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Cadmium and Phosphorous Fertilizers: The Issues and the Science

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Abstract

Non-nutritive metals, such as cadmium (Cd), occur naturally in all agricultural soils, in soil amendments (e.g. biosolids), and to varying degrees in phosphorous (P) fertilizers. Its persistence in the environment and its uptake and accumulation in the food chain make Cd a public health concern. 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), controversy exists regarding their effects. The only known case of Cd toxicity (i.e. *itai-itai* disease) occurred with subsistence farmers in Japan growing rice on soils contaminated with industrial wastes. Cadmium behaviour in soil and its accumulation by crops is complicated. Numerous factors (e.g. soil pH, organic matter content, salinity, macro and micronutrient fertilizers, crops species and cultivar, and tillage) influence the bioavailability and uptake of Cd by crops. 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, scientific risk assessments have shown that P fertilizer containing Cd is safe and does not pose risk to human health.

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1. Introduction

Cadmium is a trace element, a non-nutritive metal regarded as harmful to humans and the environment. It occurs naturally in the earth's crust and oceans and can be added to the soil through natural (e.g. volcanic activity, weathering of Cd-containing rocks, sea spray) and anthropogenic activities (e.g. mining and smelting of zinc (Zn)-bearing ores, fossil fuel combustion, waste incineration, sewage sludge, irrigation waters, manure, and fertilizers derived from phosphate rock) [1] [2]. While not essential to crop growth, or known to be essential to biological systems, agricultural crops will take up and accumulate Cd depending on its availability in the soil and their genetic characteristics [3] [4]. And, depending on its concentration in the soil, Cd can negatively impact soil organisms and soil ecology [5].

2. Health Concerns

2.1 Impacts of cadmium on human health and exposure routes

Public health concerns with Cd are primarily due to its persistence in the environment and its relatively rapid uptake and accumulation in the food chain. Although the health effects of Cd have been studied extensively, controversy exists

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regarding some of the effects. The U.S. Department of Health [6] and the European Commission's Institute of Health and Consumer Protection [7] have recently summarized the health effects of Cd, updating information published by the Organization for Economic Cooperation and Development almost 20 years ago [8]. The main toxic effect of Cd in human health is on the kidney, or renal cortex, but other adverse health effects on pulmonary, cardiovascular, and musculoskeletal systems have been reported, including Cd as a human carcinogen. The nonsmoking general population is mainly exposed to Cd through ingestion of food, and to a lesser extent by air and drinking water. Studies show the average dietary intake of Cd for nonsmokers living in uncontaminated areas is between 10 and 25 μg Cd per day and that average has been declining over the past 30 years [6] [8]. The World Health Organization has established a provisional tolerable weekly intake for Cd at 7 $\mu\text{g}/\text{kg}$ body weight, i.e. 60-70 μg Cd per day for an average 60-kg woman or 70-kg man [9]. Smoking is a significant source of Cd because tobacco leaves naturally accumulate high levels of Cd [10]. It is estimated that tobacco smokers are exposed to 1.7 μg Cd per cigarette and about 10% is absorbed by the body when smoked.

2.2 Cadmium toxicity and bioavailability in foods

While dietary intake is the primary exposure route for non-smoking adults and children, acute toxicity caused by food consumption is rare [11]. Plants can accumulate high enough concentrations of Cd to become phytotoxic, but risk of food-chain toxicity occurs before phytotoxicity is apparent because of chronic exposure through the food chain. Prolonged exposure to low levels of Cd in air, food and water can lead to its accumulation in the human body in the kidney and bone following oral exposure and kidney and lung following inhalation exposure. Its biological half-life is estimated to range from 6 to 38 years in the kidney and 4 to 19 years in the liver [12].

The adverse effects of Cd on human health were first observed in subsistence rice farmers in Japan in the mid-1950s. They contracted Cd poisoning (*itai-itai* disease) after decades of consuming home-grown rice irrigated with Cd- and Zn-enriched mine wastes. [13]. The disease caused a softening of the bones and kidney failure. Chaney [11] reports that similar Cd kidney disease has been found in other areas in Asia in populations consuming rice grown on contaminated paddy soil, but other documented cases of Cd-induced disease are rare.

The recognition by food authorities and scientists that Cd caused *itai-itai* disease in Japan prompted concern for any potential source of Cd that could introduce Cd into the food chain. Food chain risks from Cd are complicated because bioavailability of Cd in foodstuffs differs greatly. For example, documented cases of people's prolonged consumption of Cd-rich shellfish [14] [15] [16] or garden produce from soils contaminated with Cd and Zn [17] [18] show no evidence of Cd disease. Apparently when Zn accompanies Cd in contaminated soil, it can inhibit both the uptake and bioavailability of Cd [11].

2.3 Other complicating factors

Chaney [11] has thoroughly reviewed the literature demonstrating the complexity of risks from food chain Cd. Some examples he cited from controlled human and animal feeding tests are: increased dietary Zn inhibits Cd absorption while mild iron (Fe) deficiency increases absorption; Cd concentration is higher in whole wheat and bran than white flour, but its absorption from these products is less; and adding Fe to bread wheat reduces Cd retention. Based on the above examples and knowing that polished rice is deficient in Fe, Zn, and calcium (Ca), Reeves and Chaney [19] reported on their research that showed rats fed polished rice diets absorbed 10-fold more Cd than rats fed adequate levels of Fe, Zn, and Ca. They also reported that Cd absorption from sunflower kernels, which have higher levels of Fe, Zn, and Ca than polished rice, was significantly less than that from polished rice. Based on the research reported above and other published studies reviewed, Chaney [11] concluded, "... the science is clear that diet-induced Cd disease is very unusual except for rice subsistence farmers over 50 years old."

The scientific literature shows that under conditions of Fe, Zn and/or Ca deficiency or nutritional stress, Cd adsorption by the intestines is increased [20]. Compared to diets adequate in Fe and Zn, Fe and Zn deficiency can increase Cd retention 15-fold. Rice is generally deficient in Fe, Zn, and Ca for human needs. The bioavailability of Cd in food is related to the nutritional balance of Fe, Zn, and other nutrients. Dietary Fe, Zn, and Ca inhibit absorption and retention of dietary Cd and explain the lack of Cd disease in individuals exposed to extreme soil and food Cd contamination.

3. Cadmium in Soil and Fertilizer

3.1 Cadmium in Soil

Soil Cd is derived from weathering of rocks and minerals or from numerous anthropogenic sources [1]. A world literature review by Kabata-Pendias and Pendias [21] determined that 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. They cited various studies showing mean background concentrations in the USA (3045 samples) were found to be 0.27 mg/kg; 0.6-0.7 mg/kg in the UK (5692 samples); 0.5 mg/kg in the Netherlands (708 samples); and <0.3-1.0 mg/kg in Germany (2947 samples).

Natural background levels of Cd in agricultural soils can be increased through atmospheric deposition (e.g. forest fires, volcanic eruptions, soil erosion, air pollution), land application of sewage sludge and manure, and fertilizers. Incineration of municipal wastes, non-ferrous metal production, Fe and steel production, and combustion of fossil fuels contribute Cd to the air, but these sources are only significant in industrialized areas. Alloway and Steinnes [1] cited various sources showing atmospheric deposition in European countries ranges from 2.0 to 12.5 g/ha/yr while annual deposition in the USA is estimated to be less than 2.8 g/ha [22]. Sewage sludge can contain concentrations of Cd ranging from >1 to 3650 mg/kg [23]. Estimates for land receiving sludge can range from 30-40 g/ha/yr [1]. About 90% of the Cd ingested by animals from feedstuffs passes into manure, and aside from being a Cd source, manure helps mobilize soil Cd making it more available to plants [24].

3.2 Cadmium in Fertilizer

Cadmium occurs naturally in phosphate rock. The International Fertilizer Development Center (IFDC) summarized Cd content of phosphate rocks obtained from 35 sedimentary deposits in 20 countries [25]. Data for countries among the top world producers is shown in Table 1. It is apparent that concentration of Cd can vary widely between countries and within deposits in the same country. The overall average Cd concentration for sedimentary deposits was 21 mg/kg with a range of less than 1 to 150 mg/kg. Compared with non-phosphate containing rock, sedimentary phosphate rock deposits are about 69 times more enriched with Cd. Data from 11 igneous phosphate rock deposits in 9 countries surveyed by IFDC showed an average Cd concentration of 2 mg/kg and were enriched 7.5 times crustal abundance.

Table 1. Cadmium contents (mg/kg) of sedimentary and igneous phosphate rocks [25].

Country	Deposit	Average Cd	Range
Sedimentary Deposits			
China	Kaiyang	<2	—
Israel	Zin	31	20-40
	Undifferentiated	24	20-28
	Arad	14	12-17
Jordan	Oron	5	—
	El-Hasa	5	3-12
	Shidyia	6	—
Morocco	Undifferentiated	26	10-45
	Bou Craa	38	32-43
	Khouribga	15	3-27
	Youssoufia	23	4-51
Senegal	Taiba	87	60-115
Syria	Khneifiss	3	—
Togo		58	48-67
Tunisia		40	30-56
United States	Central Florida	9	3-20
	North Florida	6	3-10
	Idaho	92	40-150
	North Carolina	38	20-51
Other countries		13	<1-100
Overall Sedimentary Averages		21	<1-150
Igneous Deposits			
Brazil	Araxa	2	2-3
	Catalao	<2	—
South Africa	Phalaborwa	1	1-2
Russia	Kola	1	<1-2
Other countries		1	1-5
Overall Igneous Averages		2	<1-4

Sedimentary phosphate rock deposits dominate world production and reserves (Table 2). Approximately 85% of the world production is from sedimentary deposits. Varying amounts of Cd in the phosphate rock move through the beneficiation and acidulation processes during fertilizer manufacture. Amounts transferred depend on the manufacturing

process. For ordinary (single) superphosphate (SSP) produced by reacting phosphate rock with sulphuric acid and triple super phosphate (TSP) produced by acidulation of the phosphate rock with phosphoric acid, all of the Cd in the phosphate rock is transferred to the SSP or TSP. Depending on the phosphate rock source, SSP can contain from 2 to more the 40 mg/kg and TSP can have from less than 10 to over 100 mg/kg Cd content [25]. In wet process phosphoric acid (WPA) Cd is transferred to the acid and gypsum by-product. About 55 to 90 percent of the Cd is transferred to the acid with the balance to the gypsum. Ammonium phosphates (e.g. monoammonium phosphate [MAP] and diammonium phosphate [DAP]) are produced from WPA. Again, depending on the source of phosphate rock, their Cd content can range from less than 1 to more than 100 mg/kg.

Robarge et al. [27] surveyed the trace metal content of various fertilizers sampled from production facilities around North America over a two-year period (1999-2000). They found the average Cd content of DAP/MAP, based on 84 different samples, ranged from 16 to 22 mg/kg and 19 mg/kg for 45 samples of TSP. Samples for other fertilizer products (e.g. urea, potassium chloride, ammonium sulphate, ammonium nitrate) had negligible amounts of Cd (i.e. < 0.01 mg/kg)

Table 2. World production and reserve of rock phosphate [26].

	2010	2011	Reserves
	----- 1,000 metric tons -----		
United States	25,800	28,400	1,400,000
Algeria	1,800	1,800	2,200,000
Australia	2,600	2,700	250,000
Brazil	5,700	6,200	310,000
Canada	700	1,000	2,000
China	68,000	72,000	3,700,000
Egypt	6,000	6,000	100,000
India	1,240	1,250	6,100
Iraq	—	—	5,800,000
Israel	3,140	3,200	180,000
Jordan	6,000	6,200	1,500,00
Mexico	1,510	1,620	30,000
Morocco	25,800	27,000	50,000,000
Peru	791	2,400	240,000
Russia	11,000	11,000	1,300,000
Senegal	950	950	180,000
South Africa	2,500	2,500	1,500,000
Syria	3,000	3,100	1,800,000
Togo	850	800	60,000
Tunisia	7,600	5,000	100,000
Other Countries	6,400	7,400	500,000
World total (rounded)	181,000	191,000	71,000,000

3.3 Factors affecting cadmium accumulation, bioavailability and uptake by crops

Amounts of Cd added to agricultural soils through P fertilizer are a function of rate and frequency of application and the concentration of Cd in the fertilizer. While the net Cd balance depends on the crops grown and the fertilizer source, both the input and output of Cd tend to be low compared to the total amount of Cd present in the soil [28] [29]. The solubility of the fertilizer determines the short-term availability of the Cd. Grant [30] reviewed greenhouse studies showing Cd concentrations in crops was increased by application of fertilizers containing very high levels of Cd (417 mg/kg), but not by addition of low-solubility phosphate rock containing similar amounts of Cd. In field studies in the Canadian Prairies with durum wheat, the Cd concentration in the wheat increased with the application of MAP, but was generally not affected by

the concentration of Cd in the fertilizer [31]. For example, the Cd content of durum wheat fertilized with MAP containing varying amounts of Cd (i.e. 0.2, 7.8, and 186 $\mu\text{g/g}$) grown at 11 different locations over a three year period was not generally affected by the amount of Cd in the fertilizer. Similar results have been observed in potato field trials in Australia where the concentration of Cd in the P fertilizer had little effect on the uptake of Cd by the potatoes [32]. However, in the long-term, Cd added to the soil through P fertilization tends to accumulate if input is less than crop removal. Grant [30] reviewed numerous studies showing the application of P fertilizers containing 20 to 50 mg /kg of Cd led to significant increases in the Cd concentration of the soil, which may lead to higher crop Cd accumulation.

The risk of Cd accumulation by crops is more related to its availability due to soil, crop, management, and environment than the total Cd present in the soil. Soil pH is usually regarded as the most significant variable influencing Cd uptake from the soil (see reviews by Grant and Sheppard [4]; Chaney [11]; McLaughlin et al. [33]; Grant et al. [37]). Decreasing pH (increasing acidity) increases Cd uptake by plants, thus liming will reduce Cd bioavailability. Soil organic matter and adding organic matter to soils also influences Cd bioavailability. Soils with higher organic matter have higher cation exchange capacity, which increases Cd adsorption. Soil pH and organic matter may interact in their effects on Cd availability. Organic matter has been found to reduce Cd concentration in the soil solution in contaminated soils at pH below 6.0 and increase soil concentration at pH 6.0-8.0. Organic materials (e.g. manure and sludges) appear to reduce the availability of Cd [34]. For example, soils from the long-term trials at Rothamsted, England accumulated more Cd in the farm-yard manure treated plots, but produced wheat with lower Cd concentrations than P fertilized plots [35]. Soil chloride (Cl) increases the mobility of Cd through the formation of Cd-Cl complexes resulting in increased Cd absorption by plants in saline soils or soils irrigated with high Cl water (e.g. Norvell et al. [36]). McLaughlin et al. [33] indicated soil temperature, redox potential, and application of nitrogen (N), P, and potassium (K) and micronutrients (i.e. Zn) also affect plant uptake of Cd. However, we have little control over soil temperature or redox potential. Macronutrients can stimulate root growth, acidify the soil (i.e. N fertilizers), and increase ionic strength of the soil solution thereby reducing Cd adsorption, all of which makes Cd more available. Small applications of Zn (< 10 kg Zn/ha) in low Zn soils can reduce Cd in wheat grain and Zn applied with P fertilizer can desorb Cd from the cation exchange increasing Cd in soil solution. However, Zn also competes with Cd for uptake and translocation by plants, so Zn can also reduce Cd accumulation by crops. To further complicate Cd bioavailability, P fertilizer itself may restrict crop uptake of Zn, which also potentially increases Cd accumulation [4]. Other factors known to influence crop concentrations of Cd include soil drainage, preceding legume, and tillage [11].

It is apparent from the above discussion that Cd availability to crops is complicated and difficult to predict or manage. Another option to reduce Cd uptake is through plant breeding. Crop species and cultivars differ widely in their ability to take up and accumulate Cd [37] [38]. Cereals and legumes accumulate less Cd than leafy crops, but there also can be great differences in accumulation within cultivars. The genetic variation among cultivars means there is great potential for utilizing plant-breeding to select for low-Cd characteristics in crops.

4.0 Risk from Cd in P Fertilizer

4.1 Cadmium regulations for P fertilizer

Cadmium behaviour in the soil and accumulation by crops is complex. Fertilization can increase the risk of Cd movement into the food chain through direct addition to the soil from some P fertilizers and indirectly from fertilizer-induced changes in Cd bioavailability. Because of the potential risk to human health, several countries have implemented regulations limiting the amount of Cd that can be present in P fertilizers (Table 3).

Table 3. Limits for Cd in P fertilizers in several countries expressed as Cd:P ratio, Cd:P₂O₅ or concentration of Cd in the fertilizer product. (adapted from Chaney [11]).

Country	Limits	mg Cd/kg P	mg Cd/kg P ₂ O ₅	mg Cd/kg 45% P ₂ O ₅ Product
Limits for Fertilizer-Cd				
USA-Washington	0.0889 kg Cd/ha/yr	2040	889	400
USA-Oregon	7.5 mg Cd/% P ₂ O ₅	774	338	152
USA-California	4 mg Cd/% P ₂ O ₅	412	180	81
Australia	300 mg Cd/kg P	300	131	59
Canada	0.0889 kg Cd/ha/yr	2040	889	400
Japan		340	148	67
Austria	75 mg Cd/kg P ₂ O ₅	275	120	54
Belgium	90 mg Cd/kg P ₂ O ₅	206	90	40.5
Denmark		110	48.0	21.6
Netherlands		40	17.5	7.9
Finland	21.5 mg Cd/kg P ₂ O ₅	49	21.5	9.7
Sweden	43 mg Cd/kg P ₂ O ₅	100	43.7	19.7
EU Proposal (2001)	20 mg Cd/kg P ₂ O ₅	45.8	20	9
	40 mg Cd/kg P ₂ O ₅	91.6	40	18
	60 mg Cd/kg P ₂ O ₅	137	60	27

These limits, and the underlying assumptions upon which they are based, vary greatly. The European Commission has proposed much stricter limits transitioning from 60 to 20 mg Cd/kg P₂O₅ over a 15-year period [39] [40]. These limits are based on the conclusions of an impact assessment study that stated fertilizers containing 20 mg Cd/kg P₂O₅, or less, are not expected to result in long-term accumulation in the soil and fertilizers containing 60 mg Cd/kg P₂O₅ could result in long-term accumulation of Cd in the soil. The rationale for the limits provided by the proposal [39] provide little scientific evidence justifying a limit of 20 mg Cd/kg P₂O₅ and there is little evidence in the scientific literature suggesting that Cd would accumulate in soils through using P fertilizers containing less than 60 mg Cd/kg P₂O₅, much less pose human health risks.

4.2 Cadmium risk assessments

Chemical exposure and risk assessment is a common and accepted scientific practice used for setting health standards or safe limits as part of a risk management process [41]. Risk assessments determine the magnitude of exposure (both frequency and duration) and can be used to predict whether a sensitive receptor (e.g. farm family adult and/or child) faces a health risk. The U.S. EPA [41], the California Department of Food and Agriculture (CFDA) [42], and the Weinberg Group on behalf of The Fertilizer Institute (TFI) [43] have conducted health risk assessments examining safe limits for non-nutritive elements in fertilizers. These assessments incorporated typical agricultural practices and high-end application rates covering a wide range of agricultural NPK fertilizers and micronutrients. Woltering [41] reported that all three assessments used similar methodologies, but only TFI's assessment will be discussed here [44]. Risk-based concentrations (RBCs) in parts per million (ppm; 1 ppm = 1 mg/kg) were calculated for specific metals in NPK fertilizers, and micronutrients that do not pose a health risk, following their use and exposure over a sensitive person's lifetime.

Phosphate fertilizer products with varying concentrations of Cd (2 -150 mg/kg) and applied at typical rates (e.g. grain, 70 kg/ha; vegetables, 133 kg/ha; and root crops, 176 kg/ha) from across the USA were selected for the assessment. Exposure from dermal contact with fertilized soil, unintentional soil ingestion and eating crops (i.e. root crops, vegetables, and grains) that may have taken up metals was estimated for farm families (children and adults). The model considered metal content of the fertilizer, application rate, soil accumulation, plant uptake factors, and accepted protective levels in diets. RBCs for a given metal in fertilizer were back calculated from a protective level in the diet along with consideration of the exposure route. The RBC unit is based on 1% of the nutrient (i.e. P₂O₅) and the corresponding application rate needed to achieve its desired level in the soil. RBCs are estimates of the maximum level of a metal in the fertilizer that does not pose an

unacceptable lifetime health risk. Woltering [41] outlined the specific methodology used to determine the RBCs in detail. RBCs were calculated for three crops separately and for a multi-crop diet (50% grain, 40% vegetables, and 10% root). The RBC value for Cd was 10 mg/kg per 1% P₂O₅. For example, for MAP containing 55% P₂O₅, the RBC would be 550 (i.e. 10 mg/kg x 55), which means if the Cd concentration in the MAP is below 550 mg/kg, that fertilizer can be used without posing lifetime health risks for the most highly exposed individuals.

The three risk assessments mentioned above (i.e. the U.S. EPA, CFDA, and TFI) share much of the same methodology and underlying science; all three concluded that in nearly all cases, the metal levels found in fertilizers in North America do not pose risk to the farmers applying them, their families, or to the general public [41].

5.0 Summary and Conclusions

Cadmium is a naturally occurring, non-nutritive metal found in soil and minerals. Its persistence in the environment and its uptake and accumulation in the food chain makes Cd a public health concern. Adverse health effects from Cd exposure have been studied extensively, but the only known case of Cd toxicity (*itai-itai* disease) occurred with subsistence farmers in Japan growing rice on soils heavily contaminated with Cd from industrial wastes. Phosphate rock contains varying amounts of innate Cd and some of that Cd is transferred to fertilizer products during the manufacturing process. In addition to other anthropogenic activities (e.g. mining Zn bearing ores, combustion of fossil fuel, waste incineration, land application of sewage sludge and manure, and irrigation water), P fertilization can add Cd to agricultural soils. Cadmium behaviour in the soil and its accumulation by crops is complex; numerous factors (e.g. pH, organic matter, salinity, macro and micronutrient fertilization, crop species and cultivar, tillage, and liming) affect the bioavailability and uptake of Cd by crops. Because fertilization increases the risk of Cd movement into the food chain, several countries have implemented regulations limiting the amount of Cd that can be present in P fertilizers. Scientific risk assessments have been conducted that show that the use of P fertilizer containing current levels of Cd is generally safe and does not pose risk to the farmers that use them or the general public.

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