he did not cause the contamination himself (by his fault or otherwise) and that the contamination did not come to existence in the period of the use of the land. The owner needs to prove that next to these requirements he was not and should not have been aware of the pollution when acquiring the property. In addition is the owner for historical contamination not obliged to carry out the remediation if he proves that the contaminated land was acquired prior to 1993 and was since then exclusively used for a non-professional use although he had prior knowledge of the pollution.

The legislation with the obligation to remediate has proved to be a strong instrument to realize effective remediation works. The polluter of historical contamination is very often difficult to find. The system of exemption of the obligation has to be worked out well to keep the burden for the owners socially acceptable and fair.

Execution

The various steps in the soil remediation procedure need to be carried out under the direction of an independent soil expert accredited by the OVAM, the so-called soil remediation expert. This expert must follow the standard procedures and codes of good practice as established by the OVAM for the execution of his tasks. Likewise, sampling and analyses must be carried out by an accredited agency.

The preliminary soil investigation examines whether there are serious indications of soil contamination on a given site. This involves a limited historical examination and limited sample taking. The preliminary soil investigation will be conducted:

- on the initiative and at the charge of the transferor, before the transfer of lands at risk. These are sites on which a facility is or was established or where an activity is being or was carried out that is included in the list of potentially contaminating activities;

- on the initiative and at the charge of the operator, before the closure of a facility or the cessation of an activity on the 'list';
- on the initiative of the operator before a certain date, and, thereafter, periodically, for some categories of activities or facilities that are included in the 'list'.

The OVAM may conduct an ex officio preliminary soil investigation at any time. The OVAM can also send an investigation order to an owner if there are indications of a serious contamination.

After 20 years of experience, we know that some land with historical risk-activities is not investigated through this kind of obligations. Flanders adjusted the soil decree, so that the owners of that land have to execute a preliminary investigation before 2027. To guarantee the quality of all soil investigations and remediation works a system of independent and accredited soil experts proved to be very helpful.

Soil remediation project

The soil remediation project, drawn up by the soil remediation expert, establishes the manner in which the soil remediation works are to be carried out. In this process, consideration is given to the best available technical solutions that already have been successfully tested out in practice and whose price is not unreasonable in proportion to the achievable result in terms of protecting people and the environment (the BATNEEC principle).

Remediation of new contaminated soil is in the first place geared to the broadest realization of target values regarding soil quality. Depending on the actual situation and characteristics that are specific to the site, it may not be possible to realize the target value by application of techniques that do not result in excessive costs in some well-defined instances. In these cases, soil remediation is oriented towards the realization of a better quality than that defined by the soil remediation standards or, if this also is not possible, to the avoidance that the soil quality should constitute a risk or could/might constitute a risk for people and the environment. For historical contamination, the aim of the remediation is to remove the risk for human and the environment. For soil remediation projects, a special procedure based on input and advice has been established, taking into account the special nature of soil remediation projects and the fact that, in general, soil remediation projects are established in the public interest, and that their execution must not needlessly be delayed by an accumulation of administrative procedures.

In this respect, the involved owners and users are advised by the OVAM of the submission of a soil remediation project. They have the opportunity to check out the soil remediation project at the OVAM and at the municipal offices and are given the opportunity to raise objections and remarks. If the needed soil remediation works are subject to a permit, expert advice is also obtained from other competent administrations and local authorities.

Based on the assessment of the soil remediation project, the recommendations, objections and/or remarks and comments received, the OVAM will issue a conformance certificate or request additional information on the submitted soil remediation project. This conformance certificate serves as a permit for the planned execution of the soil remediation works.

Soil remediation works

Following the declaration of conformity by the OVAM of the submitted soil remediation project, the remediation works can be started. Soil pollution can be remediated via different remediation techniques or a combination of such techniques. These remediation techniques may include the

removal or elimination of the contamination or remain restricted to isolating and immobilizing it. Although the removal of the pollutants is in many instances the most efficient solution, this may in certain instances not prove the most advisable method (unacceptable risk factors, extremely high costs vis-à-vis other remediation techniques, etc.).

The results of the soil remediation works must be reported to the OVAM in a final evaluation report. Based on this final assessment report, the OVAM can deliver a final declaration, in which the results of the soil decontamination are listed. If further follow-up measures are deemed necessary, these will be imposed accordingly in the said final declaration.

Transfer of land

Before concluding an agreement regarding the transfer of land, the transferor must request a soil certificate from the OVAM. By transfer of land is meant, amongst others:

- the transfer inter vivos of the property title;
- the merger of legal persons, at least one of which will be owner of the land;
- the splitting of a legal person who is owner of the land.

In the event of a transfer of land on which an activity is or was carried out or a facility is or was established that is included in the 'list', it will also be necessary to conduct a preliminary soil investigation in advance of the transfer. In the event that the preliminary soil investigation indicates that a descriptive soil investigation is called for, the OVAM will inform the transferor that such a descriptive soil investigation is needed. If from the descriptive soil investigation it appears that a soil remediation project needs to be instituted, the transfer may only take place on condition that the transferor:

- has drawn up a soil remediation project in conformity with the legislation;
- has committed himself vis-à-vis the OVAM to carry out soil remediation works;
- has provided financial security.

All of the above-mentioned obligations may be assumed by the buyer of the land or by a party with legal title to proceed to the execution of transfer. The obligation to give guarantees about the soil remediation as a result of a transfer of land has proved to be a powerful instrument in the Flemish soil policy. An economical driving force has been linked to soil remediation. Soil quality has become an important element of real estate price.

Risk assessment

The methodology for site-specific risk assessment is based on the approach followed to derive soil remediation standards. A generic approach is followed for the derivation of soil remediation standards, while for site-specific risk assessments certain parameters, such as soil properties, can be adjusted.

Soil remediation standards are based on the protection of human health and on the protection of the ecosystem. Critical values for concentration in the soil are calculated based on human toxicology and others based on ecotoxicology. The most critical value is retained as soil remediation standard. Soil remediation standards for groundwater represent drinking water quality.

The use of excavated soil

During construction projects, road works, installation of utility cables and similar operations, volumes of soil are excavated or stripped from the surface. Sometimes this excavated soil is re-used as filling material on the excavation site. In most cases, however, the excavated soil will be carried off for re-use on other locations. Soil can be re-used for instance for raising the profile of a terrain or filling of pits.

If infrastructure works are carried out on a contaminated site, chances are very real that existing soil contamination will be spread. In order to prevent this dispersion of soil contamination and to offer sufficient legal security to the different actors involved in the use of excavated soil, the Flemish government drew up directives related to the use of excavated soil. In order to meet the predefined targets, the regulations on the use of excavated soil first impose a soil quality survey. The nature of the excavation works and the volume of soil that is released by them will determine the type of strategy that has to be followed. Secondly, the regulations fix the conditions for the use of the excavated soil. Depending on the soil quality, the site for re-use and the anticipated application, the excavated soil can be re-used in-situ or elsewhere under certain conditions. The basic principle here is the standstill principle, which means that no deterioration of the current environmental condition is allowed. Finally, a tracking procedure guarantees the administrative follow-up of the active soil flows.

The OVAM is acting as the supervising authority in the regulation on the use of excavated soil. The administrative follow-up of the active soil flows is carried out by different organizations (soil management organizations, interim storage facilities and centers for soil purification) that have been accredited by the OVAM.

Conclusions

After 20 years of soil remediation policy Flanders learned that most of its instruments were successful. The policy goal to remediate the historical contaminated land in a period of 40 years, so before 2036, required some adjustments to the Soil Decree in 2018. The general assessment of soil investigations was abolished. After 20 years, soil remediation experts have developed adequate maturity to work in accordance with government guidelines. To maintain the quality of the soil investigations, the decree provides an audit of the experts. In addition, Flanders adapted the soil decree, so that the owners of potentially contaminated land have to execute a preliminary investigation before 2027.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.9. The soil certificate – a tool creating awareness about soil pollution

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Abstract

Since 1996, a soil certificate must accompany each transfer of land in Flanders. The certificate contains information on soil pollution. It is a legally obliged information tool to protect acquirers. The certificate helps to raise awareness: 1) of the possible impact of soil contamination on the 'economic' value of land. It gives a stimulus to owners to take good care of the soil in order to enjoy the benefits of their land, within the framework of the free market principles; 2) of the importance of soil quality for a healthy living environment. By highlighting land as a common and adding information to the certificate that raises awareness of these issues, the OVAM stimulates the owner to consider not only his 'property rights' but also his 'property obligations' towards society.

Keywords: soil policy, soil certificate, transfer of land, awareness, residual contamination, usage recommendations

Introduction

In Belgium, the policy area 'Environment and Nature' (including the waste and soil regulations) is a strictly regional issue. As a result, Flanders was able to follow its own path in the development of a soil policy. One of the major challenges confronting the new Flemish Government in the early 1980s was the rapid increase in waste production and the related increase in uncontrolled landfills and dumpsites. In order to cope with this new societal challenge, the 'Waste Decree' was enacted in 1981, establishing a single 'waste society' for the entire Flemish territory: the 'Public Waste Society for the Flemish Region'. The OVAM was born. Initially, OVAM's task was mainly waste-oriented: waste prevention, stimulating the reuse and recycling of waste and, if necessary, the removal of dumpsites that posed a threat to public health or to the environment.

With the latter task, it became clear that in many cases, pollution had often spread to adjacent areas. The OVAM quickly acknowledged the causality between the contaminants present in the landfills and the pollution found. Based on an article from the Waste Decree that stated that the OVAM had the possibility to remove all contamination that poses a threat to public health or to the environment, the OVAM took its responsibility and increasingly paid attention to soil contamination. At the same time, in Flanders (as elsewhere in Europe) the negative effects of decades of industrial activity on soil quality became clear, requiring the authorities to react appropriately and demanding action from the involved parties. It became obvious that a specific soil policy and a separate soil regulation was needed.

From Soil Remediation Decree to Soil Decree

This specific soil regulation came with the 'Decree of February 22nd 1995 on soil remediation' (brief: 'Soil Remediation Decree'). The Soil Remediation Decree had two main objectives: the remediation of contaminated land and the prevention of soil pollution on the one hand, and the protection of new landowners against the (unexpected) presence of soil contamination on the other. Newly created contamination has to be removed immediately. A less stringent approach for contamination that had originated in the past was opted for. For this reason, the terms 'new' and 'historical' contamination were introduced and the enactment date of the Soil Decree (29 October 1995)

determined the qualification. In addition, the government's ambition was to have at least started the remediation of all historical contaminations by 2036.

In order to meet these goals and this ambition, an inventory of all contaminated sites was required. For this purpose, there had to be a way to investigate the so-called 'risk entailing sites' (sites on which potential soil-polluting activities took place or had taken place in the past). After all, one of the major problems that had led to the Soil Remediation Decree was the inability to force a party to tackle soil contamination or to have a site investigated. To achieve this, the Soil Remediation Decree defined the concept of a 'soil investigation obligation', entailing a mandatory 'preliminary soil investigation' by the transferor of the risk-entailing land. If soil contamination was found, a 'soil remediation obligation' was established, meaning the transfer could not take place before other obligations were met. In practice, this soil remediation obligation was imposed on the transferor of the land but the Soil Remediation Decree (and later the Soil Decree) provided a number of grounds for exemption. The party to whom this obligation was assigned retained at all times the right to recover the costs from the party that caused the soil pollution.

The Soil Remediation Decree remained (more or less) unchanged for about a decade, but around 2005 it became clear that it was no longer in touch with the rapidly changing economic and social reality. The Soil Remediation Decree was thoroughly revised and, in 2008, it was replaced by the 'Decree of October 27th 2006 on Soil Remediation and Soil Protection' (brief: 'Soil Decree'). The main principles of the Soil Remediation Decree were retained, but the new Soil Decree provided a simplification of existing procedures, less stringent and/or risk-based remediation targets and a number of additional instruments to make the financial burdens more bearable. In addition, the Soil Decree incorporated a newly added chapter on soil protection, shifting the focus from soil remediation to an integrated approach on soil management, paying particular attention to prevention.

The transfer of land

As mentioned above, the 'transfer of land' was the crucial policy lever to achieve the defined goals. In order to fully understand this instrument, it is important to know that the Soil Decree explicitly defines what is considered as 'land' and which legal acts are considered as 'land transfer'. Its provisions apply only when there is a 'transfer of land' in the sense of the Soil Decree. In all other cases, the Soil Decree is not applicable. A consequence of this distinction in legal acts regarded as 'transfer of land' is that the party considered as 'transferor', is also situation-dependent. For example, in the case of the sale of land, the owner is the transferor, but when a tenancy ends, the tenant is designated as the transferor. The latter is important as it is on the transferor's initiative - and at his or her expense - that a preliminary soil investigation will be conducted.

In the case of a land transfer, a distinction is made between the transfer of 'risk-entailing land' and 'non-risk-entailing land', with risk-entailing land being defined in the Decree as 'land on which risk-entailing facilities are or were present'. The Decree also defines what is meant by 'risk-entailing facilities': factories, workshops, warehouses, machinery, industrial installations and operations that carry an increased risk of soil contamination and that appear on the list drawn up by the Flemish Government.

When transferring non-risk-entailing land, the transferor has only one obligation: the notary (or the real estate agent) charged with the sale must deliver a recent soil certificate to the potential acquirer before signing the agreement. The content of the soil certificate must also be included in the property sale deed. When transferring risk-entailing land, in addition to the obligation to submit a

recent soil certificate, the report on a recently conducted preliminary soil investigation must be present.

If this preliminary soil investigation reveals the presence of a soil contamination, the transfer cannot take place, except when the transferor can demonstrate that one of the exemptions applies. In that case, the obligation to remediate shifts to another party (e.g. a user of the land in question). If the soil remediation obligation is imposed on the transferor, the transfer can only take place when all other obligations imposed by the Soil Decree are met. In case of an urgent transfer, the transferor can make use of the so-called 'accelerated transfer procedure'.

The moment of the transfer of land was chosen as a policy lever for a twofold reason: at the time of transfer, significant financial resources become available (which, if necessary, can be used by the transferor to finance soil remediation), and the sheer frequency of transfers enabled the OVAM to accelerate and continuously update its inventory process. By stipulating that the obligations had to be fulfilled prior to the transfer, the OVAM prevented contaminated land from being transferred to insolvent acquirers (which would result in community costs). On the other hand, potential acquirers were given the opportunity to, estimate possible future costs prior to the acquisition.

In the above-mentioned procedure, the importance of the notary should not be underestimated: as a notary is the only functionary authorized to execute sales deeds, he or she has to decide whether the transferred site is risk-entailing land or not and, consequently, whether the transfer can take place or not.

Soil certificate

In the transfer procedure, the soil certificate plays an important role: for a legally valid transfer of any type of 'land' (risk-entailing or not), a recent soil certificate must be present at the time of the execution of the deed. This obligation goes back to one of the original basic objectives of the soil legislation, namely to protect the acquirer by providing useful and objective information on the soil quality of the land concerned.

With this information, the potential acquirer is able to estimate any subsequent costs related to the acquisition of the land, which provides a stronger negotiating position. In this way, a wider soil awareness is created: the real estate market becomes aware of the value-influencing effect of soil contamination, and property owners become increasingly aware of the benefits of good soil care. In other words: the impact of soil contamination on property value has become important to such an extent that free market forces - perhaps even more than the obligations imposed by the government - encourage current and future land owners to prevent their soil from becoming contaminated.

In 1995, the Soil Remediation Decree introduced the concept of 'soil certificate' and stated which information it had to contain. Although this was not explicitly stated in the Soil Remediation Decree, OVAM published two types of certificates: certificates containing information on 'filed' sites (i.e.: sites that have been investigated) and so-called 'blank' certificates when no information concerning the soil quality is available yet.

When the Soil Decree came into force in 2008, there was initially only limited change in the soil certificate. In 2016, the soil certificate did change significantly. The reason for this was an OVAM policy decision to prioritize the development of the Municipal Inventories. Municipalities were already obliged from 1998 on to create a 'Municipal Inventory' ('MI' - an inventory of all risk-entailing land within the municipal boundaries), but most of them had failed to fulfill this obligation. By supporting the municipalities, the OVAM speeded up the process and, from June

2016 on, soil certificates contain information originating from the MI. This new information made it easier for notaries to decide whether a preliminary soil investigation is mandatory or not.

Nowadays, the OVAM still delivers file-bound and blank soil certificates. All certificates are either delivered ex-officio or upon request and against payment (e.g. in the context of a land transfer). Upon special request, it is possible to acquire a soil certificate for only part of a land parcel.

The current blank soil certificate contains information on the geographical location, the cadastral information, and it mentions that there is no other information on that land available at the OVAM. The file-bound soil certificate states, in addition to the geographical location and the cadastral information, all information obtained from the MI, and whether any contamination that demands further action is present. Additionally, all investigation and remediation reports are listed.

Future of the soil certificate

The Soil Decree makes risk-based remediation legally possible by redefining the Flemish general remediation targets. Historical contamination should only be remediated to reach a level that no longer poses a threat to human health or to the environment. The risks are related to and determined by the current and future use of a site. The aim of this shift to risk-based remediation is to make soil remediation economically more efficient and, consequently, to increase the number of remediation works by making the process financially more feasible. A possible side effect, however, is that a certain residual contamination remains present. This residual contamination requires no further action and, until recently, no information about it was mentioned in the soil certificate. Thus, acquirers and real estate developers were often faced with problems such as unexpectedly high costs for the disposal and/or cleaning of contaminated soil. For instance, a result of changes in spatial planning can be that the applied risk-thresholds are no longer valid, which might lead to new risks and thus extra costs for additional remediation. To avoid this kind of situation, the OVAM decided to provide additional information on the soil certificate concerning soil and groundwater pollution. More in particular, specific information on the possible impact of (residual) pollution on the use of the site is added. For example: what are the consequences of excavations, of groundwater extraction, etc.

In the meantime, OVAM has formulated a set of clear and uniform usage recommendations. These usage recommendations are intended to make the acquirer aware of possible future (negative) side-effects (such as remediation costs, limitations in use, etc.) resulting from the presence of residual contamination. For example, a usage recommendation for a residential area may imply that a new risk-assessment should be carried out if an existing surface covering is removed. The OVAM adds these usage recommendations to the soil certificate in an automated way, without decreasing its legibility and accuracy.

The OVAM has the tradition of regularly consulting with various stakeholders (acquirers, soil remediation experts and contractors), asking for formal or informal feedback on its policy instruments. This was also the case with the soil certificate, which resulted in adjustments related to the clarity and comprehensibility of the information provided. Technological evolutions allow more (and more complex) data to be filed and listed in the soil certificate, but that also increases the challenge of bringing the information to the user in a clear and comprehensible way. Customer inquiries and (self-)evaluation will therefore remain essential.

Flanders is a highly industrialized and densely populated region. Raising awareness amongst stakeholders (industry, real estate, citizens ...) on the importance of soil quality (i.e. the value of a healthy soil) and integrating this into policy and legislation is crucial for mobilizing all stakeholders to take care of the soil.

Conclusions

Since 1996, OVAM has delivered more than 4 million soil certificates, which amounts to around 200,000 blank and 17,000 file-bound certificates each year. The soil certificate evolved from a mainly informative standard document to an awareness-raising certificate, tailor-made for any specific user. The financial revenue from the retributions is used by the OVAM to optimize its data management with maximum profits for society and to financially support non-liable owners with their remediation works.

Due to the soil certificate, the OVAM succeeded, as a governmental agency, in making Flemish citizens and entrepreneurs aware of the soil legislation and the impact of soil contamination (and associated liabilities) on the financial and economic value of their land. The certificate stimulates landowners to take care of their soil, and this within the principles of the free market. The better you take care of the soil, the more you can enjoy its benefits. Objective information also protects the acquirer: proper objective information forms the basis for drawing the right conclusions.

With a future extension of the soil certificate, OVAM also aims to broaden people's awareness, particularly on the crucial role of 'soil' or 'land' as a common and the related ecosystem services provided by the soil. OVAM wants to spread the message that the prevention of pollution and the sustainable protection and management of the soil as natural capital provides a healthy living environment and many other benefits to society. Considering land as a common, the owner of a plot needs to consider not only his rights, but also his obligations towards society and the natural environment at large.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.10. Towards a holistic distributed policy cluster to prevent and remedy soil pollution

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Abstract

A distributed policy cluster to prevent and remedy soil pollution is developed here by a set of sequential steps. It begins with a survey of the established and potential generic soil pollutants, and then proceeds to suggest two strategic action pathways to counter the problem. The first include the research on emerging types of pollutant, invention of means to counter them, and improving the current preventive and remedial methods. Next, it maps sources of pollutants onto relevant areas of policy in order to design a distributed policy cluster to prevent and remedy soil pollution. It presents some of the strategic elements the cluster embodies and emphasizes the necessity of intra- and inter-policy harmony both for its success and its seamless dovetailing into its policy ambience.

Keywords: Distributed policy cluster, Subsume, Research, neutralisation, Restoration, Soil fertility, Policy harmony.

Introduction, scope and main objectives

A number of adverse effects of soil pollution on human well-being and environment are well established. However, its generic types, effects and origins, extent and distribution vary widely. Therefore, its prevention and remediation calls for a coordinated and collective effort, which could be successfully undertaken only at national and international levels. Such an action involves a successful implementation of an appropriate policy to resolve the problem.

The diversity among the generic origins of soil pollutants makes it necessary for such a policy to extend into several different areas of activity like industry, agriculture, etc. This implies that a policy to prevent and remedy soil pollution would have to be distributed among such relevant policies as a sub-set of them. This paper suggests a holistic approach to design and implement such a distributed policy cluster to achieve the present objective.

Variety in pollutant types and extent implies that no hard and fast design rules may be laid down on the composition of such a policy cluster, but ought to be in accord with the actual pollution types and levels insofar as they can be reliably established. While their suitability for the purpose depends on their scientific soundness, their appropriateness in field application depends on their affordability in terms of available local resources and skills.

Thus at the country level, the scope of this undertaking includes a survey of the incidence and distribution of known generic and specific pollutants and the sources of their release. As generic pollutants like endocrine disruptors continue to emerge, they would have to be added to the survey as more information becomes available. A similar survey may be required to ascertain the optimal ways to prevent further pollution, and its remediation.

These surveys would have to be informed by continued research into two areas; first, expanding our knowledge about the ill effects of known pollutants and better methods to neutralise them, and secondly, identification of emerging soil pollutants, how to render them harmless and restore the

affected soil. Meanwhile, design of the required policy cluster and its implementation strategies are motivated by the need for a timely resolution of the problem.

Methodology

Standard holistic analytic technique has been applied throughout to ensure the completeness of the result. Relevance to the problem with reference to established principles of natural sciences has guided the survey of generic pollutants, rendering them harmless and their restoration. Mapping them onto sources of their release has been done with respect to publicly available information on agricultural and industrial practices. Policy design has been directed by the dual need to prevent and remedy soil pollution.

It has been seen that there is a close correlation between the amount of the different types of pollutant released into soil and the degree of industrialisation and/or rate of material consumption in a country. Since there is a wide variation in this, one needs to develop a policy cluster relevant to a country, which would be flexible enough to revise both its range and scope as its general standard of living changes, while retaining its capacity to be seamlessly integrated into the general policy ambience in which it is embedded.

Types of pollutant, areas of research and sources of pollutant release

Soil pollutants may be placed in two distinct but not mutually exclusive categories. First includes those injurious to human, animal or plant health owing to their toxicity or endocrine disruption. This effect may be direct on contact or uptake, or may be mediated via an indirect pathway like the food chain or water. This generic type represents bio-active soil pollutants. Biocides, plant growth accelerators etc., are examples of this.

The second involves pollutants that make an area uninhabitable to its endemic flora and fauna by altering its chemical composition, or obstructing their access to some necessity like light. This generic type may be called obstructive pollutants. Their ill effect include soil salinization by salt accumulation or bound mineral elution due to imprudent use of fertilisers, Dumping non-toxic waste on arable land may result in predomination of certain species with serious consequences for the bio-diversity of the local soil.

Alone or in unison, both types of soil pollutants will reduce the total bio-diversity of an area. Some of the affected species may be necessary for the continued replenishment of plant nutrients by their activities, about which much remains to be understood. At present, their release via saprophytic nutrition, Nitrogen fixation and enhancement of soil porosity by earthworms' behaviour are well established. Their negative effects on soil fertility lead to a reduced food production.

A policy maker now needs to know the extent and distribution of the two types of pollutant, their identities, and origins, methods of prevention, neutralisation and soil restoration whose successful use is practicable. Often this information is either not available or very incomplete. As the first step, several surveys and a considerable amount of research seems to be needed to bridge the gaps in our knowledge to ensure the completeness of the policy cluster and the comprehensiveness of its components.

Despite these limitations, a considerable practical result may be achieved by using the available knowledge while the groundwork is done to ensure continuous narrowing of the gaps in our knowledge. As far as it is possible, the following surveys and research should be synchronous, and their continuation embodied in the national research policy.

The surveys to be undertaken include:

- A survey of national sources of soil pollutants, quantities discharged, their composition, size and location of the receiving site, modes of neutralisation and restoration in actual use. Agriculture, different industries and waste disposal are among the obvious sources of soil pollution.
- This should be complemented by a survey of published data to ascertain the known pollutants in the types of discharge found at home, ways of avoiding their release or neutralisation. This may also serve as a guide to pollution sources that may have been overlooked.
- Often a survey of reputable research on the identity, long and short-term effects of soil pollutants would indicate to an investigator what to look for in the local sources of pollution including the emerging ones. One may here refer to EU's work on endocrine disruptors for more information.
- Simultaneous with the identification of soil pollutants with respect to their negative biological effects or their impact on the habitability of the soil, another bifurcated line of research is necessary. Its first branch in applied science is intended to develop least pollutive processes to replace their current counterparts, while the other will develop methods to reclaim the already polluted areas and to neutralise the known pollutants prior to their release.
- Survey of the existing policies to deal with soil pollution and their implementation strategies of a country in order to ascertain their completeness and suitability with reference to the criteria given here, and their appropriateness with respect to the magnitude of the problem and the available resources.

Emphasis has been placed on assembling the relevant information from existing sources in order to enable the policy maker to start work which can be improved and expanded with increasing benefit. Where independent surveys and research may be undertaken, a non-exhaustive list of areas for exploration may include:

- Ascertaining what activities in a country generate organic and inorganic waste irrespective of their concentration, for some of them are highly biologically active in minute concentrations.
- Independent analyses of such waste prior to their disposal and a comprehensive and an impartial survey of where and how they have been disposed.
- Research into the long and short-term biological effects of organic and inorganic materials entering the soil in concentrations exceeding those one may justifiably expect to result from benign natural events. Inappropriate use of fertilisers, large number of biocides, and the entry of growth accelerators, etc., ought to be included here.
- Next target of the survey is to identify the pollutants-neutralisation method combinations, their stated effectiveness and the pollutants as defined above for which no effective or practical means of neutralization is available.
- Independent research is needed to discover and devise methods to neutralise the emerging soil pollutants and to improve the existing methods. Similar methods need to be developed to evaluate the industrial innovations said to be less polluting.
- It is crucial to carry out research into how polluted soil may be restored. Enabling polluted soil to regain its former fertility may be difficult, but should nevertheless remain a research goal. It may involve restoring its chemical composition, structural features, and its flora and fauna.

Towards a distributed policy cluster to prevent and remedy soil pollution

The policy design involved here is complicated by the wide distribution of the necessary preventive and remedial measures among a wide variety of policies. It is impossible to subsume them as implementation strategies of one all-embracing policy without creating a great deal of confusion, difficulties in rational delegation of responsibilities, and avoiding mismatches in

competence. Therefore, the present approach of distributing the appropriate portions of an overall policy among the relevant policies seems to be reasonable.

Information on the types and extent of soil pollution, its prevention, consequences and remediation one requires ensuring the completeness of the desired policy cluster is often inadequate. Even so, it is possible to envisage a way forward where each policy element in the cluster could be amplified as more and comprehensive data becomes available. However, there are some independent criteria of success that should be met to have a significant impact on the problem.

- The suggested non-exhaustive policy cluster consists of policy elements distributed among all policies which are relevant to prevention and remediation of soil pollution; hence, they are a distributed cluster.

- Implementation strategies of each policy to which an element in the cluster belongs, should actively support the achievement of the cluster's goal, in other words, a policy should embody intra-policy harmony. For instance, an industrial policy that merely depends on investing in decontamination equipment without a strategy to ensure the use of non-polluting methods lacks this harmony.

- Diverse policies in the ambience in which the proposed cluster is embedded, should not conflict with achieving the present objective, i.e., display inter-policy harmony. Eg. a trade policy that promotes the export of cash crops (often entails monoculture and heavy use of mineral fertilisers) undermines the success of an agriculture policy to promote the appropriate use of mineral fertilisers to avoid salination.

Subject to the caveats listed throughout the discussion, pragmatism compels one to begin an outline of the policy cluster with some means of ensuring its adequate implementation. Provided that the political authorities and the general public are willing and able to make a real contribution towards achieving this common objective, two things must be taken into consideration to achieve it.

The first is concerned with how to ensure that those releasing soil pollutants adopt more environmentally friendly methods and ensure reduced pollutant emissions, and that the affected soil is restored. A sound, enforceable legal policy will have a key role here. The part of the cluster in it should meet the following requirements:

- Acts and ordinances concerning the issue are actually enforceable with reference to the country's human and material resources.

- They deal specifically with activities producing soil pollutants, their release and neutralisation prior to waste disposal, willingness and ability to develop and/or use less pollutive methods, etc.

- Assign due responsibility for and restoration of polluted sites.

- Set sound standards of incentives and deterrents.

However, what constitutes soil pollutants and what dangers they pose, how their release into the soil may be prevented and remedied is outside the domain of legal profession, and would have to be determined by the competent scientists and analysts. Laws and ordinances to deal with the problem should be based on those findings, which would have to be updated regularly as sources of soil pollution and types of pollutant change with time.

This flow of information to legislative and legal institutions could be much enhanced by using a ministerial channel as a clearinghouse, for instance that of Environment or Internal Affairs. Its policy may actively coordinate the research and surveys required for the purpose as follows:

- Ascertain the current state of knowledge of the subject, current surveys and research in the relevant areas like agriculture and industry.
- Establish monitoring of soil pollution by independent and technically skilled inspectors.
- Compilation of a nation-wide survey on areas that need urgent inspection, research, and land restoration.
- Design a mechanism to assign research and technology development priorities with respect to its public benefit to procure state funding. This amount is often inadequate and may call for international support.
- Develop a mechanism for close cooperation with the involved sectors, and undertake coordinated action.

Other things being equal, the judicial and environmental bodies have general areas of responsibility that embrace most of our activities; hence, their policies are inclusive of the others. However, one finds greater relevant technical expertise in some other institutions those two subsume. Therefore, a non-exhaustive summary of the strategic elements in each portion of the proposed policy cluster distributed among some of the key policies might serve as a useful guide to policy design.

Part of the suggested cluster subsumed by the policies on agriculture and food supply ought to include:

- Incentives and disincentives to promote practices that minimise soil pollution.
- Surveys to ascertain the extent to which their current activities contribute to known soil pollution.
- Research to identify emerging pollutants and development of better practices to avoid or neutralise it, and means of soil restoration. Frequently, these may necessitate ear-marked international funding and technical expertise.

Industry policy may subsume a part of the cluster that contains:

- Actively discourage the processes yielding or releasing soil pollutants, and encourage the opposite.
- Provide some funding to undertake the relevant surveys and research by independent investigators.
- Make a significant contribution to the development of less pollutive industrial processes.

Finance and trade policies would subsume the portion of the policy cluster including:

- Relevant incentives and disincentives whose operational details vary with the country involved.
- Allocating some funding to surveys, research and technical development needed to resolve the problem.
- Unrestricted public access to the current industrial waste, modes and sites of its disposal.

As this approach may be easily extended into any other policy area, it would be sufficient to round it up with some strategic elements of the cluster subsumed by education policy:

- Incorporation of learning about soil pollution into an obligatory environment studies in schools including agriculture and technical institutes and public education.
- Raise the awareness among public health workers and inspectors that soil pollution may pose a direct and indirect threat to health.

Neither all the main policy areas that may have a bearing on soil pollution, nor all the implementation strategies the included part of the policy cluster have been discussed. The great diversity among countries as to the extent, rate of increase and type of soil pollution makes any such completeness tedious and irrelevant at the country level.

However, a few common policy areas have been singled out with a view to outlining an approach to policy design with the inclusion of some critical strategic elements. A line of enquiry to procure the evidence on which it is to be based, as well as an optimal means of its implementation, has been suggested.

Conclusions

Advantages of this approach include the possibility of immediate policy design and implementation, flexibility and the overview of soil pollution it could provide even when its implementation is somewhat less than adequate. It also strives to awaken a broader interest in the public, sometimes a useful motivator of political action.

Meanwhile, it has not discussed the important problem of coordinating the collection of relevant information and research by different institutions but has suggested a suitable ministry to assume this function. In the implementation of the suggested policy cluster, two difficulties remain to be overcome, viz., real inter-institutional coordination towards a common goal, and procurement of the necessary resources.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

4.1.11. Setting thresholds for addressing pollution of soils with trace metals: concepts, models, and challenges

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Abstract

Trace metals are ubiquitous soil pollutants that affect soil quality. During the last two decades, intensive research has been performed on the metal risk assessments, culminating in several new models and metal regulations accepted worldwide. This paper reviews on what basis soil or soil amendment thresholds for metals can be derived, what data and models have been used and what the challenges are that may require further study.

Setting limits starts with the evaluation of the critical pathways, e.g. food chain contamination, toxicity to soil biota or direct inadvertent soil ingestion by children. For each of these pathways, it has been demonstrated that the exposure (uptake in biota) and the adverse effects (toxicity) of the metals are only poorly related to its total concentration in soil and that they should be replaced by other expression of metal dose that take their bioavailability into account. This is mainly related to the variable metal speciation in the soil, varying with soil properties, the age of the contamination and the matrix in which the metal has been added to soil. The food chain contamination can be evaluated via empirical datasets of soil/plant relationships from the field that account for soil properties affecting the net transfer, with robust models now available for Cd and As. The toxicity to soil biota requires ecotoxicity testing for which it was shown that the limits only become field relevant after considering bioavailability. Increasing cation exchange capacity in soil was shown to mitigate the toxicity of cationic metals such as Zn, Cu and Ni. Risk of metals via soil ingestion can be critical for Pb and As. Soil ingestion by children in developing countries is largely underestimated by current models and new data are presented here. Some challenges remain: first is the source of metals in soils that is often too variable to estimate in generic approaches and that require site specific testing of bioavailability; extractions test are being calibrated to address this. Second is the mixed metal contamination, metal synergisms among cationic metals can be found in greenhouse studies but its impact at field scale is yet unknown. Finally, there is some concern about metal containing nanoparticles but its impact at field scale is yet unknown.

Keywords: metals, soil, bioavailability, risk assessment, threshold values, crops

Introduction and objective

Trace elements such as cadmium (Cd), arsenic (As) and copper (Cu) are widely known for their toxic properties. The impact of local point pollution with such elements is often obvious, *de visu*, where metals affect the vegetation leading to brownfields such as metal mining or metal smelting sites. Such clear cases have led to regulations of metal emissions and soil metal thresholds for over three decades in various jurisdictions. More subtle than the point emissions are the gradual soil enrichments with trace elements, for example through addition of animal manure containing Zn from feed supplements, land application with sewage sludge containing Cu and zinc (Zn) from diffuse emissions, the use of Cu containing fungicides or the widespread use of phosphate fertilizers containing traces of Cd. In all these four examples, the net accumulation rarely leads to risk on the short term, however the prolonged application leads to potential widespread risk

because trace elements are not biodegradable, have a long residence time and natural attenuation by fixation is often too small. The four examples selected often lead to long-term debates on the risks because of the large societal impact of the selected thresholds. As an example, this author contributed to drafting Cd limits in phosphate fertilizers more than 15 years ago, the debate has been on since then and the new regulation is not yet in place (European Parliament, 2018). There is no doubt that all these thresholds must be based on the best available knowledge and models but that all these thresholds have residual uncertainty.

This paper reviews on what basis soil or soil amendment thresholds for metals can be derived, what data and models have been used and what the challenges are that may require further study. Excellent text books are recommended on this topic (Merrington and Schoeters 2010, Swartjes 2011). This paper only summarises the most important concepts, gives an update to these books including the current challenges.

A survey of soil clean-up standards of metals worldwide has shown that these can differ up to three orders of magnitude for the same metal (Provoost *et al.* 2006). That difference is related to the different protection goals and different levels of protection. To derive a soil metal threshold, a generic risk assessment must be made and that all starts with the different risk pathways. For metals, three pathways often control the risk and only these are discussed here, that is the human food chain contamination (uptake of metals from soil in edible crops), the toxicity of metals to soil biota and the risk to humans via inadvertent soil ingestion of contaminated soil or dust. For each of these pathways, it has been demonstrated that the exposure (uptake in biota) and the adverse effects (toxicity) of the metals are only poorly related to its total concentration in soil and that they should be replaced by other expression of metal dose that take their bioavailability into account. This is mainly related to the highly variable metal speciation in the soil, varying with soil properties, the age of the contamination and the matrix in which the metal has been added to soil. As an example, total concentration of soil Cd only poorly relate to crop Cd concentrations (Figure 1). By taking into account the soil pH, significantly more variation of crop Cd can be explained since it is well established that the soil pH controls the solubility of Cd in soil (Sauvé *et al.* 2000) and, hence, its bioavailability (Jansson *et al.* 2007). The same is true in the other pathways: it is well established that toxicity of metals in soil is affected by metal bioavailability (Smolders *et al.* 2009) and that the uptake of the soil associated As from the gastrointestinal tract of swine, as an animal model, is affected by bioavailability (Rodriguez *et al.* 1999).

The risk assessments depending on the pathways considered

Cadmium and arsenic are the two main elements for which the risk to humans is most critically affected by the food chain exposure. This means that these elements exceed crop quality standards when grown in soils contamination by metals that do not yet induce effects on biota. The risk assessment can be made straightforward as the calculation of the soil concentrations of these elements at which the crops do not yet exceed the limit in the crop. This is graphically illustrated in Figure 1. We have shown more advanced options for this by making multivariate models to statistically predict crop contamination based on soil information, i.e. taking bioavailability into account. The unexplained variance can also be accounted for leading to soil metal limits for given soil types (soil pH classes) at which the likelihood is less than, for example, 5% of growing crops that exceed the food standards (Jansson *et al.* 2007). More complex risk assessment have made a food basket approach leading to limits in soil that do not lead to exceedance of the tolerable weekly intake of such elements (EU 2007). Excellent multivariate models based on large scale field surveys are available that allow making such models (Römkens *et al.* 2009)(Williams *et al.* 2011).

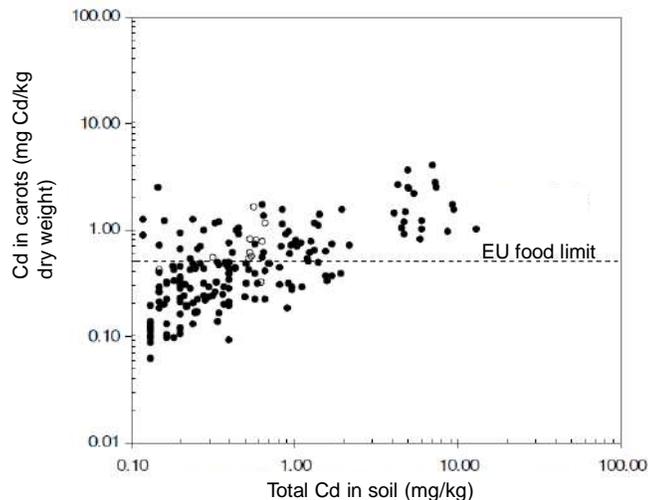


Figure 1. Cadmium concentrations in carrots sampled in Belgium and The Netherlands versus the total soil Cd concentrations. Note that the carrot concentrations vary about one order of magnitude at the same total soil Cd concentration. (Jansson *et al.* 2007).

Protecting soil biota

Zinc and Cu are elements for which the toxic effect on soil biota precede concerns for human health. Adverse effects on primary production found around Zn/Cu smelters and the presence of Zn/Cu tolerant plants indicate the toxic pressure of the soil borne metals. It has been very complicated to derive ecological limits that are above the natural background for such metals. It is well established that soil ecological limits are typically at the lower side of soil clean-up standards (Provoost *et al.* 2006). After about a decade of research with traditional lab-based toxicity studies in spiked soils, some improvements have been made yielding acceptable ecological criteria for a set of metals. Three key factors were needed to achieve this, graphically shown in Fig.2, which is the consideration of soil types affecting the toxicity, the implementation of sufficient ageing time and leaching after spiking soils with soluble metal salts and the consideration of other factors in the field, i.e. microbial adaptation and ageing. We have reviewed this entire process and refer to reader to that study (Smolders *et al.* 2009). In an associated papers shown at this conference (Oorts and Smolders), the method is given how to derive the threshold that take these three factors into account and a freeware tool is presented to do so.

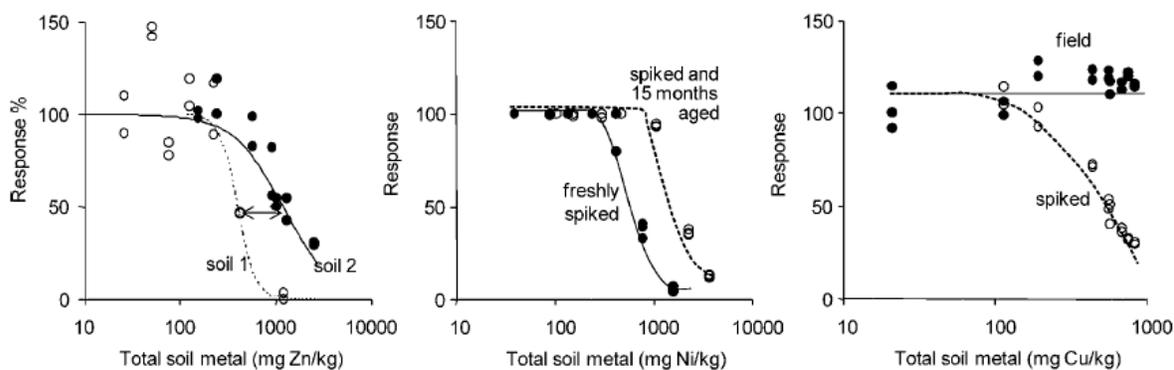


Figure 2. Metal toxicity is affected by soil type (a), by aging after metal amendment (b) and by long-term reactions in field contaminated soil (c). Panel (a): dry matter yield of wheat seedling in two ZnCl₂ amended soils. Panel (b): toxicity of Ni to barley root elongation in soil amended with NiCl₂ that was tested after 7 d (full line) or 15 months (dashed line) after amendment Panel (c): effects of Cu on microbial respiration of glucose in soil contaminated by a

CuSO₄ spill (>70 years old) versus that in CuCl₂ amended soil, differences are related to ageing and microbial adaptation. After (Smolders *et al.* 2009)

Protecting humans via soil ingestion

Children are sensitive to Pb in soil that is mainly taken up from inadvertent soil ingestion. This metal is too insoluble to be taken up by crops to a significant extent and ecological effects of soil Pb (Smolders *et al.* 2015) are found at only much larger concentrations than at those at which human health can be affected. Soil Pb bioavailability can be tested with physiologically based extractions (Ruby *et al.* 1999). This method has been used to design soil remediation methods aiming at reducing Pb exposure. For generic risk assessments and soil threshold derivation, models use a realistic worst-case estimate of soil or dust ingestion. These estimate range 0.1-0.15 g soil/day for children and are based on fecal excretion studies that measure insoluble trace elements in dust and in fecal matter (Bierkens *et al.* 2011). We have recently found that such estimates are by far not high enough for evaluating risks of metals to children in developing countries, especially in the dry season (Figure 3) and it is likely the variability of soil ingestion rate is larger than that of soil metal bioavailability.

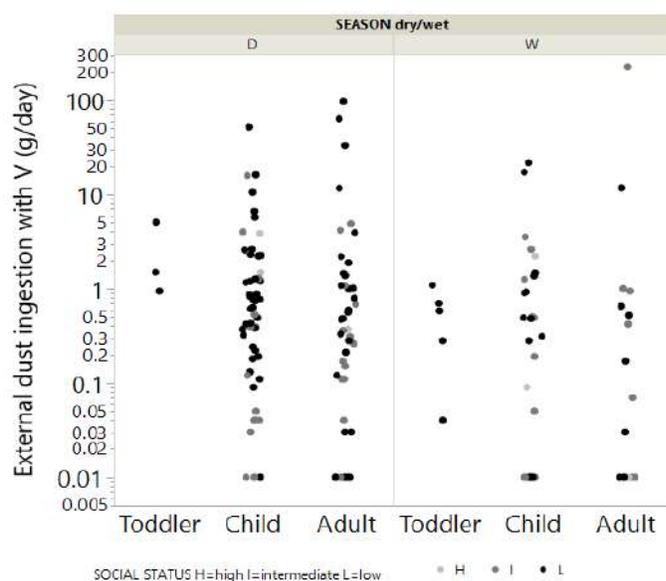


Figure 3. Soil and dust ingestion in the general population of Lubumbashi living near cobalt and copper mining sites in the dry and wet season. This ingestion was based using fecal excretion data of vanadium (V), an excellent poorly soluble soil tracer. The associated duplicate meal studies showed that, on average, 50% of the cobalt intake in the mining site is due to dust ingestion for children. Unpublished data of 2017 from this author and his colleagues of the University of Lubumbashi.

Challenges

Sparingly soluble metals compounds in soil

Soils contaminated by mining activities or by industrial waste products often contain metals present in unweathered minerals. These metals are poorly soluble and pose smaller risk than more soluble or reversely sorbed metal ions in soil. An example of this is given in Figure 4 showing that the metals from mining impacted soils, extracted with a neutral salt solution (“soluble metals”) better indicate the toxicity than the total metal concentration. Generic approaches to estimate metal solubility across soils are not very precise and it has been argued that site-specific soil extractions using neutral salts should be made as a basis of risk assessment. This also means

that the soil criteria must be expressed on the same extraction basis, i.e. all soil toxicity data with total soil based thresholds should be re-evaluated. Two independent projects in Europe now trying to re-evaluate this, potentially leading to metal legislations and thresholds expressed on a basis of metals extracted from soil with neutral salts.

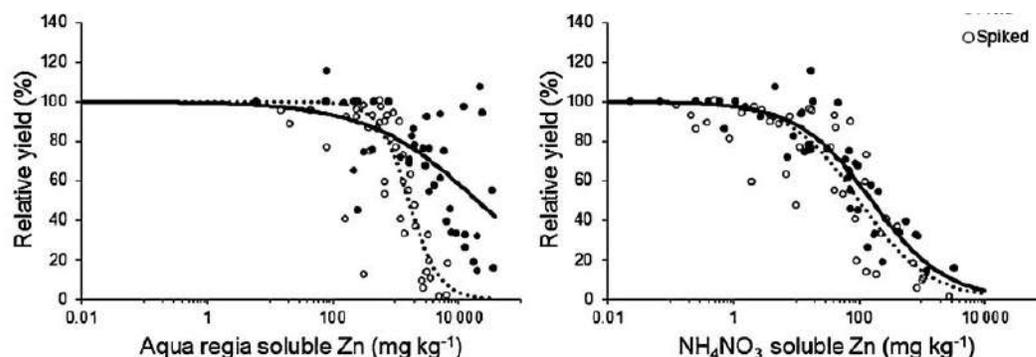


Figure 4. Comparison of Zn toxicity to barley growth in field-contaminated soils (solid circles) and in their corresponding reference soils spiked with metal salts (empty circles) with doses expressed as aqua regia and NH_4NO_3 soluble metal. Adapted from (Hamels *et al.* 2014).

Metal mixture toxicity

The ICP-MS analysis of soil metals increasingly become a routine approach and facilitate the detection of several tens of trace elements at once. This illustrates that all these elements are naturally (by definition) co-existent as a mixture. That natural mixture of elements can also become toxic upon soil pollution and mixture effects may occur, the latter defined as an adverse effect from the combination of the toxicants not to be expected if each individual contaminant were present in isolation at the same dose. This “*something from nothing*” idea can be demonstrated with, for example, plants grown in nutrient solution in small scale studies (Versieren *et al.* 2016). In addition, examples can be found of synergisms for cationic metals present in soil, largely aggravating the toxicity when dosed in combination (Qiu *et al.* 2016). The methodology to include metal mixture effects in soil are in its infancy and we have shown a potential way forward (Nys *et al.* 2017), the key question is yet the field validation, i.e. environmental significance of these predictions.

Metal containing nanoparticles

Metals can be added to soil as nanoparticles (NPs) such as Cu in fungicides or pesticides and Ag through sewage sludge. An inherent hypothesis when assessing risks posed by metal-based NPs is that the nanospecific properties (e.g., high surface area to volume ratio and high reactivity) will cause specific interactions with the test media and test organisms compared to the case of corresponding bulk particles or salt forms. As a result, new biological effects may be expected. However, a consensus on the existence of nanospecific effects has yet to be reached, especially when dealing with soils. Most comparative studies currently show that the read-across from metal salt toxicity can be adopted safely (Qiu and Smolders 2017). However, there remains concern with long-term effects of NP over several generations of that might become even larger than that of corresponding metal salts (Schultz *et al.* 2016 and Spurgeon, pers. comm). As in the previous example, it is yet to be established what this means for the field.

Conclusions

Soil chemists, ecotoxicologist, epidemiologists and risk assessors have made great progress and reached often consensus on setting soil thresholds for metals. The original large diversity of soil cleanup standards now appear to become smaller when evaluating the current or proposed legislation of metals in soil. The current scientific challenges, cited above, will soon also be followed by consensus models. The current societal challenges of trace elements may not be directly addressed given that the risks are not very immanent.

Acknowledgements

The collaborations with with scientists, regulators and industry in the metal risk assessment are acknowledged and the full list will be given at the conference. The unpublished soil ingestion data of Figure 3 were obtained through VLIR-UOS funding project ZRDC2015PR090.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.12. A flexible approach for implementation of bioavailability into derivation of thresholds for ecotoxicological effects of metals in soil for varying protection goals

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Abstract

During the last two decades, intensive research has been performed to improve the environmental effects and risk assessment of metals towards soil organisms (plants, invertebrates and microorganisms). Models were developed to correct for differences in metal bioavailability among soils and for differences between laboratory and field conditions. For many metals, sufficient chronic toxicity data for different plant and invertebrate species and microbial functions are available allowing the application of improved statistical extrapolation techniques to derive soil threshold values. This work was mainly triggered by the European legislation on chemical management (REACH) and the data and tools were therefore primarily used to ensure derivation of proper predicted no effect concentrations (PNEC) for prospective risk assessment. The information available can also be used for the derivation of metal threshold values in soil for different protection goals (e.g. remediation thresholds), jurisdictions, regions or sites by including additional options: selection of organism groups or species to be considered, selection of effect levels from the original dose-response curves, selection of protection level, bioavailability models to be included etc. A freely available threshold calculator tool for ecotoxicological effects of metals in soil has been developed for this purpose, reporting almost 1200 reliable chronic toxicity data for the direct effects of the metals Cd, Co, Cu, Pb, Mo, Ni and Zn to soil organisms. This tool that runs as Microsoft Excel integrates ecotoxicity data and models covering a wide range of soil types and properties and calculates ecotoxicological thresholds expressed as total metal concentrations in soil (mg/kg dry weight). The data and approach may be useful in various parts of the world to derive soil type-specific ecotoxicological thresholds for different protection goals.

Keywords: metals, soil, bioavailability, ecotoxicity, ecological risk assessment, threshold values

Introduction, scope and main objectives

Metals are emitted to soil via several intended applications (e.g. as micro-nutrients in fertilizers, as pesticides or biocidal products) and non-intended ways (e.g. as contaminants in sewage sludge, fertilizers and manure or via wide dispersive contamination from metallurgic activities, traffic, etc.). Risk assessments for metals in soil are part of numerous national and international regulatory programs (e.g. registration of chemicals such as plant protection products or setting contamination limits for soil remediation), resulting in a wide range of threshold concentrations for metals in soil (e.g. Provoost *et al.* 2006; Carlon *et al.* 2007).

Several aspects must be accounted for to perform a scientifically sound effects and risk assessment of trace metals in soil, such as e.g. essentiality and variability of soil properties influencing the bioavailability and toxicity of metals. During the last two decades, intensive research has been performed in these fields and numerous chronic metal toxicity data were generated for various terrestrial plant and invertebrate species and microbial functions in different soil types. Metal toxicity thresholds for the same metal and endpoint can vary up to two orders of magnitude among

different freshly spiked soils (e.g. Oorts *et al.* 2006; Li *et al.* 2009; van Gestel *et al.* 2011). The time since contamination also can significantly affect the toxicity of metals in soil due to slow equilibration processes (ageing processes, e.g. Donner *et al.* 2010; van Gestel *et al.* 2012; Smolders *et al.* 2015). It is generally accepted that the total metal concentration in soil is a poor predictor for toxicity to the environment. However, there is not yet a generally accepted method for measurement of the bioavailable fraction of metals in soil (Zhao *et al.* 2006; Menzies *et al.* 2007; Hamels *et al.* 2014), and data for (pseudo-) total metal concentrations, based on concentrated acid digestions, are most commonly available and used. The range in effect concentrations based on total metal concentrations can even overlap with the range in natural background concentrations leading to potential risk conclusions at natural background or even deficiency concentrations for essential elements such as Cu and Zn. Models were developed for correction for differences in bioavailability among soils and for differences between laboratory and field conditions (Smolders *et al.* 2009; OECD 2016). For many metals, the large amount of chronic toxicity data for different species and functions allow the application of statistical extrapolation techniques such as the species sensitivity distribution approach (SSD) to derive soil quality standards. This work was mainly triggered by the European legislation on chemical management (REACH, Registration, Evaluation, Authorisation and Restriction of Chemicals; Regulation EC No 1907/2006) and the data were therefore primarily used to derive predicted no effect concentrations (PNEC) for prospective risk assessment (e.g. Oorts *et al.* 2016). The data and models available are, however, also useful for the derivation of ecological threshold values for metals in soil for other protection goals (e.g. remediation thresholds) in various jurisdictions, regions or sites by e.g. selecting different effect and protection levels (Checkai *et al.* 2014).

This paper presents a flexible and transparent approach for the application of the available data and improved scientific methods for derivation of threshold values that can be used for environmental risk assessment of metals in soil under various ecological conditions of the world.

Methodology

A generic approach for derivation of soil threshold values is presented in Figure 1.

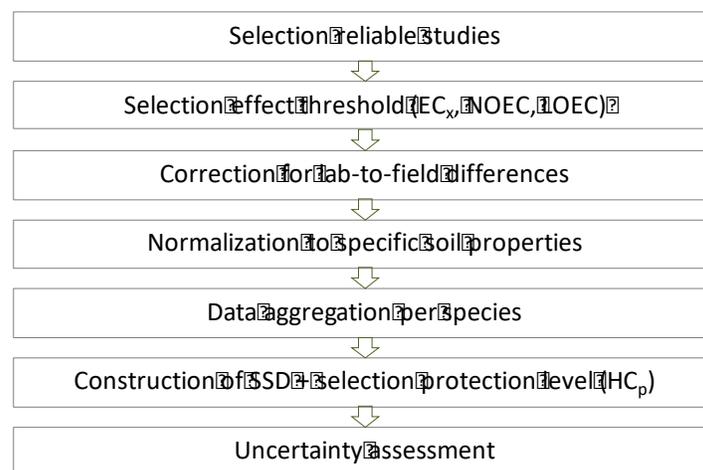


Figure 1. Different steps in the generic approach for derivation of metal threshold values in soil

Selection of reliable toxicity studies

The soil effect thresholds are based on relevant and reliable chronic toxicity data for terrestrial organisms (plants, invertebrates and microbial processes) derived from scientific literature or research projects. All data were thoroughly screened for their relevance and reliability. Acceptance criteria are summarized in Table 1. The datasets developed for the European REACH dossiers were the basis for this data collection, but all studies were re-evaluated and reliable data outside the specific scope of REACH were also included. There were no restrictions on the relevance of soil properties or species towards specific regions of the world.

Table 1. Main relevance and reliability criteria for selection of terrestrial ecotoxicity data.

Relevance	Reliability
<u>Test substance</u> : high purity soluble metal salts	<u>Description of test</u> : standard test (e.g. ISO, OECD) or not, endpoint used, test conditions
<u>Test medium</u> : only data from observations in natural and artificial (e.g. OECD) soil media; other substrates (e.g. nutrient solution, agar, pure quartz sand and farmyard manure) were judged as not representative for soils	<u>Description of test material and methods</u> : e.g. test set-up, measuring chamber/device, spiking method, test organism, including size (age), origin, number of organisms per replicate, test design (# replicates used), type of food given
<u>Test species</u> : primary producers (plants), consumers (invertebrates) and decomposers (microbial mediated processes)	<u>Description of the test soil</u> : e.g. soil type, location, pH, organic carbon, clay content, CEC
<u>Toxicological endpoints</u> : direct effects at population level, e.g. mortality, growth and reproduction for plants and invertebrates, or functional variables such as C- and N-mineralisation for soil microbial endpoints	<u>Chemical analysis</u> : test concentrations during the test are measured or evidence that the nominal concentrations are close to actual concentrations
<u>Exposure duration</u> : tests focusing on sensitive life stages (e.g. root elongation) or from “chronic exposure” (e.g. growth, reproduction)	<u>Concentration-effect relationship</u> : acceptable control response (mortality, reproduction, growth, etc.), tested concentration range is reported, at least 2 different concentrations tested besides the control, a clear concentration related response, sound statistics used to derive a suitable EC _x or NOEC/LOEC value

Selection of effect thresholds

EC₁₀ and NOEC values are used for the European REACH regulation. Other regulations however do prefer other effect thresholds (e.g. EC₂₀ for derivation soil screening levels in USA). Therefore, wherever possible, the concentration-effect relationships were re-fitted with a standard 3 parameter log-logistic dose-response curve, allowing derivation of any EC_x (Figure 2). We advise that in future reporting of results of toxicity studies, the dose-response curve parameters be also reported next to the effect thresholds to ensure maximal relevance and applicability of the results.

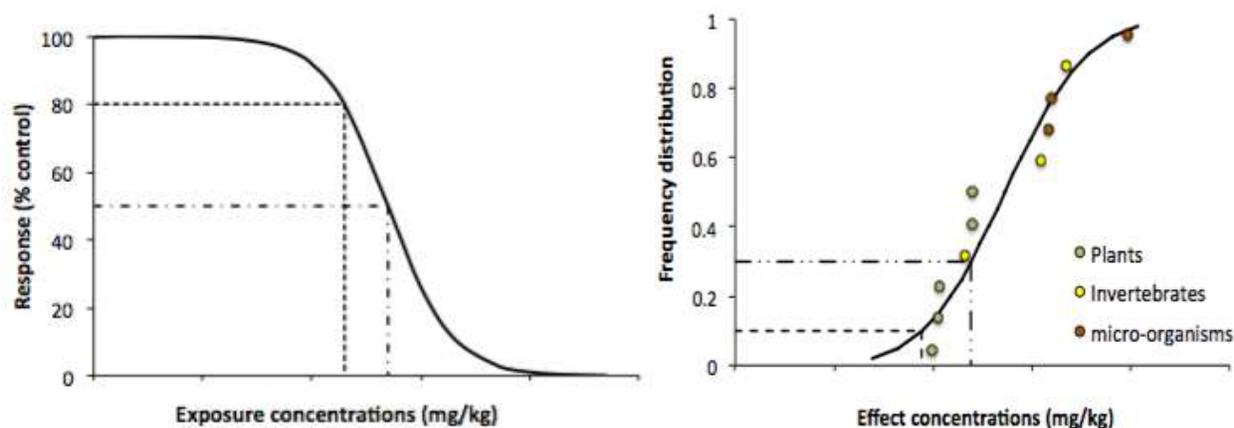


Figure 217. Selection of effect level (left) and protection level (right)

Correction for differences in toxicity between laboratory- and field-contaminated soils

Metal toxicity not only depends on the total metal dose, but also on the time since contamination and on physico-chemical soil properties (Smolders *et al.* 2009; OECD 2016). Toxicity tests in laboratory-spiked soils generally overestimate effects in field-contaminated soils due to ageing reactions and leaching of excess ions reducing the bioavailability of the remaining metal in field conditions. To account for ageing and leaching, correction factors (lab-to-field factors or leaching-ageing factors) have been derived to be applied to the added (i.e. background corrected) EC_x values from laboratory tests (Table 2). The background concentration (C_b) can be added to the corrected added EC_x to derive total metal concentrations in soil:

$$EC_{x,field} = EC_{x,lab,added} \times L/F \text{ factor} (+ C_b)$$

Normalization of EC_x values to specific soil properties

Several metal- and species-specific bioavailability models have been derived based on best correlations between soil characteristics and toxicity data (Table 2). These models can be used to normalize all toxicity data towards the soil conditions of a site of interest. The most appropriate bioavailability correction models can be selected for different regions. The input parameters required are dependent upon the metal under consideration and are generally standard soil parameters likely to be determined in routine soil analyses, such as pH, organic carbon content, clay content and eCEC (effective cation exchange capacity, i.e. CEC at prevailing soil pH).

Table 2. Available reliable chronic terrestrial effects data for higher plants, soil invertebrates (inv) and soil microbial driven processes (micro-org) and bioavailability models for selected metals

Metal	Species or processes with reliable toxicity data	Lab-to-field correction factor (L/F factor)	Number of endpoints with normalization models	Soil properties used for normalization
Cu	9 plants, 13 inv., 9 micro-org.	2	7 (European soils)	eCEC, %clay, %OC, pH
Zn	18 plants, 9 inv., 19 micro-org.	3	5 (European soils)	eCEC, pH, background Zn
Ni	11 plants, 6 inv., 25 micro-org.	1-3 (increasing as a function of pH)	7 (European soils)	eCEC
Co	7 plants, 4 inv., 3 micro-org.	1.1-3.5 (increasing as a function of pH)	10 (European + North American soils)	eCEC
Pb	16 plants, 9 inv., 5 micro-org.	4	3 (European soils)	eCEC
Mo	5 plants, 3 inv., 3 micro-org.	2	9 (European soils)	pH, clay
Cd	19 plants, 9 inv., 9 micro-org.	/	/	/

Data aggregation per species

For each species or microbial process, only data for the most sensitive endpoint are retained. In case multiple data are available for the most sensitive endpoint for a species or process, data can be aggregated by e.g. calculating the geometric mean to avoid over-representation of data-rich species in the database.

Construction of species sensitivity distribution + selection of protection level (HC_p)

For several metals, sufficient toxicity data are available to allow derivation of soil thresholds with the statistical extrapolation approach (species sensitivity distribution, SSD). Protection goals may differ among regulations (e.g. HC₅ for REACH) and e.g. land use and therefore different combinations of effect thresholds (EC_x) and protection level (HC_p) can be considered in a SSD approach for various regulatory purposes (Checkai *et al.*, 2014; Figure 2).

Uncertainty assessment

In a final step, the level of uncertainty on the soil thresholds is assessed by e.g. considering the range in abiotic factors of soils covered, the diversity and representativeness of the taxonomic groups covered by the database, the statistical uncertainties around the HC_p, a comparison of the HC_p with field and mesocosm studies.

Results

A freely available threshold calculator tool for ecological effects of metals in soil has been developed. Almost 1200 reliable chronic toxicity data points for the direct effects of the metals Cd, Co, Cu, Pb, Mo, Ni and Zn on soil organisms (plants, invertebrates and microbial processes) are included in the database. All data on test substances, organisms and endpoints, bibliographical information, soils tested (type, location, properties, analytical methods), test conditions (doses, equilibration, exposure duration, etc.), and toxicity data (NOEC, LOEC, parameters dose-response curve) were clearly reported in a searchable database.

All metals covered have sufficient chronic toxicity data allowing the derivation of an SSD (Table 2). The soils used for ecotoxicity testing cover for each metal a wide range of soil types and properties, making the results representative for most regions in the world. Several options that allow calculation of metal threshold concentrations in soil for various goals (e.g. risk assessment or setting of remediation thresholds for different land uses) include:

- selection of organism groups (trophic levels) or individual species to be considered
- selection of effect levels (x in EC_x) as a basis for the assessment (Figure 2)
- selection of protection levels (p in HC_p and potentially affected fraction in SSD) (Figure 2)
- selection of added or total approach (i.e. without or with natural background concentration included)
- soil properties

The tool presents species mean toxicity data for the selected species including the SSD of the selected EC_x values and reports the calculated soil threshold values, expressed as total metal concentrations in soil, in a user-friendly interface that runs as Microsoft Excel (Figure 3). The database and tool can be downloaded from <http://www.arche-consulting.be/tools/>.

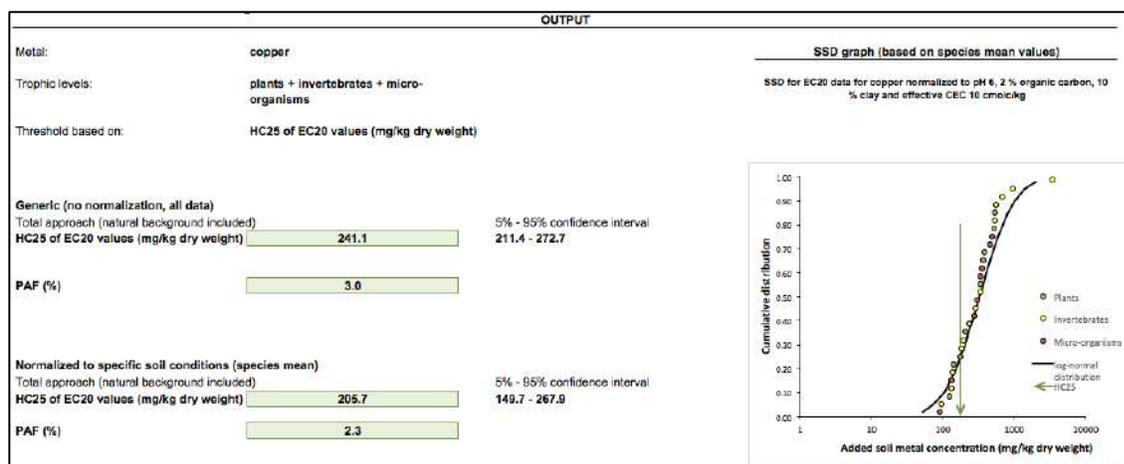


Figure 3. Example of output of the soil threshold calculator tool

Discussion

Metals are among the most widely regulated substances and soil threshold values for metals in different legislations vary strongly (e.g. Provoost *et al.* 2006; Carlon *et al.* 2007). At present, it is however often not clear how these thresholds are derived (source data, corrections, etc.), hampering their comparison and limiting their use for other areas, protection goals, etc. Following a common generic framework for the derivation of threshold values for metals in soil ensures increased transparency and comparability of the thresholds for different goals, locations, regulations, etc. This database and tool provides such a flexible approach for the derivation of thresholds for the ecological effects of metals to soil organisms.

For the metals considered, there are no major differences in sensitivity of the trophic levels covered (plants, invertebrates and micro-organisms). The sensitivity of different species to a contaminant typically varies more than the variation in effect concentrations in a dose-response

curve and the selection of the protection level (HC_p) has therefore more impact on the thresholds calculated than selection of effect values (EC_x). Choices of adverse effect levels (EC_x) must however always be made in consideration of the choices on protection levels (HC_p), and vice versa: which level of protection is most appropriate for each type of effect allowed, i.e. is a higher number of species affected reasonable when the adverse effect per species is relatively small, or is it better to have a larger effect on fewer species?

Normalization of toxicity data for varying soil properties ensures a constant protection level across soils with different bioavailability and toxicity potential of a specific metal. The observation that soil thresholds for Cu in European agricultural soil vary more than one order of magnitude and even overlap with the range in natural background concentrations (<5 to >50 mg Cu/kg) highlights the importance of consideration of variations in bioavailability across soils for setting of proper soil threshold values for metals (Figure 4).

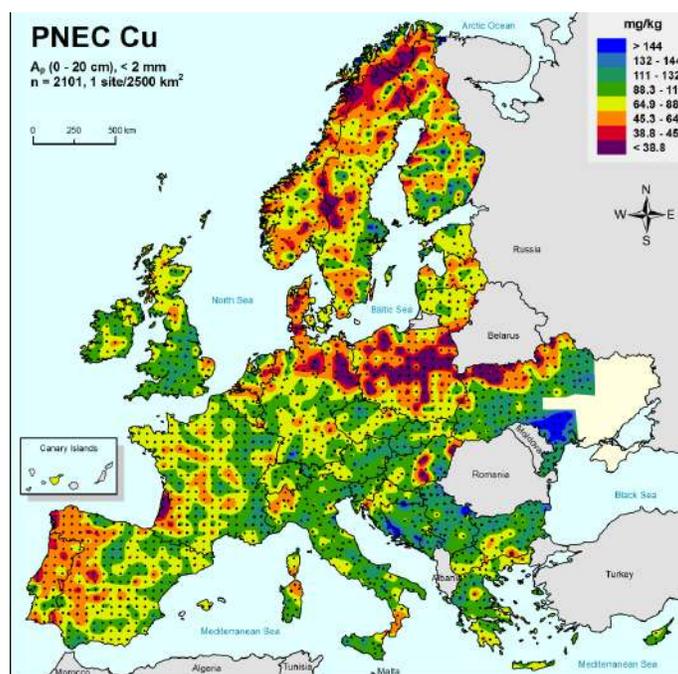


Figure 18. Predicted No Effect Concentrations (PNEC, calculated as HC_5 of EC_{10} values) for Cu in arable soils in Europe. Colour classes are based on the 5th, 10th, 25th, 50th, 75th, 90th and 95th percentiles. Data from Oorts and Schoeters 2014).

Conclusions

A generic approach is proposed for the setting of threshold values for metals in soil. This approach ensures the maximal use of available toxicity data and bioavailability corrections and increases the transparency and consistency of soil thresholds derivation, while guaranteeing flexibility for specific regulatory purposes by selection of e.g. type of soil organisms to be covered and overall protection level required.

A comprehensive database with available reliable chronic toxicity data of metals (Cu, Ni, Zn, Co, Pb, Mo and Cd) to soil organisms (plants, invertebrates and micro-organisms) and bioavailability correction models is implemented in a free user-friendly spreadsheet. The soils used for ecotoxicity testing cover for each metal a wide range of soil types and properties, making the results representative for most regions in the world. The tool allows the derivation of threshold values for

ecological risk assessment of metals in soil under variable protection scenarios and for variable soil conditions.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.13. Soil policy in the Netherlands. The dynamics of joint policymaking.

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Abstract Evolution of a soil policy towards a policy of sustainable land management

Soil differs from Member State to Member State and therefore soil policies are also different. Besides Member States, they differ in administrative organisation, geographical situation, climate and cultural aspects. The Dutch soil policy is the result of confrontation with contaminated areas in the 1980s. In 1983, a draft law was submitted focusing on remediation of contaminated sites and was finalised in 1987 in the Soil Protection Act. The law was accompanied by a system to determine historical contaminated sites by background, standard and target values, a financial framework and a knowledge programme focusing on remediation techniques. The remediation goal was multifunctional use of the soil. The Soil Protection Act also related to soil protection measures. These covered not only contamination but also erosion, salinisation and compaction. The idea was that contamination was limited and could be dealt with in a limited period. In this period, a policy was also created to prevent soil contamination resulting in the Netherlands Soil Protection Guideline for Industrial Activities (NRB) published in 2001. During the implementation of the soil policy, several aspects caused changes and thus an evolution in soil policy. What started with the legacy of soil abuse, was followed by protection measures and legislation, and now evaluates towards sustainable management of soil as part of spatial development. Soil policy in the Netherlands changed from a policy focussed on chemical contamination towards a soil policy focussed on soil services, from execution by central authorities to execution by decentral authorities, from local to area approach, from focus on environmental protection to focus on spatial planning. A paradigm shift from soil as a hindrance to soil as a partner in sustainable development to achieve societal goals.

Keywords: soil policy, paradigm shift, spatial planning, land management, sustainable development, stakeholder involvement

Introduction, scope and main objectives

Soil differs from Member State to Member State and therefore soil policies are different. Besides Member States, they differ in administrative organisation, geographical situation, climate and cultural aspects. Important characteristics specific to the Netherlands are high population density, pressure on land, delta area, many soil-based activities related to (ground)water, increasing use of top soil and sub-soil, a lot of soil excavation and a consensus-driven approach.

The Dutch soil policy is the result of confrontation with contaminated areas in the 1980s. In 1983, a draft law was submitted focusing on remediation of contaminated sites. This law was finalised in 1987, in the Soil Protection Act. The law was accompanied by a system to determine historical contaminated sites by background, standard and target values, a financial framework and a knowledge programme focusing on remediation techniques. The remediation goal was multifunctional use of the soil. The Soil Protection Act also related to soil protection measures. These covered not only contamination but also erosion, salinisation and compaction. The idea was that contamination was limited and could be dealt with in a limited period. In this period, a

policy was also created to prevent soil contamination. In 2001 the Netherlands Soil Protection Guideline for Industrial Activities (NRB) was published, forming the basis for a system of environmental licensing

Methodology

More sites than expected turned out to be contaminated. Remediation to multifunctional use was not always possible; costs were high. In the early 1990s, the targets for multifunctional use were replaced by as low as reasonably achievable and containment under management and control. The government would only provide funding for historically contaminated sites (those contaminated before 1987).

As the importance of other soil functions, both physical and biological, came into focus, the concept of sustainable use as a form of protection was introduced. This was communicated by a policy letter in 2003 and was the start of a paradigm shift in soil policy and a shift in mind-set in the sector.



In the National Environmental Policy Plan 3, 1998-2002, an inventory of potentially contaminated sites was announced for 2005. This inventory was the basis for allocation of the national remediation budget, a political agreement for the period up to 2030. The inventory brought to light more sites than expected again, the costs of after-care rose sky high and the remediation operation came to a halt. In 1995, the policy was evaluated, leading to an amended Soil Protection Act 2006. New elements were risk based solutions (source-path-threatened object), natural attenuation, monitored containment (management) groundwater. The provinces and several larger municipalities became competent authorities for soil remediation. Instruments to sustain the authorities included Sanscrit, the Soil Management and Recovery Guideline; Risk Toolbox and the soil ambitions route planner.

The amended Soil Protection Act 2006 further prioritised contaminated sites. It was politically unacceptable that sites, which presented excessively high risks to public health, as well as ecological risks and the risk of groundwater contamination spreading, were still there after decades of intervention. There was political support for an obligation to remediate in the case of unacceptable risks combined with government funding for the remediation costs for industry up to a maximum of 70% for Small and Medium-sized Enterprises (SME). It is noteworthy that a distinction was made between the right to government funding and applications for funding. Applications had an expiry date (1 January 2008). As a result, 10,000 companies signed up. This allowed the government to estimate a budget. The experience in the Netherlands is that political agreement can be achieved only once the problem has been underpinned so the budget required can be clearly estimated.

A policy evaluation in 2005 showed that the estimated costs of the remediation operation were so high that new strategies had to be considered. One of these strategies, combining remediation with development or redevelopment, so that a portion of the costs could be paid by the developers, was a real hit. 1000-1200 sites were remediated per year, all part of redevelopment projects. The aim, to quadruple the number, was not achieved. In reality, there was a doubling. Sites with actual

risks and no dynamics were left out. Thus, the benefits of remediation became a political issue. In 2007, therefore, a societal cost benefit analysis was made. This analysis showed that the benefits of remediation, although not necessarily substantial in euros, were nonetheless present. For politicians in particular, the fact that civilians were being exposed to soil contamination and were experiencing this as a serious problem was decisive. It was decided that the budget would remain but that sites with actual risks should be tackled.

The choice for prioritisation of contaminated sites made it clear that it was necessary to draw up a policy for lightly contaminated soil, excavated as part of construction work, road building etc. In 2008, the Soil Quality Decree came into force. This Decree regulates handling of lightly contaminated soil, sediment and secondary building materials. Quality control and quality assurance, certification and mapping of soil quality are an essential part of this decree. The soil quality maps are available to the public.

Before the EU Thematic Soil Strategy, the Netherlands already had knowledge development programmes. Under the Dutch Foundation for Knowledge sharing on Soil (1995-2015), with a budget of 90 million euros funded by national government and other stakeholders, 300 research projects were executed. The focus shifted from remediation techniques and in-situ techniques to area approach, land use and spatial planning and the last 5 years towards sustainable use of the ecosystem services of soil and subsoil.

From 1987 - 2006 the soil policy changed from a response to soil abuse and protection, towards a policy of sustainable use. The responsibility for soil quality became a shared responsibility of national and de-centralised authorities and end users. Instead of focusing on soil quality, the services of the soil sediment water system (SSW) became the starting point for area development. The Netherlands connected sustainable use to societal challenges like food production, climate change, energy, resources and drinking water. Using the SSW system for societal challenges means adding value to the system, making it important to protect this system and its services. Instead of focusing on soil threats, the focus shifted to benefits, soil ecosystem services and sustainable use. This demands an integrated assessment instrument. Spatial planning is considered the instrument to manage the natural system, so societal challenges can be met now and in the future. To achieve such a transition, several conditions have to be met and instruments are needed.

Results

To tackle sites with actual risks and broaden the scope to sustainable use and management, the Ministry of the Environment, the Ministry of Infrastructure and Water Management, the Ministry of Agriculture, the provinces, the municipalities and the Water Authorities drew up a Covenant on Soil and Sub-soil 2009-2015. This covenant has been successful:

- all sites presenting actual public-health risks have been identified, are under control or have been remediated;
- a thematic knowledge agenda with a connection to societal challenges has been drawn up;
- legislation and a research program on soil energy and ATEs have been drawn up and executed;
- a societal initiative on awareness building is operational, supported by ambassadors at CEO-level from societal organisations, authorities and industries;

– a research and co-operation program for area approach management has been executed, several CoPs (Communities of Practice) and other communities have been initiated and are operational (CoP Ecosystem services, Groundwater Collective, Soil and sub-soil Expertise network, Expert group soil, Network of young soil and sub-soil professionals, SURF NL).

The Netherlands have drawn up a national Environmental Planning Act, to come into force in 2021. This integrated law has a twofold purpose: 1) to set out a coherent approach to achieve and maintain a safe and healthy physical environment and good environmental standards, 2) to enable efficient management, use and sustainable development of the physical environment for social purposes. Part of this law is an integrated assessment framework, allowing local-scale tailor-made solutions, avoiding an administrative burden. The soil legislation will be integrated in this law. This means that legal decisions on remediation will be part of an integrated licence. All provinces and municipalities will become competent authorities (12+420). Therefore, special attention is needed for capacity building, knowledge development and dissemination, and data management. The basis of the integrated law is a vision document with long-term goals. The use of soil, sub-soil and its services is part of this document. Local and regional authorities draw up their own derived vision documents and policy.

Discussion

To optimise the benefits of soil ecosystem services for societal challenges, up scaling to an area approach, not only in surface but also in depth (3D) is recommended. Thus, more options for solutions can be found. Up scaling implicitly means an integral approach and the involvement of more stakeholders. More stakeholders means more people with interests and thereby investors. This heightens the pressure on the system though. It means that it takes more time to come to terms. The 'wheels' of the SSW system turn slowly, effects become visible gradually and measures to undo effects are hardly possible or take a very long time. It is therefore necessary to take into account the time factor and to monitor effects in the event of land use changes or other activities (4/5D).

To optimise is to find a balance in service demand and supply; an assessment is essential. For an assessment, the availability and quality of current services should be known and future goals and claims identified. These goals and claims can be on a national level, but also regional or local. Therefore, the Dutch Government started a national inventory of the availability of services (resources, storage possibilities, production functions etc.), of societal tasks and claims in connection with the use of soil and sub-soil, and is translating the results into a national vision in 4/5D (including the groundwater layer (up to 200m – surface level) and the layer for mining activities) for the coming 100 years (STRONG). The provinces are making their visions for the regional level and municipalities are working out their goals in a local vision. For example, the city of Rotterdam has made a vision document for use and management of the SSW system for the next 40 years.

Awareness of the importance of the SSW for societal challenges is needed. The initiative on soil-conscious use and its ambassadors are important messengers. Special programmes can also make a contribution, like a yearly 'geo-week' for schools, the soil academy with a special lectureship on the use of soil and sub-soil.

To achieve sustainable use and management of soil and sub-soil the Dutch believe in consensus and mutual agreements prior to legislation and enforcement. To facilitate bottom-up societal initiatives and enhance tailor-made solutions, specific Dutch instruments are used, such as covenants and Green deals.

This section should explore the significance of the results of the work, not repeat them. Avoid extensive citations and discussion of published literature.

Conclusions

Following on from the successful Soil and Sub-soil Covenant 2009-2015 new covenants for 2016-2020 have been signed. This time industry has been involved as well. The focus is now to identify, control or remediate the sites facing actual contamination spread and ecological risks and to facilitate the transition to the Environmental and Planning Act. The knowledge agenda has been updated, 10 million euros has been made available for knowledge development and capacity building and for co-operation with other Member States for example in the H2020 INSPIRATION project. Several green deals, agreements between private and public partners, have been made or are in preparation e.g.: Producing Landscape, Peat Substitution, Temporary Nature, Business Co-operation in Agriculture and Nature, Clean Water Netherlands.

Thus our policy has changed from

- a sectoral to an integral approach
- a site-specific to an area approach
- 2D to 4/5D
- protection against soil threats to sustainable use of the SSW connected to societal challenges
- a leading role for the national government to a co-operation of authorities, end-users and other stakeholders
- national sectoral soil legislation to a decentralised assessment framework under an Environmental and Planning Act

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.14. Contaminated land management in Malaysia: policies and legal framework.

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Abstract

The growth of Malaysia from an agricultural economy to a thriving developing country in the past 40 years has resulted an added stress to the living and natural environment. Today, we are faced with the reality of environmental degradation, exploitation of natural resources, environmental pollution, impacts from climate change and loss of biodiversity as an outcome of our development. Adding to these concerns is the need to protect our soil and groundwater. Recognising the importance of the contaminated land issues and the need to formulate specific policy and legislation to control soil pollution, a study on criteria and standard for managing and restoring contaminated land was undertaken under the Ninth Malaysia Plan (2006-2010). As a result, a contaminated land management framework, which includes soil screening guidelines values and three (3) series of guidelines, were developed as a basis to further develop regulatory elements, strategy and policy.

Under the Tenth Malaysia Plan (2011-2015) and the Eleventh Malaysia Plan (2016-2020) initiatives, the outcomes of the study on contaminated land issues focus on:

- The inventory and classification of soil pollution,
- Leaking Underground Storage Tank,
- Regulatory Impact Analysis,
- Preliminary Contaminated Land Assessments,
- Polluted Land owned by the Government,
- Development of the Training Module and Competency Course, and
- A National Plan Strategic on Contaminated Land Management.

The comprehensive nature of legislations, policies and guidelines indicate that Malaysia is moving in the right direction in term of governance of contaminated land.

Keywords: Contaminated Land Management Framework, soil, groundwater

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

4.1.15. Setting thresholds for soil pollutants: experience from legal implementation in Wallonia and specific issues around Arsenic and Lead (Belgium)

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Abstract

Soil legislation was adopted in Wallonia (Belgium) in 2008 (the Soil Decree). This legal framework proposed soil screening values established on the risk-based methodology for five land uses and 50 compounds (metals, BTEX, PAH (Polycyclic Aromatic Hydrocarbons), mineral oil, chlorinated solvents and cyanides) as well as site specific risk assessment guidelines. As new scientific data in risk assessment concerning toxicity data, soil / air transfer model, soil / plant transfer model and other parameters were available, they were taken into account in a revised soil legislation adopted in 2018. This update, based on S-RISK exposure model also used in the two other regions of Belgium in charge of polluted soils (Flanders and Brussels), allowed also to gradually harmonize the soil legislation within the country. Risk assessment models helped defining such trigger values but needed to be combined with principles linked to technical feasibility, sensitivity of the land use and observed values in the field to allow for sustainable remediation. Besides, the calculation of the new soil screening values pointed out two widespread compounds in Wallonia, arsenic and lead, for which the calculated soil screening values were below the natural background level in soil, raising the issue of needing a public health intervention. To address this situation, Wallonia decided to fund a research project about the question of commercial quality of crop production in Wallonia and the management of risks for producers, in order to give answer to worried stakeholders. Other countries might face the same situation and discussions should be triggered at the international level to share related experiences.

Keywords: soil thresholds, soil legislation, risk assessment, sustainable remediation, arsenic, lead, polluted gardens

Introduction, scope and main objectives

Setting soil thresholds is commonly seen as an approach for determining pollutants limits above which a risk is expected and therefore defining if a soil is polluted or not. However, such thresholds are highly dependent on the soil and pollutants characteristics, the target organism to protect, the land use and the site-specific conditions, which can lead to a great complexity to handle. Risk modeling can help in defining soil thresholds, but is associated to various hypotheses, and model validation is rarely undertaken. Therefore, risk assessment remains a combination of modeling exercises and expert-base discussions, keeping in mind the sustainability of the decision taken. Implementing soil thresholds in a legal framework can be useful for triggering actions (site investigations, site remediation) but cannot be directly taken as remediation objectives, which should remain based on a site-specific risk assessment. This implies that the risk assessment follows a tiered approach with increasing complexity: from screening assessment using trigger values developed on a risk-based methodology (called also generic guideline values or threshold values) to a site-specific risk assessment.

Soil thresholds integrated in some legal frameworks usually vary from one country to another reflecting the various considerations having led to their determination. Within Belgium (which is a federal state), the three regional authorities in charge of polluted soils (Wallonia, Flanders and Brussels) have different soil thresholds, showing that variability can even be considered at lower scales. In Wallonia, the risk assessment holds a central place in soil legislation adopted since 2008 as it is considered as the key tool to help in decision-making in answering the questions: does the soil quality match with the current or the future land-use? If remediation works are required, what levels of clean-up need to be reached?

Risk assessment is not a frozen framework but improves thanks to new scientific data. In 2016, Wallonia decided to update its human health risk assessment tool to take stock of new knowledge such as recent toxicity and bioavailability data and tend towards interregional harmonization by using a new exposure model called S-RISK, which was also used, in the two other regions. The objective of this paper is to explain how this could be achieved and which pending questions still need further investigation.

Methodology

In 2008, the Walloon soil legislation proposed the principle of three trigger values (VS) equal to the maximum acceptable concentrations in soil taking into account five different land uses (Type I – natural, Type II – agricultural, Type III – residential, Type IV – recreational & commercial activities, Type V - industrial). The trigger values were established for the protection of three kinds of receptors - human health (called VS_H), aquifers (called VS_N) and terrestrial ecosystems (called VS_E) - and considering fifty pollutants - metals, BTEX, PAH (Polycyclic Aromatic Hydrocarbons), mineral oil, chlorinated solvents and cyanides. Land uses were associated to adapted exposure scenario to pollutants considering the three receptors, with a specific scenario for the agricultural land use (Type II), which was based on the agricultural products quality. The minimum of the three trigger values was generally taken as the limiting one leading to the proposed final trigger value. However, to be taken on board, it should be above two times the laboratory quantification limit value, otherwise the latter was chosen. Besides, principles of gradual sensitivity of land uses had to be respected (increasing trigger values from Type I to Type V). In addition to trigger values (VS), other thresholds were defined to establish estimated levels of natural background concentration (VR – reference value) taken as ideal remediation objective, and to determine maximum levels of pollutants requiring remediation intervention (VI – intervention value). When combined with guideline values for groundwater and ecosystem protection mostly from Groundwater Directive (EC, 2006), those different values became the overall thresholds for soil and groundwater and were integrated as an annex in the legal framework, the Soil Decree (Walloon Parliament, 2008).

Human health trigger values (VS_H) were specifically calculated on “risk-based” approach following the risk assessment methodology defined by the National Research Council in USA (NRC 1983), in the reverse mode and using conservative assumptions. The trigger values were calculated with CSOIL equations (Waitz *et al.* 1996) available in RISC-HUMAN model (Van Hall Instituut, the Netherlands).

In 2017, Wallonia replaced RISC-HUMAN by S-RISK model recently developed by VITO in Flanders (Cornelis *et al.* 2017) in order to take into account its more suitable soil / air transfer model (Bakker *et al.* 2008), the calculation of exposure by age groups instead of only child/adult targets (following EPA recommendations, US-EPA 2005) and with an aim to gradually harmonize the soil legislation in the three regions of Belgium. Trigger values were calculated again for the same five land-uses and fifty pollutants, but additional generic soil standard horizons were taken

into account, including backfilled soils. For toxicity assessment, an update of reference toxicity values was done based on literature review, focusing on the selection of the most appropriate reference values for Wallonia context and not the most protective values as in 2008. While using again the reverse modeling calculation, taking into account updated laboratory quantification limits and keeping a gradual sensitivity across land uses in a similar manner than in 2008, new principles were used to finally determine the updated soil threshold values to take in the Soil Decree: the removal of terrestrial ecosystems trigger values under commercial and industrial uses due to its low relevance in such land uses (while keeping an expert committee on ecosystem issues to address case-by-case the potential impacts of the pollution of a site and to better define vulnerable areas), the use of a residential scenario for agricultural land use (allowing for an external development of a specific approach for food production issue, see discussion section below), and the requested similarity of the proposed trigger values in Type III to V land use with about 4000 observed soil pollutants values found in various databases reflecting background concentration levels (POLLUSOL 2, excavated soils – TEREX, and economic wasteland).

Finally, the reference value (VR) was withdrawn from the threshold levels and replaced by 80% of the new trigger value such that remediation objectives could be meaningful to what can be found in surrounding sites which do not need to be further investigated according to the Soil Decree, and the intervention value (VI) was also removed as already taken into account in soil investigations defining needed remediation, security and follow-up measures.

Results

Out of 255 previous threshold values set in 2008, only using S-RISK reverse modeling and removal of VS_E for Type IV and V resulted in 70 values left unchanged (as VS_N was the limiting value), 128 increased values (mainly mineral oil and PAH), and decreased 47 values (mainly heavy metals, chlorinated solvents, cyanides and ethylbenzene). In particular, due to new toxicity data, the trigger values calculated in soil for arsenic and lead compounds were below the measured natural background concentration in soil in Wallonia.

Concerning oral toxicity of arsenic, the selection of the carcinogenic value established by Health Canada (Santé Canada 1993) leads to a very low screening value in soil (0.16 mg/kg for a residential use). This screening value cannot be used as a trigger value or a remediation objective as natural background concentration in Wallonia is 12 mg/kg on average (POLLUSOL 1 study in Sonnet *et al.* 2003). The reference toxicity value ($2.80 \text{ (mg/kg.d)}^{-1}$ as oral slope factor) leading to such low screening level in soil was elaborated from a cross-sectional study of 40,000 Taiwanese exposed to arsenic in drinking water reaching 1800 $\mu\text{g/L}$ level (Tseng *et al.* 1968, Tseng 1977). Even if this study demonstrated an association between arsenic exposure and development of skin cancer, it shows several weaknesses and uncertainties.

Concerning oral toxicity of lead, the selection of the benchmark dose limit established by EFSA (EFSA 2010) also leads to a very low screening value in soil (1.4 mg/kg for a residential use). This screening value cannot be used as a trigger value or a remediation objective as such neither as natural background concentration in Wallonia is on average around 25 mg/kg. The provisional tolerable weekly intake (PTWI) of 25 $\mu\text{g/kg}$ body weight per week (or 3.6 $\mu\text{g/kg.d}$) estimated by WHO was the usual reference value, based on a 100 $\mu\text{g/L}$ blood lead level. But WHO withdrew it in 2010, considering that this value could no longer be considered health protective. In 2010, EFSA (European Food Safety Authority) decided to establish Benchmark Dose Levels for 3 health effects : neurodevelopmental effects in children and cardiovascular and renal effects in adults. Wallonia selected the Benchmark Dose Levels intake value of 0.063 $\mu\text{g/kg.d}$ for adults (renal toxicity) and 0.05 $\mu\text{g/kg.d}$ for children (neurotoxicity) which corresponds to blood lead levels

(BMDL₁₀) of 15 µg/L and 12 µg/L respectively after adding an uncertainty factor of 10 to EFSA values.

The use of others defined principles (updated laboratory quantification limits, similarity with observed background values and gradual sensitivity across land uses) allowed for balancing some outlying proposed trigger values. However, as further discussions were needed, in particular for arsenic and lead which are widespread throughout Wallonia, soil thresholds for Type I to III were left unchanged compared to 2008, while updated values for Type IV and V were taken into account. The updated soil thresholds can be found in Annex I of the revised Soil Decree (Walloon Parliament, 2018).

Discussion

The revision of soil thresholds of the 2008 Soil Decree in Wallonia allowed to take into account latest knowledge development and showed that models can be used as tools to facilitate determination of soil thresholds. However, caution is required when using such models and output values should be balanced with technical considerations and observed values in the field. Indeed, for arsenic and lead the health based guideline values became very small and lower than the background concentration in Wallonia, preventing from any sustainable soil remediation. Despite no specific health problems reported with those two elements in Wallonia, such gap between the risk assessment answer and the observed effect on the general population needs more explanation and several ways of research are currently being explored. This may be of interest for other countries facing the same challenge given the global update of arsenic and lead toxicity. Comparison between existing toxicity data and observed adverse health effects has to be especially investigated in the context of private/collective gardens and food production on potentially polluted sites. Such research has started in January 2018 in Wallonia on a specific site where a big collective garden is taking place. It is dedicated to answer the question "*Determination of pollutant content limits in the soil in order to ensure the commercial quality of crop production in Wallonia and the management of risks for producers - Development of a pilot tool via the internet to provide specific recommendations for management and management use to any producer of food biomass produced on contaminated soil in Wallonia (SANISOL)*".

Concerning arsenic, the current toxicological value for oral exposure is established based on an epidemiological study where general population was impacted due to ingestion of arsenic in water. However, absorption linked to exposure from soil ingestion can be different. Moreover, the human bioavailability of arsenic seems different depending on its origin (from geochemical background or polluted soils) or on its chemical speciation (Bradham *et al.* 2011, POLLUSOL 2 study in Pereira *et al.* 2012).

Concerning lead, recent studies show real adverse effects on population which appear at blood lead level lower than 100 µg/L (ANSES 2013). Unfortunately, there are many sources of lead contamination : dust and soil, tap water but also leaded paint from walls, lead-containing or lead-coated objects. Lead is a cumulative toxicant, particularly harmful to young children and need carefulness as a public health problem.

Conclusions

Establishing soil thresholds can be useful as screening values for triggering actions (site investigations, site remediation) but cannot be directly taken as remediation objectives, which should remain based on a site-specific risk assessment. Risk assessment models can help defining such trigger values but should be combined with principles linked to technical feasibility,

sensitivity of the land use and observed values in the field. Soil screening values set in the soil legal framework in Wallonia in 2008 were updated in 2018 due to the constant evolution in the risk assessment field and allowed for gradual harmonization with other regions of Belgium. The update exercise demonstrated the high impact that more recent toxicity data can have on soil management. Two worrying pollutants which are widespread in the soils and might need a public health intervention were pointed at: arsenic and lead. Further research is undertaken, particularly in the context of private/collective gardens and food production, aiming at developing a human health risk assessment dedicated to vegetable production, using the most suitable data and to confront results from risk assessment and human biomonitoring.

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The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.1.16. Reference values for potentially harmful elements in soils from Atlantic Rainforest, Brazil

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Abstract

The potentially harmful elements (PHE) contents in soils is a function of parent rock composition and soil forming processes. Due to requirement of Brazilian legislation, natural baseline values must be determined for each specific environment or each state in the country. The aim of this work was to access the natural baseline values for PHE in soils from Paraná's Coast Plain (Atlantic Rainforest) and to verify its correlations with soil attributes. It was crossed geological and soil maps to choose the sampling points and, performed soil fertility, texture and Fe oxides (crystalline and amorphous) determinations. Pseudo-total metal contents were accessed by microwave-assisted digestion (EPA3051A method). The positive correlation between PHE and soil clay shows the important role of pedogenetic Fe oxides on the retention of PHE in the soils. The increase of PHE contents in sandy soils from Coastal Plain occurs due to the heavy flow of vehicles for decades towards the coast of Paraná state. The following background PHE values (mg kg⁻¹) were found: Ag (0,29); As (4,78); Ba (111,4); Cd (1,02); Co (< 0,17); Cr (48,8); Cu (17,9); Mo (1,44); Ni (17,2); Pb (16,9);

Sb (3,12); V (60,2); and Zn (52,5). These contents was generally higher than studies in other states of Brazil but below the Brazilian legislation, except Sb. Therefore, our work highlights the need for determination of background PHE considering each specific environment. This procedure will increase the quality and accuracy of the intervention by environmental agencies.

Keywords: Soil Pollution, Soil Quality Reference Values, Sandy Soils, Background Potentially Harmful Elements, Inner-sphere Adsorption

Introduction, scope and main objectives

The effects of negative impacts caused by human activities must be evaluated to improve the environmental quality. In this context, governments are responsible to implement environmental laws (Santos and Alleoni, 2013). The potentially harmful elements (PHE) (e.g heavy metals) are the main inorganic pollutants present in soils and the most studied due to the deleterious effects on humans and biota. These elements are found in natural conditions due to the composition of the parent material but the anthropogenic processes change the natural content of PHE in soil promoting its enrichment (Hu and Cheng 2016). Therefore, the background contents or reference quality values (QRV) must be consider to check soil contamination. The soil formation factors and processes determines the differences between PHE contents in natural systems, so the QRV levels for PHE's must be determined for each environmental situation (Sierra *et al.* 2007). In Brazil, the National Environmental Council (CONAMA) determines that each State should have the QRV values. Considering the diversity in geologic, climate, soil and other environmental factors in our country, we understand the need to determine QRV's for each environmental situation and not for each State. The Paraná State has an area covered by Atlantic Rainforest bathed by the Atlantic Ocean. The quality of Coastal Plain soils is worldwide relevant and Atlantic Rainforest biome has one of the greatest diversity of wildlife and flora of the planet. Hence, the determination of the QRV's is essential to preserve this unique environment. The aim of this study was to determine the QRV for PHE (Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V e Zn) in soils under Atlantic Rainforest of Coastal Plain of the Paraná state, Brazil, and also establish relationships between the levels of these elements with physical, chemical and mineralogical soil properties. This work is already been published in Journal of Geochemical Exploration.

Methodology

Soil sampling, physicochemical and mineralogical soil attributes

It was collected 63 soil samples covering six soil types (Entisol, Spodosol, Inceptisol, Aquic Alfisol, Oxisol and Ultisol) and 15 geological conditions (Table 1). At a radius of 5 m of each point, five samples at 0 to 0.2 m deep were collected and homogenized (composite sample). The soil samples were collected using a non-metal instrument to avoid PHE contamination. To make sure the sampling points were in areas without or with minimal human influence (Atlantic Rainforest), they were observed through aerial images (Google Earth®). Soils samples were air-dried and passed through a 2-mm sieve and subjected to chemical and physical analyses according Embrapa (1997) method. Content and chemical composition of iron oxides of low and high crystallinity were determined by the 0.2 mol L⁻¹ pH 3.0 ammonium oxalate (AO) (McKeague 1978) and citrate-dithionite-bicarbonate (CDB) (Mehra and Jackson 1960) methods, respectively. Iron was determined by atomic absorption spectrophotometry.

Table 1. Sampling location, geology and soil order in Coastal Plain, Paraná state, Brazil. From Melo *et al.*, 2017.

Point	Coordinates		Geology	Soil
	X	Y		
1	733122	7131277	Marine sediments	Entisol
2	725403	7135095	Fluvial deposition sediments	Spodosol
3	728874	7129156	Colluvium deposits	Spodosol
4	738023	7127692	Clay and silt-sand sediments 1	Spodosol
5	741414	7132379	Marine sediments 1	Spodosol
6	741106	7128889	Marine sediments 2	Spodosol
7	745980	7140423	Marine sediments 3	Spodosol
8	748751	7157705	Old alluvium	Spodosol
9	745706	7167491	Marine sediments 4	Spodosol
10	755015	7157973	Marine sediments 5	Spodosol
11	737996	7171443	Alexandra formation	Spodosol
12	737893	7173261	Continental gravels 1	Spodosol
13	740808	7172230	Clay and silt-sand sediments 2	Spodosol
14	772893	7205442	Clay and silt-sand sediments 3	Spodosol
15	742424	7152846	Marine sediments 6	Spodosol
16	763839	7171448	Marine sediments 7	Spodosol
17	740755	7173503	Marine sediments 8	Spodosol
18	739752	7171325	Continental gravels 2	Spodosol
19	742368	7172983	Marine sediments 9	Spodosol
20	744896	7144617	Marine sediments 10	Spodosol
21	736901	7126536	Gneiss-Migmatite complex1	Inceptisol
22	724969	7145429	Fluvial sediments 1	Inceptisol
23	742191	7161689	Fluvial sediments 2	Inceptisol
24	715729	7181895	Fluvial sediments 3	Inceptisol
25	722476	7191394	Cachoeira complex	Inceptisol
26	730993	7199500	Fluvial sediments 4	Inceptisol
27	752563	7209521	Serra Negra complex	Inceptisol
28	753450	7207744	Fluvial sediments 5	Inceptisol
29	754307	7207244	Clay and silt-sand sediments	Inceptisol
30	761172	7213613	Fluvial sediments 6	Inceptisol
31	775758	7210104	Fluvial sediments 7	Inceptisol
32	731668	7125282	Marine sediments	Inceptisol
33	732668	7125610	Gneiss-Migmatite complex 2	Inceptisol
34	717455	7177483	Fluvial sediments 8	Inceptisol
35	770460	7199113	Marine sediments	AquicAlfisol
36	771247	7199510	Clay and silt-sand sediments 1	AquicAlfisol
37	771033	7200426	Colluvium deposit 1	AquicAlfisol
38	723875	7179557	Fluvial and marine sediments associated with mangroves 1	AquicAlfisol

39	729202	7176464	Continental gravels	AquicAlfisol
40	726508	7196282	Clay and silt-sand sediments 2	AquicAlfisol
41	724261	7194445	Gneiss-Migmatite complex 1	AquicAlfisol
42	732123	7198236	Colluvium deposit 2	AquicAlfisol
43	732299	7198723	Gneiss-Migmatite complex 2	AquicAlfisol
44	776677	7211331	Colluvium deposit 3	AquicAlfisol
45	714719	7178182	Gneiss-Migmatite complex 3	AquicAlfisol
46	730216	7133165	Marine sediments 1	AquicAlfisol
47	762405	7171456	Fluvial and marine sediments associated with mangroves 2	AquicAlfisol
48	748188	7169632	Fluvial and marine sediments associated with mangroves 3	AquicAlfisol
49	748188	7169632	Fluvial and marine sediments associated with mangroves 4	AquicAlfisol
50	739986	7172339	Clay and silt-sand sediments , paleo estuarines	AquicAlfisol
51	740868	7173160	Fluvial and marine sediments associated with mangroves 5	AquicAlfisol
52	723886	7189294	Fluvial and marine sediments associated with mangroves 6	AquicAlfisol
53	737136	7193658	Recent floods	AquicAlfisol
54	743197	7191262	Colluvium deposit 4	AquicAlfisol
55	772931	7210178	Gneiss-Migmatite complex 4	AquicAlfisol
56	745509	7169072	Marine sediments 2	AquicAlfisol
57	742668	7173774	Gneiss-Migmatite complex	Oxisol
58	713655	7188093	Fluvial sediments 1	Ultisol
59	712815	7186533	Colluvium deposit 1	Ultisol
60	737136	7196078	Fluvial sediments 2	Ultisol
61	736154	7195382	Gneiss-Migmatite complex	Ultisol
62	772295	7211612	Colluvium deposit 2	Ultisol
63	772104	7210026	Fluvial sediments 3	Ultisol

Potentially harmful elements (PHE) in soils

About 0.5000 g of soil was transferred to Teflon tubes in the presence of 9 mL of concentrated HNO₃ and 3 ml of concentrated HCl. The tubes were held in a microwave (Mars Xpress 6, CEM) for 8 min and 40 s to ramp temperature reach 175 °C; then this temperature was maintained for an additional period of 4 min 30 s (EPA 3051A; Usepa 1998). The solution was filtered and transferred to a 25 mL volumetric flask. All extracting solutions and volumetric flasks were filled with ultra-pure water (18.2 MΩ.cm at 25 °C - Millipore Direct-Q System). High purity acids were used in the analyses (Merck PA) and all extracts were filtered in a slow filter paper (Macherey Nagel®). The PHE concentrations (Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V, Zn) were determined by atomic emission spectroscopy with plasma coupled inductively (ICP-AES). It was established the detection limit (DL) of ICP-AES. The DL for each PHE was calculated using Eq. (1).

$$DL = \text{average concentration of 10 blank samples} + 3s \quad (1)$$

where: s is the standard deviation of the readings.

It was calculated the practicable DL of the soil, multiplying the DL by the dilution factor of the samples (50 times). Analysis quality control was performed with certified soils (NIST SRM2709 San Joaquin soil) (Nist 2010).

Soil quality reference values (QRV) for potentially harmful elements (PHE) in soils

The QRV values for each PHE in soils were determined through percentile diagrams analyzes (Sierra *et al.*, 2007). The statistical procedure was performed from the normal distribution curve, settling the 75 percentile (superior quartile) of the frequency distribution of analytical results. The anomalies (outliers) were previously withdrawn (Alfaro *et al.*, 2015). When the analytical results of all samples were less than the practical DL, this variable was considered as the QRV of the heavy metal. When some analytical results were less than the practical DL, it was considered on the data matrix the value practical DL/2 and, when all analytical results were above practical DL it was remained the proper levels (Paye *et al.* 2010; Santos and Alleoni 2013).

Statistical analysis

The results were evaluated by descriptive and Pearson correlation analysis ($P < 0.05$). It was used the PHE levels versus physical, chemical and mineralogical soil attributes for Pearson correlations. For explain possible effects of soil types in their mineralogical characteristics and PHE content, box-plot graphics were built. All statistical procedures were performed using the Statistic version 8.0 program.

Results and discussion

The pH average values (Table 2) reduces outer-sphere adsorption of cations in variable charge minerals and increases the mobility of most PHE in the soils (Bednářová *et al.* 2016). The influence of marine sediments in the Coastal Plain explain the sandy texture of the most soil samples. Therefore, the soil organic matter upper to 0.2 m from soil surface was responsible for the CEC at pH 7.0. The correlation between Fe_2O_3 -CDB and clay content was positive ($r = 0.83$, $P < 0.005$) for samples 3, 21, 33, 41, 43, 45, 55, 57, 59, 61 and 62 (formed by colluvium deposits and gneiss-granite complex) (Table 1). The Fe_2O_3 -CDB values varied from 5 to 40 mg kg^{-1} and Fe_2O_3 -AO 5 to 10 mg kg^{-1} (data not showed)

The background levels (Atlantic Rainforest samples) of PHE in the soils were highly variable compared to the international standards and other states of Brazil (Table 3). They were generally lower than the obtained in Cuba, Italy, China, Ireland, USA and Minas Gerais state (Brazil) and generally higher than the Poland, Espirito Santo state (Brazil), Mato Grosso state (Brazil), Rondonia state (Brazil) Pernambuco state (Brazil), Piauí state (Brazil) and Brazilian Organosols (OR) levels. The Paraná Coastal Plain soil has higher average of PHE than the other Brazilian states due to strong influence of sandy marine sediments. Comparing to a similar environment (formed by fluvial and marine sediments) in Parnaíba River Delta (de Paula Filho *et al.* 2015), our contents for Cr, Cu, Pb e Zn are at least 1.5 times higher. The Pb content was higher than other Brazilian States (Minas Gerais, Espirito Santo, MatoGrosso/Rondônia and Piauí) (Table 3). It must be consider the heavy traffic occurring during the summer. From Pb emissions released by

automobiles, 20 to 60% are deposited close to the source, which is observed by high content in plants and soils along the roads (Turer and Maynard 2003; França *et al.* 2017).

Table 2. Physical and chemical soil attributes. From Melo *et al.*, 2017.

Descriptive variables	pH _{H2O}	Sand	Clay	OC	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	CEC pH 7.0	V
Average	4.4	488	257	29.6	1.12	0.20	0.31	0.25	2.57	13.3	10.2
Median	4.4	497	233	20.2	0.08	0.12	0.15	0.12	1.88	11.0	4.7
Maximum	5.4	936	634	187.3	52.17	3.17	2.31	2.15	7.80	69.7	85.8
Minimum	3.3	2	23	6.1	0.03	0.03	0.07	0.01	0.09	2.15	2.0

Table 3. Background levels of Heavy metals (mg kg⁻¹) from samples with concentration higher than the detection limit (DL) (maximum number (N^o) of samples = 63) for soils of Paraná state Coastal Plain and reference levels from Cuba (CU), China (CHI), Ireland (IRL), Italy (ITA), United States (USA), Poland (POL) and Minas Gerais (MG), Espírito Santo (ES), MatoGrosso/Rondônia (MT/RO), Pernambuco (PE), Piauí (PI) Brazilian states and Organosols from Brazil (OR). From Melo *et al.*, 2017.

Metal	N ^o	Mean	CU ^a	CHI ^b	IRL ^c	ITA ^d	USA ^b	POL ^e	MG ^f	ES ^g	MT/RO ^h	PE ⁱ	PI ^j	OR ^l
Ag	30	0.4	2.0	10.0	-	-	-	-	-	-	-	-	-	-
As	47	4.4	10.8	9.2	-	-	5.2	2.6	-	6.8	-	0.4	-	-
Ba	63	70.8	128.7	-	-	-	-	271.2	-	-	-	99.1	-	117.0
Cd	55	0.6	1.2	0.1	0.5	-	1.6	-	0.5	-	-	0.6	-	-
Co	7	0.2	31.4	-	-	-	20.0	3.6	16.5	8.6	20.3	3.5	-	-
Cr	63	44.2	463.2	53.9	49.5	100.0	37.0	16.8	100.1	41.1	39.4	27.1	18.0	21.0
Cu	59	12.1	83.7	20.0	16.9	51.0	17.0	6.3	30.9	5.6	16.5	7.2	6.8	33.0
Mo	49	1.6	1.7	1.2	-	-	0.6	-	-	1.4	-	-	-	-
Ni	60	13.5	294.2	23.4	13.5	46.0	13.0	7.4	30.1	6.7	1.3	6.0	-	12.0
Pb	62	10.4	34.6	23.6	30.4	21.0	16.0	18.8	3.9	8.8	8.1	11.2	5.9	18.0
Sb	39	3.4	6.9	-	-	-	-	-	-	-	-	-	-	-
Se	10	1.4	-	-	-	-	-	0.1	-	-	-	-	-	-
V	63	37.1	-	-	-	87.0	-	18.4	-	-	-	-	-	-
Zn	63	30.4	90.7	67.7	70.3	89.0	48.0	40.3	13.1	22.6	6.8	22.5	13.4	34.0

Note: - data not valuated. ^a Alfaro *et al.* (2015); ^b Chen *et al.* (1991); ^c Salonen and Korkka-Niemi (2007); ^d Angelone and Bini (1992); ^e Dudka (1992); Dudka and Markert (1992); ^f Souza *et al.* (2015); ^g Paye *et al.* (2010); ^h Santos and Alleoni (2013); ⁱ Biondi *et al.* (2011); ^j de Paula Filho *et al.* (2015); ^l Lima *et al.* (2016).

The pedogenic iron oxides (Fe₂O₃-CDB) was positive related to the most PHE contents in soils (0.57 < R < 0.82, P < 0.05) (Fadigas *et al.*, 2006; Paye *et al.*, 2010; Ramos-Miras *et al.*, 2014; de Paula Filho *et al.*, 2015; Lawson *et al.*, 2016; Lima *et al.*, 2016). These minerals have high pH of point of zero charge (pH_{PZC} ~8 to 9). In other words, at pH below 7.0 predominates anion exchange capacity (AEC). Thus, the adsorption of cationic PHE occurs by ligand exchange or inner-sphere formation. This mechanism is very important on environmental terms due to its greater stability.

Our QRV values were large variable than the other regions of Brazil (Fadigas *et al.*, 2006). These differences is mainly due to parent material composition, soil forming processes and differences between analytical techniques. Except for Sb, the natural contents of all elements studied are above the prevention values suggested by Brazilian Environmental Agency (Conama, 2009). The Sb are used as a catalyst in plastics, hardener of lead alloys in batteries and ammunition and the lubricant in automotive brake and clutch linings (Filella *et al.*, 2009). Therefore, the heavy traffic on the roads of Coastal Plain can contribute to this result.

Table 4. Quality reference values (QRV) (mg kg⁻¹) for soils in the Coastal Plain of Paraná compared to values obtained for other states of Brazil. From Melo *et al.*, 2017.

	Ag	As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Se	V	Zn
P 75	0.29	4.78	111.4	1.02	<0.17	48.7	17.8	1.44	17.2	16.9	3.12	<1.28	60.2	52.5
MG ^a	-	8.00	-	<0.4	-	75.0	49.0	-	21.5	19.5	-	-	-	46.5
ES ^b	-	<12.83	-	<0.13	10.21	54.1	5.9	1.74	9.1	<4.5	-	-	-	29.8
RO/MT ^c	-	0.44	-	<0.3	21.30	44.8	20.6	-	2.1	9.0	-	-	-	3.0
SP ^d	0.25	3.50	75.0	<0.5	13.00	40.0	35.0	<0.4	13.0	17.0	<0.5	0.25	275.0	60.0
PV ^e	2.00	15.00	150.0	1.30	25.00	75.0	60.0	30.00	30.0	72.0	2.00	5.00	-	300.0

Note: - data note valuated. ^a Minas Gerais state - Souza *et al.* (2015). ^b Espírito Santo state - Paye *et al.* (2010). ^c Rondônia e Mato Grosso states - Biondi *et al.* (2011). ^d São Paulo state - Cetesb (2005). ^e Prevention values suggested by Brazilian environmental agency (CONAMA, 2009).

Conclusions

- Soils under Atlantic Rainforest of the Paraná Coastal Plain showed relatively high average levels of PHE when compared with data from other studies in Brazil and some countries in the world. The dispersion of air pollutants from vehicles increased PHE background in plain soils;
- The pedogenetic Fe oxides had important role in the adsorption and maintenance of PHE in soil. Special attention should be given to Sb, due its concentration in soil is over the critical environmental level.
- The great differences in QRV for PHE between the Coastal Plain of Paraná and other national and international data highlights the need for determination of QRV locally, considering the great differences in the parent materials that reflect in distinct soil classes. The local determination of QRV will increase the quality and accuracy of the intervention of environmental agencies.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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Sub-theme 4.2: Global status of soil pollution

4.2.1. Heavy metal soil pollution in Russian Federation: a review

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Abstract

Based on available data published in open academic papers and reporting documents of environmental organizations, heavy metal (HM) pollution assessment in soils of Russian Federation was compiled. It is shown that since 2007 HM soil pollution in impact zones of large industrial centres practically does not occur. However, despite a sharp decline in the inputs of HM into soil, the level of pollutants in soils of industrial territories remains high.

Keywords: heavy metals, industrial contamination, monitoring

Introduction, scope and main objectives

Regular monitoring of soil heavy metal (HM) contamination levels on the territory of the Russian Federation is carried out by Federal Service on Hydrometeorology and Monitoring of the Environment (Roshydromet). The obtained data on HM content in soils are compared with national standards. As reference values for certain elements maximum allowable concentrations (MAC) and tentative allowable concentrations (TAC) are applicable, whether for complex pollution Z_b index is used. Z_b is the sum of concentration coefficients K of pollutants normalized by background values for corresponding elements. It is calculated as

$$Z_b = \sum_{i=1}^n K_{bi} - (n-1)$$

where n is the number of detected metals, K_{bi} is the metal concentration coefficient equal to the ratio of i^{th} metal concentration in contaminated soil to its concentration in background area ($K_b = C_i/C_{background}$).

At $Z_b < 16$, pollution is considered harmless; at $16 < Z_b < 32$ as moderately dangerous; at $32 < Z_b < 128$ as dangerous; and at $Z_b > 128$ as extremely dangerous (Roshydromet 2017).

In average over the past 10 years about 2.2% of the surveyed settlements in Russian Federation can be classified as belonging to dangerous category, about 9.3% to moderately dangerous, and 88.5% to permissible level of soil contamination (Minprirody RF 2017). Soils in which an excess of MAC of HM was detected cannot be attributed to the permissible category of contamination. National regulations of MAC and TAC (Roshydromet 2017) are comparable with European standards adopted for soils with the most stringent requirements: agricultural soils and soils of children's playgrounds (Motuzova and Karpova 2013).

The objective of this work is to evaluate the levels and dynamics of HM-polluted soils in Russia over the last 20 years, using available published data from open academic papers and environmental organizations' reporting documents.

Methodology

Assessment of HM soil pollution level was compiled using published data. Values of HM content in soils of various surveyed sites were compared with MAC, TAC or Z_b .

Results

The most powerful sources of soil pollution by HM are mining enterprises, large non-ferrous metallurgy plants. Content of metals in soils near some of these sources is given in Table 1. Of these, the largest are located in Arctic: in Norilsk industrial region and in Kola Peninsula. From these sources the impact zone of HM soil contamination extends up to 50-200 km.

Table 1. Heavy metal content (ppm) in soils of Russia with high contamination level

Town, area	Source of pollution	Territory of survey	Cu	Ni	Co	Pb	Zn	Cd	Data source
Monchegorsk, Zapolyarny, Nikel, Pechenga: Murmansk Region, Kola Peninsula	"Severonickel" and "Pechenganikel"	< 3 km	950-7000	2000 – 10000	100-800				Koptsik <i>et al.</i> 1998; Kashulina <i>et al.</i> 2007, 2017; Evdokimova <i>et al.</i> 2011, 2014; Evseev and Krasovskaya 2017
Norilsk, Krasnoyarsk Territory	"Nornickel": nickel and palladium mining and smelting plant	Urban territory and suburb up to 15 km	1536-16000 546-3092	415-3469 274-1736	384-1229	12-150 12-49	94-348 43-143		Vodyanitskii <i>et al.</i> 2011; Yakovlev <i>et al.</i> 2008
Revda, Sverdlovsk Region, Middle Urals	Middle-Uralian Copper-Smelting Plant	< 1 km 7 km	1084-2400 170-424			290-1148 50-215	160-969 100-257	4-6 2-5	Vodyanitskii <i>et al.</i> 2011; Vorobeichik and Kaigorodova 2017
Karabash, Chelyabinsk region, Southern Urals	Copper smelting plant	2 km	4340	280		900	1877	13	Tatsiy 2012
Rudnaya Pristan, Pacific coast of Primorsky Krai	Lead smelting plant	2 km 4,5 km	331-1451 118-781	126-621 32-186	172-302 84-210	1848-4148 330-1667	1205-3331 515-1340	12-26 2-8	Timofeeva 2012

In Murmansk region areas of the greatest soil HM-contamination are near to enterprises of nonferrous metallurgy "Pechenganikel" (towns Zapolyarny, Nikel, Pechenga) and "Severonickel" (Monchegorsk). Within 3 km radius from the enterprises, the contents of priority pollutants (nickel, copper, and cobalt) in upper soil layer in average achieve 60 and 30 MAC. In this area high

accumulation of metals occurs not only in top soil organic horizons, but also in mineral horizons B. Territory with the maximum contamination achieves 3.2 thousand sq. km. These contaminated areas are man-made barrens, in which vegetation has been almost completely destroyed, soil cover structure has changed, and surface waters are highly contaminated.

In Norilsk the major sources of HM- contamination are large Russian metallurgical enterprises producing nickel, copper, cobalt, platinum group metals: structural subdivisions of Polar Division of Mining and Metallurgical Company Norilsk Nickel. Ministry of Natural Resources and Ecology of Krasnoyarsk Territory assesses the ecological state of Norilsk urban district in 2015 as "crisis" and assigns this territory as a zone of emergency in terms of ecological situation (Minprirody Krasnoyarsk region 2016). The city of Norilsk belongs to the first dozen of the most polluted cities in the world. Content of metals in soils of the city exceeds TAC levels 30-240 -folds for copper, 10-86 folds for nickel, and 23 folds for cobalt (Yakovlev *et al.* 2008; Vodyanitskii *et al.* 2011). In soils directly adjacent to metallurgical plants, the excess can reach 350 (Cu), 500 (Ni), and 70 (Co) times (Zachinyaev and Zachinyaeva 2011; Evseev and Krasovskaya 2017). Impact zone with high contamination level extends for 25 km from the city.

The greatest density of industrial sources for complex soil HM-contamination is observed in Middle and Southern Urals, the largest mining and metallurgical base of the country. In some cities content of metals in soils 5-10 folds or more exceed TAC levels (towns Kirovgrad, Rezh, Asbest, Revda). In urban area of Chelyabinsk there are about 600 industrial enterprises. About 12% of its territory (in the city center) can be attributed to the zone of ecological disaster: content of Zn, Pb in soil is 25 times higher than the TAC. TAC levels of these HM are also exceeded in soils of residential zone. Soils of Magnitogorsk and Karabash are heavily polluted (Tatsiy 2012).

A high level of technogenic load is observed in the town of Belovo, Kemerovo region, where a zinc plant has been operating for 80 years. Industrial giants of Baikal region have composed zones of contaminated soils in the cities of Bratsk (aluminum plants, ferroalloys), Svirsk (metallurgical plant), Irkutsk (construction, machine-building plants), Cheremkhovo (heavy engineering, mechanical, chemical plants, and open-pit mining). In Svirsk soils, MAC levels for lead are exceeded in 9-63 times (Minprirody RF 2017).

In the Far East the most unfavorable region is Dalnegorsk and the nearby village Rudnaya Pristan. Industrial centers of the Primorye are widely known. In Dalnegorsk there is a huge quarry of Mining & Chemical Combine, in Rudnaya Pristan there is a shed of mining and smelting combine (created more than 100 years ago for lead production). In 30 km zone away from them, Pb content in soils reaches 17-42 MAC (Timofeeva 2012; Minprirody RF 2017). This village is included in the list of the most polluted sites in the world.

In the south of Russia, unfavorable environmental situation in respect to soil HM-contamination has developed in Vladikavkaz (main sources of pollution are OJSC Electrozinc, and Pobedit). Content of HM in soils exceeds TAC for Zn 27 and 40 times, Cd in 94 and 324 times, Pb 10 -30 times, Ni 3-4 times (Kabaloev 2014; Minprirody RF 2017).

In Central Chernozem area soil contamination with HM is concentrated around iron ore mining enterprises in Belgorod and Kursk regions. Content of such metals as Zn, Cu, Pb, Co in these soils does not exceed MAC by more than 2 times (Zamotaev *et al.* 2017).

In soils of most of the medium and large cities of Russia, excesses of a wide range of HM over their background contents have been recorded. Sources of pollution are power engineering companies (coal-operating power plants) and vehicles, but the mostly recorded excess of TAC levels is not more than 2-folds.

In Moscow the results of soil survey using Z_b index showed that soils can be classified as weakly (permissible) polluted at 95% of observation sites (Department... 2017).

Soils of agricultural and forest lands are affected by the megapolices nearby. Results of arable soils survey in European part of Russian Federation show that the proportion of soils with HM-levels of 1.5-2 MAC composes only 2-3%.

Discussion

Over the past 25 years, emissions of industrial enterprises as a whole have decreased both due to the economic recession, and due to the modernization of production, introduction of new environmental technologies. Nickel Plant in Norilsk (2016) and the lead-melting plant Rudnaya Pristan have been stopped. All operating large metallurgical enterprises currently introduce modern ecological technologies. But for natural processes of soil self-cleaning from HM a long time period is required. Figure 1 shows the dynamics of copper and lead emissions from Sredneuralsky Copper Smelting Plant (SUCSP) and metal content in upper soil horizons (O and AY) at distances of 1 and 7 km from the plant (Vorobeichik and Kaigorodova 2017).

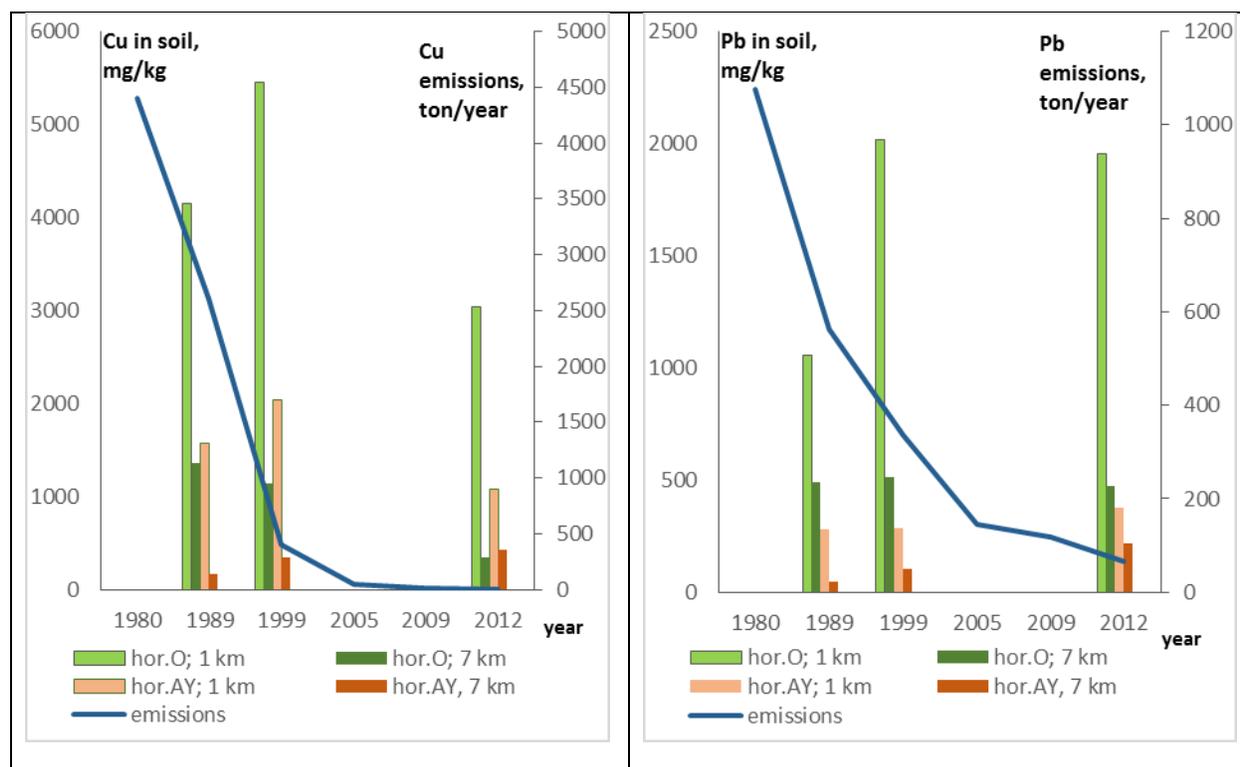


Figure 1. Dynamics of Cu and Pb emissions from SUCSP and metal content in upper soil horizons (O and AY) at distances of 1 and 7 km from the plant (compiled according to Vorobeichik and Kaigorodova 2017).

Despite a sharp reduction in metal emissions over a 23-year period, a decrease in lead content in soil is not recorded. The content of copper in litter in 2012 compared with 1989 decreased in all sites, but in the humus horizon only directly near the plant.

Period of semi-removal from soil surface layer as a result of leaching, consumption by plants, erosion and deflation can reach from 13 to 110 years for Cd, from 70 to 510 years for Zn, from 310 to 1500 years for Cu, and from 740 to 5900 years for Pb (Kabata-Pendias 2011). Period of HM removal from podzolic soils with washing water regime to the background level, calculated on the

basis of long-term data is estimated as 2090 and 90 years for copper and nickel, respectively (Evdokimova 1995). To accelerate soil cleansing from high HM content, land remediation measures or a complete replacement of contaminated soil layer may be promising.

Basically, since 2007, the apparent accumulation of total HM content in soils surveyed in 2016 has not been recorded, with the exception of some local survey sites (Minprirody RF 2017). Soil pollution in impact zone of Pechenganikel and Severonickel remains constant over the past decade (Evdokimova *et al.* 2014), (Lyanguzova *et al.* 2016).

Comparison of monitoring results for the period 2011-2016 showed that the average content of mobile HM species in soils of Moscow as a whole remains stable; there was a decrease in lead mobility during the period from 6.9 to 6.1 ppm (Department... 2017).

Conclusions

1. Since 2007 in Russian Federation soil pollution with HM in zones of large industrial centers and their suburbs resulting from functioning of enterprises practically does not occur.
2. Despite the sharp decline in HM-input in soils, the level of pollutants in soils located in impact zones of industrial enterprises remains high. Depending on the degree of pollution, processes of soil self-cleaning from HM can take a long time. Therefore in some cases, measures for remediation or complete replacement of contaminated ground can be reasonable.

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4.2.2. Deterioration of soil quality of tropical home gardens- a case study from Kerala, India

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Abstract

Tropical home gardens are rich sources of biodiversity. In addition to providing resources for the sustenance of life in the form of food and fodder, they also provide a number of soil ecosystem functions. In this study, the home gardens of an industrial area and non-polluted area in Kerala, India were compared. The microarthropod fauna were examined for the presence of soil health indicators, collembola and acari. It was found that the home gardens in industrial area showed acidic soils than non-polluted area. The soil health indicating microarthropods were absent in the home gardens of industrial area. The study shows the deterioration of home garden soil quality and the need for undertaking proper management measures for sustaining the soil quality of home gardens of tropical regions. These management measures include periodical monitoring of home garden soils, preservation of vegetative cover in the home gardens and management of industrial pollution.

Keywords: Soil microarthropods, home gardens, soil quality, monitoring, collembola, acari

Introduction, scope and main objectives

Soil ecosystems have a number of functions like supporting life, providing habitat for plants, animals and microorganisms. In addition to these, they also contribute to a number of ecosystem functions like nutrient cycling, buffering of pollutants by chelation and provision of water for oil organisms. The soils in tropical home gardens are much important, as they are unique and subjected to many amendments. Hence monitoring of tropical home garden soils is important to maintain its quality in the future, providing food security by supporting agricultural production and maintaining soil ecosystem balance.

This study was conducted in home gardens of two sites, Eloor and Chengamanad regions in Kerala, India. Chengamanad region is a rural agricultural area with more than 25% of the land under agricultural use while Eloor region is a low lying industrial area near Periyar river with less than 25% agricultural land, holding a number of small and large scale industries. Eloor region is an urban industrial belt described as a 'toxic hotspot' by Greenpeace (Kumar *et al.* 2010). The home garden

soils in Chengamanad are not much subjected to the use of insecticides and pesticides and many of the home gardens are older when compared to Eloor home gardens. The objectives of the study was to compare the soils in the home gardens of the two sites, compare the soil quality indicating microarthropods of two sites and thus get an overview regarding the soil quality of these home gardens. Additionally, management measures to improve the soil quality of home gardens will be also addressed. The study will thus act as a representative study of the home gardens of developing countries which faces many problems like land degradation and soil quality deterioration.

Methodology

Soil samples were taken from twenty five home gardens in Eloor and Chengamanad by random sampling method during summer and north east monsoon in 2014. The physicochemical parameters like soil temperature, soil pH, soil moisture and organic matter were assessed. Soil temperature and soil pH were measured using probes in the field. Soil moisture was determined using gravimetric method and organic matter by Walkley Black method. Microarthropods were sampled using TSBF protocol. Soil monoliths of about 10cm x 10 cm x 10 cm were taken and microarthropods were extracted using Berlese tullgren funnel apparatus (Swift and Bignell 2001). After 72 hours of extraction, they were preserved (70% ethanol:glycerol, 1:2), identified upto group level and enumerated. Among the soil microarthropod fauna, collembolans and acari were given more attention and their population was monitored.

Results

The soil samples of the two sites showed variation in physicochemical properties during summer and monsoon. The Details of physicochemical parameters of the two home gardens are given in Table 1.

Table 1. Physicochemical parameters of home gardens in Eloor and Chengamanad, Kerala, India

Soil parameters	Mean values	
	Eloor	Chengamanad
Temperature	30±1.45	27.8± 1.26
pH	5.94±0.65	6.5±0.65
Moisture content	12.38±6.87	14.48±3.85
Organic carbon	1.76±0.48	2.92±1.47

The enumeration of microarthropods showed that soil microarthropods in Chengamanad region were represented by collembola, coleoptera, hymenoptera, araneae, acari and diplopoda. While in Eloor, the microarthropod population was represented by coleoptera, hymenoptera, araneae and diplopoda. The disappearance of collembola and acari in Eloor home gardens indicate a reduction in soil quality.

Parameters	Comparison	
	Eloor	Chengamanad
Average area of home gardens	0.02-0.04 ha	0.02-0.20 ha
Vegetation cover	Represented by herbs, shrubs and trees	Represented by herbs, shrubs and trees
Microarthropod groups	coleoptera hymenoptera araneae diplopoda	collembola coleoptera hymenoptera araneae acari diplopoda
Management practices	no management	mulching, providing manure like cowdung

Discussion

The results from the analysis of physicochemical parameters show an increase in value for pH, moisture and organic carbon in the home gardens of Chengamanad. The decreased average pH value in Eloor soils indicate a chance of soil quality deterioration compared to Chengamanad home gardens. A high value for soil moisture content in Chengamanad home gardens is a positive factor while considering the survival of microarthropod fauna and survival of plants, as soil moisture supports the survival of microarthropods, especially collembolans. The absence of collembolans and acari in the home gardens of Eloor points to disturbance in soil ecosystem. As these two microarthropod groups form a part of soil food web (Seastedt and Crossley 1981), their survival is much important for a healthy soil ecosystem. Another study by the same authors have shown that there is relationship between soil microarthropod abundance and vegetation cover in the home gardens of Chengamanad region. While observing the average size of home gardens, the home gardens in Chengamanad had larger area, thick canopy cover with a number of trees especially Jackfruit, Mango and Teak which formed the upper strata of home garden canopy. In Eloor, the average area of home gardens was less, with shrubs forming about 50% of the home garden vegetation. The number of trees represented only 25% of the total sampled area in Eloor region. This observation has significance, as the reduction of canopy cover may influence soil moisture content, leading to disappearance of collembolans. Hence variation in soil physicochemical properties, reduction of vegetation cover and reduction of average area of home gardens may be the factors which contribute to the reduction in the population of collembolans and acari, which are the soil quality indicators.

Conclusions

The results from the study show that there is difference in soil quality of home gardens in Eloor region while compared to that of Chengamanad region. This observation is supported by the absence of collembolans and acari in Eloor region. The absence of soil health indicating microarthropods may be also due to industrial pollution. Eloor region is already declared as a toxic hotspot by Greenpeace and the soils in Eloor are polluted. The study points out to the need for improvement of soil quality of home gardens by increasing the soil health indicating microarthropods. Soil quality can be improved by management measures like maintaining trees which forms the top canopy layer. The soil carbon content and moisture content can be increased by providing mulches to the planted trees in the home gardens, instead of burning them. This will create a microclimate required for the survival of microarthropods. Whenever possible, the large and old home gardens should be kept as such without much manipulation. Constructions can be made in such a manner that the total free land space available in a locality is kept constant. In industrial areas, especially low lying areas like Eloor, soils has to be periodically monitored for pollutants which check the survival of soil organisms and pollution abatement measured has to be undertaken.

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4.2.3. Crude oil spillage, soil pollution and farmers' livelihoods in Nigeria's Niger Delta: Case study of Ogoniland

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Introduction, scope and main objectives

Nigeria's economy is dominated by the crude oil and gas industry, which accounts for 70% annual government revenue; 15% of Gross Domestic Product (GDP) and over 90% of the country's export earnings. The dominance of the oil industry is traceable to the early 1970s, when it replaced agriculture as the mainstay of the Nigerian economy. The nation's oil-driven economy has elevated Nigeria to the eleventh largest crude oil reserves holding in the world, estimated at 37 billion barrels in 2015. Nigeria is also ranked as the sixth largest crude oil exporter and Africa's largest producer. In 1956, oil was discovered in the Niger Delta, which accounts for the bulk of the nation's oil exploration and production activities. Among other oil infrastructure in the region, the Niger Delta features 606 oil fields, with 360 distributed over land, swamps and mangroves, while the balance or 246 are located offshore in the Gulf of Guinea. In 2015, Nigeria's daily crude oil production is estimated at 2.3 million barrels per day, both within and off-shore the Niger Delta. However, production of crude oil in Niger Delta is often accompanied by widespread spillage, creating huge environmental degradation and the loss of peoples' livelihoods in the oil-producing communities.

The Niger Delta is a region located in Southern Nigeria, measuring 75,000sq.km² and comprising 7.5% of Nigeria's landmass. Administratively, the Niger Delta comprises nine oil-producing states and 185 Local Government Areas (LGAs), with a population estimated at 35 million people. The region is also acknowledged with the world's third largest wetland and Africa's largest, rich in biological diversity. However, the region's agro-ecological zones are rather fragile, comprising coastal barrier islands, mangrove swamp forests, fresh water swamps and lowland forests. Niger Delta's natural resource-endowment is abundant, comprising crude oil and natural gas, lead, coal, zinc, salt, arable land and sea foods, among others. The demographic profile of the region reveals about half of the population are either farmers or artisanal fisher men and women. Following the

discovery of crude oil in the Niger Delta by Shell Petroleum (now Royal Dutch Shell) in 1956; production and exportation began in 1958, a watershed that drew other multi-national oil corporations into the Niger Delta. Apart from Shell, other major multi-national oil entities that are engaged in oil exploration and production activities in the region include: Chevron, Mobil, Elf, Agip, Texaco, among others. However, several decades of crude oil exploration and production activities are creating externalities and exerting a toll on the environment of the Niger Delta. Externalities attributed to oil production include crude oil spills and gas flaring.

The major objective of this paper is to shed light on crude oil spills and their effects on farmers' livelihoods in the Niger Delta, with Ogoniland as case study.

Keywords: Niger Delta, Oil, Pollution, Land, Water, Farmers, Environment, Ogoniland.

Methodology

The study employed empirical data to analyze the scope of crude oil spillage in the Niger Delta. Secondary data for the study were sourced from various publications, including journal articles and periodicals within and outside Nigeria. Data were also sourced from governmental agencies associated with the Nigerian oil and gas industry, as well as the Central Bank of Nigeria and the nation's Bureau of Statistics. Additional data were sourced from International agencies, including the World Bank and United Nations Environment Programme. Data analyzed for the study include socio-economic characteristics of the Niger Delta, rural and farmers' livelihoods, as well as soil pollution and productivity. Analytical methods employed include descriptive and inferential statistics.

Results

In the context of the Niger Delta, oil spillage is attributable to sabotage, theft, human error, accidents or equipment failure. For example, the Department of Petroleum Resources (DPR) Annual Statistical Bulletin (2014) reveals that while 65.13% of oil spills during that year was caused by sabotage; 17.38% was yet to be determined; while 14.35% was as a result of natural accidents, corrosion, equipment failure and human error; 3.00% was also due to 'mysterious' circumstances. Over time, oil spillage began to assume an obnoxious dimension in the Niger Delta, with the impact of recurring spills manifesting in negative environmental and health outcomes; posing grave implications for industry players, policy makers and oil-producing communities. The scale of the challenge was revealed in a major report, which estimated the volume of oil spills as at June, 2010 at about 546 million gallons of crude oil discharged annually in the Niger Delta over the previous 50 years. The report was also complemented by the National Oil Spills Detection and Response Agency (NOSDRA) (2011), which shows that the region experienced, on average, 273 oil spills, with an average of 115,000 barrels of crude oil spilled annually between 1976 and 2001. In addition, about 6,333 oil spill incidents were recorded between January, 2010 and August, 2015. The enormity of oil spills in the Niger Delta is brought into limelight, when contrasted with other oil producing regions in the world. For example, it is noteworthy that only 10 oil spills were recorded across Europe between 1971 and 2011, in sharp contrast to similar incidents in the Niger Delta.

The consequences of oil spillage on land and other ecosystems in the Niger Delta are particularly worrisome. Extensive land degradation attributed to oil spills across the region are undermining environmental integrity and fueling a loss of biological diversity. Farmers, who depend upon arable soils for their livelihoods have witnessed degradation of land, associated with crude oil spills, with grave economic losses, particularly in the fragile estuarine agro-ecological zone. The discharge of crude oil over soils is detrimental to land and the crops grown on it. It contaminates

the land, rendering it unsuitable to support crops. In the Niger Delta, severely affected communities feature oil spillage penetrating the soil to the depth of 0.65 meters, damaging the sub-soil and its fertility. The incineration of crude on soil surfaces prevents aeration and water filtration into sub-soil layers. Crude oil spill on land becomes a physical and artificial barrier between the air and the soil. Contamination also undermines the physio-chemical properties of the soil, including temperature, structure, nutrient status and pH. The consequences of oil spills are devastating to crops, as roots are starved of oxygen and water-use. Thus, oil spills, potentially, have either acute or chronic toxicity or a combination of both on soil properties and micro-flora. Severe contamination of soils with crude oil unleashes damages on plant growth, affecting normal photosynthesis and transpirational processes, resulting in chlorophyll deficiency and ultimate demise of crops. Indeed, studies on pollution in the Niger Delta reveal loss of efficiency and productivity in affected areas; with mean technical efficiency of 78% observed in polluted areas, against 88% in unpolluted areas. The consequences in affected oil-producing communities are particularly serious, with farmers losing their sources of livelihoods and rendering families vulnerable to extreme deprivation, while trapped in a vicious circle of poverty, hopelessness, helplessness, voicelessness and lack of dignity.

The study adopts Ogoniland as case study on crude oil pollution in the Niger Delta. With a landmass covering 1,000 km², Ogoniland is located in the Southeastern region of the Niger Delta basin. The community's 2006 census reveals a population of about 832, 000 people, which has risen to 1.2 million, and covering four Local Government Areas (LGAs): Eleme, Gokana, Khana and Tai. The community also comprises six traditional kingdoms: Babbe, Eleme, Gokana, Ken-Khana, Nyo-Khana and Tai. The residents are socially and culturally tied to natural resources in agriculture and fisheries derived from land the coastal areas, respectively. Oil exploration commenced in Ogoniland in the 1950s, with Shell Petroleum prospecting for crude oil in the community.. The striking of oil marked the commencement of extensive oil production activities, accompanied by an elaborate oil infrastructure deployed across the community's farmlands and fragile freshwater systems. The oil infrastructure across Ogoniland is part of elaborate, complex, multi-faceted projects, comprising: land survey, land clearance for seismic lines, establishment of seismic and drilling camps, site preparation, infrastructure construction, drilling for oil and development of transportation infrastructure. Once the oil-producing infrastructure is in place and streamed; it is usually accompanied by a variety of challenges, including spills associated with oil production and the disposal of water (a salty liquid, otherwise known as 'produced water'). These activities result in land degradation, which leaves an environmental footprint in the oil-producing areas of Ogoniland.

Discussion

The Environmental degradation in the Niger Delta, fueled by oil spills over the past several decades, has assumed a problematic dimension in the past couple of decades. The development has triggered violence and conflict in the oil-producing communities across the Niger Delta. This is particularly the case in Ogoniland. Incessant oil spills in Ogoniland over several decades began to provoke civil unrests in the community in the late 1980s, unleashing hostilities against oil Shell Petroleum, the multi-national oil corporation operating in the area. The development was fueled by the loss of livelihoods of farmers and artisanal fishermen and women attributed to oil pollution. The conflict and unrest in Ogoniland escalated into the 1990s, with increasing sabotage against oil infrastructure, as well as attacks on oil workers and security agents, in a development that attracted the attention of the international community. In response to the volatile developments, and the risk posed to its employees; in 1993, Shell Petroleum suspended oil production in Ogoniland. While oil production was suspended in Ogoniland, the damaging impacts of the spills on land and freshwaters presented a severe environmental disaster demanding remediation. This

imperative forced policy makers to approach development partners to find lasting solutions. Consequently, the United Nations Environment Programme (UNEP), in 2011, conducted an Environmental Impact Assessment on Ogoniland. The report reveals, among other things, that pollution of soil by crude oil is extensive in land areas, sediments and swampland. The report further reveals that two-thirds of the contaminated land sites close to oil industry facilities features a degree of contamination exceeding the Nigerian National Standards elaborated in the Environmental Guidelines and Standards for Petroleum Industries in Nigeria (EGASPIN).

Conclusions

The scope of oil spill in the Niger Delta is extensive, revealing considerable degradation of land and resulting in the loss of farmers' livelihoods, triggering an environmental emergency. The development has unleashed violence and conflict across oil-producing communities in the region. This has led to concerted efforts by government, in partnership with international development agencies, to provide long-term solutions that can restore environmental integrity and the People's confidence in oil corporations. The study presents a policy framework underpinned by deepening enforcement of environmental standards in the Nigerian oil and gas industry; swift compensation to victims of oil spill and decontamination of soil and water exposed to crude oil spillage across the Niger Delta.

The views expressed in this information product are those of the author(s) and do not necessarily reflect the views or policies of FAO.

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4.2.4. Assessment of pesticides in soil from obsolete pesticides stores: A Caribbean case study

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Abstract

The fate of highly hazardous or persistent pesticides in soils and their potential for environmental and health risks depends on the physical and chemical properties of the pesticide, soil properties including biological health and climatic conditions. Assessing the fate and impact of pesticides in soil is complicated in the Caribbean due to high diversity of soils and duality of climate. The FAO has supported national competent authorities from eleven countries in the Caribbean to safeguard and dispose of 320 tons of obsolete pesticides and continues to engage some of these countries in the assessment and remediation of contaminated soil. Two countries will be identified following preliminary site investigations that utilise the rapid environmental assessment (REA) methodology, for detailed assessment and bioremediation. Pesticide toxicity, solubility and absorption coefficient will be combined with soil characteristics to qualitatively determine the impact on soil health and quality, water, biodiversity and human health. Bioremediation will be explored as an environmentally safe and cost effective strategy to remediate soils and reduce negative impacts. Overall, assessment of soil pollution from stored obsolete pesticides will be shown to be important for rational decision making regarding fate and potential impacts.

Keywords: rapid environmental assessment, risk assessment, obsolete pesticides, Caribbean, soil pollution

Introduction, scope and main objectives

A project implemented by the FAO and funded by the European Union (EU) and Global Environmental Fund on safe-guarding and disposal of obsolete pesticides, pesticide management and sustainable pests management utilized the pesticide stock management system (PSMS) database to generate an inventory of obsolete pesticides across participating Caribbean countries. The presence of contaminated sites from storage of obsolete pesticide stockpiles were identified in six countries namely; Trinidad and Tobago, Suriname, St. Kitts and Nevis, Dominican Republic, Dominica and Barbados. This information contradicts Williams (2007), who previously stated that Haiti and Saint Lucia have performed inventories of sites contaminated with persistent toxic substances and reported extensive contamination. This may infer that the current inventory is not accurate or complete. In any regard, there is need for review, ratification and probably further probing to identify all possible stockpiles. For most countries, stockpiles of obsolete pesticides represent centralised storage locations associated with public health or manufacturer and retailer inventories and large-scale monoculture cropping systems, prevalent as economic drivers in the countries' recent history. The current inventory may not account for decentralised storage of small scale stocks including agro-shops, farmer associations and individual farmers. However, whether storage is centralised or not, the public health and environmental risk associated with site contamination from obsolete pesticides has yet to be assessed.

FAO (2010) indicated that estimates of annual pesticide poisonings range in the millions and often exposed persons are unaware of the potential danger. An FAO survey in 2011 showed that all Caribbean countries face problems of unintentional human and animal poisonings and

environmental contamination from pesticides (including new and obsolete). Regionally, pesticide storage is not controlled, regulated or monitored, resulting in a high risk of exposure. Notably, the environmental risk may far exceed the direct health hazard. Soil and water contamination is a grave concern as the exposure pathways allows for larger geographic distribution and increases the exposure routes. The normal climate for the Caribbean has a wet season characterised by intense storm events. These conditions aggressively favour the movement and contamination of natural resources including soil and water. Incidents of floods and hurricanes exposing pesticides to the environment have been noted. Variability in climate will create challenges for any risk reduction strategy the longer the pesticide stocks remain unmanaged. This situation is further complicated by the large diversity in soil series across the region (Ahmad, 2011), which may limit general strategies geared at reducing risk. A case study in Martinique identified contaminant levels of obsolete pesticides in seven rivers and coastal water 10 years after these pesticides were banned (Bocquene, 2005). The need to assess the extent of contamination at storage sites and associated risk assessment is fundamentally important.

The PSMS ranked the storage sites for each country according to environmental risk in the following order: Trinidad and Tobago, Dominica, St. Kitts and Nevis, Suriname and Jamaica. However, Williams (2007) stated that some sites may be privately managed and such decentralisation across and within countries will affect the accuracy of reported information entered into PSMS. Site selection should also consider the public and ecological risk through application of the rapid environmental assessment and preliminary site investigation for pesticide contaminated locations. Where obsolete pesticide stockpiles have been inventoried and visual observation and assessment identified site contamination, very little progress has been made in risk assessment and management. Although the region has had some experience in site characterisation and risk assessment of chemical contaminated sites, fragmentation exist in the institutional framework, as many organizations are involved with sometimes conflicting objectives. This is compounded by insufficient funds to execute specific target actions as well as limited technical capacity.

The project specific objectives were to perform preliminary site assessment of obsolete pesticide contaminated soils to assist in ranking and identification of pilot remediation sites. Selected sites would undergo detailed assessment followed by remediation. This paper presents information to date on preliminary site investigations.

Methodology

Approaches used in the Caribbean to characterise, assess and manage chemical contaminated sites have followed international benchmarks for reducing risks associated with pesticide stockpiles. Harmson *et al.* (2010) identified the first step in the methodology, which entails preparatory activities, preliminary site visits and investigations related to contamination on the site, followed by intense investigation of the site (historical use, hydrology, climate, transport).

The obsolete pesticide project involved several countries of the Caribbean including Antigua and Barbuda, The Bahamas, Barbados, Cuba, Belize, Dominica, Dominican Republic, Guyana, Jamaica, Saint Kitts and Nevis, Saint Lucia, Saint Vincent and the Grenadines, Suriname, and Trinidad and Tobago (Figure 1). Countries completed online inventories of obsolete pesticide stocks using the FAO PSMS. The Environmental Management Tool Kit (EMTK) Series (FAO, 2008) was then used to generate an estimate of the environmental and public health risks.

Tool A was used to calculate the risk factor for each product stored. The sum of each factor gives an indication of the overall quantity, condition and risk associated with the products at a

particular store, termed **F_p**. Stocks held at the store that are characterized by greater toxicity (described as WHO groups Ia, Ib, II, III or U) or those that whose packaging is in poor condition are given a higher **F_p** factor. During the inventory the condition of the storage facility was assessed from which an environmental risk factor **F_e** is calculated. By plotting the **F_e** factor and normalized product of the **F_p** factor for each store, the relative risk to the environment and public health was estimated.



Figure 1. Map of the Caribbean showcasing participating countries.

Rapid environmental assessments were conducted by national competent authorities following procedures including forms from FAO (2016). This was followed by preliminary site investigations by an expert team to sites where soil contamination was reported (Table 1). Site assessments were conducted at obsolete pesticide storage sites in St. Kitts and Nevis, Dominica, Barbados, Trinidad and Tobago and Suriname. Table 1 also identifies the specific sites within country along with the EMTK site assessment and prioritization.

A total of eight composite soil samples (0-20 cm) were taken following procedure from FAO (2016). The quadrant procedure was used to collect samples at all sites except for Fond Cole Sanitary Landfill, Dominica, where the pesticides were buried. At this site, samples were taken along a transect at the bottom of an incline in the direction of water movement. Soils from all sites were contaminated with a range of pesticides (Table 1). Method 1699 was used to quantify pesticide content in soils by high resolution gas chromatography and high resolution mass spectrometry (US EPA, 2007). Collected samples were air dried, crushed to pass a 200 mesh sieve and forwarded to a commercial laboratory for analysis.

Results

Environmental fate of Obsolete Pesticides

Results of the EMTK analysis and prioritization identified the Fond Cole and Camden Base sites in Dominica and Trinidad and Tobago respectively as the only critical sites. Dicofol and Actellic were identified as the obsolete pesticides, an organochlorine and organophosphate respectively at the Fond Cole site. The physical properties of these pesticides indicate moderate persistence in soils,

with low volatility and leaching, although the organic phosphate has a relatively higher leaching potential associated with a higher solubility (Table 2). Dicofol is more strongly adsorbed than Actellic which supports the lower groundwater ubiquity score (GUS) leaching potential. Preliminary site investigation revealed that the exposure pathways are mainly associated with leaching and water contamination as the site has porous geology (pumice) and the pesticides were buried several feet below the surface in a restricted access area. This inference is further supported by the high sand content (69.7 %) and correspondingly low cation exchange capacity ($6.05 \text{ cmol}^+ \text{ kg}^{-1}$) (Table 3). Soil samples were not collected at the Camden Base site as the investigators concluded that the contamination was restricted to an impervious layer above the soil with minimal hazard.

Of the other stocks all but the New River Estate and Department of Agriculture sites were listed as problematic related to an environmental hazard. The environmental index Fe decreased in the order: Marienburg obsolete storage, Pepperpot, Grantley Adams international airport, Sugar manufacturing association. Malathion was reported at the New River Estate site. Although the volatility is reported as low there was a residual odour at the site. This organophosphate pesticide has moderate solubility and is moderately mobile (Table 2). This is important in the context of the calcareous geology and ground water resources of the site. A similar feature was noted at the two reported contaminated sites in St. Kitts. Both sites were categorised as problematic and were exposed to the chemical Buctril. This herbicide is shown to have a high solubility and moderate sorption coefficient (Table 2). During the site assessment, it was reported that a major aquifer was situated within the contamination zone.

Contrastingly, the reported contaminated sites in Suriname were at low elevation (sea level). The water table was at, or near the surface for all sites, with a predominance of sandy soils. HCH and Chlorpyrifos, organochlorine and organophosphate pesticides respectively were identified as the main obsolete pesticides. Both possess relatively high GUS leaching potentials, but the former has a lower sorption coefficient.

Of the soils analysed for respective pesticides, reported values were all below the method detection limit (Table 4).

Table 1. Location and site assessment of obsolete pesticide stocks for countries where soil contamination was reported.

Country/ District	Site/Store	Pesticide	Fp	Fe	Site Prioritization	Samples
Suriname: Commewijne	Marienburg obsolete storage	Chlorpyrifos, HCH (Hexachlorocyclohexane)	204,800	64	Problematic Site (environment)	1*
Suriname: Nickerie	Airfield Alibux Wageningen	HCH (Hexachlorocyclohexane)	ND	ND	ND	1
Suriname: Commewijne	Pepperpot	Cupravit (Copper Oxychloride)	3716	58	Problematic Site (environment)	1
Dominica	Fond Cole Sanitary Landfill	Dicofol, Actellic (Pirimiphos-methyl)	352,000	65	Critical site	1*
Nevis	New River Estate	Malathion	718,796	43	Problematic Site (pesticide)	1*
St. Kitts	Department of Agriculture	Buctril (Bromoxynil)	2093	41	Non-priority	1
St. Kitts	Sugar Manufacturing Association	Buctril (Bromoxynil)	81,845	54	Problematic Site (environment)	1
Barbados	Grantley Adams International Airport	Carbaryl, Endrin	107,265	55	Problematic Site (environment)	1*
Trinidad and Tobago	Camden Base (Airstrip)	Imidacloprid, Fenobucarb	54,306,536	58	Critical Site	0

*Indicates sites where samples were analyzed for respective pesticides.

ND means “not determined”

Table 2. Properties of obsolete pesticides related to the environmental fate. Data sources from <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>

Name	Group	Half-life (days)	Koc (Sorption Coefficient)	GUS Leaching Potential	Solubility (mg/l)	Vapour pressure at 25°C (mPa)	Henry's Law Coeff. (Pa m ³ mol ⁻¹)
Dicofol	Organochlorine	80 (MP)	6064 (NM)	0.36 (L)	0.8 (L)	0.25 (LV)	2.45 × 10 ⁻⁰² (NV)
Chlorpyrifos	Organophosphate	386 (VP)	5509 (NM)	3.36 (H)	1.05 (L)	1.43 (LV)	0.478 (MV)
Endrin	Organochlorine	4300 (VP)	10000 (NM)	0.00 (L)	0.24 (L)	2.00 × 10 ⁻⁰⁷ (LV)	1.48 × 10 ⁻⁰¹ (MV)
Actellic (pirimiphos-methyl)	Organophosphate	39 (MP)	1100 (SM)	1.03 (L)	11 (L)	2.00 × 10 ⁻⁰³ (LV)	6.08 × 10 ⁻⁰⁵ (NV)
Malathion	Organophosphate	0.17 (NP)	1800 (SM)	-1.28 (L)	148 (M)	3.1 (LV)	1.00 × 10 ⁻⁰³ (NV)
Carbaryl	Carbamate	16 (NP)	300 (MM)	2.02 (TS)	9.1 (L)	0.0416 (LV)	9.20 × 10 ⁻⁰⁵ (NV)
Cupravit (copper oxychloride)	Inorganic Compound	10000 (VP)	NA	NA	1.19 (L)	0.00001 (LV)	NA
HCH (Hexachlorocyclohexane)	Organochlorine	980 (VP)	1270 (SM)	3.95 (H)	8.52 (L)	4.4 (LV)	1.483 × 10 ⁻⁰⁶ (NV)
Buctril (bromoxynil)	Hydroxybenzoxynil	0.63 (NP)	302 (MM)	-0.34 (L)	38000 (H)	0.12 (LV)	8.7 × 10 ⁻⁰⁷ (NV)
Imidacloprid	NeoNicotinoid	191 (VP)	225 (MM)	3.74 (H)	610 (H)	4.0 × 10 ⁻⁰⁷ (LV)	1.7 × 10 ⁻¹⁰ (VN)
Fenobucarb	Carbamate	18.5 (NP)	1068 (SM)	1.23 (L)	420 (M)	48 (HV)	NA

NP, MP and VP represents non, moderately and very persistent; NM, SM and MM represents non, slightly and moderately mobile; L, M, H and TS represents low, moderate, high and transition state; LV and NV represents low volatility and non-volatile. NA means "not available"

Table 3. Selected soil properties of study sites

Country	pH	EC	TOC	TKN	C/N	CEC	Sand	Silt	Clay
		mS cm ⁻¹	← % →			cmol ⁺ kg ⁻¹	← g kg ⁻¹ →		
Barbados	8.06	1.03	2.48	0.28	8.86	12	517	209.9	273
Dominica	7.63	0.25	0.33	0.05	6.60	6.05	697.3	218.1	84.6
St. Kitts and Nevis	8.42	0.48	2.94	0.02	147.00	10.8	654.9	230.2	114.9
Suriname	7.90	0.29	1.02	0.16	6.38	6.92	778.7	123.7	97.6

Table 4. Concentration of obsolete pesticides in soils from contaminated sites

Country	Pesticide	Concentration (µg kg ⁻¹)
Barbados	Endrin	< 5*
	Carbaryl	ND
Dominica	Actellic (pirimiphos-methyl)	< 2.5*
	Dicofol	< 5*
St. Kitts and Nevis	Malathion	< 2.5*
	Buctril (Bromoxynil)	ND
Suriname	Chlorpyrifos	< 2.5*
	HCH (Hexachlorocyclohexane)	ND
	Cupravit (copper oxychloride)	ND

* Results are less than the method detection limit

Discussion

The EMTK tool A and tool B was relatively effective in identifying the environmental hazard posed by obsolete pesticide stocks. It was less effective in prioritizing the sites. When combined with preliminary site assessment data, a more accurate ranking was possible. The properties of the obsolete pesticides and the associated soils further contributed to understanding their environmental fate. Pesticides such as Buctril and Malathion, which possess moderate to high solubility and are relatively mobile, may have greater hazard potential due to the edaphic, geological and climatic conditions under which the contamination exists in St. Kitts and Nevis. Although neither pesticide persists in the soil, the high permeability of the soils (inferred based on the high sand content and geologic material) may contribute to ground water contamination. Atypically, soils across countries showed similar chemical and physical properties; alkaline pH, non-saline with low CECs and being composed mainly of sand sized separates. These properties may partly explain the low pesticides levels detected in the samples. Tested pesticides were non-volatile (Table 2), which support minimal loss during storage and processing. Schneider *et al.* (2013) stated that during the drying process pesticides adhere to mineral surfaces, protecting them from volatilization. However sorption in soils is associated with colloidal particles with large surface area. The studies soils showed low CEC and potential for sorption. Accordingly, the likely fate of the pesticides are degradation and leaching. Degradation is likely for Dicofol, Actellic and Malathion which are moderately to non-persistent in soil. Kerle *et al.* (2007) reported that microbial degradation of pesticides are favoured in warm, well aerated soils with a neutral pH. Soil properties also favour leaching of pesticides, even where pesticide properties infer otherwise. It is likely that duality of climate in the Caribbean fosters leaching and movement of pesticides in surface and ground waters. This exposure pathway requires further investigation.

Conclusions

A combination of the EMTK tool kit and site investigation allowed for assessment and prioritization of pesticide contaminated sites across participating Caribbean countries. Concentration of analyzed pesticides in soils were below detection limits. The fate of obsolete pesticides may be beyond the immediate soil matrix and require further assessment.

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4.2.5. Effect of combined application of subsurface drainage and mineral fertilization on iron-reducing bacterial populations' developments and Fe²⁺ uptake by two rice varieties in an iron toxic paddy soil of Burkina Faso (West Africa)

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Abstract

Rice is one of the staple crops in Burkina Faso. However, the local production covers only 47% of the population demands. One of the main reasons of the poor productivity in Burkina Faso is iron toxicity which is related mainly to the activity of Iron Reducing Bacteria (IRB) in the rice field's ecosystems. In order to control the harmful effects of IRB populations and to improve rice productivity, a pots experiment was conducted at the experimental site of the University Ouaga I Pr. Joseph KI-ZERBO. An iron toxic soil from Kou Valley (West of Burkina Faso) and two rice varieties, BOUAKE-189 and ROK-5, sensitive and tolerant to iron toxicity, respectively, were used for the experiment. The pots were drained for 14 days (D2) and amended with chemical fertilizers (NPK+Urea and NPK+Urea+Ca+Mg+Zn complexes). Control pots without drainage and fertilization (Do/NF) were prepared similarly. The kinetics of IRB populations and ferrous iron content in soil near rice roots were monitored throughout the cultural cycle using MPN and colorimetric methods, respectively. The total iron content was evaluated in rice plant using a spectrometric method. Data obtained were analysed in relation to drainage and fertilization mode, rice growth stage and rice yield using the Student's t-test and XLSTAT 2014 statistical software. The experiment showed that the combined application of subsurface drainage and NPK+Urea+Ca+Mg+Zn fertilization, reduced significantly the number of IRB in the soil near rice roots for both rice varieties ($p = 0.050$ and $p = 0.020$) increased the leaf tissue tolerance to excess amounts of Fe, and rice yield.

Keywords: Iron Reducing Bacteria, Rice Variety, Iron Uptake, Subsurface Drainage, Fertilization

Introduction, scope and main objectives

The iron toxicity is recognized as one of the most widespread nutritional disorders and one of the major edaphic constraints of lowlands in West Africa that affects crop growth, especially rice growth (Becker and Asch 2005). Chérif *et al.* (2009) reported also that about 55% of the rice area is affected by Fe toxicity in three West African countries, with about 10% of rice cultivation area abandoned due to severe iron toxicity.

In Burkina Faso, iron toxicity affects many agricultural plains like Moussodougou, Tiéfora and Kou Valley (Wellens and Nitchou 2010). For the latter, since 1986, 300 ha of fields were

abandoned because of ferrous intoxication, and most among these intoxicated fields remained uncultivated up to date (Keita *et al.* 2013).

Iron reduction into ferrous form is largely controlled by microbial processes (Otoïdobiya *et al.* 2015). In anoxic conditions, Fe (III)-compounds are reduced and it results in ferrous ions production (Olaleye, *et al.* 2001). Iron toxicity occurs when the rice plant accumulates a toxic concentration of Fe in the leaves, causing bronzing symptoms of leaves, blackening of roots and damage to cellular membranes (Sahrawat 2004).

Benckiser *et al.* (1984) and Becker and Asch (2005) reported that iron-induced yield is frequently associated with a poor nutrient status of the soil. Kosaki and Juo (1986) underlined also that the poor level of development of lowlands in West Africa, epitomized with bad water management which generates favourable conditions for the occurrence of iron toxicity (Audebert and Sahrawat 2000).

The present experiment was developed in the sensitive site of Kou Valley, to determine the effects of chemical fertilization and subsurface drainage on microbiological and chemical parameters sustaining iron toxicity in paddy fields and on rice yield.

Therefore, plastics pots were filled with a sensitive soil, amended by chemicals fertilizers and drained periodically during rice cultivation. The Iron Reducing Bacterial (IRB) populations' density, Fe²⁺ content in the paddy soil and iron accumulation in rice plant, were recorded during the cultural cycle of BOUAKE-189 and ROK-5 rice varieties (sensitive and tolerant to iron toxicity, respectively).

Methodology

Soil Sampling and Experiments Sites Location

The soil used for the experiments was collected at Kou Valley, located at the West of Burkina Faso (11° 23'12" N and 4° 23'25" W) (Figure 1). The soil collected was carried out to the experimental site of the University Ouaga I Pr. Joseph KI-ZERBO (12° 22'45.7" N and 1° 29'52.5" W, Figure 1). The experiments were performed from June to October 2014.

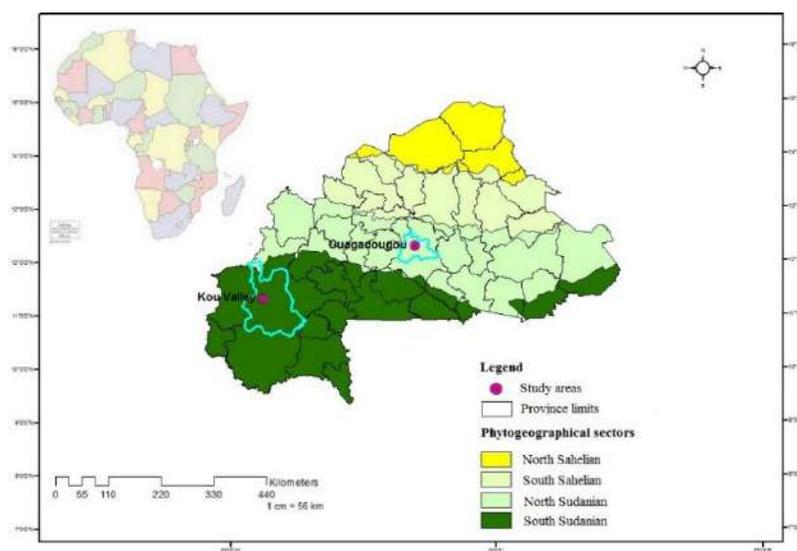


Figure 1. Location of sampling and experimental sites.

Climatic Characteristics of the Experimental Site Area

The experiments site was located in the central plateau of Burkina Faso consisting of a rainy season. During the experiments period, sixty-two rainy days were recorded, with an average rainfall of 743.5 mm (Figure 2). The average daily temperature was 29.03 °C with minimum at 27.6 °C and maximum at 30.7 °C (Figure 3). The daily relative hygrometry (RH), varied from 45% to 77% (Figure 3), with a sunniness average of 7.26 hours/day.

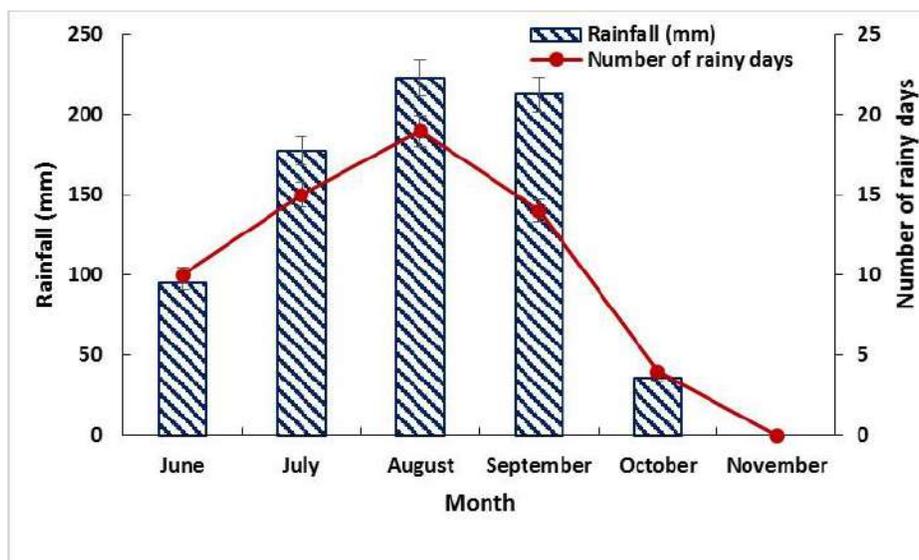


Figure 2. Monthly rainfall and monthly number of rainy days from June to November 2014.

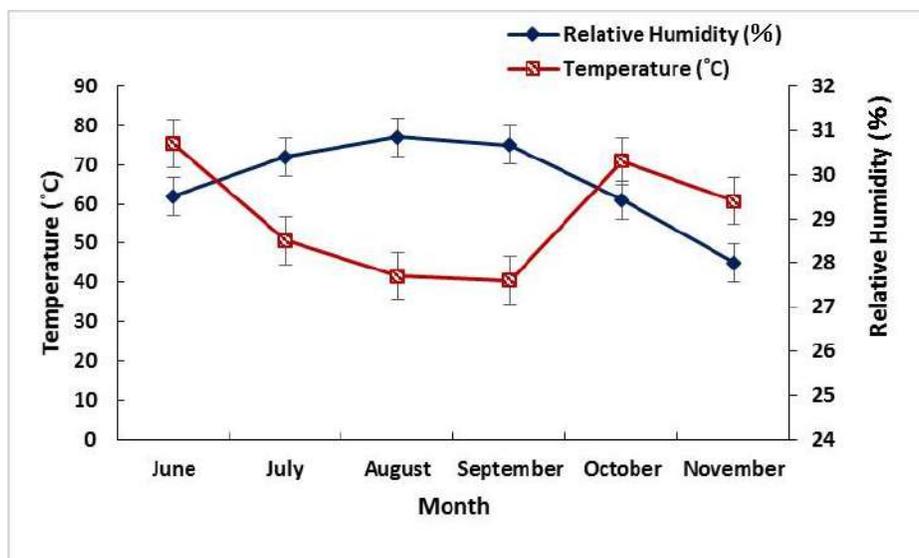


Figure 3. Monthly temperatures and monthly relative humidity from June to November 2014.

Plant Material

Plant materials used for experiments were BOUAKE-189 and ROK-5 rice varieties, originating from the Asian species *Oryza sativa* L. (Indica varietal group), respectively (ISRA 2012).

Pots Experiments

Experiments were carried out as previously described by Otoidobiga *et al.* (2016). Seventy two plastics pots with 25 cm³ of bulk were used in 3 replications throughout the study. At the bottom of each pot, an external tap was installed to sub-drain the soil.

After 2 weeks of flooding, 15 day-old rice plants were transplanted. The soil was continuously flooded until rice harvest (120 days after flooding). Three replications and three modes of fertilization were performed throughout the study: without fertilization, NPK+Urea and NPK+Urea+Zn+Ca+Mg, respectively. The doses of N-P-K (14-23-14), CaCO₃, ZnO and MgCl₂ application in pots were in the ratio of 720:50:22.4:20 mg/kg of dry soil according to the recommended doses of 300 kg/ha for N-P-K, 10 kg/ha for ZnO, 250 kg/ha for CaCO₃ and 8.92 kg/ha of MgCl₂ at the rice transplanting.

The Urea fertilizer (240 mg/kg of dry soil) was applied in two further dressings (at rice transplanting, and 60 days after transplanting, respectively) according to the recommended dose of 100 kg/ha. Two modes of drainage were applied during the study: without drainage (Do) and drainage for 14 days (D2), respectively by regulating the drained water flow from the bottom (Otoidobiga *et al.* 2015). Control pots, without drainage and fertilization (Do/NF) were prepared similarly.

Iron Reducing Bacterial Populations Monitoring

The number of IRB in the soil were determined by the most-probable-number (MPN) method, and a culture medium adapted from Hammann and Ottow (1974) as described by Otoidobiga *et al.* [2016]. The enumeration of bacteria was performed before flooding when the soil was dried, on transplanting day and during the rice growth stages until harvest near rice hills.

Determination of Ferrous Iron Concentration in Soil

From the soil sampled for bacterial enumeration and at the same periods during the rice cultural cycle, Vizier (1969) method was used to measure the content of ferrous iron in the soil solution, using 0.2% ortho-phenantroline and 10% acetic acid reagents as described above (Otoidobiga, 2016).

Determination of Fe Content in Rice Plant

The total Fe was analysed in the leaves and roots of the two rice varieties described above. Young leaves were taken from each pot during the cultural cycle of rice. At harvest, the aerial biomass and the roots of each plant were also collected. Completely dried plant parts were digested in a diacid mixture of nitric acid (HNO₃) and perchloric acid (HClO₄) (15:2) and analysed as described by Chapman and Pratt (1961). The total Fe content was determined by Atomic Absorption Spectrometry (Murphy and Riley 1962).

Statistical Analysis

Data obtained were subjected to analysis of variance (ANOVA) with regard to the IRB populations' development and activity, drainage and fertilization modes and rice yield using XLSTAT 2015 software. Mean variables were compared using the Fishers' test at probability level $p = 5\%$ (Otoidobiga *et al.*, 2016).

Results

The experiment showed that the number of IRB and the concentration of ferrous iron in the soil near rice roots increased after two weeks of flooding in all pots for BOUAKE-189 and ROK-5 rice varieties (Figures 4-5). The number of IRB and content of ferrous iron in soil near rice roots increased gradually with fluctuations from transplanting day to rice flowering and maturity stages in all the paddy pots (Figure 4-5).

In most pots, the highest densities of IRB and content of ferrous iron were recorded from rice tillering and flowering to maturity stages (Figures 4-5).

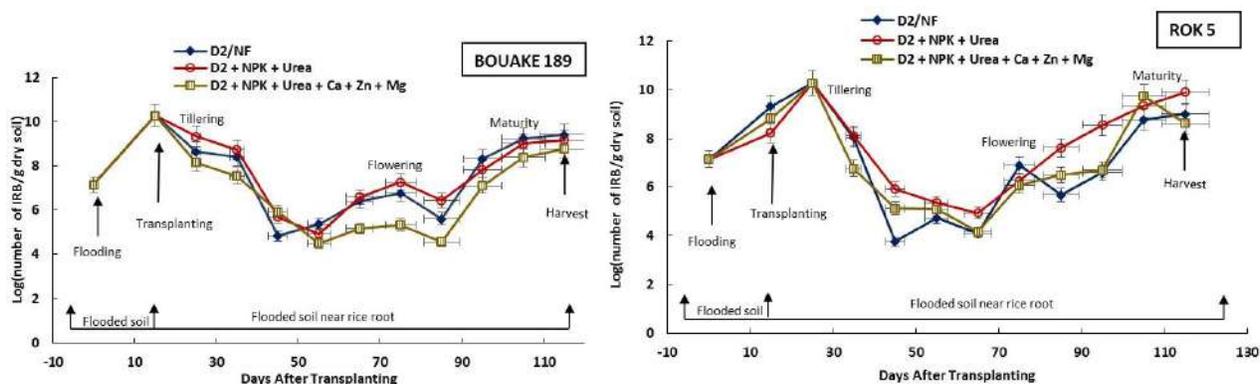


Figure 4. Densities of IRB in soil before flooding, at transplanting day and in soil near rice roots during the cultural cycle of varieties in drained pots for 14 days without fertilization (D2/NF) and combined application of D2 drainage, NPK+Urea and NPK+Urea+Ca+Zn+Mg fertilization, respectively (means of 3 replicates)

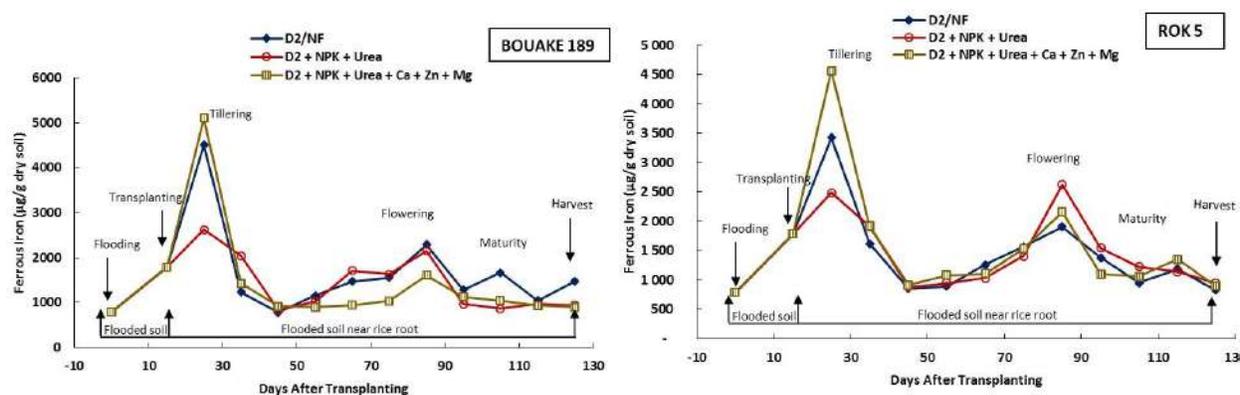


Figure 5. Evolution of soil ferrous iron content during the cultural cycle of rice varieties in drained pots for 14 days without fertilization (D2/NF), and combined application of D2 drainage NPK+Urea and NPK+Urea+Ca+Zn+Mg fertilization, respectively (means of 3 replicates).

The Fishers' test (Table 1) revealed that the number of bacteria in the soil near BOUAKE-189 and ROK-5 rice roots wasn't significantly related to the subsurface drainage ($p = 0.891$ and $p = 0.941$, respectively). However, the IRB number was significantly related to the combined both factors ($p = 0.050$ and $p = 0.020$, Table 1). Thus, the D2 drainage in the NPK+Urea+Ca+Zn+Mg amended pots showed the lowest average number of IRB in soil near rice roots, during the cultural cycle of both rice varieties (2×10^7 and 2.6×10^7 cells/g dry soil, for BOUAKE-189 and ROK-5 rice variety, respectively).

Table 1. Variance of IRB number in soil near rice roots in relation to subsurface drainage and fertilization, during the cultural cycle of rice varieties.

Source of variation	df	log (IRB number/g dry soil)			
		BOUAKE-189		ROK-5	
		F	p	F	p
Drainage	1	0.019	0.891 ^{ns}	0.005	0.941 ^{ns}
Drainage*Fertilization	2	2.914	0.050*	3.998	0.020*

df = degree of freedom; F = Fisher F; *significant $p < 0.05$; ^{ns}not significant $p > 0.05$.

The variance of ferrous iron content in soil near rice roots in relation to subsurface drainage and combined application of subsurface drainage and fertilization for BOUAKE-189 and ROK-5 rice varieties are reported in Table 2. From the study, no significant effect of subsurface drainage and combined application of both factors was observed on the ferrous iron content in soil near rice roots, for BOUAKE-189 rice variety ($p = 0.676$ and $p = 0.940$, respectively), and for ROK-5 rice variety ($p = 0.746$ and $p = 0.750$, respectively), (Table 2).

Table 2. Variance of ferrous iron content in soil near rice roots in relation to subsurface drainage and fertilization, during the cultural cycle of rice varieties.

Source of variation	df	Ferrous iron content ($\mu\text{g/g}$ dry soil)			
		BOUAKE-189		ROK-5	
		F	p	F	p
Drainage	1	0.175	0.676 ^{ns}	0.006	0.940 ^{ns}
Drainage* Fertilization	2	0.294	0.746 ^{ns}	0.288	0.750 ^{ns}

df= degree of freedom; F= Fisher F; ^{ns}not significant $p > 0.05$.

The study showed, however that the total iron accumulation in BOUAKE-189 and ROK-5 rice aerial biomass was significantly related to subsurface drainage ($p = 0.011$, Table 3). However, no significant effect of combined application of both factors was observed for the two rice varieties ($p = 0.056$, Table 3).

Moreover, the total iron contents of aerial biomass in the drained (D2) pots were significantly high comparatively to the controls (Do) pots ($p = 0.011$). The experiment revealed also that the total iron content in aerial biomass of pots which received combined application of subsurface drainage and fertilization (D2+NPK+Urea and D2+NPK+Urea+Ca+Zn+Mg) were higher relatively to D2 drained and non-drained pots (Do) (Figure 6), for both rice varieties.

Table 3. Variance of total iron content in rice plant in relation to subsurface drainage and fertilization, during the cultural cycle of rice varieties.

Source of variation	df	Total Biomass iron content ($\mu\text{g/g}$ dry soil)			
		BOUAKE-189		ROK-5	
		F	p	F	p
Drainage	1	6.840	0.011*	6.840	0.011*
Drainage* Fertilization	2	3.034	0.056 ^{ns}	3.034	0.056 ^{ns}

df = degree of freedom; F = Fisher F; *significant $p < 0.05$; ^{ns}not significant $p > 0.05$.

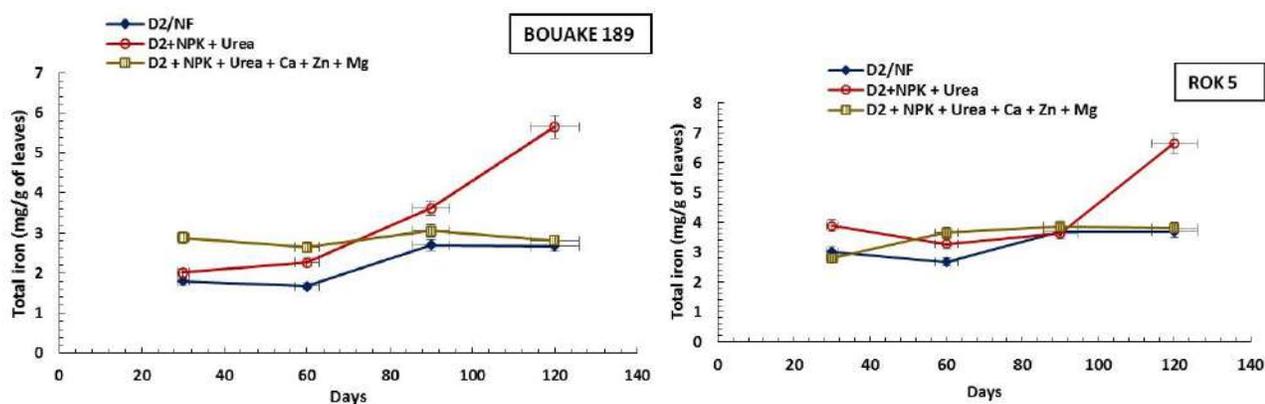


Figure 6. Evolution of the aerial biomass total iron content during the cultural cycle of rice varieties in drained pots for 14 days without fertilization (D2/NF), and in pots with combined application of D2 drainage NPK+Urea and NPK+Urea+Ca+Zn+Mg fertilization, respectively (means of 3 replicates).

Throughout the study, a significant difference was observed on rice biomass yield for subsurface drainage and combined effects of both factors ($p = 0.001$ and $p = 0.000$, respectively) for ROK-5 rice varieties (Table 4).

Furthermore, the experiment revealed that the biomass yield of BOUAKE-189 rice variety was related to subsurface drainage ($p = 0.007$, Table 4), while combined effects of both factors showed no significant difference ($p = 0.108$, Table 4).

However, among all treatments, the D2+NPK+Urea+Ca+Zn+Mg treatment showed the highest yield (296.6 and 433.7 g/pot, respectively), for both rice varieties (Figure 7).

Table 4. Variance of total biomass yield in relation to subsurface drainage and fertilization, for rice varieties.

Source of variation	df	Yield of plant total biomass (g/pot)			
		BOUAKE-189		ROK-5	
		F	p	F	p
Drainage	1	12.867	0.007**	28.469	0.001**
Drainage* Fertilization	2	2.981	0.108 ^{ns}	26.482	0.000**

df = degree of freedom; F = Fisher F; **significant $p < 0.01$; ^{ns}not significant $p > 0.05$.

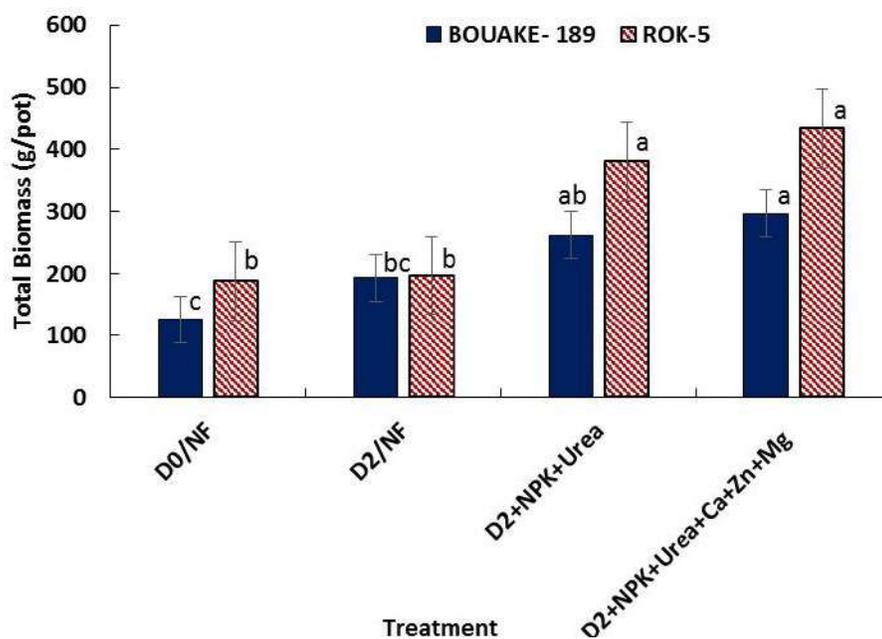


Figure 7. Total biomass yield of rice varieties in drained (D2) in drained pots for 14 days without fertilization (D2/NF) and combined application of D2 drainage, NPK+Urea and NPK+Urea+Ca+Zn+Mg fertilization, respectively (means of 3 replicates). Yields sharing the same letter are not significantly different according to Fishers' test $p > 0.05$.

Discussion

The kinetics of IRB populations and ferrous iron content in soil near rice roots indicate that the growth of IRB is stimulated by flooding (Betremieux 1951). Thus, in spite of drainage and fertilization mode, and according with previous studies rice plant remains the main factor that modulates the dynamic of IRB during rice cultural cycle, as reported by Jacq *et al.* (1991).

From the experiment, and in agreement with our previous study (Otoïdobi *et al.* 2015), the application of subsurface drainage alone, doesn't reduce significantly the number of IRB and ferrous iron content in soil near rice roots for both varieties (Tables 1 and 2). These results can be explained by surviving facultative anaerobic IRB which can survive and grow in aerobic compartments in the presence of low pressure of oxygen (Jacq *et al.* 1991; Liesack *et al.* 2000). The heterogeneous distribution of oxygen through the drainage can also create anoxic compartments where ferrous iron can be reduced by surviving anaerobic IRB population (Ponnamperuma 1972).

The experiment evidenced that the IRB number was significantly reduced by the combined application of both factors (Table 1). In fact, Trollenier (1977) showed that a sufficient mineral nutrition of potassium was important in maintaining the oxidising power of rice roots and in the reducing of IRB populations' activities in rice fields. Thus, we can deduct that the D2 subsurface drainage-combined to mineral fertilization may contribute to the decrement of IRB growth-in rice paddy soil.

Moreover, it appeared that D2+NPK+Urea+Ca+Zn+Mg treatments showed the highest ferrous iron content in the soil, in aerial biomass and the highest rice biomass yield, for the two rice varieties, respectively (Figure 7), for the two rice varieties. Thus, the application of plant essential nutrients counteracts negative effects of excess amounts of iron, by competing with Fe^{2+} uptake

at the sites of ion adsorption on roots or by enhancing plants' defence or tolerance mechanisms (Panda *et al.* 2012). Therefore, in combined application of subsurface drainage and mineral fertilization condition, the drainage favours oxidation and precipitation of Fe²⁺ into Fe³⁺ forms, while the mineral fertilization contributes to Fe³⁺ acquisition by enabling the plant to synthesize more photosynthetic assimilates (NADPH⁺, H⁺) (Ethan, and Odunze 2011), and improving plant growth and yield (Panda *et al.* 2012).

Conclusions

The experiment showed also that the rice plant remains the main factor which modulates the dynamic and activity of IRB during rice cultural cycle.

From the results obtained in this study, subsurface drainage combined with NPK+Urea+Ca+Zn+Mg fertilization decreases the number of IRB in an iron toxic paddy soil under BOUAKE-189 and ROK-5 rice varieties cultivation. Thus, oxygenation throughout drainage and mineral fertilization of the soil maintains the oxidising power of rice roots and reduces the IRB population's number. Moreover, the low level of ferrous iron content in the soil near rice roots, for both rice varieties in the D2+NPK+Urea pots, indicates that the combination of drainage and mineral fertilization may decrease iron reduction and/or optimize the absorption of Fe(II) complexes into the rice plant. However, the subsurface drainage combined to NPK+Urea+Ca+Zn+Mg complex amendment recorded high level of ferrous iron content in the soil near rice roots, high content of total iron in the aerial biomass and the highest mean of rice biomass yield for both rice varieties. Indeed, combined application of drainage and mineral fertilization seems to have a synergic effect on improving rice yield. The oxidation power of the subsurface drainage combined to the mineral fertilization may optimize the acquisition of Fe by rice plant for an improved growth and yield.

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4.2.6. Use of red mud as a pyrolysis catalyst and a carbonated soil amendment

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Abstract

Catalytic pyrolysis may be an alternative production strategy to petroleum-derived fuels and chemicals. Furthermore, red mud, a toxic industrial bauxite byproduct, may serve as a sustainable catalyst, thereby overcoming the need for more robust catalysts. To test this, *in situ* catalytic pyrolysis was run on a semi-pilot scale with various ratios of red mud and switchgrass (*Panicum virgatum*) feedstock. Authors hypothesized that the coking process would render red mud environmentally benign and could, like biochar, improve soil quality and health for bioenergy crop production. Therefore this work investigated i) red mud's capability to enhance bio-oil quality, and ii) how the modified biochar produced from *in situ* pyrolysis affected switchgrass establishment, seedling vigor, and root and shoot mass. Results indicate that red mud is effective at increasing soil pH and reducing the total acid number in bio-oil. While high loading of reacted red mud had a negative impact on plant yield, adding uncatalyzed biochar to pure red mud significantly improved seedling yield on marginal soils. These results suggest that this technology has potential for valorizing a waste stream and creating a soil amendment from red mud; thereby closing nutrient and bioenergy production cycles.

Keywords: bioremediation; red mud; pyrolysis; in situ catalyst; bauxite; bioenergy

Introduction

Red mud, or bauxite residue, is a well-known industrial waste product generated by the Bayer process in during the production of aluminum. This waste stream is generated at a massive scale;

for every 1 kg of aluminum produced there are 2.5-3.0 kg of red mud created. This equates to 44 million tons of red mud produced annually (Hammond *et al.* 2013). It is estimated that there are currently 3 billion tons of red mud stockpiled worldwide (Elham *et al.* 2013). Currently, red mud slurries are spread over large fields and set to dry. Red mud is a highly basic mixture of metal oxides; however, the specific composition varies greatly with the bauxite mineral's geographic origin. Reserves of red mud are ecologically hazardous, and developing its use as a catalyst could turn this waste into a value-added product.

Pyrolysis, the thermal conversion of biomass under anaerobic conditions, could prove to be a viable strategy to produce fuels and chemicals from non-food crops. However, there are many challenges to convert biomass into a petroleum alternative. Developing catalysts that are both active towards deoxygenation and selective against carbon (C)-C cleavage is a significant challenge, considering the harsh reaction conditions and the complexity of the chemical species present. In order to create an economically viable bio-oil, novel catalysts must be either extremely inexpensive and be able to withstand the harsh pyrolysis environment. Recently, researchers have shown red mud to be an effective post-pyrolysis bio-oil upgrading (Karimi *et al.* 2010) and an *in-situ* catalyst (Yathavan and Agblevor 2014). This technology has the potential to generate revenue from unwanted materials, both crop and bauxite residues. However, red mud's toxicity must be neutralized during pyrolysis in order to be used downstream as a soil amendment.

While bio-oil has the potential to be a valuable source of energy, biochar a co-product of pyrolysis is also potentially valuable. Biochar has shown to improve soil quality, sequester carbon, and act as a sorbent for environmental toxins (Mohan *et al.* 2007; Sadaka *et al.* 2014). Specifically, red mud could be rendered less toxic due to carborization, as it has been proposed that the coking process lowers the pH of the red mud and makes potentially harmful metals (such as sodium and heavy metals) less bio-available. This mixed oxide product is expected to be coated in about 30% C making it a modified biochar product. This modified biochar could enhance soil properties as seen in many agronomic studies (Ashworth *et al.* 2014). In order for this novel catalytic reaction to be industrially viable, red mud should be rendered environmentally benign. If this modified biochar is valuable, then two revenue streams could be realized from remediating an immense waste stream. Therefore, authors investigated red mud as an *in-situ* catalysts on a semi pilot-scale pyrolysis reactor. Switchgrass, the biomass feedstock, was pre-mixed with various loadings of red mud to investigate its catalytic effect. The resulting biochars were tested as soil additives to evaluate potential plant toxicity to pyrolyzed red mud and determine its potential end-use as a soil amendment.

Methodology

Bauxite residue was supplied by Alcoa Inc. (Point Comfort, TX). The material was dried for 24 h at 106°C, then crushed and sieved to a particle size between 180-850µm. Switchgrass biomass was supplied by Genera Energy Inc. (Vonore, TN) and was air-dried, ground to a particle size less than 2 mm, and a moisture content of ~16 wt%. Catalytic pyrolysis was conducted by a semi pilot-scale auger pyrolysis system, which was equipped with a feeding system, an auger pyrolysis reactor, a biochar collector, a particle-precipitating chamber, and a condensation section (Fig. 1). Four loadings of red mud were used in this study, switchgrass (SG): red mud (RM) mass-based ratios were as follows: 1:0, 5:1, 1:1, and 1:3. Uncatalyzed pyrolysis (1:0) was used as a control. Feedstock mixtures were subjected to the same continuous operation conditions in the auger pyrolysis reactor and sweeping gas (nitrogen gas, 20 L/min). Bio-oils collected from three condensers were immediately combined and mixed for homogeneity and frozen at -20°C until characterization. The methods used for calculating the aqueous modified total acid number (AMTAN) and the component analysis are reported elsewhere (Connatser *et al.* 2014).

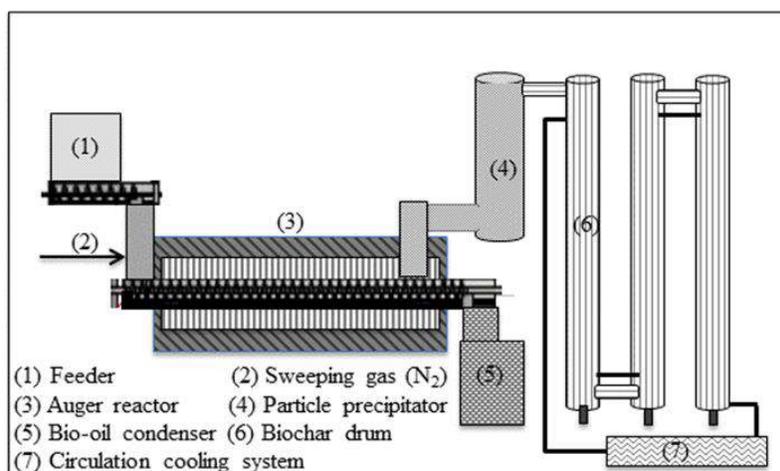


Figure 1. Illustration of the auger style pyrolysis reactor.

A switchgrass cv. Alamo establishment and growth study was conducted on a local soil (Etowah series; Fine-loamy, siliceous, semiactive, thermic Typic Paleudults) that had been autoclaved to 250°C for two 24-hr cycles to kill any pathogens, or beneficial bacteria, and then dried down. Biochars produced from the pyrolysis experiment were mixed at two rates (10 and 20 wt%). Germination was counted every week. After the 6th week, shoots and roots were harvested. Plant material was washed, weighed, dried for 4 h at 105°C, and then re-weighed. Dried root and shoot material was sent to University of Tennessee Soil, Plant and Pest Center, (Nashville, TN, USA), for elemental plant tissue analysis in order to investigate uptake of various elements. Scanning electron microscopy images were collected for each treatment.

Germination and yield data were analyzed to determine soil amendment treatment impact on seedling emergence and vigor with soil amendment considered a fixed effect with replication assumed to be random.

Analysis of variance tests were performed using the Mixed procedure [(SAS V9.3; SAS Inst., Cary, NC) (SAS-Institute 2007)]. When main effect differences were found, mean separations were performed by the SAS macro 'pdmix800' (Saxton 1998) with Fisher's LSD and a Type I error rate of 5%.

Results

The addition of red mud to switchgrass feedstock had dramatic effects on the yield of biochar, oil and, gas. Generally, bio-oil and biochar yields were enhanced with increased loading of red mud. In general, as switchgrass: red mud ratios increased, less paracrystalline visible secondary cell wall occurred along with greater degradation, likely owing to greater heavy metal contributions. Chemical and physical properties of bio-oil were affected by red mud's presence during pyrolysis. The C/H ratio decreased as a result of red mud's presence. Bio-oil heat of combustion was not severely changed by the addition of red mud, but was surprisingly lowered due to its addition.

Modified biochar effected switchgrass growth ($P < 0.05$). High loadings of modified red mud were used to test the upper limit of its application in marginal soils. Considering this, those treated with the higher loading (20 wt%) typically resulted in reduced biomass yield. The highest root and shoot yields were seen for the uncatalyzed biochar at 10 wt% loading. Surprisingly, soils treated

with 10 wt% red mud showed similar, if not enhanced biomass yield as compared to the control. However, adding modified biochar from the 3:1 (RM:SG) pyrolysis reduced root and shoot yields at both high and low loading ($P < 0.05$; Fig. 2). These trends could potentially be explained by the bioavailability of sodium, considering a significantly negative relationship was observed between plant growth (root and shoot yield per pot) and bioaccumulated sodium. It was thought that the biochar present in the post catalytic pyrolysis would help sequester sodium along with other elements present in red mud; however, it appears that at high red mud to switchgrass loadings, biochar helped facilitate ion exchange in the case of sodium. Therefore, metals oxides comprising red mud increased as expected in the catalyzed biochars.

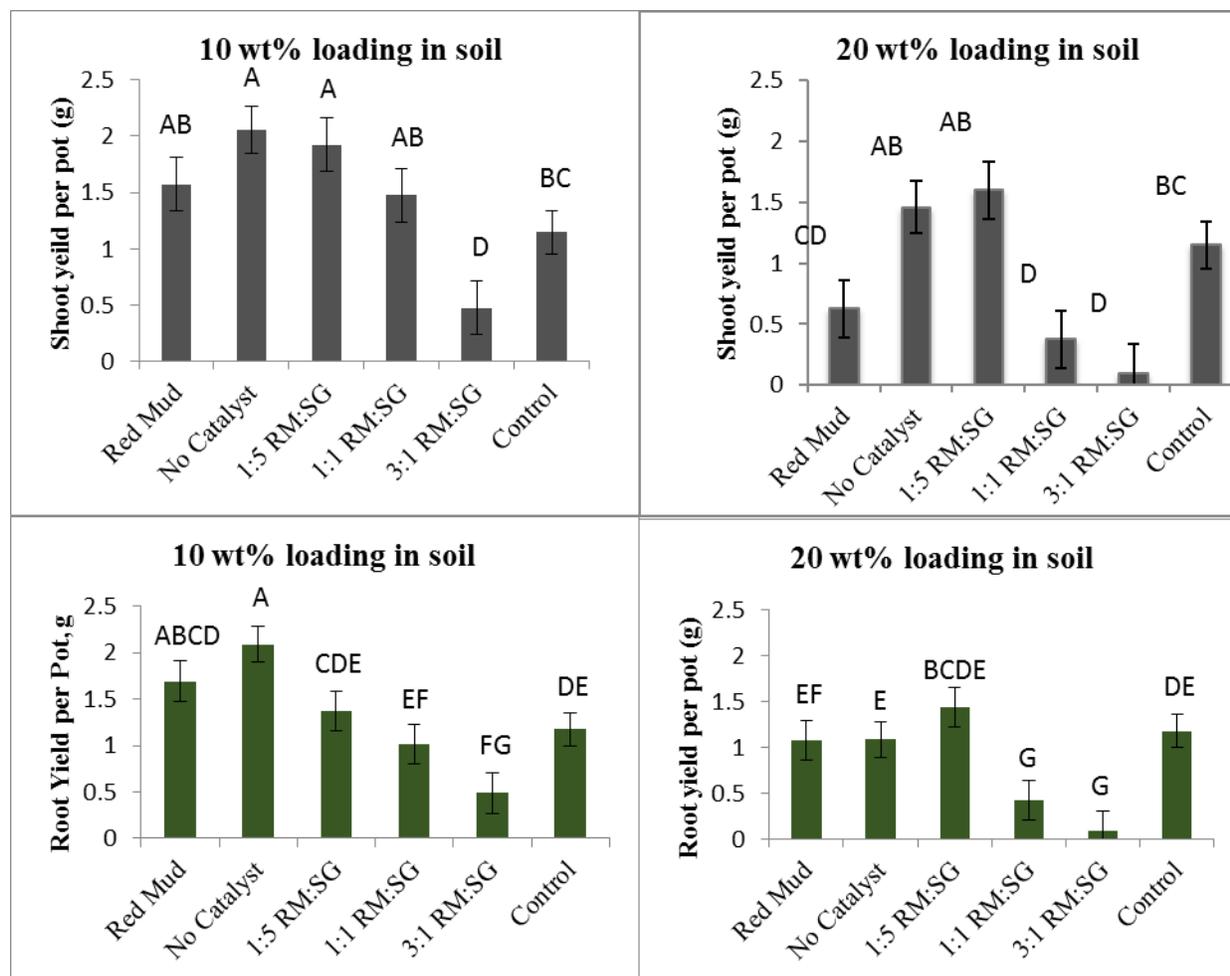


Figure 2. Root and shoot yield per pot based on dry mass with various soil treatments. Loading of red mud (RM) to switchgrass (SG) is pre-pyrolysis. The resulting biochar was added on a weight basis into the soil. Different letter denotes significant difference within 5% confidence.

In previous work by Ruyters *et al.* (2011) increasing red mud applications by 5 and 25% increased soil pH and impacted shoot yield of barley (*Hordeum vulgare*), as well as increased shoot metal uptake; although neither rate exceed toxic limits. In addition, this study suggested that NaOH was one of the main drivers of adverse growth effects from red mud (Ruyters *et al.* 2011). Therefore, it appears that higher red mud dosage results in salt injury in plants, which has implications for bioremediation and may be one of the major limitations for red mud use in closing bioenergy nutrient cycles. Further research is needed to test additional soil amendment combinations such as gypsum to improve red mud structure and composition.

Conclusions

Pyrolysis of biomass may be one viable pathway to create renewable fuels and chemicals. Although, this technology hinges on valorizing a waste stream; hence the exploration of creating a soil amendment material from red mud. The ultimate fate of this technology will be decided based on overall process economics and whether or not red mud is remediated or valorized. Specifically, our findings suggest:

1. That red mud is able to produce a better bio-oil, however, the loading of the catalyst must be considered carefully. In addition, red mud is effective at increasing soil pH and reducing the total acid number in bio-oil.
2. The use of modified biochar as a soil amendment on marginal soil may enhance its fertility; however, this is highly dependent on the nature of the soil and the extent of loading.
3. This technology has the potential to create multiple revenue streams from a longstanding waste material, however, future investigation of red mud's catalytic ability and its presence in the soil post-reaction need further investigation.

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4.2.7. Indian nitrogen assessment, environmental impacts and sustainable development

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Abstract

Nitrogen Cycle is one of the most anthropogenically altered nutrient cycles on Earth. Agricultural soils are the main source of the greenhouse gas N₂O, mainly due to inefficient or unbalanced usage of fertilizer N. The environmental accumulation of reactive N compounds such as nitrate, ammonium, urea etc. from agriculture and NO_x, NO and particulate N compounds (PM) from fossil fuel burning and N₂O from all these activities goes far beyond the denitrifying capacity of earth. They cause soil, water and air pollution affecting health, biodiversity, ecosystem services and climate change. The challenge of nitrogen assessing and managing reactive N species is compounded by the diverse sources of its origin. The just published Indian Nitrogen Assessment (Elsevier, 2017), is a result of about a decade of interdisciplinary assessment process fostered by the Indian Nitrogen Group, a voluntary body of over a hundred scientists and other stakeholders co-founded by the authors. It deals with various aspects of the reactive nitrogen biogeochemical cycle in India from diverse sources, including agricultural soils. It also captures its impacts on food security, health, environment, climate change, biodiversity etc., and the projected scenarios for the future. India is the first developing country to bring out such a comprehensive assessment and we are now leading a South Asian assessment for the next 3 years as a part of a UNEP-GEF

project on International Nitrogen Management System in association with the International Nitrogen Initiative. The lecture will present the highlights of the Indian N assessment including soil pollution and the opportunities it presents to India for evidence-based national/state/regional policies to reduce soil and water pollution due to N. Two major policy initiatives, namely the mandatory use of neem coated urea and 10% reduction in the size of urea fertilizer bag and other measures under consideration are expected to achieve major reduction in urea consumption in the decade ahead. The findings emerging from Indian N assessment also aid in informed international negotiations on various sustainable development goals, especially climate change, health, agriculture, energy, biodiversity and environment.

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4.2.8. The soil pollution of agricultural solving by organic farming for food safety and friendly environment- Case Study from Thailand.

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Abstract

This work is part of the *Bakery loop for tomorrow* and *ECO Bakery for Friendly Environments* projects, which focus on producing safe food to achieve zero hunger and a healthy environment to support the SDG 2030. In Thailand, the problem of soil pollution is rising, due to the used of agro-chemicals that can have harmful effects on humans, both farmers and consumers, and on the environment, as well as on the rice, which is the main food in Asia. To tackle this problem and improve soil quality, several agricultural methods are proposed such as organic agriculture and crop rotation, which also have benefits on food safety and the environment. This research proposes the use of organic fertilizers such as legumes, prior to planting the rice, thus ensuring the safety of the ingredients for bakery and safety rice for human consumption.

In Thailand, there is the increasing problem of soil pollution from the dangerous chemical usage which has an effect on humans, both the farmers and consumers and on the environment by agricultural such as in the rice planting. Normally, the rice can be planted 2 times per year together with other crops or plants such as groundnut, which has a short life cycle. They can cultivate plants that use to be the ingredients of bakery such as leguminous. Their root can be plowed and buried as the bio-fertilizer for the rice, which has become the organic matter to improve the soil biological and chemical qualities. Researchers have launched this concept for testing the conducted research in the land where rice has planted.

The random sampling was carried out at 302 sites where farmers were previously known, including to the water qualities and soil properties, to reduce uncertainties. Biological, chemical and physical soil tests were carried out before and after the planting of legumes. The results were analysed for statistical significance by used t-test based on different sample pairs, with the SPSS program. The mean and SD values were taken with tolerance limits of 5%.

All data have been evaluated into 4 levels: excellent, good, moderate and poor. The result of this experimental research has shown that the soil quality has improved after the testing. In the biological parameters, we find soil bio-indicators, such as the peanut bugs, the macro-fauna and the forest lice, which accelerated the rates of the decomposition of soil organic matter. Through the chemical qualifications, it was observed an improvement in soil cation exchange capacity (CEC), an increase in soil buffering capacities, and the increasing of the soil organic matter content, which has reduced the toxicity of aluminium and manganese. The physical qualification had shown an increase in soil productivity. The descriptive statistics of the soil pollution of agricultural solving by organic farming for food safety and friendly environment research has significant $\alpha = 0.05\%$ or 95% , $Z = 0.512$, and critical $t < 1.49$ to $t > 2.82$.

The legumes such as peanuts, green beans, red beans, or soybeans, are suitable for live amendment and the seeds can be used as the ingredients of the bakery. Because they grow fast, once the seed is harvested, they can be incorporated into the soil by ploughing and decompose in 15-30 days. The leaves and root will serve as fertilizer to increase soil nutrients, improving rice productivity in the next crop.

Keywords: soil pollution, agricultural solving, Organic farming for food safety and friendly environment, Soil pollution solving, Safety Organic farm, Organic plant, Organic Bakery, Bakery loop for tomorrow, ECO Bakery for Friendly Environments in Ecological,

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4.2.9. Decontamination of agricultural fields and mitigation of radioactive cesium uptake after nuclear contamination by TEPCO's FDNPP accident – situation after 7 years -

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Abstract

The 2011 Great East Japan Earthquake and Tsunami caused the accident at Tokyo Electric Power Company (TEPCO)'s Fukushima Daiichi Nuclear Power Plant (FDNPP) in Japan and released a large amount of radioactive materials (¹³¹I, ¹³⁴Cs and ¹³⁷Cs are of concern) to the agricultural products and fields. Evergreen plants (tea), winter crops (winter wheat, pasture) and orchard plants were directly contaminated by fall out. As in the case of paddy and upland crops, most of them were before cultivation and only the soil surface was contaminated. The countermeasure was mainly dependent on how the plant and/or field was contaminated. Removal of attached radionuclides from the plant body was effective at reducing the harvest radioactivity, and large areas of tea and fruit orchard were treated by mid place cutting and bark removal by a high water pressure machine, respectively. On the other hand, when the soil was directly contaminated, decontamination of soil was introduced in a large area. Several methods were developed, and in paddy fields, about 5 cm of topsoil was removed and then non-contaminated soil was dressed. Since the radioactive materials were not able to be removed completely from the field, a substantial amount of radioactive cesium still remained in the soil. To mitigate the radioactive cesium transfer from the soil to the plants, increasing the exchangeable potassium level in the soil was carried out. These methods successfully

reduced the radioactivity of the agricultural products in the disaster area. Based on the inspection of all bags of brown rice (more than 10 million 30-kg bags), there were no reports exceeding the limitation value for shipment (100 Bq/kg) since the 2016 fiscal year.

Keywords: Nuclear disaster, Radioactive cesium, Top soil removal, Potassium application, All bags inspection, Fukushima

Introduction, scope and main objectives

When a large area is contaminated, some radioactivity will still remain in the soil even after the decontamination process (*e.g.*, top soil removal and reverse tillage). To overcome this problem, the major countermeasure for reducing the uptake of radioactive Cs (^{134}Cs + ^{137}Cs) is to apply a sufficient amount of potassium to the field. In 2011, after the FDNPP event, there was an urgent request to overcome the contaminated area in Fukushima prefecture and the surrounding prefectures (*e.g.*, Miyagi, Tochigi, Chiba, Gunma, and Niigata prefectures). Based on research on the rice plant, which was carried out about 50 years ago (*e.g.*, Tensho *et al.* 1959), research using global fallout data (Komamura *et al.* 2001), and research on the Chernobyl event (Komamura *et al.* 2001, Tsukada *et al.* 2002), it is estimated that a higher transfer factor (radioactivity of Cs in brown rice / radioactivity of Cs of grown soil) is lower than 0.1 (Uchida *et al.* 2005). Based on this observation, the provisional limitation value for rice was determined as 500 Bq/kg in 2011, which means that rice was allowed to be planted in paddy fields with radioactivity lower than 5,000 Bq/kg in 2011.

To renovate the agriculture after a disaster, one countermeasure, *i.e.*, the decontamination of contaminated soil from the field, is required, as the downward movement of radioactive Cs is rather slow (Yamaguchi *et al.* 2012). The Ministry of Agriculture, Forestry and Fisheries of Japan introduced several methods as early as 2011, and these techniques have been applied to agricultural fields in a large area of contamination. It should be mentioned that physical decontamination is not a perfect method. Some of the radioactivity still remained in the decontaminated soil. To further reduce the radioactivity of soil and recover the amount of field soil, non-contaminated soil was dressed and mixed with some fertilizers, zeolite and/or manure after the decontamination. Because the required amount of soil was too large, the mountainous soil around the area was collected and used. This soil was primarily weathered granite and/or soil containing a large amount of sand, and thus, the fertility was poor (Photo 1).



Photo 1. Large amount of non-contaminated soil (degraded granite soil taken from nearby mountains) dressed after decontaminating the paddy soil in Kawamata town, Fukushima (2016).

In 2011, a rice bag survey for radioactivity was carried out by a monitoring survey (more than 20,000 bags were checked). Some samples (0.2%) exceeded the provisional regulation value even though the cultivation area was determined based on the radioactivity of the soil (Fig. 1). The soil chemical properties gave an answer to explain this inconsistency. When the soil exchangeable potassium level was plotted against brown rice radioactivity, it is clearly demonstrated that the soil exchangeable potassium strictly regulated the transfer of radioactive Cs from the soil to brown rice (Fig. 2). Based on these observations, it is recommended to apply 25 mg of K_2O 100 g^{-1} (207 mg of $K\text{ kg}^{-1}$) in addition to conventional fertilization (MAFF 2014a, Kato *et al.* 2015).

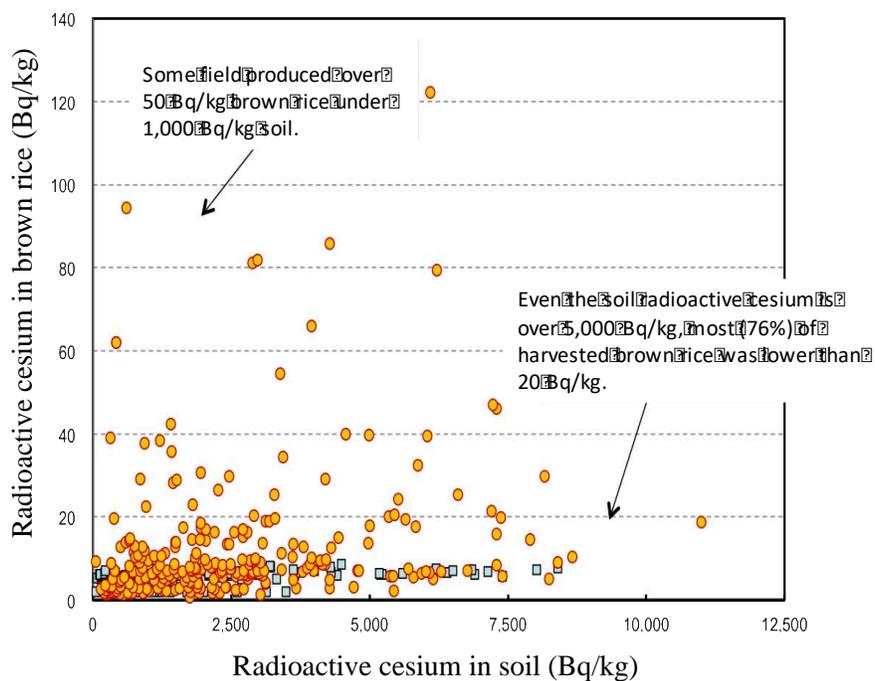


Figure 1. Radioactive cesium concentration of soil and harvested brown rice in Fukushima prefecture, cultivated outside of the Special Decontamination Area (MAFF *et al.* 2014).

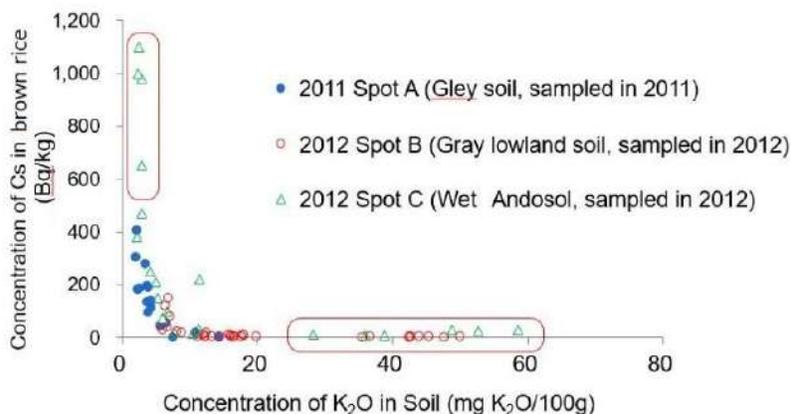


Figure 2. The relationship between the exchangeable potassium concentration in soil and the radioactive Cs concentration in brown rice (MAFF *et al.* 2014).

Methodology

Physical decontamination methods have been summarized in MAFF (2013).

Detailed analytical information for rice is obtained in Kato *et al.* (2015).

For soybean and buckwheat, countermeasures to decrease the radioactive Cs transfer from the soil to the plant have been carried out. Different levels of potassium fertilizer have been applied in the field after decontamination, and then the growth and radioactivity were determined. To describe the effect of the potassium level on the migration of radioactive Cs to the harvest at different contamination levels of the soil, the transfer factor (TF: TF = radioactivity of harvest / radioactivity of soil) is introduced.

Results and discussion

Several decontamination methods have been developed and are summarized in Table 1. Based on these data, most of the top soil removal was carried out by removing 5 cm.

Decontamination (which was carried out in the relatively highly contaminated area only) and subsequent countermeasure by applying a sufficient amount of potassium fertilizer (which was carried out in a wide area of contaminated area) gave a tremendous effect for rice production. In Table 2, the result of brown rice monitoring (FY 2011) and all bags inspection (from FY 2012) is demonstrated, and it is shown that there were no rice bags that exceeded the standard limitation value (100 Bq kg⁻¹) since FY 2015.

Table 1. Change in the radioactive Cs concentration of brown rice after 2011. (Fukushima prefecture)

Decontamination method	Characteristics	Radioactivity (Bq kg ⁻¹)	
		Before	After
Top soil removal	Remove the few cm top soil (4cm)	10,370	2,599
	Remove the top soil using hardner (3cm)	9,616	1,721
	Remove the top soil with grass (3cm)	13,600	327
Stirring cleaning method	Remove clay fraction selectively	16,052	9,859
Reverse tillage	Turn over more than 30cm	-	-

Table 2. Change in the radioactive Cs concentration of brown rice after 2011. (Fukushima prefecture)

		≤ 50 Bq kg ⁻¹	51-75 Bq kg ⁻¹	76-100 Bq kg ⁻¹	100 Bq kg ⁻¹ <	Monitored number
FY 2011	actual no.	20,295	364	219	311	21,189
	ratio (%)	95.78%	1.7179%	1.0336%	1.4677%	100%
FY 2012	actual no.	10,343,548	1678	389	71	10,345,686
	ratio (%)	99.98%	0.0162%	0.0038%	0.0007%	100%
FY 2013	actual no.	10,951,351	492	323	28	10,952,194
	ratio (%)	99.99%	0.0045%	0.0029%	0.0003%	100%
Fy 2014	actual no.	11,014,636	1	1	2	11,014,640
	ratio (%)	100%	0.00001%	0.00001%	0.00002%	100%
Fy 2015	actual no.	10,496,518	4	0	0	10,439,072
	ratio (%)	100%	0.00004%	0	0	100%
Fy 2016	actual no.	10,264,859	0	0	0	10,264,859
	ratio (%)	100%	0%	0%	0%	100%
Fy 2017	actual no.	9,813,530	0	0	0	9,813,530
	ratio (%)	100%	0%	0%	0%	100%
(2018.2.1)	ratio (%)	100%	0%	0%	0%	100%

For soybean and buckwheat, the TF is also regulated by the soil exchangeable potassium (Fig. 3). It seems that the TF decreased as the years passed, while the decrease seems to cease after 2015.

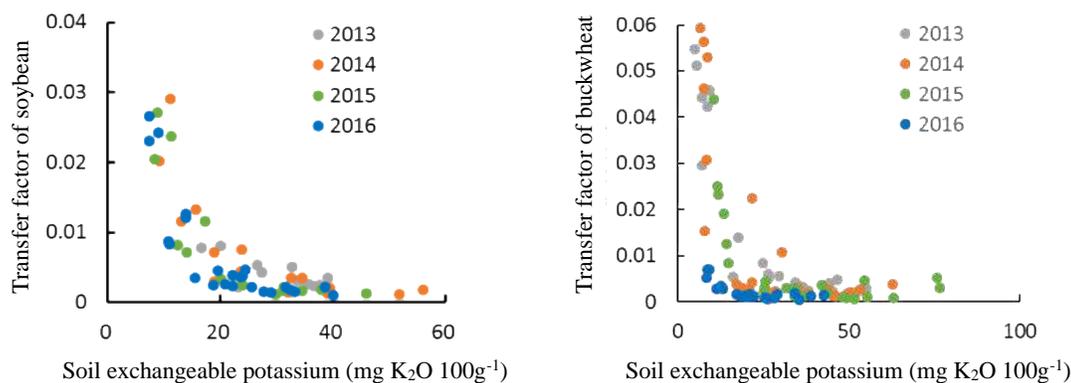


Figure 3. Successive change in the relationship between the exchangeable potassium concentration in soil and the transfer factor of soybean (Left) and buckwheat (Right). (NARO/TARC ARRC 2018).

The TF of soybean and buckwheat is much higher than that of rice (Kato *et al.* 2015). Though the standard application for soybean addition to the conventional fertilization is 25 mg of K₂O 100g⁻¹, it is recommended to increase this value up to 50 mg of K₂O 100g⁻¹ (415 mg of K kg⁻¹) in the case of an initial trial after an accident and/or in areas where the harvest radioactivity is high (MAFF *et al.* 2015). Moreover, for buckwheat, the recommendation is 30 mg of K₂O 100g⁻¹ (249 mgK kg⁻¹) (MAFF *et al.* 2014b).

Conclusions

Countermeasures against radioactive cesium contamination to the agricultural fields were carried out for 7 years in Japan. Based on the characteristics of cesium, it is recommended to remove the top soil if the contamination level is high. Though the downward migration is slow in the case of cesium, an earlier application gave a better result. On the other hand, it is not possible to remove all of the radioactive materials from the soil even by top soil removal. Continuous countermeasures to mitigate the transfer from the soil to the plant are still required.

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