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ORIGINAL PAPER

Fertilizer usage and cadmium in soils, crops and food

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Abstract Phosphate fertilizers were first implicated by Schroeder and Balassa (Science 140(3568): 819–820, 1963) for increasing the Cd concentration in cultivated soils and crops. This suggestion has become a part of the accepted paradigm on soil toxicity. Consequently, stringent fertilizer control programs to monitor Cd have been launched. Attempts to link Cd toxicity and fertilizers to chronic diseases, sometimes with good evidence, but mostly on less certain data are frequent. A re-assessment of this "accepted" paradigm is timely, given the larger body of data available today. The data show that both the input and output of Cd per hectare from fertilizers are negligibly small compared to the total amount of Cd/hectare usually present in the soil itself. Calculations based on current agricultural practices are used to show that it will take centuries to double the ambient soil Cd level, even after neglecting leaching and other removal effects. The concern of long-term agriculture should be the depletion of available phosphate fertilizers, rather than the negligible contamination of the soil by trace metals from fertilizer inputs. This conclusion is confirmed by showing that the claimed correlations between fertilizer input and Cd accumulation in crops are not robust. Alternative scenarios that explain the data are presented. Thus, soil acidulation on fertilizer loading and the effect of Mg, Zn and F ions contained in fertilizers are considered using recent Cd^{2+}, Mg^{2+} and F^{-} ion-association theories. The protective role of ions like Zn, Se, Fe is emphasized, and the question of Cd toxicity in the presence of other ions is considered. These help to clarify difficulties in the standard point of view. This analysis does *not modify* the accepted views on Cd contamination by airborne delivery, smoking, and industrial activity, or algal blooms caused by phosphates.

Keywords Cadmium · Metal toxins · Phosphate · Crops · Fertilizers · Soils · Food

Introduction

That fertilizers could be a serious source of Cd contamination of agricultural soils, and consequently, the diet was suggested almost half a century ago by Schroder and Balassa (1963). This view has now become a mainstream paradigm (McLaughlin and Singh 1999; Loganathan et al. 2008; Grant and Sheppard 2008) that has raised much public concern (Wales University 2013; Tòth et al. 2016), as also with the overuse of pesticides (Lechenet et al. 2017). Cd is a prime example of trace elements (TE)

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that have caused concern. Sheppard et al. (2009) state that the "key question for agriculture is, after decades of use, could these trace-element additions result in the deterioration of soil quality?" The presence of Cd in the environment, augmented by industrial activity, years of coal and fossil-fuel usage, mining, etc., is a serious health hazard and its monitoring is essential, given its known accumulation in the food chain with the potential for causing chronic diseases of the renal, pulmonary, cardiovascular and musculoskeletal systems (ATSDR 2013; Jarup et al. 1998). However, controversy exists regarding a number of aspects (Chaney 2012; Roberts 2014), and a re-assessment of the "accepted" view of Cd enrichment of soils by Cd in P-fertilizers is timely, given the larger body of data available on fertilizer use (Sillanpää and Jansson 1992; World Bank 2016).

Many tropical agricultural communities (e.g. in India, Sri Lanka, El Salvador, Nicaragua, Egypt, China) are facing a new type of chronic kidney disease of unknown aetiology (CKDu) appearing even though recognized causes (e.g. diabetes, hypertension) are absent (Jayatilake et al. 2013; Gifford et al. 2017). Such CKDu is also found in the developed world including Canada (Arora et al. 2013). Some authors (excluding the present author) have proposed that Cd, etc. from agrochemicals to be factors causing such chronic kidney disease (Wanigasuriya 2012; Jayatilake et al. 2013; Mott et al. 2013). The existence of CKDu communities adjacent to non-CKDu communities subject to similar agrochemical exposure is inconsistent with agrochemical-origin theories of CKDu (Dissanayake and Rohana 2005; Illeperuma et al. 2009; Wasana et al. 2017; Dharma-wardana 2017; Edirisinghe et al. 2017). Traditional agricultural communities have a relatively low fertilizer usage. For instance, in 2002 El Salvador (which has CKDu) used about 71 kg/ha, while New Zealand (no significant CKDu) used 1836 kg/ha according to World Bank (2016) data. These show an anti-correlation with fertilizer use and chronic disease, but many authors readily implicate the "green revolution" and P-fertilizers for chronic health issues of unknown aetiology, e.g. Bandara et al. (2010).

In this study, we deal mainly with Cd toxicity, while our discussion can be easily adapted to other heavy-metal contaminants as well. We review the evidence and counter-evidence that exist to claim that increased fertilizer usage is correlated with increased metal toxin levels in the soil, together with an increase in Cd in crops grown in such soil. International regulatory bodies have set a 60–70 µg tolerable maximum daily intake for an average adult (JECFA 2011). However, some societies traditionally consume rice, or sea food in diets with Cd exceeding such limits, while remaining quite healthy (Sirot et al. 2008). Hence, noting possible counter-action among heavy-metal contaminants and micronutrients, a simple model for joint toxicity effects is considered in the last part of this study.

Phosphates have been mined for the last 150 years. It is a non-renewable resource that must be mined from nature and cannot be artificially produced. This is a powerful argument for the reduction in mineral phosphate inputs in agriculture where possible. However, it is argued here that contrary to the commonly held paradigm that "the addition of phosphate fertilizers to the soil proportionately increases the bio-available soil Cd", simple mass conservation limits any such increase to extremely small margins, well within the uncertainties of soil chemistry, bio-availability and uptake of metal ions by crops. It is suggested that controlling the Cd content in fertilizers will have no discernible effect on the Cd content in soil and in crops. Hence, the increasingly restrictive efforts of some governments, esp. in the EU to minimize dietary Cd inputs via fertilizer control, will prove to be futile. The European Food and safety Authority (EFSA) set the recommended tolerable weekly level in the diet at 2.5 µg Cd/kg of body weight in 2012, and proposals to reduce the Cd content in fertilizers correspondingly have been made. Even according to 2001 regulations more than a decade ago, the amount of Cd allowed was set at 400 mg/kg of fertilizer in USA (e.g. in Washington state, for, 45% P_2O_5 product), while the EU countries proposed setting limits averaging close to 20 mg/kg of P_2O_5. In countries like Sri Lanka where public concern has been raised by groups pushing for "traditional agriculture", impractical limits as low as 3 mg/kg of fertilizer have been imposed with no basis in science (SLSI 2016). Roberts, commenting on this restrictive trend, remarks in 2012 that "the rationale for the limits provided by the proposal provides little scientific evidence justifying a limit of 20 mg Cd/kg P_2O_5 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 P_2O_5, much less pose human health risks" (Roberts 2014). Similar views are found in recent risk-assessment studies by other authors, e.g. Chaney (2012), or the Wageningen University report (Rietra et al. 2017).

In the following, we present further evidence against the conventional paradigm of Cd accumulation by fertilizer inputs and examine mechanisms where fertilizer addition into soils triggers *existing soil Cd* making it bio-available to plants. Mechanisms like (1) the effect of increased acidulation due to fertilizer addition, (2) competition from ionic forms of Zn, Se, Fe, (3) salinity effects, (4) dissolved organic carbon, soil and plant characteristic are usually examined, but in addition we consider ionic mechanisms due to added F and Mg ions, previously inadequately treated in discussions of Cd dynamics in soils. Hence, if the analysis given here is found to be valid on further investigation, Cd uptake by crops from soils may also require controlling the Mg and F content in fertilizers and in the soil and ensuring an excess of bio-available zinc ions over bio-available Cd ions.

Cadmium accumulation in the soil and fertilizer use

Subsequent to the suggestion of Schroeder and Balassa (1963) that the use of phosphate fertilizer leads to Cd accumulation in soils, interest in monitoring soils for cadmium grew rapidly, with Kjellstrom reporting in 1979 that measured Cd levels in wheat doubled from 1920 to 1979 (Kjellstrom 1979), while Singh claimed in (1994) that the application of phosphate fertilizer for a period of 36 years resulted in a 14-fold increase in Cd content of surface soils (Singh 1994). Sheppard et al. (2009) considered not only inputs from fertilizers, but also inputs from the atmosphere, manures and municipal bio-solids. They concluded that in many cases, steady-state concentrations for Canadian soils could be toxic and that in 100 year, the soil concentrations may be up to threefold higher than the present background. In contrast to Singh (1994), Sheppard et al. (2009) considered that contributions from trace elements in fertilizers are perhaps the most uncertain.

A noteworthy step was the publication of the soil bulletin No. 65 (FAO65) of the Food and Agriculture Organization (FAO) (Sillanpää and Jansson 1992), presenting the status of Cd, Co and Se in soils and plants of thirty countries, determined within a uniform protocol enabling international comparisons. The publication by Sillanpää and Jansson (1992) sponsored by the FAO will be referred to as FAO65 when convenient. Data from Figure 5 given in FAO65 are shown in Fig. 1, where a clear correlation of the Cd content in the soil extracted using a mild reagent (see below) is shown for a time duration of three years of P-fertilizer application.

Sillanpää and Jansson concluded that "although the fertilization data covers only three years, the relatively firm correlations leave no doubt as to the increasing effect of phosphorous fertilization on the Cd contents of both plants and soils". However, from this observation it also needs one further tacit *assumption* to conclude that this increased Cd comes from the Cd impurities contained in the P-fertilizers *added* to the soil annually. Sillanpää and Jansson do not in fact make that assumption, but many readers may easily do so. This may be called the "Soil-Cd Enhancement by Fertilizers" (SCdEF) assumption and is articulated quite clearly in many other works (Mulla et al. 1980; McLaughlin et al. 1996; Eriksson 2001; Moolenaar 1999; Jansson 2002; Premarathne 2006; Tòth et al. 2016). In the following, we argue that the data can be more correctly interpreted as a case of the P-fertilizer triggering the conversion of already existing soil Cd to an "available form" of Cd extractable by mildly acidic reagents.

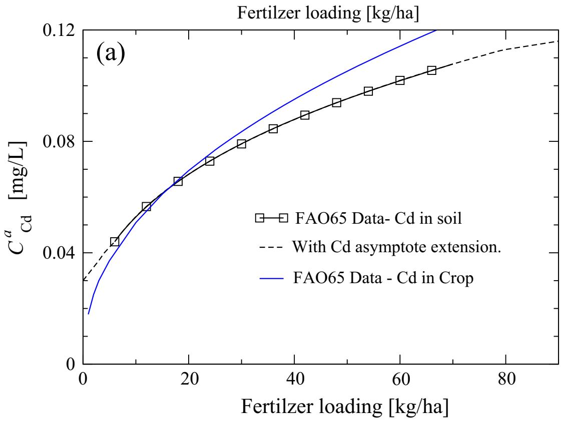

Fig. 1 (Online colour) Soil Cd (extracted using a mild regent) C^a_{Cd} as functions of P-fertilizer input, (FAO Soil Bulletin No. 65, Sillanpää and Jansson 1992) and its extension (dashed lines) using asymptotic constraints

Hence, it is instructive to re-examine many of the studies of the period when the SCdEF paradigm was developed. McLaughlin et al. (1996) present a soil-balance calculation in the caption to their Table 2 which states the following. "Assumes 20 kg P/ha applied per wheat crop and 80 kg P/ha per potato crop and fertilizer contains (per kg P) 50 mg As, 300 mg Cd (250 mg Cd for potatoes), 5 mg Hg, 200 mg Pb and 200 g F. Element inputs in irrigation water assumed to be negligible, although F may be a significant impurity in some waters". They also assume a fertilizer-application depth of 10 cm of soil, taken to have a density of 1.3 kg per litre. No leaching of the metal impurities added to the soil via the fertilizer is included, but such corrections can be easily applied. McLaughlin et al. (1996) report analytical data for a variety of phosphate fertilizers. We have included a selection of these in Table 1 together with other data, e.g. for Sri Lanka and India, where some regions are affected by chronic kidney disease. Columns 2 and three in the table enable one to roughly convert among the various methods of indicating the Cd concentration in rock phosphates, viz. as mg/kg of rock, mg/kg of P or mg per kg of P_2O_5, with the P/P_2O_5 also dependent on the origin of the mineral although a factor of around 0.4 is sometimes used. In citing published work, we have retained the units used by the cited authors.

Table 1 Cd and P concentrations in some rock phosphate sources for fertilizers

Source	Cd (mg/kg)	P%	Cd (mg Cd/kg P)
Russia[a]	0.2	17	1
China(Yunan)[a]	5	14	35
Sri Lanka			
(Eppawala)[†]	<3	14	34
(imported)[b†]	2.3–46	7–20	325
India (Mussoorie)[c†]	8	12	62
Egypt[a]	8–9	13	61–67
Morocco[a]	12–34	14–15	88–240
USA (N.C.)[c]	33	15	240
Florida	8–9	13	69
Nauru (NZ)[a]	100	15.6	641

The total P_2O_5 contents are very variable, ranging from 15–17% (Russia, Chile) to 35–36% (Senegal, Togo), with an average of 27%. Phosphate rocks containing less than 20% P_2O_5 need beneficiation to justify transportation costs. A minimum of 25% P_2O_5 is usually required

[a] McLaughlin et al. (1996)

[b] Zapata and Roy (2004)

[c] Van Kauwenbergh (1997), [†] Estimated

For single superphosphate (SSP) produced by reacting phosphate rock with sulphuric acid, produced by acting on phosphate rock with phosphoric acid, most of the Cd in the phosphate rock is transferred to the SSP. In wet-process phosphoric acid (WPA), about 55–90% of the Cd is transferred to the acid with the balance to the gypsum (a byproduct). Ammonium phosphates (e.g. monoammonium phosphate [MAP] and diammonium phosphate [DAP]) are produced from WPA. Their Cd content can range from <1 to >100 mg/kg, depending on the mineral.

Cadmium input into the soil on application of phosphate fertilizer.

In order to examine more closely the validity of the SCdEF assumption, we recalculate the incremental change in the soil Cd concentration, ΔC^s_{Cd} on addition of P-fertilizer to the soil. We summarize the result using the symbols A^F for the amount of fertilizer (kg/ha) applied annually, C^F_{Cd} for the concentration of Cd (mg/kg) in the fertilizer, d_s the depth of the soil layer in cm, while ρ_s is the density of the soil in kg/l. The total concentration of soil Cd is denoted by C^s_{Cd}. Then, the change ΔC^s_{Cd} on fertilizer loading is:

$$\Delta C^s_{\mathrm{Cd}} = \frac{A^F C^F_{\mathrm{Cd}}}{d_s \rho_s} \times 10^{-8}, \quad \text{Cd, g/kg of soil} \qquad (1)$$

$$= \frac{10 A^F C^F_{\mathrm{Cd}}}{d_s \rho_s}, \quad \text{Cd ng/kg of soil} \qquad (2)$$

The change of Cd concentration, being very small, is given in nanograms per kg of soil in Eq. 2. We have ignored the additional inputs (e.g. via airborne Cd and via irrigation water) although airborne Cd may be a major source of Cd deposited on soils in industrialized countries. The Cd inputs via irrigation water can be neglected in normal farming environments in most countries like the EU, Canada and USA, and even in less regulated non-industrial environments.

For instance, in a publication relating to CKDu in Sri Lanka (Dharma-wardana et al. 2015) the authors considered the non-point source transport of phosphate by the irrigation waters of one of the major rivers (Mahaweli) of Sri Lanka, but the amounts of Cd and other metal toxins transported in the same manner would be quite negligible, being present in parts per million compared to macronutrients. Thus, consider one hectare of the tea growing region where the rivers originate, with an average annual rainfall of 2 m, and an annual average fertilizer input of 100 kg/ha, containing 30 mg/kg of Cd (or any such impurity like As). If half the rainfall contributes to the river run-off, the concentration of Cd from the fertilizer inputs is only 0.3 parts per trillion. On the other hand, macronutrients (e.g. phosphates) are important pollutants that cause algae blooms. Diyabalanage et al. (2016a) confirmed by detailed analytical studies of Mahaweli river water that metal toxin levels are indeed below maximum allowed limits (MALs). What is measured is the wash-off from the *existing* soil cadmium, as the contribution from fertilizer inputs is negligible. Similarly, Jayasinghe et al. (2015) showed that toxin levels in irrigation waters were well below the usual MALs and hence required no reverse-osmosis treatment to render them safe. McLaughlin et al. (1996) also disregard irrigation-water inputs of Cd into farm soils. A study of the translocation and dispersion of pesticides by irrigation waters of the Mahaweli river also showed the effect to be negligible (Aravinna et al. 2017). That this should be so is also easily ascertained by a simple calculation based on mass balance.

Essentially, the same analysis as for Cd can be used for As, Pb and other heavy-metal additions to crops via fertilizers, be they wheat, barley, rice or any other crop, and the concentration *increment* $\Delta C^{s}_{\mathrm{Cd}}$ turns out to be in parts per trillion to fractions of parts per billion (μg/kg of soil). Only a fraction of this would be bio-available. This is further lowered if we take into account any leaching effects of rain fall and irrigation wash-off (esp. under monsoonal conditions in the tropical belt).

Thus, even after a millennium of industrial agriculture using a typical rock phosphate fertilizer (see Table 1), the total Cd inputs will remain negligible even for accumulations over centuries (Dharma-wardana 2017).

In contrast, the calculations of the "Cd budget" given in publications by various authors usually extract a different conclusion that supports the SCdEF paradigm. The ambient total Cd in the soil, C^{s}_{Cd}, in European soils (within the "plough layer") can range from 0.05 mg/kg to higher values (in industrialized areas e.g. in Belgium, Hungary, see FAO65, i.e. Sillanpää and Jansson 1992). Soil Cd amounts in Shipham, Wales, UK, rang from 9–360 mg/kg (Wales University 2013). A mean value of 0.4 mg/kg is sometimes used in model calculations for the EU (Rietra et al. 2017), while 0.3 mg/kg has been proposed by Smolders and Six (2013) as an average for the EU. Scandinavian soils have a lower average of 0.2 mg/kg (Eriksson et al. 1997).

Interestingly, the Cd concentrations in the soil of Sri Lanka are reported to range from 0.42 mg/kg in forest soils, to as high as 5 mg/kg in lake sediments (Rohana Chandrajith and Dissanayake 2012), and are consistent with values found in the WHO-sponsored study (Jayatilake et al. 2013). However, most of the Cd in Sri Lankan soils is found as bound Cd, since the Cd contents in water and in soil solution were found to be < 3 μg/L and are below the WHO MAL (Jayatilake et al. 2013).

Tòth et al. (2016) raised the interesting possibility that the low values of Cd in E. Europe, in comparison with W. Europe, are possibly due to the use of Russian P-fertilizer in E. Europe, as opposed to Moroccan fertilizer used in W. Europe. However, the calculations presented in section "Cadmium input into the soil on application of phosphate fertilizer" show that the Cd content of Moroccan P-fertilizer cannot account for such a difference. The high content of soil Cd in industrialized regions (e.g. in W. Europe) should be attributed to industrial activity, coal-power production and Cd deposition from emissions. These are far more important than Cd inputs via P-fertilizer applications. Fortunately, according to Smolders and Six (2013), airborne Cd sources have decreased by a factor of five between 1980 and 2005. They propose a 0.35 g $\mathrm{ha}^{-1}\,\mathrm{y}^{-1}$ as the mean Cd airborne deposition rate for the EU region currently. We limit our study to soil Cd and Cd from fertilizer inputs.

In order to understand the difference between our conclusions and the traditional approach to the soil budget for Cd, we review such a calculation (Eriksson 2001) for southern Sweden extracted from the Doctoral thesis of Jansson (2002), Table 1, column 2. Eriksson considers the Cd inputs and outputs (g $\mathrm{ha}^{-1}\,\mathrm{y}^{-1}$) in his Cd budget.

1. P-fertilizer, 0.12g from 10 kg P ha^{-1} containing 12 mg Cd kg^{-1} of fertilizer.

2. Deposition: 0.7g from airborne sources, rain, etc. (Note that Smolders and Six 2013 proposed a 0.3 g annual addition from deposition as an EU average in 2013.)
3. From lime, 0.02g Cd added to the soil.
4. Hence, total Cd input = 0.84 g ha^{-1} y^{-1}.

Cd removal from soil is evaluated as follows:

1. Crops, 0.23g by plant uptake, removal of roughage, stubble, etc.
2. Leaching, 0.40g Cd, assuming a top soil layer 25 cm deep.(N.B., much higher leaching rates are proposed in recent studies as European averages, e.g. in Smolders and Six 2013).
3. Total amount removed = 0.63g.

From the above date, we calculate the change in the soil Cd concentration purely due to fertilizer input.

1. Hence, amount of Cd claimed for fertilizer = 0.12 g ha^{-1} y^{-1}.
2. Soil depth 0.25 cm, soil volume = 25 × 10^5 litres/ha.
3. Soil density 1.3 kg/L, soil weight = 3.25 × 10^6 kg/ha.
4. Total soil Cd in the plough layer with 0.2mg Cd/kg of soil = 650 kg/ha.
5. Change in soil Cd concentration= $\Delta C^s_{\mathrm{Cd}} = 43 \times 10^{-9}$ g/kg.

This leads to a total accumulation of 0.21 g ha^{-1} y^{-1}, 1/3 of which is due to deposition. The amount that may be claimed for P-fertilizer is 0.12 g ha^{-1} y^{-1}, and this is taken to support the SCdEF paradigm, leading to the conclusion that accumulation of Cd impurities in fertilizers poses a serious health risk. However, this accumulation produces only a *change* in Cd concentration $\Delta C^s_{\mathrm{Cd}} = 43 \times 10^{-9}$ g/kg of soil, i.e. a change of the order of 40 ng/kg which is truly negligible. Thus, Eriksson's Cd budget and those of other workers are consistent with our calculation giving mere nanogram/kg changes in Cd *concentration* in the soil. The mean median Cd concentration in top soils (0.2 mg/kg) as reported by Eriksson et al. (1997) is 0.47 × 10^4—some ten thousand times bigger than the increase. Hence, the parts-per-trillion increase (43 × 10^{-9} g/kg/y) in Cd concentration due to fertilizers is negligible. However, unlike the 0.12 g ha^{-1} y^{-1} Cd input of the P-fertilizer, the 0.7 g ha^{-1} y^{-1} airborne deposition of airborne Cd does not necessarily get ploughed into a 25-cm-deep soil layer, but affects a few centimetres of the topmost layer, causing more drastic changes in the soil Cd concentration in the near surface.

McLaughlin et al. (1996) and Loganathan et al. (2008) have given estimates for the doubling of the background soil Cd and F due to fertilizer addition. We take Loganathan et al. (2008) as an example of such calculations and review their Table 2 with suitable complementary information in Table 2. It is of course not the doubling of the ambient levels that matter, but their reaching the maximum allowed limits (MALs) for agricultural soils. However, since the determination of the MALs is itself an uncertain toxicological issue, the doubling time is an important measure.

We re-evaluate the above data using fertilizer inputs based on current farming practices where smaller amounts of fertilizer are used, since the fertilizer input is based on the soil Olsen-P levels as well. The amount of P-fertilizer/ha/y needed depends on the target harvest/ha as well as on the available phosphorous in the soil (Table 3). Furthermore, since a large fraction of the world consumes rice, we have included recommended fertilizer additions, as given by the Dept. of Agriculture, Sri Lanka (DOA-SL 2016), noting that TSP is recommended for paddy cultivation (3–4 month irrigated crop) as the phosphate is needed in the short term. Current agricultural practice is to use a mixture of mineral fertilizers and other (e.g. compost) fertilizers to get higher yields. Hence, based on Table 3, we have chosen the amount of fertilizer to be a phosphate fertilizer equivalent to 70–100 kg/ha rock phosphate, which corresponds to the 15–9 Olsen-P type of soil for potatoes. Wheat needs about a fourth of the amount of fertilizer, and hence, we may assume it to be similar to paddy cultivation discussed below. In practice, the harvest can be significantly increased by using a mineral+-compost mixture, without going to higher mineral-fertilizer inputs. Similarly, targeted application of fertilizer to the root zone, or banded-application methods can be used to reduce the needed fertilizer input, as is increasingly the current agricultural practice.

Hence, we use the figure of 70–100 kg/ha/y of rock phosphate (RP) or 15 kg P/ha/y as our nominal fertilizer input for potato cultivation for typical soil Olsen-P levels. Rock phosphate will be assumed to

Table 2 Estimated time for doubling the concentrations of Cd and fluoride as given by Loganathan et al. (2008), assuming a soil density 1.0 kg/l, a soil depth of 10 cm, and ignoring small corrections due to pasture and animal uptake, removal, leaching, etc.

Element *X*	Input of P-fert. (kg p/ha/y)	Equiv. kg of rock fertilizer	*X* in fert. (mg/kg)	Rate of *x* added. (g/ha/y)	Soil conc. of *X* (mg/kg)	Years to double the conc. (y)
Cd	30	200	42	~ 8.4	0.3	36
F	30	200	30,000	~ 6000	300	51

Table 3 (a) P-fertilizer requirement as a function of (Olsen-P) phosphate availability in the soil and the target harvest for potatoes, based on agricultural practices in southern Ontario and northern Minnesota (Rosen and Bierman 2018). (b) Recommended TSP fertilizer for rice cultivation in Sri Lanka as a function of Olsen-P phosphate (mg/kg) in the soil (DOA-SL 2016). Note that the P-fertilizer amounts for paddy cover two rice-growing seasons of the year

↓ Target harvest[a] 30–35 tonnes/ha/y potato	Olsen-P → (ppm)	0–3	4–7	8–11	12–15
Fertilizer[b], as P_2O_5	(kg/ha/y)→	112	82	55	28
As P	”	42	31	20	10
As Rock P	”	280	205	135	70
Paddy cultivation	Olsen-P→	0–5	5–10	10–15	15–20
Triple super phosphate	(kg/ha/y)	70	40	0	0

[a] Increased harvest, e.g. 45 tonnes/ha/y, can be obtained by using the inputs recommended for the lower Olsen-P range

[b] P_2O_5 concentration in concentrated superphosphates ~45%, while typical rock phosphates may contain about 38–42%

contain 30 mg/kg of Cd and 30 g/kg of F (e.g. as in Moroccan RP). In the case of paddy cultivation, we take 40 kg/ha/y of TPS as the typical input, based on DOA-SL (2016), Amarasiri (2016), specifications for both cultivation seasons. Since the conversion of RP to TSP leads to the transfer of a part of the Cd and F content to gypsum and other by-products, the Cd and F content in the TSP will be taken as 15–20 mg of Cd per kg and 15–20 g F per kg of TSP, respectively, while the parent rock phosphate may have contained 25–30 mg/kg. Hence, our calculations which revise those of Loganathan et al. (2008) are given in Table 4.

Currently, there is greater effort to reduce fertilizer usage than in an earlier era, and our calculations (using quantities conforming to current usage patterns) give room for greater optimism. It may take timescales of a millennium to double the concentration of Cd in soils under paddy cultivation, even if we neglect removal processes (leaching, monsoonal run-off and removal when crops, roughage, straw, etc., are taken away from farmland). Even in the case of potato farming, even if we adopt 200 kg/ha/y rock phosphate inputs (as in Loganathan et al. 2008), it will take over a century to double ambient soil concentrations of Cd or F. When such timescales are considered, the effect of other ions and the incorporation of Cd, F into bio-unavailable forms in the clay need to be considered. Hence, the major concern of long-term agriculture should be the depletion of stocks of P-fertilizer and not below-threshold contributions to the concentration of trace metals coming from fertilizer inputs.

Fertilizer inputs for wheat are a factor of 4 less than for Potato (McLaughlin et al. 1996). As seen from Table 4 and the associated discussion, fertilizer inputs for rice are also low. Hence, Cd and other fertilizer-based inputs can be cut down by perhaps a factor of 4, thereby increasing the soil Cd doubling time to millennium timescales by adopting the following steps.

1. Potato diets could be increasingly replaced by rice or wheat-based diets as the needed fertilizer inputs are much smaller.
2. In addition, genetically modified potato cultivars which mimic rice-like fertilizer response may be possible.

Some caution must be used with published data. Page 27 of the Wageningan study (Rietra et al. 2017) states

Table 4 Estimated time for doubling the concentrations of Cd and fluoride using current farming inputs for potatoes, and for paddy, assuming a soil density 1.3 kg/l, a soil depth of 20 cm, and ignoring corrections due to pasture and animal uptake, removal, leaching, etc.

Element × Potato	Input of P-fert. (kg P/ha/y)	Equiv. kg of rock fertilizer	X in fert. (mg/kg)	Rate of x added. (g/ha/y)	Soil conc. of X (mg/kg)	Years to double the conc. (y)
Cd	15	100	30	3.0	0.3	260
F	15	100	30,000	3000	300	260
Paddy	(kg/ha/y)	–	(mg/kg)	(g/ha/y)	(mg/kg)	(y)
Cd	40 (TSP)	–	20	0.8	0.3	975
F	40 (TSP)	–	20,000	800	300	975

In the case of paddy cultivation, leaching and run-off due to monsoonal rains can be considerable and increases the time for doubling ambient concentrations

that "the average annual inputs of fertilizers to agricultural soils are of the order of one to three g/ha/y. At a Cd level in soil of 0.4 mg/kg, assuming a rooting zone of 20 cm and bulk density of 1.2 kg/L, this amounts to a total Cd pool of approx. 960 g/ha". In effect, the correct value is 960 kg/ha; we give this simple calculation for the convenience of the reader.

1. Soil volume/ha $= 10,000\,\text{sq. m} \times 0.2\,\text{m, i.e.}\,2000\,\text{m}^3.$
   $= 2 \times 10^6$ litres
2. Soil mass/ha $= (2 \times 10^6) \times (1.2)$ kg.
   $= 2.4 \times 10^6$ kg.
3. Mass of Cd/ha $= (2.4 \times 10^6) \times (0.4 \times 10^{-3})$ kg.
   $= 0.96 \times 10^3\ \text{kg} = 960\ \text{kg}.$

Thus, the maximum 3 g/ha/y corresponds to a change of about three parts per million, and not parts per thousand, as implied in the Wageningen study. Nevertheless, the authors had correctly noted that "reducing the Cd load by fertilizer would have a very minor effect on the Cd pool during the first few decades...". In fact, it can be further strengthened to say that there would be a very minor effect even in centuries, rather than decades. That is, European data also give us room for more optimism than the prognosis from McLaughlin et al. (1996), Loganathan et al. (2008) and other pioneering studies. A similar analysis can be used to show that trace amounts of arsenic found in P-fertilizers have a negligible effect on the ambient concentration of soil arsenic (Dharmawardana 2017). Hence, extreme public policies on Cd and As content in P-fertilizers, driven by the SCdEF paradigm, cannot be justified by the available scientific data. In fact, the available world reserves of P-fertilizers would probably run out long before the soils reach anywhere near the MALs for adverse health effects.

Similarly, the conclusion by Jayasumana et al. (2015) that trace amounts of Cd, As, etc., found in agrochemicals have an environmental effect leading to chronic kidney disease is completely in error, as the trace elements, when distributed in farm applications contribute mere fractions of parts per billion which are far below accepted MALs for chronic toxicity.

Furthermore, the origin of the increased Cd concentration detected in the soil, and in crops, c.f., Fig. 1, using a mild regent, cannot be due to the Cd coming from the fertilizer. It is released from the soil itself, by the action of the fertilizer on the ambient soil Cd. We examine this further in the next section.

The effect of P-fertilizer on available soil Cd.

The discussion in the previous paragraphs shows that modifying the Cd content in the P-fertilizer, e.g. using a low-Cd fertilizer as opposed to a high-Cd fertilizer, should show no effect on the Cd levels available in soil solution to crops grown in most soils. In this section, we give experimental evidence in support of this conclusion that we obtained from considerations of mass conservation.

Figure 1 usually invoked to support the SCdEF paradigm actually implies the opposite (see section "Change of soil pH due to P-fertilizer loading, releasing Cd into the soil solution"). Soil Cd data reported in Sillanpää and Jansson (1992) had been determined using the acetate–ammonium acetate Na_2EDTA (AAAc-EDTA) reagent which measures "available" or "easily extractable" Cd rather than the total concentration of Cd per kg of soil. The plot shows that on application of 70 kg ha^{-1} y^{-1} of P-fertilizer for three years, the available soil Cd concentration had reached 0.12 mg/L, while a much weaker loading at $\simeq 5$ mg/kg gives $C_{\rm Cd} \simeq 0.04$ mg/L. Taking the density of soil to be 1.3 kg/L, mean increment, $\Delta C^s_{cd} = (0.12 - 0.04)/(3 \times 1.3) = 0.0205$ mg/(kg.year). However, typical ΔC^s_{cd} are in the nano- to microgram range (at the most), as seen from Sect. "Cadmium input into the soil on application of phosphate fertilizer" and Eq. 1.

Hence, this result is 20,000 to 20 times too large for it to have originated from the Cd amounts that were input via the P-fertilizer used. As airborne Cd and other inputs were excluded in the experiments reported in FAO65 (Sillanpää and Jansson 1992), conservation of mass implies that almost all of it originated from *the pre-existing Cd pool* in the soil.

The Cd was initially not extractable using AAAc-EDTA. It is converted to "available" Cd by some mechanism (see below) activated by the agrochemical inputs, and converted to ionic Cd accessible with the mild reagents like AAAc-EDTA, and by plants. Of course, the total Cd concentration $C^s_{\rm Cd}$ can be determined by standard methods using extraction with strong acids (e.g. 2M nitric acid). Experimental data fitted to algebraic formulae connecting the AAAc-EDTA extractable Cd, taken to be of the form $C^a_{\rm Cd} = a + bC^s_{\rm Cd}$ or expressed as log-scaled regressions have been quoted by many authors (McLaughlin et al. 1996; Smolders and Six 2013), and in FAO65.

Field experiments showing that the Cd content of the fertilizer may have little or no impact on the soil Cd concentration and on the crop-Cd content are found even in the literature of the period and are alluded to in reviews by various authors, e.g. McLaughlin et al. (1996), and Grant et al. (2002). Here we refer to a number of such examples,

(a) Sparrow et al. (1992) compared Cd uptake by potatoes fertilized with both low- and high-Cd DAP in field trials. They found little differences in Cd uptake between the two cases, with Cd concentration in tubers being related to the rate of P applied, rather than to the amount of Cd applied.

The Cd content of durum wheat fertilized with MAP containing varying amounts of Cd (0.2, 7.8, and 186 mg/kg) and grown at 11 different locations over a three-year period had no significant dependence on the Cd content in MAP (Grant et al. 2002). Thus, in spite of soil differences in the 11 locations, the result remained robust.

(b) P-fertilizers are usually applied to the soil together with N and K fertilizers. Nitrogen fertilizers (e.g. urea, ammonium salts) are converted by soil bacteria to nitrates, generating acids (H^+ ions) in the soil, while base ions are transferred to plants. Hence, additional availability of Cd in the presence of phosphates may also be caused by accompanying N fertilizers. This may be viewed as due to increased leaching of Cd fixed in the soil and conversion to Cd^{2+} in soil solution, caused by decreased pH.

Already in 1976 Williams and David (as reviewed in McLaughlin et al. 1996) showed that the concentration of Cd in wheat grains harvested from soils treated with superphosphate and ammonium nitrate exceeded that with superphosphate alone by a factor of two.

(c) McLaughlin has also discussed the work of Sillanpää and Jansson (1992), (and those of Williams and David as reviewed by McLaughlin 1992) where it is shown that the addition of P to a soil (with no change in Cd input) increases Cd uptake through a stimulation of root proliferation in the zone into which P is added.

(d) Onyatta and Huang (2005) report an increase in available Cd in the soil, induced by the use of P-fertilizer used in the form of Idaho monoammonium phosphate. They attribute their observations to the release of pre-existing Cd from the soil as well as to the Cd coming from the fertilizer.

(e) Comparisons between Cd content in crops grown using commercial P-fertilizer and organic fertilizers in field experiments for rye, carrots, potatoes showed no significant differences in Cd levels (Jorhem and Slanima 2000),

(f) In fact, livestock manure from animals fed with soybean and other relatively Cd-rich grains provides more Cd to fields than from phosphate fertilizers Keller and Schulin (2003), and hence, organic-farming practice may also need monitoring for Cd inputs.

Effect of phosphate fertilizer on the soil.

Soil is a complex subsystem containing clay, sand, organic materials loosely called "humus", water, electrolytes and dissolved gases, interacting with an interpenetrating subsystem consisting of living organisms made up of micro-organisms, insects, "bugs" and plants. The plants as well as the soil organisms need the mineral nutrients, water as well as some of the organic matter for their existence, and exchange material among them mostly via the soil. The exchange of nutrients between the plant subsystem and the soil can be described by transfer coefficients, and they need to be determined by experiment.

Even the processes that occur entirely in the soil, e.g. the behaviour of the added fertilizer, and its partitioning among clay, humus and the aqueous phase of the soil (called the "soil solution") are too complex for us to treat using first-principles atomistic models. Hence, it has become the practice to characterize the soil using various macroparameters of the soil, e.g.

(a) The pH, soil texture characterized by a texture index (TI, see FAO65), organic matter content (OMC) γ, cation-exchange capacity (CEC) ξ, salinity ζ, hardness η and electrical conductivity σ;
(b) The concentrations of specific ions (micronutrients) like B, Cu, Mn, Mo, Zn;
(c) Elements toxic to humans, like Cd, Pb, Hg, As.

However, while concentrations of micronutrients and toxins are specified in "defining" a soil, macronutrients like N, K, P are not specified as they are overwhelmingly controlled by fertilizer loading. Fertilizers themselves affect the pH of the soil, and nitrogen fertilizers trigger soil-microbial action generating acids. Hence, the crop soils need pH adjustments which are usually achieved by the addition of ag-limes like calcite and dolomite.

An element like Cd can exist in several forms in the soil:

1. Cd ions chemically replacing Al or Mg atoms in octagonal environments, or replacing Si atoms in tetrahedral environments in clays. Here we are not implying any Cd-based crystal types, but only point-defect substitutions. These are soil-bound Cd with a concentration C^{b}_{Cd} and are intermediate in stability.
2. Fully or partially hydrated exchangeable Cd ions electrostatically attached to edges, oxide groups, etc., with a concentration $C^{\mathrm{xb}}_{\mathrm{Cd}}$. These ions may migrate into internal sites with time, becoming more strongly bound, though never as strongly as Mg or Al.
3. Fully hydrated Cd ions "available" in soil solution at a concentration of C^{a}_{Cd}. These aqueous Cd ions carry a solvation sheath of water molecules. However stable associations with other ions like fluoride forming a strong $(\mathrm{Cd\text{-}F})^{+}$ complex ion (see Fig. 2) can occur. It can be shown that such complexes are more stable than the hydrated Cd^{2+} ion or the hydrated F^{-} ion existing without ion association (Dharma-wardana 2017). In such cases, essentially all the aqueous Cd ions are in associated from since the F^{-} concentration is largely in excess of the Cd^{2+} concentration in most soil solutions. To complicate matters, such associated ions can also attach electrostatically to edges, and surfaces of soil particles, and hence also contribute to $C^{\mathrm{xb}}_{\mathrm{Cd}}$. As they have a lowered positive charge, they are more weakly bound electrostatically.

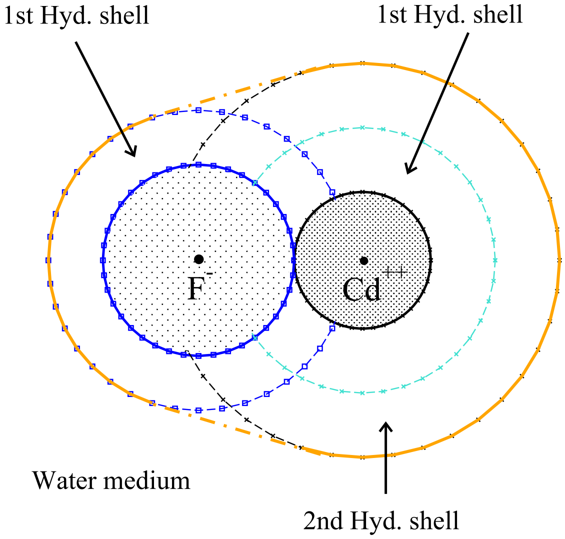

Fig. 2 (Online colour) A schematic diagram of the $(\mathrm{Cd{-}F})^{+}$ ion pair together with the hydration shells of the Cd^{2+} ion and the F^{-} ion prior to pairing. The divalent Cd^{2+} ion holds tightly two hydration shells, while the 'monovalent F^{-} holds only a single hydration shell. The water outside the joint hydration shell of the pair "sees" an ion of effective charge $Z_p = 1$. The reduction in solvation energy on pairing is offset by the paring energy when persistent ion pairs are formed

4. Although CdF_2 is rather insoluble, its solubility and concentrations in the rhizosphere are sufficient to cause a synergistic action of fluoride with regard to Cd uptake (Chen et al. 2017; Liu et al. 2003). The stability of the hydrated CdF^+ ion is hence of significance.

Thus, while even the specification of the concentration of Cd is complex due to the several forms, viz. (i)–(iii), reagent chemistry can usually distinguish only between "total Cd" concentration (extracted using strong acids), and the "available" Cd concentration extracted using milder reagents like AAAc-EDTA. Their dependence on macrosoil parameters is obtained from field trials. The use of such macroparameters without using a more microscopic physico-chemical model of the soil implies that experimental data connecting them have to be linked by purely numerical regression relations (curve fitting) containing coefficients without a clear physical meaning. For instance, the bio-available or "accessible" Cd concentration C^a_{Cd} in a soil measured (with a mild reagent) as a function of the P-fertilizer loading A^F can be fitted to a regression relation as given in Figure 5 of FAO65 (reproduced here in Fig. 1),

$$\log(C^a_{\mathrm{Cd}}) = -1.641 + 0.365\log(A^F). \tag{3}$$

Logarithms to the base 10 are implied. Similar empirical relationships have been constructed connecting other pairs of parameters like pH, OMC, but it is hard to assign error bars and domains of validity to them. Usually, additional field trials fail to reproduce such fits in actual farm situations as a multiplicity of factors weighs in. Furthermore, the use of log-scaled parameters drowns much sensitivity and renders such equations to be full of pit falls if one were to use several equations in succession to eliminate variables and link a pair of parameters which have not been directly fitted to experiments from field trials. Nevertheless, currently used computer codes make wide use of such empirical fits and results of "regression trees" to provide databases for algorithms whose outputs are rarely physically transparent.

Another approach useful in colloid chemistry is to exploit surface complexation modelling of titration data on clean minerals like gibbsite, kaolinite, providing rate constants for Cd absorption, retention, etc (Weerasooriya et al. 2002). However, most such experiments deal with Cd^{2+} solutions in the 0.01 molar solution range or higher, where as the ambient exchangeable Cd levels in soil solutions are in the milli-molar regime (the bound part of the Cd pool may be 10 times larger in more alkaline soils). Nevertheless, as valid microscopic models are not available, we follow a strategy where empirical regression fits are judiciously used by constraining them to known asymptotic behaviour within simplified physico-chemical models.

It is instructive to look at a possible first-principles model of soil even though we cannot exploit such models in this study. The clay component can be modelled using a crystal structure where tetrahedral SiO_2 sheets and octahedral sheets (mainly Al or Mg oxide sheets with various cations replacing them) are the building blocks, as in montmorillonite (MMT), illite or vermiculite. The highly reactive edge sites and surface defects control the stabilization of soil organic matter, colloidal and rheological properties (Sposito 2008; Tombacz and Szekeres 2004) The edges of the sheet structure of MMT-type clays represent the boundary that solutes must cross in going between interlayer nanopores and micropores. The dissolution of clay nanoparticles has been observed to proceed predominantly from such edge surfaces (Bickmore et al. 2001). Hence, we may consider such structures where Cd, Mg, Zn and other ions may replace the Al ions in the MMT-type octahedral sites, while some cationic substitutions of the tetrahedral Si sites are also possible. Hydrated ions can remain in the channels between layers and constitute electrostatically held exchangeable cations in equilibrium with the cations in the soil solution.

The addition of P-fertilizers and other agrochemicals can influence the ambient pool of Cd in the soil in a variety of ways. These are:

1. Change of soil pH due to P-fertilizer loading, releasing soil-bound Cd into the soil solution,
2. Change of concentration of competing ions like Zn, Ca and micronutrient ions,
3. We examine the effect of fluoride and magnesium added to the soil via fertilizer loading, and their ion-pair formation, topics which have not been adequately addressed in the past.
4. The effect of agrochemicals via their ionicity and ionic strength in modifying the OMC of the soil. Here we use "ionic strength" as used in the theory

of strong electrolytes, while “ionicity” is used to indicate the capacity of an ionic mixture for denaturing or breaking up complex structures (e.g. in humus, or in proteins) by the Hofmeister mechanism (Dharma-wardana et al. 2015; Baldwin 1996).

In the following, we examine the first three items in greater detail.

Change of soil pH due to P-fertilizer loading, releasing Cd into the soil solution

Although the data given in the FAO soil bulletin No. 65 (FAO65) are somewhat dated, they form a consistent set of continued interest for theoretical modelling. Here we examine the data given by Sillanpää and Jansson (1992), reproduced here as Fig. 3(a), using the regression equations given there to clarify possible mechanisms for the increase in Cd content in the soil as P-fertilizer is loaded over a time period (Fig. 1).

The amount of Cd in the soil available to plants depends on the soil pH and its cation-exchange capacity (CEC), as the H^+ ions compete with the Cd ions for electrostatic binding to edges and surfaces of octahedral and tetrahedral building blocks of clays. This binding is weak compared to Mg and Al ions; hence, such ions are partially available. Also, decrease in pH hydrolyzes ions bound to humic acids as they are weak organic acids. The data for the Cd content in soil used in Fig. 1, obtained from Sillanpää and Jansson (1992), are for Cd determined using the AAAc-EDTA reagent as described in FAO65. This in effect extracts essentially the bio-available Cd, with a concentration C^a_{Cd}, while bound Cd located on clay sites is not extracted. Plants are also able to serve themselves of this “available” Cd. Sillanpää and Jansson (1992) give the regression relation, Eq. 3, connecting C^a_{Cd} with the P-fertilizer loading A^F. Here we examine the extent of pH change that is needed to explain these data (Fig. 1) and if such a pH-based model is plausible.

The change in the pH associated with the loading of fertilizer may be due to its intrinsic acidity (or alkalinity, see Table 5), or acidification due to bacterial action triggered by increased availability of fertilizer.

At the high-loading end, we may assume that almost all the exchangeable Cd in the soil has been released. The large-x asymptote to the curve, being a log–log regression, is somewhat poorly defined, as the fitting has not used such a boundary condition. Nevertheless, we can judiciously take it to be close to the value attained at the highest loading, viz. $C^a_{\mathrm{Cd}} = 0.12$ mg/L. Furthermore FAO65 provides a

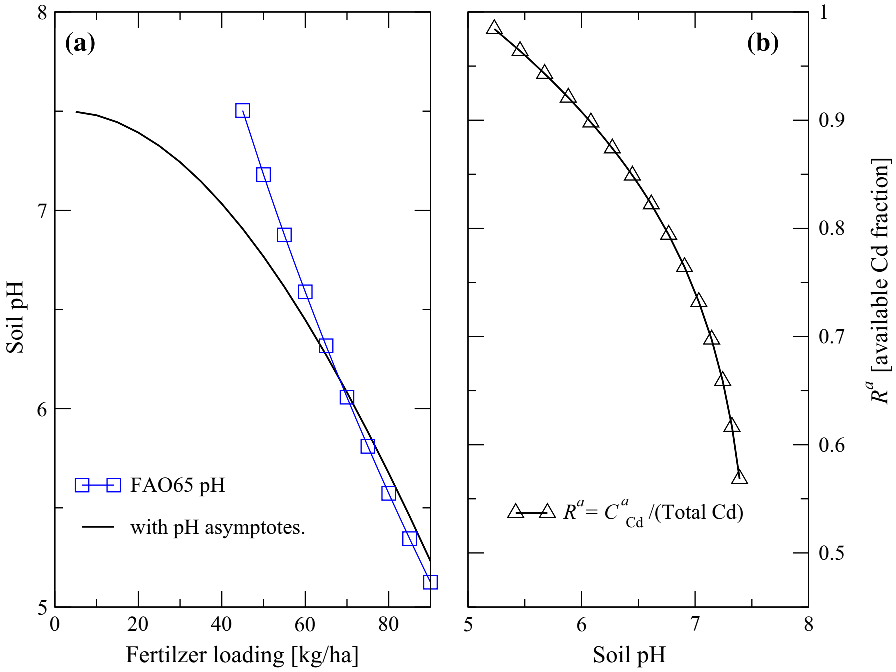

Fig. 3 (Online colour) (**a**) Soil pH calculated using a regression relation between pH and C^a_{Cd} from FAO65 (Sillanpää and Jansson 1992)and after constraining the alkaline regime (pH $>$ 7) to ambient natural C^b_{Cd}. (**b**) The fraction of available Cd in the soil, where the mean total soil Cd is taken as 0.12 mg/L of soil

Table 5 Initial pH effect of some common fertilizers on soil acidity, and their nominal Ca and Mg content

Source	Initial pH effect	Ca (%)	Mg (%)
MAP	Decreases to ∼3.5	–	–
DAP	Increases to ∼8.5	–	–
Rock P	Needs low pH to act	5–25	5–20
SSP	Negligible effect	5–20	5–15
TSP	”	5–13	5–8
Dolomite	Increases pH	22	12

Sources: CTAHR-Hawaii (2018) and Manufacturers' data sheets

regression equation connecting the available Cd and the pH, viz.

$$C^{a}_{\mathrm{Cd}} = 0.175 - 0.0111\ \mathrm{pH} \tag{4}$$

The pH used in this equation is the pH determined using a $CaCl_2$ buffer as defined in FAO65. The use of this equation with Eq. 3 by eliminating C^{a}_{Cd} is justified only for $\mathrm{pH} \leq 7$ as the AAAc-EDTA extraction becomes ineffective in alkaline media. At C^{a}_{Cd}=0.10 mg/L, this equation predicts a pH of 6.1. Thus, the acidulation needed to achieve the observed increase in available soil Cd is eminently reasonable as continuously fertilized soils are known to reach even higher acidity (pH close to 4) unless treated with ag-lime. In order to model the higher (alkaline) range of pH, we assume (using the data in Appendix 1, FAO65) that the unfertilized initial soil had been adjusted to a pH of 7.5 at a zero fertilizer loading, viz. $A^F = 0$, while the available Cd in the initial neutral soil is 25% of the total available soil Cd. In effect, we constrain the regression to satisfy the (asymptotic) boundary conditions for small x and large x. The resulting acidulation curve, i.e. pH due to fertilizer loading A^F, is shown in Fig. 3(a).

The purpose of the exercise is to demonstrate that while we may qualitatively state that increased acidulation of the soil triggered by fertilizer inputs can explain soil Cd enhancement data like those of the FAO65 set, they can in fact be addressed *quantitatively* and the results are indeed quite plausible. However, while this might constitute an explanation, it is by no means the only possible scenario that could lead to the observation that the addition of P-fertilizer to the soil increases the Cd available in the soil and hence in crops grown therein. In fact, given that there are many factors affecting the concentrations of available C^{a}_{Cd} and bound soil Cd C^{b}_{Cd} soil have to be given as a function of al least the major variables. For instance, a popular empirical model is to use the form

$$C^{s}_{\mathrm{Cd}} = C^{b}_{\mathrm{Cd}} + C^{a}_{\mathrm{Cd}}, \quad C^{b}_{\mathrm{Cd}} = K_D C^{a}_{\mathrm{Cd}} \tag{5}$$

$$\log K_D = a_1 + a_2\ \mathrm{pH}\ + a_3 \log C^{b}_{\mathrm{Cd}} + a_4 \log \gamma + a_5 \log(C_{Clay}) + a_5 \xi + \cdots, \tag{6}$$

where five variables are included via the coefficients $a_i, i = 1, 2, \ldots,$. Equation 5 is written in the form of a mass-action law using the constant K_D although this may not be justifiable as full equilibrium is rarely attained. C^{b}_{Cd} consists of lattice-Cd atoms which may be embedded in the tetrahedral -Si and octahedral -Al lattice sites of the clay particles, as well as Cd adsorbed to edges and surfaces of the nanopores and channels of the clay particles and humic acids. The adsorbed Cd is likely to be in equilibrium with the "available" Cd present in the soil solution, but not with the lattice-embedded Cd which only occupy point-defect sites. In fact, no microscopic model will lead to such a form as the above equation. That is, Eqs. 5, 6 are really a testimony to our lack of a quantitative understanding of the processes involved. When data are analysed using such fits, in most cases one finds that the pH dependance associated with the fit parameter a_2 carries the dominant effect, providing a basis for the use of the simpler form given in Eq. 4.

As a counter-argument to focusing on pH, we note that there are many inconsistent results obtained in attempts to control the available soil Cd by controlling the soil pH using, say, ag-lime addition (e.g. see Jansson 2002 and references therein).

Effect of competing ions like Zn, Mg, Fe on the available Cd in the soil

Equation 6 does not make a serious attempt to take account of the effect of other ions like Zn, Mg, Fe on the Cd balance in the soil solution. Zn is in the same group of elements as Cd in the periodic table and has very similar chemical properties, with Zn being by far the more reactive of the two. The radii of the hydrated Cd^{2+}, Mg^{2+} and Zn^{2+} ions are nearly equal, being about 4.2–4.4 Å depending on the aqueous environment. The evidence for such competition between Zn and Cd is widely available in the literature. In addition to their co-action in the aqueous "soil solution" phase, they also compete for sites for incorporation in the inner substitution sites in octahedral and tetrahedral locations of clay crystals. The ionic radii in the crystal lattice largely favour Mg (0.86 Å), then Zn (0.88 Å) and least of all Cd (1.09 Å). Thus, long-term fixation by incorporation into the clay lattice applies for Mg, and Zn, but less so for Cd. More attention has been paid in the literature to exchange with Ca^{2+} ions (radius in crystals, 1.14 Å), but its ionic radius is less favourable than that of Mg^{2+} which is likely to have a larger impact on Cd dynamics in the soil, as further discussed below.

Nevertheless, effects of such competing ions are all lumped into the exchangeable cation term ξ in Eq. 6 and in many Cd "risk-assessment" simulations. This shortcoming is also reflected in the reports of experiments on Cd in soil and in crops that fail to report the amount of Zn present together with Cd, leading to inconsistent conclusions. Greenhouse pot experiments using "simulated" fertilizer mixtures using pure phosphates and Cd salts cannot be used to derive conclusions about actual farming outcomes where fertilizers typically have a Cd/Zn ratio (Table. 6) that may range from 1/10 to 1/100 (Chaney 2012). That is, Zn largely dominates the Cd input from fertilizers and this effect cannot be ignored, or lumped into a global "cation-exchange" term.

The role of Zn has two contradictory effects. We examine them below:

(i) In Sect. "Cadmium input into the soil on application of phosphate fertilizer", we showed that the effect of the Cd input from P-fertilizers can be neglected, but the Zn input, being possibly a ten to hundred times lager than the Cd input, cannot be neglected and has a strong impact on the *pre-existing* available soil Cd C^{a}_{Cd} as the Zn ions will free up many Cd ions (denoted by $\mathrm{Cd}^{\mathrm{bx}}$) bound on to soil particles and humic acids moieties.

$$\mathrm{Cd}^{\mathrm{bx}} + \mathrm{Zn}^{2+} \rightleftharpoons \mathrm{Cd}^{2+} + \mathrm{Zn}^{\mathrm{bx}} \tag{7}$$

The above equations must be coupled with the equation for the solubility product for the Cd^{2+} and PO_4^{3-} equilibrium since Cd phosphate is relatively insoluble and the phosphate concentrations in the plough layer are quite high, thereby suppressing Cd dissolution into the soil solution.

By making the assumption that the exchangeably bound zinc, $\mathrm{Zn}^{\mathrm{xb}}$, and also the available zinc (i.e. Zn^{2+}) concentrations are quite large compared to the corresponding Cd amounts, the observed enhancement of available Cd on fertilizer addition displayed in Fig. 1 can be explained using a rate constant K_D used in Eq. 5, with K_D in the range of 1–100 depending on various reasonable assumptions that one may make regarding the initial amounts of bound and available Cd, Zn, etc., in the soil prior to fertilizer application. Here we keep the pH fixed as we wish to see whether the data of Fig. 1 can be explained purely in terms of the impact of Cd dynamics in the soil. As reported by Smolders and Six (2013), values for K_d obtained by fitting to databases can vary up to even 2300. Hence,

Table 6 Cadmium, selenium, zinc and fluoride concentrations in some rock phosphate sources for fertilizers

Source	Cd (mg/kg)	Se (mg/kg)	Zn (mg/kg)	F (g/kg)
USSR[a,d]	0.1–0.2	n.a	19	n.a.
Tunisia[a,d]	38–53	11	385	41
Morocco[a,d]	3–34	3	209	n.a.
USA (N.C.)[c,d]	39	5	333	35
Nauru (NZ)[a,d]	100	n.a.	1000?	30

The indicated Zn concentrations are a lower bound

[a] McLaughlin et al. (1996)

[b] Zapata and Roy (2004)

[c] Van Kauwenbergh (1997)

[d] Bech et al. (2010)

we see that the increase in available Cd concentration in soils as observed on fertilizer loading can also be accounted for quite easily by just the effect of Zn addition that occurs automatically via the fertilizer loading, even if the pH was kept constant by calcite addition.

(ii) Even when the available Cd concentration is augmented by various means, this may not be reflected to the same extent in the plant because the Zn ions will also compete with Cd ions in the rhizosphere. Rice accumulates Cd using several cadmium transporters which may include NRAMP and HMA transporters (Uraguchi and Fujiwara 2012) that do not invoke Zn but use other ions like Mn. Furthermore, the plant will take up both Cd and Zn ions in parallel, and the high Zn component in the soil will also be reflected in the chemical content of the plant. For instance, taking the rice plant *Oriza Satavia*, a strong phyto-accumulator of Cd as an example, we show in Table 7 a typical 1:1000 Cd/Zn ratio in both CKDu-endemic regions and CKDu-free regions. While the Cd-to-Zn ratio in the soil may be typically only 1:10 to 1:100, the phyto-accumulation of Zn may be much stronger than that of Cd, further increasing the plant Zn content compared to Cd. It is believed that this high intake of Zn (and also Se) suppresses the Cd intake in the gut and may account for the physiological counter-action of Zn in the diet (ARL 2012), and indeed such information has been available in the literature for perhaps over four decades (Jacobs et al. 1978). These suggest that there is little reason to associate Sri Lankan CKDu with dietary cadmium although suggestions to that effect have been made (Jayatilake et al. 2013; Bandara et al. 2010).

Table 7 Concentrations of Cd, Zn and Se present in rice grown in the endemic "dry zone" (DZ) of Sri Lanka (where a form of chronic kidney disease is found) and in the "wet zone" (WZ) which is free of the disease

Rice	Unit	DZ	DZ[a]	WZ
Cd	μg/kg	52	41.2	79
Se	μg/kg	26	–	19
Zn	mg/kg	14	22.3	16

Median amounts have been used where possible using the data from Diyabalanage et al. (2016b) and Meharg et al. (2013). The data are for the grain, while the straw usually has 2–3 times more Cd and Zn content (n.b. Zn in mg/kg)

[a] Mean values, CKDu-endemic area in the DZ, from Levine et al. (2016)

Magnesium and Fluoride mediated enhancement of available Cd in the soil

McLaughlin et al. (1994), also Sparrow et al. (1993), drew attention to the impact of salinity and chloride ions on the available Cd concentration in P-fertilized soils, and proposed that CdCl complex formation in the soil solution has to be taken into account as a function of the chloride concentration in the soil solution. Smolders (2001) reported similar results and a linear trend between crop Cd and soil Cd. Similarly, Loganathan et al. (2008) drew attention to the importance of fluoride added to soils via P-fertilizer loading, where they considered mainly fluoride toxicity.

Most of the multiple ionic interactions occur in the *aqueous phase* of the soil solution, and hence, they can in fact be treated rather rigorously using methods of electrochemistry and thermodynamics. Manoharan et al. (2007) have discussed the complex formation between Al^{3+} ions and fluoride as a function of soil pH. However, possible interactions of the fluoride with Cd ions were not discussed.

In Dharma-wardana (2017), it is shown by calculations of the change in Gibbs free energy that Cd forms a complex CdF^{+} which is more stable than $CaCl^{+}$. Thus, the increased presence of F^{-} ions in the soil solution will bring pre-existing exchangeably soil-bound Cd into soil solution by forming CdF^{+} ions. This effect can contribute to an observed Cd enhancement associated with fertilizer addition, as in Fig. 1(a). However, while Mg, or Al, taken individually with fluoride may show complex formation, a mixture of many ions tends to have a buffering action on each other, and the effects of multiple ions become less marked. This was found to be the case not only from calculations of ionic Gibbs free energies, but also from studies of nephrotoxicity using laboratory mice (Wasana et al. 2017). These conculsions apply to a certain range of Ca-concetrations, but not to a higher range when the cadmium fioride solubility limit is reached.

Another aspect of complex formation that we do not discuss in detail in this study is the effect of herbicides like glyphosate applied to crops. This leads to a presence of glyphosate and its breakdown products in the top soil in the short term. They have a salutatory effect on heavy-metal content in forming insoluble complexes with, e.g. cadmium, lead, and making them not available to plants and soil organisms like earthworms, e.g. by diminishing the bio-available soil Cd and making earth worms thrive (Zhou et al. 2014).

Cadmium content in crops like rice (*Oriza sativa*)

Figure1 shows the close correlation of the Cd content in soil and in the plant. Although the rate of uptake of Cd from the soil solution during the growth of a plant depends on the growth stage, sunlight, water availability, etc., it is possible to make a simple estimate of the final concentration of Cd, e.g. in paddy and in the water in which it is grown, using a number of simplifying assumptions. We present two simple but fairly robust models for the Cd uptake by a grass or a rice-like plant.

Model based on water intake

We begin by applying a simplified version of the more detailed analysis (given below) to compare the predicted Cd uptake values with the Cd data given in Table 7 and reported for Sri Lanka by Diyabalanage et al. (2016b). A 90-day irrigated rice crop in the rice-growing north-central province of Sri Lanka takes up about 500 mm water (DOA, Sri Lanka 2017), i.e. 5×10^6 litres of water per hectare as an upper bound. Typical values of Cd concentrations are 0.24 µg/L in canal water (Jayatilake et al. 2013), or 0.11 µ g of Cd per kg of soil as reported by (Levine et al. 2016). Hence, we may take a range of values from 0.5 g–1.2 g of Cd uptake by paddy per hectare per season.

An independent calculation which brings us to consistence with the above numbers is obtained by looking at the output of paddy (with husk), rice (without husk), straw and stubble, produced per hectare. Using statistical information for the four years 2011–2015 (Paddy Statistics, Sri Lanka, Paddy Statistics 2015), we have:

$$\begin{aligned}&\text{Number of hectares averaged over} = 0.69 \times 10^6\\&\text{Average yield of rice, m.tonnes} = 3.90\\&\text{Average yield of husk, m.tonnes} = 0.43\\&\text{Yield of straw + stubble, m.tonnes} = 4.96\end{aligned}$$

Using the above figures and the Cd content C_{cd} of 52 µg/kg in the grain, $2.5C_{cd}$ and $3C_{cd}$ for the Cd content in the husk and straw respectively, the total Cd absorbed from the water works out to an upper bound of about 1.03 g/ha, which can be compared to the upper bound of 1.2 g/ha Cd estimated from the water intake.

Thus, we have consistence with the experimental data given in Table 7. However, a more detailed discussion is useful.

Minerals enter the plants through water intake as well as via aerial deposition. Here we ignore the aerial delivery which may be important in industrial neighbourhoods. The water supply needed through out the plant's life is used up partly in evaporation and partly by uptake into the plant. If the daily water supply is stated as a height h_w (e.g. 0.10 m), the water volume V_w per hectare is $10^4 \times h_w$ m^3 per day. Of this, a fraction f_e is lost by evaporation and the uptake by the plant is $10^4 h_w(1-f_e)$. We define the uptake factor $f_u = (1-f_e)$. At planting and at the initial stages, f_e is significant and may be as high as 50–60% of that of the grown plant, while most of the water is taken up by the plant during its mid-season growth when the crop is fully developed and in the flowering and grain-setting stage. In "dry-harvested" crops like maize, sunflower or paddy, the end-season water needs are minimal. Thus, $h_w(t)f_u(t)$ are functions of the growth time t, which extents from $t = 0$ at planting to $t = T$ at harvesting. Let the Cd concentration in the water near the roots at the time t be $C_w(t)$. The soil-to-plant transfer coefficient is $f_{sp}(t)$. Thus, the total mass of Cd (or any other ion) absorbed is

$$M_{\mathrm{Cd}} = \int_0^T dt 10^4 \times C_w(t)h_w(t)f_u(t)f_{sp}(t). \tag{8}$$

If C_w, f_u, f_{sp} are replaced by their average values during growth, and treated as constants, then we may write the total Cd absorbed by one hectare of crop during its growth season T as

$$M_{\mathrm{Cd}} = 10^4 \times C_w h_w f_e T = C_w f_e V_w. \tag{9}$$

Here $V_w = V_w$ is the total water input during the season. For a 90-day crop requiring an average of 5–7 mm per day of water, this amounts to 450–600 mm of water per hectare for the whole growth period. Using the average values $f_{sp} \simeq 1$, $f_e \simeq 0.2$, $h_w = 7$ mm $C_w = 0.24$µ g/l, we can estimate the Cd uptake by one hectare of a rice plantation during a putative 90-day growth season. Assuming this to yield 4 metric tons of rice grain, and assuming a distribution of 2:1 or possibly 2.5:1 of Cd between the straw and grain, the calculated concentration in the rice grain (30–80 µg/kg) is completely consistent with the values given in Table 7.

Similar calculations can be done for other ions like Zn or F. Zinc is found in large excess over Cd according to Table 7. Such calculations show that the measured concentrations of ions in crops (e.g. as given in Table 7) are in *grosso modo* agreement with the concentrations of ions measured in the soil solution, establishing their consistence.

Model based on harvest volume

The rice plant absorbs water and Cd from the ground and grows from a negligible volume v_0 to its final large volume V_F during its lifetime. The water absorbed is in fact proportional to this increase in volume $V_F - v_0$. Let the volume *change* at any moment of its growth be dV. Let the concentration of Cd in the neighbourhood of the roots be denoted by C_w at the moment when the plant has a volume V.

Then the amount of Cd absorbed by the plant in changing its volume by dV is $C_w dV$. There is also a transfer coefficient f_{sp} connecting the Cd concentration in the soil and the Cd concentration in the plant. As seen from Fig. 1, this factor f_{sp} may be taken to be of the order of unity in typical cases. Hence, the total mass of Cd M_{Cd} absorbed by the plant is:

$$M_{\mathrm{Cd}} = \int_{v_0}^{V_F} f_{sp}.C_w.dV \tag{10}$$

If we assume that f_{sp} and C_w can be replaced by their average values during the lifetime of the plant, we can take them out of the integral sign and write:

$$M_d = C_w.f_{sp}.(V_F - v_0) \tag{11}$$

So, neglecting v_0, setting $f_{sp} = 1$ the Cd absorbed by the plant during its life is $M_{\mathrm{Cd}} = C_w V_F$. The final volume V_F used here is the *wet volume at harvest* and not the dry volume. We consider a crop grown on a hectare of land. Let the average height of a plant to be h_p, while the packing fraction is taken to be f_p. Then the volume of plant matter and also the weight W_F of the total wet growth are given by

$$V_F = (1 \text{ hectare }) \times (h_p f_p); \quad W_F = V_F \rho. \tag{12}$$

In the above, ρ is the density and may be taken to be close to that of water (i.e. 1 kg per litre for order of magnitude calculations). The packing fraction f_p allows for the fact that there is space among plants unoccupied by them. In the case of paddy, we may assume that h_p at harvest is 0.5 to 0.75 m, while the packing fraction f_p may be 0.75–0.95 in the full grown condition at harvest time. The above analysis assumes that the water supply to the soil solution remains more or less unchanged at saturation level during growth. In dry-zone cultivation, the soil water may be cut off at later stages of growth, but such correction effects are indirectly included in the final plant height and hence on the average high h_p used in the model. Thus, given experimental values for the quantities needed in the last equation, one may compare field data with theoretical expectations.

Toxicity effects of Cd in the presence of other ions

Crops grown in soils contaminated by mining and smelting activities usually contain extreme amounts of metal toxins, and they are not considered here as their nephrotoxicity, etc., are easily understood. In normal circumstances, many ions occur and their co-actions become important, but they are often neglected. The neglect of competitive ionic effects seen in many reported experiments is also seen in the dietary specifications on Cd intake. Thus, as already stated, Se, Zn, Mg and Fe in the diet have an antagonistic action on Cd toxicity (ARL 2012; Brzóska and Moniuszko-Jkoniuk 2001; Matović et al. 2011; Chaney 2012), but this is not included or even alluded to in specifying the recommended tolerable monthly intake limits (TMIL) on Cd in the diet as indicated in the Codex Alimentarius (CCF12 2018) stipulations. Of course, local authorities have the freedom to reinterpret the TMIL to mean that if the Zn inputs are over-overwhelmingly large, then the Cd inputs may be ignored. This usually happens mainly on the strength of tradition rather than on the basis of science. Sunflower kernels and other foods like shellfish are high in Cd and yet show no adverse effects when consumed (Sirot et al. 2008). Farming communities in the UK in regions with high Cd in the soil consume diets rich in potatoes and cereals without any adverse effects (Chaney 2012). Similarly, the lack of chronic

Cd toxicity in many communities, where rice containing Cd in amounts exceeding the TMILs has been consumed for generations, can be explained by the protective action of adequate amounts of ions like Zn, Se or Fe in the diet (see Dharma-wardana 2017, and Sect. 5.4 of Chaney 2012). Conversely, when Cd toxicity from crop products occurs, it is mostly likely that the diet is grossly deficient in protective micronutrients like Zn or Se. Table 7 shows that Sri Lankan chronic kidney disease is uncorrelated with Cd in rice. Hence, other explanations have been considered (Wasana et al. 2017; Thammitiyagodage et al. 2017). The Codex Alimentarius (CCF12 2018) uses a single-variable step-function model for stipulating a chronic toxicity-onset amount m_{Cd} per kg of body weight per day, week or month, as is appropriate. No synergies or counter-effects of other contaminants are included in the specification. If, for example, the daily inputs of Cd, Zn, Fe, etc., are $I_{\mathrm{Cd}}, I_j, j = \mathrm{Zn, Fe}$, only the amounts scaled by their bioavailable fractions f_j^a are of importance. Many studies, e.g. those of Premarathne (2006), Smolders et al. (2013), show that f_j^a if the order of 30–50% for common vegetables, rice, etc., i.e. $f_j^a \sim 0.4$. Furthermore, each ion has an uptake factor f_j^u for intestinal absorption. Only about 2.5–6% of the bioavailable Cd is absorbed in the intestines, with $f_{\mathrm{Cd}}^u \sim 0.05$ (ASTDR 2008). According to Kim et al. (2007), Cd absorption in the gut involves a ferrous transporter, which also takes up Zn, while Zn has other transporters associated with its uptake, and hence, the details are unclear (Pullakhandam and Nair 2009). Furthermore, iron deficiencies can cause higher Cd absorption. Both ferrous ions and Zn ions are believed to be more actively taken up by this transporter, but even if we assume that the uptake factors f^u are the same for the three elements, the Cd uptake will be reduced to a third or less if ferrous and Zn ions are present in equal amounts to compete with Cd. That is, using the simplest picture (i.e. without including synergies), it is only if the potential amount of Cd available in the gut for uptake exceeds the total amount of its competitor ions that there would be absorption. That is, it is reasonable to conclude that the condition

$$I_{\mathrm{Cd}} f_{\mathrm{Cd}}^a f_{\mathrm{Cd}}^u > \Sigma_j I_j f_j^a f_j^u \tag{13}$$

has to be satisfied for any significant Cd absorption by the gut to set in.

Conclusion

We have reviewed the widely held hypothesis that “soil Cd concentrations get enhanced by the use of P-fertilizer at rates which are likely to create dangerous conditions for human health in a few decades”, and conclude the following. (a) This strong concern is not justified at current levels of fertilizer usage where the doubling of the Cd content in soils would take centuries and not decades. (b) The causes of increased bioavailable soil Cd on fertilizer addition are most probably found in other factors that cause the release of *pre-existing* Cd found in the soil.

These conclusions follow since the incremental change in the bio-available soil Cd concentration on addition of P-fertilizer is in fractions of mg/kg of soil per year, while ambient soil Cd levels are millions of times larger. The factors that cause the increase in bio-available soil Cd are most likely to be the following: (1) change in soil pH due to fertilizer action and associated action of micro-organisms, (2) the effect of ionic forms of Zn, Mg, F, Cl, Ca, etc., on the ionic equilibria of the soil solution, given that such ionic forms are found in P-fertilizers, ag-lime and such agrochemicals, (3) competitive effects on clay adsorption sites, humic acid moieties, and in the rhizosphere, (4) proliferation of the root system and its activity under fertilizer addition, leading to increased dissolved Cd in the soil (and in the plant) and (5) ionicity effects on organic matter and other effects that we have not discussed in this study.

We have also pointed out that the neglect of ion synergies (e.g. Zn in suppressing Cd toxicity) in specifying tolerable maximum weekly intake values can lead to paradoxical situations where healthy communities have been found to be consuming diets that would appear to be dangerous to health if the Codex Alimentarius stipulations are applied naively.

Furthermore, we conclude that attempting to control the enhancement of bio-available Cd in soils caused by P-fertilizer loading may require controlling their fluoride, magnesium and Zn content rather than the Cd content. Reducing potato diets in favour of wheat and rice diets would cut down fertilizer inputs perhaps by a factor of four. In addition, the push by the European Food Safety Agency (as well as similar organizations) to reduce the Cd content in crops by continued lowering of the allowed Cd levels in

P-fertilizers would turn out to be an expensive and futile exercise.

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