Food and Agriculture Organization of the United Nations

13–15 JUNE, 2023

Cadmium content in fertilizers and its impacts on soil health

Ms Vinisa Saynes Santillán,

INFA coordinator

INTERNATIONAL NETWORK ON SOIL POLLUTION

CHANNELLING COLLECTIVE ACTION TOWARDS ZERO POLLUTION

1st Meeting of the International Network on Soil Pollution (INSOP)

GLOBAL SOIL PARTNERSHIP

We are dependent on fertilizers; prices have increased and are expected to do so for another two years

Uneven distribution of nutrient stocks
90% of phosphorus (P) reserves are concentrated in five countries, while over half of the potassium (K) is found in three countries.

Social factors change the global outlook
The high concentration of minerals, coupled with the war conflicts, leading to an acute energy and fertilizer crisis.

Supply shortages triggering price hikes and risking farmers
Sanctions and supply cuts in Russia and Belarus are leaving about **40% of the world's potassium supply out of the market,** leading to shortages and rising prices. Energy plays an important role. **Reduced natural gas restricts the fertilizer industry**, leading to supply shortages, especially of nitrogen.

Higher prices leading to soil nutrient crisis
According to the Commodity Price Outlook report, fertilizer prices were 70% higher in 2022 than in 2021, and the World Bank forecasts that high fertilizer prices could remain in place for up to two more years, putting farmers at risk.

Additional challenges in P-fertilizers

Approximately half of the world’s agricultural lands are low in P

We are mining P

To grow our crops, we have dug up about 22 × 10^{12} g P from geological phosphate reserves to produce fertilizers.

We have been doing that every year for more than 50 years, quadrupling the environmental flow of P.

The P used in fertilizers is obtained from rock phosphate, which is a non-renewable resource that should be efficiently used

P reserves are concentrated

The mined deposits of phosphate rock we need to produce fertilizers are limited and concentrated in less than 10 countries

There is no replacement

Unlike nitrogen, phosphorus cannot be pulled from the air and, unlike the carbon in our energy system, there is no known replacement

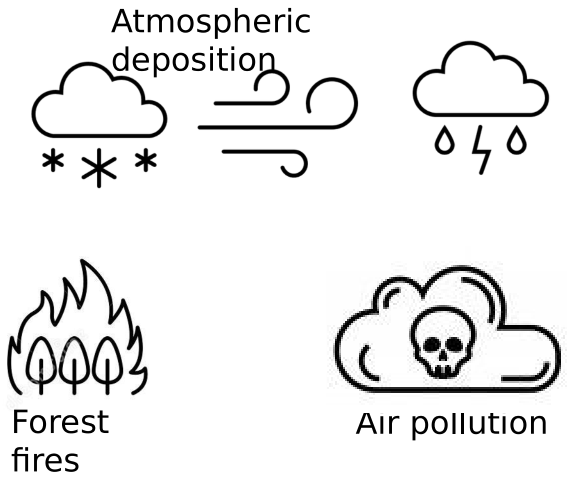
We are wasting P

80 % of phosphorus mined in 2005 was used in fertilizer, but only 17 % made it to the fork (or chopstick). The largest loss — around 46 %— was directly from farms through soil leaching and erosion.

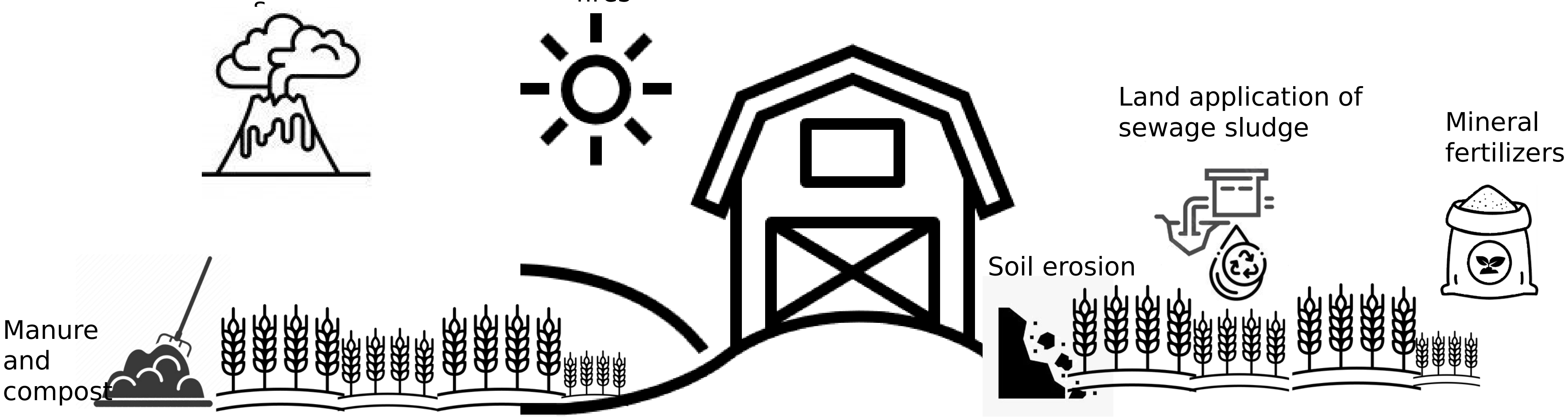
30–40% of food produced is spoiled or wasted, and this wastes around 1 million t P/yr

Where does Cd come from?

Cd can be released into the environment through natural activities (erosion, river transport, and volcanic activity) and, above all, through phosphate fertilizers, which can cause pollution.



- Significant sources in industrialized areas
- Incineration of municipal wastes
- Non-ferrous metal production, Fe and steel production
- Combustion of fossil fuels contribute Cd to the air



Average concentrations of Cd in non-polluted soils are between 0.06 to 1.1 mg/g, with a minimum of 0.01 and a maximum of 2.7 mg/g (Kabata-Pendias and Pendias, 1992)

Quality issue: potential content of heavy metals

Cd persistence in the environment and its uptake and accumulation in the food chain make Cd a public health concern.

- Cadmium (Cd) is a relatively rare metal in nature and belongs to the group of "heavy metals"
- Cd is the third most dangerous pollutant to the environment after mercury (Hg) and lead (Pb).
- It is biopersistent and, once absorbed by an organism, can remain in it for many years.
- The United States Environmental Protection Agency (US EPA, 2021) and the International Agency for Research on Cancer (IARC2021) classify Cd as a human carcinogen due to its ability to accumulate in the body and cause serious and permanent damage.

Table 18.7

SOURCES AND HEALTH EFFECTS OF SELECTED INORGANIC SOIL POLLUTANTS

Chemical	Major uses and sources of soil contamination	Organisms principally harmed[a]	Human health effects
Arsenic	Pesticides, plant desiccants, animal feed additives, coal and petroleum, mine tailings, detergents, and irrigation water	H, A, F, B	Cumulative poison, cancer, skin lesions
Cadmium	Electroplating, pigments, plastic stabilizers, batteries, and phosphate fertilizers	H, A, F, B, P	Heart and kidney disease, bone embrittlement
Chromium	Stainless steel, chrome-plated metals, pigments, refractory brick manufacture, and leather tanning	H, A, F, B	Mutagenic; also essential nutrient
Copper	Mine tailings, fly ash, fertilizers, windblown copper-containing dust, and water pipes	F, P	Rare; mental problems, fatigue; essential nutrient
Lead	Combustion of oil, gasoline, and coal; lead-acid batteries; iron and steel production; solder in water-pipes; paint pigments	H, A, F, B	Brain damage, convulsions
Mercury	Pesticides, catalysts for synthetic polymers, metallurgy, and thermometers; from coal burning	H, A, F, B	Nerve damage
Nickel	Combustion of coal, gasoline, and oil; alloy manufacture; electroplating; batteries; and mining	F, P	Lung cancer
Selenium	High Se geological formations and irrigation wastewater in which Se is concentrated	H, A, F, B	Deformities; essential nutrient
Zinc	Galvanized iron and steel, alloys, batteries, brass, rubber manufacture, mining, and old tires	F, P	Rare; essential nutrient

[a]H = humans, A = animals, F = fish, B = birds, P = plants.

Why do fertilizers contain Cd?

Origin	Cadmium content (mg per kg P205)		
IGNEOUS	**(1)**	**(2)**	**(3)**
Kola (Russia)	< 13	0.3	0.25
Phalaborwa (South Africa)	< 13	0.1	0.38
SEDIMENTARY			
Florida (USA)	23	19.8 - 32.7	24
Jordan	< 30	12.01.28	18
Khouribga (Morocco)	46	17 – 63	55
Syria	52	13 – 46	22
Algeria	60	42 – 62.6	
Egypt	74		
Bu-Cra (Morocco)	100	101 – 115	97
Nahal Zin (Israel)	100	81 – 112	61
Youssoufia (Morocco)	121	164.7	120
Gafsa (Tunisia)	137	94	173
Togo	162	164 – 179	147
North Carolina (USA)	166	125	120
Taiba (Senegal)	203	165 – 180.6	221
Nauru	243		

Sources: **(1)** *Davister (1996);* **(2)** *Botschek and Van Balken (1999);* **(3)** *Demandt (1999).*

Compared with non-phosphate containing rock, sedimentary phosphate rock deposits are about 69 times more enriched with Cd.

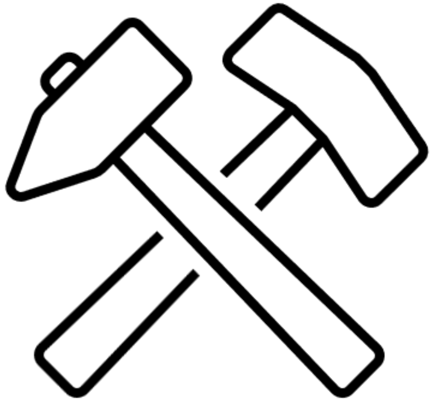
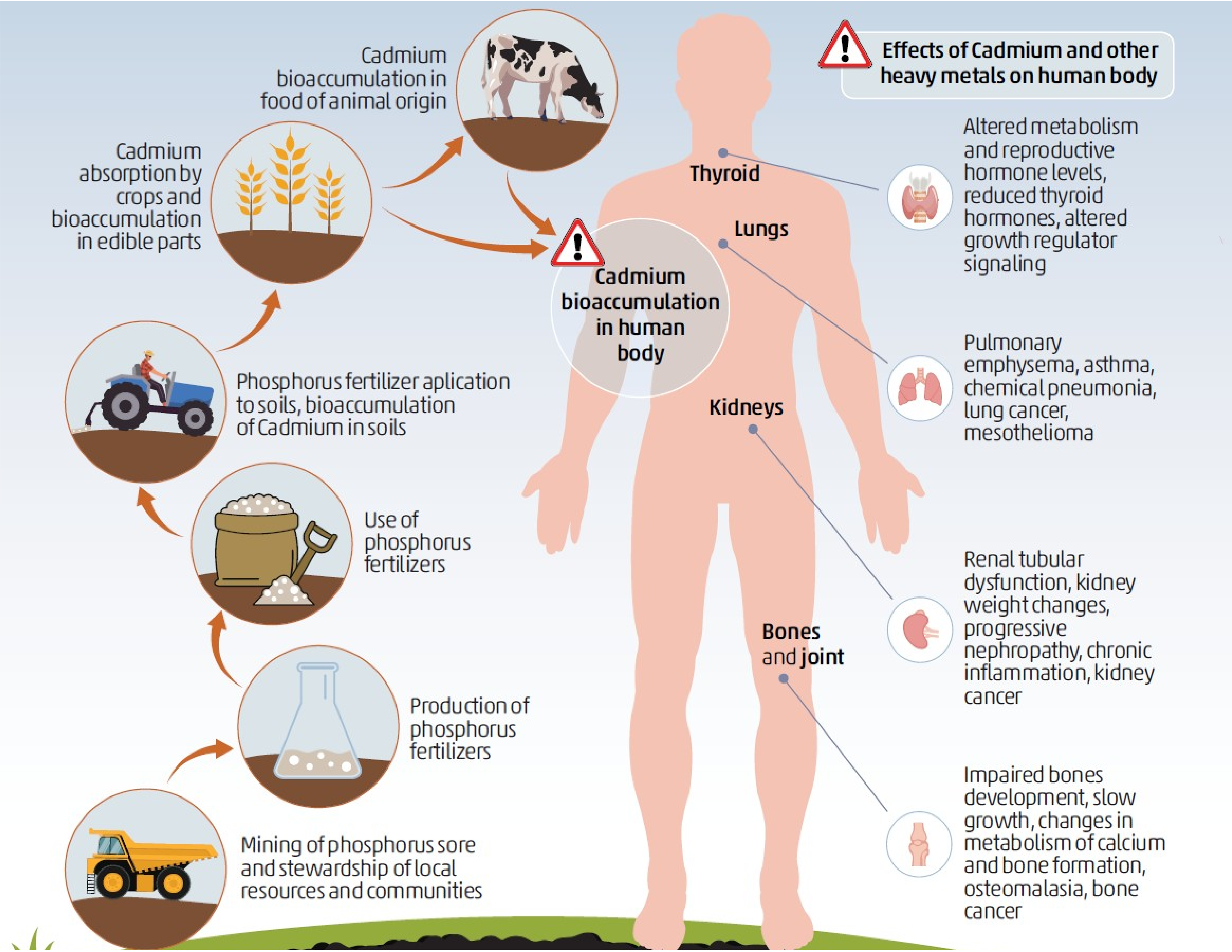


Table: Cadmium contents of main commercial P rocks according to different sources

The effects of cadmium on health and the environment

The main effect of Cd on human health is kidney disease, and although other adverse effects have been reported
(e.g. pulmonary, cardiovascular, and musculoskeletal systems)



Sources and methods for analyzing Cd content

SOURCES

Manure and

Mineral fertilizers

Sampling, sample handling and sample preparation play a significant role

The accuracy of obtained result is strongly related to chemist's decision in choosing the proper and most suitable analysis method. So, the question is, what is the most suitable method?

FRACTION

EXTRACTION METHODS

The different methods for recovering metals from fertilizers produce highly variable results for a same sample, making comparisons difficult.

CONCENTRATION DETERMINATION

Atomic absorption spectrometry (AAS)

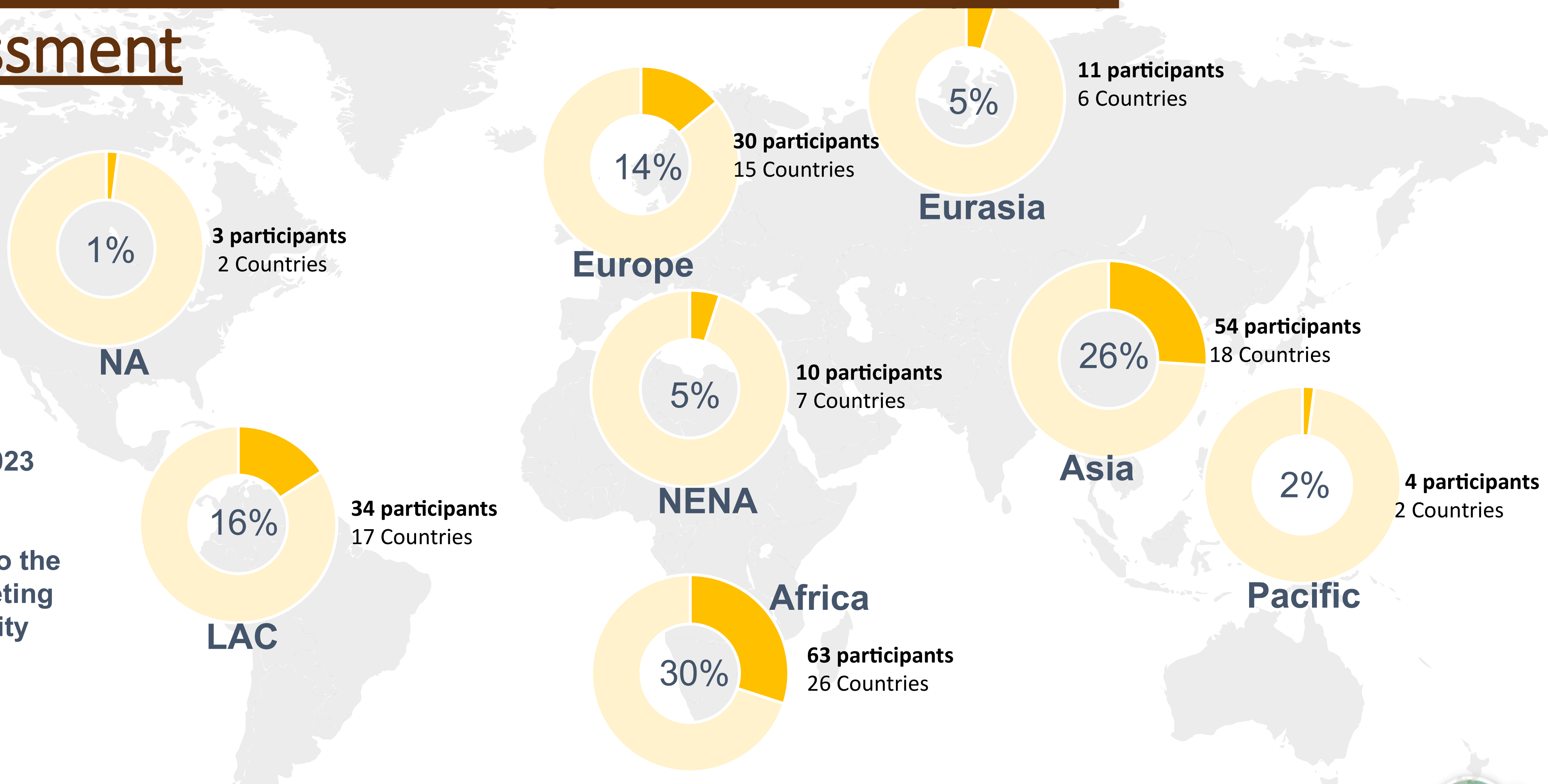
How can INFA and INSOP contribute to monitoring and reducing the contamination and health problems associated to certain sources of mineral P-fertilizers?

First INSOP-INFA meeting on fertilizer quality assessment

28th February 2023

209 participants joined virtually to the INSOP-INFA meeting on fertilizer quality assessment

51 % INSOP
49 % INFA

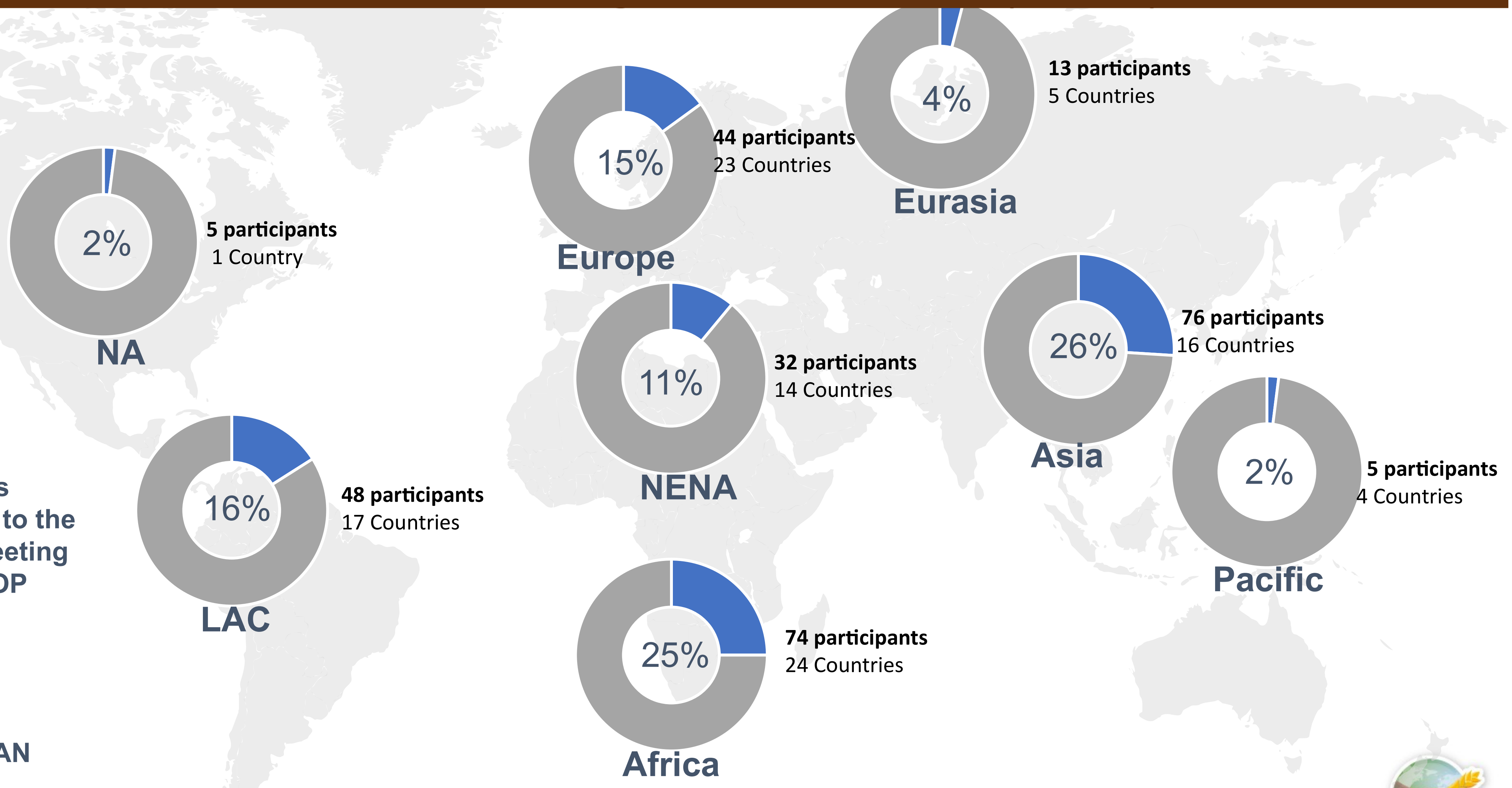


The proposed areas of collaboration are

A joint collaboration with INFA will address important gaps and, in 2023 will work together towards achieving the following tasks:

- Identifying the **main fertilizer** sources to be analyzed
- Identifying the most frequently used **methods**
- **Optimizing and harmonizing** of standard operating procedure (SOP) for the analytical evaluation of **heavy metal content in phosphate fertilizers**
- **Raising awareness** on the importance of environmental and health safety of mineral and organic fertilizers and recycled nutrient

Second INSOP-INFA meeting on fertilizer quality assessment



1st June 2023

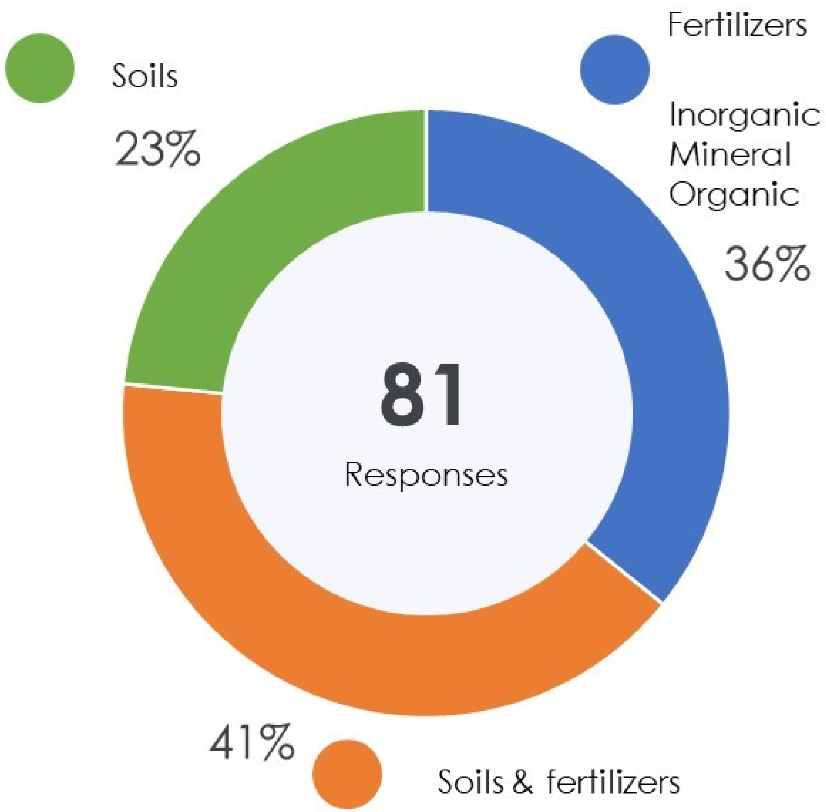
297 participants joined virtually to the INSOP-INFA meeting on cadmium SOP harmonization

31 % INSOP
20 % INFA
49 % GLOSOLAN

69 laboratories from 49 countries completed the template for collating information on the methods for Cd content analysis in soils and fertilizers

B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	
Latin America and the Caribbea	**Country**	**Fertilizer name or type**	**Fertilizer form**	**Sample preparation procedure**	**Sieve size for analysis (mm**	**Sample weight (g)**	**Equipment used for analys**	**Reagents Used**	**Chemical Manufacturers for Reagen**	**Catalyst/s add**	**Catalyst/s weight (g)**	**Volume and concentration of reagents (**	**Reagents weight (g)**	**Mixing/Standing time (min)**	**Analysis type (Digestion, distill**	**Analysis time (min)**	**Cost of analysis (US dollars**	**Reference materials used**	**Qu**
Pacific	Australia	Compost and Soils	Any form	Dry 105°C	then ring	0,4	ICPMS	Aqua regia (3HCL;1HNO3)	approved	None	NA	20ml			Digestion	120min	element	variety	ISO
Europe and Central Asia	Austria	Soils	solid	Air drying for samples sieved through 2 mm sieve	2 mm	0,5	ICPOES, ICPMS	Aqua regia (6 ml HCL;2ml HNO3)	VWR	No	NA	6 ml HCl (34-36 %);2 ml HNO3 (67-69 %)			microwave digestion, ICPOES; ICPMS	Digestion (70 min), Measurement (about 3-6 min per sample)	Prüfstelle		ISO
Asia	Bangladesh	Inorganic and Organic Fertilizer	soid	Drying at 105°C C and Grinding	2mm	2g	AAS	Nitric Acid	BDH, Merck,Fisher or other equivalent manufacturers	No	N/A	10 ml/per sample and 68% HNO3	N/A	30 minutes	Digestion,Volume and filter and then taking the reading in AAS.	Digestion will be continued until the clear digestion formed.	Government organization Approx. 3 US dolar and private 6 US dolar.	CRM	ILC with Acr
Latin America and the Caribbean	Brazil	Soil only	solid (2 mm)	drying at 40 °C	2 mm	0.5 g	ICP-OES	HNO3, H2O2, HCl	Scharlau, Sigma			10 ml			microwave digestion		US$ 10	2711a Montana soil (NIST)	Lab
Africa	Côte d'Ivoire	Soils, plants and fertilizer	Any form	Air drying for samples sieved through 2 mm sieve	2 mm	0.3g	Digester bloc; distillation unit; Spectrophotometer and Atomic absorption	Sulfuric Acid 98%		Mixed 6g (CuSO4.5 H2O) + 94g (K2SO4)	1	3 ml H2SO4 98%			for total Nitrogen; Spectrophotometer for total Phosphorus and Atomic Absorption for Heavy and leaght elements		It depends on the parameters but an average of 5 USD per sample	Yes	Yes

Matrix type



Agreed to:

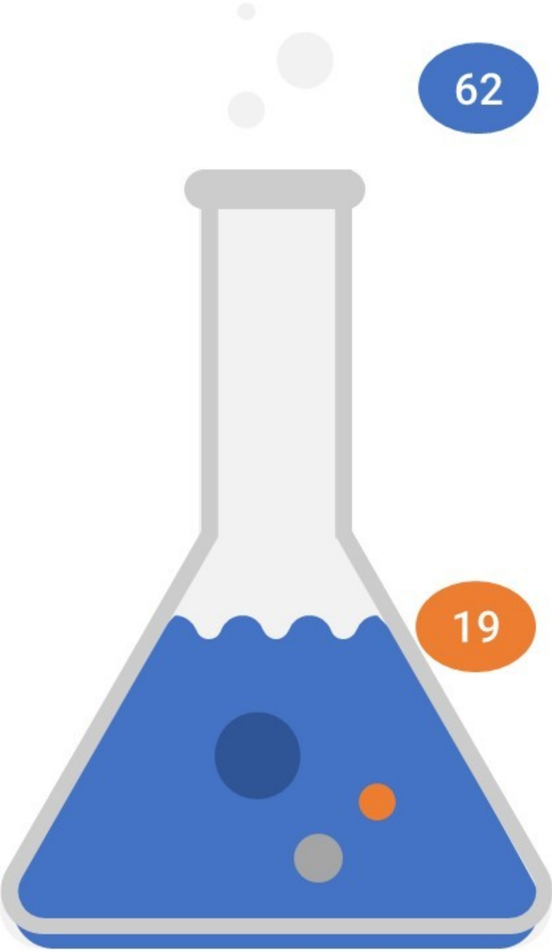
- Develop and harmonize the SOP on Cd determination in mineral **fertilizers and soils**.
- Mineral fertilizers:

multi-nutrient fertilizers (NPK)

triple superphosphate (TSP)

rock phosphate fertilizers.

Methods for extraction



Some form of digestion

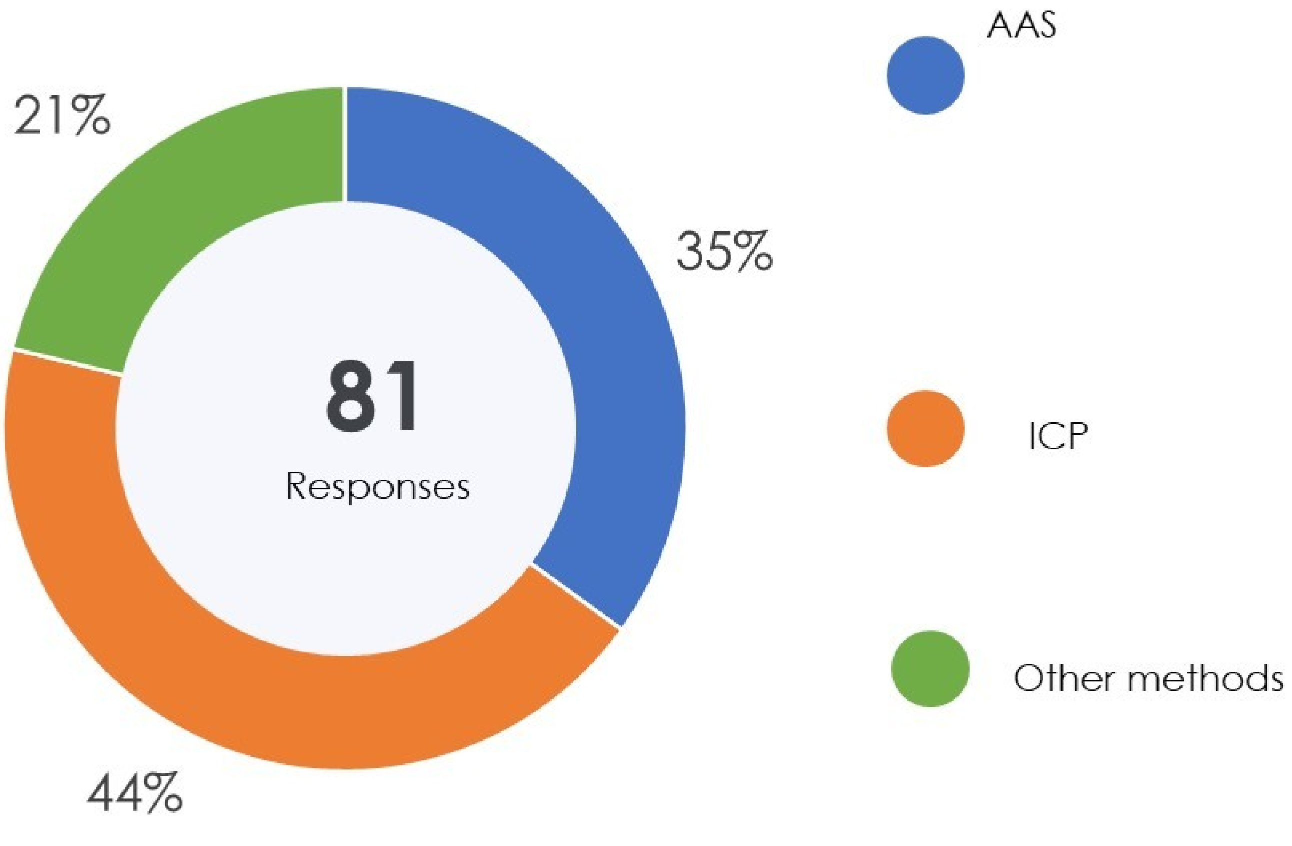
Block digestion
Closed digestion
Digestion
Digestion on plate
Hot block extraction and AAS (or MP-AES determination)
Hot block digestion
Microwave
Titration, digestion, and weighting

Other methods

Dry analysis (no reagents used)
Flux
Filtration
Drying, weighing

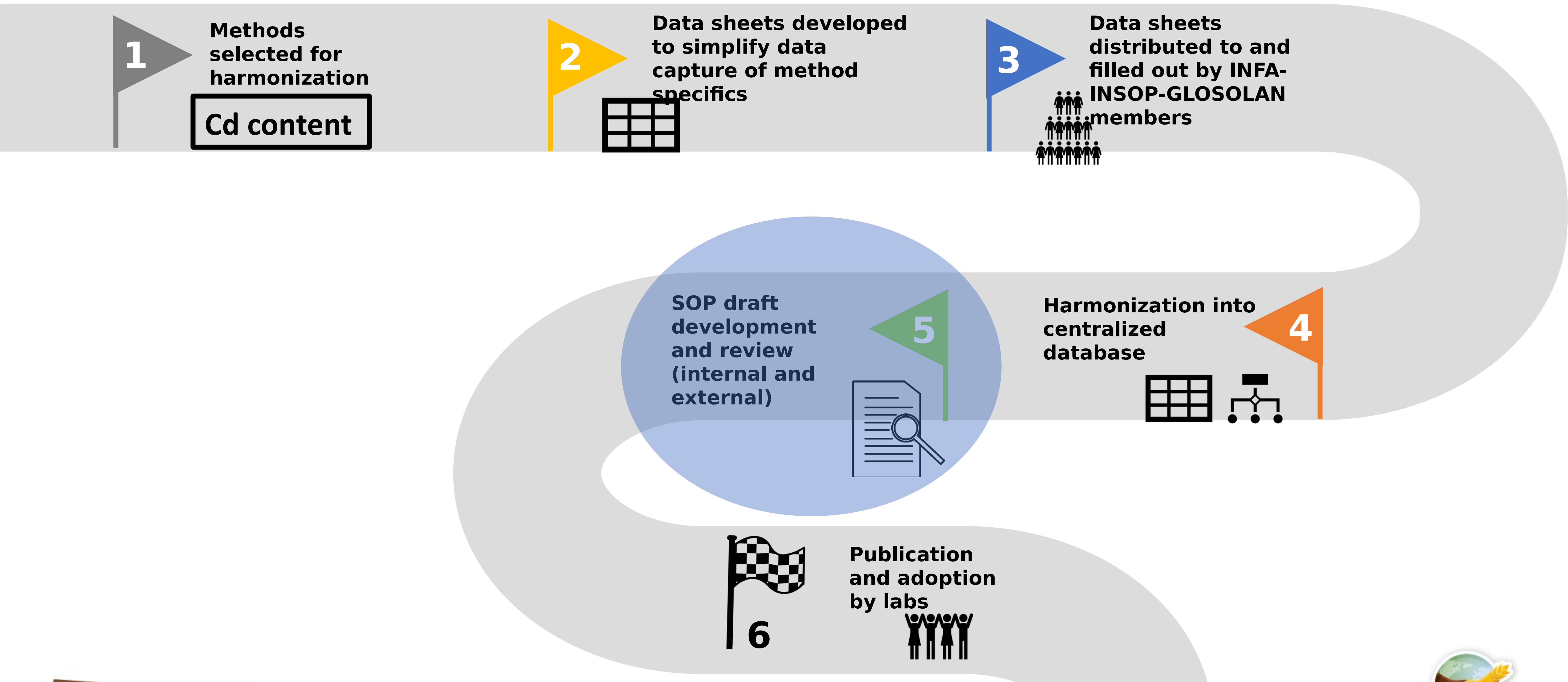
- Develop the SOP with two widely used extraction methods: open and microwave digestion.

Equipment for Cd determination



- Develop the SOP with two comprehensive used equipment: ICP and AAS.

Analytical balance
FAAS/GAAS
Graphite atomic absorbance spectroscopy
MPAES
Portable XRF
UV
Flame


1
Methods selected for harmonization
Cd content
2
Data sheets developed to simplify data capture of method specifics
3
Data sheets distributed to and filled out by INFA-INSOP-GLOSOLAN members
4
Harmonization into centralized database
5
SOP draft development and review (internal and external)
6
Publication and adoption by labs

Advantages for harmonization

- Provides a standardized and robust procedure to laboratories
  - Procedure works to produce both accurate and precise results

- Ensures results are comparable between laboratories

- Improves fertilizer analysis at a global level
  - Improves resultant decision making

- Capacity building for developing nations

Harmonization process

INSOP-INFA-GLOSOLAN teamwork

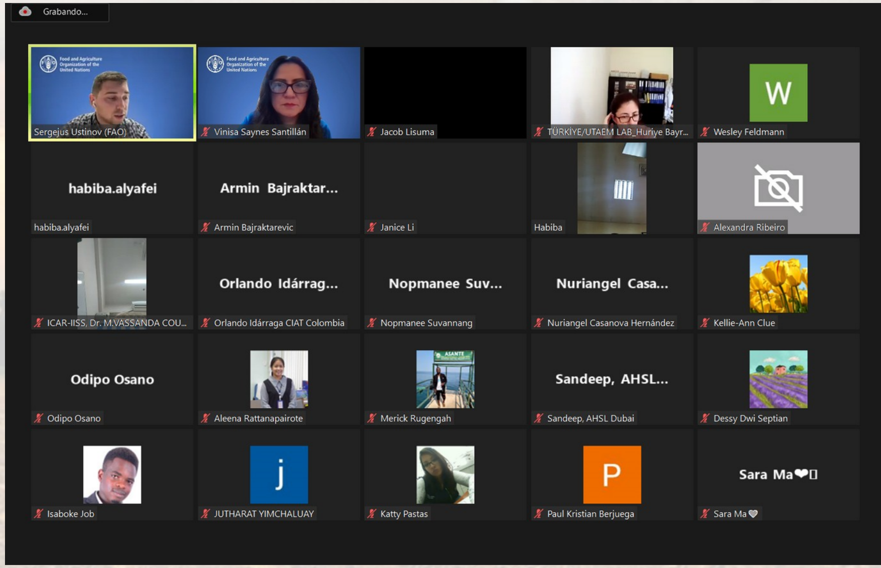
5 experts agreed to create a team to help develop the SOP for determining Cd levels in fertilizers and soils

Food and Agriculture Organization of the United Nations

INTERNATIONAL NETWORK ON SOIL POLLUTION

CHANNELLING COLLECTIVE ACTION TOWARDS ZERO POLLUTION

Thank you for your attention



GLOBAL SOIL PARTNERSHIP

Vinisa.saynessantillan@fao.org

Permited limits in soils and fertilizers

Table 3. Limits for Cd in P fertilizers in several countries expressed as Cd:P ratio, Cd:P_2O_5 or concentration of Cd in the

P_2O_5

Because fertilization increases the risk of Cd transfer to the food chain, some governments have imposed limits restricting the Cd content of P fertilizers.

However, it is variable or not defined in different countries

Regardless limits in the different regions **it is necessary to quantify and monitor the heavy metal content with standardized methods**

Austria	75 mg Cd/kg P_2O_5	275	120	54
Belgium	90 mg Cd/kg P_2O_5	206	90	40.5
Denmark		110	48.0	21.6
Netherlands		40	17.5	7.9
Finland	21.5 mg Cd/kg P_2O_5	49	21.5	9.7
Sweden	43 mg Cd/kg P_2O_5	100	43.7	19.7

Cd classification as a human carcinogen goes back to the 1990s. The European Union adopted Regulation (EU) 2019/1009, limiting Cd content in phosphate fertilizers at **60 mg/kg**.

Roberts, 2014