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# Sludge-Derived Cu and Zn in a Humic-Gley Soil: Effect of Dissolved Metal-Organic Matter Complexes on Sorption and Partitioning

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*A sequential extraction scheme was combined with sorption isotherm analysis in order to investigate sorption of sewage sludge-derived Cu and Zn to the A-horizon of a humic-gley soil as a whole, and to the operationally defined exchangeable (1 M $MgCl_2$), carbonate (1 M NaOAc), Fe/Mn oxide (0.04 M $NH_2OH.HCl$), and organic (0.02 M $HNO_3$ + 30% $H_2O_2$) soil fractions. Sorption parameters were compared for a sample of sludge leachate (with 97.4% of Cu and 63.2% of Zn present as dissolved metal-organic matter complexes, as calculated by geochemical modeling involving MINTEQA2 and verified using an ion exchange resin method) with that of a reference solution exhibiting the same chemical characteristics as the leachate, except for the presence of dissolved organic material. Dissolved metal-organic matter complexes were found to significantly ($P < 0.05$) depress sorption to the bulk soil and each fraction. The greatest depression of Cu and Zn sorption was observed for the exchangeable, carbonate, and Fe/Mn oxide fractions, while the organic fraction of the soil was the least affected. This reflects a greater affinity for the exchangeable, carbonate, and Fe/Mn oxide fractions by the free divalent metal ($Cu^{2+}$, $Zn^{2+}$), with sorption by these fractions attributed to cation exchange, chemisorption, and co-precipitation processes. The sorption characteristics of the organic fraction indicated that Cu and Zn sorption by soil organic matter mostly involved dissolved metal-organic matter complexes. This may be attributed to hydrophobic interactions between non-polar regions of the dissolved metal-organic matter complexes and solid-phase soil organic matter.*

**Key Words:** *heavy metals, speciation, sequential extraction.*

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## INTRODUCTION

The disposal of municipal sewage sludge in an environmentally sound manner presents a challenge to environmental scientists and policymakers worldwide. Application to agricultural soil is a method of disposing of this waste, which may have beneficial rather than adverse environmental consequences if well regulated. Agricultural reuse is limited, however, by relatively high concentrations of potentially toxic metals typically present in sewage sludge from urban areas (Alloway, 1995; Smith, 1996). Copper (Cu) and zinc (Zn) are important heavy metals of interest in the land application of sewage sludge (Barry *et al*., 1998). In general, Cu is regarded as relatively immobile due to its high affinity for soil organic matter, and Zn is highly mobile due to its association with labile geochemical fractions (Keller and Vedy, 1994; Li and Shuman, 1996; Wasay *et al*., 1998; Basta and Sloan, 1999).

Sorption is the most important process controlling the solubility, and therefore mobility, of these heavy metals in soils (McBride, 1989; Alloway, 1995). Heavy metal sorption is frequently described in terms of the total solid phase concentration of a particular metal. That is, by partitioning the metallic species between the solution and solid phase and determining the equilibrium phase concentrations (Barry *et al*., 1995; Gao *et al*., 1997; Phillips, 1999). However, the widespread utilisation of sequential extraction techniques which partition heavy metals into operationally defined geochemical fractions, with each fraction exhibiting differing degrees of availability and mobility, is indicative of the limited value of bulk solid-phase analysis (Basta and Sloan, 1999; Almas *et al.,* 2000; Sutherland *et al*., 2000).

The examination of sorption by distinct geochemical fractions traditionally has been restricted to an examination of pure soil mineral or organic components (Forbes *et al*., 1976; Fu *et al*., 1991). However, this approach fails to consider the important interactions that occur between individual fractions in real soils. For example, Davis (1984), Anderson and Benjamin (1990), and Meng and Letterman (1993) have shown that various soil components, such as amorphous Fe oxides and humic acid, tend to interact and consequently exhibit quite different sorptive properties when aggregated together in a natural soil compared with when examined in isolation as pure sorbents.

Recently, Salim *et al*. (1996) developed an approach to sorption analysis that took account of sorption by separate environmentally relevant geochemical fractions, thereby allowing heavy metal mobility to be semiquantitatively estimated prior to the application of the heavy metal bearing waste. Salim *et al*. (1996) combined the batch approach of sorption isotherm analysis with a sequential extraction scheme and generated sorption isotherms for five individual geochemical fractions in addition to the traditional bulk solid-phase isotherm.

It is generally accepted that heavy metal speciation in the soil solution has a major influence on sorption characteristics (McBride, 1989; Alloway, 1995). In particular, recent work by Romkens and Salomon (1998) and Almas *et al*. (2000) has shown that the presence of dissolved metal-organic matter complexes can substantially depress heavy metal sorption. This is especially important in relation to land disposal of sewage sludge, as work by Fotovat *et al*. (1997) suggests that large proportions of dissolved sludge-derived metals exist as organic complexes. However, studies into the sorption of sludge derived heavy metals by soils traditionally have used solutions generated from inorganic salts and have failed to consider the influence of dissolved metal-organic matter complexes (Barry *et al.,* 1995; Redding, 1997). Furthermore, the effect that these complexes have on the geochemical partitioning of sludge-derived heavy metals in soil has received little attention.

Given the need for research into the effects of dissolved metal-organic matter complexes on the sorptive and partitioning behavior of sewage sludge-derived Cu and Zn, the objectives of this study are to (1) generate Cu and Zn sorption isotherms for a humic-gley soil as a whole and for each of the individual geochemical fractions targeted by a sequential extraction scheme, and (2) investigate the influence of dissolved metal-organic matter complexes present in sewage sludge leachate on the sorption isotherms produced.

## METHODS

### Soil and Sewage Sludge Characterization

The humic-gley soil used was collected at a rural site (153°23E, 24°48S) approximately 40 km southeast of Brisbane, Queensland, Australia. Samples were obtained from the A-horizon (0 to 30 cm) of a hand-dug pit. The anaerobically digested sewage sludge sample employed was collected from a stockpile, prepared in anticipation of transport to a landfill, at a wastewater treatment facility operated by Brisbane City Council. The samples were dried (soil 40°C; sludge 50°C) and ground to obtain the <2 mm fraction by sieving. Each sample was then characterized in terms of pH and electrical conductivity (1:5 soil to water suspension), texture (pipette method; Gee and Bauder, 1986), organic carbon content (Walkley-Black method; Nelson and Sommers, 1996), carbonate content (acetic acid dissolution method; Loeppert and Suarez, 1996), cation exchange capacity (Gillman and Sumpter, 1986), exchangeable acidity (Thomas, 1982), and Fe-oxide and Mn-oxide content (determined by measuring Fe and Mn in step 4 below; Tessier *et al*., 1979).

The partitioning of Cu and Zn found in the soil and sewage sludge samples into different geochemical fractions was achieved by using a modification of the sequential extraction procedure developed by Tessier *et al*. (1979). This particular technique was employed because it is the most thoroughly validated and widely utilized sequential extraction scheme available (Almas *et al*., 2000; Basta and Sloan, 1999; Sutherland *et al*., 2000).

It should be noted that sequential extraction procedures have been criticized due to the "operationally defined" nature of the extracted fractions, and the potential redistribution of metals between individual fractions during the extraction process (Nirel and Morel, 1990; Kim and Fergusson, 1991; Bermond, 2001). Nevertheless, such procedures have been shown to provide useful information relating to the geochemical behavior of heavy metals in soil (Howard and Sledzinski, 1996; Salim *et* al., 1996)

The sequential extraction procedure, with each operationally defined geochemical fraction involved and each extraction step, is described below:

- ***Soluble*** — 10 mL deionized water with 2 g of sample at room temperature for 1 h.
- ***Exchangeable*** — 20 mL of pH 7, unbuffered 1 *M* $MgCl_2$ for 1 h at room temperature.
- ***Carbonate*** — 20 mL of 1 *M* NaOAc, adjusted to pH 5 with HOAc, for 6 h.
- ***Fe/Mn oxides*** — 40 mL of 0.04 *M* $NH_2OH.HCl$ in 25% HOAc (v/v) for 6 h at 96°C with 10 min shaking every hour.
- ***Organic*** — 6 mL of 0.02 *M* $HNO_3$ + 10 mL of pH 2 (adjusted with $HNO_3$), 30% $H_2O_2$ (v/v) for 2 h at 85°C with occasional shaking. An additional 6 mL of pH 2 (adjusted with $HNO_3$), 30% $H_2O_2$ (v/v) for 3 h at 85°C with occasional shaking. A further addition of 10 mL of 3.2 *M* $NH_4OAc$ in 20% $HNO_3$ (v/v) is made with continuous shaking for 30 min at room temperature.
- ***Residual*** — boiled, with continuous reflux, in 30 mL of concentrated $HNO_3$ for 5 h. The suspension was then allowed to cool for 1 h.

All extractions, except the final digestion, were conducted in 50-mL polypropylene centrifuge vials in order to minimize losses of solid material. Between each successive extraction, separation was achieved by centrifuging at 3500 rpm for 15 min. The supernatant was then removed with a pipette and analyzed, while the residue was washed with 10 mL deionized water, centrifuged, and the supernatant discarded.

## Production and Characterization of Sewage Sludge Leachate

A sample of sewage sludge leachate was obtained by passing deionized water through a column (rate = 100 mL/h) containing the sludge sample and acid washed (0.1 *M* HCl) quartz sand (1:3 sludge to sand). The resultant effluent (termed "leachate") was filtered (0.45 µm) and characterized in terms of the concentrations of Cu, Zn, Ca, Mg, Mn, Na, Fe, S, Al, Ni, Sr, and Ba (ICP-AES analysis), organic and inorganic carbon (Dohrman-100 total organic carbon analyzer), chloride (Activon $Cl^-$ Ion Selective Electrode), and nitrate (Orion $NO_3^-$ Ion Selective Electrode). These leachate characteristics were used as input into the geochemical speciation model MINTEQA2 (Allison *et al*., 1991) and used to create a reference solution (which mimicked the leachate, except for dissolved organic matter). The concentration of metal and ligand species in the leachate were calculated with the MINTEQA2 model and also determined with the cation exchange resin method developed by Sanders (1983) and Holm *et al*. (1995). Chelex-100, a chelating resin based on polystyrene with iminodiacetic acid as the functional group that retains free hydrated metals, was used in accordance with the procedures of Dang *et al*. (1996).

### Combined Sequential Extraction – Sorption Isotherm Analysis

A range of five total Cu and Zn concentrations (0 to 3 mg/L) were prepared from the leachate and reference solution. Sorption isotherms were created with the batch approach as explained by Salim *et al*. (1996) and involved shaking each of the Cu and Zn concentrations separately with 2 g of soil for 100 h (previous kinetic studies on a soil similar to that used in this work suggest that Cu and Zn approach equilibrium within this time; Redding, 1997). The equilibrium supernatant solutions were obtained by centrifugation at 3500 rpm for 15 min. The residual soil was then subjected to the sequential extraction scheme described above. This allowed sorption isotherms to be generated for the bulk soil, and also for the exchangeable, carbonate, Fe/Mn oxide, and organic fractions. Isotherm parameters were obtained for the bulk soil and the individual fractions by least squares analysis according to Linear, Freundlich, and Langmuir isotherms described in Eqs. 1, 2, and 3, respectively:

$$C_s = K_d C_a \tag{1}$$

$$\log C_s = \log K_f + n \log C_a \tag{2}$$

$$1/C_s = 1/m + 1/K_l m C_a \tag{3}$$

where $C_a$ = equilibrium solution phase concentration (mg/L), $C_s$ = equilibrium sorbed concentration (mg/kg), $m$ = Langmuir isotherm sorption capacity (mg/kg), $n$ = Freundlich isotherm constant, and $K_d$, $K_f$, and $K_l$ are constants for the Linear, Freundlich, and Langmuir equations, respectively, indicating relative affinity for sorption. For the bulk soil and each fraction, the $K_d$, $K_f$, and $K_l$ values describing Cu and Zn sorption were compared between the leachate and reference solution using techniques for comparing simple linear regression equations as discussed by Zar (1999).

### General Analytical Techniques and Quality Control

All analyses involved three separate replicates, with relative standard deviations generally less than 15%. Except where otherwise stated, all Cu and Zn concentrations were analyzed with a Varian SpectrAA 20 Plus flame atomic absorption spectrophotometer (AAS) with an air/acetylene flame. Calibration was done by either the standard curve or standard additions, depending on concentration and sample volume. Calcium and Mg concentrations were also measured by flame AAS, while Na and K levels were determined by atomic emission spectrometry. Working standards of the metals, created from the $NO_3^-$ salt of the cations, were freshly prepared prior to each stage of the experiment.

## RESULTS AND DISCUSSION

### Soil and Sewage Sludge Characterization

The study soil was described by Holz (1979) as a humic-gley and was selected for study based on its proximity to a large and rapidly expanding urban population and its widespread occurrence in coastal Australia. The A-horizon is acidic (pH 5.5) with a clay loam texture, abundant organic matter, and moderate levels of Fe/Mn oxides (Table 1). Despite this relatively high clay, organic matter, and Fe/Mn oxide content, the CEC value was moderately low (14.6 cmol/kg).

The sewage sludge sample had a pH of 7.4, which was reflected in the relatively high carbonate content (7.9% calcium carbonate equivalent). Total Cu (683 mg/kg) and Zn (2244 mg/kg) levels were moderate in comparison to the mean Cu (662 mg/kg) and Zn (1309 mg/kg) levels reported by Barry *et al.* (1998) for sludge from 33 treatment plants in coastal Queensland. The sludge sample contained 20.1% or-

**Table 1. Characteristics of the soil and sludge sample employed in this study.**

| Property | Soil | Sludge |
|---|---|---|
| pH | 5.5 | 7.4 |
| EC, mS/cm | 1.92 | 3.6 |
| Organic C, % | 5.7 | 20.1 |
| Texture | Clay-loam | *nd* |
| Calcium Carbonate Equivalent, % | 1.1 | 7.9 |
| Mn oxides[A], g/kg | 0.06 | 0.14 |
| Fe oxides[A], g/kg | 7.8 | 1.5 |
| CEC, cmol/kg | 14.6 | 2.7 |

[a] Fe and Mn oxides are expressed on an elemental basis as hydroxylamine hydrochloride extractable Fe and Mn.

ganic carbon, with 95.6% of Cu and 29.2% of Zn associated with this sludge organic matter (Figure 1). The Fe/Mn oxide content was moderate and was particularly important for Zn, with 55% associated with this fraction. Less than 2% of the sludge Cu and total Zn concentration was found to be water soluble.

### Leachate Characterization

The leachate Cu (0.33 mg/L) and Zn (0.69 mg/L) concentrations exceeded the relevant water quality criteria for the maintenance of aquatic ecosystems (0.005 mg-Cu/L and 0.05 mg-Zn/L; ANZECC, 1992) by a factor of 66 for Cu and 14 for Zn (Table 2). The dissolved organic carbon content of the leachate was relatively high (4890 mg/L). The release, with leaching water, of high levels of dissolved organic matter derived from sewage sludge is consistent with previous work (Christensen and Lun, 1989; Redding, 1997), and has been shown to favor the formation of dissolved metal-organic matter complexes (Elliot and Denneny, 1982).

The MINTEQA2 speciation shows that the majority (97.4%) of leachate Cu is associated with dissolved organic matter, with insubstantial proportions as free $Cu^{2+}$ and inorganic ion pairs (Table 3). The strong association of Cu with dissolved organic matter has been well documented (Christensen and Lun, 1989; Holm *et al.,* 1995) and is a consequence of the high formation constants for organo-Cu complexes (Stumm and Morgan, 1981). Similarly, Zn is also present mostly as organo-Zn complexes (63.2%). However, in contrast to Cu, a substantial proportion of leachate Zn is also present as free $Zn^{2+}$ (25.1%), which is consistent with previous

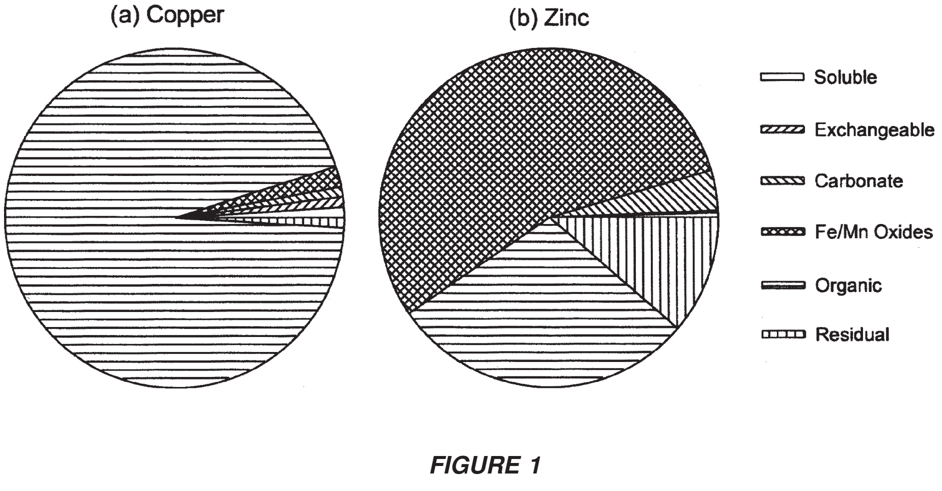

***FIGURE 1***

*Geochemical partitioning of sludge Cu and Zn.*

**Table 2. Comparison of the Reference solution with the Leachate. The pH, and concentrations of major cations and anions are equivalent for both solutions. The sodium concentration, however, is greater for the reference solution than the leachate.**

| | Leachate | Reference solution |
|---|---|---|
| Component | mg/l | |
| $Ca^{2+}$ | 185 | 185 |
| $Mg^{2+}$ | 60 | 60 |
| $K^{+}$ | 180 | 180 |
| $Na^{+}$ | 210 | 2660 |
| $Ni^{2+}$ | 10 | 10 |
| $Zn^{2+}$ | 0.69 | 0.69 |
| $Cu^{2+}$ | 0.33 | 0.33 |
| $SO_4^{2-}$ | 1200 | 1200 |
| $NO_3^{-}$ | 247 | 247 |
| $Cl^{-}$ | 2000 | 2000 |
| Inorganic C | 40 | 40 |
| pH | 6.7 | 6.7 |

**Table 3. Speciation of leachate Cu and Zn as determined by MINTEQA2.**

| Copper | | Zinc | |
|---|---|---|---|
| Species | % of total Cu | Species | % of total Zn |
| Organo-Cu | 97.4 | Organo-Zn | 63.2 |
| $Cu^{2+}$ | 1.5 | $Zn^{2+}$ | 25.1 |
| $CuSO_4^{0}$ | 0.6 | $ZnSO_4^{0}$ | 8.9 |
| $CuCO_3^{0}$ | 0.3 | $ZnCl^{+}$ | 1.4 |
| $CuOH^{+}$ | 0.1 | $Zn(SO_4)_2^{2-}$ | 0.9 |
| $CuCl^{+}$ | 0.05 | $ZnHCO_3^{+}$ | 0.15 |

research by Dang *et al*. (1996), Fotovat *et al*. (1997), and Fotovat and Naidu (1997).

The proportions of free $Cu^{2+}$ and $Zn^{2+}$ as determined by the cation exchange resin method (6% as $Cu^{2+}$; 34% as $Zn^{2+}$) and calculated from MINTEQA2 (1.6% as $Cu^{2+}$; 25.1% as $Zn^{2+}$) are in good agreement, although the exchange resin method produced slightly higher proportions. Fotovat and Naidu (1997) found a similar result for their study of Cu and Zn in soil solutions and suggested that the resin method produces results of higher proportions of free metals ($Cu^{2+}$, $Zn^{2+}$) due to the adsorption of positively charged hydroxy-complexes. A correction factor accounting for the metal-hydroxy complex effect has been proposed by Christensen and Lun (1989). However, this correction factor has not been applied here because the MINTEQA2 speciation shows that negligible proportions (< 0.1%) of Cu and Zn were present as hydroxy complexes. The adsorption of positively charged complexes, other than hydroxy complexes, may also result in the resin method, producing slightly higher free $Cu^{2+}$ and $Zn^{2+}$ proportions in comparison to MINTEQA2.

The MINTEQA2 speciation (validated by the resin method results) demonstrates that, while many researchers (Sposito, 1984; Ankomah 1992) consider the hydroxide ion as the most important solute ligand affecting metal speciation, in sewage sludge leachate, dissolved organic ligands are much more important and exert a dominating effect on metal speciation. This finding reinforces the work of Fotovat *et al*. (1997) and Lebourg *et al*. (1998), who emphasized the importance of dissolved metal-organic matter complexes in influencing the geochemical behavior of sewage sludge derived heavy metals in soil

### Geochemical Partitioning at Background Levels of Cu and Zn

Good agreement is exhibited between the Cu and Zn totals obtained by summing the individual fractions (Cu = 15.5 mg/kg, and Zn = 33.2 mg/kg) and that obtained from a total digest (Cu = 17.5 mg/kg, and Zn = 37.8 mg/kg). Small variations, such as reported here, have been reported by other authors, such as Howard and Sledzinski (1996) and Salim *et al*. (1996), and have been attributed to inevitable losses of solid material during the sequential extraction process. The fairly successful mass balance between "total digest" and "summed total" values suggests that the proportions of Cu and Zn determined for the individual fractions are reasonably accurate (Table 4).

The sequential extraction of Cu and Zn naturally present in the study soil shows both metals to be mostly associated with the residual fraction (Figure 2). The dominant importance of the residual fraction (i.e., metals bound within the crystal lattice of soil minerals) in uncontaminated soil is consistent with previous research (Iyengar, 1981; Chang *et al*., 1984; Saha *et al*., 1991). The association between heavy metals and the residual fraction of uncontaminated soil is so strong that high

**Table 4.** Geochemical fractionation and total solid-phase Cu and Zn results for the humic gley soil after equilibration with a range of soluble Cu and Zn concentrations (referred to as "spike concentration"). Results presented are the means of triplicate analyses, with standard deviations shown in parentheses.

| Spike Concentration | Targeted Geochemical Fraction | | | | | | | | | | Sum Total | Total Digest | Mass Balance (summed vs. digest total) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Exchangeable | | Carbonate | | Fe/Mn oxides | | Organic | | Residual | | | | |
| mg/l | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | mg/kg | % |
| **Copper - Reference** | | | | | | | | | | | | | |
| 0.37 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 1.4 (0.1) | 8.1 (0.6) | 6.7 (0.2) | 39 (1.2) | 8.8 (0.2) | 51.2 (1.2) | 17.2 (0.3) | 19.3 (0.1) | 10.8 |
| 0.6 | 0 (0) | 0 (0) | 1.4 (0.1) | 7.4 (0.5) | 2 (0.1) | 10.6 (0.5) | 7.4 (0.3) | 39 (1.6) | 8.5 (0.2) | 44.9 (1.1) | 18.9 (0.1) | 20.7 (0.3) | 8.7 |
| 1.03 | 0 (0) | 0 (0) | 1.4 (0.1) | 6.6 (0.5) | 2 (0.1) | 9.5 (0.5) | 8.5 (0.1) | 40.3 (0.5) | 9.1 (0.2) | 43.1 (0.9) | 21.1 (0.5) | 23.8 (0.1) | 11.3 |
| 1.36 | 0 (0) | 0 (0) | 2.4 (0.1) | 10.3 (0.4) | 2.1 (0.1) | 9.1 (0.4) | 9.6 (0.1) | 41.4 (0.4) | 8.8 (0.1) | 37.9 (0.4) | 23.2 (0.2) | 27.4 (0.4) | 15.3 |
| **Copper - Leachate** | | | | | | | | | | | | | |
| 0.3 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 7.9 (0.2) | 47 (1.2) | 8.7 (0.3) | 51.7 (1.8) | 16.8 (0.1) | 19.6 (0.5) | 14.3 |
| 0.62 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 10 (0.2) | 54.9 (1.1) | 8 (1.5) | 43.9 (8.2) | 18.2 (0.1) | 20.9 (0.4) | 12.9 |
| 0.93 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 13.2 (0.4) | 68 (2.1) | 5.3 (0.4) | 27.3 (2.1) | 19.4 (0.2) | 21.8 (0.4) | 11.1 |
| 1.24 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 15.3 (0.5) | 73.5 (2.4) | 4.5 (0.4) | 21.6 (1.9) | 20.8 (0.1) | 24.2 (0.2) | 14 |
| **Zinc - Reference** | | | | | | | | | | | | | |
| 0.71 | 2.8 (0.3) | 7.9 (0.8) | 0.4 (0.1) | 1.1 (0.3) | 6.3 (0.4) | 17.8 (1.1) | 0.32 (0.3) | 0.9 (0.8) | 24 (0.7) | 67.8 (2.0) | 35.4 (0.5) | 38.7 (2.2) | 8.5 |
| 1.43 | 3.8 (0.4) | 9.7 (1.0) | 0.6 (0.1) | 1.5 (0.3) | 7.6 (0.6) | 19.5 (1.5) | 0.21 (0.2) | 0.6 (0.6) | 24.5 (0.7) | 62.8 (1.8) | 39 (0.5) | 42.1 (4.3) | 19.2 |
| 2.09 | 5.3 (0.4) | 12.7 (1.0) | 1.2 (0.4) | 2.9 (1.0) | 9.1 (0.5) | 21.9 (1.2) | 0.2 (0.2) | 0.5 (0.5) | 22.9 (0.3) | 55 (0.7) | 41.6 (0.6) | 44 (4.9) | 5.5 |
| 2.78 | 7 (0.5) | 15.9 (1.1) | 2.3 (0.4) | 5.2 (0.9) | 10.4 (0.6) | 23.6 (1.4) | 0.4 (0.4) | 0.9 (0.9) | 20.8 (0.3) | 47.2 (0.7) | 44.1 (0.8) | 47.5 (5.5) | 7.2 |
| **Zinc - Leachate** | | | | | | | | | | | | | |
| 0.74 | 2.1 (0.1) | 5.9 (0.3) | 0.2 (0) | 0.6 (0) | 6 (0.2) | 16.9 (0.6) | 3.2 (0.4) | 8.9 (1.1) | 23.4 (0.7) | 65.7 (2.0) | 35.6 (0.5) | 41 (0.9) | 13.2 |
| 1.37 | 3 (0.1) | 8.1 (0.3) | 0.3 (0.2) | 0.8 (0.5) | 7 (0.1) | 18.9 (0.3) | 4.1 (0.3) | 11.1 (0.8) | 20.8 (0.2) | 56.1 (0.5) | 37.1 (0.3) | 41.9 (0.7) | 11.5 |
| 2.1 | 3.7 (0.5) | 9.1 (1.2) | 0.3 (0.1) | 0.7 (0.2) | 8.4 (0.3) | 20.7 (0.7) | 5.5 (0.3) | 13.6 (0.7) | 19.9 (0.1) | 49 (0.2) | 40.6 (0.4) | 47.6 (1.0) | 14.7 |
| 2.73 | 4.1 (0.2) | 9.7 (0.5) | 0.2 (0.1) | 0.5 (0.2) | 9.1 (0.3) | 21.7 (0.7) | 5.9 (0.2) | 14 (0.1) | 19.4 (1.1) | 46.2 (2.6) | 42 (0.5) | 48 (1.0) | 12.5 |

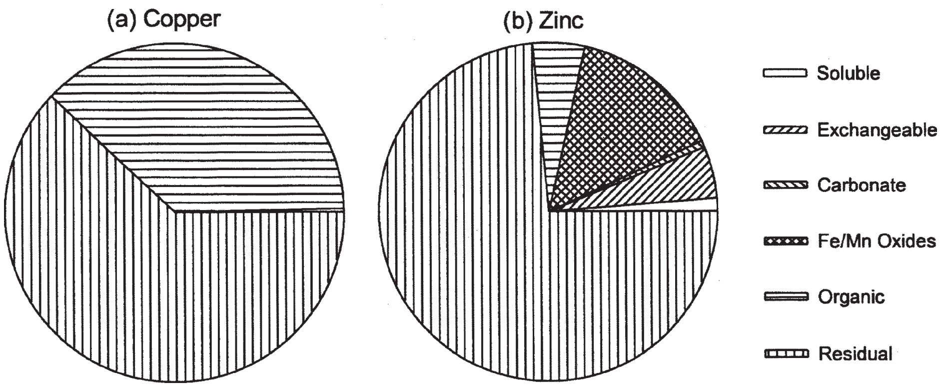

***FIGURE 2***

*Geochemical partitioning of Cu and Zn naturally present at background levels in the study soil.*

proportions of soil heavy metals associated with nonresidual fractions has been used by Arakel and Hongjun (1992) and Sutherland *et al*. (2000) as an indicator of anthropogenic contamination.

A large proportion (37%) of Cu at natural background levels was also associated with the organic fraction of the study soil. This association with soil organic matter is to be expected given the high values for formation constants of organo-Cu complexes (Stumm and Morgan, 1981). As a consequence of the affinity of organic ligands for Cu, studies into the geochemical partitioning of Cu frequently have reported that a substantial proportion of total Cu is organically bound (Keller and Vedy, 1994; Ma and Rao, 1997; Basta and Sloan, 1999; Hsu and Lo, 2000). In the study soil, exchangeable, carbonate-bound, and Fe/Mn oxide associated Cu was below the analytical detection limit, while soluble Cu contributed less than 2% of total Cu.

Aside from the residual fraction (72.8%), the majority of Zn was associated with Fe/Mn oxides (14.5%). This association has been observed by a number of workers and is attributed to chemisorption reactions with hydroxyl groups on oxide mineral surfaces and the ability of Zn to substitute for Fe and Mn in mixed oxide minerals (Ma and Rao, 1997; Ma and Uren, 1997; Han *et al*., 2000; Hsu and Lo, 2000).

In contrast to Cu (which had an exchangeable concentration below the analytical detection level), a detectable proportion (4.9%) of total Zn was exchangeable. This is due to the greater tendency of Zn to exist in solution as free divalent cations compared with Cu at the pH range typically found in soils (Dang *et al*., 1996; Fotovat and Naidu, 1997). It is generally accepted that this tendency is directly related to the hydrolysis of the metal cation (McBride, 1989). The first stage of metal hydrolysis can be expressed in the general form (Alloway, 1995):

$$xM^{n+} + yH_2O \rightarrow M_x(OH)_y^{(xn-y)+} + yH^+$$

Hydrolysis of $Cu^{2+}$ reportedly occurs at pH of 5.9, whereas $Zn^{2+}$ hydrolysis occurs at pH of 7.6 (Lindsay, 1979). At the study soil pH of 5.5, a large proportion of indigenous soil solution Cu, therefore, is expected to be present as $Cu(OH)^+$, while Zn will exist primarily as the free divalent cation ($Zn^{2+}$). Free divalent cations exhibit great affinity for negatively charged exchange sites and are consequently adsorbed by cation exchange reactions. This explains the observed association of Zn with the exchange phase of the study soil.

In the study soil, organic ligands also contributed to Zn partitioning, with 5% of total Zn being organically bound. This is generally consistent with previous research and is due to solid-phase organic complexation processes (Shuman, 1999b; Han *et al*., 2000). Small proportions of Zn (less than 1%) were also associated with both the carbonate fraction and the soluble phase.

## Geochemical Partitioning of Cu and Zn at Various Levels of Contamination

The sequential extraction of soil Cu and Zn after equilibration with either the leachate or reference solution shows that the geochemical partitioning behavior is substantially different to background partitioning (Figure 3). This observation is consistent with previous studies and is the basis of the "geochemical signatures" used by Arakel and Hongjun (1992) and Sutherland *et al*. (2000). These geochemical signatures refer to the differences and similarities in partitioning behavior of contaminated soils and uncontaminated soils and are used to determine whether the contamination is anthropogenically derived (Arakel and Hongjun, 1992).

At the lowest total Cu concentration (0.30 mg-Cu/L) from the leachate, 47% of Cu was organically bound following equilibration with the soil, compared with only 39% after equilibration with the reference solution Cu and 37% for Cu at background levels. The difference between this organically bound Cu derived by equilibration with the leachate and that derived from equilibration with the reference solution is due to the effect of dissolved organo-Cu complexes (present in the sludge leachate). This suggests that soil organic materials have a greater affinity for soluble organo-Cu complexes than for inorganic complexes or free $Cu^{2+}$. A similar result occurred for Zn, with 8.9% of Zn associated with the organic phase of the study soil as a result of equilibration with the lowest leachate concentration (0.70 mg-Zn/L). However, in comparison, only 0.9% of Zn derived from the reference solution was organically bound after equilibration with the soil. This result for equilibration of reference solution Zn at the lowest level of contamination is particularly interesting compared with background organically bound levels

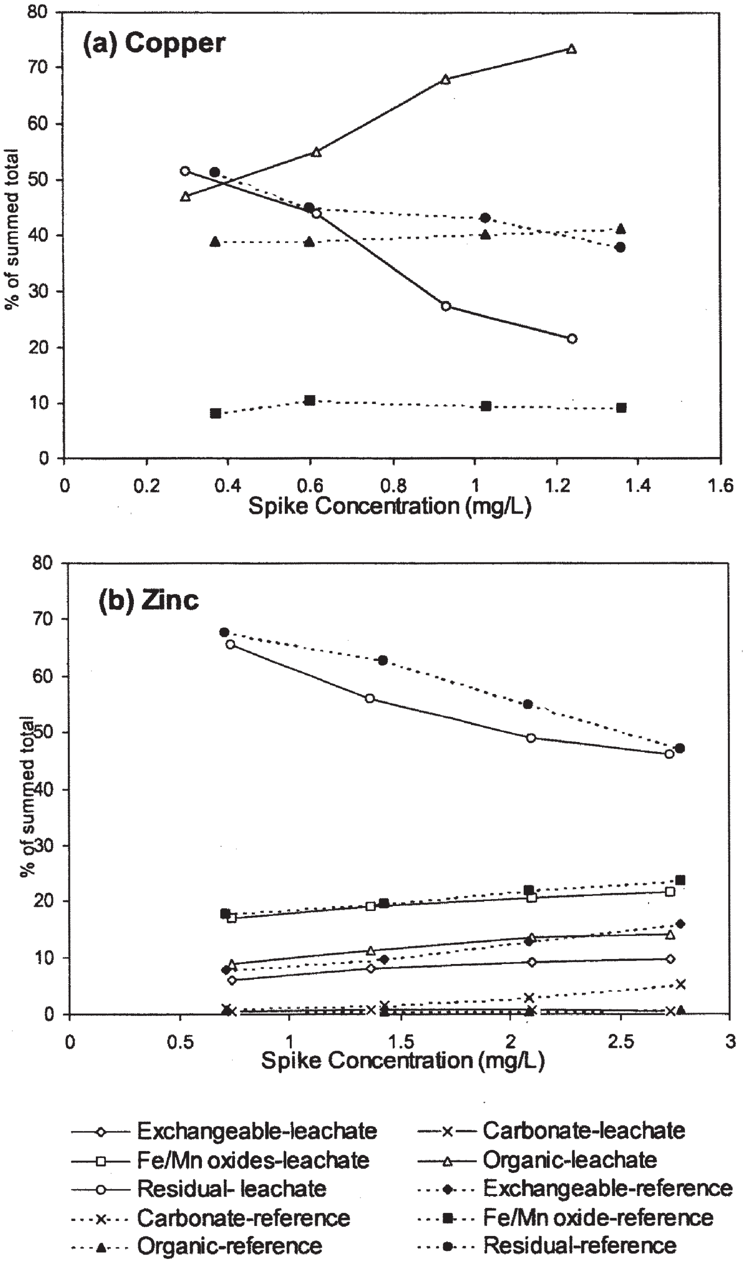

*FIGURE 3*

*Partitioning of Cu (a) and Zn (b) among the various geochemical fractions after equilibration with a range of equilibrating solution concentrations (referred to as "spike concentration") from sludge leachate and a reference solution (which mimicked the leachate, except for dissolved organic material).*

because the organic fraction was less important for Zn retention after equilibration with the reference solution.

This decrease in importance, as measured by the proportion of total Zn, was due to the increasing importance of other fractions, namely, exchangeable and Fe/Mn oxide associated Zn. The Fe/Mn oxide fraction for Cu was also far more important after equilibration with the reference solution. This demonstrates that $Cu^{2+}$, $Zn^{2+}$ or weak inorganic ion pairs have a much greater affinity for surface sites on Fe/Mn oxides than do more stable organic complexes (i.e. the dissolved metal-organic matter complexes of Cu and Zn present in the leachate). This is consistent with sorption due to cation exchange, chemisorption, and co-precipitation processes as reviewed by McBride (1989).

Howard and Sledzinski (1996) and Salim *et al.* (1996) reported that in similar studies the importance of the exchangeable and carbonate fraction increased with increasing heavy metal spike concentration. In these two studies, the partitioning of heavy metals at relatively high levels of contamination was examined. The concentrations, which for Salim *et al*. (1996) ranged from 0 to 100000 mg/L, were so high that increasing heavy metal sorption by the carbonate fraction could be easily attributed to precipitation of pure Cd-, Ni-, and Pb-carbonates. Contrary to the results for Cu and Zn reported in this study, the proportions of Cd, Ni, and Pb associated with the organic and Fe/Mn oxide fractions were found by both Howard and Sledzinski (1996) and Salim *et al*. (1996) to decrease with increasing spike concentration. This outcome was not observed here because both the leachate and reference solution Cu and Zn concentrations did not result in an exceedance of the sorption capacity of the organic and Fe/Mn oxide fractions (as is evident by the linearity of the sorption isotherms discussed below).

As the levels of Cu and Zn contamination increased, the importance of the residual fraction decreased. This is attributed to a combination of the increasing importance of other fractions and possibly the kinetically limited rate of sorption for the residual fraction. It is possible that the 100 h equilibration period employed in this work was insufficient for complete diffusion of Cu and Zn into the crystal lattice of the soil minerals.

### Cu and Zn Sorption Isotherms for the Bulk Soil

Sorption of Cu from both the leachate ($K_d = 11.5$ L/kg, $r^2 = 0.99$) and a reference solution ($K_d = 119$ L/kg, $r^2 = 0.96$) by the bulk soil was best described by a Linear isotherm equation (Figure 4a). Although L-type (Freundlich or Langmuir) equations generally perform poorly compared with C-type (Linear) equations at low equilibrating solution concentrations, the sorption of Zn from both the leachate ($K_f = 1.3$ L/kg, $n = 0.6$, $r^2 = 0.93$) and reference solution ($K_f = 5.7$ L/kg, $n = 0.4$, $r^2 = 0.92$) by the bulk soil was best described by a Freundlich isotherm equation (Figure 4b).

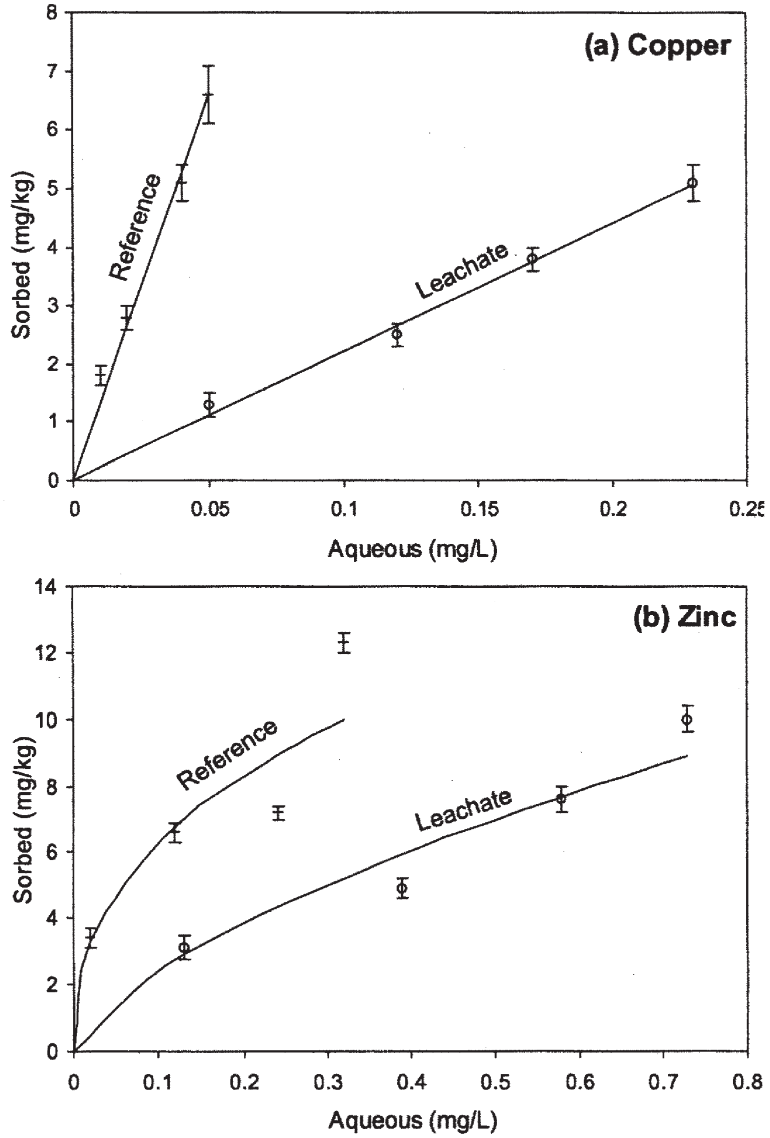

***FIGURE 4***

*Isotherms describing Cu (a) and Zn (b) sorption by the bulk soil determined by equilibration with sludge leachate and a reference solution (which mimicked the leachate, except for a lack of dissolved organic material).*

L-type isotherms reflect a strong affinity at low concentrations, but lesser affinity at higher levels due to a limiting number of sorption sites and a decrease in sorbing surface as the excess of sorbate increases. This isotherm shape, which typifies heavy metal sorption at high concentrations, is thought to be produced when cation exchange is the dominant form of sorption (Sposito, 1984). Despite this belief, the geochemical partitioning of Zn at various levels of contamination in this work (Figure 3b) shows that cation exchange is not the dominant sorption mechanism. This is consistent with Lake (1984) and McBride (1989), who report that adsorption by cation exchange processes does not limit heavy metal solubility in low to moderately contaminated soil.

The parameters describing Cu and Zn sorption by the bulk soil allow an assessment of the sorptive effect of dissolved metal-organic matter complexes by comparing the results for the reference solution with those of the leachate. The MINTEQA2 speciation results show that the majority of leachate Cu (97.4%) and Zn (63.2%) was present as dissolved metal-organic matter complexes. These complexes exerted a significant effect on Cu and Zn sorption by the bulk soil sample, with the $K$ value for sorption from the reference solution being five times greater for Zn ($P < 0.001$) and 10 times greater for Cu ($P < 0.0001$) than the corresponding value for the leachate. These $K$ values (both $K_d$ and $K_f$) give an indication of the affinity that the bulk soil has for Cu and Zn sorption and are dependent on several factors. In this study all factors previously shown to influence Cu and Zn sorption were the same for both the leachate and reference solution, with the exception of dissolved metal-organic matter complexes. Therefore, in the case of the leachate, the presence of dissolved metal-organic matter complexes and dissolved organic ligands has resulted in depressed Cu and Zn sorption compared with the reference solution. This supports work by Lebourg *et al*. (1998), Shuman (1999a), and Almas *et al*. (2000), demonstrating the sorption depressing influence of dissolved metal-organic matter complexes.

### Cu and Zn Sorption Isotherms for the Individual Fractions

Salim *et al*. (1996) showed that it is possible to investigate sorptive behavior of heavy metals with the individual geochemical fractions of soils determined on the basis of sequential extraction analyses. This is done by plotting the amounts recovered in each step of the sequential extraction procedure after equilibration with a contaminant solution against the corresponding equilibrium solution concentration determined using the bulk soil. This approach has a definite advantage over traditional methods in that it allows direct measurement of sorption by individual fractions, rather than indirect inference from a correlation or regression with soil characteristics.

It was possible to construct sorption isotherms for most of the targeted geochemical fractions with least squares linear regression ($P_{crit.} < 0.05$). However, excessive scattering of data and/or the Cu or Zn concentrations in some fractions being below the analytical detection limit prevented the construction of statistically significant isotherms for all fractions.

The experimental data for organically complexed Cu displayed good fits ($r^2 >$ 0.95) to the Linear, isotherm equation (Figure 5). Comparison of the $K_d$ value for organically bound Cu derived from equilibration with the leachate (41.1 L/kg, $r^2$ = 0.96) and that for the corresponding reference solution system (73.7 L/kg, $r^2$ = 0.97) show that the sorption affinity of this fraction from the reference solution system is significantly greater ($P < 0.001$) compared with the leachate system. This depressed sorption was observed with the bulk Cu isotherm and is due to the sorption depressing effect of dissolved organo-Cu complexes. The $K_d$ value for the reference solution equilibrated system is only 1.7 times greater than for the leachate for organically bound Cu, whereas for the bulk soil there was a 10-fold difference. This comparison suggests that soil organic matter has a greater affinity for dissolved organo-Cu complexes than does the bulk soil, even though such complexes actually depress sorption for both the bulk soil and the organic fraction.

The Cu sorption data for the organic fraction can also be significantly ($P <$ 0.05) fitted to a Langmuir isotherm. The maximum capacity ($m$) of the organic fraction to sorb Cu derived from the leachate is 84.7 mg/kg ($r^2$ = 0.98), and the corresponding capacity for Cu retention from the reference solution was only 11 mg/kg ($r^2$ = 0.99). While the absolute accuracy of these sorption capacities are questionable, they allow a comparison between the leachate (which contained 97.4% organically complexed Cu) and the reference solution (which was com-

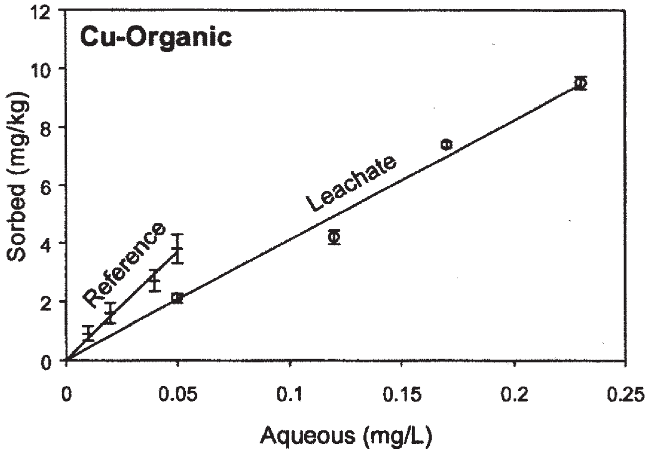

**FIGURE 5**

*Isotherms describing Cu sorption to the organic fraction of the study soil determined by equilibration with sludge leachate and a reference solution (which mimicked the leachate, except for a lack of dissolved organic material).*

prised of $Cu^{2+}$ or inorganic ion-pairs). It is evident by this comparison that soil organic matter has a greater capacity to sorb metal-organic matter complexes compared with inorganic ion pairs or $Cu^{2+}$. This may be related to hydrophobic interactions between dissolved organic material, with which leachate Cu was complexed, and soil organic matter (Jardine *et al.*, 1989). This view conflicts with Gu *et al.* (1994) and Edwards *et al.* (1996), however, who argue that electrostatic interactions or chemisorption processes are primarily responsible for dissolved organic matter sorption. Based on the work of these authors, the Fe/Mn oxide fraction of the study soil would exhibit the greatest affinity for dissolved metal-organic matter complexes. This notion is not supported by the results presented in this study.

Unfortunately, excessive scattering of data for organically bound Zn derived from the reference solution prevented the creation of a statistically significant (at $P < 0.05$) isotherm. Therefore, it was not possible to make the same comparison with Zn sorption by the organic fraction as was made with Cu. The sorption of organically bound Zn derived from the leachate was best described by a Linear equation ($K_d = 4.7$ L/kg, $r^2 = 0.97$) (Figure 6a). This $K_d$ value of 4.7 for organically bound Zn is much less than the corresponding value of 41.1 for Cu. This may be attributed to the much lower formation constants for organo-Zn complexes compared with organo-Cu complexes (Stumm and Morgan, 1981).

It was also possible to successfully construct sorption isotherms for exchangeable, carbonate bound, and Fe/Mn oxide-associated Zn. The sorption of Zn by the exchangeable fraction from both reference ($K_d = 13.7$ L/kg, $r^2 = 0.98$) and leachate solutions ($K_d = 3.4$ L/kg, $r^2 = 0.99$) was best described by a Linear equation (Figure 6b). The $K_d$ value describing sorption by the exchange phase for the reference solution system therefore is some four times greater than that of the leachate system. This significantly greater ($P < 0.001$) $K_d$ value for the reference solution is not surprising given that negatively charged surface sites of the exchangeable fraction exhibit a much greater affinity for free $Zn^{2+}$ (present in the reference solution) than for organo-Zn complexes (present only in the leachate). The fact that the ratio of $K_d$ value for the reference solution system to $K_d$ value for the leachate system for sorption by the exchange phase (ratio = 4) is so similar to the corresponding ratio for sorption by the bulk soil (ratio = 5) indicates similar affinity of soluble Zn species for the exchangeable fraction and the bulk soil. This suggests that in the study soil as a whole, Zn was mostly sorbed as the $Zn^{2+}$ species.

As for the bulk soil and the exchangeable fraction, sorption of Zn by Fe/Mn oxides from both the reference solution ($K_d = 13.5$ L/kg, $r^2 = 0.99$) and leachate ($K_d = 5.3$ l/kg, $r^2 = 0.98$) was best described by a Linear equation (Figure 6c) and was significantly ($P < 0.001$) depressed for the leachate equilibrated system compared with the reference solution equilibrated system. The ratio of reference solution $K_d$ to leachate $K_d$ is similar to the corresponding ratio for the bulk soil and the exchangeable fraction, indicating that the sorption of Zn to the Fe/Mn oxide fraction also primarily involved $Zn^{2+}$.

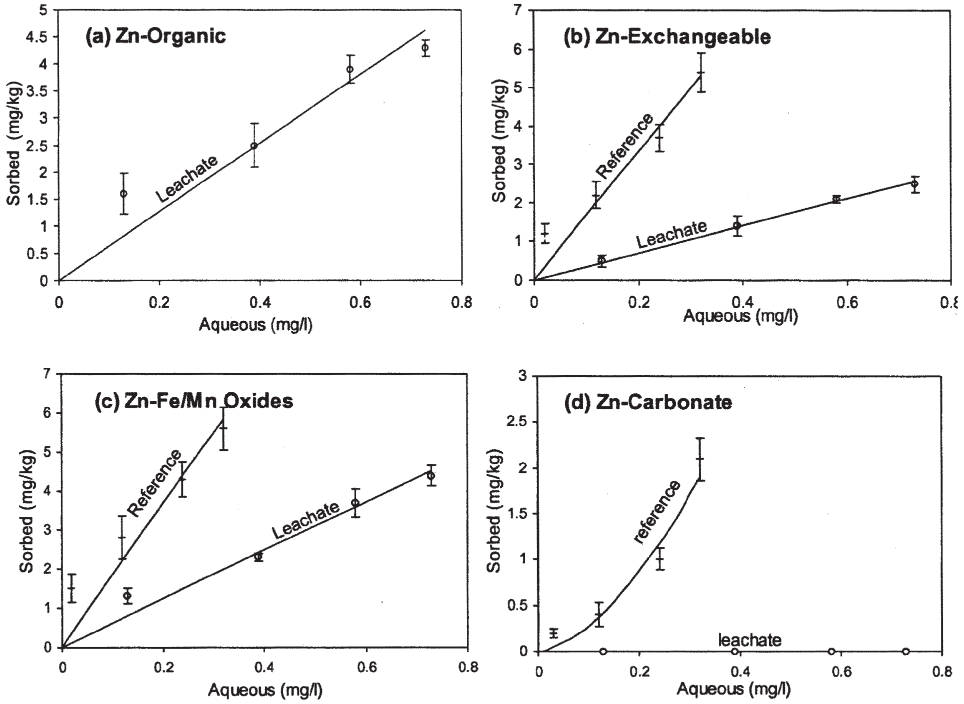

***FIGURE 6***

*Isotherms describing Zn sorption to the organic (a), exchangeable (b), Fe/Mn oxide (c), and carbonate (d) fractions of the study soil determined by equilibration with sludge leachate and a reference solution (which mimicked the leachate, except for a lack of dissolved organic material).*

It was not possible, due to concentrations being below detection limits, to fit a sorption curve for leachate-derived Zn in the carbonate fraction. It was possible, however, to model sorption of the reference solution equilibrated Zn with the Freundlich equation ($K_f$ = 12.9 L/kg, $n$ = 1.7, $r^2$ = 0.92; Figure 6d). Freundlich isotherms with $n > 1$ have been rarely reported in the literature. Sposito (1984) reports that the shape of such isotherms is generally due to precipitation reactions. A comparison of the expected Zn solubility (based on the solubility product constant of $ZnCO_3$) with measured soluble Zn concentrations suggests that it is unlikely that Zn has precipitated in the form of a pure carbonate mineral.

The formation of solid solutions, as discussed by McBride (1989), with a composition $Zn_{1-x}Ca_xCO_3$ would greatly reduce the effective solubility of $ZnCO_3$. Solid solution formation has been shown by Davis *et al.* (1987) to be important for Cd sorption in the presence of $CaCO_3$. These workers reported that the formation of a solid solution of composition $Cd_{1-x}Ca_xCO_3$ controlled Cd levels in solution in association with solid-phase $CaCO_3$. Similar to the results shown in Figure 6d, Davis *et al*. (1987) found that Cd sorption became more prominent as the quantity of $CaCO_3$ surface increased and proceeded even though the solution was undersaturated with respect to solid $CdCO_3$. It seems that a similar mechanism could explain the shape of the sorption isotherm for carbonate bound Zn; however, more research is needed.

## GENERAL DISCUSSION

The bulk soil sorption isotherms demonstrate that sludge-derived dissolved metal-organic matter complexes substantially depress Cu and Zn sorption. This overall result (depressed sorption) is consistent with previous research and shows that dissolved organic ligands exert a powerful role in controlling the speciation and solubility of Cu and Zn in sludge-amended soil environments (Lebourg *et al*., 1998; Shuman, 1999a; Almas *et al*., 2000). Examination of heavy metal behavior, through the use of sorption isotherm analysis, traditionally involves equilibration of a soil sample with electrolyte solutions containing a single metal of interest or a limited suite of metals (Schulte and Beese, 1994; Barry *et al*., 1995; Gao *et al*., 1997; Phillips, 1999). At best, such studies account for the sorption-depressing influence of cationic competition but do not quantitatively consider the effect of dissolved metal-organic matter complexes. Based on the results presented here, this approach appears to underestimate Cu and Zn mobility even if the effects of cationic competition, pH, ionic strength, and inorganic ion-pair formation are considered.

In addition to causing depressed sorption, dissolved organic ligands also influenced the geochemical partitioning behavior, with the organic fraction of the study soil exhibiting a greater affinity for metal-organic matter species compared with other dissolved Cu and Zn species. The importance of organic matter to the sorption of non-polar organic compounds is well established (Karickhoff *et al*., 1979). It may be valid to consider that, although dissolved humic and fulvic acid macromolecules exhibit surficial ionic characteristics, such molecules are still likely to contain areas of a non-polar nature. Such areas of their molecular structure would be hydrophobic and would be passively attracted to non-polar, solid-phase soil organic matter. Therefore, the organic fraction of the soil would be expected to exhibit a greater affinity for dissolved organic matter than would other geochemical fractions. This is consistent with Jardine *et al*. (1989), who reports that physical adsorption (hydrophobic interaction) is the primary mechanism controlling the sorptive behavior of dissolved organic matter with soil.

This importance of hydrophobic interaction explains the observation that the organic fraction of the study soil displayed a greater affinity for dissolved metal-organic matter complexes compared with other soluble Cu and Zn species. This suggests that the solid phase organic matter in the study soil was primarily responsible for sorption of dissolved metal-organic matter complexes. However, this conclusion conflicts with previous research by Kaiser and Zech (1997), who found that mineral surfaces, particularly Fe/Mn oxides, were mostly responsible for the sorption of dissolved organic matter in soil. These researchers studied dissolved organic matter sorption by soil rich in Fe/Mn oxides and low in organic matter and found that ligand exchange of $OH^-$ and $H_2O$ from Fe/Mn oxides by organic polymers was more important for sorption than hydrophobic interactions. This suggests that the influence of dissolved metal-organic matter complexes on the geochemical partitioning of heavy metals may be largely dependent on soil characteristics, with particular variation between Fe/Mn oxide-rich soils (e.g., oxisols) and highly organic soils (e.g., the study soil). The role of contrasting soil characteristics on the sorptive and partitioning effects of sludge-derived dissolved metal-organic matter complexes is an area requiring further research.

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