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ACCUMULATION OF POTENTIALLY TOXIC ELEMENTS IN PLANTS AND THEIR TRANSFER TO HUMAN FOOD CHAIN

Key Words: Heavy metals, environmental contamination, risk assessment

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ABSTRACT

Contaminated soils can be a source for crop plants of such elements like As, Cd, Cr, Cu, Ni, Pb, and Zn. The excessive transfer of As, Cu, Ni, and Zn to the food chain is controlled by a "soil-plant barrier"; however, for some elements, including Cd, the soil-plant barrier fails. The level of Cd ingested by average person in USA is about 12 μg/day, which is relatively low comparing to Risk Reference Dose (70 μg Cd/day) established by USEPA. Food of plant origin is a main source of Cd intake by modern society. Fish and shellfish may be a dominant dietary sources of Hg for some human populations. About half of human Pb intake is through food, of which more than half originates from plants. Dietary intake of Cd and Pb may be increased by application of sludges on cropland with already high levels of these metals. Soils amended with sludges in the USA will be permitted (by USEPA-503 regulations) to accumulate Cr, Cd, Cu, Pb, Hg, Ni, and Se, and Zn to

levels from 10 to 100 times the present baseline concentrations. These levels are very permissive by international standards. Because of the limited supply of toxicity data obtained from metals applied in sewage sludge, predictions as to the new regulations will protect crop plants from metal toxicities, and food chain from contamination, are difficult to make.

INTRODUCTION

Soils are a geochemical sink for contaminant elements and a natural buffer controlling the transport of elements to the atmosphere, aquatic ecosystems, and plants. Natural concentrations of elements in soils vary greatly depending on composition of parent rocks, mineralization, and soil processes (Table 1).

Trace elements originated from various anthropogenic sources (Table 2), when reach the surface soil, tend to accumulate there.

Trace metals are persistent in soils for very long periods of time; loses from the site by uptake and removal by crops and by leaching are normally low (Chang et al., 1984; Dowdy et al., 1991). Therefore, soils once contaminated with metals can be a potential source of contamination for plants and animals for long time. Wide spread increases of metal concentrations (e.g. Cd, Hg, and Pb) in agricultural soils in Europe resulting from long-range transport of contaminants have been estimated to be in order of 10-15% since beginning of this century (Jones, 1991). They are small, however, when compared with the possible localized increases in soil metal concentrations from sewage sludge use in agriculture (Table 3).

Trace elements can enter the human food chain by way of water, soil, plants, and animals. Many trace elements (e.g. Cr, Co, Cu, Se, Mn, Mo, Zn) are essential to

TABLE 1
Baseline Concentrations of Trace Elements in Soils

Element	Podzols		Cambisols		Histosols	
	Range	Mean	Range	Mean	Range	Mean
As	<0.1-30	4	1.3-27	8	<0.1-65	9
Cd	0.01-0.6	0.1	0.01-1	0.3	0.2-2	0.7
Cu	1-70	13	4-100	23	1-110	16
Hg	0.001-0.7	0.05	0.01-1	0.1	0.04-1	0.3
Mo	0.2-4	1.3	0.1-7	3.0	0.3-3	1.5
Ni	1-80	13	3-100	26	0.2-120	12
Pb	2-20	12	2-30	16	2-170	44
Se	0.05-1	0.1	0.02-2	0.3	0.1-2	0.4
Zn	3-100	30	5-200	45	5-250	50

Source: Holmgren et al., 1993; Dudka, 1992; Kabata-Pendias and Pendias, 1992

TABLE 2
Worldwide Inputs of Trace Elements into Soils (Thousand tons/year)

Source	As	Cd	Cr	Cu	Hg	Pb	Zn
Agricultural & Animal Wastes	5.8	2.2	82	67	0.85	26	316
Wood Wastes	1.7	1.1	10	28	28	7.4	39
Urban Refuse	0.4	4.2	20	26	0.13	40	60
Sewage Sludge	0.25	0.18	6.5	13	0.44	7.1	39
Solid Wastes from Metal Fabrication	0.11	0.04	1.5	4.3	0.04	7.6	11
Coal Ashes	22	7.2	298	214	2.6	144	298
Discarded Products	38	1.2	458	592	0.68	292	465
Fertilizers and peat	0.28	0.20	0.32	1.4	0.01	2.9	2.5
Atmospheric Fallout	13	5.3	22	25	2.5	232	92
Total input	**82**	**22**	**898**	**971**	**8.3**	**759**	**1322**

Source: Nriagu, 1990

TABLE 3
Potential Increases of Trace Element Concentrations in Soils from Sludge Use in Agriculture

Element	Initial[a] soil level(I) mg/kg	Loading[b] with sludge kg/ha	Final soil level(II) mg/kg	Ratio II:I	Sludge[c] level mg/kg	Amount of sludge to reach final soil level tons/ha
As	6.5	20	14	2	41	500
Cd	0.2	20	7	35	39	500
Cr	40	1500	540	13	1200	1200
Cu	18	750	270	15	1500	500
Hg	0.07	8	3	43	17	500
Mo	2	9	5	2.5	18	500
Ni	16	210	86	5	420	500
Pb	11	150	61	5.5	300	500
Se	0.3	50	17	57	36	1400
Zn	43	1400	500	12	2800	500

Source: Dudka and Miller, 1995 (Personal communication)
[a] mean concentrations in uncontaminated mineral soils
[b] 50% of maximum cumulative loading (USEPA, 1993)
[c] maximum concentrations in 'clean' sludge (USEPA, 1993)

metabolic functions of the human body. Others, such as Cd, Hg, Pb, have no known positive effect, and their excessive intake can lead to health problems. Essential elements produce positive metabolic effects in certain concentration ranges. Values below those ranges can lead to deficiencies, and concentrations exceeding those ranges can be toxic. Nonessential elements become hazardous in concentrations higher than tolerance limits. Plants most often suffer toxicities from B, Cu, Ni, and Zn, while animals are sensitive to As, Be, Cd, Cr, Cu, Mo, Ni, Pb, Se, whereas Cd, Hg, and Pb have the greatest potential to affect human health (Logan and Traina, 1993). The trace element contamination of plants can be a problem due to crop yield decrease and accumulation of potentially toxic elements in plant parts used as food or feed. It is generally agreed that phytotoxicity from B, Cr, Cu, Ni, Zn is the main limitation for these elements (Chaney and Ryan, 1993; Chang et al., 1992). Plant uptake and transfer to the human food chain is the limit for Cd. Direct digestion of contaminated soils by animals and humans, especially children, is the primary limitation for Pb (Chaney and Ryan, 1993).

The objective of this paper is to give the overview of accumulation of potentially toxic elements in plants and element transfer to the human food chain. The emphasis will be given to Cd because of its potential risk to the food-chain.

EFFECT OF SOIL PROPERTIES ON ACCUMULATION OF TRACE ELEMENTS BY PLANTS

Soil properties that affect plant uptake of trace element from soils include pH, organic matter, cation exchange capacity (CEC), iron and aluminum oxides, texture, aeration, specific sorption sites, and water availability. The factors which tend to be stable soil properties are: texture, CEC, organic matter, and Fe and Al oxides. On the other hand, properties such as pH, water content or soil aeration vary frequently or are relatively easy to adjust. Soil pH, for example, can be increased by liming while ammoniacal fertilizers acidify soils. Among the soil properties, pH is considered to have the strongest impact on metal accumulation by plants. Generally, metal availability decrease with liming, except for Mo and Se. Usually, lime applications reduce uptake of Zn and Ni more than Cd (Singh and Narwal, 1984). Metal uptake in response to liming may also vary among plant species. Liming decreased more Cd uptake by lettuce and carrot than by potatoes and peanuts (Chaney et al., 1987). Likewise liming reduced Zn concentrations in soybean seeds to a greater extend than in corn grains or cotton seeds (CAST, 1980). There is some evidence (Vlamis et al., 1985) that pH about 6 is high enough to regulate metal uptake. Increase of pH to 6.5, recommended for controlling metals in food chain, does not seem to be necessary. This finding is of a practical importance because liming of acidic soils to pH 6.5 is often costly and can require considerable amount of lime.

The effect of other soil properties on element uptake by plants is less evident than that of pH, and the results are often conflicting. Hinsley et al. (1982) conducted a study to determine the effect of CEC on Cd uptake by corn. The soil CEC inversely affected Cd uptake by corn when the metal was applied as a soluble salt, but not when Cd was supplied as constituent of municipal sludge. This conclusion was confirmed in greenhouse studies conducted by Korcak and Fanning (1985). Some trace elements exhibit affinity for soil organic matter (OM), which has both the cation exchange property and chelating ability. Therefore, addition of sewage sludge, peat or plant residues can bind trace elements in soil. On the other hand, because of chelating ability, OM is viewed as a source of soluble complexing agents for trace elements. The binding ability of OM is not permanent. It is generally agreed that the organic mater level in soil must eventually return to a value not much greater than that of original soil (McBride, 1995). The half-life of OM decomposition has been estimated to be about 10 years.

It has to be stressed that the impact of soil contamination on trace element uptake by plants should be based on field studies rather than on pot studies. In addition the contaminant should be introduced to soils in the same forms that those one wants to evaluate. Metals applied as a salt, commonly a sulfate, chloride, or nitrate salt, accumulate in plants more readily than the same quantity of metal added in sewage sludge, flue dust, or fly ash (Dudka et al., 1994; Dudka et al. 1996; Logan and Chaney, 1983). Metal salt additions to soils can cause formation of metal chloride complexes and ions pairs which may increase metal diffusion to the roots and plant uptake. There are data indicating the stimulating effect of soil salinity on Cd uptake by crops in Australia (McLaughlin et al., 1994). The enhanced uptake of trace elements in pot or greenhouse study generally results from: (i) use of acid-forming fertilizers; (ii) increased soluble salt content from fertilizers in smaller soil volume than in the field; (iii) root confinement; and (iv) unnatural watering pattern.

TRACE ELEMENTS IN PLANTS

The element load of food or feed depends on the conditions under which food and feed are produced, processed, and stored. Trends in metal availability as a function of metal content in soils can be described by three models: (i) linear (constant partitioning model), (ii) plateau (saturation model), and the Langmuir sorption model (Figure 1). Usually uptake of metals by plant tops does not occur in linear response to concentrations of the metal in soils, except at a low range of concentrations (Chaney and Ryan, 1993; Dudka et al., 1994; McBride, 1995). Uptake of metals by plants become less efficient at higher metal loadings in soil, and the plateau relationship is used to describe this saturation effect (Dudka et al., 1994 and 1996). Soils have a finite capacity to immobilize metals by adsorption or precipitation. When this protective potential is exceeded a Langmuir-type of relationship is expected (Figure 1). This is the relationship found sometimes for metals added to soils in soluble salt forms (Hendrickson and Corey, 1981).

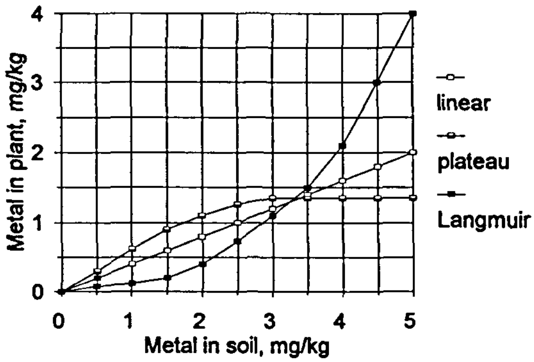

FIGURE 1
Metal availability as a function of metal content of soils.

Under more realistic field conditions when metals are introduced to soil with sewage sludges, or aerial deposition, or with industrial wastes, the plateau model prevails (Figure 2). Dudka et al. (1996) conducted the field experiment with several crops (barley, red clover, potatoes) grown in rotation on a soil contaminated by flu dust form a Pb-Zn smelter. The soil had pH 7-8 and contained trace metals up to Cd 106, Pb 5450, and Zn 11400 mg/kg. Despite high metal contents of the soil, the metal level in the plants remained low (Table 4).

The plant response to increased metal concentrations in the soil was the best described by the plateau model (Figure 2).

The simple soil-plant relationship of plant element uptake is often modified by environmental, plant, and soil factors. As a result, only a small proportion of elemental variability in plants can be explained by element concentrations in soils. An aerial deposition of contaminants onto plant surfaces and subsequent assimilation of elements by the plant tissues can be an important source of metals for plants in areas with strong

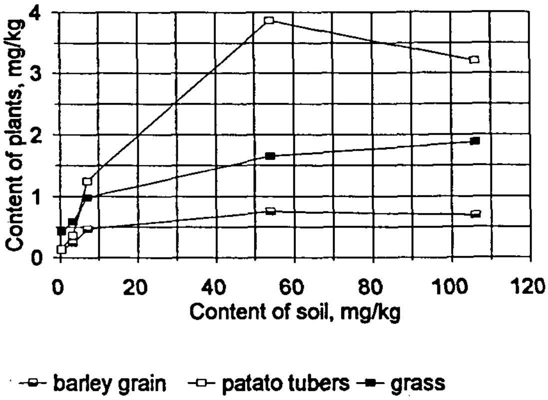

FIGURE 2
Dose response curve: Cd in plants vs. Cd in soil; Source: Dudka et al. (1997).

TABLE 4
Trace Element Concentrations (mg/kg, dry wt.) in Crops Grown on Soil Contaminated with Flu Dust from a Zn-Pb Smelter

Crop		Barley		Potato tubers	
		straw	grain	intact	pealed
Cd	control	0.34	0.12	0.15	0.16
	contaminated	2.40	0.70	3.21	1.67
Pb	control	7.3	0.4	0.24	0.21
	contaminated	13.0	2.0	15.4	0.89
Zn	control	25	29	25	23
	contaminated	99	58	172	55

Source: Dudka and Piotrowska, 1995 (Personal communication); Soils were between pH 7-8 and contained (mg/kg): Cd 0.3, Pb 6.8, Zn 25 Cd (control) and Cd 106, Pb 5450, Zn 11400 (contaminated), and about 0.8% organic matter.

atmospheric contamination. Davies and Thornton (1989) reported that about 60-80% of Pb in vegetables grown in industrial sites of England came from atmospheric deposition. Food processing has a marked impact on decontamination for those elements that adhere to the surface of plants. For example, the content of Pb or Tl can be reduced by 80% in certain plants by intensive washing (Weigert, 1991). Such concentration reduction is not possible for Cd. On the other hand, the concentrations of Fe, Pb, Zn, Sn can be substantially higher in canned foods than in the original raw plant products. Pealing of potatoes can substantially reduce Pb concentrations in tubers (Table 4), even though the tubers were rigorously washed before analysis.

Plants can accumulate trace elements, especially metals, in their tissues due to their ability to adopt to various environmental conditions. Plant uptake of elements from the soil solution requires positional availability to the plant root. Either the element must be moved to the root through diffusion or mass flow, or the root must grow to the element. This transfer requires that the element move through a solution phase. Therefore, water solubility and a variety of complexation, chelation, and other chemical reactions controlled by pH, become important in regulating element availability. Except for a few special cases (Lund et al., 1981), plant tissue concentrations do not positively correlate with total element content of untreated soils. The element concentration in plant tissues varies greatly depending on species and cultivar, plant organ, age, and environmental conditions (Chang et al., 1987; Dudka et al., 1996; Kubota et al., 1992; Piotrowska et al., 1994; Wolnik et al., 1983ab and 1985). The results of survey conducted by USDA-USEPA-FDA for a variety of crops in major regions of U.S. show that the Cd, Pb, and Zn content of different crops varies by 1 to 3 orders of magnitude (Table 5).

The mean concentrations of Cd and Pb were highest in leafy vegetables (spinach and lettuce) and lowest in grains. Mean concentrations of Zn across the 12 crops were more uniform. The data were collected for crops grown on soils located far away from sources of contamination. Therefore, the data may not be representative of the crops for U.S. agricultural soils in general.

It is interesting to note that cultivars (also referred to as varieties genotypes, or selections) within a crop species vary significantly in uptake of trace elements. An extensive characterization of relative corn cultivar variation in uptake of sludge-applied Cd and Zn was reported by Hinsley et al. (1982). Uptake of Cd and Zn by 20 corn cultivars was studied in a long-term field experiment with soils having high level of available metals resulted from sewage sludge application. Leaf Cd concentrations ranged from 0.88 mg/kg Cd in inbred R805 to 30.3 mg/kg Cd in inbred B37. Grain Cd ranged from 0.05 mg/kg Cd in inbred H96 to 1.81 mg/kg Cd in inbred B37. The grain and leaf concentrations were highly correlated as were the ranks among cultivars of grain Cd concentrations and leaf concentrations. However, the grain Cd to leaf concentration varied from 0.02 to 0.1. This wide range in grain Cd to leaf Cd ratio indicate that breeding program to lower Cd transfer to food chain should be based on both leaf and grain concentrations of Cd. The selection of a particular variety would depend on whether one wants to reduce Cd load of grains or silage. Differences in corn Zn concentrations were smaller, ranging from 44 to 152 mg/kg Zn in corn leaves and 32 to 58 mg/kg Zn in grains. Studies with cultivars of other crops (Bogges et al., 1978;

TABLE 5
Trace Element Concentrations (mg/kg, dry wt.) in the Edible Part of Crops Grown on Untreated Soils

Element	Cd		Pb		Zn	
	Mean	95th[a]	Mean	95th[a]	Mean	95th[a]
Lettuce	0.44	2.1	0.19	1.0	46	78
Spinach	0.80	1.5	0.53	1.2	43	128
Potatoes	0.14	0.36	0.03	0.10	15	27
Wheat	0.04	0.12	0.02	0.17	29	48
Rice	0.01	0.03	0.01	0.03	15	20
Sweet corn	0.01	0.06	0.01	0.06	25	46
Field corn	0.01	0.07	0.01	0.03	22	30
Carrots	0.16	0.79	0.05	0.24	20	48
Onions	0.09	0.24	0.04	0.09	16	26
Tomatoes	0.22	0.61	0.03	0.11	22	29
Peanuts	0.07	0.21	0.01	0.03	31	42
Soybeans	0.04	0.18	0.04	0.10	45	59

Source: Wolnik et al. 1983ab and 1985; [a]95th percentile

Harrison, 1986) revealed only about 3-4 fold variation in Cd concentrations. Chaney et al. (1987) concluded that the inclusion of various cultivars in the food supply would not significantly alter chronic exposure to Cd due to increased crop uptake, because the cultivar variation should average out. However, cultivar selection can be used to reduce food-chain transfer of elements from contaminated soils (Chaney et al. 1987).

The extend of increase in trace element concentration above control for crops grown on metal-contaminated soils is strongly affected by crop species. The studies conducted in England (Carlton-Smith and Davies, 1983) report the response of many crop species grown in the same experiment on 2 soils contaminated by long-term sludge application. The authors developed the tables of relative element concentrations for Cd, Zn, Cu, Ni, and Pb. The concentrations in each crop was expressed as a percent of that in the crop with highest uptake of a given element. The raw plant data were averaged across the 2 soils; then the normal background element concentration in each crop was subtracted from the mean level in the crop, and ratio of element in crop X to the mean Cd level in lettuce was calculated. The relative crop uptake remove factors other than crop species (or cultivar). Leafy vegetables, and interestingly wheat grains, had the highest relative increased uptake of Cd (Table 6).

DIETARY INTAKE OF TRACE ELEMENTS BY HUMANS

Plants can be an important source of trace elements for humans and animals. Because of minimal soil ingestion by humans and the elimination of metals from vegetable and animal foods during processing, serious metallic contaminants in humans are confined to Cd, Hg, and PIn specific cases, exposure of local populations to Cr^{6+} and As in drinking water can be a problem (Logan and Traina, 1993). The concern about food-chain contamination by metals arouse because of Cd poisoning of Japanese farmers who ate rice grown on Cd-contaminated paddy field (Asami, 1991), and due to high blood Pb levels in U.S. children partly resulted from Pb contamination of commercial foods (Jelinek, 1987).

Cadmium is regarded as one of the most toxic trace elements for humans and animals. The human health significance of Cd can be placed in perspective by comparison with the situation for Pb. For Pb, there is now a consensus that children, particularly in urban locations, are at risk from neurobehavioral effects of the metal (Hutchinson and Meema, 1987). In contrast, reports of health effects of Cd in environmentally exposed populations

TABLE 6
Cadmium Levels in Edible Tissues of Crops Grown on Sludge Treated-soils

Crop	Sludged soil	Background	Increased crop Cd	Relative increased Cd uptake
Lettuce	7.1	0.7	6.4	111
Spinach	5.0	0.7	4.3	67
Kale	1.3	0.27	1.0	16
Cabbage	0.97	0.27	0.70	11
Wheat	0.75	0.08	0.67	10
Leek	0.73	0.27	0.46	7
Turnip	0.58	0.21	0.37	6
Rape	0.54	0.08	0.46	7
Onion	0.52	0.21	0.31	5
Beetroot	0.41	0.21	0.20	3
Tomato	0.40	0.32	0.08	1
Radish	0.33	0.21	0.12	2
Carrot	0.33	0.25	0.08	1
Barley	0.28	0.08	0.20	3
Potato	0.20	0.13	0.07	1
Oat	0.18	0.08	0.10	2
Squash	0.17	0.11	0.06	1
Sweet corn	0.16	0.11	0.05	1
Field corn	0.13	0.08	0.05	1
Beans	0.08	0.06	0.02	<1

Cd in sludged soil: 7.4-69 mg/kg; soil pH 6.7-7.4; Sources: Carlton-Smith and Davies, 1983; Wolnik et al., 1983ab and 1985; Chaney et al., 1987.

have been restricted to certain communities in Japan and elderly populations from an industrialized city in Europe (Roles et al., 1981). For occupationally non-exposed persons and nonsmokers food is the main source of Cd. In general, about one-third of the total Cd burden originates from animal products and two-thirds from plant products (Hapke, 1991). Weekly uptake of Cd (100 to 250 μg/week) in most Western countries is about 20-50 percent of the Provisional Tolerable Weekly Intake (PTWI) of 400-500 μg of Cd per person (WHO/FAO, 1972).

Plants absorb only small amounts of Hg through their roots, even from highly contaminated soils; most plant Hg is a result of surface contamination by Hg-containing aerosols (Hutchinson and Meema, 1987). Foods and animal feed derived from plants usually have Hg contents between 0.001 and 0.03 mg/kg. Marine organisms have an exceptional ability to transform inorganic Hg to organic compounds, which makes Hg more easily transferred through the aquatic food chain (Hapke, 1991). As a result, marine organisms have Hg levels up to 5 mg/kg. Consumption of fish and other aquatic animals is the main source of the Hg burden in man (Hutchinson and Meema, 1987).
A PTWI of 300 μg Hg is only achieved through occupational exposure or by consumption of large amounts of contaminated fish or organ meats (liver, kidney). Otherwise, weekly Hg intake through food remains low (30 and 50 μg).

Lead in food and animal feed comes mainly from aerial deposition and Pb-rich soil particles adhering to plant surfaces (Chaney and Ryan, 1993). Industrial contamination can result in plant Pb concentrations of 30 mg/kg and more (Piotrowska et al., 1994; Dudka et al., 1996). Plant foodstuffs contain more Pb than foodstuffs of animal origin. Average intake of Pb through food is about 0.3 to 1.0 mg Pb per week per person. The PTWI of Pb is fairly high (3 to 4 mg/person) because Pb resorption in the human gastric tract is low (WHO/FAO, 1972). About half of human Pb intake is through food, of which more than half originates from plants (Adams, 1991). The normal food chain from soil to plant to animal to man causes dilution of the metal. No acute hazard from Pb in food chains has been determined so far. However, there is no doubt that where soil Pb concentration is high, some vegetables (brassicas, lettuces, leeks) have high surface contamination. Consequently, people consuming large amounts of these vegetables are likely to increase their Pb intake. High Pb concentrations in drinking water (in areas where lead pipes are still in use) considerably increases the Pb intake both in beverages and in food cooked in water. People consuming large quantities of canned food used to have significantly higher intake, but this source has now been largely removed (Simms and Beckett, 1987). Children in some areas can exceed their PTWI for Pb from hand-to-mouth transfer of contaminated soil (Thornton et al., 1985 and 1988).

Since 1960 when the itai-itai disease of Japanese farmers was attributed to consumption of Cd contaminated rice (Asami, 1991), high concern has been expressed about food Cd and about Cd contamination of soils. However, now it is known that this concern was based on ignorance of the factors controlling risk to humans from soil having increased levels of total Cd (Chaney and Ryan, 1993). Excessive dietary Cd intake can accumulate in the kidney cortex and cause renal tubular dysfunction (Fanconi syndrome), a disease in which low molecular weight proteins are excreted in urine. The Japanese farm families experienced Itai-itai (acute form of renal tubular dysfunction) after prolonged consumption of rice grown on highly Zn and Cd contaminated paddies, the properties of rice and flooded soils, and malnutrition in Japan at that time, played very important roles in allowing high transfer of soil Cd to kidneys. The rice grain was increased in Cd but not in Zn, because ZnS was formed in flooded soils (Chaney and Ryan, 1993). Crops grown on aerobic soils have greater increase in Zn than in Cd in edible crop tissues. In another case, New Zealand oyster fishers and their families consumed high amounts of Cd-rich oysters, ingesting nearly as much Cd as the Japanese farmers who suffered Cd disease. However, the oysters and the total diet are not deficient in Ca, Zn, and Fe, the affected persons did not accumulate high amounts of Cd in their kidneys and did not suffer tubular proteinuria. This difference between effect of Cd in rice and Cd in other foods is evidence that Cd has different bioavailablity depending on the presence of different nutrients in the same food (Chaney, 1992).

Since sludge utilization in agriculture can be the most important source of Cd enrichment in arable soils (Table 3) and crop plants, much research was conducted to assess the risk from Cd in sewage sludge (Logan and Chaney, 1983; Page et al., 1987; Page et al., 1988; Page et al., 1989). Estimation of Cd food chain transfer is critical to valid estimation of the potential for risk. These estimations are made by considering: (i) relative increased uptake of Cd by various crops from sludge-amended soils; (ii) rate of consumption of different crops by the population; (iii) the bioavailability of the increased amount of an element in crops; (iv) transfer coefficient from sludge-amended soil to edible crop tissues (Chaney et al., 1987; Ryan and Chaney, 1993). In order to estimate the maximum allowable increase in Cd in garden crops, Cd in lettuce was related to Cd in the garden foods which make diet grown on a Cd enriched soils. According to the pathway approach to risk assessment (Ryan and Chaney, 1993) it is assumed that an individual who consumes high proportion of garden foods (60%), produced on sludge-amended soils converted to residential home garden, is very likely to expose to increased amount of dietary Cd. Such individual is called Most Exposed Individual (MEI). It is assumed that if the MEI is protected form hazardous exposure to Cd from food, the general population is also protected.

In strongly acidic soils which cause increased Cd levels in foods, the relative uptake of Cd is very constant (Table 7). By multiplying the dry weight of each food group by its relative increased Cd uptake on acidic sludge amended soils, one can estimate that diet Cd will be increased 1.67 µg/day when lettuce is increased by 1 µg/g dry weight (100% of garden foods grown on the amended soil). To estimate allowable increase in concentration, the average intake (12 µg Cd/day) was subtracted from the Risk Reference Dose (70 µg/day) yielding 58 µg/day allowed increase. If we divide 58 µg/day (allowed Cd intake increase) by 1.67 µg of increased dietary Cd, we find that leafy vegetables could safely reach 35 µg/g dry wt. of Cd contents for 100% vegetable diet from sludged soils. The increase of Cd concentrations in leafy vegetables can be connected to cumulative Cd loading with sludge applications. Based on a plateau model of regression analysis (Chaney and Ryan, 1993), it was estimated that one can add to soil up to 39 kg/ha of sludge Cd without appreciable risk for food chain (Table 8). Taking into account results of dietary Cd risk assessment, Chaney and Ryan (1993) concluded that "we should no longer consider that Cd in sludge comprise any food-chain Cd risk to humans consuming Western diets under any conditions."

METAL GUIDELINES RELEVANT TO HUMAN FOOD CHAIN

During the last decades concern about the hazards of toxic metals for human health and the environment has increased worldwide. In many countries legislative and administrative measures have been taken to reduce environmental contamination and to prevent adverse effects resulting from environmental exposure to chemicals. Since there is a general consensus that metals in soil may be taken up by plants and thus enter the

TABLE 7
Home Garden Dietary Cd Risk Assessment

Food Group	Food intake (g DW/d)	Relative Cd Uptake (μg/g)	Increased Diet Cd (μg/d) if lettuce Cd increased by 1 μg/g, DW
Lettuce	-	1.00	-
Leafy Vegetables	1.97	0.536	1.065
Potato	15.60	0.020	0.312
Root vegetables	1.60	0.096	0.154
Legumes	8.75	0.010	0.088
Garden Fruits	4.15	0.014	0.058
All Garden Foods	-	-	1.67

Source: Chaney and Ryan, 1993

food chain, limit values for maximum tolerable metal concentrations in agricultural soils were set in various countries (McGrath et al., 1994). Because sewage sludge can be the most important localized source of heavy metal increases in agricultural soils, the existing limits have been developed to regulate sludge application in agriculture. There are three basic methods for formulating limits to metal additions in soils receiving sewage sludges: (i) analysis of pathways of metal transfers; (i) limits consistent with the no-observed adverse effect level (NOAEL); and (iii) metal balance approach (McGrath et al., 1994).

The governing principle of the pathway approach (USEPA, 1993) is that cumulative pollutant loading limits, which were derived from the analyses of various exposure pathways, will not be exceeded. To protect public health and the environment against the impact of high-metal sewage sludges, this regulation also defines maximum concentrations for metals present in the sewage sludge beyond which land application of the sludge is not permitted. This upper limit was the calculated maximum concentration allowed according to the cumulative pollutant loading limits assuming sludge is applied at the annual rate of 10 tones per hectare for 100 years. The Netherlands has developed a Soil Protection Policy with associated soil quality standards known as 'ABC' values (McGrath et al., 1994). The Dutch 'action value' (or 'C') indicates concentrations above which there is a danger of a reduction in the functional properties which soils have to animals and plant production. Although the integrated 'C' values were based on ecotoxicological and human toxicological studies similar to that used by the USEPA, they are appreciably lower, except for Pb, than the USEPA derived limits (Table 8). This is surprising since the C-values indicate the concentration at which there is considered to be serious soil contamination and a need for further action or for soil remediation, whereas the USEPA (1993) limits indicate the level which is considered to pose no significant threat to public health and to protect terrestrial and aquatic ecosystems (McGrath et al., 1994).

Limits consistent with the no-observed adverse effect level (NOAEL) are based on actual cases of effects due to metals, but not necessarily derived from studies which involved land application of sewage sludge. The Commission of the European Communities (CEC) issued a Directive to limit the inputs of potentially toxic metals to soil from sewage sludge, so as to protect plant growth, crop quality, and human and animal health (CEC, 1986). The Directive has three types of metal limits: (i) concentrations allowed in sludges used for agriculture; (ii) maximum concentrations permitted in sludge-treated soils; (iii) the 10-year average annual rate of addition of metals in sludge. For most metals the EC limits are more restrictive than USEPA limits (Table 8).

TABLE 8
Maximum Metal Concentrations (A - mg/kg, dry wt.) and Annual Loading Limits (B - kg/ha/year) for Sewage Sludges Used in Agriculture and Maximum Allowed Metal Concentrations (mg/kg, dry wt.) in Agricultural Soils

Country		Cd	Cu	Ni	Pb	Zn	Hg
Germany	A	10	800	200	900	2500	8
	B	0.15	6	1	6	15	0.13
	C	1.5	60	50	100	200	1
Holland	A	-	-	-	-	-	-
	B	0.003	0.15	0.076	0.45	0.6	0.0015
	C	0.8	36	35	85	140	0.3
UK	A	-	-	-	-	-	-
	B	0.15	7.5	3	15	15	0.1
	C	3	135	75	300	300	1
US	A	85	4300	420	840	7500	57
	B	1.9	75	21	15	140	0.9
	C	20	750	210	150	1400	8

Sources: McGrath et al., 1994; USEPA, 1993; CEC, 1986

The third category of defining rules for metals in soils, the metal balance approach, is concerned with the fact that in industrial countries the metal inputs to soil minus losses through crop removal, leaching and erosion is positive for all metals studied (Andersson, 1992; van Driel and Smilde, 1990). These observations have led to a very cautious approach to the intentional additions of metals to soils. In both the Netherlands and Sweden, no accumulation of possibly hazardous elements in the soil is allowed under any type of soil management, including land application of sewage sludge. The idea of no metal accumulation does not appear to be achievable in the short term because non-point source metal inputs are still significant. Therefore, a decision has been made to minimize intentional inputs as much as possible (McGrath et al., 1994).

All the discussed limits on metal additions in sewage sludge are lacking high quality data from long-term field experiments to support them. Data needed to construct comprehensive dose-effect curves are not present for many crop species, as well as for other organisms and important microbial processes. The approach adopted in the US regulations pushes the pollutant loading limits along the plateau of the dose response curve as far as possible. The USEPA-503 rule will permit accumulation in sewage sludge-amended soils metals such Cr, Cu, Cd, Pb, Hg, Ni, Se, and Zn to levels from 10 to 100 times the baseline concentrations of these metals in most soils. The US rules also allow the largest rate of annual input of metals to soil and the highest metal concentrations in sewage sludges which can be used in agriculture (Table 8). Although the supporters of the 503- Regulations believe that sludge-amended soil will maintain an ability to immobilize toxic metals in unavailable forms, it is impossible to predict long-term consequences of high metal loadings of soils. Predictions of no-adverse effects on crops and food chain employ the sludge protection hypothesis, which states that the specific adsorption capacity added with sludge will persist in soils and will be effective in metal immobilization as long as metals are present in soils (Chaney and Ryan, 1993). The experimental data, however, suggest that immobilization of metals in sludge-amended soil is due in some part to sludge organic matter. Therefore, the sludge time bomb hypothesis points out that slow mineralization of organic matter added with sludges could release metals into more soluble forms, which eventually will adversely affect crop productivity and food chain quality (McBride, 1995).

From the ecotoxicological point of view, any addition of heavy metals will have some 'impact' on organisms in the soil and in the food chain (Nriagu, 1988). If no-metal enrichment policy of environmental protection is followed, the potential adverse effects of sewage sludge application to soils can be diminished by adopting the approach of maintaining the metal balance in soils. If an accumulation of metals in sewage-treated soils is accepted, the maximum permissible metal concentrations in the soil are dependent upon the organisms that regulations are intended to protect, assuming that the cause-effect relationships are known. In adopting the environmental exposure pathway approach, one must select a target organism for each pathway. The process of selecting the contaminant loading limit for each pathway is also based on no-observed adverse effect level (NOAEL). From the long-term perspective it is very difficult to foresee if the approach to setting limits for metals in soils allowing substantial increase in soil metal concentrations, will be effective in protecting environment, food chain, and human health form adverse effects of potentially toxic metals.

SUMMARY

Plants can be sources of toxic elements for humans. Cadmium, Hg, and Pb are the most serious human contaminants both in terms of intensity of the toxic effect and the magnitude of contamination. For occupationally non-exposed persons and nonsmokers, food is the main source of Cd. About one-third of the total Cd burden originates from animal products and two-thirds from plant products. An average daily Cd intake of Cd by US population (12 μg/person/day) is less than 20 percent of the Risk Reference Dose (70 μg/person/day) established by USEPA. Consumption of fish and other aquatic animals is a main source of Hg intake by humans. In general population, Hg intake through food remains low. About half of human Pb intake comes from food, of which

more than half originates from plants. Drinking water and ingestion of Pb-rich soil and dust make another half of the Pb burden in humans. No acute hazard from Pb in the food chain has been determined so far. Generally there are two approaches to setting limits for metals in soils. One states that no enrichment of potentially toxic constituents is allowed in soils. Another option stresses that the basis for regulating land application of metals (with sludge, compost, etc.) should be the potential to cause adverse effect on agriculture or on environment, not the simple soil enrichment with potentially toxic metals.

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