Copper Solubility in Myersville B Horizon Soil in the Presence of DTPA

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ABSTRACT

Organic ligands greatly affect the speciation and solubility of heavy metals in soils, depending on complex interactions of pH, ligand-to-metal ratio, and the order of application of metals and ligands to soils. To understand how these variables influence the fate of metals added to soil, we investigated the solubility of Cu(II) in Myersville B horizon soil (Ultic Hapludalf) in the presence of diethylenetriaminepentaacetic acid (DTPA), a strong complexing agent. Copper solubility was studied as a function of soil pH, individual and relative concentrations of Cu^{2+} and DTPA, and the order of application of these components to the soil. In the presence of DTPA (1.0 and 10 mmol kg^{-1} soil), Cu(II) solubility (0.1 and 1.0 mmol kg^{-1} soil) increased with an increase in pH (4 to 7). However, this occurred only when DTPA concentration $\geq$ Cu(II) concentration, implying that the relative concentrations of DTPA and Cu(II) were critical in controlling Cu(II) solubility. The order of application of Cu(II) and DTPA to the soil also strongly influenced Cu solubility. The three orders of application of these components were (i) application of premixed stock solutions of Cu(II) and DTPA in specified ratios and concentrations to the soil, (ii) equilibration of Cu(II) with the soil followed by application of DTPA, and (iii) equilibration of DTPA with soil followed by Cu(II) application. Of these three, the highest Cu solubility was observed in the third case when DTPA > Cu(II). This was attributed to surface coordination of DTPA, which prevents Cu from binding with soils. Also, an increase in background electrolyte concentration was accompanied by a decrease in the pH and, therefore, a change in Cu(II) solubility. These results have several implications in the field of contaminant and nutrient management in soils.

THE TOXICITY AND BIOAVAILABILITY of certain heavy metals such as Cu, Fe, Zn, and Mn depends on their activity and speciation in soils (Lehman and Mills, 1994; Buffle et al., 1990; Adriano, 1986; Brown et al., 1985). The ultimate fate of these metals is dependent on their dynamic interactions with various soil components, especially the organic fractions (Harter and Naidu, 1996; McLean and Bledsoe, 1992; Evans, 1989; McBride, 1989). Solubility of heavy metals in soils and mineral oxide surfaces as a function of pH is often dictated by the presence of organic and inorganic ligands (Harter and Naidu, 1996; Sparks, 1995; McBride, 1989). Sorption of heavy metals onto mineral oxide surfaces and soils typically increases with an increase in pH in the presence of inorganic ligands. Organic ligands such as acetate, oxalate, and nitrilotriacetate have been found to promote sorption at low pH (Elliott and Huang, 1980, 1979), and it has been found that the presence of ligands such as EDTA and DTPA enhances heavy metal solubility with a corresponding increase in pH (Harter and Naidu, 1996).

This study concerns itself with metal–organic interactions in soils. Heavy metals have been known to be incorporated into soils due to various waste disposal practices, environmental pollution, or fertilizer application. Inputs of organic acids in soils are seasonal in nature due to plant growth or due to waste disposal practices. Metals are commonly added to agricultural production systems as chelates (Mortvedt et al., 1991). Organic-rich metal wastes might enter the soil as components of sewage effluent or sludge. Organic acids from root exudates come in contact with metal-rich soils (Mortvedt et al., 1991). Weathering of soil minerals by organic acids added to metal-rich soil systems are commonly encountered (Stumm and Wollast, 1990). Finally, the addition of metals to organic-rich systems in which the organic acids have already reacted with the soil could affect the fate of the metals in that soil. Thus, the solubility and degree of complexation of metals in any soil system may depend on whether organic ligands or metals react with the soil first, i.e., the order of application of the components to the soil. This behavior may be simulated to some extent using a laboratory soil system in the presence of low molecular weight organic acids (such as EDTA and DTPA). These organic acids have functional groups similar to those found in humic and fulvic acids (such as carboxylic acid and amino groups). The following have been found to affect the sorption behavior of metals onto mineral oxide surfaces in the presence of organic acids: pH, heavy metal and organic acid type (Elliott and Huang, 1980, 1979; Davis and Leckie, 1978; Vuceta and Morgan, 1978), the relative concentrations of the metals and organics (Elliott and Huang, 1979), their individual concentrations (Basta and Tabatabai, 1992a,b) the ionic strength (Elliott and Huang, 1985), and the order of application of each of these components to the medium (Bryce et al., 1994).

The results from this study are specific to Cu solubility in Myersville B horizon soil in the presence of DTPA. Copper is a very important element found in terrestrial systems. It is an essential micronutrient for plants, and is also required in metabolic processes of various organisms (Flemming and Trevors, 1989; Adriano, 1986). Though Cu is considered nontoxic to mammals, it has been found to be extremely toxic to aquatic biota at higher concentrations (Flemming and Trevors, 1989; Adriano, 1986). Copper is also a high-priority pollutant on U.S. Environmental Protection Agency's assessment lists (Lehman and Mills, 1994). A very strong chelating agent, DTPA has been commonly used in the assessment of long-term availability of metals exposed to plants in soils (O'Connor, 1988; Lindsay, 1979). Myersville B horizon soil contains large amounts of Si, Al, and Fe oxides that

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Table 1. Selected properties of Myersville B horizon soil material.

Classification†	fine-loamy, mixed, mesic Ultic Hapludalf (Dystric Eutrochrept)
Textural class†	Silt loam
Particle-size distribution, g kg^{-1}†	Sand, 363; silt, 452; clay, 185
Clay mineralogy‡	Mixed, dominated by vermiculite
Total chemical analyses of the >0.2-mm clay fraction for:	
Macro minerals, g kg^{-1}†	SiO$_2$, 394; Al$_2$O$_3$, 247; Fe$_2$O$_3$, 207
Microelements, mg kg^{-1} soil†	Cr, 342; Mn, 987; Ni, 140; Cu, 230; Zn, 188
Organic matter, g kg^{-1}§	9.0 (measured by wet oxidation)
Soil pH¶	5.7
pH-dependent CEC and AEC in the soil for a pH range of 3.4–7.7#	
CEC	Increased from 55 to 96 mmol$_c$ kg^{-1} soil
AEC	Decreased from 12 to 2 mmol$_c$ kg^{-1} soil
Average moisture content of the pH-adjusted soils¶	19.4 ± 0.8%

† Johnson and Chu (1983).
‡ Stahl and James (1991).
§ Korcak and Fanning (1985).
¶ Vulava (1994).
# Stahl (1990).

influence the adsorption characteristics of the soil (Table 1). The presence of Al, Fe(II, III), and other major cations could affect Cu solubility in the soil solutions, as can be seen from the stability constants for these elements involving DTPA (Table 2) depending on their relative concentrations in the soil solutions at any given pH. Also, the soil being low in indigenous organic matter, DTPA may not be affected by the organic matter significantly enough to change the solubility patterns.

The primary emphasis in this study was placed on exploring the possibility of creating a laboratory setup to simulate the factors affecting the heavy metal fate and speciation in soils in the presence of strong chelating agents. The effects of the above-mentioned factors (soil pH, relative and individual Cu and DTPA concentrations applied to the soil, order of Cu and DTPA application, and the concentration of background electrolyte) on Cu solubility were investigated.

MATERIALS AND METHODS

Reagent Solutions

Stock solutions of 4.8 × 10^{-3} M Cu(NO$_3$)$_2$; 10^{-2} and 10^{-3} M DTPA; 1.0 and 0.1 M KNO$_3$; and 2.0, 1.0, and 0.1 M KOH were prepared with analytical grade reagents (J.T. Baker, Phillipsburg, NJ) and distilled water. Two, 1.0, and 0.1 M HNO$_3$ stocks were prepared from 5.0 M stock. All the reagents were stored in acid-washed polyethylene storage bottles. Copper standards for atomic absorption measurements were prepared from certified Cu standards (1000 mg L^{-1}) in 10^{-4} M DTPA and 0.01 M KNO$_3$.

Soil pH and pH Adjustment

Soil pH was adjusted before conducting the experiments to control the variability of soil pH due to treatment. "Soil pH" was operationally defined as follows: A 1:10 soil-to-solution ratio (2.5 g soil dry-weight basis) in 0.01 M KNO$_3$ followed by shaking (reciprocating shaker) for 1 h and centrifugation (14 600 × g, 20°C, 10 min). The pH of the decanted extract was measured potentiometrically in equilibrium with the atmosphere. The unadjusted soil pH was 5.7.

The pH adjustment was done by adding 1.0 or 2.0 M HNO$_3$ or KOH to 500 g of field-moist soil (approximately −10 kPa water potential) depending on the pH required. The acid or base was thoroughly kneaded into the soil in a polyethylene bag, and then stored (at 25 ± 2°C in diffuse room light,

double bagged with moist towelettes between the bags to prevent moisture loss). The soils were allowed to equilibrate for 7 d before the measurement of soil pH by the above procedure. The soil pH was measured again after another week and very slight deviation (±0.1 pH unit) from previous measurements were observed. The soil pH following equilibration ranged from 4.2 to 7.2. Soil samples with a pH of 4.2, 4.5, 5.0, 5.8, 6.6, and 7.2 were used extensively for all studies.

Adsorption and Solubility Experiments

The following conditions were used consistently throughout the study, unless mentioned otherwise. For pH studies, soils with pH of 4.2, 4.5, 5.0, 5.8, 6.6, and 7.2 were used. Extraction conditions were as described for defining soil pH operationally, except an equilibration period of 16 ± 1 h was provided in a reciprocating shaker. A preliminary study demonstrated that Cu concentration in solution did not change significantly in the presence of DTPA after 5 h, so 16 h of shaking was deemed adequate to characterize an "equilibrium" condition (data not shown). All treatments were replicated three times.

Table 2. Stability constants (K_{eq}) used in equilibrium calculations.

Reaction	log K_{eq}†
H$^+$ + DTPA^{5-} = HDTPA^{4-}	10.49
2H$^+$ + DTPA^{5-} = H$_2$DTPA^{3-}	19.09
3H$^+$ + DTPA^{5-} = H$_3$DTPA^{2-}	23.39
4H$^+$ + DTPA^{5-} = H$_4$DTPA$^-$	25.99
5H$^+$ + DTPA^{5-} = H$_5$DTPA	27.99
Cu^{2+} + DTPA^{5-} = CuDTPA^{3-}	21.42
Cu^{2+} + H$^+$ + DTPA^{5-} = CuHDTPA^{2-}	26.22
Cu^{2+} + 2H$^+$ + DTPA^{5-} = CuH$_2$DTPA$^-$	29.18
Cu^{2+} + 3H$^+$ + DTPA^{5-} = CuH$_3$DTPA	31.74
2Cu^{2+} + DTPA^{5-} = Cu$_2$DTPA$^-$	28.21
K$^+$ + DTPA^{5-} = KDTPA^{4-}	0.9‡
Ca^{2+} + DTPA^{5-} = CaDTPA^{3-}	10.75
Ca^{2+} + H$^+$ + DTPA^{5-} = CaHDTPA^{2-}	16.86
2Ca^{2+} + DTPA^{5-} = Ca$_2$DTPA$^-$	12.35
Mg^{2+} + DTPA^{5-} = MgDTPA^{3-}	9.34
Mg^{2+} + H$^+$ + DTPA^{5-} = MgHDTPA^{2-}	16.19
Fe^{2+} + DTPA^{5-} = FeDTPA^{3-}	16.4
Fe^{2+} + H$^+$ + DTPA^{5-} = FeHDTPA^{2-}	21.7
Fe^{2+} − H$^+$ + H$_2$O + DTPA^{5-} = FeOHDTPA^{4-}	7.41
Fe^{2+} − 2H$^+$ + 2H$_2$O + DTPA^{5-} = Fe(OH)$_2$DTPA^{5-}	− 2.22
2Fe^{2+} + DTPA^{5-} = Fe$_2$DTPA$^-$	19.38
Fe^{3+} + DTPA^{5-} = FeDTPA^{2-}	28‡
Fe^{3+} + H$^+$ + DTPA^{5-} = FeHDTPA$^-$	31.56
Fe^{3+} − H$^+$ + H$_2$O + DTPA^{5-} = FeOHDTPA^{3-}	18.12
Al^{3+} + DTPA^{5-} = AlDTPA^{2-}	18.7
Al^{3+} + H$^+$ + DTPA^{5-} = AlHDTPA$^-$	23
Al^{3+} − H$^+$ + H$_2$O + DTPA^{5-} = AlOHDTPA^{3-}	11.3

† For all constants I = 0.1 M, 25°C. All constants have been obtained from Martell and Smith (1974) and their subsequent supplements.
‡ Estimated at 20°C rather than 25°C.

Copper Adsorption

Initial $Cu(NO_3)_2$ concentrations of 2.5×10^{-3}, 5×10^{-4}, 1×10^{-4}, and $1 \times 10^{-5}\ M$ were applied to the soils at different pH values and in the presence of the background electrolyte ($0.01\ M\ KNO_3$). Following equilibration, the soil samples were centrifuged and the supernatant solutions were poured off into polyethylene vials for pH measurement and Cu analysis. Copper(II) adsorbed was calculated as the difference between the applied Cu and the Cu remaining in solution at equilibrium. All other conditions were similar to those in soil pH measurements.

Effect of Relative Concentrations and Order of Application

Molar ratios of Cu^{2+}/DTPA applied to the soil were 1:1, 1:10, 1:100, and 10:1. The individual initial concentrations of Cu^{2+} applied were 10^{-4}, 10^{-5}, and $10^{-6}\ M$ while those for DTPA were 10^{-3}, 10^{-4}, 10^{-5}, and $10^{-6}\ M$. Copper and DTPA were applied to the soil in three different orders, designated as Orders I, II, and III. The description for orders of application follows:

Order I (Cu + DTPA). Premixed solutions of $Cu(NO_3)_2$ and DTPA were prepared in designated concentrations and ratios in the presence of the background electrolyte. These solutions were then applied to the soils and equilibrated, followed by centrifugation. Soil extracts were then decanted into vials for pH and atomic absorption measurements.

Order II (Cu first). Only $Cu(NO_3)_2$ at various concentrations was applied to the soil samples (six replicates), and the soil suspensions were equilibrated. Soluble $Cu(II)$ at equilibrium was measured in three of the replicates. Then, DTPA was applied to the other three replicates, and the soluble $Cu(II)$ was measured following another 16-h equilibration period.

Order III (DTPA first). This order was the reverse of Order II, with DTPA being applied to the soil in the first stage followed by Cu^{2+} application in the second stage.

Effect of Background Electrolyte

The effect of change in ionic strength was measured by keeping soil pH and added Cu^{2+} and DTPA concentrations constant, while varying the concentration of the background electrolyte, KNO_3. Levels of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and $0\ M$
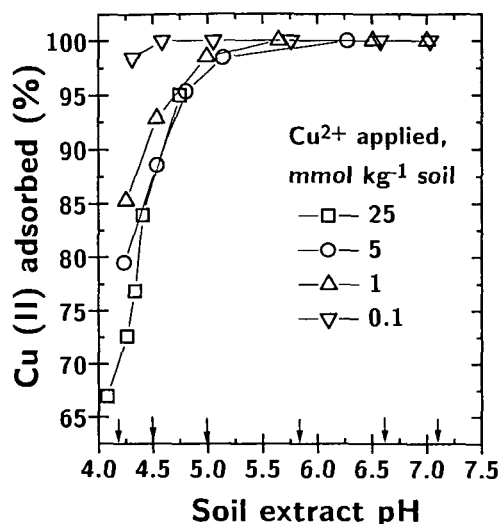

Fig. 1. Adsorption of Cu^{2+} onto the soil without DTPA. The arrowheads indicate the soil pH before application of Cu to the soil. Note: all points are arithmetic means of triplicate results. All standard errors of the means are smaller than the data points.

KNO_3 were applied to the soil containing 1.0 mmol of Cu^{2+} kg^{-1} soil in the presence and absence of 1.0 mmol DTPA kg^{-1} soil. After equilibration, soluble Cu and the extract pH were measured following centrifugation.
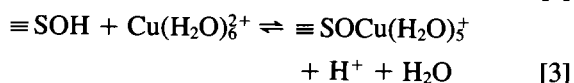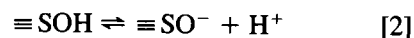
Extractability of Indigenous Copper

Some indigenous soil $Cu(II)$ was expected to interfere with the solubility measurements. To account for this, various concentrations of DTPA were applied to the soil and the extractable $Cu(II)$ was measured in the solution. A maximum of 2.1×10^{-3} mmol of $Cu(II)\ kg^{-1}$ soil was extracted with a DTPA concentration of 10 mmol kg^{-1} soil (highest concentration of DTPA used in the solubility studies). Based on the amount of DTPA applied in each of the treatments, the indigenous Cu extracted was subtracted from all $Cu(II)$ solubility calculations.
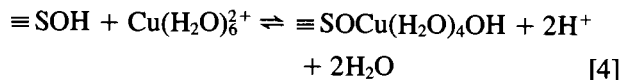
RESULTS AND DISCUSSION
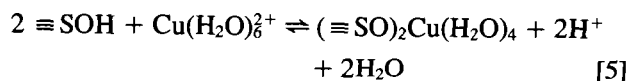
Copper Sorption in the Absence of DTPA

Copper sorption by soil in the absence of DTPA correlated with the initial aqueous Cu concentration. The results indicate that Cu sorption increased with increasing pH (Fig. 1), which is expected based on thermodynamic predictions and other research (Allison et al., 1991; McBride, 1989). At a concentration of 25 mmol kg^{-1} soil, about 67% of $Cu(II)$ was adsorbed onto the soil surface at pH 4.2. Compared with this, about 97% of $Cu(II)$ was adsorbed at the same pH for an initial Cu^{2+} concentration of 0.1 mmol kg^{-1} soil. Other intermediate concentrations showed intermediate values. Some researchers have concluded that the adsorption mechanisms of Cu onto mineral oxide surfaces principally involve the adsorption of Cu^{2+} and Cu-OH species (Elliott and Huang, 1981; Davis and Leckie, 1978). This has been represented as:

$$\equiv SOH_2^+ \rightleftharpoons\ \equiv SOH + H^+ \qquad [1]$$

$$\equiv SOH \rightleftharpoons\ \equiv SO^- + H^+ \qquad [2]$$

$$\equiv SOH + Cu(H_2O)_6^{2+} \rightleftharpoons\ \equiv SOCu(H_2O)_5^+$$
$$+ H^+ + H_2O \qquad [3]$$

Equations [1] and [2] represent generic reactions for deprotonation of the mineral oxide surfaces as weak acids with $\equiv SOH_2^+$ favored at low pH and $\equiv SO^-$ at high pH (Schindler, 1990). These models may be applicable to our system as the soil is a heterogeneous mixture of several such mineral oxides (Table 1). From Eq. [3] it may be observed that one H^+ is released for every Cu^{2+} complexed, assuming that the soil surface is represented by $\equiv SOH$ in the pH range 4 to 7. More H^+ may be released if surface hydrolysis of the adsorbed Cu occurs:

$$\equiv SOH + Cu(H_2O)_6^{2+} \rightleftharpoons\ \equiv SOCu(H_2O)_4OH + 2H^+$$
$$+ 2H_2O \qquad [4]$$

or if two surface sites are involved in the surface hydrolysis (Eq. [2]) followed by the sharing of a Cu^{2+}, resulting in the release of two H^+

$$2 \equiv SOH + Cu(H_2O)_6^{2+} \rightleftharpoons\ (\equiv SO)_2Cu(H_2O)_4 + 2H^+$$
$$+ 2H_2O \qquad [5]$$

Reactions such as Eq. [4] have been found to be thermo-dynamically more favorable than Eq. [3] and [5] on mineral oxide surfaces (Davis and Leckie, 1978). Assuming similar characteristics with soil surfaces, Eq. [4] and [5] can each release more than one H^+ per mole of $Cu(H_2O)_6^{2+}$ adsorbed. But, the soil being very heterogeneous, many adsorption sites may not favor reactions such as Eq. [4] and [5]. The reactions occurring at the surface may, therefore, be summed up as a combination of Eq. [3], [4], and [5]. Thus, the number of H^+ released per $Cu(H_2O)_6^{2+}$ adsorbed may lie between one and two depending on the speciation of the metal and the surface charge characteristics (Kooner, 1993; Hayes and Leckie, 1987; Davis and Leckie, 1978). Davis and Leckie (1978) concluded that the models of Eq. [3] and [4] most likely explain the Cu adsorption patterns, with Eq. [4] becoming predominant at higher pH. Different concentrations of Cu were applied to the soil at different initial pH values and the soluble Cu and pH were measured following equilibration. As can be seen in Fig. 1, at all pHs the addition of 0.1 mmol Cu kg^{-1} soil produced the smallest pH shift. An increase in applied Cu concentration increased the pH shift as well. For example, for an initial soil pH of 7.2, the application of 0.1 mmol Cu kg^{-1} soil did not change the equilibrium pH significantly, while the pH dropped to 4.7 following the application of 25 mmol Cu kg^{-1} soil (other intermediate Cu applications showed intermediate trends). Hence, our results indicate that the amount of H^+ released into solution increases as the applied Cu concentration increases.

More Cu(II) remained in solution at higher initial applied concentration than at lower concentrations, i.e., the adsorption percentage was greater at lower concentrations. The availability of surface sites is pH dependent and therefore affects the adsorption of Cu. As the pH increases, the number of negative sites increases (Eq. [2]); therefore, Cu(II) that was available in solution at
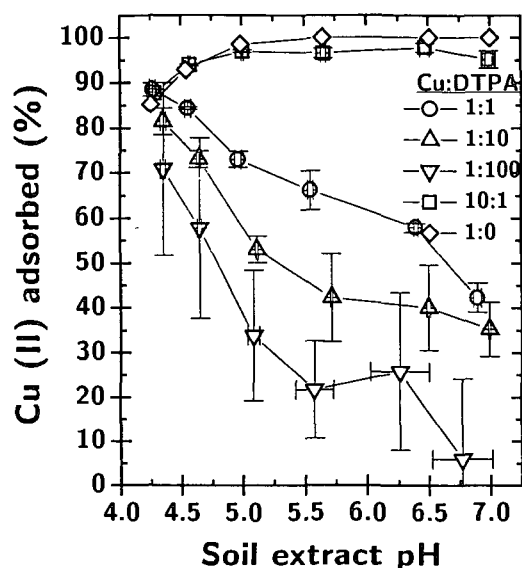
a lower pH adsorbs onto the new sites. If the sites available are insufficient for complexation and the pH is high, Cu(II) undergoes hydrolysis and precipitates as $Cu(OH)_2$, as is generally the case in aqueous solutions (Basta and Tabatabai, 1992b). In other words, surface-induced hydrolysis of Cu occurs—especially at lower concentrations. This phenomenon is strongly dependent on the relative concentrations of Cu^{2+} and the charged surface sites.

Effect of Relative Concentrations on Copper Solubility

In the presence of DTPA, Cu(II) solubility increased with an increase in pH (Fig. 2). However, this occurred only when [DTPA] $\geq$ [Cu^{2+}]. When [DTPA] $<$ [Cu^{2+}], Cu solubility followed the typical cation-like solubility trends as discussed above. The DTPA forms very strong complexes with Cu compared with any other inorganic ligands that might be present in the soil suspensions (Martell and Smith, 1974). Furthermore, DTPA could also form stronger complexes with Cu than with soil surfaces, thereby preventing Cu from sorbing onto the surface (McBride, 1994; McLean and Bledsoe, 1992). Equilibrium speciation calculations for [DTPA] = [Cu^{2+}] indicate that Cu remains complexed with DTPA for all pHs >4 (Fig. 3c). This implies that Cu exhibits
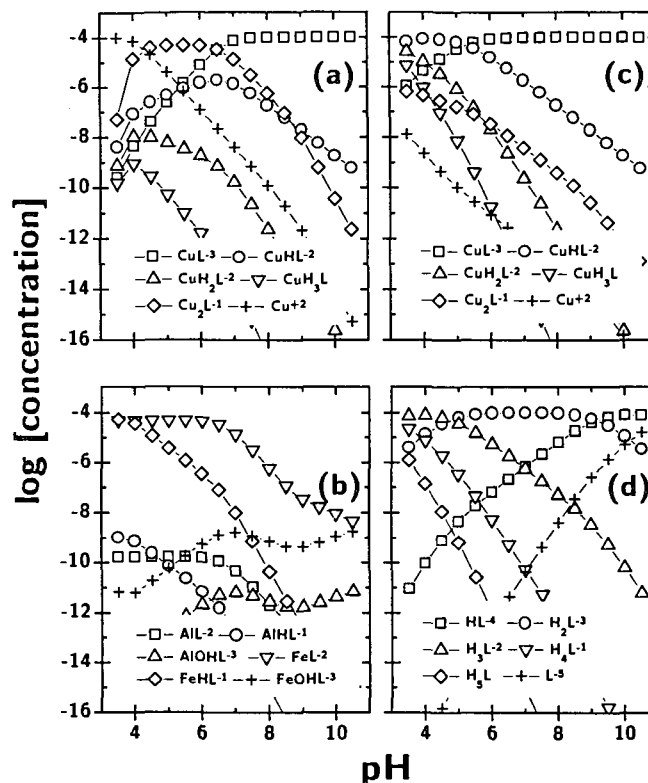
Fig. 3. Equilibrium aqueous speciation of Cu and DTPA in aqueous solutions ($Cu^{2+} = 10^{-4}$ M, DTPA = 10^{-4} M, and ionic strength = 0.01 M): (a) speciation of Cu in the presence of DTPA and Al(III) and Fe(III) solid phases, (b) speciation of Al and Fe for the previous case, (c) speciation of Cu in the presence of DTPA but without Al(III) and Fe(III) solid phases, and (d) speciation of DTPA without any other cations. Calculations were done with MINTEQA2 (Allison et al., 1991).

Fig. 2. The overall Cu^{2+} adsorption pattern as a function of Cu/DTPA and soil extract pH. All points are arithmetic means of results obtained in the three orders of addition of Cu and DTPA, with standard errors shown.

anion-like adsorption behavior (decrease in sorption with an increase in pH) in the presence of DTPA. This behavior has been observed for several metals in the presence of EDTA (which is expected to behave similarly to DTPA) on mineral oxides and soils by several researchers (Nowack and Sigg, 1996; Zachara et al., 1995; Bryce et al., 1994; Girvin et al., 1993; Bowers and Huang, 1986; Elliott and Denneny, 1982). Deprotonation of DTPA occurs as pH increases, i.e., it becomes more anionic in nature (Table 2, Fig. 3d). Also, the negative surface sites on the soil increase as the pH increases (Eq. [2]) implying that more DTPA becomes soluble due to unavailability of positive surface sites for its adsorption. This is supported by the fact that the CEC of the soil varies from 55 to 96 $mmol_c$ kg^{-1} soil and the AEC varies from 12 to 2 $mmol_c$ kg^{-1} soil in a pH range of 3.4 to 7.7 (Table 1). Compared with this, Cu additions ranged between 0.2 and 2.0 $mmol_c$ kg^{-1} soil, which is lower than than the AEC of the soil and much less than the CEC of the soil. The DTPA levels were 1.0 and 10 mmol DTPA kg^{-1} and their equivalents of charge depended on pH and concentration. That is, the anion-like behavior of Cu–DTPA complexes are strongly pH dependent. The Cu–DTPA complex formation and hence Cu solubility strongly depend on the availability of soluble DTPA at any given pH.

Although an increase in the solubility of Cu(II) accompanied an increase in DTPA concentration, not all added

Cu(II) became soluble. That is, some DTPA was still unavailable for complexing Cu. As observed from the results, a Cu/DTPA of 1:100 solubilized as much as 95% of the Cu^{2+} applied at pH 6.8, while a Cu/DTPA of 1:10 extracted only about 60% of the applied Cu^{2+} at the same pH (Fig. 2). This implies that other cations present in the soil suspensions such as Fe(III) and Al(III) were competing with Cu for DTPA. Figures 3a and 3b are the equilibrium aqueous speciation calculations for Cu and DTPA in presence of Fe and Al solid phases. Comparing Fig. 3a and 3c (in the presence and absence of Fe and Al solid phases, respectively), one can easily observe the change in speciation patterns.

At Cu/DTPA of 10, stoichiometrically 90% of Cu remains in solution as free Cu and hence the sorption behavior of this system would resemble the one observed in Fig. 1. If the anion-like adsorption behavior is true, one would expect a small increase in the sorption of Cu at low pH. This can be observed from Fig. 2 for a Cu/DTPA of 10:1 and 1:0. Also, the adsorption maxima never attained 100% in the case of Cu/DTPA of 10:1 and the Cu solubility seemed to slightly increase beyond pH 6.5. This is due to the presence of a small amount of DTPA in the system. This increase seemed to correspond to the decomplexation of DTPA with Fe(III) and Al(III) as one would expect from equlibrium aqueous speciation calculations (Fig. 3b).

Effect of Order of Application on Copper Solubility

Our observations indicate that the order of application of Cu and DTPA to the soil greatly influenced Cu solubility under quasi-equilibrium conditions (Fig. 4). Three discrete phenomena occur if one considers a system consisting of three components (DTPA, Cu(II), and soil). As the pH of the solution increases, (i) DTPA deprotonates, (ii) soil surfaces become increasingly negative, and (iii) Cu hydrolyzes. The combination of phenomena (ii) and (iii) has already been discussed above. Solubility patterns resulting from the combination of all three of these factors are considered here. The order in which each of these occurs affects the final Cu solubility. The type of reactions between Cu^{2+}, DTPA, and the soil surfaces that occur in these three orders result in different intermediates, which may orient differently at the soil surface and hence affect the Cu solubility patterns (Schindler, 1990). Also, the speciation of each of these components varies in each of these orders.

The results obtained from these three orders are summarized in Fig. 4. First, compare Fig. 4a and 4b where Cu(II) applied is 1.0 mmol kg^{-1} while DTPA concentration is 10 times less than (Fig. 4a) and equal to that of Cu (Fig. 4b). The pH has very little effect on Cu solubility across the whole pH range in Fig. 4a, while it has a strong effect on Cu solubility in Fig. 4b. This clearly indicates the influence of DTPA on Cu solubility irrespective of the order of application. Also note that the Cu solubility remains nearly constant in all the three orders. Now, compare Fig. 4c and 4d [both at Cu(II) of 0.1 mmol kg^{-1}]. Increasing Cu/DTPA from 1:10 to 1:100
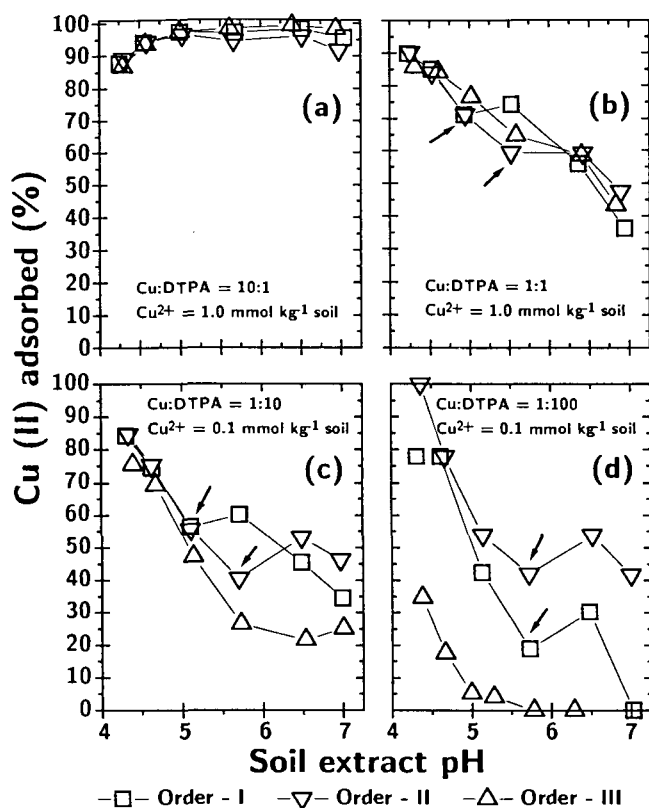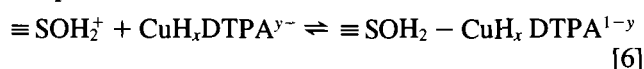
Fig. 4. Copper adsorbed onto the soil as a function of Cu/DTPA, soil extract pH, and mode of application of Cu^{2+} and DTPA to the soil. The arrowheads point to the change in solubility patterns. Note: all points are arithmetic means of triplicate results. All standard errors of the means are smaller than the data points.

affects the Cu solubility the most in Order III (DTPA first) and the least in Order II (Cu first). These results are important in that they show that at low levels of Cu addition (0.1 mmol kg^{-1}), increasing DTPA level and changing the order of application strongly affect the Cu retention, but at higher levels of Cu, a different pattern is observed.

In Order I, Cu^{2+} and DTPA were mixed and then applied to the soil, i.e., Cu already exists as a Cu–DTPA complex before it comes in contact with the colloid surface. Equilibrium aqueous speciation calculations with MINTEQA2 (Allison et al., 1991) predicted that Cu is mostly present as Cu–DTPA complexes when [DTPA] $\geq$ [Cu^{2+}] (Martell and Smith, 1974). The species CuDTPA^{3-} and CuHDTPA^{2-} predominate in the pH range of 4 to 7 (Fig. 3c). Hypothetically, the Cu–DTPA complexes can adsorb on soil surfaces as follows:

$$\equiv SOH_2^+ + CuH_xDTPA^{y-} \rightleftharpoons \equiv SOH_2 - CuH_x DTPA^{1-y}$$
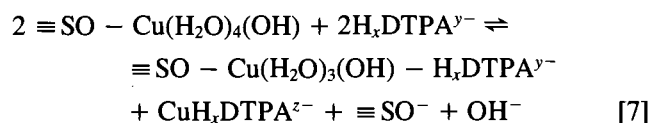[6]

This reaction denotes the formation of a ternary Cu–DTPA complex at the surface, where x and y are 0, 3 or 1, 2, respectively. As positive complexation sites are required, this reaction is favored at low pH (where soil surfaces are predominantly positive), i.e., the complex will exhibit anion-like behavior.

Orientation of these complexes may be another important factor. An orientation of the ligand closer to the soil surface is favored when the soil has a predominantly positive charge, while an orientation with Cu^{2+} closer to the soil surface is favored when the surface charge is negative (Elliott and Huang, 1979). While this is applicable in the case of ion-pair formation, more specific interactions such as ligand exchange are possible at the surface. If ion pairs are formed, no adsorption may be seen at any pH. But this is not the case, as can be seen in Fig. 4. This may be attributed to: (i) specific adsorption of these complexes, particularly at low pH (irrespective of surface charge), (ii) some Cu^{2+} not remaining complexed with DTPA when the complexes contact the soil surfaces (decomplexation and hydrolysis), and (iii) some DTPA applied being unavailable for complexation either because of its adsorption onto soil surfaces or due to dissolution of other cations such as Al and Fe(II, III) from soil minerals and their competition with Cu for DTPA, particularly in low-pH regions. As is the case with most organic anions, DTPA desorbs from soil surfaces as pH increases, i.e., more DTPA is available for Cu complexation. This explains to a certain extent the increase in the solubility of Cu(II) in the presence of DTPA as pH increased. The higher the DTPA applied relative to initial Cu^{2+}, the higher the solubility (Fig. 2 and 4). This is due to the fact that more DTPA remains in solution in spite of some of it being subjected to specific sorption. As Cu/DTPA ratio increased, less DTPA was available for complexation, resulting in the hydrolysis and sorption of Cu^{2+} by the soil.

In Order II, Cu^{2+} contacted the soil first, and following equilibration, DTPA was added. When DTPA is applied in the second stage, it may complex with the sorbed or precipitated Cu(II) followed by either the formation of

a ternary complex at the surface or desorption of Cu(II) from the soil surface and subsequent soluble Cu–DTPA complex formation. The following reaction is suggested for the second stage of Order II, while the first stage is represented by Eq. [4]:
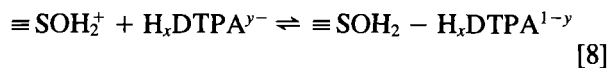
$$2 \equiv SO - Cu(H_2O)_4(OH) + 2H_xDTPA^{y-} \rightleftharpoons$$
$$\equiv SO - Cu(H_2O)_3(OH) - H_xDTPA^{y-}$$
$$+ CuH_xDTPA^{z-} + \equiv SO^- + OH^-$$
[7]

where x, y, and z are 2, 3, 1 or 3, 2, 0, respectively, depending on the equilibrium pH. The results indicate that Cu desorption from the surface occurred as pH increased. Due to more specific interaction with the soil surface or due to slower Cu desorption kinetics than in the other orders, less Cu(II) remained in solution in Order II, especially at higher pH (Fig. 4). For instance, for a Cu/DTPA of 1:100 at a pH of 7.0, about 60% of applied Cu^{2+} remained soluble, compared with nearly 100% in the other two orders. A similar trend was observed at all Cu/DTPA ratios. When Cu(II) is specifically complexed with the soil surface, a greater activation energy is required for desorption than is required for adsorption. The rate of desorption of the applied Cu is slower than the rate of sorption and therefore more time is required to be able to extract as much Cu as in Order I (McBride, 1991). Hering and Morel (1990) have shown that the kinetics of metal exchange by complexing agents on heterogenous surfaces is very complex and time scales can be very large. In the other orders, Cu(II) was not sorbed specifically to the surface (either Cu is already complexed or DTPA was applied to the soil first, preventing specific interaction of Cu with the soil) and therefore this was not observed. This also leads to the observation that uniform equilibrium conditions did not exist in all these orders.
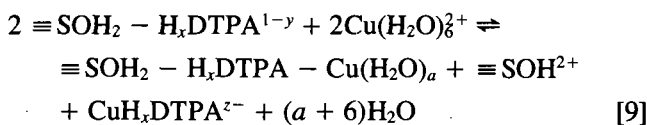
A decrease in Cu solubility with an increase in pH in the presence of DTPA (arrowheads in Fig. 4) was observed for Orders I and II in the pH range of 4.7 to 5.7. In this pH region, Fe and Al from soil mineral constituents may have dissolved into the solution. As can be seen from Table 2, Fe and Al form very strong complexes with DTPA and could easily compete with Cu for the available DTPA (also compare Fig. 3a and 3c). If some Cu decomplexes due to this, it hydrolyzes and sorbs onto the soil and hence the solubility decreases. This type of metal behavior in the presence of EDTA has been observed on mineral oxide and soil surfaces by several researchers (Nowack and Sigg, 1996; Zachara et al., 1995; Girvin et al., 1993; Jardine et al., 1993; Bowers and Huang, 1986; Elliott and Denneny, 1982). This decrease also seemed to correspond with pK_3 (4.7) of DTPA and with pH where [CuDTPA^{3-}] and [CuHDTPA^{2-}] are equal (Fig. 3c). The decrease in the solubility may be occurring due to the transition from a lower negative charge (CuHDTPA^{2-}), to a higher one (CuDTPA^{3-}).

In Order III, DTPA was applied to the soil in the first stage, followed by the application of Cu^{2+} in the second stage. As shown in Fig. 4, the amount of Cu adsorbed decreased significantly in some cases, compared with

Orders I and II. We postulate that DTPA sorbed to the soil surface during the first stage. When Cu was applied to the soil–DTPA solution, most of the Cu was effectively left out of complexation with soil surfaces. The following hypothetical mechanisms are proposed:

$$\equiv SOH_2^+ + H_xDTPA^{y-} \rightleftharpoons \equiv SOH_2 - H_xDTPA^{1-y} \tag{8}$$

This is a possible reaction in the first stage where x, y are 2, 3 or 3, 2, respectively.

$$2 \equiv SOH_2 - H_xDTPA^{1-y} + 2Cu(H_2O)_6^{2+} \rightleftharpoons$$

$$\equiv SOH_2 - H_xDTPA - Cu(H_2O)_a + \equiv SOH^{2+}$$

$$+ CuH_xDTPA^{z-} + (a + 6)H_2O \tag{9}$$

Equation [9] denotes a second-stage reaction at the soil surface where x, y, z, a are 2, 3, 1, 4 or 3, 2, 0, 5, respectively. Complexation of DTPA at the surface is favored at low pH where more positive surface sites may exist (Eq. [1]) The addition of Cu^{2+} at a later stage may result in a mechanism suggested by Eq. [9], which is similar to Eq. [7] with the exception that DTPA acts as bridge between the soil surface and Cu. Hence, the solubility patterns in Order III were not similar to those of the other orders. The amount of Cu(II) remaining in solution in this order increased as Cu/DTPA decreased and was much higher than the corresponding values from the other orders (Fig. 4). Surface coordination of DTPA may have prevented Cu from binding with the soil.

As indicated in Fig. 2, averages of Cu solubilities in the three orders increased as Cu/DTPA decreased, with the highest variability for a ratio of 1:100. The average "equilibrium" pH for similar Cu and DTPA applications was also affected. The largest variations observed were for Cu/DTPA of 1:100, which also increased with an increase in the "equilibrium" extract pH. Overall, the maximum variation was due to the patterns from Order III. We also did not observe a decrease in solubility in Order III in the pH range of 4.7 to 5.7, as was the case in the other two orders (arrowheads in Fig. 4), suggesting that the application of DTPA to the soil altered the soil properties. The surface charge may have been redistributed sufficiently to change the solubility patterns within the working pH range. The pH$_{ZPC}$ of soil is known to shift due to charge modification by electrolytic ions (McBride, 1989).

Thus our results indicate that the order of application of Cu and DTPA can significantly influence the solubility of metals in complex systems. Furthermore, Cu is known to complex with natural organic matter (NOM) very strongly (Harter, 1983; Oates and Kamprath, 1983). Also, NOM dissolves easily in organic solvents (Schwarzenbach et al., 1993). This could result in preferential binding of DTPA with NOM and thereby affecting Cu solubility. In addition, some indigenous Cu associated with the NOM may have been displaced by DTPA if it prefers similar surface sites. The NOM compounds are also more soluble at higher pH than at lower pH. When DTPA was in contact with the soil in Order III, some organic fractions in the soil may have dissolved and increased the organic acid available for solubilizing Cu. This

is in addition to the normal desorption of DTPA from the surface with an increase in pH. The dissolved NOM may also complex Al and Fe(II, III) and hence the decrease in Cu solubility similar to the other orders will not be discernible. This was clearly observed (Fig. 4).

Effect of the Background Electrolyte

In all the experiments, KNO₃ was added to the soil at a concentration of 0.01 M to simulate the ionic strength of a well-drained soil (Lindsay, 1979). However, to observe the effect of ionic strength on the Cu adsorption patterns, a series of experiments was conducted varying the concentration of KNO₃ and the soil pH (in the presence and absence of DTPA). The results showed a clear change in the solubility patterns of Cu(II) and the solution pH as a function of the KNO₃ concentration (Fig. 5). A change in the K^+ concentration may be accompanied by a change in the thickness of the electric double layer at the soil–water interface. Increase in K^+ increases the ion density within the double layer (diffuse layer). This is accompanied by H^+ displacement from the surface by increasing K^+ concentration close to the soil surface and resulting in a pH reduction. This was clearly observed from the experiments (Fig. 5). As the concentration of K^+ increased, the pH decreased. The pH stabilized between the concentrations of 10^{-3} and 10^{-4} M KNO₃ soil around pH 6.1 to 6.3, indicating that the ionic strength of the original soil solution was in this region. The presence of DTPA (at 1.0 mmol kg^{-1} soil) in a similar setup did not considerably affect the soil pH (Fig. 5).

The adsorption patterns of Cu were affected accordingly in the presence and absence of DTPA. This behavior may be an indirect effect of pH, which in turn
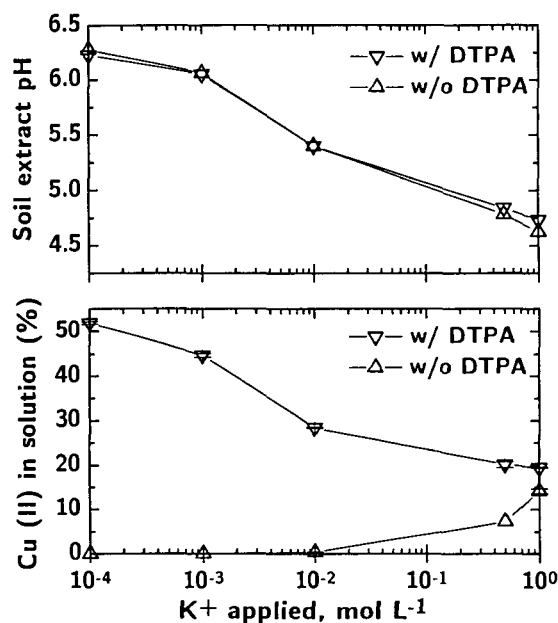

Fig. 5. Effect of varying ionic strengths on Cu(II) remaining in solution and the extract pH with and without DTPA. The pH values correspond with the percentage of Cu(II) remaining in solution. Starting Cu^{2+} = 1.0 mmol kg^{-1} soil and DTPA = 1.0 mmol kg^{-1} soil. Note: all points are arithmetic means of triplicate results. Standard errors smaller than data points do not appear.

was affected by K^+ applied. As K^+ decreased (i.e., pH increased), the adsorption of Cu(II) increased or decreased in the absence and presence of DTPA, respectively, for reasons explained above. At a K^+ of 0.1 M (equilibrium pH of 4.7), 15 and 20% of applied Cu^{2+} remained soluble in the absence and presence of DTPA, respectively. But, at a K^+ concentration of $10^{-4} M$ (equilibrium pH of 6.2), 0 and 52% of the applied Cu^{2+} remained soluble in the absence and presence of DTPA, respectively (Fig. 5). This difference in Cu solubility cannot be specifically attributed either to the direct effect of the presence of K^+ or to the indirect effect of pH. To determine this nature, the solubility patterns from the solubility and background electrolyte studies have been compared in Fig. 6. For 85% of applied Cu^{2+} adsorbed, the H^+ released was less in electrolyte studies (by 0.4 pH units). Shuman (1986), Elliott and Huang (1985), Petruzelli et al. (1985) concluded, however, that an increase in ionic strength results in higher metal solubility. The trend in the presence of DTPA showed a similar difference at some percentage of Cu(II) adsorbed (high pH) (Fig. 6a). At high background electrolyte concentrations, the K^+ in solution may compete with Cu^{2+} for complexation with DTPA and adsorption sites due to sheer numbers though Cu-DTPA complexes are more stable than K-DTPA complexes (Table 2). If K^+ competes with Cu^{2+} for DTPA, less DTPA is available for complexation and hence Cu solubility decreases. However, if K^+ competes with Cu^{2+} for adsorption sites, it could result in two totally different patterns: (i) more Cu^{2+} is released into solution because of displacement

from the surface, i.e., increase in Cu solubility (alteration of free energy of adsorption) (Elliott and Huang, 1985) and (ii) DTPA may be adsorbed onto the soil surface due to the increased positive sites created by the K^+ adsorption onto the surface (Davis and Leckie, 1978), i.e., reduction in Cu solubility. At a pH of 6.2, about 48% of applied Cu(II) was measured in solution during background electrolyte experiments, while about 62% of applied Cu(II) was in solution during adsorption experiments. This decrease during ionic strength experiments may hence be due to K^+ competition with Cu^{2+} for complexation by DTPA.

CONCLUSIONS

The presence of strong chelating agents affected Cu solubility in soils as a function of various environmental parameters. The quasi-equilibrium solubility strongly depended on soil pH, the absolute and relative concentrations of Cu^{2+} and DTPA, the concentration of the background electrolyte, and most importantly the order of application of these components to this soil. Copper solubility in the soil increased or decreased in the presence or absence of DTPA, respectively, as the soil pH increased. When DTPA $\geq Cu^{2+}$, the Cu solubility pattern exhibited anion-like behavior. This became more evident with an increase in DTPA relative to Cu. This was attributed to increased availability of DTPA, which promotes Cu solubility patterns especially at high pH. Also, the differences in Cu solubility between the three orders of application increased as DTPA increased relative to Cu(II) applied. Depending on when each of the main components contacted the soil surface, the nature of interactions at the soil surface changed significantly. The highest solubility was observed when the soil was preequilibrated with DTPA before the application of Cu^{2+}.

The study was based on quasi-equilibrium processes with almost 100% of the applied Cu^{2+} remaining in solution in some orders of application. This may not be the case in long-term studies where kinetics and aging processes could play a very important role. Another implication of this study is the nonsuitability of equilibrium models used in risk assessment and remediation technology feasibility studies. Since equilibrium conditions are rarely reached within a short period of time, the metal solubility may be over- or underestimated.
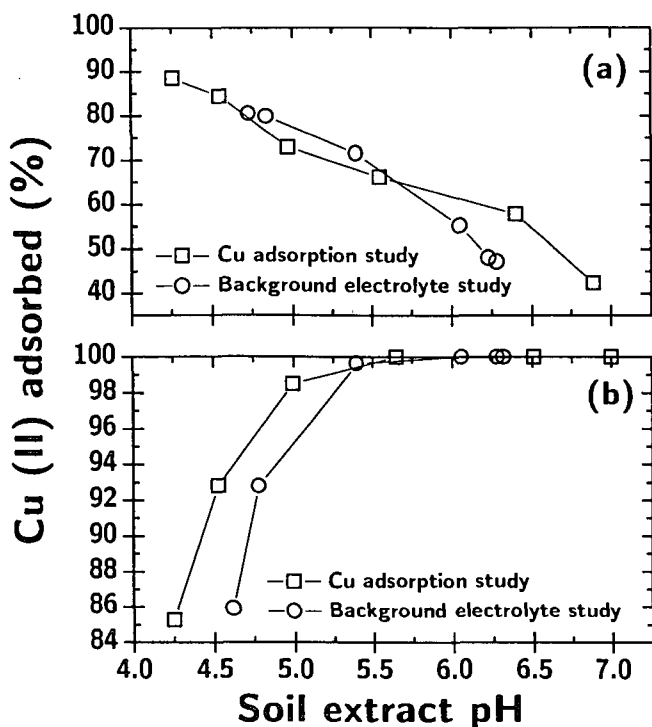

Fig. 6. Comparison between solubility patterns obtained during ionic strength and solubility studies in the (a) presence of DTPA at Cu/DTPA = 1:1 and Cu^{2+} = 1.0 mmol kg^{-1} soil and (b) absence of DTPA at Cu^{2+} = 1.0 mmol kg^{-1} soil.

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