

Cd content in phosphate fertilizer: Which potential risk for the environment and human health?

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Abstract

Cadmium (Cd) is a heavy metal that accumulates in soil and in living organisms and causes severe and permanent damage. Its presence in the soil depends largely on the use of phosphate fertilizers. Phosphorite and apatite rocks used in phosphate fertilizers production contain several other minerals, including Cd. The amount of Cd incorporated in phosphate fertilizers depends on the type of phosphorite and apatite rocks (with low or high Cd content). Cd is present in soil mainly in insoluble form and has no bioavailability for plants. However, plants can increase Cd solubility by releasing root exudates that change the pH of the rhizosphere, therefore increasing Cd accumulation. Once crops absorb Cd, it enters the food chain. Food is the primary source of Cd exposure (for the non-smoking population), with cereals, nuts and legumes, and fish and shellfish being the major contributors. Progressive accumulation of Cd in humans impairs kidney function, affects the liver, and causes bone demineralization. Cd classification as a human carcinogen goes back to the 1990s. The European Union adopted Regulation (EU) 2019/1009, limiting Cd content in organo-mineral fertilizer having total phosphorus (P) content of 5% P₂O₅ equivalent at 60 mg kg⁻¹ P₂O₅. This threshold seems inadequate compared to the threshold values for Cd currently in place in some EU countries: 12 member states have a Cd threshold between 20 and 50 mg kg⁻¹ P₂O₅, 8 have the same threshold as that proposed in the regulation, and 2 have a higher threshold. Meanwhile, the new EU Regulation on CAP Strategic Plans explicitly references soil health and fertility protection and the limitation of contaminants in fertilizers. Fertilizers with low Cd content, with thresholds no higher than 20 mg kg⁻¹ P₂O₅, would effectively limit bioaccumulation. As stopping P fertilizer application cannot be an option, strategies such as the use of P fertilizers with low Cd content, the use of cultivars that accumulate less Cd in their consumed parts, production of mineral P fertilizers with higher nutrient use efficiency than those actually produced, the decadmiation of P rocks from the raw materials, soil phytoremediation before crops cultivation, and increased use of recovered nutrients, should be adopted.

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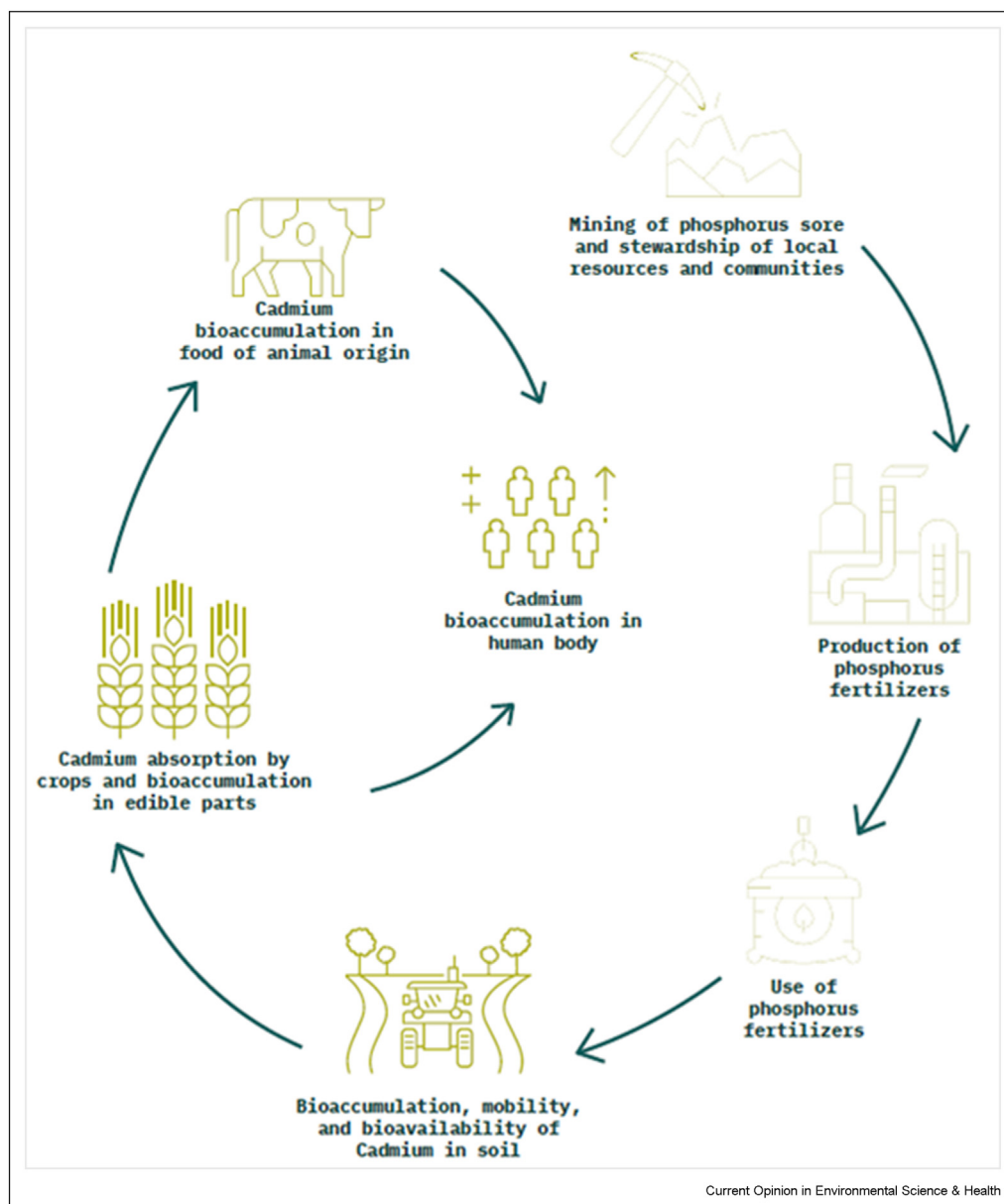
Keywords

Cadmium, Heavy metals, Environmental contamination, Human health exposure, Sustainable agriculture.

Background

Several studies point to the impact of mineral fertilizers as a significant source of Cadmium (Cd) contamination in agricultural soils and, consequently, in Europeans' diets (Figure 1) [1]. Cd is a toxic contaminant that can have severe and often irreversible effects on human health and natural ecosystems [2–4]. The application of mineral phosphate (P) fertilizers is mainly responsible for the accumulation of Cd in agricultural soils and watersheds [5]. Accumulation in the soil increases Cd levels in plants and the potential for humans to ingest amounts that exceed the level at which no adverse health effects occur [6]. In addition, Cd can enter freshwater reservoirs and animal feed [4,7]. In Europe, mineral P fertilizers contribute 45% of the total Cd contamination of cropland. At the same time, 55% of the total dietary Cd intake of the average European consumer is related to Cd accumulation in soil [8].

Figure 1



Life cycle of cadmium in phosphorous fertilizers.

The long-term consequences of Cd contamination on the soil ecosystem are not entirely predictable. Moreover, some studies show that even at low Cd concentrations in soil, in the presence of efficient Cd transfer from soil to plants, the Cd accumulations in the edible parts of plants may exceed the values recommended for human consumption, with no toxicity symptoms for plants [9]. Therefore, although current concentrations of soil Cd are estimated to meet provisional safe intake limits for Cd uptake in Europe ($2.5 \mu\text{g kg body weight}^{-1}$ per week), several studies pointed out that other jurisdictions like the US have set much lower limits ($0.7 \mu\text{g kg body weight}^{-1}$ per week). These limits are

exceeded in most of the world [10]. Furthermore, concentrations of Cd in foodstuffs are important in relation to the trade of food commodities and are the subject of disputes regarding restrictive trade rules under the World Trade Organization's jurisdiction [11]. Hence it is prudent that agricultural systems be managed to limit Cd accumulation in soil, and to utilize agronomic and genetic management to minimize Cd uptake by crops and animals prone to Cd accumulation. The main scope of the present review is to assess and identify future actions and research directions, to meet European consumers' requirements for safe food and environment.

Research and actions to fill the gaps

Use of phosphate fertilizers in Europe

Although the non-substitutable nutritional element secures our food production, P fertilization in European agriculture is often inefficient. While soils in some regions of Europe are showing nutrient deficiencies and thus losing their productive capacity, elsewhere, especially in regions with high livestock density, large amounts of P accumulate in the European soils [12]. The European Union (EU) relies on more than 90% of mineral P imports [13]. Based on supply risk and economic importance, the EU continues to identify phosphate rock and white phosphorus as Critical Raw Materials in 2020 [14], and the Stockholm Resilience Centre places the cycles of P and N in the risk zone of 'planetary boundaries' [15]. Recent studies highlighted natural radioactivity and radiation hazard associated to mineral phosphate fertilizer production [16]. Along with the world population growth, P demand in both agriculture and biofuels sectors is increasing over the years. Europe has an unsustainable consumption of P, with only 16% of the P present in fertilizer reaching human food, while the main fraction is lost through net accumulation in agricultural soils, soil erosion, or crop residues [17]. According to EUROSTAT [18], the consumption of inorganic fertilizers based on P reached about 1.1 Mt P₂O₅ in 2018 in the EU countries, with a slight reduction of 1.2% since 2008. USA has an average consumption of about 4.0 Mt of P₂O₅ (1990–2015), almost four times higher than in the EU [19]. As announced in the New Circular Economy Action Plan, the EU revised the previous 2003/2003 fertilizer regulation also to encourage the supply of safe and high-quality fertilizer products coming from domestic organic sources [8]. Thus, it is expected that the European Commission develop shortly the Integrated Nutrient Management Action Plan (INMAP), to ensure more sustainable application of nutrients and boost the markets for recovered nutrients [20].

Cd content in fertilizers and its transfer to soil

Cd in mineral phosphate fertilizers depends on phosphate rocks (apatite and phosphorite), by far the most important phosphorus-bearing raw material used in the fertilizer industry [21]. Different types of phosphate rocks have different levels of Cd, based on the type of ore (igneous or sedimentary) and geographic provenance. It is well established that phosphate from igneous deposits contains low Cd concentrations (range 1–4 mg kg⁻¹) and such deposits are in South Africa and Russia. Higher Cd concentrations (range < 1–150 mg kg⁻¹) are reported in phosphate rock from sedimentary deposits derived from Morocco, Togo, Senegal, and Idaho, USA [11]. Data for countries among the top world producers is shown in Table 1 [22,23].

Table 1

Cadmium content (mg/kg) and dominant minerals in phosphate rocks around the world [22,23].

Origin	Dominant minerals	Cd content (mg kg ⁻¹)
Wyoming–USA	Fluapatite	1.45
Florida–USA	Hydroxyapatite	3.31
Idaho–USA	Hydroxyapatite, carbonate fluorapatite	199
Morocco	Carbonate fluorapatite	507
Sludanka - Russia	Hydroxyapatite	0.15
Okinawa - Japan	Hydroxyapatite	29.5
Taiba Senegal	–	87
Zin- Israel	–	31
Tunisia	–	40
Phalaborwa -South Africa	–	1
Araxa -Brazil	–	2
Tongo	–	58
El-Hasa - Jordan	–	5
Kaiyang - China	–	<2

When a phosphate fertilizer comes into contact with the soil, it undergoes various biochemical, microbiological, and physical processes through which it is progressively reduced and retained in the soil. The contaminants in the fertilizers (mineral/chemical) tend to follow the same destiny [24] even if studies show that on addition to moist soil, granules of single superphosphate (SSP) lost all their P in 8 days but 60% of the Cd (and Ca) was retained in the granule [11]. Soil organic matter, oxyhydroxides of Al, Fe, and Mn and clay minerals are the main Cd sorbents in soil. Cd is strongly bound in soil and only minute fractions of it are present in soil solution and, hence, Cd removal by vertical leaching is small unless the soils are very acidic and low in organic matter. Despite this, the vertical leaching of Cd has become a focal point of attention and even controversy in the debate on the Cd limits in fertilizer in Europe that took place between about 1998 and 2018 [5,11]. Annual net accumulation of Cd in the soil is about 1% of the amount already present in agricultural soils [25]. In New Zealand from the 1950–2000s, the Cd presence in P fertilizers determined an enrich of soil Cd by 50–400% above natural background concentrations [10]. The researchers estimated that stopping P fertilizer applications in New Zealand soil reduced Cd concentrations after more than 21 years. Nevertheless, another recent study of a no-P pasture found no change in total soil Cd concentrations over 22 years [26]. Additional studies highlighted that in soils fertilized with products containing 1–20 mg kg⁻¹ P₂O₅, Cd tends to accumulate very slowly or even decrease after 100 years, whereas at a concentration of more than 60 mg kg⁻¹ P₂O₅, soil accumulation would be relatively high [25].

Strategies to reduce soil Cd concentrations other than stopping P fertilizer would be required to prevent production losses. Such strategies could include substantially lowering the Cd concentration in P fertilizers, lowering soil pH, or using plants that hyperaccumulate Cd [10,27,28]. However, their efficacy is unproven in the long term. It is therefore likely that a mix of strategies is required that considers the local production system, climate, and soil type [10].

Cd accumulation in crops

Cd is present in soil mainly in insoluble form and has no bioavailability for plants. However, plants can increase Cd solubility by releasing root exudates that change the pH of the rhizosphere, therefore increasing Cd accumulation, despite it varies between and within plant species [29]. Cd behavior is very similar to that of zinc (Zn), an element that is necessary for good plant development. When the soil has an insufficient mineral supply of Zn to meet the crop's needs, the similarity between the two elements causes the plant to take Cd instead of Zn [30]. Recently, in maize, Tan et al. [31] individuated double mutations of two Zn transporter genes, that synergistically regulate the uptake of Zn and Cd. Therefore, Cd contamination is a significant stressor for plants that may result in genotoxic effects, leaf chlorosis, reduced growth rates, inhibition of respiration and photosynthesis, increased oxidative damage, and reduction in nutrient uptake ability [30].

A widespread low concentration of soil contamination together with efficient transfer of Cd from soil to plants means that even in the presence of low levels of contamination, and even if the plants do not exhibit symptoms of toxicity, the edible parts of plants may exhibit Cd accumulations higher than those allowed for human consumption [32]. Over the two last decades, numerous publications have addressed the biomolecular processes of Cd accumulation in plants with the scope of creating cultivars that accumulate less Cd in their consumed parts [33]. Targets for future research should include the crystal structure of plant Fe/Zn/Mn transporters, identification of desirable allelic variants, and design of a protein specific for substrate transport [30].

The impact of Cd on human health

Cadmium is a non-essential element for humans that is almost absent from the body at birth and accumulates with age in the kidney and liver to peak at around age 50 [11]. It can cause bone demineralization and it is classified as a human carcinogen [1]. Foods are the primary source of Cd exposure, accounting for approximately 90% of the total Cd intake for the non-smoking general population [3]. Cereals and cereal products, vegetables, nuts and legumes, and fish and shellfish are the most significant contributors to human exposure [11].

Most of the Cd absorbed by the human body is excreted, but between 5% and 10% is retained, mostly (>50%) in the kidneys [11]. The biological half-life of Cd is within 6–38 years in the kidneys and 4–19 years in the liver [1]. Damage to the kidneys occurs when the Cd concentration in the renal cortex exceeds approximately 200 mg kg^{-1} (wet weight), as evidenced by the excretion of proteins (proteinuria) and calcium (Ca). The latter leads to osteomalacia which is the underlying cause of itai-itai disease [34]. Recent European and French studies have shown that the risk related to Cd dietary exposure cannot be ruled out for a part of the population [1].

EU and MSs position on Cd limits

The European Union has been concerned about Cd since the 1970s, but it was only in June 2019 that the EU Council officially adopted the Regulation 2019/1009, which introduced limits on the Cd content in organo-mineral fertilizer having total phosphorus (P) content of 5% P_2O_5 -equivalent set at $60 \text{ mg/kg P}_2\text{O}_5$ [1]. The new limit of 2019 is based on the “stand still principle” or “zero net accumulation”, not on health risk assessment and several member states (MSs) had claimed to have local soil, climate, land use, or crop use conditions that justified their national limit [11]. Indeed, 12 MS already adopted lower threshold values, 8 MS have similar values, and 2 MS have set higher thresholds so that it is challenging to consider the new limit a breakthrough or a harmonization of the internal market. Harmonized rules provide a transparent and predictable legal framework for all businesses (e.g., agricultural technology providers, farmers, food processors, and distributors), which is a prerequisite for healthy competition and greater awareness along the value chain of risks and risk mitigation strategies.

In October 2020, the European Parliament successfully adopted a few amendments during the current CAP review process, linking the CAP to reducing heavy metals in fertilizers. The text was part of the European Parliament's negotiating position with the Council. In June 2021, EU agriculture ministers confirmed the preliminary agreement with the European Parliament on CAP reform. On September 9, 2021, the European Parliament's AGRI Committee approved by a large majority the complete CAP package agreed upon during the informal triologue in June. The preliminary agreement contained an explicit reference to protecting soil health and fertility and reducing contaminants in fertilizers. Art. 47 of Regulation (EU) 2021/2115 on CAP Strategic Plans was adopted on 21 December 2021 and is set to enter into force on 1 January 2023. This explicitly refers to the reduction of contaminants in fertilizers as one of the measures where MS interventions could be envisaged. This creates first-ever financial incentives for farmers to use low-Cd phosphates [24].

Remarks

Cd dietary exposure cannot be ruled out for a part of the European consumers. Progressive accumulation of Cd in humans impairs kidney function, affects the liver, and causes bone demineralization. Mineral phosphate (P) fertilizers are the main source of Cd in the environment and food. The European Union adopted Regulation (EU) 2019/1009, limiting Cd content in organo-mineral phosphate fertilizers at 60 mg kg⁻¹ P₂O₅. This threshold seems inadequate compared to the threshold values for Cd currently in place in some EU countries: 12 member states have a Cd threshold between 20 and 50 mg kg⁻¹ P₂O₅, 8 have the same threshold as that proposed in the regulation, and 2 have a higher threshold. Stopping P fertilizer cannot be an option and strategies able to reduce soil Cd concentrations, by considering the local production system, the climate, and the soil type should be adopted. Such strategies could include (i) the use of P fertilizers with low Cd content, (ii) the use of cultivars that accumulate less Cd in their consumed parts, (iii) soil phytoremediation before crops cultivation, (iv) the production of mineral P fertilizers with higher nutrient use efficiency than those actually produced, (v) the decadmiation of P rocks from the raw materials, and (vi) increased use of recovered nutrients. For all these options additional research is needed for a better understanding and optimization of the processes and an evaluation of the economic benefits and impacts.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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