



Project Summary

Factors Affecting the Bioavailability of Cadmium

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Results are presented from two studies designed to identify factors affecting the bioavailability of Cd and other trace metals in soils amended with municipal sewage sludges and to develop analytical methods for measuring those factors. The research included field, greenhouse, growth-chamber, and laboratory studies. The field studies were conducted on the agricultural research stations at Arlington and Hancock, Wisconsin. Growth-chamber studies were done at the University Biotron, and the greenhouse and laboratory studies were conducted in Department of Soil Science facilities at the University of Wisconsin-Madison.

The first study was entitled "Heavy Metal Bioavailability in Sludge-amended Soils" and included (1) field studies with two sludges containing about 200 mg Cd/kg to determine the effects of application rate, sludge properties, soil texture, and liming on uptake of Cd and other trace metals by corn, (2) greenhouse studies of the same factors but with three sludges and ten soils, and (3) laboratory studies to develop methods for measuring parameters that have been shown to affect bioavailability of the trace metals. The second study was entitled "Bioavailability of Cadmium" and was concerned mainly with further developing and applying methods for predicting bioavailability of Cd and other trace metals in soils amended with sewage sludge.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Municipal sewage sludges have been shown to be effective sources of plant nutrients, particularly N and P, when applied to agricultural land. However, some sludges contain relatively high levels of trace metals, which under some circumstances can produce toxic reactions in plants and/or animals. The trace metal Cd is of particular concern because it can accumulate in sufficient quantities in plant tissues to be toxic to animals or humans ingesting those tissues over an extended period. The purpose of the investigations reported here was to identify sludge and soil characteristics that affect the bioavailability of Cd and other trace metals and to develop analytical methods for measuring those factors. As our knowledge of the sludge-soil-plant system increased during these studies, it became apparent that a particularly effective research approach would be to devise methods that would provide inputs to a computer model describing solute transport and plant uptake.

Transport of solutes in a soil system can occur by mass flow (moving with the labile soil water) or by diffusion (moving in response to a concentration gradient). Transport of metal downward in the soil profile occurs dominantly by mass flow, whereas transport to plant roots is mainly a diffusion process (even for some conservative solutes such as nitrate), except when the species being absorbed are at very high concentrations. The soil and plant factors that affect the rate at which a plant absorbs a given metal from solution in a diffusion-limited system are shown in Equation 1. This equation is a modification of an uptake equation that describes the diffusive radial flux of solute

(in our case a metal) from an isotropic medium (soil) to a cylindrical sink (plant root), in time, t assuming depletion of a cylindrical volume of soil surrounding each segment of root.

$$U = C_{ii}b(1 - \exp \frac{-2\pi\alpha A_i r_o L_v t}{b(1 + \frac{\alpha A_i r_o}{D_i \theta f} \ln \frac{r_h}{1.65 r_o})}) \quad (1)$$

Soil factors: C_{ii} = initial concentration of metal in soil solution

b = buffer power, the change in concentration of total labile forms (adsorbed + dissolved) per unit of change in concentration of dissolved metal

A_i = fractional area of water contacting root

θ = volumetric water content

D_i = diffusion coefficient for the metal in soil solution

f = conductivity factor related to length of diffusion path

Plant factors: U = uptake per unit volume of soil in time, t

α = root-absorbing power (uptake flux density)/ (conc. at root surface)

r_o = root radius

r_h = half-distance between roots

L_v = root density

We have developed analytical methods that determine the proportions of metals present as dissolved free ions, dissolved complexes, and reactive adsorbed (labile forms). These methods allow us to calculate the dissolved metal concentration, C_{ii} , and buffer power, b , in Equation 1. We also developed methods for controlling metal-ion activities at realistic soil-solution levels in solution cultures to study the effects of speciation of dissolved metals on the root-absorbing power, α , and on competition among metal ions in the uptake process.

Development of Analytical Methods

Total Labile Metals

The accepted standard method for determining labile elements is isotopic exchange if suitable isotopes are available. Thus, ^{109}Cd and ^{65}Zn were equilibrated with samples of sand and silt loam

soils with and without addition of 102 Mg sewage sludge/ha. Isotopically exchangeable Cd and Zn were determined after 16 hr, and the results were compared with amounts of Cd and Zn extracted by various diethylenetriamine-pentaacetic acid (DTPA) and ethylenediaminetetracetic acid (EDTA) solutions. Metal extraction by 0.005M EDTA in 0.01M CaCl_2 at a 1:2.5 soil:solution ratio gave the best agreement with isotopically exchangeable values. DTPA extraction consistently gave low results.

Metal Speciation In Soil Suspensions

The method developed for determining metal speciation in soil suspensions involves equilibration of separate soil samples with each of four solutions: (1) 0.01M $\text{Ca}(\text{NO}_3)_2$, (2) 0.01M CaCl_2 , (3) 0.01M $\text{Ca}(\text{NO}_3)_2$ + $10^{-4.5}\text{M}$ EDTA (or hydroxyethylenediaminetriacetic acid (HEDTA), and (4) 0.01M CaCl_2 + 0.005M EDTA. If Cd is not detectable in the 0.01M $\text{Ca}(\text{NO}_3)_2$ solution, $\text{Cd}(\text{NO}_3)_2$ is added to all solutions to give a final Cd concentration of 5 mg/L. Equilibration with Solution 1 gives total dissolved metals. The increase in Cd concentration in Solution 2 over Solution 1 results from the formation of cadmium chloride complexes. Because the stability constants for these complexes and the Cl^- activity are known, the activity of Cd^{2+} can be calculated. The increases in metal concentrations in Solution 3 over Solution 1 result from the formation of metal-EDTA complexes. The activity of any divalent metal ion, (M^{2+}), can be calculated from Equation 2 once the Cd^{2+} activity and relevant competitive stability constant (K) are known:

$$(\text{M}^{2+}) = K(\text{Cd}^{2+}) \frac{[\text{M-EDTA}]}{[\text{Cd-EDTA}]} \quad (2)$$

If concentrations of any of the metals are below detection limits in Solution 1 but are detectable in Solution 2, activities can be calculated, but information on dissolved complexes cannot be obtained. The Solution 4 extract is a measure of labile metals. From the ratio of metal activities in solution to labile metal concentrations, distribution coefficients can be calculated for the partitioning between solution and solid phases. Concentrations of these metal ions can be determined from the calculated activities and ionic strength. Concentrations of dissolved metal complexes (M-ch), are determined by subtracting the calculated metal ionic concentration from the respective total metal concentration determined in Solu-

tion 1. An overall competitive stability constant (K_N) for the natural complexes can be calculated from Equation 3.

$$K_N = \frac{(\text{M}^{2+})[\text{Cd-ch}]}{(\text{Cd}^{2+})[\text{M-ch}]} \quad (3)$$

The method used for calculating free metal ion activities assumes that the addition of CaCl_2 in Solution 2 or EDTA in Solution 3 does not alter the equilibrium significantly; that is, the amount extracted into solution is not a significant part of the labile fraction. If this assumption does not hold, the calculated activities will be lower than those in a natural system.

Speciation of Dissolved Metals

Dissolved metals are partitioned between hydrated free-ions, ion pairs, and organic and inorganic complexes. The concentrations of total dissolved species are usually within the detection limits of sensitive analytical methods such as flameless atomic absorption spectrophotometry (FAAS), but present methods that measure activities of free metal ions are either not sensitive enough to measure the low activities present in most soil solutions, or they are subject to interference by components of the solution. The method for determining metal speciation in soil suspensions estimates free-ion activities, but it requires contact with a solid phase to maintain a constant metal activity. In order to overcome these limitations a sensitive method utilizing a Donnan* equilibrium system was developed. In this method a cation-exchange membrane separating a donor compartment (through which the test solution is pumped) from a much smaller compartment containing an acceptor solution. The latter is similar in composition to the test solution with respect to major cations. Free metal ions equilibrate across the membrane in about 1 hr, but transfer of complexed species is greatly retarded. Thus, analysis of the acceptor solution after 1 hr by FAAS gives the concentration of the free ion, from which an activity may be calculated. The detection limit is determined by the detection limit of the FAAS analysis.

Characterization of Soluble Complexing Agents

Chelating resins which provide a reservoir for metal ions and maintain

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use

constant metal ionic activity are used to control metal-ion activities so that competitive selectivity coefficients can be determined for dissolved ligands. The chelating resin is placed in a dialysis bag and equilibrated with the solution which originally contains the dissolved ligand or ligands but not the metal ion. The amount of metal complex formed is the difference between the total metal concentration and the metal ion concentration supported by the resin. Competitive stability constant (K) is calculated from the following equation where M and N are different metals, L is the dissolved ligand and ML and NL and the concentration of metal ligands:

$$K = \frac{[ML]}{[NL]} \frac{(N^{2+})}{(M^{2+})} \quad (4)$$

A method was developed for estimating the Cu-complexing capacity of dissolved ligands. In this method, samples of solution containing the dissolved ligand received varying amounts of added Cu^{2+} . The difference between the total Cu concentration determined by FAAS and Cu^{2+} concentration (determined either with the Donnan-equilibrium/cation-exchange membrane system or with an ion-specific electrode when Cu^{2+} activities are above $10^{-6}M$) gave the Cu-complexing capacity at the measured Cu^{2+} activity.

Cadmium Adsorption Isotherms

A method was developed for adsorbing Cd onto soil surfaces under conditions of constant pH and Cd^{2+} activity. To produce solutions with known and constant Cd^{2+} activity varying ratios of Cd-saturated chelating resin to Ca-saturated chelating resin were mixed and added to a dialysis bag. A pH-adjusted, weak-acid resin was also added for pH control. The resin mixture in a dialysis bag was then equilibrated with a soil sample in $0.01M$ $Ca(NO_3)_2$, and the Cd adsorbed on the soil was extracted with acid and determined. The Cd adsorbed on the soil must be small compared with that contained in the chelating resin so that a nearly constant, known Cd^{2+} activity is maintained. Competition for adsorption sites on the soil is limited to Cd^{2+} and Ca^{2+} as the resin adsorbs other metals that were originally adsorbed on the soil. Competitive adsorption at known metal activities could be studied by including other metals in the chelating resin.

Control of Solute Concentrations in Nutrient Solutions

If nutrient solutions are to be used for determining root-absorbing powers for

trace metals, concentrations of those metals at the root surfaces must be known. However, the nutrient solutions do not buffer metal concentrations, and even rapidly flowing solutions do not maintain constant metal concentrations at root surface when concentrations are in normal soil solution ranges. For this reason, a resin-buffered nutrient solution system was developed. In this system, a strong-acid resin controls the ratios of Ca^{2+} , Mg^{2+} , K^+ , and Mn^{2+} ; a weak-acid resin buffers pH and assists in controlling ratios of the previously mentioned cations; a chelating resin controls the ratios of trace metals, including Cd^{2+} , Zn^{2+} , and Cu^{2+} ; and a strong-acid resin partially saturated with $(Al(OH)_2^+)_n$ polynuclear complexes controls P concentrations and assists in controlling ratios of the major cations. Anions such as NO_3^- and SO_4^{2-} must be maintained by periodic additions. For most of the cations, the ratios are controlled by the resins; but the absolute concentrations are a function of ionic strength. Thus the total solute concentration as indicated by electrical conductivity must be controlled within rather narrow limits. This system has been used successfully with the resins enclosed in filter membrane bags, floating free in the pot, or contained in a column through which the nutrient solution is recirculated.

Factors Affecting Cadmium Bioavailability

Sludge Characteristics

Data from laboratory, greenhouse, and field all show that sludge characteristics are extremely important, if not dominant, in controlling Cd (and Zn) availability to plants. From 18% to 63% of the total Zn, and from 12% to 63% of the total Cd in the sewage sludges studied was isotopically exchangeable. The greatest percentage was for Chicago sludge, whereas the lowest was for a sludge that received soluble Fe during the treatment process. When corrected for the effects of pH, the fractions of isotopically exchangeable Zn and Cd extracted by $0.01M$ $Ca(NO_3)_2$ were about the same for all sludges and soils studied. This result suggests that the mechanism by which solubility is controlled is coprecipitation (solid solution) of Zn and Cd with phosphates of Fe, Al, or Ca, with hydrous oxides of Fe or Al, or with $CaCO_3$ during the treatment process.

According to solid solution theory, the solubility of a trace constituent should be proportional to its relative concentration

on the surface of the precipitate. Thus for equal concentrations of Cd in different sludges, the solubility should decrease as the amount of the precipitate's major component ($FePO_4$, $AlPO_4$, etc.) increases with respect to the Cd concentration. This effect is apparent when comparing results for the Chicago sludge (low Fe, Al, and P) with those for the Wisconsin Rapids sludge (high Fe and P). Although total concentrations of Cd were nearly the same for both sludges, the isotopically exchangeable Cd, solution Cd, and Cd in barley leaves in the field were all much higher for the Chicago sludge.

Similarly, in sludges with similar levels of the major precipitant, the solubility of Cd should increase with the total Cd concentration. This result is borne out (although not as clearly as would be desired because of the low additions involved) in the greenhouse study comparing plant uptake of Cd at equal Cd additions from the Oshkosh (9 mg Cd/kg) and Wisconsin Rapids (180 mg Cd/kg) sludges.

If these observations on a few sludges were found to hold as a general rule, Cd solubility might be predicted on the basis of sludge composition and verified by analyzing for the capacity factor by isotopic dilution or ligand extraction and for the intensity factor by equilibration with $Sr(NO_3)_2$ or $Ca(NO_3)_2$.

Sludge Application Rate

At high sludge application rates, the properties of the sludge tend to determine Cd and Zn availability, with the effects of soil properties being limited primarily to pH control. At low sludge rates, the adsorptive properties of the soil appear to exert some control.

Increasing additions of the high-Cd Wisconsin Rapids sludge to soils in the greenhouse resulted in proportionate increases in DTPA-extractable Cd. Similar increases in the levels of soluble DTPA-extractable and isotopically exchangeable Zn and Cd were observed in the field as the rate of sludge application was increased. However, these proportionate increases in labile metal levels were not consistently reflected in crop uptake. The Cd concentration in corn tissue, particularly in the third greenhouse crop, tended to plateau at about 80 Mg/ha (18.3 kg Cd/ha) in the Plainfield sand and 160 Mg/ha (36.6 kg Cd/ha) in the Plano silt loam. Tissue Cd levels in the field also tended to plateau at higher sludge rates, but the effect was not as apparent as in the greenhouse because

of the lower rates used in the field. This relationship was somewhat confounded in the field by lower pH induced by the high sludge rates.

In the field, the concentrations of Cd in corn ear leaves tended to reach a plateau between 1 and 1.5 mg/kg. Very little Cd was found in the corn grain. In the greenhouse, the Cd concentration in plant tissue from the third corn crop reached a plateau at about 7 mg/kg. This level is much higher than in the field, even considering that the greenhouse tissue was less mature. This result suggests that the greater transpiration ratio of the greenhouse crop may have resulted in greater Cd uptake because of the increased amount of Cd arriving at the root surface by mass flow. Alternatively, Cd uptake in the field may have been reduced by root penetration into deeper soil regions not affected by sludge addition.

Time Following Sludge Application

In both the greenhouse and field studies, DTPA-extractable Cd tended to increase with time, but the effect extended over a longer period in the field, probably because the sludge particles were coarser and took longer to interact completely with the soil. Mixing sewage sludge with soil did not change the isotopic exchangeability of either component immediately (i.e., the concentration of isotopically exchangeable Zn in the mixture remained the weighted average of the values for the soil and sludge). However, mixing did increase the concentration of isotopically exchangeable Cd by 30% to 40% in the mixture after 1 year.

The concentration of Cd in tissue tended to increase from crop-to-crop, both in the greenhouse and the field. This result is contrary to those of most field studies reported in the literature. However, interpreting year-to-year differences in crop Cd concentrations as due to changes in lability of sludge Cd alone is questionable because Cd uptake from a given soil might also be affected by changes in environmental conditions such as temperature, moisture, pH, soluble salts, and evapotranspiration.

Soil pH

The combination of liming and sludge application resulted in a wide pH range — greater than 2 pH units in the Plano field plots. Isotopic exchange studies on soil samples from these plots indicated that the concentration of isotopically ex-

changeable Zn in the sludge-amended soil was independent of pH. However, isotopically exchangeable Cd at pH 6.2 after 1 year was only 80% of that measured at pH 5.4. Similarly, DTPA-extractable Cd on the limed plots in 1979 (after 3 years of equilibration) averaged 67% of that of the unlimed plots. Graphs of the negative logarithms of solution concentration versus pH for control and sludge-treated plots gave a slope of 1.0 for Zn and 0.7 for Cd over a pH range of 4.6 to 6.8. An increase in 1 pH unit therefore decreased the intensity factor of bioavailability (concentration in solution) tenfold for Zn but only fivefold for Cd. The values of the slopes were independent of the sludge application rate.

This marked decrease in soluble Cd with increasing pH is not consistently reflected in a corresponding decrease in Cd uptake in the field, however. Although the limed and unlimed plots on the Plano soil differed by approximately 1 pH unit, no significant effects of pH on Cd concentration in the leaves of corn or barley were observed. Only in the corn leaf tissue from Hancock at the high rates in 1978 and at all rates in 1979 was there a markedly greater Cd concentration in corn ear leaves from unlimed plots. Why the increased solution Cd at lower pH did not result in consistently greater Cd uptake from the Plano soil is not apparent.

In contrast to the field studies, where there was little effect of pH on Cd uptake, addition of excess CaCO_3 to 10 soils in the greenhouse caused marked decreases in Cd uptake. This result is consistent with others in the literature, indicating relatively low Cd availability in calcareous soils. The pH range in the greenhouse study was higher than those used in the field study, so the results are not directly comparable.

Soluble Salts

Equilibration of Wisconsin Rapids sludge with solutions of varying Ca concentrations resulted in solution Cd levels that were directly related to Ca concentration. This result is in accord with Cd-Ca reactions on the chelating resin. Zinc, Ni, and Fe also increased with increasing Ca concentration, but only about half as much as Cd. Similar results were obtained with soils from the field plots when equilibrated with varying concentrations of Ca or Sr.

Tissue Cd levels in the second greenhouse corn crop tended to be lower for high-sludge treatments that had been leached than for lower-sludge treatments

that had not been leached. This suggests that Cd levels in the soil solution may have been increased at higher salt levels. Such a response implies that either the salts in the sludge were present in the Ca form or that the other cations induced greater displacement of Ca from exchange sites, which then competed with Cd for more selective adsorption sites. This relationship is by no means clearcut, but it does point out the need to control soluble salt concentration following sludge application, especially in greenhouse studies.

Speciation of Dissolved Cd

Speciation studies indicated that most of the Cd and Zn in the soil solution were in the free-ion form, whereas Cu was more than 90% complexed. In a Biotron study using the resin-controlled nutrient solution system, the Cd^{2+} , Zn^{2+} , and Cu^{2+} activities were controlled at levels characteristic of a sludge-amended soil, but total metal concentrations were changed two to four orders of magnitude by complexing with EDTA. Concentrations of Cd in the plant shoots were not affected by the presence of the soluble complex, and concentrations of Zn and Cu were increased less than 30% even though the total Cu concentration in solution increased 10,000 times. Metal uptake therefore appears to be a function of the free-ion concentration at the root surface.

Speciation results with Cd and Cu in soil solutions from control and sludge-amended soils by the Donnan membrane equilibrium technique were compared with those calculated by the GEOCHEM program. The nine-ligand Mixture Model of GEOCHEM generally tended to predict higher proportions of free Cd^{2+} and Zn^{2+} than those experimentally determined.

Buffer Power

The Cd buffer power is the change in total labile Cd per unit change in dissolved Cd. If curves relating adsorbed Cd to solution Cd were linear, the distribution coefficient, $\text{Cd}_{\text{adsorbed}}/\text{Cd}_{\text{solution}}$, would equal the buffer power. A survey of literature values showed that distribution coefficients decreased dramatically as Cd/Ca ratios increased. The reason is probably that sites with a very high affinity for Cd are available at low Cd concentrations; but at higher Cd concentrations, these sites are filled, and Cd has to compete with Ca for sites of lower Cd specificity. Under these conditions, Cd buffer powers determined at relatively high Cd/Ca ratios drastically underesti-

mate buffer powers at Cd/Ca ratios occurring in normal soil solution. In fact, the literature survey indicates that most distribution coefficients have been determined at unrealistically high Cd values and that buffer powers derived from those values may be as much as three orders of magnitude too low for normal soils. The relationship of buffer power to uptake shown in Equation 1 indicates that a difference of this magnitude would have a very great effect on predicted uptake.

Cadmium-Zinc Interactions

The addition of $Zn(NO_3)_2$ to unamended Plainfield sand resulted in increased uptake of Cd by plants grown in the greenhouse, most likely as a result of increased Cd in solution caused by displacement from the relatively small number of adsorption sites in this soil. Similar Zn additions to Plano soil and to both soils containing sludge resulted in little additional Cd uptake, probably because the greater quantity of sorption sites furnished by the soil and the sludge could accommodate the Zn with little Cd displacement. These assumptions were supported by the Cd concentrations determined in 0.01M $Ca(NO_3)_2$ extracts from the above soil treatments. Zn addition to the Plainfield soil greatly increased relative solution Cd levels, whereas the increases in solution Cd levels in the Plano soil and the sludge-amended soils were much smaller.

Effects of Cd/Zn ratios in solution on Cd and Zn uptake by tomatoes grown in the resin-controlled nutrient system were studied in a Biotron experiment. Ratios of Cd/Zn were varied over four orders of magnitude, with Cd varying from $10^{-9.3}$ to $10^{-7.5}M$ and Zn from $10^{-7.9}$ to $10^{-5.2}M$. Cu was maintained at $10^{-11.3}M$. A linear relationship ($r^2=0.94$) was found between $\log (Zn/Cd)$ in tissue and $\log (Zn/Cd)$ in solution. A slope value of 0.74 indicated that the plant preferentially absorbed the metal at the lower concentration. At constant Cd^{2+} activities in solution, Cd concentration in the plant decreased with increased Zn concentrations, but the decrease was not large except at very high Zn concentrations.

Conclusions

1. Bioavailability of a given amount of Cd applied to soil as a constituent of sewage sludge depends on both sludge and soil characteristics.
2. Other compositional factors being equal, the bioavailability of a given amount of Cd applied as sludge ap-

pears to increase as the concentration of Cd in the sludge increases.

3. Bioavailability of Cd from sludges with equal Cd concentrations was observed to be lower for sludges with high concentrations of hydrous oxides or phosphates of Fe or Al on which the Cd can be adsorbed or with which it might be coprecipitated during the treatment process.
4. Adsorption properties of the soil affect the bioavailability of sludge-applied Cd, particularly at low sludge applications. As sludge applications are increased, metal adsorption sites on the soil become saturated, and the sludge properties seem ultimately to control bioavailability. This conclusion is supported by the tendency of metal uptake to approach a maximum with increasing sludge application.
5. Concentrations of metals in the soil solution increase as the pH of the sludge-soil system decreases or as the Ca concentration in solution increases. Such conditions usually result in increased metal uptake by plants, but not always.
6. Diffusion-convection models of solute transport can be used to model trace metal uptake. The advantage of this approach is that the parameters in the model indicate the factors that must be determined analytically to successfully use the model.
7. Most of the methods described in this report were designed to provide data on metal speciation in the soil-sludge-water system that (1) permit calculation of solution concentrations and buffer powers and (2) contribute to our estimate of root-absorbing power. All of these parameters are variables in the uptake model.
8. Further research is needed to improve methods for determining metal-desorption characteristics of soils under the conditions of competitive adsorption existing in soil-sludge systems.

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J. A. Ryan is the EPA Project Officer (see below).

The complete report, entitled "Factors Affecting the Bioavailability of Cadmium," (Order No. PB 87-147 435/AS; Cost: \$30.95, subject to change) will be available only from:

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