

The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution

Abdul Kadir Salam ^{a,*}, Philip A. Helmke ^b

^a *Department of Soil Science, Faculty of Agriculture, University of Lampung, Bandarlampung 35145, Indonesia*

^b *Department of Soil Science, University of Wisconsin-Madison, Madison, WI 53705, USA*

Received 21 May 1996; revised 4 December 1997; accepted 4 December 1997

Abstract

Concentrations of total dissolved Cu and Cd and activities of their free ions in soil solution are suggested to be influenced by soil pH. The objective of this research was to study the relationships between free ionic activities and total dissolved concentrations of Cu and Cd and soil pH. Soil samples from Elkhorn, WI, USA (Typic Argiudoll), were used as a model. Free ions Cu^{2+} and Cd^{2+} were determined in the soil saturation extracts by using Donnan analysis with graphite furnace AAS. The values of soil pH beyond their indigenous values were obtained by additions of dilute nitric acid to the soil–water mixtures. The results showed that logarithmic concentrations of total dissolved Cu and Cd showed curve–linear relationships with soil pH. Free ionic Cu^{2+} and Cd^{2+} activities were negatively correlated with soil pH. The slopes of $\log(\text{Cu}^{2+})$ vs. pH plots were -0.10 and -0.30 and those of $\log(\text{Cd}^{2+})$ vs. pH plots were -0.60 and -0.70 for the control soil and the sewage-sludge-treated soil, respectively. © 1998 Elsevier Science B.V.

Keywords: cadmium; copper; free ions; metal solubility

1. Introduction

The concentrations of soluble Cu and Cd and their free ionic activities in soil solution have been repeatedly reported to be affected by soil pH (Ma and Lindsay, 1995; El-Falaky et al., 1991; Workman and Lindsay, 1990; Brummer et al., 1988; Harsh and Doner, 1984; Elliott, 1983; Kuo and Baker, 1980).

* Corresponding author.

Generally soil researchers agree that concentrations of dissolved Cu and Cd and their free ionic activities in soil solution decrease with the increase in soil pH. For example, El-Falaky et al. (1991) found that logarithmic activities of free Cd^{2+} decreased by two units with a unit increase in soil pH. The reason for decrease with increase in soil pH is that the adsorption capacity of soils, particularly of those with colloids dominated by pH-dependent charges, increases with the increase in soil pH, theoretically due to the deprotonation of the surface-bound H on the soil-exchange sites (Kabata-Pendias and Pendias, 1992; Kishk and Hassan, 1973). Helling et al. (1964) reported that the cation-exchange capacity (CEC) of both clay and organic matter increased linearly with soil pH. This process decreases the soluble Cu and Cd concentrations and their free ionic activities in soil solution. Some authors even propose that this process may change the predominantly exchangeable metal cations to the predominantly nonexchangeable (Stahl and James, 1991).

The free ionic forms of dissolved metals in soil solution (Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , etc.) are of interest because they are important in determining metal bioavailability and toxicity to plants (Chekai et al., 1987a,b; Allen et al., 1980). These species are also important in chemical reactions that occur in the soil–water system, such as adsorption/desorption, precipitation/dissolution, and complexation (Alloway, 1990; Bowman and O'Connor, 1982; Sanders, 1982). However, data on the relationships between free ionic Cu^{2+} and Cd^{2+} activities and soil pH are scarce, probably due to the difficulties in measuring the activities of the free metal ions in soil solutions, which are generally very low. The activities of free Cu^{2+} and Cd^{2+} in natural soil solution are in the order of nanomolar (El-Falaky et al., 1991; Workman and Lindsay, 1990). These values are below the detection limits of ion-selective electrodes and most other easily available devices. Most data on the activities of free metal cations are estimated values, usually calculated with computer-implemented speciation programs such as the program GEOCHEM-PC and MINTEQA2 from concentrations which are generally much higher than their natural activities in soil–water systems.

The only available data on the ion activity vs. soil pH relationships for Cu and Cd and for other heavy metals are those reported by Lindsay and his coworkers (Kalbasi et al., 1995; Ma and Lindsay, 1995; Ma and Lindsay, 1993; El-Falaky et al., 1991; Workman and Lindsay, 1990; Lindsay, 1979; Norvell and Lindsay, 1972, 1969). The activities of free Cu^{2+} and Cd^{2+} were measured indirectly by competitive chelation method (Ma and Lindsay, 1995; Workman and Lindsay, 1990). To measure Cd^{2+} ion activity, they reacted a series of 10 μM DTPA (diethylenetriaminepentaacetic acid) solutions containing varying initial fractions of Cd and Pb with soil for 140 h. The free Pb^{2+} was used as a competing cation, with an activity assumed to be controlled by PbCO_3 , which was added to the system. During the reaction period in which DTPA equilibrated with soil minerals and PbCO_3 , some solutions gained Cd and lost Pb

while others gained Pb and lost Cd. The activities of Cd^{2+} in soil solution were calculated based on the mole fraction at which the composition of the solution did not change during the equilibration. The assumption that Pb^{2+} was controlled by PbCO_3 , however, could not be verified since the Pb^{2+} ion activities could not also be measured directly. The activity of Pb^{2+} in soil solution was in the order of 10^{-7} M, calculated by the solubility of PbCO_3 , while the detection limit of ion-selective electrode was in the order of 10^{-6} M.

The explanations above suggest that a direct measurement of free ionic Cd^{2+} and other free ions is necessary. The objective of this research was to study: (1) the activity–pH relationships of free ionic Cu^{2+} and Cd^{2+} measured experimentally by Donnan analysis and (2) the concentration–pH relationships of total dissolved Cu and Cd in soil–water systems.

2. Materials and methods

Soil samples (Typic Argiudoll) collected from field plots in Elkhorn, WI, USA, were used in this study. Selected element contents in the soils and in their solution phases are listed in Table 1. Soil 1 was from a control plot and Soil 2 was from a plot treated with 6.7 t ha^{-1} of Milwaukee sewage sludge annually since 1979. The plots have been in continuous culture with various crops since the sludge was first incorporated. All soil samples were collected in July 1991. The samples were air dried, sieved to 2 mm, and stored in plastic bags for analysis.

A batch equilibration method was used to obtain the soil saturation extracts. A series of 500 g soil samples were weighed into centrifuge bottles. Deionized-distilled water and dilute nitric acid were added to the soil samples to reach a 1-to-1 soil-to-water ratio. The amounts of dilute nitric acid added were determined previously by trial-and-error experiments with small samples to set up soil mixtures with pH ranging approximately from 4 to 7. This pH range was chosen because it represented the natural pH values of most soils. All treatments were done in duplicate.

The soil mixtures were shaken in an over-end shaker for 24 h. After equilibration, the mixtures were centrifuged at $4200 \times g$ for 1 h. The liquid fractions were separated and re-centrifuged at $4200 \times g$ for another hour. The clear supernatant was then filtered through Millipore* FH 047 $0.50 \mu\text{m}$ filter. This solution was used as donor solution in the Donnan analysis.

Donnan analysis specifically measures Cd^{2+} , Cu^{2+} , and other cationic forms of these elements by exchanging the cations from the donor solution (the soil saturation extract) with Sr^{2+} in the acceptor solutions during the Donnan equilibration. To do this analysis, about 100 ml of donor solution was placed in contact with 400 μl (200 μl in each of two cells) of an acceptor solution separated by a sheet of cation-exchange membrane (Nafion*-117). The donor

Table 1
Elemental contents of soils and soil solutions^a

Property	Soil 1 ^b	Soil 2
<i>Soil (mg kg⁻¹)^c</i>		
Total Cu	60.0	82.1
Total Cd	0.53	1.23
Total Zn	110	180
<i>Soil solution</i>		
pH	6.97	6.14
Total DOC ^d (mg l ⁻¹)	102	183
Water soluble and free metal ions		
Total Cu (nM)	419	902
Cu ²⁺ (nM)	7.12	7.41
Total Cd (nM)	1.70	9.84
Cd ²⁺ (nM)	0.49	1.91
Total Zn (μM)	9.52	12.4
Zn ²⁺ (μM)	6.89	7.18
Water soluble and free metal ions (acidic values)		
Total Cu (nM)	326	663
Cu ²⁺ (nM)	14.3	29.2
Total Cd (nM)	197	367
Cd ²⁺ (nM)	17.1	36.9
Total Zn (μM)	7.37	32.0
Zn ²⁺ (μM)	1.89	12.3
Major ions (mM)		
Ca ²⁺	1.32	2.40
Mg ²⁺	1.10	1.55
K ⁺	0.16	0.25
Na ⁺	0.16	0.29
NH ₄ ⁺	0.10	0.10
SO ₄ ²⁻	0.58	0.97
NO ₃ ⁻	0.37	1.36

^aAverage of two replicates. All ions are in activity term. Cu²⁺, Cd²⁺, and Zn²⁺ were determined with Donnan analysis technique and all other ions were estimated by MINTEQA2.

^bSoil 1 is the control and Soil 2 is the sewage-sludge-treated soil.

^cTotal contents of elements in soils were obtained by soil digestion with concentrated nitric acid in an oven (130°C) and were measured with ICP-AES for Cu and Zn and with graphite furnace AAS for Cd.

^dDOC is dissolved organic carbon, determined with Shimadzu 5000 TOC Analyzer.

solution was circulated constantly past the surface of the membrane opposite the acceptor solution until Donnan equilibrium was reached. A Teflon bellows pump was used to pump the solution. The Donnan equilibrium instrument design was reported previously (Kadir, 1993; Fitch and Helmke, 1989). An equilibration time of 2 h was used.

Nafion*-117, a strong-acid, cation-exchange membrane, is a copolymer of

tetrafluoroethylene and sulfonyl fluoride vinyl ethers produced by E.I. Dupont de Nemours. It has a thickness of 0.18 mm and an exchange capacity of 0.83 mmole_c dry g⁻¹ in H-form. For the purpose of these experiments, sheets of membrane with diameters of 1.98 cm were soaked in elixir to replace adsorbed cations with H⁺ (Elixir is a high purity cleaning solution that our laboratory makes and uses to clean plastic wares in preparation for trace metal analysis. Elixir contains 10% methyl alcohol, 10% concentrated HCl, and 80% deionized water). After 24 h, the membrane sheets were rinsed several times with deionized water and soaked in water for 5 h. The membranes were then soaked in fresh acceptor solutions. The solution was replaced three times within 24 h prior to the membranes being used. The ionic strength of the solution used to prepare the membrane was identical to that of the related donor solution as estimated from its composition by the program GEOCHEM PC.

The attainment of equilibrium between the donor and acceptor solutions is dependent on the ionic strengths of both solutions and the volume of the acceptor solution. The ionic strengths of the acceptor solutions were made identical to those of the donor solutions to minimize the transfer of water across the membrane. The donor solutions for each treatment unit obtained from a small scale extraction before the experiment were analyzed for pH with a pH meter, total dissolved Ca, Mg, K, Na, and S with ICP-AES; and total dissolved Cu, Cd, and Zn with graphite furnace AAS. The results were used to estimate the ionic strengths of the donor solutions by the program GEOCHEM-PC. The concentration of SO₄²⁻ was calculated based on the measurement of total dissolved S and assuming that the organic S was small. This anion is important because it affects the speciation of metal cations significantly. The acceptor solutions were then prepared from an analyte-free Sr(NO₃)₂ with ionic strengths identical to their respected donor solutions.

To monitor and correct potential errors in matching the ionic strengths, carrier-free ²²Na radiotracer was added to the donor solutions before the Donnan analysis. Sodium is relatively free from complexation reactions. At equilibrium, the concentrations of Na⁺ in the donor and acceptor solutions must be identical if the ionic strengths are identical. A 4-ml aliquot of the donor and a 50-μl aliquot of the acceptor solution were radioassayed to determine the ²²Na ratio using high resolution gamma-ray spectroscopy.

Differences in radioactivity of donor and acceptor solutions indicate that their ionic strengths differ and corrections in the measured activities in the acceptor solutions are needed. The effects of small differences in the relative ionic strengths of the acceptor and donor solutions on the ratio of the activities of analyte divalent cations in the acceptor and donor solutions were corrected by the following equation:

$$\left(\frac{A}{D}\right)_{\text{corrected}} = \left(\frac{A}{D}\right)_{\text{measured}} \left(\frac{D}{A}\right)_{\text{Na-22}}^2$$

where A and D are the activities of the analyte cation or the radioactivity of ^{22}Na in the acceptor and donor solutions.

The concentrations of Cd and Cu in the acceptor and donor solutions were determined with graphite furnace AAS (detection limits for Cu 1 ppb and Cd 0.025 ppb). The concentrations of other elements in the donor solution were measured with ICP-AES and the pH of the donor solutions were measured with a pH meter. Activity coefficients were calculated from the extended Debye–Huckel theory to convert concentrations to activities (Lindsay, 1979).

The Donnan analysis has been used to measure very low activities of Cu^{2+} , Cd^{2+} , and Zn^{2+} in pure laboratory solutions, and its use with natural solutions is shown in the subsequent data and discussion. The technique has several advantages: (1) it is free from interference from neutral and anionic species; (2) it does not alter the equilibrium composition of the sample solution, and (3) it is relatively sensitive.

3. Results and discussion

3.1. Free ionic activities of Cu and Cd

Free Cu^{2+} comprised a very small part of the total dissolved Cu. On average, free Cu^{2+} comprised 1–20% of the total dissolved Cu in soil solution. In contrast, free Cd^{2+} comprised 20–40% of the total dissolved Cd. This observation is in agreement with previous reports (Kabata-Pendias and Pendias, 1992; Ellis and Knezek, 1982). The relatively low activities of free Cu^{2+} and Cd^{2+} compared to their total dissolved concentrations are related to the relatively high formation constants of Cu- or Cd-complexes. The activities of free Cu^{2+} and free Cd^{2+} are presented as a function of soil pH in Fig. 1. Logarithms of both free Cu^{2+} and Cd^{2+} activities showed strong, linear relations with soil pH.

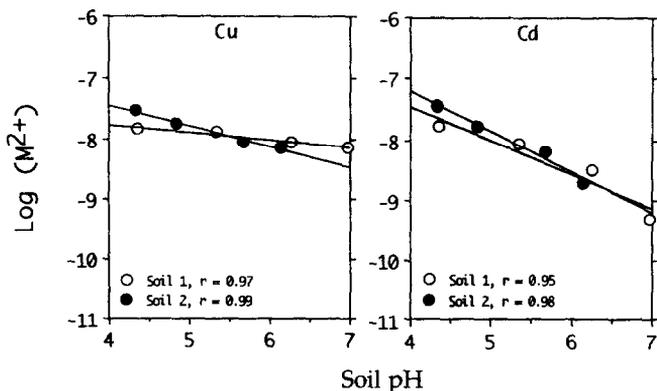


Fig. 1. Relationships between free ionic Cu^{2+} and Cd^{2+} activities and soil pH.

The logarithmic activities of Cu^{2+} decreased with the increase in soil pH with slopes of -0.10 in Soil 1 (control soil) and -0.30 in Soil 2 (sewage-sludge-treated soil). These values were much less negative than -2 reported for calcareous soils (Lindsay, 1979), indicating that the activities of Cu^{2+} in these soils were less dependent on soil pH. The logarithmic activities of Cd^{2+} also decreased with the increase in soil pH, with slopes of -0.60 and -0.70 for Soil 1 and Soil 2, respectively. These values were also much less negative than -2 reported for calcareous soils (Ma and Lindsay, 1995; El-Falaky et al., 1991; Workman and Lindsay, 1990). In addition, the values of the slopes (Fig. 1) suggest that in Soil 2, Cd^{2+} activities were twice more dependent on soil pH than were the Cu^{2+} activities, and in Soil 1 Cd^{2+} activities were 6 times more dependent.

The decreasing trends in free Cu^{2+} and Cd^{2+} activities with soil pH were due to the increase in the adsorptive capacity of the soils as pH increased. This reasoning is in agreement with previous reports that proposed as soil pH increases the adsorptive capacity of soil solids increases due to the deprotonation of surface-bound H (Kabata-Pendias and Pendias, 1992; Alloway, 1990; Kishk and Hassan, 1973). The soil solid surfaces may include clays with variable charges and organics possessing carboxylic and phenolic functional groups. The increase in soil pH also influences the dissociation of H^+ ions bound on functional groups of dissolved organic chelating agents in soil solution (Alloway, 1990). Because the resulting negative charges may adsorb or complex metal cations, all of these phenomena result in a decreasing trend in free ionic Cu^{2+} and Cd^{2+} activities in soil solution when soil pH increases.

The slope values in Fig. 1 show that addition of the sewage sludge increased the dependence of free ionic Cu^{2+} and Cd^{2+} on soil pH. For example, at pH below 5.5, the activities of free Cu^{2+} in Soil 2 were higher than that in Soil 1. The higher free Cu^{2+} in Soil 2 originated from the sewage sludge addition. Because more functional groups in the chelating agents were protonated in pH range below 5.5, parts of the added Cu^{2+} from the sewage sludge (sewage sludge was a source of Cu and Cd) remained as free cations. As the soil pH increased, the concentrations of the active chelating agents in Soil 2 increased as a result of deprotonation of chelating agents of the sewage sludge origin and their concentrations were higher than those in Soil 1. Active chelating agents were dissolved and surface ligands with deprotonated functional groups. These chelating agents complexed with more Cu^{2+} so that decreased the activities of Cu^{2+} more significantly as soil pH increased. As a result, the soil pH increased beyond pH 5.5, the activities of Cu^{2+} in Soil 2 became lower than those in Soil 1. This shows that a more negative slope value in Soil 2 than in Soil 1 was due to the difference in concentrations of complexing agents in the two soils and their deprotonation characteristics with respect to pH changes.

The difference in concentrations of organic chelating agents in Soil 1 and Soil 2 did not affect the $\log(\text{Cd}^{2+})$ vs. soil pH plots as much as the $\log(\text{Cu}^{2+})$ vs.

pH plots (Fig. 1). However, careful observation of the curves in Fig. 1 revealed a similarity between the $\log(\text{Cu}^{2+})$ and the $\log(\text{Cd}^{2+})$ vs. pH plots. At pH below 6.25, the activities of Cu^{2+} in Soil 2 were slightly higher than that in Soil 1. The value of the crossover point for the $\log(\text{Cu}^{2+})$ vs. soil pH plot (5.5) was lower than that for the $\log(\text{Cd}^{2+})$ vs. pH plot (6.25), suggesting that the active chelating agents preferentially complexed with Cu^{2+} ions. Free Cu^{2+} was complexed stronger than was Cd^{2+} ion, and the complexation reaction was more important for predicting the free Cu^{2+} behavior in soil solution. It was also reported previously that the formation constants for Cu-complexes were higher than for Cd-complexes (Kerndorff and Schnitzer, 1980). This theory may to some extent explain the fact that Cd^{2+} activities are more dependent on soil pH than Cu^{2+} activities are (Fig. 1).

3.2. Total dissolved concentrations of Cu and Cd

Copper and Cd in soil solution exist as free ions (Cu^{2+} and Cd^{2+}) and complex species such as $\text{Cu}(\text{OH})^+$, CuSO_4^0 , $\text{Cd}(\text{OH})_2^0$, CdCl^+ , CdCO_3^0 , Cu-fulvate, Cd-fulvate, etc. The total dissolved concentration of Cu or Cd is the sum of its free ions and complex species. Cadmium is a weaker acid than Cu (Kerndorff and Schnitzer, 1980) and, hence, the relative concentration of total Cd complexes was less than that of Cu. For example, in Soil 2 (pH 6.14), the total Cd complexes comprised 68% of the total dissolved Cd, while at the same pH the total Cu complexes comprised almost all of the total dissolved Cu. The concentrations of total dissolved Cu and Cd in soil solution are presented as a function of soil pH in Fig. 2.

The total dissolved Cu decreased with the increase in soil pH below pH 5.5 and increased above pH 5.5. The relationships between logarithms of total dissolved Cu concentrations and soil pH were best fitted with quadratic equa-

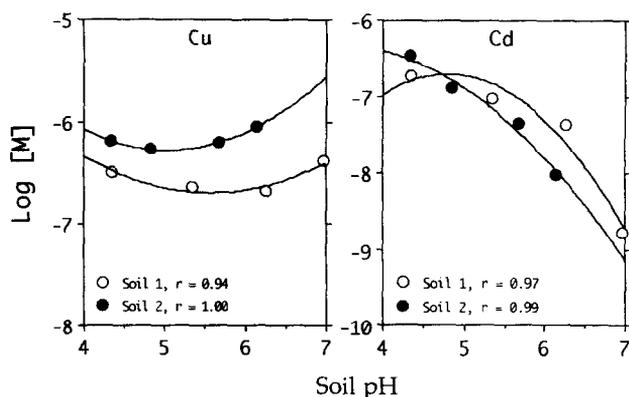


Fig. 2. Relationships between concentrations of total dissolved Cu and Cd and soil pH.

tions, different from those for the logarithmic free Cu^{2+} that showed a linear relationship with soil pH. In relation to this pattern, complexation reaction is believed to be the most important governing process for Cu concentrations in soil solution. Hence, it can be understood that the sewage sludge addition, that introduced organics into the soil system (shown by higher DOC in Table 1), increased the concentrations of total dissolved Cu in soil solution and that the total dissolved Cu increased at pH above pH 5.5 (Fig. 2). It occurred because the concentrations of active chelating agents in soil solution were, as discussed previously, higher at higher pH so that they complexed with more Cu^{2+} as soil pH increased. Because the total concentrations of chelating agents were higher in sewage-treated soil (Soil 2), the total dissolved Cu in Soil 2 was also higher than that in Soil 1.

Sewage-sludge addition, however, affected total dissolved Cd behavior differently. The logarithms of total dissolved Cd and soil pH was also best fitted with quadratic equations but, unlike Cu that shows a U-shape relation with soil pH, the total dissolved Cd concentrations decreased with the increase in soil pH between pH 4 and 7. At pH below 4.75, the total dissolved Cd concentrations in Soil 2 were higher than those in Soil 1. At pH above 4.75 the total dissolved Cd concentrations in Soil 2 were lower than in Soil 1. This relation is also different from that for free ionic Cd^{2+} activities (Fig. 1).

The higher concentrations of total dissolved Cd in Soil 2 below pH 4.75 were a result of the Cd added through the sewage-sludge treatment. In this pH range, the concentrations of active chelating agents were lower than that at higher pH due to the protonation of their functional groups and, therefore, a part of Cd introduced by sewage-sludge treatment remained as free ions. As the soil pH increased, the concentrations of active chelating agents increased, but most of these chelating agents complexed with Cu^{2+} and other free cations that had higher complex formation constants than did Cd^{2+} . Some soil researchers have reported previously that Cu^{2+} had a higher complex formation constant than did Cd^{2+} (Kerndorff and Schnitzer, 1980). For example, the complex formation constant for Cu-fulvate is even higher than those for Ca-, Mg-, and Zn-fulvate (Schnitzer and Khan, 1972). Some Cd^{2+} previously complexed with chelating agents may have been displaced by these free ions.

Most of the free Cd^{2+} is believed to have been adsorbed by the soil adsorptive surfaces that become more important with the increase in soil pH. It has been shown previously by Kadir (1993) that logarithmic activities of Cu^{2+} is linearly correlated with that of $(\text{Ca}^{2+} + \text{Mg}^{2+})$, suggesting a cation-exchange mechanism. As a result, at pH above 4.75 the total dissolved Cd concentrations in Soil 2 were lower than those in Soil 1. The total contents of Cd in soil increased by the sewage-sludge addition (Table 1) but most of the added Cd was likely adsorbed by the soil adsorptive surfaces. The importance of soil adsorptive capacity in affecting the activity of Cd^{2+} in soil solution cannot be explained by the current data.

4. Summary and conclusions

Activities of free ionic Cu^{2+} and Cd^{2+} as well as total dissolved concentrations of Cu and Cd showed a strong dependence on soil pH. The relationships between logarithms of total dissolved concentrations of Cu and Cd with soil pH were best fitted with quadratic equations while those of the logarithmic activities of Cu^{2+} and Cd^{2+} with soil pH were linear. The slopes of $\log(\text{Cu}^{2+})$ vs. soil pH were -0.10 and -0.30 and those of $\log(\text{Cd}^{2+})$ vs. soil pH were -0.60 and -0.70 for Soil 1 and Soil 2, respectively. These values are less negative than those determined in calcareous soils by the competitive chelation method.

References

- Allen, H.E., Hall, R.H., Brisbin, T.D., 1980. Metal speciation, effects on aquatic toxicity. *Environ. Sci. Technol.* 14, 441–443.
- Alloway, B.J., 1990. Soil processes and the behavior of metals. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*. Blackie, pp. 7–28.
- Bowman, R.S., O'Connor, G.A., 1982. Control of nickel and strontium sorption by free metal ion activity. *Soil Sci. Soc. Am. J.* 46, 933–936.
- Brummer, G.W., Gerth, J., Tiller, G., 1988. Reaction kinetics of the adsorption of nickel, zinc, and cadmium by goethite: I. Adsorption and diffusion of metals. *J. Soil Sci.* 39, 37–52.
- Chekai, R.T., Hendrickson, L.L., Corey, R.B., Helmke, P.A., 1987a. A method for controlling the activities of free metal, hydrogen, and phosphate ions in hydroponic solutions using ion exchange and chelating resins. *Plant Soil* 99, 321–334.
- Chekai, R.T., Corey, R.B., Helmke, P.A., 1987b. Effect of ionic and complexed metal concentrations on plant uptake of cadmium and micronutrient metals from solution. *Plant Soil* 99, 335–345.
- El-Falaky, A.A., Abouloos, S.A., Lindsay, W.L., 1991. Measurement of cadmium activities in slightly acidic to alkaline soils. *Soil Sci. Soc. Am. J.* 55, 974–979.
- Elliott, H.A., 1983. Adsorption behavior of cadmium in response to surface charge. *Soil Sci.* 136, 317–321.
- Ellis, B.G., Knezek, B.D., 1982. Adsorption reactions of micronutrients in soils. In: Mortvedt, J.J., Giordano, P.M., Lindsay, W.L. (Eds.), *Micronutrients in Agriculture*. SSSA, pp. 57–78.
- Fitch, A., Helmke, P.A., 1989. Donnan equilibrium/graphite furnace atomic absorption estimates of soil extract complexation capacities. *Anal. Chem.* 61, 1295–1298.
- Harsh, J.B., Doner, H.E., 1984. Specific adsorption of copper on an hydroxy–aluminum montmorillonite complex. *Soil Sci. Soc. Am. J.* 48, 1034–1039.
- Helling, C.S., Chesters, C., Corey, R.B., 1964. Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. *Soil Sci. Soc. Am. Proc.* 28, 517–520.
- Kabata-Pendias, A., Pendias, H., 1992. *Trace Elements in Soils and Plants*, 2nd ed. CRC Press, London.
- Kadir, A., 1993. Control of indigenous levels of cadmium, copper, and zinc ion activities in soil solution. PhD Diss. University of Wisconsin-Madison, Madison, USA.
- Kalbasi, M., Peryea, E.J., Lindsay, W.L., Drake, S.R., 1995. Measurement of divalent lead activity in lead arsenate contaminated soils. *Soil Sci. Soc. Am. J.* 59, 1274–1280.

- Kerndorff, H., Schnitzer, M., 1980. Sorption of metals on humic acid. *Geochim. Cosmochim. Acta* 44, 1701–1708.
- Kishk, F.M., Hassan, M.N., 1973. Sorption and desorption of copper by and from clay minerals. *Plant Soil* 39, 497–505.
- Kuo, S., Baker, A.S., 1980. Sorption of copper, zinc, and cadmium by some acid soils. *Soil Sci. Soc. Am. J.* 44, 969–974.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley, New York.
- Ma, Q.Y., Lindsay, W.L., 1993. Measurement of free zinc²⁺ activity in uncontaminated and contaminated soils using chelation. *Soil Sci. Soc. Am. J.* 57, 963–967.
- Ma, Q.Y., Lindsay, W.L., 1995. Estimation of Cd²⁺ and Ni²⁺ activities in soils by chelation. *Geoderma* 68, 123–133.
- Norvell, W.A., Lindsay, W.L., 1969. Reactions of EDTA complexes of Fe, Zn, Mn, and Cu with soils. *Soil Sci. Soc. Am. Proc.* 33, 86–91.
- Norvell, W.A., Lindsay, W.L., 1972. Reactions of DTPA chelates of iron, zinc, copper, and manganese with soils. *Soil Sci. Soc. Am. Proc.* 36, 778–783.
- Sanders, J.R., 1982. The effect of pH upon the copper and cupric ion concentrations in soil solution. *J. Soil Sci.* 33, 679–689.
- Schnitzer, M., Khan, S.U., 1972. *Humic Substances in the Environment*. Marcel Dekker, New York.
- Stahl, R.S., James, B.R., 1991. Zinc sorption by iron oxide-coated sand as a function of pH. *Soil Sci. Soc. Am. J.* 55, 1287–1290.
- Workman, S.M., Lindsay, W.L., 1990. Estimating divalent cadmium activities measured in arid-zone soils using competitive chelation. *Soil Sci. Soc. Am. J.* 54, 987–993.