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Bioavailability of Cd to Food Crops in Relation to Heavy Metal Content of Sludge-Amended Soil

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Results of greenhouse and laboratory experiments on factors influencing uptake and accumulation of Cd by economic crops are summarized.

Tolerance to Cd is highly crop-specific. For example, 21 different economic crops were grown in pots filled with a calcareous soil treated with increasing amounts of Cd. Yields versus Cd addition rate relations showed yield reductions to occur with Cd sensitive plants (spinach, soybean, curlycress, and lettuce) at addition rates varying from 5 to 15 μg Cd/g soil, whereas tolerant crops (tomato, squash, cabbage, and rice) did not suffer a yield reduction when treated at rates less than 150 μg Cd/g soil. Nutrient solution experiments likewise revealed marked differences in growth of crops. Corn, turnip, beets, bean, and tomato plants grown in solution cultures containing 0.1 μg Cd/ml accumulated different amounts of Cd in leaf tissue depending upon crop species; leaf Cd concentrations ranged from a low of 9 μg Cd/g leaf for beans to 200 μg Cd/g leaf for beets. Large differences also occur with regard to distribution of Cd within the plant. Fruit and seed tissue contain less Cd than leaves. Experiments comparing the toxicity of Cd to Cu, Ni, and Zn in an acid soil ± lime showed Cd to be the most phytotoxic. While interactive effects occur with regard to metal uptake and accumulation by plants, Cd uptake is essentially dependent upon the Cd concentration of the soil. Studies of chemical speciation of Cd in relation to Cd availability indicate that the free Cd^{2+} concentration correlates better with Cd uptake than Cd total of the soil solution.

Introduction

In the early 1970's, our laboratory group initiated a research program for identifying and evaluating various soil and plant factors having an influence on uptake and accumulation of Cd by economic crops. Experiments were designed to illustrate the importance of factors such as Cd concentration in soil, soil pH, other metals (Cu, Ni, and Zn), oxidative state of soil, and plant species. The principal results of such experiments serve as the basis for this review paper.

Substrate Concentration Relationship

A series of nutrient solution culture experiments were carried out with the objective of establishing Cd uptake and accumulation characteristics for a number of economic crops in relation to substrate Cd concentrations ranging from 0.10 to 10.0 μg Cd/ml of nutrient solution. These experiments were also designed to indicate the minimum Cd concentration of the solution culture associated with a yield depression and visual symptoms of Cd injury. The results of the above experiments clearly showed that plants differed greatly with respect to being able to grow in the presence of Cd (Cd tolerance) and Cd accumulation characteristics. Table 1 contains a list of crop species tested under known levels of Cd in nutrient solution cultures, a ranking according to Cd tolerance as indicated by the nutrient culture level associated with a 25% reduction in growth [compared to yield of plants in the −Cd solutions (controls)], and corresponding leaf Cd values of plants showing a 25% yield reduction. Visual leaf injury symptoms consisted of chlorosis, similar to that due to Fe deficiency, and in some instances, leaf burn.

The influence of crop species is strongly reflected in response of test plants to Cd present in nutrient solutions. The lowest Cd concentration utilized as a treatment was excessive for three of the nine crop

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Table 1. Solution culture concentration of Cd associated with a 25% reduction in growth, leaf Cd concentration of plants manifesting a 25% reduction in growth, and visual leaf symptoms of plants under stress from Cd.

Crop species	Solution culture concentration producing a 25% growth depression, μg Cd/ml	Leaf Cd content at 25% growth depression, μg/g	Visual leaf symptoms
Beet	0.05	150	wilting
Bean	0.08	9	wilting
Turnip	0.10	160	chlorosis
Lettuce	0.25	150	chlorosis
Corn	0.35	200	chlorosis
Pepper	0.50	60	chlorosis
Barley	0.75	50	none
Tomato	1.00	175	chlorosis
Cabbage	4.00	600	none

species tested in terms of limiting growth. The concentration of Cd limiting yield 25% varied from 0.05 (extrapolated) to 4.0 μg Cd/ml depending upon crop species. Likewise, markedly different amounts of Cd accumulated in leaf tissue depending upon the crop species. The range of leaf Cd contents of plants receiving the 0.10 μg Cd/ml treatment varied from 9.0 μg Cd/g for bean to 280 μg Cd/g for beet. Additional information about the above solution culture experiments is contained in the publication by Page, Bingham, and Nelson (*1*).

The influence of substrate Cd concentration on growth characteristics of economic crop species was also carried out by growing a wide variety of food crops to maturity in pots containing soil treated with low to phytotoxic amounts of Cd. In these experiments, the procedure entailed amending 7 kg lots of a soil with a municipal sewage sludge (10 g sludge/kg soil) pretreated with different amounts of $CdSO_4$. This procedure produced Cd addition rates of 0.0, 5.0, 10.0, 20.0, 40.0, 80.0, 160, 320, and 640 μg Cd/g soil. A calcareous soil (pH 7.5) was used for this series of experiments. Various crop species (14 in all) were grown to maturity, at which time yield weights were obtained and samples of leaf and edible tissue (fruit, seed, lettuce head, etc.) were collected for chemical analysis. Results of this series of experiments provide information pertaining to Cd tolerance as well as Cd uptake and accumulation characteristics; the principal results of the study are summarized in Table 2. The addition of 10 μg Cd/g soil curtailed yields 25% of sensitive crops such as spinach, soybean, and curlycress. Crops such as tomato, zucchini squash, cabbage, and swiss chard were able to grow normally at Cd addition rates up to 100 μg Cd/g. Rice under flood management showed no decrease in yield at any of the Cd treatment rates ($\leq$ 640 μg Cd/g). There were also large differences in the Cd content of leaf and edible tissue associated with the plant species under test.

Table 2. Soil and plant tissue Cd levels associated with a 25% decrement in yield.

Crop species	Soil Cd rate causing a 25% yield decrement, μg Cd/g	Plant tissue Cd at 25% yield decrement, μg/g: Leaf	Plant tissue Cd at 25% yield decrement, μg/g: Edible tissue
Spinach	4	75	75 (leaf)
Soybean	5	7.0	7.0 (seed)
Curlycress	8	80	80 (leaf)
Lettuce	13	48	70 (head)
Corn	18	35	19 (kernel)
Carrot	20	32	19 (tuber)
Turnip	28	120	15 (tuber)
Field bean	40	15	1.7 (seed)
Wheat	50	33	12 (grain)
Radish	96	75	21 (tuber)
Tomato	160	125	7.0 (fruit)
Zucchini squash	160	68	10 (fruit)
Cabbage	170	160	11 (head)
Swiss chard	250	150	150 (leaf)
Rice	>640	3.0[a]	2.0 (grain)[a]

[a] Maximum values for plants receiving the 640 μg Cd/g treatment; no yield depression noted.

Table 3. Cd content of edible portion of crops cultivated on a calcareous soil receiving 0.1 and 5 μg Cd/g soil in sludge form.

Crop species	Edible tissue analyzed	Cd content of edible tissue, μg/g tissue: Plants receiving 0.1 μg Cd/g	Cd content of edible tissue, μg/g tissue: Plants receiving 5 μg Cd/g
Paddy rice	Seed	<0.1	0.2
Field bean	Seed	<0.1	0.4
Zucchini squash	Fruit	<0.1	0.4
Sweet corn	Kernel	<0.1	0.5
Cabbage	Head	0.2	1.3
Tomato	Fruit	<0.1	1.6
Table beet	Tuber	0.2	1.8
Radish	Tuber	0.2	2.5
Wheat	Grain	<0.1	2.8
Turnip	Tuber	<0.1	4.9
Soybean	Seed	0.7	6.8
Carrot	Tuber	0.9	8.2
Swiss chard	Leaf	1.4	21
Romaine lettuce	Leaf	0.8	27
Curlycress	Leaf	2.4	55
Spinach	Leaf	3.6	91

The Cd content of edible tissue is of particular concern from a public health consideration because of the toxic nature of Cd to animals. Part of the experiments, testing tolerance of crops to Cd, included treatments with low additions of Cd to soil, simulating levels of Cd that conceivably could exist in agricultural soils treated with large amounts of sewage sludge. Table 3 contains Cd concentrations in the edible portion (part harvested and consumed as food) of a number of important field and vegetable crops grown on a calcareous soil pretreated with sewage sludge enriched with $CdSO_4$ sufficient to produce Cd concentrations of 0.1 and 5.0 μg Cd/g soil. In general, seed and fruit contain the lowest Cd concentrations and leafy tissue from plants such as chard, lettuce, curlycress and spinach contain the highest Cd concentrations. Leaf Cd values for the latter plants grown in soil treated at the 5 μg Cd/g rate vary from 21 to 91 μg Cd/g leaf tissue. Seed, however, contains much lower Cd concentrations. As examples, plants under the 5 μg Cd/g soil treatment contained the following Cd levels in seed: rice, 0.2; bean, 0.4; sweet corn, 0.5; wheat, 2.8; and soybean, 6.8 μg Cd/g tissue. Detailed information on Cd content of food crops as influenced by soil Cd concentrations is given in publications by Bingham et al. (*2*, *3*).

Relative Toxicity of Cd to Food Crops

Toxicity of Cd was compared to that of Cu, Ni, and Zn using two widely different soils and indicator plant species. Our procedure entailed amending an acid soil (pH 5.2) and a calcareous soil (pH 7.5) with a municipal sewage sludge (10 g sludge/kg soil) which had been pretreated with different amounts of $CdSO_4$, $CuSO_4$, $NiSO_4$, or $ZnSO_4$. The metals were not combined; four sets of treated soil were prepared each for the acid and calcareous soils. Approximately 7 kg of treated soil was placed in pots and cropped with romaine lettuce and wheat. The plants were permitted to grow to maturity, at which time they were harvested for measurement of yields (lettuce head and wheat grain) and samples of lettuce and grain collected for analysis of heavy metals. By plotting yield as a function of metal addition rate, we were able to determine the addition rate (threshold rate) causing a 25% depression in yield for each metal-soil-plant combination. These threshold rates which were expressed relative to that for Zn are summarized in Table 4. In all combinations, Cd was more toxic than any of the other metals, ranging from 2 to 20 times more toxic than Zn. The publication by Mitchell, Bingham, and Page (*4*) gives a detailed discussion of the above relative toxicities of heavy metals.

Table 4. Toxicity of heavy metals expressed relative to Zn for wheat and lettuce grown on an acid and a calcareous soil.

Heavy metal	Relative toxicity			
	Acid soil		Calcareous soil	
	Wheat	Lettuce	Wheat	Lettuce
Zn	1	1	1	1
Cu	4	1	1	3
Ni	6	2	1	2
Cd	12	2	6	20

A multiple metal system was subsequently investigated to evaluate interactive effects of heavy metals. This experiment involved treating an acid soil (pH 5.2) with municipal sewage sludge (10 g sludge/kg soil) enriched with different amounts of $CdSO_4$, $CuSO_4$, $NiSO_4$, and $ZnSO_4$ such that each metal was present at a low, intermediate, and high concentration in complete factorial combination with the other metals. A total of 81 treatments were prepared ($3^4 = 81$ metal combinations). A duplicate set of treatments were applied to the acid soil limed to pH 6.7 making a total of 162 treatments. Wheat was grown to maturity, harvested, and weighed. Grain production per plant was related to metal addition rates through multiple regression analysis. Table 5 contains stepwise regression equations for the above yield-metal relationships. The best-fit equation for grain yield of wheat cultivated on an acid soil may be written as follows:

$$y = 3.71 - 0.0036(1.00\ \mathrm{Zn} + 1.44\ \mathrm{Cu} + 2.06\ \mathrm{Ni} + 4.03\ \mathrm{Cd})$$

where y is yield in g grain/plant and the metals are expressed as μg/g soil. If we consider yield reduction equated with toxicity, Cd is 4.03-fold more toxic than Zn, 2.8-fold more toxic than Cu, and 1.96-fold more toxic than Ni. Upon liming, Ni and Zn were not toxic at any levels tested ($\leq$ 80 μg Ni and $\leq$ 200 μg Zn); thus the best-fit multiple regres-

Table 5. Stepwise multiple regression equations relating grain yield to addition rate of metals to an acid soil ± lime.

Soil type	Equation[a]	R^2
Unlimed	$y = 2.50 - 0.0145\ \mathrm{Cd}$	0.30[b]
	$y = 3.06 - 0.0145\ \mathrm{Cd} - 0.0052\ \mathrm{Cu}$	0.47[b]
	$y = 3.45 - 0.0145\ \mathrm{Cd} - 0.0052\ \mathrm{Cu} - 0.0036\ \mathrm{Zn}$	0.55[b]
	$y' = 3.71 - 0.0145\ \mathrm{Cd} - 0.0052\ \mathrm{Cu} - 0.0036\ \mathrm{Zn} - 0.0074\ \mathrm{Ni}$	0.62[b]
Limed	$y = 2.24 - 0.0083\ \mathrm{Cd}$	0.22[b]
	$y' = 2.44 - 0.0083\ \mathrm{Cd} - 0.0018\ \mathrm{Cu}$	0.26[b]

[a] y' = best-fit equation by F-test.

[b] Significant at the 0.001 level of probability.

Table 6. Toxicities for heavy metals relative to Cd.

	Cd	Cu	Ni	Zn
Unlimed soil	1.0	0.36	0.50	0.25
Limed soil	1.0	0.22	0.33	0.14

sion equation included only Cd and Cu. Writing the best-fit equation as

$$y = 2.44 - 0.0018\ (\mathrm{Cu} + 4.61\ \mathrm{Cd})$$

gives an expression of Cd toxicity relative to Cu, i.e., Cd is 4.61 times more toxic than Cu. As mentioned earlier, the Ni and Zn addition rates did not extend into a toxic range for limed soil. Results of a current experiment with this limed soil indicate toxicity (wheat) at treatment rates of 200 μg Ni/g and 600 μg Zn/g. Accordingly, toxicities for heavy metals relative to Cd for wheat are as shown in Table 6. Liming reduces the toxicity of Cu, Ni, and Zn expressed relative to that for Cd. As example, Cd was 4.0 times more toxic than Zn in the unlimed soil and after liming, Cd becomes 7.1 times more toxic than Zn.

Although information pertaining to soil Cd–yield relationships is of interest, the likelihood of Cd attaining a phytotoxic concentration in agricultural soils is low. However, pollution of soils by Cd to levels permitting uptake and accumulation of Cd in food crops to concentrations rendering the food crop unsafe for consumption is a real possibility. Concentrations of 5 to 10 μg Cd/g soil are sufficiently high for a number of crop plants to accumulate excessive amounts of Cd (Tables 2 and 3). Hence the Cd uptake data for wheat are relevant to entry of Cd into the food chain. The Cd treatment rates for the above experiment with an acid soil ± lime were 0.1, 20, and 80 μg Cd/g soil in combination with three concentrations each of Cu, Ni, and Zn. The grain Cd values for the unlimed soil experiment varied from 0.11 to 0.24 μg Cd/g grain for the 0.1 μg Cd/g soil treatment, 9.3 to 16.4 μg Cd/g grain for the 20 μg Cd/g soil treatment, and from 21.3 to 37.0 μg Cd/g grain for the 80 μg Cd/g soil treatment. In general, liming reduced grain Cd concentrations 50%.

A quantitative relationship between the Cd content of wheat grain and addition rate of heavy metals was obtained through multiple regression analysis (Table 7). These equations predict accurately grain Cd levels over the entire range of addition rates of heavy metals. Essentially all of the variation in grain Cd data is accounted for by the addition rate of Cd; however, inclusion of other metals leads to equations with slightly higher coefficients of multiple determination (R^2). The R^2 values for the best-fit equations were 0.99 and 0.98 for the unlimed and limed soil experiments, both being unusually high (note that the equations are $\log_{10}$ transformed). These equations also indicate a significant negative effect of Zn applications on Cd uptake by wheat grain. The interested reader is referred to the paper by Bingham et al. (*5*) for further details of interactive effects of heavy metals on wheat.

pH Effects on Cd Availability

In the experiment with wheat described earlier in this paper, adding lime to the acid soil raised the pH from 5.2 to 6.7. The Cd content of grain from plants cultivated on the limed soil was approximately 50% of that from plants in the unlimed soil. This decrease in Cd content of grain is ascribed to a pH effect rather than to a Ca^{2+} per se. Additional details pertaining to availability of Cd as influenced by changes in soil pH stem from a recent investigation reported by Mahler, Bingham, and Page (*6*). The latter investigation consisted of amending four acid and four calcareous soils with sewage sludge (10 g sludge/kg soil) enriched with low to phytotoxic concentrations of $CdSO_4$. The range of pH values for the acid soils was from 4.8 to 5.7; and for the calcareous soils, 7.4 to 7.8. These soils were cropped with romaine lettuce and swiss chard to have a biological measurement of soil Cd. In essence, the experiment was designed to compare Cd response

Table 7. Stepwise regression equations for Cd content of wheat grain in relation to addition rate of heavy metals to an acid soil ± lime.

Soil type	Equation	R^2
Unlimed	$\log y = -0.0152 + 0.795 \log \mathrm{Cd}$	0.985[b]
	$\log y = -0.0315 + 0.795 \log \mathrm{Cd} - 0.0004\ \mathrm{Zn}$	0.986[b]
	$\log y = -0.0128 + 0.795 \log \mathrm{Cd} - 0.0004\ \mathrm{Zn} + 0.0004\ \mathrm{Cu}$	0.987[b]
	$\log y' = -0.0389 + 0.795 \log \mathrm{Cd} - 0.0004\ \mathrm{Zn} + 0.0004\ \mathrm{Cu} + 0.0007\ \mathrm{Ni}$	0.988[b]
Limed	$\log y = -0.2682 + 0.763 \log \mathrm{Cd}$	0.970[b]
	$\log y = -0.1492 + 0.763 \log \mathrm{Cd} - 0.0011\ \mathrm{Zn}$	0.977[b]
	$\log y' = -0.2009 + 0.763 \log \mathrm{Cd} - 0.0011\ \mathrm{Zn} + 0.0005\ \mathrm{Cu}$	0.978[b]

[a] y' = best-fit equation by *F*-test.

[b] Significant at the 0.001 level of probability.

of two crop species under the influence of soil pH.

Multiple regression analysis of yields of lettuce and chard in relation to various soil properties revealed that Cd addition rate, % organic carbon, % clay, and soil pH were the principal soil properties exerting an influence on Cd availability in the eight soils as reflected by shoot weights of indicator plants. The best-fit equations for yields were as follows:

Lettuce:

$$y = 5.66 - 0.02 \text{ Cd added} + 3.40 \text{ \% OC} - 0.14 \text{ \% clay} + 1.93 \text{ pH}$$
$$R^2 = 0.82$$

Chard:

$$y = -0.88 - 0.06 \text{ Cd added} + 1.77 \text{ \% OC} + 0.17 \text{ \% clay} + 3.40 \text{ pH}$$
$$R^2 = 0.93$$

where y is in g/plant, Cd is in μg Cd/g soil, and OC is organic carbon.

These equations indicate that the phytotoxic effect of a given rate of Cd applied is moderated as soil pH and % OC increase.

Leaf tissue from lettuce and chard plants grown on these soils was analyzed for Cd to have another measure of available Cd. Multiple regression analysis of leaf Cd content in relation to selected soil properties [pH, Cd concentration of saturation extract (SE Cd), % sand-silt-clay, % $CaCO_3$, and cation exchange capacity (CEC)] showed most of the variation in leaf Cd to be related to SE Cd (R^2 = 0.771 and 0.766 for lettuce and chard). The coefficient of multiple determination (R^2) was increased slightly upon inclusion of CEC and pH parameters with SE Cd. The best-fit equations were:

Lettuce:

$$y = 21.97 + 20.43 \text{ SE Cd} + 3.92 \text{ CEC}$$
$$R^2 = 0.82$$

Chard:

$$y = 629.02 + 31.79 \text{ SE Cd} - 93.46 \text{ pH}$$
$$R^2 = 0.89$$

Comparison of leaf Cd values as a function of a given concentration of Cd in saturation extracts of acid soils as a group versus calcareous soils showed greater leaf Cd values for plants grown on the acid soils.

Thus the evidence on hand shows Cd availability to decrease with increasing soil pH. An explanation of reduced availability of Cd existing in soils at identical soil solution concentrations upon increasing pH is lacking. Possibly root activity controlling Cd uptake is favored by acid pH conditions. Preliminary studies of the chemical species of Cd existing in acid versus calcareous soil systems have not led to a satisfactory explanation of the greater Cd uptake under acid soil conditions.

Conclusions

Plants differ greatly in tolerance to Cd as well as in Cd uptake and accumulation characteristics. Leafy plants such as spinach, lettuce, curlycress, and swiss chard are accumulators of Cd.

Based upon solution culture experiments, Cd concentrations as low as 0.05 μg Cd/ml in soil solutions (or saturation extracts of soils) are sufficiently high for a number of crop species to accumulate Cd in levels rendering the plant unsafe for consumption. Likewise, Cd addition rates as low as 5 μg Cd/g soil are excessive for such crops.

Soil pH is a dominant factor influencing the availability of Cd added to soil. Liming an acid soil from pH 5.2 to 6.7 was associated with marked reduction of Cd uptake and accumulation by wheat. Comparison of Cd availability to lettuce and swiss chard grown on acid soils with that on calcareous soils also revealed less Cd uptake by plants under alkaline soil conditions.

Speciation of Cd in soil solutions of the four acid and four calcareous soils examined indicates approximately 50% of the total Cd solubilized is free Cd^{2+}; Cl, SO_4, and fulvate-Cd species account for the remainder. Cd availability appears to be more closely related to the concentration of free Cd^{2+} in the soil solution than to that of Cd total or Cd complexes.

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