

Heavy metal mobility and PAHs extractability relationships with soil hydrophobicity in coal ash reclaimed technogenic soils (Technosols)

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INTRODUCTION

The overburden dumps at Maritsa-Iztok coal mine in South-Eastern Europe are characterized by elevated bioavailability of metals, lack of enough moisture, increased compaction and water repellency. In the beginning of the reclamation period (1970s) 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, a waste product from the nearby coal incineration thermal power plant. The objective of the present study was to assess mobile (soluble and exchangeable) metals, and labile (organic solvent extractable) polycyclic aromatic hydrocarbons (PAHs) in hydrophobic Technosols reclaimed with coal ash and investigate links with soil hydrophobicity (soil water repellency).

METHODOLOGY

Total organic carbon (TOC), by oxidation with $K_2Cr_2O_7/H_2SO_4$ and

humic organic carbon (HOC) and fulvic organic carbon (FOC) by 0.1 $MNa_4P_2O_7$ and 0.1 M NaOH; cation exchange capacity (CEC), by buffer K-malate at pH 8.2; electrical conductivity EC by ISO 11265; texture, by Kachinski method; soil water-repellency, by the water drop penetration time (WDPT); statistical analysis (Principal component analysis PCA and cluster analysis by SPSS 22. Heavy metals in: H_2O in soil:water ratio 1:5; 0.01M $CaCl_2$ in soil:solution ratio (1:5); pseudo-total forms of metals (PT) in aqua-regia digestion (ISO 11466:1995); exchangeable cations in 1M NH_4NO_3 analysed by AAS. Anions in the soil solution including dissolved organic carbon (DOC) through analysis with Spectroquant tests, Merck Millipore. Heavy metal speciation, by using Visual Minteq V. 3.1. The analysis of H_2O and 0.01M $CaCl_2$ by ICP-OES; PAHs by 1:1 v/v acetone:hexane extraction (ISO 18287:2006 and GC-MS analysis).

MAIN RESULTS

The non-vegetated Technosol (Fig. 1) has higher contents of sand than the pine-vegetated soil, however the CEC, EC and TOC are higher

due to the accumulation of coal particles in the sand fraction and the high proportion of humified organic matter in coal. PCA and cluster analysis involving exchangeable and soluble forms of Co, Cu, Fe, Mn, Ni, Zn, Pb and other soil properties and characteristics revealed that soil hydrophobicity and soluble and exchangeable forms of most heavy metals have a similar source. All heavy metals (1M NH_4NO_3 , 0.01 M $CaCl_2$), except Pb were positively related with % sand. Water extracts of Fe (Fe_W) were significantly correlated with WDPT ($r=0.80$, $p<0.003$) and Fe_W, WDPT and OC loaded on one component and constituted a sub-branch of the dendrogram (Fig. 2). The majority of heavy metal species in the Technosols were represented by free ions (M^{2+}) and neutral sulfate complexes (MSO_4^0). The metal speciation showed that: (i) in the more acidic non-vegetated plot (pH~3.0) mono- and disulphate complexes were the most dominant for Al, and M^{2+} were the most common for Cu, Fe, Mn, Ni and Zn; (ii) the distribution of Fe species is controlled by the pH/Eh conditions and SO_4^{2-} concentration in solution. In the

non-vegetated plot with a pH~3.0 ($Eh<150$ mV), Fe was found as free Fe^{2+} and $FeSO_4^0$. In addition, the H_2O and 0.01 M $CaCl_2$ soluble Fe, Mn, Ni, Cu and Zn, were higher than the maximum permissible levels for surface waters and may become a source of contamination. Soil organic matter (SOM) in water repellent soils is more chemically inert, than SOM in wettable hydrophilic soils, due to hydrophobic interactions in the soil organic matrix thus decreasing the release of organic colloids.

PCA did not reveal links of individual or total PAHs with WDPT or TOC. The extremely acidic soil reaction prevents dissolution and mobilization of hydrophobic compounds through sorption to dissolved organic carbon and organic colloids. The high contents of acenaphthylene (Table 1) may originate from the fly ash amended waste dumps (Liu et al. 2000). PAHs are strongly adsorbed by inert and hydrophobic insoluble organic matter (bound residues in SOM), and are therefore not released through extraction with organic solvent.



Fig.1: Non-vegetated Technosol.

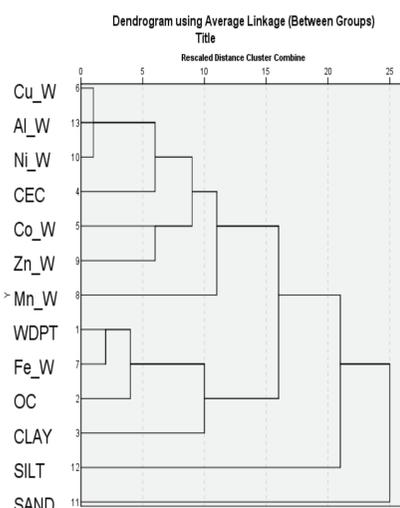


Fig.2: Cluster analysis of H_2O soluble forms of metals and other soil characteristics.

| PAH $\mu g/kg$ | 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 | |
| | BaA | CHR | BbF | BkF | BaP | IND | Dbah | B | |
| mean | 4,88 | 9,46 | 5,86 | 3,63 | 4,28 | 3,56 | 0,90 | 2,89 | 1876 |
| SD | 2,39 | 5,12 | 3,59 | 1,75 | 1,99 | 1,95 | 0,43 | 0,98 | 901 |

Table 1: PAHs contents (means) +/- SD. 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

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