

Predicted Solution Phase Forms of Heavy Metals in Sewage Sludge-Treated Soils¹

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ABSTRACT

Chemical speciation of selected elements in the soil solution of sewage sludge-treated soils was studied with aid of the computer program, GEOCHEM. Soil solutions were obtained by the saturation extract method from reconstructed soil profiles where anaerobically digested sewage was incorporated into the top 15 cm of the soil and the soils were leached for 25 months. Total concentrations of Cd, Cu, Ni, and Zn in the soil solutions were elevated by the sewage sludge addition, but in most cases were within ranges found in a survey of soils untreated with sludge. Concentrations of the metals were so low that their contribution to metal movement over the duration of the study was negligible. Concentration changes in solution metals across the sludge-soil interface in most columns was dramatic. For Cd, Ni, and Zn between 50 and 60, 60 and 70 and 60 and 70%, respectively, of the total metal in solution was found to be in the free ionic form. Copper was almost exclusively in organically complexed forms in sludge-soil layers, and below these layers the form of Cu shifted to the free ionic form as the pH decreased. Activities of the metals indicated undersaturation with respect to established minerals in soils.

Additional Index Words: cadmium, copper, nickel, zinc, GEOCHEM, metal activity.

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Reports in the literature on the chemical forms of heavy metals in soil solutions are limited. This is probably due to the large number of possible chemical forms in which the metals can exist and the analytical problems associated with their determination. Environmental scientists are becoming increasingly aware of the need for reliable methods that can differentiate the chemical forms of heavy metals in natural waters. The often-reported measurement of the total concentration of a particular metal in a water sample may be very misleading. For example, ionic Cu is far more toxic towards aquatic organisms than complexed Cu, and the more stable the Cu complex the lower is its toxicity (Steemann and Wium-Andersen, 1970). Also in soil solutions, a neutral or anionic species of the metal is more likely to move through a negatively charged soil matrix than a positively charged form.

Florance and Batley (1977) presented three general methods for the determination of chemical forms of metals in natural waters. The three methods are: separation, physicochemical, and calculation. Separation methods include a wide variety of techniques such as dialysis, ultrafiltration, centrifugation, solvent extraction, ion exchange resins, and gel filtration. A number of investigators have used these different techniques with varying degrees of success (Lagerwerff et al., 1976; Bender et al., 1970; Hodgson et al., 1965). The major disadvantage of separation methods is the

uncertainty in the recovered chemical species. Instead of a specific chemical species, it often recovers a category of similar or overlapping chemical forms. Many times, it is desirable to know the concentration of a specific species (i.e., Cd^{2+} , NiOH^+ , CdCl_3^- , $\text{Cu}(\text{OH})_2^0$) in solution, and this is not possible with these methods. Physicochemical methods include ion-selective electrodes and determination of shift in polarographic half-wave potential with changes in pH. Street et al. (1977) evaluated the use of a Cd ion-selective electrode to determine the activity of Cd in soils amended with Cd and sewage sludge, but the activity in many of the soils was below the detection limit of the electrode. Polarographic half-wave potential shifts and ion-selective electrodes also suffer from the same problems of low metal concentrations in natural waters and interferences due to complexing agents. Therefore, these methods frequently are of limited value in the determination of species of metals in soil solution.

The use of the chemical equilibrium concept to calculate the chemical speciation of aqueous systems has been reviewed by Jenne (1979). One of the more comprehensive aqueous chemical models for computing equilibria in aqueous chemical systems was developed by McDuff and Morel (1974) and Morel and Morgan (1972). Extending this work, Sposito and Mattigod (1980) developed a computer program (GEOCHEM) for soil solutions. The improvements and problems associated with the development and use of the computer program, GEOCHEM, have been discussed by Mattigod and Sposito (1979).

The objectives of this study were (i) to determine the total metal concentrations and through the use of GEOCHEM evaluate the chemical forms of the metals, Cd, Cu, Ni, and Zn, in the soil solution of soil profiles that had received surface applied sewage sludge; and (ii) to determine the changes with depth in the chemical forms of heavy metals in the soil solution of soil profiles with surface-applied sewage sludge. An attempt was also made to determine the solid phase controlling the activity of the metals in the soil solutions through the use of stability diagrams.

MATERIALS AND METHODS

The soil solutions analyzed in this study were obtained from a column study described completely by Emmerich et al. (1982) and Emmerich (1980). A brief description of the column study is as follows. Profiles representing three soil series were reconstructed in columns and anaerobically digested sewage sludge in either liquid (wet) or air-dried (dry) form was incorporated into the top 15 cm of the soils. The columns were leached for 25 months and then sectioned. The sectioning consisted of dividing the sludge-soil layer into two equal increments and, starting at the sludge-soil interface (i.e., the separation between the sludge-soil layer and the soil portion of the column) the soil portions of the columns were sectioned into 5-cm increments. From each increment, a 20-g sample was taken for moisture analysis to be used in calculation of species concentration in the soil solution. Saturation extracts were prepared for each increment from the remaining soil or sludge-soil mixture (Richards, 1954), with weights being recorded before and after ion exchange water was added so the concentration of the constituents in the soil solution could be cal-

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culated. For simplicity in designating the samples, A and B will be used for the top and bottom halves of the sludge-soil layers, respectively, and 5 and 10 for the first and second 5-cm increment below the sludge-soil interface, respectively.

The saturation extracts were analyzed as completely as possible for total metals and ligands and the concentrations were converted to a soil-solution basis. The computer program, GEOCHEM, was used to speciate the metals in solution using the total concentrations of the metals and ligands in the soil solutions (Sposito and Mattigod, 1980). The analytical methods used were as follows: Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Si, and Zn were determined by atomic adsorption spectrophotometry (AAS) with a Perkin-Elmer model 5000; CO₃ and HCO₃ by titration (Bower and Wilcox, 1965); NO₃-N and SO₄ on a Technicon AutoAnalyzer II industrial method no. 102-70W/B and 118-71W/B, respectively; Cl using a Aminco chloride titrator; P colorimetrically (Murphy and Riley, 1962); Cd following organic extraction (Sprague and Slavin, 1964) using a Perkin-Elmer model 306 AAS equipped with a HGA-2100 graphite furnace; organic C using a Beckman model 915 total organic C analyzer with a model 215B infrared analyzer; and pH with a Beckman model 3550 pH meter.

RESULTS AND DISCUSSION

Total metal concentrations in the soil solutions are given in Table 1. The added sludge metals increased the soil solution concentrations of all the metals in the sludge-soil layers over the concentrations found lower in the columns. The change in concentrations across the sludge-soil interface for most metals was dramatic. This large concentration gradient across the interface was an indication that the metals had not moved out of the sludge-soil layers, and this was confirmed by a total metal analysis of the soils below the sludge-soil layers and the leachates from the columns (Emmerich et al., 1982).

The total soil solution concentrations of most metals in the sludge-soil layers and below (Table 1) were generally within the ranges observed for soils untreated with sludge (Bradford, 1979, personal communication; Bradford et al., 1971). In fact, they were so low that they did not contribute significantly to metal movement (Emmerich et al., 1982). Bradford collected 68 soil samples representing 30 soil series in California and measured the concentrations of numerous metals in soil saturation extracts. The range of concentrations for Cd, Cu, Ni, and Zn were <10, 10–200, 10–90 and 10–400 ppb, respectively. The concentrations of most of the metals within and below the sludge-soil layers in the columns were within the ranges found by Bradford, except for Cu and Ni in two different columns. Bradford's ranges were for saturation extracts and values here are for soil solutions. Comparison on a saturation extract basis shows only Cu and Ni in the sludge-soil layers of the Ramona and Helendale columns exceeded concentration ranges for non-sludge-treated soils reported by Bradford. The significance of these results is that even after the addition of sewage sludge to soils, the solution concentrations of the total metals for the most part were comparable to those that could be found in some native soils without sludge additions.

The GEOCHEM program is a chemical equilibrium model. All results are calculated by computer, based on thermodynamic association and solubility product constants in the model and the analysis of the solution being studied. There are a number of important theoretical problems associated with the use of GEOCHEM; they have been discussed by Mattigod and Sposito (1979).

Table 1—Total metal concentrations expressed on a soil solution basis of the Holland, Ramona, and Helendale† columns.

Sample‡	Cd		Cu		Ni		Zn	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
µg/liter								
Holland								
A	1.1	1.2	210	180	140	90	130	50
B	1.5	2.6	130	200	80	130	110	80
Sludge-soil interface								
5	0.2	0.5	40	70	20	20	90	60
10	0.2	0.5	30	70	30	10	70	60
Ramona								
A	1.3	7.6	190	1,350	120	460	140	360
B	3.1	4.7	200	1,500	190	440	140	200
Sludge-soil interface								
5	0.2	0.5	50	120	40	100	90	100
10	0.3	0.3	50	90	30	60	110	90
Helendale								
A	5.8	11.2	280	1,590	150	620	150	410
B	4.5	4.7	600	1,130	180	340	70	230
Sludge-soil interface								
5	0.9	0.3	70	340	20	80	50	90
10	1.0	0.3	70	280	20	50	60	150

† Holland sandy loam: fine-loamy, mixed, mesic Ultic Haploxeralf; Ramona sandy loam: coarse-loamy, mixed, thermic Typic Haploxeralf; and Helendale loamy sand: coarse-loamy, mixed, thermic Typic Haplargid.

‡ A and B = top and bottom halves of the sludge-soil layers, respectively, and 5 and 10 = first and second 5-cm increment below the sludge-soil layer interface, respectively.

The problem of stability constants for trace metal complexes with organic ligands is of concern in this paper and the results of organic complexes must be tempered with this in mind.

The GEOCHEM program calculated the concentrations of hundreds of complexes in the soil solutions. These data were condensed by grouping the metals into free ionic and organic and inorganic complexed forms. The percentages of the three forms for the metals are given for the Ramona columns in Table 2. The data for the other columns and those in Table 2 reveals that for a certain metal and similar location in a column, there was a range of 10% for a particular form between the three soils and the form of the added sludge (i.e., wet or dry). The exceptions to this were Cu below the sludge-soil interface and Ni in the sludge-soil layers. The differences in Cu below the sludge-soil interfaces could be explained by the change in the pH with depth; the pH values are given by Emmerich et al. (1982). In the sludge-soil layers Cu was almost entirely complexed with the organics and as the pH decreased there was a shift to the free ionic form even with ample organics to complex the Cu. There was no obvious explanation as to the greater variability of Ni speciation in the sludge-soil layers, but the pH change was probably involved.

The data also revealed lack of a change in chemical form in almost all of the columns, especially for the metals Cd and Zn across the sludge-soil interfaces. In contrast, the total solution metal concentrations across the sludge-soil interfaces changed dramatically (Table 1). The stabilization of chemical forms in the soils suggested that there was perhaps an equilibrium between

Table 2—Percent of metal in the free ionic (F) and inorganic (I) and organic (O) complexed forms in the soil solution of the Ramona columns.

Sample†	Wet			Dry		
	F	I	O	F	I	O
%						
Cd						
A	59	39	1	49	47	3
B	52	46	2	51	45	4
Sludge-soil interface						
5	52	46	1	49	49	2
10	53	47	1	53	46	1
Cu						
A	3	4	94	1	1	98
B	1	1	98	1	1	98
Sludge-soil interface						
5	4	3	93	6	4	90
10	23	11	66	39	20	41
Ni						
A	65	22	13	53	21	26
B	50	22	29	42	20	38
Sludge-soil interface						
5	67	24	9	63	29	9
10	73	25	3	69	28	3
Zn						
A	71	27	2	64	32	4
B	66	31	3	61	33	5
Sludge-soil interface						
5	68	30	1	62	35	2
10	69	30	1	66	33	1

† A and B = top and bottom halves of the sludge-soil layers, respectively, and 5 and 10 = first and second 5-cm increment below the sludge-soil layer interface, respectively.

free ionic, organic, and inorganic forms. As more metals were added to the system, they were partitioned according to the existing equilibrium, and therefore the percentages of each form remained unchanged. This equilibrium was probably influenced by many factors, with pH being one of the more important ones. Changes of soil pH probably caused metals in solution to shift from organically complexed toward the free ionic form as exemplified by the changes of Cu and Ni in the soil profiles. The effect of pH on the equilibrium was likely different for each metal. Since only small percentages of Cd and Zn were in organic forms, the effect of pH on chemical forms of Cd and Zn were less apparent.

The chemical properties of the sludge and soils were also expected to affect the equilibrium. The properties of the soil seemed to dominate for the metals Cd and Zn, as there was no significant change in percentages across the sludge-soil interfaces. For Cu and Ni the properties of the sludge seemed to dominate in the sludge-soil layers, but below the sludge-soil interfaces the soil properties seemed to dominate, as there was a change in the percentages across the interfaces.

The activities of the metals of interest were calculated using the single-ion activity coefficient (Davies, 1962) and the free ion concentration (GEOCHEM). The ionic strength for the Davies equation was calculated by GEOCHEM. The results of the calculations are presented in Table 3. The values obtained using this

Table 3—Activities† of free metal ions in the soil solution of the Holland, Ramona, and Helendale columns.

Sample‡	Cd		Cu		Ni		Zn	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
× 10 ⁻² M								
Holland								
A	3.2	3.0	3.5	3.7	8.1	4.8	8.0	2.5
B	4.1	5.7	8.2	2.0	5.1	5.8	6.6	3.6
Sludge-soil interface								
5	0.6	1.1	2.0	16.8	1.5	1.1	5.0	2.6
10	0.6	1.0	1.6	27.1	1.7	0.7	3.7	2.7
Ramona								
A	3.7	1.4	4.0	9.8	6.8	17.6	7.9	15.3
B	6.7	9.7	0.9	4.9	7.3	14.3	6.6	8.5
Sludge-soil interface								
5	0.5	1.1	1.6	5.4	2.0	5.2	4.5	4.7
10	0.5	0.6	8.5	27.6	1.6	3.7	5.4	4.5
Helendale								
A	13.1	21.6	5.4	11.9	7.6	24.1	7.2	17.4
B	10.2	8.6	6.4	3.5	8.0	22.2	3.2	9.8
Sludge-soil interface								
5	2.1	0.6	6.2	4.2	0.9	3.7	2.4	3.7
10	2.2	0.6	7.4	41.4	1.0	2.7	2.7	6.6

† Activity = single-ion activity coefficient (Davies equation) × free ion concentration (GEOCHEM).

‡ A and B = top and bottom halves of the sludge-soil layers, respectively, and 5 and 10 = first and second 5-cm increment below the sludge-soil layer interface, respectively.

method were very low and for all practical purposes below the detection limit of ion-selective electrodes and many analytical instruments. Therefore, if the activities of metals in soil solutions at these low values are to be determined a calculation method must be employed.

The sewage sludge added to the soils increased the activity of the metals in the soil solution of sludge-soil layers. For Cd, Ni, and Zn the activity was almost always greater in the sludge-soil layers than the soil profile below. Copper has some significantly greater activities in the samples below the sludge-soil interfaces. The reason for the increase in activity below the sludge-soil interfaces for Cu was the change in the form of Cu in solution. In the sludge-soil layers the Cu was almost entirely complexed with the organics, whereas below, the form shifted to a considerable extent to the free ionic form, hence the increased activity. This shift was probably due to the decrease in pH. As the pH decreased the H⁺ ion could successfully compete for the organic ligands and release the Cu as a free ion.

Activities of the metals in the soil solutions were plotted on stability diagrams along with the solid phase that would produce the lowest activity as determined by Lindsay (1979) or Sillen and Martell (1964) (Fig. 1-4). The indication was that the activities of the metals were independent of pH. The absence of the normally observed logarithmic decrease in activity with increasing pH could be explained by any of the following: (i) equilibrium conditions did not exist, (ii) the solid phase controlling the metal activity is unknown, (iii) the GEOCHEM program is in error due to thermodynamic data used, and/or (iv) the solid phase controlling the metal activity is not in its standard state. The columns were open systems with water being continually added

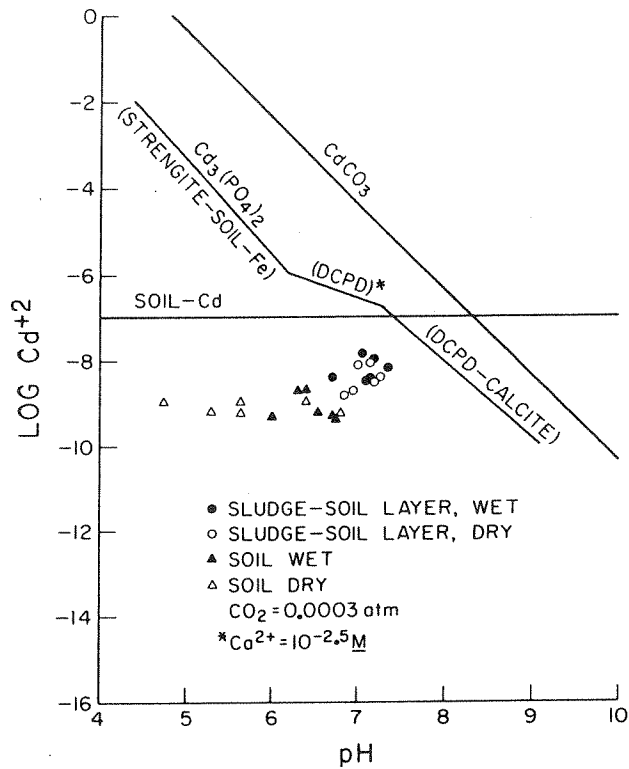


Fig. 1—Activity of Cd in solution vs. pH in the A, B, 5, and 10 samples of all the columns. (Strengite-soil-Fe) and soil-Cd lines were taken from Lindsay (1979).

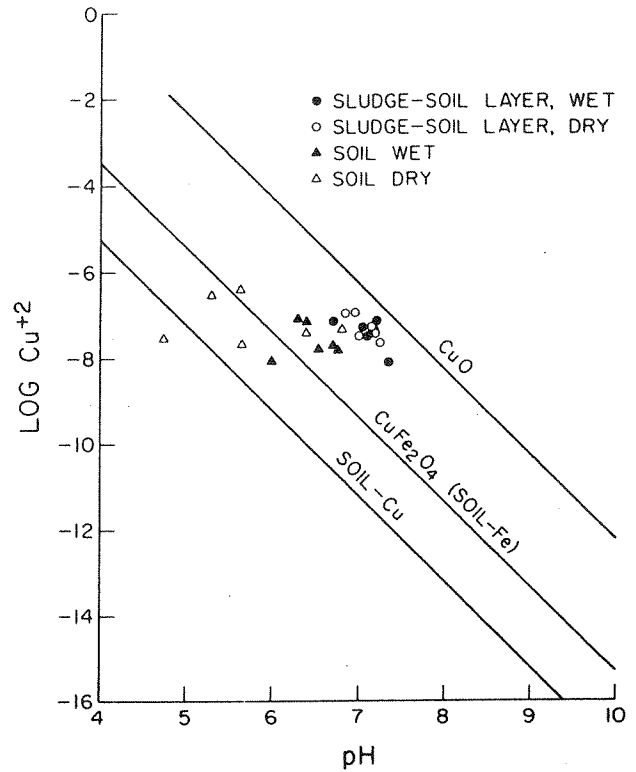


Fig. 2—Activity of Cu in solution vs. pH in the A, B, 5, and 10 samples of all the columns. CuFe_2O_4 (soil-Fe) and soil-Cu lines were taken from Lindsay (1979).

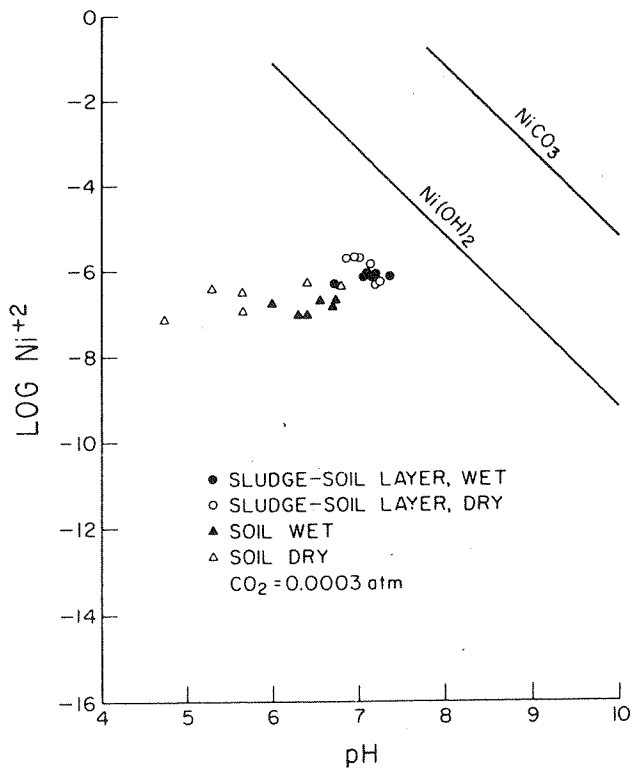


Fig. 3—Activity of Ni in solution vs. pH in the A, B, 5, and 10 samples of all the columns.

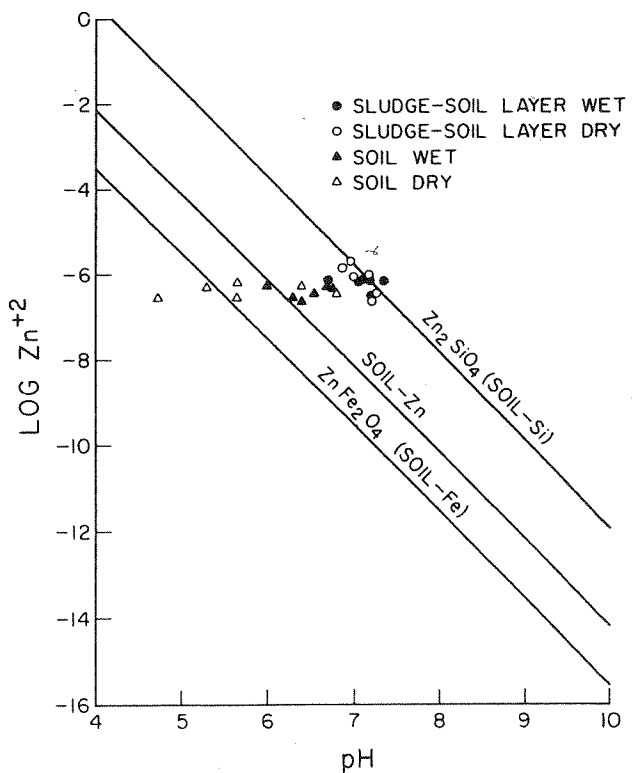


Fig. 4—Activity of Zn in solution vs. pH in the A, B, 5, and 10 samples of all the columns. Zn_2SiO_4 (soil-Si), soil-Zn, and ZnFe_2O_4 (soil-Fe) lines were taken from Lindsay (1979).

and removed, hence, it is unlikely equilibrium did exist, but some form of steady state should have been reached after 2 years of leaching. Therefore, a lack of equilibrium could account for the observed activities.

The standard state of a solid consists of a solid in the most stable form for the pure solid under a pressure of 1 atm, at a specified temperature (i.e., usually 298.15°K), and with an activity of the solid equal to 1. Without hesitation it can be said most solid phases in soils are not in their standard states, and this could account for some of the deviation from a significant decreasing activity with increasing pH.

There is the possibility that the solid phase controlling the activity of the metals in solution is unknown and not plotted on the stability diagrams. In Fig. 1-4 all of the activities of the metals were undersaturated with respect to established minerals that could be found in soils. The soil-metal solid phases as determined by Lindsay (1979) to be controlling the activity of the metals in soil solutions are uncharacterized and subject to question, hence are only used as guides. This presents the possibility that a specific solid phase is not controlling the activity of a metal and that other mechanisms may be involved.

Some of the mechanisms involving the solid phases in soils that could be controlling the activity of metals are exchange, sorption, specific adsorption, precipitation, coprecipitation, and complexation. The specific adsorption of heavy metal cations from solution by hydrous oxide gels is very effective (Kinniburgh et al., 1976). With Fe and Al gels, Kinniburgh et al. (1976) were able to remove 100% of the metals Cd, Cu, Ni, and Zn at a concentration of $10^{-4}M$ from a $1M$ $NaNO_3$ solution at pH 7.2. Oxide surfaces are ubiquitous in soils, hence, specific adsorption should be playing a role in controlling the activity of metals in soil solutions. In studies of adsorption of metals in soils, McBride and Blasiak (1979) and Cavallaro and McBride (1978) found that Cd, Cu, and Zn were undersaturated with respect to the least soluble investigated mineral phases (i.e., $CdCO_3$, CuO , and $Zn(OH)_2$) of these metals. Cavallaro and McBride also observed a shift in the adsorption equilibria for Cd with competing ions, such as Ca, suggesting that ion exchange is responsible for Cd adsorption. For Cu the shift was less, indicating that it may be bonded more specifically.

This serves to point out that metals in soil solutions are generally undersaturated with respect to the least soluble mineral phases evaluated, and that the solid phase that is controlling the activity of a metal is unknown. The identification of the solid phases in soils that are controlling the activity of heavy metals in soil solutions is an area where research is needed.

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