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Heavy Metals and Naturally Occurring Radionuclides in Agricultural Soils from Phosphorus Fertilizers: A Review

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ABSTRACT

The aim of this study was to summarize and critically assess available data on the content of heavy metals (HM) and naturally occurring radionuclides (NOR) in mineral phosphorus fertilizers, their entry into agricultural soils, and associated ecological and human health hazards. The systematic Scopus database search (2004–2024) was supplemented by highly cited earlier works and authoritative monographs to introduce historical and methodological depth. The search term "heavy metals/ radionuclides and agricultural soils and phosphorus fertilizers" was used in English and Russian. The publications were sorted by date, selecting the first 250 relevant papers for 2020–2024, 100 for 2014–2020, and 50 for 2004–2014. The analysis suggests that mineral phosphorus fertilizers are an essential agrogenic source of ecotoxicants in agroecosystems, which may contain unregulated and, in some cases, high levels of HM and NOR, primarily cadmium (Cd) and arsenic (As). Long-term regular application can result in the gradual buildup of these elements and in the exceedance of safe levels in soils. Risk assessment should consider the phosphate rock origin, fertilizer type and norm of application, soil physicochemical properties, climate, crop biology, and agronomic practice, all of which influence contaminant bioavailability and transfer in the "crop–(livestock)–human" food chain. The results highlight the urgent need for comprehensive risk assessment schemes and stricter regulation of HM and NOR in fertilizers. Future research activities should focus on region-specific contamination pathways, innovative mitigation technologies, tightened fertilizer quality standards, and long-term environmental monitoring in support of food security, ecosystem stability, and sustainable agricultural production.

Keywords: *Soil contamination, Ecotoxicants, Agroecosystems, Environmental risk, Public health risk*

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INTRODUCTION

Modern intensive agriculture depends on fertilizers that replenish nutrients removed with harvested crops, accounting for an estimated 30–50% of global crop yields (Gupta *et al.*, 2014). Over the past six decades, mineral fertilizer use has increased substantially, with China, the USA, India, Brazil, and Indonesia accounting for approximately two-thirds of global agrochemical consumption. In contrast, fertilizer use in Europe declined approximately fourfold between 1980 and 2010, and further reductions are projected through 2031 for phosphorus, potassium, and nitrogen fertilizers (Fertilizers Europe, 2021). Nevertheless, fertilizer application remains high in many regions, particularly in Asia, where reported rates range from 277 kg/ha in South Korea to 436–750 kg/ha in China (Jiao *et al.*, 2012; Cai *et al.*, 2015; Peng *et al.*, 2019; Chen *et al.*, 2022; Fei *et al.*, 2022).

Along with essential macronutrients such as nitrogen (N), phosphorus (P), and potassium (K), fertilizers can introduce heavy metals/metalloids (HM) and naturally occurring radionuclides (NOR) into agricultural soils. Their gradual accumulation in arable horizons may pose environmental risks because of their persistence, adverse effects on biota, and potential migration into adjacent environmental compartments

(Jiao *et al*., 2012; Deng *et al*., 2020; Liu *et al*., 2021a, 2021b; Angon *et al*., 2024; Anas *et al*., 2025).

Some metals, including copper (Cu), zinc (Zn), molybdenum (Mo), and nickel (Ni), are essential micronutrients and may be deliberately incorporated into fertilizers. However, excessive concentrations can become phytotoxic, impairing photosynthesis, respiration, chlorophyll formation, protein synthesis, and enzymatic activity. In particular, excessive Cu and Zn may cause effects comparable to or greater than those associated with some non-essential heavy metals (He *et al*., 2005; Broadley *et al*., 2012; Marschner 2012; Gupta *et al*., 2014; Georgiadou *et al*., 2018).

Heavy metals and NOR also enter arable soils through organic fertilizers, sewage sludge, manure, compost, soil amendments, pesticides, and contaminated irrigation water (Chen *et al*., 2007; Kabata-Pendias, 2010; Bigalke *et al*., 2017). However, mineral fertilizers represent an important and continuous anthropogenic source, with the highest concentrations of HM and NOR impurities generally associated with phosphate rocks and phosphate-containing fertilizers (Jiao *et al*., 2012; De Vries & McLaughlin, 2013; Bolan *et al*., 2014; Gupta *et al*., 2014; Kratz *et al*., 2016; Bigalke *et al*., 2017).

Among the ecotoxicants introduced through mineral phosphorus fertilizers, cadmium (Cd) and uranium (U) are of particular concern because of their mobility and potential bioavailability in agricultural soils. Their accumulation may facilitate transfer through food chains and, under certain conditions, migration into groundwater. Phosphorus fertilizers may also contain rare earth element impurities with potentially toxic effects, further increasing environmental risks associated with intensive fertilizer use (Silva *et al*., 2019).

The aim of this study was to critically review current data on heavy metals (HM) and naturally occurring radionuclides (NOR) in mineral phosphorus fertilizers, their input into agricultural soils, and the associated ecological and human health risks arising from their accumulation and bioavailability in agroecosystems.

MATERIALS AND METHODS

Study design and scope

This study was designed as a critical review of peer-reviewed scientific publications in high-impact international journals indexed in the Scopus bibliographic and abstract database, covering the period from 2004 to 2024. Additionally, highly cited publications from earlier periods and authoritative scientific monographs were included for historical and methodological context.

Literature search strategy

The literature search was conducted in Scopus using the keywords "heavy metals/ radionuclides and agricultural soils and phosphorus fertilizers" in both Russian and English. Publications were sorted by date of publication. The selection included:

- **2020–2024:** first 250 publications relevant to the query;
- **2014–2020:** first 100 publications;
- **2004–2014:** first 50 publications.

All retrieved publications were screened for relevance by title and abstract. Full texts were reviewed when necessary to confirm inclusion.

Inclusion criteria

Studies were included if they met the following criteria:

1. Focused on heavy metals or radionuclides in agricultural soils in the context of phosphorus fertilizers.
2. Published in peer-reviewed journals or as authoritative monographs.
3. Provided quantitative or qualitative data relevant to the review objectives.

Exclusion criteria

Publications were excluded if they were:

- Not peer-reviewed;
- Conference abstracts without full papers;
- Focused on unrelated topics despite matching keywords.

Data extraction and synthesis

Relevant information from each selected publication was extracted, including study location, types of phosphorus fertilizers investigated, analytical methods, and reported concentrations of cadmium (Cd) and other trace elements. Data were synthesized qualitatively to identify key trends, knowledge gaps, and methodological approaches.

Ethical and licensing considerations

All cited works were used in accordance with their publication licenses. No permission was required for the use of bibliographic data and summaries. When methods or descriptions were adapted from previously published works, the original sources were cited, and wording was modified to avoid verbatim reproduction.

Mineral phosphorus fertilizers as a source of HMs in agricultural soils

HMs in mineral phosphorus fertilizers

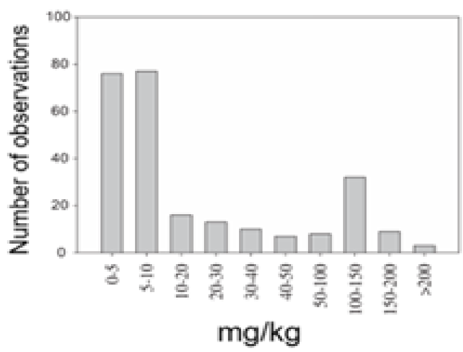
Phosphate rock mining is an important industry in more than 40 countries. Of approximately 150 million tons mined annually, around 90–95% is used for fertilizer production (Aydin *et al*., 2010; Mar & Okazaki, 2012; Hartley *et al*., 2013). About 75–85% of global phosphorus reserves occur in sedimentary phosphate rocks, particularly in the Mediterranean phosphogenic province, while igneous and metamorphic apatite ores account for 15–20% and are concentrated, among other areas, in the Khibiny Massif (Russia). Small amounts are also obtained from bird and bat guano (Aydin *et al*., 2010; Mar and Okazaki, 2012; Gupta *et al*., 2014; Kratz *et al*., 2016). Global phosphate rock production is projected to peak around 2030, with reserves potentially becoming depleted within 50–100 years (Cordell *et al*., 2009).

Commercial phosphate deposits generally contain apatite-group calcium phosphate minerals, including hydroxyapatite, francolite, and collophane, with P_2O_5 contents above 20% (Silva *et al*., 2010). Crystal lattice defects and chemisorption favor the incorporation of HMs into these minerals. As, Cd, and Pb concentrations in phosphate rocks from different regions may reach 21, 130, and 43 mg/kg, respectively, with reported mean concentrations of 0.7, 19.1, and 13.2 mg/kg (Jiao *et al*., 2012).

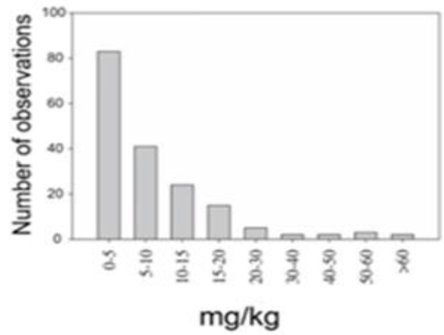
During processing, HM concentrations may remain unchanged or increase by up to 1.5 times (Schipper *et al*., 2011; Bigalke *et al*., 2017).

Cadmium contamination frequently exceeds regulatory limits. Among 414 fertilizers analyzed in Europe and Norway, 10% contained more than 60 mg Cd/kg P_2O_5 (Verbeeck *et al*., 2020). In Switzerland, 45% exceeded the national limit of 50 mg/kg P, with concentrations reaching 220 mg/kg P (Bigalke *et al*., 2017). Similarly, analysis of 162 phosphate fertilizers marketed in Germany showed that many single, triple, and partially acidulated phosphate fertilizers exceeded the national Cd limit of 50 mg/kg P_2O_5 (Kratz *et al*., 2016).

The composition and concentration of HMs in mineral phosphorus fertilizers may vary by 10–1000 times depending on raw material, production technology, and product type **(Figure 1)**. Fertilizers derived from sedimentary phosphate rocks tend to contain higher levels of As, B, Be, Cd, Cr, Mo, Ni, Pb, Sb, Se, Tl, U, Zn, and Al, whereas Co, Cu, Sn, and Sr are generally more abundant in fertilizers produced from igneous and metamorphic apatites (Kratz *et al*., 2016). Cd concentrations may range from 0.15 to more than 640 mg/kg P, while reported ranges for other HMs are As 0.5–20, Cr 63–896, Cu 0.2–1170, Ni 0.5–151, Pb 1–200, V 49–721, and Zn 31–1150 mg/kg (Chen *et al*., 2007; Aydin *et al*., 2010; Kabata-Pendias, 2010; Jiao *et al*., 2012; Kratz *et al*., 2016; Bigalke *et al*., 2017; Hu *et al*., 2024).



a)



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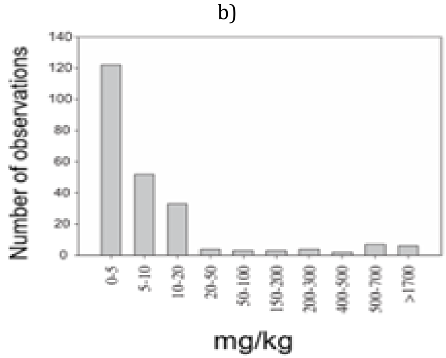

c)

Figure 1. Frequency distribution of Cd (a), As (b), and Pb (c) concentrations in phosphorus fertilizers produced in the USA (Jiao *et al*., 2012)

The leading global producers and regional differences in Cd concentrations are summarized in **Table 1**. In the EU, where the average Cd concentration in phosphate fertilizers is approximately 30 mg/kg P_2O_5, relatively low impurity levels are reported in Scandinavian products and higher concentrations in fertilizers from the Iberian Peninsula (Silva *et al*., 2010). U, V, Sb, Cr, As, and Ni concentrations also positively correlate with phosphorus and Cd levels (Silva *et al*., 2010).

Table 1. Optimal proportions of nutrients for growing conifer seedlings

No.	Country	Cd in phosphate rocks, mg/kg	Cd in simple superphosphate, mg/kg	Sources
1	China	4	—	Robarge *et al*. 2003; Aydin *et al*. 2010; Silva *et al*. 2010; Mar and Okazaki 2012
2	Morocco	3–165	≈30; 200–300	Robarge *et al*. 2003; Aydin *et al*. 2010; Schipper *et al*. 2011; Chauhan and Chauhan 2014; Hu *et al*. 2024; United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1977, …
3	USA	3–186	≈20; ≈140–160	Aydin *et al*. 2010, …
4	Russia	0.1–<13	≈20	Aydin *et al*. 2010, …
5	Tunisia	38–173	≈50	Aydin *et al*. 2010, …
6	Togo	44	≈70	Aydin *et al*. 2010, …
7	Jordan	6–23	—	Aydin *et al*. 2010, …
8	Brazil	4	≈40; ≈70	Aydin *et al*. 2010, …
9	Israel	12–32	≈30; ≈50	Aydin *et al*. 2010, …
10	Syria	6–52	≈140–160	Aydin *et al*. 2010, …
11	Pakistan	5–14	≈20	Aydin *et al*. 2010, …

12	South Africa	2–<13	—	Aydin *et al*. 2010, …
13	Egypt	8–74	—	Aydin *et al*. 2010, …
14	Australia	7–43	≈40	Aydin *et al*. 2010, …
15	Senegal	37–221	≈70	Aydin *et al*. 2010, …
16	India	—	—	Aydin *et al*. 2010, …
17	Togo*	44–179	≈70	Aydin *et al*. 2010, …
18	Canada	—	—	Aydin *et al*. 2010, …
19	Nigeria	—	≈30	De Vries and McLaughlin 2013, …
20	Saudi Arabia	—	≈40	De Vries and McLaughlin 2013, …
21	New Zealand	—	≈50	De Vries and McLaughlin 2013, …
22	Algeria	—	200–300	De Vries and McLaughlin 2013, …

Fertilizers produced and used in Asia generally contain higher HM concentrations than European products. In Chinese phosphate fertilizers, reported As, Cd, Cr, and Pb concentrations are 15, 4, 25, and 56 mg/kg, respectively (Chen *et al*., 2020), although fertilizers manufactured from domestic Chinese raw materials may contain lower concentrations than imported products (Peng *et al*., 2019). Pakistani phosphate fertilizers reflect the characteristics of local sedimentary ores and contain relatively high Cd and Pb concentrations, with reported levels of Cd 9, Cr 40, Cu 9, Ni 25, Pb 67, and Zn 102 mg/kg (Sabiha-Javied *et al*., 2009).

Substantial variability may also occur within individual countries and even within the same phosphate deposit as mining progresses (Jiao *et al*., 2012; Mar & Okazaki, 2012). In Germany, sedimentary-rock-based fertilizers were enriched in Al, As, B, Be, Cd, Cr, Mo, Ni, Pb, Sb, Se, Tl, U, and Zn, whereas magmatic apatite products contained relatively more Co, Cu, Sn, Mn, Ti, Fe, and Sr (Kratz *et al*., 2016). In the United States, fertilizers derived from eastern Pliocene phosphate formations contain less than 10 mg/kg Cd, whereas products from western Permian deposits may contain up to 174 mg/kg (Mortvedt, 1995).

Because of these risks, some U.S. states and other jurisdictions regulate Cd and As concentrations in phosphate fertilizers. At the same time, B, Co, Cu, Mo, and Zn may be deliberately added to mixed mineral fertilizers as essential micronutrients, increasing the total HM load on agricultural soils (He *et al*., 2005; Kratz *et al*., 2016). European regulation of several trace elements, particularly Cd, As, Cr, Pb, Hg, and Ni, has also been under discussion (Kratz *et al*., 2016; Fertilizers Europe, 2021).

The impurity profile also depends on fertilizer formulation. Single, double, and triple superphosphates and monoammonium and diammonium phosphates differ markedly in TM composition (Chauhan & Chauhan, 2014). Single superphosphate is often enriched in Cu, Hg, Ni, Pb, and Zn, whereas monoammonium and diammonium phosphates may contain higher As levels (Peng *et al*., 2019). Overall, single superphosphate tends to contain higher concentrations of several TMs, whereas calcium phosphate fertilizers show comparatively low contamination levels **(Table 2)**.

Table 2. Average concentrations of TMs in different types of phosphate fertilizers, mg/kg (after (Kratz *et al*., 2016))

Element	Ground phosphate rock	Partially acidulated phosphate rock	Single superphosphate	Triple superphosphate	Dicalcium phosphate	Element
As	8.3 ± 4.0	13.5 ± 9.9	8.5 ± 4.8	8.2 ± 3.8	n.d.	As
Cd	12.5 ± 6.9	23.4 ± 7.9	34.0 ± 25.0	24.4 ± 9.4	n.d.	Cd
Co	0.96 ± 0.56	0.77 ± 0.26	1.5 ± 1.8	0.73 ± 0.33	0.28	Co
Cr	113 ± 25.4	148 ± 56	90 ± 48.9	171 ± 66	0.92	Cr
Cu	15.1 ± 7.4	31.2 ± 11.3	92 ± 98	21.5 ± 14.0	1.1	Cu
Mo	6.6 ± 5.0	11.3 ± 6.8	15.5 ± 1.0	8.4 ± 3.2	3	Mo
Ni	22.0 ± 12.2	41.3 ± 12.1	38.9 ± 1.1	26.5 ± 13.1	3.5	Ni
Pb	6.9 ± 4.5	3.8 ± 1.8	3.0 ± 0.67	3.9 ± 4.4	1.1	Pb
Sn	0.38 ± 0.32	8.9 ± 16.9	n.d.	0.15 ± 0.05	n.d.	Sn
Sr	1449 ± 247	1057 ± 368	1102 ± 197	909 ± 82	36.7	Sr
Tl	1.1 ± 0.79	0.36 ± 0.15	0.59 ± 0.34	0.39 ± 0.11	n.d.	Tl
U	89 ± 54	141 ± 42.1	140 ± 79	125 ± 68	0.16	U
V	112 (n=1)	n.d.	n.d.	n.d.	5.1	V
Zn	239 ± 127	426 ± 185	469 ± 136	390 ± 190	95	Zn

Temporal changes are also evident. In 196 phosphate fertilizer samples from European countries, mean concentrations were 7.4 mg/kg Cd, 7.6 As, 14.8 Ni, 89.5 Cr, 2.9 Pb, and 166 Zn (Nziguheba & Smolders, 2008). Later European data showed lower mean As, Cd, Ni, and Cr levels but increased Pb and Zn concentrations (Verbeeck *et al*., 2020). In contrast, 30 phosphate fertilizers used in Germany showed higher mean concentrations of Cd (20.5 mg/kg), As (10.4), Ni (33.8), Cr (135), and Zn (354), while Pb averaged 1.7 mg/kg (Kratz *et al*., 2016). Depletion of relatively "clean" phosphate deposits may therefore increase HM concentrations in future fertilizers and intensify ecotoxicant inputs into agroecosystems (Jiao *et al*., 2012; Kratz *et al*., 2016).

Input of heavy metals through mineral phosphate fertilizers into soils

In tropical agroecosystems, phosphorus is frequently a major factor limiting crop productivity because P-bearing minerals are resistant to weathering and phosphate ions are strongly fixed in soils through chemisorption (Corguinha *et al*., 2012; Gupta *et al*., 2014). Consequently, phosphate fertilizer application rates should balance crop requirements with the need to minimize HM contamination and environmental dispersion.

A single application of 500 kg/ha phosphate fertilizer containing 20 mg/kg Cd would theoretically increase Cd concentration in a 20-cm plow layer by only 0.0033 mg/kg, generally below analytical detection limits (Jiao *et al*., 2012). At an application rate of 20 kg P/ha, annual inputs have been estimated at approximately 55.4 g/ha Zn, 25 g/ha Cr, 12.3 g/ha Cu, 7.7 g/ha Pb, 0.13 g/ha Cd, and 0.01 g/ha Hg (Hu *et al*., 2013; Gupta *et al*., 2014).

Actual inputs vary with crop requirements and fertilizer composition. In the EU, average phosphorus fertilizer application rates are approximately 21 kg P_2O_5/ha for cereals and 45 kg P_2O_5/ha for potatoes. With an average fertilizer Cd concentration of 36 mg/kg P_2O_5, this corresponds to annual Cd inputs of approximately 0.8 and 1.6 g/ha, respectively (Six & Smolders, 2014). Brazil uses higher P_2O_5 rates—approximately 66 kg/ha for soybean and 430 kg/ha for potatoes—but fertilizers generally contain only 2–12 mg/kg Cd (Corguinha *et al*. 2012). Vegetable production may involve particularly high fertilizer inputs because of crop nutrient requirements and economic incentives (Qiutong & Mingkui, 2017).

Long-term field observations confirm that repeated applications can alter soil Cd concentrations. After 31 years and a cumulative application of 930 kg P/ha in Irish pasture soils, Cd increased by 0.05 mg/kg above a background concentration of 0.20 mg/kg (McGrath & Tunney, 2010). In the USA, 36 years of fertilizer use based on Florida phosphates containing <10 mg/kg Cd produced no significant increase, whereas fertilizers containing 174 mg/kg Cd increased soil concentrations from 0.07 to 1.0 mg/kg (Mortvedt, 1995). In Australia, long-term single and triple superphosphate applications increased pasture-soil Cd by 0.015–0.045 mg/kg above a background of 0.020 mg/kg (Schipper *et al*., 2011).

Thus, substantial changes in soil HM concentrations generally develop over decades and depend strongly on impurity levels and cumulative fertilizer inputs. Cd accumulation in European agricultural soils correlates with phosphorus fertilizer use and P_2O_5 accumulation (Pan *et al*., 2010), while long-term experiments in China also indicate an effect of phosphorus fertilization on Hg concentrations in soils with initially low background levels (Zheng *et al*., 2008). Meta-analytical evidence identifies phosphate fertilizers as a major agrogenic and, in some systems, principal anthropogenic source of Cd, with total P, Cd, and U concentrations closely linked to fertilizer type and application rate (Schipper *et al*., 2011; Jiao *et al*., 2012). Historical soil archives from the UK, France, and Denmark further indicate a 1.3–2.6-fold increase in soil Cd accompanied by increasing concentrations in wheat grain (Six & Smolders, 2014).

Evaluation of fertilizer-derived contamination requires consideration of natural TM backgrounds, atmospheric deposition, agricultural inputs, crop removal, runoff, and leaching. Across Europe and the USA, phosphate fertilizers contribute approximately 0.2–4.0 g/ha Cd, 2.3–6.0 g/ha As, and 61–1083 g/ha Zn annually, with atmospheric deposition often providing comparable amounts (Keller & Schulin, 2003; Kratz *et al*., 2016). Some studies estimate that fertilizers account for 54–74% of total TM inputs to arable soils (Chen, W. *et al*., 2007; Grant *et al*., 2010), although the relative contribution varies considerably among elements and countries (Nziguheba & Smolders, 2008). For EU countries and Norway, the annual Cd balance in the arable layer may approach zero because fertilizer inputs are partly offset by downward leaching (Six & Smolders, 2014).

Regional studies illustrate this variability. In England and Wales, atmospheric deposition dominates total HM inputs, but phosphorus fertilizers contribute approximately 25% of Cd and 32% of Cr loading (Nicholson *et al*., 2003). At Rothamsted, annual application of 35 kg P/ha containing 401–1575 mg/kg As between 1856 and 1948 approximately doubled soil As concentrations; after fertilizer As concentrations declined to 1.6–20.3 mg/kg, soil levels stabilized (Hartley *et al*., 2013). In France, mineral fertilizers account for approximately 2–5% of annual Pb, Cu, and Zn inputs, 8–18% of Hg, Ni, Mo, and As, and 40–55% of Cr, Se, and Cd (Belon *et al*., 2012). In Switzerland, Cd stocks in arable horizons were significantly higher than in parent materials and correlated with phosphate fertilizer application (Bigalke *et al*., 2017).

In California, atmospheric deposition, irrigation, and phosphorus fertilizers contribute differently to As and Cd loading. Modeling suggests that the long-term topsoil As balance may become negative, whereas Cd may continue to accumulate by approximately 11 g/ha annually; fertilizers with higher impurity concentrations could raise annual inputs to 330 g/ha As and 89 g/ha Cd (Chen, W. *et al*., 2007).

China provides one of the most extensively studied examples. Approximately 20% of agricultural soils are reported to be contaminated with TMs (Shi *et al*., 2019), with industrial activity, lithogenic sources, and agriculture contributing approximately 28%, 27%, and 21%, respectively (Fei *et al*., 2019). Cd represents one of the principal ecological hazards (Khatun *et al*. 2022), although industrial and agricultural soils differ substantially in contamination patterns (Yang *et al*., 2018). Atmospheric TM inputs remain particularly important in rapidly industrializing regions, with an atmospheric-to-agrochemical input ratio of approximately 4:1 in some areas (Luo *et al*., 2009; Pan *et al*., 2010; Shi *et al*., 2018). Nevertheless, fertilizer use contributes to positive annual TM balances and may increase the relative importance of agricultural Hg inputs as atmospheric emissions decline (Hu *et al*., 2013; Peng *et al*., 2019).

In southern China, intensive fertilizer use increases both HM loading and the mobility of cationic TMs in acidic soils (Peng *et al*., 2019). Source-apportionment studies in Sichuan attributed 18% of TM inputs to agriculture, compared with 26% to natural materials, 31% to metallurgical emissions, and 25% to coal combustion (Shi *et al*., 2024). In Guangdong, mean Cd concentration under long-term phosphorus fertilization was 0.60 mg/kg, and 90% of samples exceeded the Chinese environmental quality standard (Cai *et al*., 2015). The same study associated Cr, Ni, and Co primarily with lithogenic sources and As and Hg largely with atmospheric inputs.

Urbanization further modifies these patterns. Around Shanghai, industrial emissions dominate Pb and part of the Cr load, coal combustion contributes Hg, fertilizer application is an important Cd source, and As is primarily geogenic (Fei *et al*., 2019, 2022). In suburban Nanjing, mineral fertilizers contribute only small proportions of total Cd, Pb, Cu, and Zn inputs (Hu *et al*., 2013), whereas around Hanzhong fertilizer application was identified as the main factor behind an 85% increase in Cd in the 0–20 cm arable layer (Xiao *et al*., 2019). In Shandong, agrochemical sources contribute substantially to elevated Cu concentrations (Wen *et al*., 2025).

Outside major urban and industrial zones, the contribution of fertilizers may become more pronounced. In Henan, agrochemical and transport sources account for approximately 61% of Cd accumulation (Wang *et al*., 2025). In the Yangtze River Valley, current Cd trends suggest that the agricultural safety threshold of 0.3 mg/kg could be reached within nine years (Shao *et al*., 2016). In Jilin Province, phosphate fertilization accounts for approximately 59% of Cd in chernozems and 70% in aeolian arenosols, while severe Cd and Hg contamination increased between 1998 and 2022 (Ren *et al*., 2022; Wang *et al*., 2023; Zhou *et al*., 2024).

These risks are widely incorporated into Chinese land-use assessments (Li *et al*., 2005; Chen, S. *et al*., 2007; Chen, W. *et al*., 2007; Luo *et al*., 2009; Jiao *et al*., 2012; Niu *et al*., 2013; Cai *et al*., 2015; Fei *et al*., 2019; Peng *et al*., 2019; Chen *et al*., 2020, 2022; Fei *et al*., 2022; Shi *et al*., 2024). Evidence from other Asian countries remains more limited. In central Bangladesh, more than 99% of analyzed arable soils were contaminated with Ni and Cd, with agrochemical sources contributing up to 29% (Proshad *et al*., 2024). In Iran, fertilizer use increased from 2.4 million t in 1999 to 4.4 million t in 2018, while agricultural soils in many provinces showed elevated Ni, As, Pb, Cd, and Cr concentrations (Jahandari & Abbasnejad, 2024). In Qazvin Province, only 5% of assessed soils met the "very high quality" criterion (Rahmanipour *et al*., 2014).

In Australia and New Zealand, phosphate fertilizers are regarded as the principal anthropogenic source of Cd in arable and improved pasture soils. Surface-layer Cd concentrations increased 7–8 times in some long-term systems (Chen, W. *et al*., 2007; Schipper *et al*., 2011; Bolan *et al*., 2014; Salmanzadeh *et al*., 2016). In Australia, modeled and field-verified increases during 1900–2000 averaged 0.21 mg/kg under rainfed cereal production, 0.42 mg/kg under irrigation, and 0.68 mg/kg under fodder production (De Vries & McLaughlin, 2013). Agricultural phosphate fertilizer use may influence TM concentrations at distances of up to 20 km and increase Cd, Zn, Cu, and Pb in arable horizons relative to background soils (Rodríguez *et al*., 2008).

Ecological consequences and risks from the input of TMs via mineral phosphate fertilizers into agricultural soils

The bioavailability of TMs and their transfer from soil to crops depend strongly on pH, redox potential, organic matter, clay minerals, Fe and Mn oxides, carbonates, soil solution mineralization, and related precipitation–dissolution, adsorption–desorption, and complexation processes (He *et al*., 2005; Zhang *et al*., 2018). Soil pH is particularly important for Cd: root uptake generally increases as pH decreases (Kirkham, 2006), making acidic systems such as the "red soil–rice–human" food chain especially vulnerable (Li *et al*., 2005). Humus depletion and acidification associated with agricultural degradation can further increase TM mobility (Zhou *et al*., 2024).

Fertilizer-derived TMs are generally considered more mobile than geogenic forms, while soil organic matter promotes immobilization (Jiao *et al*., 2012; Niu *et al*., 2013; Zhang *et al*., 2018). However, isotope-tracing experiments indicate that only 6.5–15% of Cd found in wheat shoots originated directly from recently applied ^{109}Cd-labeled triple superphosphate, with most fertilizer-derived Cd retained in soil and roots (Wiggenhauser *et al*., 2019). Huang *et al*., (2004) similarly found that less than 1% of fertilizer-derived Cd accumulated in lettuce biomass. These results demonstrate that direct crop uptake from newly applied fertilizers remains incompletely understood.

Field and laboratory studies also demonstrate interactions among elements. In the Yangtze River Delta, extractable TM fractions in soils correlated with pH, humus content, CEC, and other physicochemical properties (Ran *et al*., 2016). Triple superphosphate and monoammonium phosphate increased Cd in flax seed and wheat grain, while a four-year experiment showed increasing Cd and decreasing Zn in flax, rapeseed, and spring wheat after monoammonium phosphate application, suggesting competitive interactions (Grant *et al*., 2010). Cd and Zn also compete for sorption sites, while phosphate fertilizers may alter ionic strength and pH; in one experiment, fertilizer application increased Cd concentrations in soil extracts by 87% relative to the control (Lambert *et al*., 2007). Crop uptake additionally varies with edaphic and climatic conditions (Perilli *et al*., 2010).

The effect of phosphate fertilizers on Cd mobility remains controversial. Immobilization has been reported in some studies (Knox *et al*., 2006; Hong *et al*., 2008), whereas others indicate enhanced mobilization of Cd and As in contaminated soils (Sabiha-Javied *et al*., 2023). Predictions therefore include both decreases (Azzi *et al*., 2017) and increases (Grant *et al*., 2013) in Cd mobility. Competition between Cd and Zn occurs both in the soil sorption complex and during plant uptake and translocation (Zhao *et al*., 2005). Overall, fertilizer-induced changes in Cd bioavailability are considered relatively limited because Cd mobility is controlled by multiple interacting factors (Jiao *et al*., 2012).

Effects on other elements are also element-specific. Phosphate fertilizers can increase total Hg in paddy soils while simultaneously reducing Hg bioavailability to rice under certain conditions (Tang *et al*., 2018). In contrast, Pb mobility generally decreases because phosphate promotes stable organic complexes and precipitation of poorly soluble pyromorphite (Chen, S. *et al*., 2007; Udeigwe *et al*., 2011; Bolan *et al*., 2014; Gupta *et al*., 2014). Increasing soil phosphorus may similarly enhance immobilization of Cu, Pb, and Ni, with single and triple superphosphate considered particularly effective for Pb stabilization (Jiao *et al*., 2012; Chen *et al*., 2022).

For As and Sb, phosphate application can increase mobility through competition of arsenates and antimonates with phosphates for sorption sites or through isomorphic substitution in the solid phase (Cao *et al*., 2003; Gupta *et al*., 2014). At Rothamsted, long-term As accumulation in vegetation declined toward background levels after contaminant concentrations in fertilizers were reduced (Hartley *et al*., 2013). In suburban Beijing soils, mobile Cu and Zn fractions were higher in arable horizons, whereas Cr and As showed more uniform profiles, suggesting different anthropogenic and natural origins (Heimann *et al*., 2015). More than 90% of fertilizer-derived As may eventually be leached from the root-inhabited layer because phosphate competes with arsenate for adsorption sites on Fe and Al oxides and hydroxides (Chen, W. *et al*., 2007; Jiao *et al*., 2012).

The rhizosphere strongly modifies TM mobility and uptake. Root exudates, microbial activity, redox processes, and local pH changes can either mobilize or immobilize elements (Gupta *et al*., 2014). Rhizosphere soil contains more organic compounds and available N but less available P than bulk soil, indicating intense plant–microbial competition (Gupta *et al*., 2014; Liu *et al*., 2022). A review of 123 studies showed that mineral elements are generally more mobile in the rhizosphere because of microbial activity and chelation by root exudates (Bertin *et al*., 2003; He *et al*., 2005; Kim *et al*., 2010; Heimann *et al*., 2015; Zhong *et al*., 2025). Amino acids such as mugineic and avenic acids in cereals and phenolic compounds in dicots can mobilize metals, whereas other root-derived chelates reduce TM availability and contribute to rhizostabilization (He *et al*., 2005; Bais *et al*., 2006; Gupta *et al*., 2014; Aslan *et al*., 2024; Česaitis *et al*., 2024; He *et al*., 2024; Jeung, 2024; Miranda *et al*., 2024; Varoneckaitė *et al*., 2024; Cai *et al*., 2025; Castro & Billones, 2025; Li *et al*., 2025; Oud *et al*., 2025; Joyson & Rajasekar, 2026; Muradov *et al*., 2026; My & Tam, 2026).

Rhizosphere microorganisms and roots also catalyze redox and acid–base reactions that influence TM uptake (Gupta *et al*., 2014). Arbuscular mycorrhizal associations, present in approximately 80% of vascular plant species, expand the effective absorptive surface through fine hyphae and can substantially modify trace-element uptake (Grant *et al*., 2010; Smith *et al*., 2010).

Actual accumulation in crops therefore depends not only on soil availability but also on plant physiology (Nziguheba & Smolders, 2008). Toxic TMs such as As, Cd, and Pb may enter plants through transport systems for chemically similar essential nutrients (Kabata-Pendias, 2010; Penrose *et al*., 2016). Cd can be transported with Fe, Mn, Zn, Ni, Cu, and Co through ZIP and NRAMP transporters, while As may enter through phosphate- or silicon-transport proteins (Sasaki *et al*., 2012; Gupta *et al*., 2014; Bin *et al*., 2018; Ajeesh Krishna *et al*., 2020; Bandi *et al*., 2024; Chen *et al*., 2025; Jannath *et al*., 2025; Makoae *et al*., 2025; Salem *et al*., 2025).

Consequently, crop species differ markedly in TM accumulation. In the Yangtze River Delta, mobile soil fractions followed Cd > Cu > Pb > Ni > Zn, whereas bioconcentration in wheat grain followed Zn (0.47) > Cd (0.36) > Cu (0.19) > Ni (0.01) > Pb (0.004) (Ran *et al*., 2016). In Shandong, peanut showed relatively high Cd, Cu, and Pb bioconcentration, wheat accumulated Zn most strongly, sweet potato showed the highest Cr value, and maize most effectively restricted TM uptake (Wen *et al*., 2025). In Pakistan, wheat grain bioconcentration after phosphate fertilization followed Zn > Pb > Ni, Cu > Cr > Cd, demonstrating the influence of soil and pedoclimatic conditions (Sabiha-Javied *et al*., 2023; Alhossan *et al*., 2024; Danchin *et al*., 2024; Frost *et al*., 2024; Hillman, 2024; Cuenca-Martínez *et al*., 2025; Ismail *et al*., 2025; Laaksonen & Virtanen, 2025; Mishra *et al*., 2025; Peterson & Rogers, 2025; Torres *et al*., 2025).

Fertilizer type is another important factor. Soluble complex P-containing fertilizers (NPK) increased Cd concentrations in carrot, lettuce, oats, ryegrass, and wheat, whereas phosphate rock with comparable Cd concentrations did not produce the same effect (Gupta *et al*., 2014).

Finally, increased TM mobility may affect aquatic environments. Agricultural sources account for approximately 36% of TM fluxes, particularly Zn, Pb, and Cd, in the Huanghe River watershed (Li *et al*., 2024). Agricultural activity has also been associated with As accumulation in Erhai Lake sediments (Lin *et al*., 2016) and progressive Cd, Pb, and Zn accumulation in Chaohu Lake sediments (Tang *et al*., 2010). In ponds between the Huanghe and Yangtze rivers, most investigated TMs increased between 1980 and 2004; Cd rose fourfold from 0.08 to 0.33 mg/kg, and the temporal trend corresponded to increasing phosphate fertilizer application (Zhang & Shan, 2008).

Assessment of human health risks

Five trace metals (TMs), including As, Cd, Cr, Pb, and Hg, are considered the most hazardous to human health and are classified as “known” or “probable” carcinogens by the International Agency for Research on Cancer (IARC) (Khatun *et al*., 2022). Recently, assessments of human health risks of both carcinogenic and non-carcinogenic nature, associated with TM accumulation in arable soils, have become increasingly popular. For example, an analysis of the combined use of phosphorus fertilizers at a dose of 25 kg/ha and zinc micronutrients applied to maize on neutral, saturated soils at the Quzhou experimental station in Hebei Province (China) showed that this scheme met the crop’s requirements for essential Zn and Cu while simultaneously reducing potential human health risks associated with Cd and Pb, whereas phosphorus fertilizer doses above 50 kg/ha led to increased carcinogenic risks associated with Cr impurities (Chen *et al*., 2022).

However, a slightly earlier 10-year field experiment conducted by the same authors at the same Quzhou station, assessing the effect of phosphorus fertilizer application in doses from 25 to 400 kg/ha, showed that, with the relative accumulation of Zn, Pb, Cd, and As in the plow horizon, only the concentrations of Cd and As in wheat grain increased (without exceeding the respective safety thresholds), whereas the concentrations of Zn, Cu, Pb, and Ni, on the contrary, decreased, and the transfer of Cr from soil to wheat grain remained invariant with respect to the fertilizer doses. The optimal dose in terms of minimizing TM soil contamination was recognized as 50 kg/ha (Chen *et al*., 2020).

In areas with pronounced contamination of vegetable-growing soils in the suburban zone of Nanjing (China) and with elevated concentrations of Cd, Pb, Cu, and Zn accumulated in the plow horizons, the estimated intake of TMs through plant products was much lower than the risk-inducing dose for both children and adults (Hu *et al*., 2013). In the industrial-agricultural Shandong Province, the main route of TM entry into the human body, by contrast, was alimentary intake; Cd was the most significant element posing carcinogenic risks, while Cu was responsible for non-carcinogenic risks for adults and children (Wen *et al*., 2025). According to a nationwide assessment of human health risks in China caused by agricultural soil contamination, the hazard from ingestion of TM-containing dust was higher than the risk from dermal adsorption of ecotoxicants (Yang *et al*., 2018). In agricultural regions, the assessment of non-carcinogenic health risks is generally lower than in industrial areas. The disease risk for adult men is negligible, but the hazard of diseases caused by TM-contaminated soils exists for women and children, especially in the agricultural provinces of Guangxi and Hubei, and to some extent in the farming regions of Hunan, Jiangxi, and Yunnan (Yang *et al*., 2018).

An assessment of human health risks associated with contamination of agricultural soils in various provinces of Iran indicated the pressing need to mitigate ecological hazards posed by As, Cd, and Cu, mainly related to the ingestion of TM-containing dust blown from the surface of over-dried arable land (Jahandari & Abbasnejad, 2024).

Thus, the application of mineral phosphorus fertilizers contributes noticeably to the contamination of agricultural soils with TMs from anthropogenic sources and may affect crop quality, potentially creating health risks for the population. Children are almost always more vulnerable to TM exposure than adults (Ran *et al*., 2016; Yang *et al*., 2018).

Input of naturally occurring radioactive materials (NORM) via mineral phosphorus fertilizers into agricultural soils

The primary specific source of NORM entry into arable soils, as in the case of trace metals, is mineral phosphorus fertilizers (Kabata-Pendias, 2010; Chauhan & Chauhan, 2014; Kratz *et al*., 2016; Bigalke *et al*., 2017).

Phosphate-containing raw materials used for fertilizer production typically contain elevated concentrations of naturally occurring radionuclides of the ^238U series. Activities of ^238U and ^226Ra in phosphate rocks can reach up to 4800 Bq/kg, while the activity of ^232Th is lower, up to 163 Bq/kg (United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR], 1977, 1982; Ajiboye *et al*., 2024; Ashwin *et al*., 2024; Jin *et al*., 2024; Konaparthi *et al*., 2024; Li *et al*., 2024; Owusu *et al*., 2024; Alves *et al*., 2025; Chen *et al*., 2025).

Processing phosphate-containing mineral raw materials and disposal of associated waste can lead to increased NORM content in the soils of industrial sites and surrounding areas. For example, in soils at a phosphorus fertilizer production facility near Mumbai (India), ^226Ra and ^238U concentrations reach 50% of their levels in phosphate raw materials, which is 30–35 times higher than the background concentrations in Indian soils. In soils adjacent to the plant, ^226Ra and ^238U concentrations are elevated 1.5–2.5 times above background levels (Sahu *et al*., 2014).

During the processing of raw phosphate-containing materials, a significant redistribution of ^226Ra, ^238U, ^232Th, and other NORM isotopes occurs. Almost all ^238U and substantial portions of ^226Ra and ^232Th can transfer into the final product. In phosphorus fertilizers, NORM activities vary widely: 55–1100 Bq/kg for ^226Ra and ^238U, and 7–100 Bq/kg for ^232Th in single superphosphate; 100–800 Bq/kg ^226Ra, up to 2100 Bq/kg ^238U, and 6–540 Bq/kg ^232Th in triple superphosphate; 75±11 Bq/kg ^226Ra and 65±3 Bq/kg ^232Th in diammonium phosphate (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1982; El-Taher & Althoyaib, 2012; Chauhan & Chauhan, 2014; Gupta *et al*., 2014; Hameed *et al*., 2014; Sahu *et al*., 2014; Uosif *et al*., 2014; Punniyakotti *et al*., 2020; Bouargane *et al*., 2023).

Phosphorus fertilizers produced from sedimentary phosphate rocks contain on average 50–200 mg/kg (620–2500 Bq/kg) ^238U and 2–20 mg/kg (8–81 Bq/kg) ^232Th, whereas those produced from apatite ores contain less than 10 mg/kg (<125 Bq/kg) ^238U, but higher amounts of ^232Th and rare earth elements (Chauhan & Chauhan, 2014).

^238U concentrations in phosphorus fertilizers manufactured in different countries vary as follows: Brazil – 5–185 mg/kg (62–2300 Bq/kg), Germany – 3–186 mg/kg (37–2320 Bq/kg), India – 16–36 mg/kg (199–448 Bq/kg), Serbia – 13–1778 mg/kg (162–22100 Bq/kg), USA – 9–221 mg/kg (112–2750 Bq/kg), Uzbekistan – 11–70 mg/kg (137–871 Bq/kg), Croatia – 66–127 mg/kg (822–1580 Bq/kg), Japan – 31 mg/kg (386 Bq/kg) (Yamazaki & Geraldo, 2003; Takeda *et al*., 2006; Avelar *et al*., 2016; Kratz *et al*., 2016; Vranješ *et al*., 2020). In fertilizers produced in EU countries, the average ^238U content is 94 mg/kg (1170 Bq/kg) (Verbeeck *et al*., 2020).

In phosphorus fertilizers, ^238U can exist in a relatively mobile and potentially plant-available form. For example, phosphorus fertilizers used in central Italy have been shown to contain 30–65% of ^238U in a plant-available form in triple superphosphate, diammonium phosphate, and organo-mineral NPK fertilizers, respectively (Roselli *et al*., 2010).

Regular and long-term application of phosphorus fertilizers with elevated NORM content leads to their accumulation in soils over extended periods, even after the cessation of fertilizer use. In soils of North Carolina, ^238U content increased by 1.4–1.7 times compared to unfertilized soils (Hu *et al*., 2024); in the United Kingdom – by 1.3 times (Ahmed *et al*., 2014); in soils of India – by 1.3–1.5 times (Hameed *et al*., 2014; Punniyakotti *et al*., 2020); in soils of Thailand – more than 2 times (Porntepkasemsan *et al*., 2018); in soils of Japan – by 1.4–3.9 times (Takeda *et al*., 2006; Yamaguchi *et al*., 2009); in soils of central Russia – by 1.3–1.9 times (Manakhov *et al*., 2022); and in soils of Kenya, Tanzania, and Uganda – by 2.3–4.0 times (Mwalongo *et al*., 2023).

In addition, a portion of ^238U remains in a plant-available form in soils: from 2% in soils of North Carolina (Hu *et al*., 2024) and 2.5% in soils of Japan (Takeda *et al*., 2006) to 7% in soils of southern Kazakhstan (Nursapina *et al*., 2022) and 24% in soils of the United Kingdom (Ahmed *et al*., 2014). The fraction of plant-available ^226Ra in soils of central Russia reaches 8–13% of its total activity (Manakhov *et al*., 2022).

The accumulation of NORM in crops grown on soils fertilized with phosphorus fertilizers occurs more intensively than on unfertilized soils. The ^238U accumulation factor in crops on fertilized soils in Brazil was on average 1.5–2 times higher than on unfertilized soils (Lauria *et al*., 2009). In soils of southern Kazakhstan, the accumulation factor of radish on soil fertilized with potassium monophosphate exceeded 4 (Nursapina *et al*., 2022). At the same time, in tobacco grown on fertilized soils in Kenya, Tanzania, and Uganda, the ^238U accumulation factor was almost two times lower than on background soils (Mwalongo *et al*., 2023). For acidic soils in Croatia, it was shown that the intensity of ^238U and other NORM accumulation by maize grown on soils with phosphorus fertilizers containing elevated NORM decreases with increasing doses of applied phosphorus and nitrogen (Zgorelec *et al*., 2021).

According to the United Nations Scientific Committee on the Effects of Atomic Radiation, NORM accumulation in soils leads to a slight increase in the external dose to the population and the possible dose from intake of radionuclides via crops grown on soils fertilized with phosphorus fertilizers containing elevated NORM. Slightly higher exposure may occur for populations living in close proximity to phosphorus fertilizer production facilities: up to 100 μSv/year, which constitutes about 4% of the total annual effective dose from all natural radiation sources (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2000). For workers directly handling phosphorus fertilizers and mineral raw materials with elevated NORM content, the increase in radiation dose, both from external exposure and inhalation, can reach 10–25% of the total annual effective dose (Gezer *et al*., 2012).

The chemical hazard of ^238U for biota components exceeds the radiological component: it has been established that an ecotoxicological effect can manifest at a load of more than 1 kg (12.8 MBq) of ^238U/ha per year. In Germany, the use of phosphate fertilizers over a 60-year period from 1951 to 2011 led to a total input of approximately 14,000 t of ^238U into arable soils, which corresponds to an average cumulative load of 1 kg ^238U/ha (Schnug & Lottermoser, 2013). A unique analysis of the impact of phosphorus fertilizer application to the arable soils of the Rothamsted Research station (UK), conducted from 1876 to the 2010s, showed that the average annual accumulation rate of ^238U in the arable horizon varied across experimental sites from 2.8 to 6.1 μg/kg (35–76 mBq/kg) per year and did not affect the mobility and, consequently, the bioavailability of the radionuclide for plants (Sun *et al*., 2022).

For agricultural lands in different countries, the average increment of ^238U levels in the arable horizon with continuous use of mineral phosphorus fertilizers is estimated at 0.85 μg/kg of soil (11 mBq/kg of soil). Thus, the accumulation of ^238U derived from fertilizers is a global issue, even if the rates of manifestation vary (Sun *et al*., 2022). Some studies report an increase in the reserves of terrigenous radionuclides in arable soils compared to virgin soils, which correlates with the duration of phosphorus fertilizer use (Yamazaki & Geraldo, 2003; Takeda *et al*., 2006; Schnug & Lottermoser, 2013; Verbeeck *et al*., 2020), while others note no significant changes over the observed period (Roselli *et al*., 2010; El-Taher & Althoyaib, 2012; Guidotti *et al*., 2015).

CONCLUSION

Providing food safety necessitates a careful evaluation of human health and environmental risks due to the contamination of agricultural soils with heavy metals (HMs) and naturally occurring radionuclides (NOR). Mineral phosphorus fertilizers constitute a considerable anthropogenic source of ecotoxicants in agroecosystems since they contain unregulated (in most nations) and sometimes high levels of HMs and NOR, notably Cd and As. Repeated inputs of these elements into arable soils can, in the long term, result in exceedances of safe threshold concentrations. Risk evaluation should consider the region of phosphate rock mining, doses and types of phosphorus fertilizers applied, soil type, climate and weather patterns, and biological characteristics of crops in rotation and agronomic management, all of which affect the bioavailability of HMs and NOR to plants and, as a consequence, their transfer along the food chain from "crop – (livestock) – human.

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