Fertilizer usage and cadmium in soils, crops and food.

M.W.C. Dharma-wardana
National Research Council of Canada, Ottawa, Canada, K1A 0R6 and Département de Physique, Université de Montréal, Montréal, Québec, Canada.
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Phosphate fertilizers were first implicated by Schroeder and Balassa in 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 contamination of the soil by trace metals. 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-ion-association theories. The protective role of ions like Zn, Se, Fe, etc., 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.

I. 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 Schroeder et al [57]. This view has now become a mainstream paradigm [40, 42] that has raised much public concern [68, 70], as also with the overuse of pesticides [38]. 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 [5, 30]. However, controversy exists regarding a number of aspects [13, 54], 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 [58, 71].

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 etiology (CKDu) appearing even though recognized causes (e.g., diabetes, hypertension, etc.) are absent [24, 33]. Such CKDu is also found in the developed world including Canada [3]. Some authors have suggested Cd and other heavy metals to be factor causing such chronic kidney disease [32, 48, 71]. However, the existence of CKDu communities adjacent to non-CKDu communities subject to similar agrochemical exposure is consistent with other explanations [16, 18, 20, 72]. 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 [74] 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., [7].

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 of Cd in crops grown in such soil. International regulatory bodies have set a 60-70 μg tolerable maximum daily intake for an average adult [34]. However, some societies traditionally consume rice, or sea-food in diets with Cd exceeding such limits, while remaining quite healthy [60]. 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 of 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 \(\mu g\) 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[61]. 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”[54]. Similar views are found in recent risk-assessment studies by other authors, e.g., [13], or the Wageningen University report[58].

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 trigger existing soil Cd making it bioavailable to plants. Mechanisms like (i) the effect of increased acidulation due to fertilizer addition, (ii) competition from ionic forms of Zn, Se, Fe, (iii) salinity effects, (iv) dissolved organic carbon, soil and plant characteristic etc., 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.

II. CADMIUM ACCUMULATION AND FERTILIZER USE

Subsequent to the suggestion of Schroeder and Baldass 57 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[37], 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[59]. A noteworthy step was the publication of the soil bulletin No. 65 (FAO65) of the food and agriculture organization (FAO) 58, 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 Silanpää 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) are shown for a time duration of three years of P-fertilizer application.

Silanpää 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. Silanpää 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[22,29,43,47,49,51,68]. 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.

Hence it is instructive to reexamine 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”.

![figure](image-url)
TABLE I. Cd and P concentrations in some rock phosphate sources for fertilizers. The total P$_2$O$_5$ 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$_2$O$_5$ need beneficiation to justify transportation costs. A minimum of 25% P$_2$O$_5$ is usually required.

| Source                              | Cd (mg/kg) | P %   | Cd (mg/kg) |
|-------------------------------------|------------|-------|------------|
| Russiaa                             | 0.2        | 17    | 1          |
| China (Yunan)b                      | 5          | 14    | 35         |
| Sri Lanka:                          |            |       |            |
| (Eppawala)†                         | < 3        | 14    | 34         |
| (imported)†                         | 2.3-46     | 7-20  | 325        |
| India (Mussoorie)c†                 | 8          | 12    | 62         |
| Egypta                             | 8-9        | 13    | 61-67      |
| Moroccoa                            | 12-34      | 14-15 | 88-240     |
| USA (N.C.)c                         | 33         | 15    | 240        |
| Nauru (NZ)a                         | 100        | 15.6  | 641        |

a [45]  
b [75]  
c [69]  
†Estimated.

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 I 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$_2$O$_5$, with the P/P$_2$O$_5$ also dependant 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.

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 gyspum (a by product). 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.

### A. 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, $\Delta C_{\text{Cd}}^s$ 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, $C_{\text{Cd}}^F$ for the concentration of Cd (mg/kg) in the fertilizer, $d_s$ the depth of the soil layer in cm., while $\rho_s$ is the density of the soil in kg/litre. The total concentration of soil Cd is denoted by $C_{\text{Cd}}^s$. Then the change $\Delta C_{\text{Cd}}^s$ on fertilizer loading is:

$$\Delta C_{\text{Cd}}^s = \frac{A^F C_{\text{Cd}}^F}{d_s \rho_s} \times 10^{-8}, \text{ Cd, g/kg of soil}$$  \hspace{1cm} (1)

$$\Delta C_{\text{Cd}}^s = \frac{10A^F C_{\text{Cd}}^F}{d_s \rho_s}, \text{ Cd ng/kg of soil}$$  \hspace{1cm} (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 [17] 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 macro-nutrients. Thus, consider one hectare of the tea growing region where the rivers originate, with an average annual rainfall of 2 meters, and an annual average fertilizer input of 100 kg/ha, containing 30 mg/kg of Cd (or any other such impurity). If half the rainfall contributes to the river run off, the concentration of Cd from the fertilizer input is only 0.3 parts per trillion. On the other hand, macro-nutrients (e.g., phosphates) are important pollutants that cause algal blooms. [19] 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 washoff from the existing soil cadmium, as the contribution from fertilizer inputs is negligible. Similarly, [31] showed that toxin levels in irrigation waters were well below the usual MALs and hence required no reverse-osmosis treatment to render them safe. [15] 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 [1]. 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 $\Delta C_{\text{Cd}}$ turns out to be in parts per trillion to fractions of parts per billion ($\mu g/kg$ 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 I), the total Cd inputs remain negligible even for accumulations over centuries [10].

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, $C_{\text{Cd}}^s$, 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., Sillenpää and Jensson 1992).

Soil Cd amounts in Shipham, Wales, UK, ranges from 9 mg/kg – 360 mg/kg [70]. A mean value of 0.4 mg/kg is sometimes used in model calculations for the EU [53], while 0.3 mg/kg has been proposed by [62] as an average for the EU. Scandinavian soils have a lower average of 0.2 mg/kg [23].

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 [55], and are consistent with values found in the WHO-sponsored study [33]. 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 $\mu g/L$ and are below the MAL [33].

[68] raises the interesting possibility that the low values of Cd in E. Europe, in comparison to 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 Sec. HA 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 [63] airborne Cd sources have decreased by a factor of five between 1980 and 2005. They propose a 0.35 g ha$^{-1}$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 [22] for southern Sweden extracted from the Doctoral thesis of Jansson (2002), Table 1, column 2. Eriksson considers the Cd inputs and outputs (g ha$^{-1}$y$^{-1}$) in his Cd budget.

1. P-fertilizer, 0.12g by plant uptake, removal of roughage, stubble etc.
2. Deposition: 0.7g from airborne sources, rain etc.

(Note that [63] proposed a 0.3 g annual addition from deposition as an EU average in 2013).

3. From lime, 0.02g added for soil remediation.
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 [62]).
3. Total amount removed = 0.63g.

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 occurs in a soil volume 25 cm deep over an area of a hectare, i.e., in a soil volume of $25 \times 10^6$ liters, corresponding to a soil weight of 3.25 $\times 10^6$ kg with a soil density of 1.3 kg/L, producing a change in Cd concentration $\Delta C_{\text{Cd}} = 43 \times 10^{-9}$ 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) and subsoils (0.1 mg/kg) as reported by [23] are trillion times bigger. The total soil Cd in the plough layer is 650 kg/ha. Hence the parts per trillion increase in Cd concentration due to fertilizers is negligible. 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 centimeters 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 [40] as an example of such calculations and review their table 2 with suitable complementary information in Table II. 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 III). Furthermore, since a large fraction of
TABLE II. 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 & animal uptake, removal, leaching, etc.

| Element | Input of Equiv. kg X in P-Fert. or rock fert. (kg p/ha/y) | rate of x added. conc. of X double the conc. of X | Years to double the conc. |
|---------|---------------------------------------------------------|--------------------------------------------------|--------------------------|
| Cd      | 30                                                      | 200                                              | 42                       | ~8.4                    | 0.3                      | 36                       |
| F       | 30                                                      | 200                                              | 30,000                   | ~6000                   | 300                      | 51                       |

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 III 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 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) 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 byproducts, 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 IV.

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 time scales of a millennium to double the concentration of Cd in soils under paddy cultivation, even if we neglect removal processes (leaching, monsoonal runoff, 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 time scales 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 Potatoes (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

TABLE III. (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 [56]. (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.

| Olsen-P | 0-3 4-7 8-11 12-15 | 30-35 tonnes/ha/y potato [ppm] |
|---------|------------------|-------------------------------|
| Fertilizer, as P<sub>2</sub>O<sub>5</sub> [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 |

<sup>a</sup>Increased harvest, e.g. 45 tonnes/ha/y can be obtained by using the inputs recommended for the lower Olsen-P range.<br><sup>b</sup>P<sub>2</sub>O<sub>5</sub> concentration in concentrated superphosphates ~ 45%, while typical rock phosphates may contain about 38-42%.
be cut down by perhaps a factor of 4, there by increasing the soil-Cd doubling time to millennium time scales 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 Wageningen study [53] states 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 sq. m \times 0.2 m, i.e., 2000 m$^3$
   = 2\times10^6 litres.
2. Soil mass/ha = (2\times10^6) \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 kg = 960 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 [15]. 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 content 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.

B. 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 Sec. [III A].

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**TABLE IV.** 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 & animal uptake, removal, leaching, etc. 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.

| Element | Input of X | Equiv. kg X in P-fert. | Rate of X x added conc. of X | Years to double the conc. [y] |
|---------|-------------|------------------------|-----------------------------|-------------------------------|
| Potato  | Cd          | 15                     | 100                         | 30                            | 3.0                           | 0.3                           | 260                           |
|         | F           | 15                     | 100                         | 30,000                        | 3000                          | 300                           | 260                           |
| Paddy   | Cd          | 40 (TSP)               | -                           | 20                            | 0.8                           | 0.3                           | 975                           |
|         | F           | 40 (TSP)               | -                           | 20,000                        | 800                           | 300                           | 975                           |
Soil Cd data reported in [58] had been determined using the Acetate-Ammonium Acetate Na\textsubscript{2}EDTA (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\textsuperscript{-1}y\textsuperscript{-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 \( C_{Cd} \simeq 0.04 \) mg/L. Taking the density of soil to be 1.3 kg/L, mean increment, \( \Delta C_{cd} = (0.12 - 0.04)/(3 \times 1.3) = 0.0205 \) mg/(kg.year). However typical \( \Delta C_{cd} \) are in the nano to micro-gram range (at the most), as seen from calculations given in sec. [11] 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 \textit{pre-existing} Cd \textit{pool} in the soil, but 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 \( C_{Cd} \) 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 \( C_{cd} = a + bC_{Cd} \) or expressed as log-scaled regressions have been quoted by many authors [42, 63], 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., [25, 15]. 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 [25]. 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\textsuperscript{+} 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\textsuperscript{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 Sparrow et al (1992), and those of Williams and David (1977) 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) 50 report an increase of available Cd in the soil, induced by the use of P-fertilizer used in the form of Idaho mono-ammonium 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 [43].

III. 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 macro-parameters of the soil, e.g., (a) the pH, soil texture characterized by a texture index (TI, see FAO65), organic matter content (OMC) \( \gamma \), cation-exchange capacity (CEC) \( \xi \), salinity \( \zeta \), hardness \( \eta \), and electrical conductivity \( \sigma \); (b) the concentrations of specific ions (micronutrients) like B, Cu, Mn, Mo, Zn etc.; (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:
(i) Cd ions chemically replacing Al or Mg atoms in octahedral 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 \( C_{\text{Cd}} \). They can be dislodged using strong reagents.
(ii) Fully or partially hydrated exchangeable Cd ions electrostatically attached to edges, oxide groups etc., with a concentration \( C_{\text{a,Cd}} \). These ions may migrate into internal sites with time, becoming strongly bound.
(iii) Fully hydrated Cd ions ‘available’ in soil solution at a concentration of \( C_{\text{av,Cd}} \). These aqueous Cd ions carry a solvation sheath of water molecules. However stable associations with other ions like fluoride forming a strong (Cd-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 without ion association [10]. In such cases, essentially all the aqueous Cd ions are in associated form 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, oxide groups, surface defects, etc., to carry a solvation sheath of water molecules. However, their concentration is largely in excess of the Cd\(^{2+}\) and the F\(^-\) ions. As they have a lowered positional stability, they can be dislodged using strong reagents.

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 AAx-EDTA. Their dependence on macro-soil parameters is obtained from field trials. The use of such macro-parameters 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 \( C_{\text{av,Cd}} \) 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),

\[
\log(C_{\text{av,Cd}}) = -1.641 + 0.365 \log(A^F). \quad (3)
\]

Logarithms to the base 10 are implied. Similar empirical relationships have been constructed connecting other pairs of parameters like pH, OMC etc., 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 additional factors weigh in. Furthermore, the use of log-scaled parameters drowns much sensitivity, and renders such equations to be full of pitfalls 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 data bases for algorithms whose outputs are rarely physically transparent.

Another approach useful in colloid chemistry is to exploit surface complexation modeling of titration data on clean minerals like gibbsite, kaolinite, providing rate constants for Cd absorption, retention etc [23]. 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 millimolar 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 will not exploit it fully in this study. The clay component can be modeled using a crystal structure where tetrahedral SiO\(_4\) 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 [65, 67]. The edges of the sheet structure of MMT-type clays represent the boundary that solutes

![FIG. 2. (On line colour) A schematic diagram of the (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\(^-\) ion 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.](image)
must cross in going between interlayer nanopores and micropores. The dissolution of clay nanoparticles has been observed to proceed predominantly from such edge surfaces \[^9\]. 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:

(i) change of soil pH due to P-fertilizer loading, releasing soil-bound Cd into the soil solution,

(ii) change of concentration of competing ions like Zn, Ca, and micronutrient ions,

(iii) 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.

(iv) 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, proteins etc.) by the Hofmeister mechanism \[^6,\,17\].

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

A. 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 modeling. Here we examine the data given by \[^58\], reproduced here as Fig.2(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. 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. Also, decrease of 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 \[^58\] for Cd determined using the AAAc-EDTA reagent as described in FAO65. This in effect extracts essentially the bio-available Cd, with a concentration \(C_{Cd}^a\), while strongly bound Cd located on clay sites are not extracted. Plants are also able to serve themselves of this ‘available’ Cd. Sillanpää and Jansson (1992) give the regression relation, Eq. \[^3\] connecting \(C_{Cd}^a\) with the the P-fertilizer loading \(A\(^P\).\) Here we examine the extent of of pH increase that is needed to explain these data (Fig.1) and if such a pH-based model is plausible. The rise in the pH associated with the loading of fertilizer may be due to its intrinsic acidity (Table \(V\)), or due to bacterial actions 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. \(C_{Cd}^a=0.12\) mg/L. Furthermore FAO65 provides a regression equation connecting the available Cd and the pH, viz.,

\[
C_{Cd}^a = 0.175 - 0.0111pH
\]

The pH used in this equation is the pH determined us-

![FIG. 3. (On line colour) (a) Soil pH calculated using a regression relation between pH and \(C_{Cd}^a\) from FAO65 (Sillanpää and Jansson, 1992)and after constraining the alkaline regime (pH > 7) to ambient natural \(C_{Cd}^b\). (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 V. 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 5-25 | 5-20 | 5-20 |
| SSP    | negligible effect | 5-20 | 5-15 |
| TSP    | , | 5-13 | 5-8 |
| Dolomite | increases pH | 22 | 12 |

Sources: \(^{15}\) and Manufacturers’ data sheets.
ing a CaCl₂ buffer as defined in FAO65. The use of this equation with Eq. [3] by eliminating \( C_{\text{Cd}}^a \) is justified only for pH ≥ 7 as the AAAC-EDTA extraction becomes ineffective in alkaline media. At \( C_{\text{Cd}}^a = 0.10 \) mg/L, this equation predicts a pH of 6.1. Thus the acidification needed to achieve the observed increase in available soil Cd is eminently reasonable as continuously fertilized soils are known to reach even higher pH (close to 4) unless remedied with ag-lime. In order to model the higher (alkaline) range of pH, we assume (using the data in the 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. 2(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 available Cd in the soil and hence in crops grown therein. In fact, given that there are many factors affecting the concentrations of available \( C_{\text{Cd}}^b \) and bound soil Cd \( C_{\text{Cd}}^a \), we have to give as a function of all the major variables. For instance, a popular empirical model is to use the form

\[
C_{\text{Cd}}^a = C_{\text{Cd}}^b + C_{\text{Cd}}^a, \quad C_{\text{Cd}}^b = K_D C_{\text{Cd}}^a \tag{5}
\]

where five variables are included via the coefficients \( a_i, i = 1, 2, \cdots \). 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. \( C_{\text{Cd}}^b \) 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. In fact, no microscopic model will lead to such a form as the above equation. In fact, Eqs. 5, 6 are really a testimony to our lack of a quantitative understanding of the processes involved. When data are analyzed 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. 3.

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 soil-pH remediation using, say, ag-lime addition (e.g., see [29] and references therein).

### B. Effect of competing ions like Zn, Mg, Fe, etc., 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 etc 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 favours Mg (0.86Å), then Zn (0.88Å) and least of all Cd (1.09Å). 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) and Zn\(^{2+} \) ions are 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 \( \xi \) 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

### TABLE VI. Cadmium, selenium, zinc and fluoride concentrations in some rock phosphate sources for fertilizers. The indicated Zn concentrations are a lower bound.

| Source       | Cd    | Se   | Zn   | F    |
|--------------|-------|------|------|------|
|              | [mg/kg] | [mg/kg] | [mg/kg] | [ 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    | 299  | n.a. |
| USA (N.C.)\(^{c,d}\) | 39     | 5    | 333  | 35   |
| Nauru (NZ)\(^{a,d}\) | 100    | n.a. | 1000?| 30   |

\(^{a}\) FAO65; \(^{b}\) USSR; \(^{c}\) Tunisia; \(^{d}\) Morocco; \(^{e}\) USA; \(^{f}\) Nauru
ratio (Table. VI) that may range from 1/10 to 1/100 [13]. 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 Sec. [14] 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 larger than the Cd input, cannot be neglected, and has a strong impact on the pre-existing available soil Cd $C_{\text{av}}^D$ as the Zn-ions will free up many Cd ions (denoted by Cd$^{\text{bx}}$) bound on to soil particles and humic acids moieties.

$$\text{Cd}^{\text{bx}} + \text{Zn}^{2+} \rightleftharpoons \text{Cd}^{2+} + \text{Zn}^{\text{bx}}$$

(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, Zn$^{\text{bx}}$, 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. (4) 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 if the data of Fig. 1 can be explained purely in terms of the impact of Cd dynamics in the soil. As reported by [63], values for $K_D$ obtained by fitting to data bases can vary up to even 2300. Hence 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 were 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 rizosphere. Furthermore, the plant will take up both Cd and Zn ions, and the high Zn component 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 VII 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 counteraction of Zn in the diet [2], and indeed such information has been available in the literature for perhaps

| Rice unit | DZ | DZ* | WZ |
|-----------|----|-----|----|
| Cd $\mu$g/kg | 52 | 41.2 | 79 |
| Se $\mu$g/kg | 26 | 19 | |
| Zn $\text{mg/kg}$ | 14 | 22.3 | 16 |

* mean values, CKDu-endemic area in the DZ, from [39].

over four decades [28].

C. Magnesium and Fluoride mediated enhancement of available Cd in the soil.

[44] drew attention to the impact of salinity and chloride ions on the available Cd concentration in P-fertilized soils, and proposed that Cd$^{2+}$+$\text{Cl}^-$ complex formation in the soil solution has to be taken into account as a function of the chloride concentration in the soil solution. [62] reported similar results and a linear trend between crop Cd and soil Cd. Similarly, [40] drew attention to the importance of fluoride added to soils via P-fertilizer loading, where they considered mainly fluoride toxicity.

However at the time the impact of fluoride ions on the Cd balance, or possible synergies of fluoride, magnesium and Cd were not suspected. Recently such synergies among F, Mg and Cd have been proposed to cause enhanced nephrotoxicity [16, 72] via naturally occurring fluoride and hard water in dug wells rather than from agricultural inputs. Unfortunately, it is not easy in field trials to control or recognize the role played by many variables like fluoride, chloride, and Cd levels etc. Furthermore, glass-house experiments do not simulate the multiple interactions present in actual soils [13]. Of course, results of simplified experiments can be used in principle to construct the synergies and buffering actions that come in to play, but in practice this is full of pitfalls.

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. [41] have discussed the complex formation between A$^{3+}$ ions and fluoride as a function of soil pH. However, possible interactions of the fluoride with Cd ions were not discussed.

In [16] we show 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 en-
hancement 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 [72].

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 salutary effect on heavy-metal content in forming insoluble complexes with, e.g., cadmium, lead etc., 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 (Chui-Fan Zhou et al 2014).

IV. CADMIUM CONTENT IN CROPS LIKE RICE (ORIZA SATIVA)

Fig.1 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.

A. 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 VII and reported for Sri Lanka by [20]. A 90-day irrigated rice crop in the rice-growing north-central province of Sri Lanka takes up about 500 mm water [52], i.e., $5 \times 10^6$ litres of water per hectare as an upper bound. Typical values of Cd concentrations are 0.24 $\mu$g/L in canal water [52], or 0.11 $\mu$g of Cd per kg of soil as reported by [39]. 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 consistency 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 [12] we have:

- Number of hectares averaged over = $0.69 \times 10^6$
- Average yield of rice, m. tonnes = 3.90
- Average yield of husk, m. tonnes = 0.43
- Yield of straw+stubble, m. tonnes = 4.96

Using the above figures and the Cd content $C_{cd}$ of 52 $\mu$g/kg in the grain, 2.5$C_{cd}$ and 3$C_{cd}$ 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 upperbound of 1.2 g/ha Cd estimated from the water intake.

Thus we have consistency with the experimental data given in Table VII. 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 neighbour-hoods. 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 $10^3 h_w (1 - f_e)$. 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

$$M_{Cd} = \int_0^T dt 10^4 \times C_w(t) h_w(t) f_u(t) f_sp(t).$$

(8)

If $C_w$, $f_w$, $f_sp$ 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

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

(9)

Here $V_w = V_w$ is the total water input during the season. For a 90-day crop requiring an average of 5mm-7mm 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 $C_w = 0.24 \mu$g/litre, 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 $\mu$g/kg) are completely consistent with the values given in Table rice-tab.

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

B. 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 life time. 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 \( C_v \cdot f_p \cdot V \). 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:

\[
M_{Cd} = \int_{v_0}^{V_F} f_{sp} \cdot C_w \cdot dV
\]  

(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:

\[
M_d = C_w \cdot f_{sp} \cdot (V_F - v_0)
\]  

(11)

So, neglecting \( v_0 \), setting \( f_{sp} = 1 \) the Cd absorbed by the plant during its life is \( M_{Cd} = C_w \cdot V_F \). 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

\[
V_F = (1 \text{ hectare}) \times (h_p \cdot f_p); \quad W_F = V_F \rho.
\]  

(12)

In the above, \( \rho \) 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 to 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 cutoff 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.

V. TOXICITY EFFECTS OF Cd IN THE PRESENCE OF OTHER IONS.

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 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, say, CODEX alimentarius stipulations. Of course, local authorities have the freedom to re-interpret 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. Farming communities in the UK in regions with high Cd in the soil consume diets rich in potatoes and cereals without any adverse effects. 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 Dharmawardana, 2017, and Sec. 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 VII shows that Sri Lankan Chronic Kidney disease is uncorrelated with Cd in rice. Hence other explanations have been considered. The Codex Alimentarius 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, and Zn, Fe ... are \( I_{Cd}, I_{j}, \ j = \text{Zn, Fe} \), only the amounts scaled by their bioavailable fractions \( f_{j}^{a} \) are of importance. Many studies, e.g., Smolders et al., 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 \( f_{Cd}^{u} \sim 0.05 \). According to 30 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. 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 \( f_{j}^{u} \) 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 exceed the total amount of its competitor ions that there would
be absorption. That is, it is reasonable to conclude that
the condition
\[ I_{Ca} f_{Ca}^a f_{Cd}^u > \sum_j I_j f_j^a f_j^u \]  
(13)
has to be satisfied for any significant Cd absorption by the gut to set in.

VI. 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. (i) Change in soil pH due to fertilizer action and associated action of microorganisms, (ii) 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, aglime and such agrochemicals. (iii) Competitive effects on clay adsorption sites, humic acid moieties, and in the rizosphere, (iv) Proliferation of the root system and its activity under fertilizer addition, leading to increased dissolved Cd in the soil (and in the plant). (v) 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 perpahs 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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