

## SHORT REVIEW

# Phosphate mineral fertilizers, trace metals and human health

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**Abstract:** Fertilizers, indispensable as they may seem, are nevertheless materials that also clearly cause serious environmental contamination notably in the agricultural soils. The dire necessity for increased food production has been more marked than ever before. Mineral fertilizers, which are indeed an important nutrient source used for enhanced food production, have unfortunately now become a 'necessary evil'. Excessive and continuous use of nitrogen and phosphorous fertilizers for decades have converted the agricultural soils into virtual chemical time bombs.

Phosphate rocks by their very geological and mineralogical nature contain a host of environmentally hazardous chemical elements such as Cd, Pb, Hg, U Cr and As among others. The superphosphates are particularly abundant in these hazardous elements and they contaminate the agricultural soils through the use of fertilizer. The leachability and dispersion of some of these toxic elements are most pronounced in some types of soils such as andisols. After the discovery of the dreaded disease 'Itai-Itai' cadmium has been listed as one of the most potentially dangerous elements found in phosphate fertilizers. Uranium, apart from its radiotoxicity, is chemotoxic and on account of these two properties, it is considered as a disease causing element. The geochemical pathways lead these toxic elements into food crops, soil, water, air and ultimately the human body tissues *via* the food chain. Several diseases are known to be caused by the excessive presence of the toxic elements and among them gastrointestinal, pulmonary and kidney ailments are most noteworthy.

**Keywords:** Geochemical pathways, heavy metals, mineral fertilizers, superphosphates.

## INTRODUCTION

This review provides information on the abundance of toxic metals in phosphate rocks and phosphate fertilizers and their impact on soil pollution, accumulation in plants and effects on human health. Two elements, namely

cadmium (Cd) and uranium (U) are considered in detail due to their importance as potent toxic materials as well as the availability of much data.

Much of the world's phosphate fertilizers are produced from phosphate rocks which contain the mineral apatite  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}, \text{F}, \text{Cl}]$ . The term phosphate rock<sup>5</sup> however is rather vaguely defined and generally encompasses naturally occurring geological materials that contain one or more phosphate minerals suitable for commercial use. The term rock phosphate is also used mainly in the field of agriculture. Mineralogically, the phosphate rocks have different origins and chemical and physical properties. The principal phosphate minerals in them are the apatite (Ca phosphates). Chemically, a pure fluor-apatite would contain 42%  $\text{P}_2\text{O}_5$  while francolite, another mineral found in phosphate rocks has 34%  $\text{P}_2\text{O}_5$ . The five main types of phosphate deposits mined are:

- i) marine deposits
- ii) igneous deposits
- iii) metamorphic deposits
- iv) biogenic deposits
- v) secondary deposits formed by weathering

It has been estimated that 75% of the world's phosphate resources are obtained from sedimentary, marine rock deposits while 15-20% are obtained from igneous and weathered deposits. The biogenic resources account only for 1-2%<sup>1</sup>. Fluoro-apatite  $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$  is found mainly in igneous and metamorphic deposits and the hydroxyl-apatite  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$  is found in biogenic deposits such as bone and teeth in addition to igneous and metamorphic types. Francolite  $[\text{Ca}_{10-x-y}\text{Na}_x(\text{PO}_4)_{6-z}(\text{CO}_3)_2\text{F}_{0.4}\text{F}_2]$  is common in the marine phosphates and to a lesser extent in carbonatite, an igneous type of phosphate.

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Phosphorus (P), like potassium and nitrogen is an essential element for plant growth and the phosphate fertilizer industry is therefore a major global concern. Very large phosphate deposits are mined in many parts of the world (Tables 1 and 2), while the small to medium deposits often lie dormant due to economic, geographic and technological reasons. In international trade, phosphate ranks just below coal and hydrocarbons, indicating its major importance in agriculture and industry. During the last two decades, 80-90% of world phosphate rock output had been used in the fertilizer industry. The phosphate fertilizer categories include the basic slag (12-18%  $P_2O_5$ ), single superphosphate (17-20%  $P_2O_5$ ), rock phosphate (26-37%  $P_2O_5$ ), dicalcium phosphate (35-52%  $P_2O_5$ ) and triple superphosphate (44-48%  $P_2O_5$ ). Generally, phosphate fertilizers are produced by the acidulation of crushed and powdered phosphate

rock. Single superphosphate (SSP) is produced by the use of sulphuric acid while triple superphosphate (TSP) uses phosphoric acid for acidulation (Figure 1).

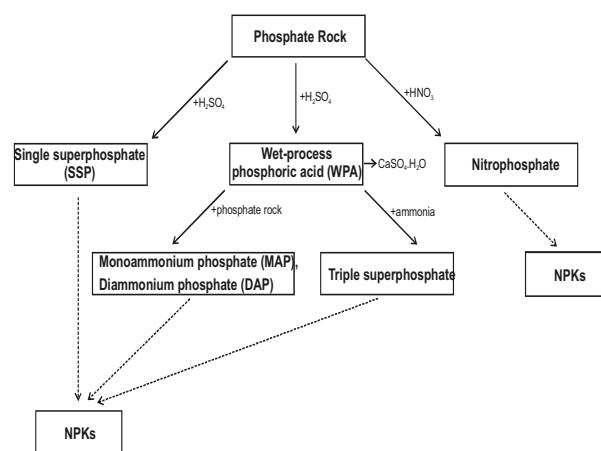
Contamination of phosphate fertilizer by toxic elements has been observed during their processing using the above methods. Fluorides, metals such as Cd, mercury (Hg), lead (Pb), U and chromium (Cr) have been found to be significantly high in some of the final products ready for marketing. Radionuclides are also often carried through from the phosphate rock and become accumulated. The quantities of these undesirable toxic materials can be dangerously high if the processing does not include adequate cleaner production methodology. Precipitation of heavy metals is highly desirable, particularly when the raw phosphate materials contain an abundance of toxic material. Due to the presence of these toxic elements that have a major negative impact on the environment many countries have enforced stringent laws on the maximum permissible levels of the toxic elements in fertilizer products.

**Table 1:** World phosphate rock production, 1999 (Source: Mew)<sup>60</sup>

Country	Product (1 000 tones)	World total %
United States of America	40 867	28.1
China	30 754	21.1
Morocco and Western Sahara	21 986	15.1
Russian Federation	11 219	7.7
<b>Subtotal top four</b>	<b>104 826</b>	<b>72.0</b>
Tunisia	8 006	5.5
Jordan	6 014	4.1
Brazil	4 301	2.9
Israel	4 128	2.8
South Africa	2 941	2.0
Syrian Arab Republic	2 084	1.4
Senegal	1 879	1.3
Togo	1 715	1.2
<b>Subtotal top twelve</b>	<b>135 894</b>	<b>93.4</b>
India	1 623	1.1
Algeria	1 093	0.8
Egypt	1 018	0.7
Mexico	955	0.7
Kazakhstan	900	0.6
Finland	734	0.5
Vietnam	710	0.5
Christmas Island	683	0.5
Nauru	604	0.4
Iraq	415	0.3
Venezuela	366	0.3
Canada	350	0.3
Australia	145	0.1
Uzbekistan	139	< 0.1
Zimbabwe	124	< 0.1
Democratic People's Republic of Korea	70	< 0.1
Sri Lanka	30	< 0.1
Peru	15	< 0.1
Colombia	4	< 0.1
<b>World total</b>	<b>145 472</b>	<b>100.0</b>

### Hazardous elements in phosphate fertilizers

The entry of various heavy metals into the human food chain *via* various agricultural products has been given increased attention in recent years due to their possible health impacts. Some potentially toxic metals and trace elements present in agricultural soils enter the human body easily through the food chain. Low levels of all of these elements occur naturally in soils and some are essential for plants or animals. Even the essential trace elements create a toxicity problem if high levels are present in the environment<sup>2</sup>.



**Figure 1:** Relationship of phosphate rock and phosphate fertilizers<sup>4</sup>

Application of inorganic fertilizers frequently results in the addition of certain trace elements that are already present in soils as traces. Depending on their origin,

inorganic fertilizers such as superphosphates and rock phosphates may also contain different quantities of potentially toxic heavy metals or compounds derived mainly from parent rock materials. They may also result from other sources, such as corroded equipment, catalysts, reagents and materials added to commercial preparates as fillers, coaters, conditioners, etc. (i.e. gypsum, kaolin, limestone)<sup>3</sup>. Application of such fertilizers could lead to a modification of the natural geobiochemical equilibria which may affect human health adversely. Application of potentially toxic metals into agricultural soils is of great concern because they do not degrade and remain in the soil indefinitely<sup>3</sup>. Fertilization coupled with irrigation can cause substantial changes in the hydrology and chemistry of groundwater in agricultural areas. Trace substances in mineral fertilizers added to the soils could easily leach and contaminate groundwater resources. It is now an established fact that mineral fertilizers are a major source of the inorganic elements that enter food materials. The raw materials used to produce the fertilizers are the ultimate sources of these elements and the phosphate fertilizers are therefore particularly rich in toxic elements (Table 3). The global application of these phosphate fertilizers is enormous (Figure 2).

During the late 1960's, Japan experienced the disastrous effects of cadmium, when the dreaded “*Itai-Itai*” disease was discovered. The rice plant (*Oryza sativa*) which produces the staple diet of millions of people in Asia was known to absorb cadmium readily and any input into a rice field of a Cd-rich fertilizer (i.e. phosphates) was considered to be dangerous. Austria,

**Table 2:** Reserve base world rock phosphate deposits<sup>61</sup>.

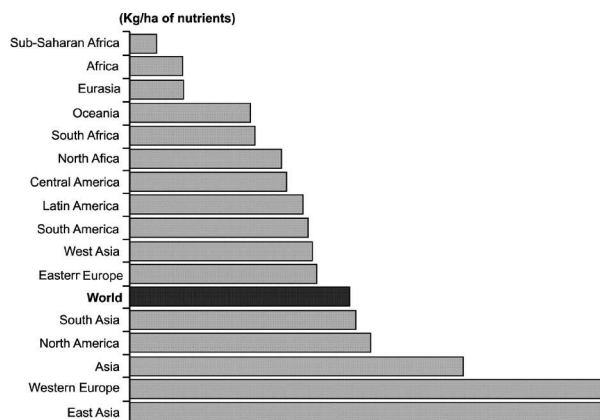
Country	(In '000 tones)
Australia	1200000
Brazil	370000
Canada	200000
China	13000000
Egypt	760000
India	160000
Israel	800000
Jordan	1700000
Morocco and Western Sahara	21000000
Russia	1000000
Senegal	160000
South Africa	2500000
Syria	800000
Togo	60000
Tunisia	600000
USA	4000000
Other countries	2000000
World total	50000000

Finland and Sweden enforced limits for Cd in fertilizers at the international level<sup>5</sup>. As a result of this, the average Cd content of fertilizers in Sweden fell from 80 mg/kg to about 8 mg/kg P<sub>2</sub>O<sub>5</sub>.

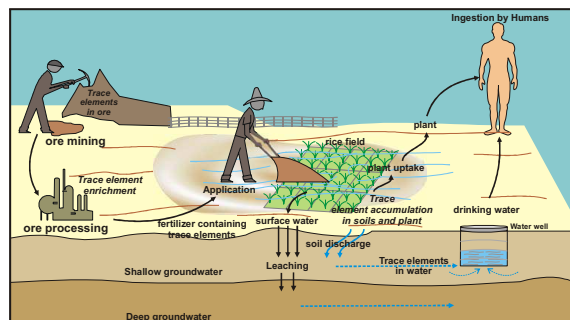
The two main geochemical pathways of trace elements are:

- i) Raw materials (phosphate rocks) → fertilizer → soil → plant → food → human body
- ii) Raw materials (phosphate rocks) → fertilizers → water → human body

Figure 3 illustrates a model depicting these different geochemical pathways of toxic trace elements affecting human health. It is clearly seen that the toxic elements have their origin in the phosphate ores and from the phosphate fertilizer production processes. If stringent precautions are not taken and the proper regulations not implemented, the agricultural fields such as the rice fields of tropical Asia would be a sink for these hazardous elements. Considering the very large quantities of phosphate fertilizers added and that too in several seasons annually, the danger posed to human health is very large.



**Figure 2:** Per hectare fertilizer use by markets, 1998/99 <sup>60</sup>



**Figure 3:** Conceptualized model showing geochemical pathways of metals

**Table 3:** Concentrations of hazardous elements in phosphate rocks (mg/kg) <sup>62</sup>

Element	Morocco Bu Craa	Morocco Khouribga	Togo Benin	Senegal Taiba	Eshidia	Jordan El-Hasa	Tunisia Gafsa	Algeria Djebel Onk	USA Florida	Israel Nahal Zin	Syria Kneifiss	Russia Kola	Russia Kovdor	South Africa Phalaborwa
Cd	25-42	3.0-27	53-65	53-110	3.0-9.6	2.7-34.7	15-63	11-22.5	6.8-11.2	20-30	5-15	0.05-0.12	0.5-0.9	0.04-5.0
Hg	0.1	0.03-0.1	-	0.1-0.5	0.03	0.01-0.5	0.05-0.2	0.3-5.0	0.08	0.4-0.6	0.01-0.1	<0.01	0.1	0.15-0.2
As	3.9	6-13	-	1.0-3.6	5-7	2.6-27.5	1.5-31.9	10-22.6	8.0-9.0	3-10	15-30	0.2-1.0	2-4	3-15
Pb	1	1-1.3	-	4-5	3.4	1-16.2	4-11.4	6-20	18	2-7	2-10	0.6-2.0	2-14.3	2-19
Cr	130	300	30	6-200	60-100	72-100	81	200	91	50-70	-	2.1-3.0	1-69	7-10
Sb	-	-	-	-	-	-	-	10-15	-	-	-	1.0-4.0	1.0-4.0	-
Ba	-	-	-	100	-	-	-	-	-	-	-	70-690	70-690	-
F	3.9-4.5	3.9-4.1	3.8	3.7-3.9	3.6-4	3.7-3.8	3.54-4.9	3.3-3.7	3.8	3.3-4.0	3.6-4.0	0.96-1.01	0.96-1.01	0.22-2.25
Cu	14	39-47	-	50-70	21	9-27	19-28	15-24	9.0	20-40	5-29	4-40	4-40	105-130
Ni	40	41	-	28-53	11	15-71	28	16-20	30	35	53-61	14-28	14-28	14-40
Zn	66-120	200-255	-	-	135-164	85-420	151-370	185	95	300-500	320-340	23-64	23-64	6-20
Co	-	-	-	1	6	9-26	17-20	17	-	-	8	5	5	-
Mn	200	-	200	20	11.6	30-77	35-37	14-35	290	5.0-10	6-7	300-1100	300-1100	200
Sr	-	150	30	120-800	-	1100-2500	1925	2022	-	2000-4000	1900	1600-2830	1600-2830	4650-5500
V	122	21	-	140	50-70	32-70	62	45	70	100-160	-	3-90	3-90	8-15

### Cadmium in soils and phosphate fertilizers

van Kauwenbergh<sup>4</sup> has considered about 16 elements that are associated with phosphate rocks and fertilizers which are potentially hazardous to human health. Mineralogically, the apatite structure is known to host more than 25 elements which include hazardous elements such as Cd, As, Cr, Hg, Pb, Se, U and V<sup>5</sup>. These elements are probably found as substituents within the apatite structure or substituting in other associated minerals within the phosphate rocks or as adsorbants on the apatite surface. It is generally proposed that divalent calcium is replaced by many other divalent cations including Hg or Pb. In the case of other ions such as V, Cr or U, coupled replacement can be expected.

Weathering processes, which bring about secondary mineral deposits, also contribute quite significantly to the enrichment of metals in the phosphate deposits. Uranium accumulations in the Florida phosphate deposits are known to be caused by such processes<sup>6</sup>. U and Rare Earth Elements (REE) in phosphate rocks of Morocco and Queensland in Australia are accumulated in this manner<sup>7</sup>. An interesting study by van Kauwenbergh<sup>8</sup> showed that approximately 25% of Cd in the highly weathered zone of the Togo phosphate deposit is associated with the calcite component and that phosphate and cadmium tend to concentrate during the leaching of carbonate-bearing beds and removal of calcite.

Table 4 shows the enrichment (depletion) factors of some toxic elements. It is observed that Cr, Hg and V are considered normal in abundance in sedimentary phosphates rocks. The most significant feature is that Cd and U are the most enriched and potentially hazardous elements in sedimentary phosphate rocks with enrichment factors of 69 and 30, respectively. Table 5 shows the phosphate and cadmium contents of some sedimentary

phosphate rocks from some countries with phosphate deposits.

### Uranium in soil and phosphate fertilizers

Uranium has five main oxidation states (+2, +3, +4, +5 and +6). Of these +4 and +6 are commonly found in the natural environment. Out of the three naturally occurring isotopes (<sup>234</sup>U, <sup>235</sup>U and <sup>238</sup>U), 99% is <sup>238</sup>U which has a half life of 4.46x10<sup>9</sup> years. It emits alpha, beta and gamma emissions<sup>9</sup>. Apart from the radioactive emissions, uranium is also chemo-toxic and hence it is considered as an element of great environmental concern.

Mineralogically, uranium is found as uraninite (UO<sub>2</sub>), brannerite (U,Ca,Ce)(Ti,Fe)<sub>2</sub>O<sub>6</sub> and carnotite K<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>.3H<sub>2</sub>O. As an accessory element, it is found in the minerals apatite, zircon, allanite and monazite as well as in complexes with organic matter and phosphatic ironstone. Uranium is found in a variety of chemical forms in soils, food and drinking water<sup>10</sup>. In the earth's crust, uranium is generally found as oxides (UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>). In soils, about 80-90% of uranium is present in the +6 state as the uranyl cation (UO<sub>2</sub><sup>2+</sup>)<sup>11</sup>. This ion is predominant under acidic reducing conditions in the soil and under neutral conditions hydroxide complexes such as UO<sub>2</sub>OH<sup>+</sup>, (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, (UO<sub>2</sub>)<sub>3</sub>(OH)<sup>5+</sup> and (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>7</sub><sup>-</sup> and phosphate complexes such as UO<sub>2</sub>HPO<sub>4</sub><sup>0</sup> and UO<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub><sup>2-</sup> form. In alkaline conditions, carbonate complexes such as UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> are predominant.

It has been reported that the global uranium concentrations in soils range from 0.3 to 11.7 mg/kg<sup>12</sup>, the average background concentration being 2 mg/kg<sup>13</sup>. In the soils, conditions such as high biological and chemical oxygen demand (BOD and COD), water saturation, carbonate content, organics, pH and parent

**Table 4:** Potentially hazardous trace element abundances in sedimentary phosphorites, sedimentary phosphate rock, and average shale<sup>4</sup>

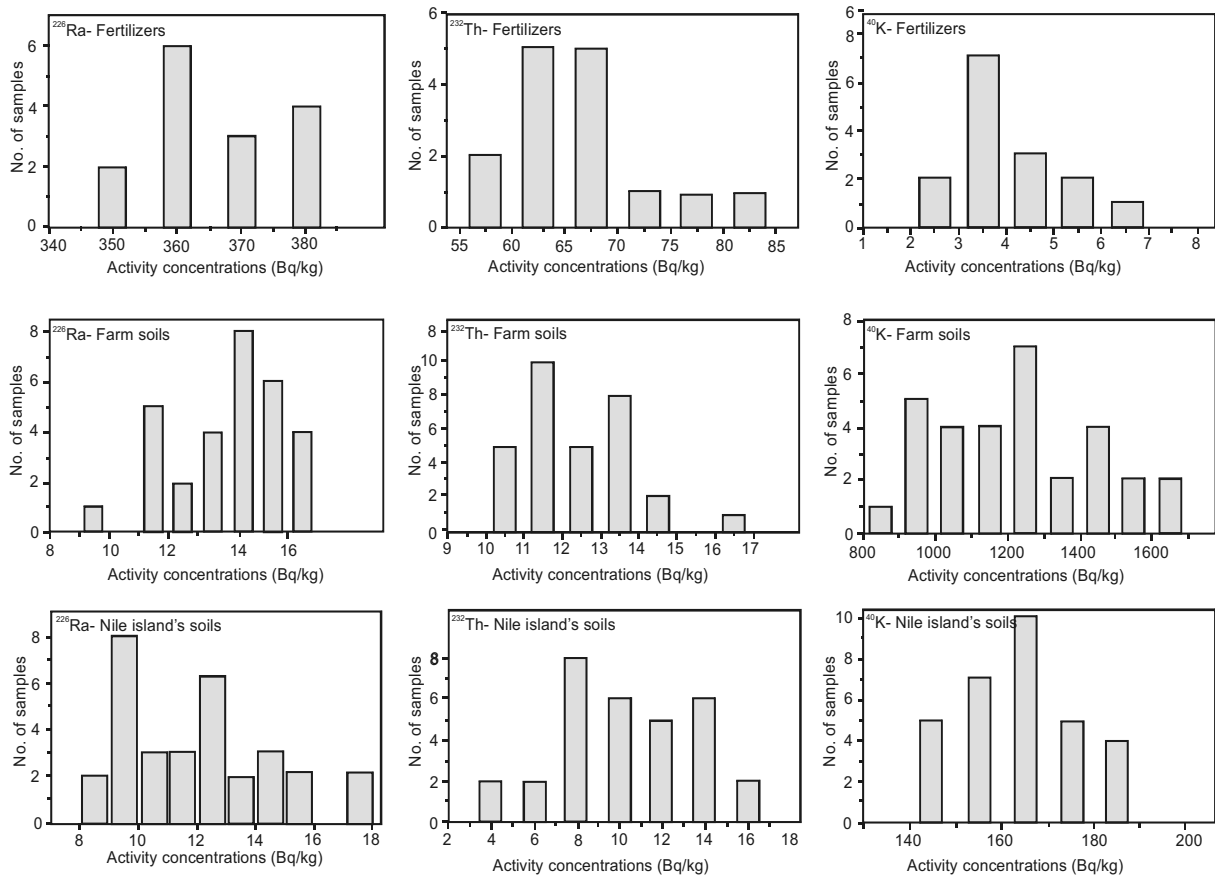
Element	Atschuler (1980)			Van Kauwenbergh (1997)		
	Average shale (mg/kg)	Average phosphorite (mg/kg)	Enrichment (depletion) factor	Average shale (mg/kg)	Average phosphorite (mg/kg)	Enrichment (depletion) factor
As	13	23	1.8	6.6	13.2	2.0
Cd	0.3	18	60	0.3	20.6	68.7
Cr	90	125	1.4	100	129.2	1.3
Hg	0.4	0.055	(7.3)	0.4	0.4	1.0
Pb	20	50	2.5	20	8.4	(2.4)
Se	0.6	4.6	7.7	0.6	4.8	8.0
U	3.7	120	32.4	3.2	96.1	30.0
V	130	100	(1.3)	130	129.6	1.0

**Table 5:** Phosphate and cadmium contents of sedimentary phosphate rocks <sup>4</sup>

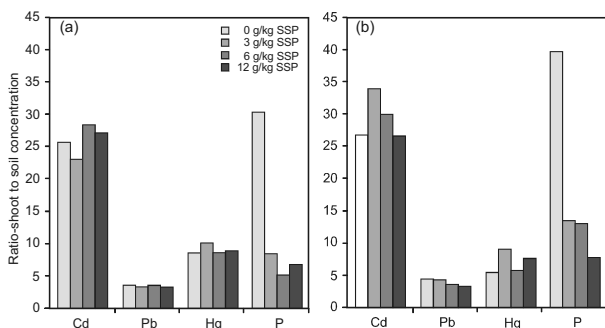
Country	Deposit	Average P <sub>2</sub> O <sub>5</sub> wt %	Range of Cd (mg/kg)
Algeria	Djebel Onk	28.8	13-32
Australia	Duchess	31.2	0.5-5
China	Kaiyang	35.9	<2
Colombia	Sardibnata	35.4	12-19
Egypt	Abu Tartur	29.9	3-10.5
Israel	Zin	31.3	20-40
Jordan	El-Hasa	31.9	3-12
Mali	Tilemsi	28.8	8
Morocco	Khouribga	32.6	3-27
Senegal	Taiba	35.9	60-115
Togo		36.7	48-67
Tunisia		29.9	36-56
USA	Florida	32.1	3-20
Sedimentary Averages		31.3	0.5-150

**Table 6:** Comparison of the intervals of uranium concentrations in phosphate fertilizers produced in different countries <sup>63</sup>

Country	Uranium concentration (ppm)	Method of determination
USA	8.9 – 221.0	γ-Ray spectrometry
Germany	3.2 – 185.5	γ-Ray spectrometry
Uzbekistan	11 – 70	Fission track
India	15.9 – 35.8	Fission track
Croatia	66 – 127	γ-Ray spectrometry
Yugoslavia	58.9 – 162.0	Spectrophotometry
Brazil	5.17 – 54.3	Fission track



**Figure 4:** Distribution of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K in phosphate fertilizers, farm soils and Nile island's soils <sup>30</sup>



**Figure 5:** The magnitude of shoot to soil ratios for the heavy metals and phosphorous<sup>39</sup>

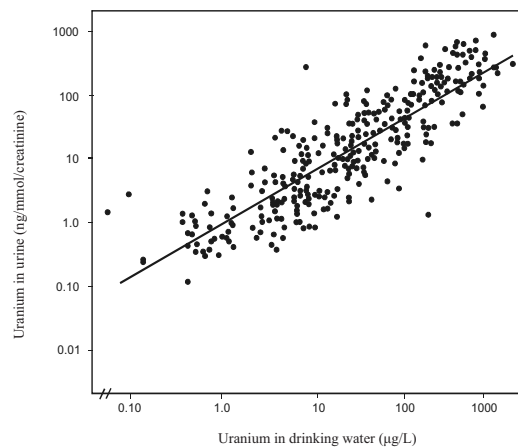
material are particularly significant in uranium mobility. An increased soil cation-exchange capacity (CEC) will retain more uranium while carbonates present increases the mobility of uranium<sup>14,15</sup>. Acidic soils with poor adsorption characteristics, alkaline soils with carbonate minerals and the presence of chelates such as citric acid are known to increase uranium mobility and plant accumulation<sup>16</sup>.

In water, the mobility of uranium depends on factors such as pH, redox status and the concentration of dissolved ions. Even as a metal, it shows high solubility particularly in oxidizing, alkaline and carbonate-rich waters. It is also soluble in strongly acid waters. Under these conditions the main species in solution is the uranyl cation ( $UO_2^{2+}$ )<sup>17</sup>. In neutral to alkaline oxidizing conditions, soluble uranyl-carbonate complexes i.e.  $UO_2(CO_3)_2^{2-}$  are most common<sup>18,19</sup>. Under reducing conditions, insoluble  $UO_2$  can be observed. Uranium is known to be sensitive to redox conditions and occurs in  $U^{6+}$  state under oxic conditions. It is found as a complex ion solution, mostly with carbonate ligands and phosphate, fluoride and sulphates. In the groundwater, uranium occurs in higher concentration as compared to surface water on account of the large solid/solution ratios in aquifers and the greater influence of water-rock interactions<sup>20</sup>. The affinity of uranium for organic matter and phosphates is marked and hence the importance of uranium contamination in agricultural fertilizers.

**Table 7:** Pb and Cd contents in the phosphate fertilizers used and metals quantities incorporated by the highest rate<sup>41</sup>

Fertilizer	Pb	Cd
Gafsa rock phosphate	238 (355.4)	61 (91.1)
Triple superphosphate	45 (45.9)	28 (28.5)
Yorin thermophosphate	110 (256.3)	11 (25.6)
Araxá rock phosphate	51 (55.7)	15 (16.4)

Numbers in parenthesis refer to g/ha



**Figure 6:** Correlations of the uranium concentration in drinking water and in urine [ $\log(y) = 0.01 + 0.80 \log(x)$ ; Pearson correlation = 0.85]<sup>56</sup>.

Takeda *et al.*<sup>21</sup> showed the accumulation of uranium in a cultivated Andisol in Japan subjected to long term application of fertilizers. The large quantities of uranium contained in phosphate fertilizers was expected to enrich agricultural soils in uranium after application of the fertilizer<sup>22-24</sup>. Guzman *et al.*<sup>25</sup> noted that the uranium concentration in the phosphate fertilizers used on Mexican lands ranges between 70 and 200 mg/kg. They were of the view that it is capable of generating toxic effects in all the trophic levels if 2.1 mg/L are surpassed in soil and 20 µg/L in the water supply<sup>26-28</sup>.

Under flooded conditions such as those observed in rice fields, virtually all water soluble uranium in fertilizers was absorbed by Andisols 24 hours after application<sup>29</sup>. Soil types, quality of fertilizer and its application rate are among some of the factors that influence the accumulation of uranium in surface soils. In view of the fact that about 90% of uranium input to the field was attributable to superphosphate, Takeda *et al.*<sup>21</sup> estimated that the annual input of uranium from the application of fertilizer material was 3.0 mg/(m<sup>2</sup> y).

**Table 8:** Analytical results of triple super phosphates collected from different locations in Sri Lanka (in mg/kg)<sup>58</sup>

Collected location	Al	Cr	Ni	Cd	Pb	U
Anuradhapura	9949	52.9	35.2	3.6	50.7	107
Medawchchiya	9405	43.6	27.1	4.0	79.2	76
Medirigiriya	8563	59.5	22.3	46.1	41.1	5.8
Giradurukotte (1)	9016	65.9	24.2	39.8	58.2	64.1
Kandy	10113	62.1	27.3	4.3	80.2	166
Giradurukotte (2)	5177	19.2	10.6	2.3	67.2	364
SLS			N/A	10	250	

Ahmed and El-Arabi<sup>30</sup> carried out a study on the natural radioactivity in farm soil and phosphate fertilizer in Qena, Upper Egypt. Since phosphate fertilizers are used extensively in agriculture, uranium concentrations in phosphate fertilizers obtained from different parts of the world are most useful. This is particularly important for those developing countries of the tropical belt, where laws pertaining to radio- and chemo-toxicity of the metals in fertilizers may not be rigidly enforced. Further, in the tropical countries in view of the high rain fall and leaching, dissolution of metals may be intense, and their geochemical distributions are such that there may be a great impact on the environment and the food chain.

It has been shown that the concentration of uranium correlates with the  $P_2O_5$  concentration of fertilizers<sup>31,32</sup>. It was noted that the  $^{232}Th$  series contributes only in a minor way to the radioactivity in phosphates compared to the uranium series<sup>33,34</sup>. The naturally occurring<sup>40</sup>K is also known to be present in soils and phosphate fertilizers. Figure 4 shows the distribution of  $^{226}Ra$ ,  $^{232}Th$  and  $^{40}K$  in phosphate fertilizers, farm soils and Nile Island soils in the Upper Egypt<sup>30</sup>. A study by Makweba and Holm<sup>35</sup> in Arusha, Tanzania had shown that the radioactivity of superphosphate, triple superphosphate and phosphogypsum had activity concentrations as high as 400 Bq/kg. Phosphate fertilizers from Pakistan had the  $^{238}U$  activity concentrations of 799 Bq/kg while that from Jordan was 4.28 Bq/kg<sup>36</sup>. Further, the activity concentration of Ra in the SSP fertilizer was found to be 1043 Bq/kg which is significantly higher than normal background values. The uranium concentrations in the Brazilian phosphate fertilizers ranged from 5.17 to 54.3 mg/kg and were in good agreement with the results reported for similar fertilizers in other countries (Table 6).

The use of phosphate fertilizers was also considered as a uranium enrichment factor in soils and groundwater<sup>37</sup>. After investigating the effect of decades-long application of uranium rich fertilizer on the uranium concentration of irrigation drainage, Zielinski *et al.*<sup>38</sup> showed that there was a minimal impact of fertilizer-U compared to natural uranium leached from local soils.

### Heavy metals entering the food chain from fertilizers

As mentioned earlier, Cd has been intensively studied for its impact on the environment and human health. Plants are known to show highly variable capacities to absorb and translocate metals from vegetative tissues to grain and subsequently to the human body. Further, this is also of great importance to grazing animals who may ingest Cd and other heavy metals from a source of phosphate fertilizer quite easily.

Phosphate fertilizers contain toxic elements such as Cd, U, Hg, Pb, Fe, Mo, Ra, rare earth elements and Cr among others and these tend to accumulate in the agricultural soils over many years. Many experiments have been carried out on the labile nature of toxic elements, notably Cd. Even though Cd accumulation poses a threat of contamination of agricultural soil from the more soluble phosphate fertilizers such as triple superphosphate. Due to slow leaching out of the metal bioaccumulation is considered by some workers to be not too intensive, though some other experiments suggest a significant accumulation of the metal in plant tissues. The soil conditions, notably pH and the plant varieties however, play a major role in the bioaccumulation of cadmium.

The accumulation of heavy metals in some vegetables after phosphate fertilizer application was studied by Oyedel *et al.*<sup>39</sup>. They showed that the Cd, Pb and Hg contents of the soils had increased significantly with the addition of fertilizer by the 14-60% over the control soil. Root and shoot accumulation of the heavy metals by the plants had also increased after fertilizer application, with Cd and Pb being particularly high. From among the metals, Cd showed the highest transfer ratio from soil to plant tissues (Figure 5). Guzman *et al.*<sup>40</sup>, in their study of contamination of corn growing areas due to intensive fertilizer application in the high plane of Mexico had pointed out that the occurrence of phosphate was approximately 100 times greater in the agricultural areas compared to the non-agricultural areas. They quantified the entry of phosphate and uranium in the vadose zone, where the quantity of phosphate was 443 g/kg and that of uranium was 198 mg/kg. They observed that from the total phosphate, a fraction of 15-20 % was assimilated by crops while the rest remained in the inter phase vadose zone-water.

Mendes *et al.*<sup>41</sup> studied the bioavailability of cadmium and lead in a soil amended with phosphorus fertilizers in Brazil (Table 7). In spite of the relatively high concentration of Pb in the fertilizers, this element was not detected in the shoots of the velvet bean plants. They attributed this result as being due probably to the low Pb translocation in plants and its preferential accumulation in roots. However, the low availability of this metal in alkaline soils as the one used in the work of Mendes *et al.*<sup>41</sup>, along with the low solubility of Pb phosphates<sup>42</sup>, seemed to be a significant factor. The application of agronomic rates of the phosphates fertilizers may not increase the Pb concentration above the levels naturally found in soils. They emphasized however, that monitoring Pb uptake by plants in soils needs to be done in the long term, since Pb availability can increase due to chemical alterations in the soil, particularly those with low pH.



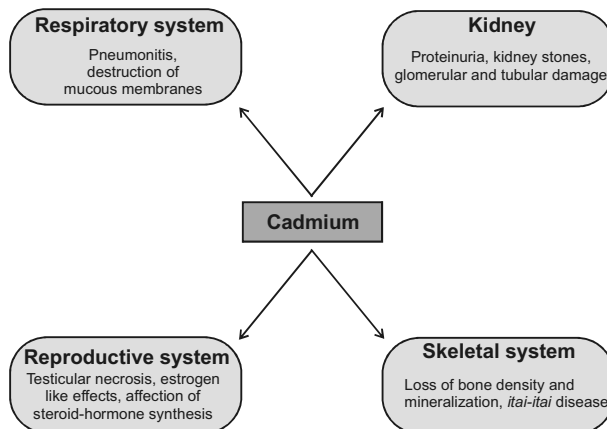


Figure 7: Effects of cadmium on several organ systems<sup>57</sup>.

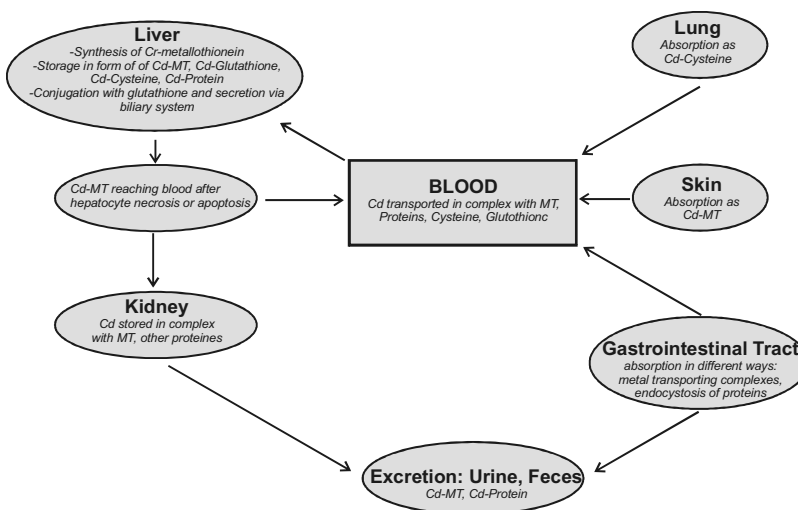


Figure 8: Metabolism, storage and excretion of cadmium in the human body<sup>57</sup>.

**Plant uptake of heavy metal contaminants in phosphate fertilizers**

As discussed by Mortvedt and Beaton<sup>43</sup>, plant species differed considerably in their ability to take up Cd. Leafy vegetables absorb more Cd than grasses, and only 12-18 % of the Cd in cereal plants was translocated into the grain. However, soil application of TSP containing Cd resulted in increased Cd concentrations in both cereal grains and the edible portions of vegetables. Top dressing pastures with TSP also resulted in increased Cd of pasture species, especially that of subterranean clover (*Trifolium subterraneum* L.)<sup>44</sup>. Reuss *et al.*<sup>45</sup> had also found greater Cd uptake by radish (*Raphanus sativus* L.), lettuce (*Latuca sativa* L.) and peas from soil applications of TSP containing 870 mg Cd/kg P than from Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>,

which is the main P compound in TSP. In plants the uptake of Cr, Ni, and Pb was quite variable and was not directly related to their concentrations in P fertilizers<sup>46</sup>. It should however be mentioned that there are significant differences among plant species in their ability to take up Cd and other heavy metals.

Mortvedt and Beaton<sup>43</sup> report that the average weekly per capita Cd intake in the USA was estimated at about 100 µg, compared to the maximum weekly Cd intake of 400-500 µg approved by the World Health Organization<sup>47</sup>. Estimated per capita weekly Cd intake in Australia was 125-225 µg<sup>48</sup>. While Cd uptake by crops might be somewhat higher on P-fertilized acid soils, doubt has been expressed about the weekly Cd intake by humans increasing significantly.

## Health aspects

As shown in the model depicted earlier, the geochemical pathways of metals which had originated from the source phosphate rocks and the phosphate fertilizers produced from them ultimately enter the human tissues resulting in diseases thereafter. Even though some studies have shown that there is only a low entry of these hazardous metals into the human tissues from the soils and plants fed with phosphate fertilizers, the cumulative effects over a long period of time, certainly is a matter of concern. This is particularly so, when low quality phosphate fertilizers (generally known to contain an array of trace metals) are applied over several years. Cd, U, Hg and Pb have been studied extensively for their health effects.

Even though uranium is rather abundant in the environment, it has no known metabolic functions in animals and hence, it is regarded as being non-essential<sup>49</sup>. The absorption of uranium from the gastrointestinal tract depends upon the solubility of the uranium compound<sup>49</sup>, previous food consumption<sup>50,51</sup>, and the concomitant administration of oxidizing agents such as Fe<sup>3+</sup> ion and quinhydrone. The average human gastrointestinal absorption of uranium is 1-2%<sup>52</sup>. After the ingestion of uranium, it is rapidly taken up into the bloodstream<sup>51</sup>, where it becomes associated mainly with red cells<sup>53</sup>. A non-diffusible uranyl-albumin complex is known to form in equilibrium with a diffusible ionic uranyl hydrogen carbonate complex (UO<sub>2</sub>HCO<sub>3</sub><sup>+</sup>) in the plasma<sup>54</sup>. The uranyl compounds are known to show high affinity for phosphate, carboxyl and hydroxyl groups and therefore, they combine readily with proteins and nucleotides to form stable complexes. Removal of uranium from the bloodstream takes place rapidly and it accumulates in the kidneys and skeleton. The latter is the major site of uranium accumulation of the uranyl ion replacing calcium in the hydroxyapatite complex of bone crystals. Chemically, the main effect of uranium in humans is nephritis<sup>55</sup>. Nephrotoxicity of uranium has been studied by Kurtio *et al.*<sup>56</sup> who measured uranium concentration in drinking water and urine in 325 persons who had drilled wells for drinking water. They observed that the median uranium concentration in drinking water was 2 µg/L and in urine 13 ng/mmol creatinine, resulting in the median daily intake of 39 µg. They have concluded that uranium exposure is weakly associated with altered proximal tubular function suggesting that even low uranium concentrations in drinking water can cause nephrotoxic effects. Figure 6 shows the correlation of uranium concentration in drinking water and that of urine.

The effect of Cd on human health has been studied intensively, particularly after the discovery of the *Itai-Itai* disease in Japan. Cadmium has no particular

physiological function within the human body and as shown in Figure 7, cadmium poisoning can lead to kidney, bone and pulmonary damage. There are three main ways of cadmium resorption in the human body, namely, gastrointestinal, pulmonary and dermal. The uptake of Cd through the human gastrointestinal system is about 5% of the total amount ingested, depending on the exact dose and nutritional composition<sup>57</sup>. It has been reported that an average German citizen has a daily intake of 3.0-35 µg of Cd, 95% of which comes from food and drink. Of particular importance was the fact that people with low iron supplies showed a 6% higher uptake of Cd, than those with normal iron contents. This may have an important impact on anaemic people, notably in the developing countries, exposed to excessive cadmium ingestion. Within the body, once taken up by the blood, most of the Cd is transported to proteins such as albumin and metallothionein (Figure 8). The main organ for long term Cd accumulation is the kidney, where the half-life period of Cd is about 10 years. Extensive accumulation of Cd in the kidney results in tubules cell necrosis. Accordingly, the blood concentration of Cd serves as a reliable indicator of recent exposure, while the urinary concentration reflects past exposure body burden and renal accumulation. There is a correlation of urinary Cd excretion with the degree of Cd-induced kidney damage. A urinary excretion of 2.5 µg Cd per g of creatinine reflects a renal tubular damage degree of 4%. Cadmium poisoning and bone damage is well known, the *Itai-Itai* disease being a good example. Several studies had come to the conclusion that environmental exposure to Cd can cause skeletal demineralization. Even though the exact manner in which Cd affects bone mineralization is not known, there appears to be a direct influence on osteoblast and osteoclast function *via* renal dysfunction.

## Metals in phosphate fertilizers used in Sri Lanka

Phosphate fertilizers are widely used in agricultural activities in Sri Lanka to supply crops with adequate amounts of P for growth and development. Mainly two types of phosphate fertilizers are available in the Sri Lankan market. The Eppawala rock phosphate produced in Sri Lanka has very low solubility and hence it is used only for long term crops such as tea, rubber and coconut. The other variety is imported granular TSP which is used mainly for perennial crops such as rice and vegetables.

Chandrajith *et al.*<sup>58</sup> described the heavy metals and activity concentration of radionuclides such as <sup>40</sup>K, <sup>226</sup>Ra and <sup>232</sup>Th in rice field soils and commonly used fertilizers in Sri Lanka. Table 8 shows the heavy metal contents of the TSP available in the Sri Lankan market. The results

indicate that the trace element levels vary widely in the TSP available in the local market, probably depending on the country of origin. However, identification of the origin of the fertilizers is not possible with the samples collected from the market. In some samples extremely high amounts of uranium were recorded. It is also noted that in some cases, the trace metal contents exceed the standard values recommended by the Sri Lanka Standards Institute. The results obtained from their study indicated that the U content in TSP collected from the local market varies from 5.8 to 364 mg/kg. However the content of U in rice field soils samples was below 7 mg/kg with an average of 3.6 mg/kg. In Sri Lanka, farmers use TSP twice a year (three times in some cases) for their rice cultivations and the average amount of TSP applied for rice fields is 85 kg/ha per season. Similarly higher <sup>40</sup>K levels were noted in both rice paddy soils and TSP available in the local market.

The activity values of <sup>40</sup>K in rice paddy soils collected from Anuradhapura, Giradurukotte and Kandy ranged from 542 to 680, 308 to 637 and 296 to 846 Bq/kg, respectively. These values are greater than the typical world average value of 370 Bq/kg (UNSCEAR 1993)<sup>12</sup>. The radioactivity of <sup>40</sup>K in two reference sites (undisturbed natural forests) from the dry zone and the wet zone respectively were 258 and 138 Bq/kg, and these <sup>40</sup>K values are lower than that of paddy soils, which are highly modified by anthropogenic activities such as puddling, submerging and by artificial fertilizer applications. The activity values of <sup>40</sup>K obtained from different fertilizers collected from the Sri Lankan market were 103-15606 Bq/kg.

Effect of fertilizer applications to rice fields in Sri Lanka should be investigated fully in terms of accumulation of metals in soils and their transfer into drinking water and finally into the human body particularly<sup>14</sup> because of the widespread chronic kidney disease in the dry zone region with an uncertain aetiology.

### Setting regulations for heavy metals in fertilizers

Curtis and Smith<sup>59</sup>, who developed a model for the setting up of regulations for heavy metals in fertilizers, stated that a mathematical model for fertilizer application (fertilizer risk model) has 3 principal components;

- i) A description of metal accumulation in soil.
- ii) A description of exposure pathways to humans.
- iii) A description of toxicity risk associated with exposure.

Each part of the model represents an approximation of what might happen in an actual agricultural setting. The selection of model parameters is always intended to over-estimate the actual potential risk to human health in order to provide maximum health protection. An acceptable risk level is given and a corresponding maximum 'safe' threshold concentration of a heavy metal in a fertilizer is assigned. Therefore, concentrations higher than this threshold will result in risk levels higher than those deemed to be acceptable.

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