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SOLUBILITY RELATIONSHIP OF COPPER IN CALCAREOUS SOILS

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In the present study, Cu activities in 12 calcareous soils were obtained by chelation. The Cu activities (pCu) ranged from 11.5 to 13.0. A positive correlation between $CaCO_3$ concentration and Cu^{2+} activities was observed, whereas negative correlation was found with Fe_2O_3. Direct identification of solid phases controlling Cu solubility in these soils has not been achieved. From the solubility isotherms, it became evident that in most soil solutions, the concentration of Cu was much lower than that determined by the solubility of inorganic precipitates of hydroxides or carbonates. A significant positive correlation between Cu^{2+} and Fe^{3+} activity does suggest some kind of mechanism which involves copper and iron but which is independent of pH. However, formation of cupric ferrite ($CuFe_2O_4$) is unlikely as the shape of the isotherm does not support this hypothesis.

INTRODUCTION

The mechanism that controls the Cu solubility relationships in soils is poorly understood. Experimental studies are hampered by low concentrations of soluble Cu and by the presence of uncharacterized inorganic and organic complexes of Cu, especially in well-aerated soils in the neutral to alkaline pH range. These problems can be partially overcome by the chelation method of Norvell and Lindsay (1982). With this method, a well-characterized complexing or chelating agent is added to a soil suspension, the activity of one of the metal is determined, and the activity of the second metal is calculated from the ratio of the two chelated metal species of those metal ions. This method is effective for obtaining free metal cation concentrations or activities in neutral or alkaline soils.

Previous studies have measured Cu adsorption in neutral and alkaline soils, which may show Cu deficiency (McLaren and Crawford, 1973 a; Cavallaro and McBride, 1978) and in acid soils where toxicity is likely to occur (McBride and Blasiak, 1979). Copper adsorption in soils is affected by soil pH, clay minerals, iron and manganese oxides, organic matter and carbonates (McBride, 1981). The mechanisms and specific ion species involved in Cu adsorption are not still fully understood. Adsorption mechanisms suggested to include specific adsorption (McLaren and Crawford, 1973 b) or physisorption and chemisorption (McBride and Bouldin, 1984). One of the major problems in studying Cu adsorption in soils has been the failure to consider which of the various species of Cu in solution are sorbed.

In most studies, concentrations of free Cu have not been measured. Usually total concentrations have been used directly or total Cu has been speciated using only inorganic models. Lindsay and Norvell (1969) used the following empirical relationship to express the Cu activity relationships:

$$\text{Soil - Cu} + 2H^+ \rightleftharpoons Cu^{2+}$$

Their results gave a log K^O for this reaction of 2.8.

Rearranging this equilibrium reaction:

$$\log (Cu^{2+}) = 2.8 - 2\,pH$$

Our objective was to obtain activities in calcareous soils using the chelation method to see if the soil-Cu solubility relationships reported earlier are observed generally in calcareous soils. A modification of the original chelation method was used in this study.

MATERIALS AND METHODS

Twelve calcareous soils from 6 series from England and Pakistan were chosen for this study (Table 1). The soils were air-dried and passed through 2 mm stainless steel sieve and stored in polyethylene-lined containers. Solutions ranging from 0 to 1 mole fraction (MF) of EDTA as Cu-EDTA were prepared. Reagent-grade Na_2H_2EDTA (99.7% assay) was used to prepare the EDTA-chelate solutions. The ^{14}C-labeled EDTA (^{14}C in carboxyl groups) was added to give a solution with 4.92×10^8 Bq mol^{-1} of EDTA. Calcium was used as the counter ion to saturate the remaining EDTA not complexed with Cu. The chelate solutions were all adjusted to pH 7.0 initially using dilute HCl or KOH.

Soil suspensions were prepared which contained 25 g of soil and a final suspension volume of 50 ml. The soils suspension were aerated with moist air and shaken vigorously two or three times daily in the dark at 25 ± 1 ° C except for the experiment which was conducted in the closed system. All suspensions were shaken for 7 days before the EDTA chelate were added because earlier experiments (Chaudhri, 1989) showed that appreciable quantities of Mn temporarily entered the solution for 2 or 3 days when the air-dry soils were first wetted. Experiments continued for an additional 14 days after EDTA chelates were added to allow equilibrium to be approached as established in earlier experiment (Chaudhri and Rowell, 1991). A few drops of chloroform were also added to check the microbial growth. The initial EDTA concentrations in all the cases was 100 μM. Deionized distilled water plus soil was used as the blank treatment.

Suspensions pH was measured immediately after the reaction period, for it approximates the pH of the solution better than filtrate pH. Clear supernatants were obtained by centrifuging for 20 minutes at 3000 rpm and electrical conductivity was measured. A portion of the solution was finally passed through XAD-2 resin for the separation of organically complexed metals. This treatment was not given in the closed system. Supernatants were analyzed for cations by atomic absorption spectrophotometer using appropriate standards. The total concentration of ^{14}C-labeled EDTA was determined by radioassay with a liquid scintillation spectrophotometer.

Measured concentrations of Cu, Zn, Fe and Mn were assumed to represent their respective EDTA chelates because these metals form stable chelates leaving little free cation. The concentration of Ca-EDTA was estimated as the difference between total EDTA and the EDTA chelates of Cu, Zn, Fe and Mn. Changes in the concentrations of Cu-EDTA and Ca-EDTA chelates were used to obtain the unique ratio of chelated metals that neither lost nor gained Cu and Ca from the chelate. A range of initial mole fraction (MF) of Cu-EDTA and Ca-EDTA was used so that equilibrium could be approached from both undersaturation and supersaturation that is Cu could be either gained or lost from solution. The equilibrium speciation of EDTA chelates, in combination with chemical analyses of the soil solution, provided the information needed to calculate the concentration of Cu^{2+} in equilibrium with soil. The expression for calculating the free metal ion concentrations was derived by taking the ratio of appropriate chelate reactions as outlined by Lindsay and Norvell (1969). For example, the expression for calculating the concentration of Cu^{2+} has the form:

$$\begin{array}{lclll} Cu^{2+} + L^{4-} & == & CuL^{2-} & K^{m}_{CuL} & (3) \\ Cu^{2+} + CaL^{2-} & == & Ca^{2+} + L^{4-} & -K^{m}_{CaL} & (4) \\ \hline Cu^{2+} + CaL^{2-} & == & CuL^{2-} + Ca^{2+} & K^{m}_{cul} - K^{m}_{CaL} & (5) \end{array}$$

Rearranging Eq. (5) gives:

$$[Cu^{2+}] = \frac{[CuL^{2-}]\,[Ca^{2+}]\,10^{-8.09}}{[CaL^{2-}]} \qquad (6)$$

where L represents the free EDTA ligand, brackets indicate molar concentrations and K^m for the indicated species is the mixed equilibrium constant expressed in terms of concentrations (except for H, OH and e^-, which if present, are expressed as activities). The formation constants for EDTA were selected from those compiled by Lindsay (1979). Similar expressions were derived for computing the concentrations of other metal ions.

Measured inputs to Eq. (6) included [Ca], [CuL] and [CaL]. Total EDTA in the soil extract was taken as the sum of all metal chelate concentrations, including [CaL], [FeL], $[Fe(OH)L^{2-}]$, $[CuL^{2-}]$, $[ZnL^{2-}]$ and $MnL^{2-}]$ (Lindsay, 1979). Thus, [CaL] was obtained by difference, i.e. total EDTA concentration minus the sum of all metal chelates (Table 2). The concentration of Ca^{2+} was obtained by difference between the total calcium determined in the solution and the CaL^{2-}. Values for [CuL] were taken as the total soluble Cu measured by atomic absorption spectrophotometer. The final Cu MF in the filtrate, expressed as [CuL]/([CaL] + [CuL]), were plotted against the initially added Cu MF. The point of intersection of these lines represents the equilibrium Cu MF, or the unique Cu MF such that no loss or gain of Cu from the solution occurred (Lindsay, 1979). Graphs were obtained for each of the 12 soils for each system. A typical example for the Tandojam (P-31) soil is given in Figure 1.

The ratio of [CuL]/[CaL] needed to solve Eq. (6) was obtained from the equilibrium Cu MF estimated from the graph, and Cu concentration was then calculated (Eq. 6). Formation constants for the EDTA metal chelates were taken from Lindsay (1979) and corrected for the ionic strength using the Debye-Huckle equation.

RESULTS AND DISCUSSION

The total concentrations of EDTA, Cu, Zn, Fe and Mn, suspension pH, initial Cu MF and calculated final Cu MF for the Tandojam soil are presented in Table 2. Similar data on suspension pH concentration of Ca^{2+}, equilibrium mole fractions of CaL^{2+}, CuL^{2+}, ZnL^{2+}, FeL^{2+} and MnL^{2+} and negative logarithm (pM) values of Cu^{2+}, Zn^{2+}, Fe^{3+} and Mn^{2+} activities for the 12 soils are summarised in Table 3. Under the present experimental conditions, pH bore no

Table 1. Physical and chemical properties of the soils

Soil series	Soil number	Particle size analysis: Sand	Silt	Clay	pH: H_2O	0.01 M $CaCl_2$	Total $CaCO_3$	Organic matter	Free Fe as Fe_2O_3	Free Mn oxides
		(%)	(%)	(%)			%	%	%	%
Wantage	(A-1)	37.5	20.0	42.5	7.22	7.00	6.8	10.04	0.76	0.42
Wantage	(B-5)	35.5	22.0	42.5	7.57	7.40	16.4	3.75	0.59	0.28
Blewbury	(C-7)	41.5	28.5	30.0	7.27	7.02	24.3	21.68	0.82	0.16
Blewbury	(C-10)	40.3	27.0	32.5	7.27	7.11	23.6	16.88	0.66	0.27
Broad	(C-13)	49.0	13.5	37.5	7.28	7.08	1.1	10.31	7.82	0.24
IcKnield	(F-17)	50.5	29.5	20.0	7.98	7.60	12.5	12.68	3.48	0.86
Upton	(G-20)	44.0	36.0	20.0	7.88	7.50	51.1	10.21	1.12	0.23
Tandojam	(P-31)	31.4	22.4	46.2	8.24	7.86	8.5	3.31	0.89	0.04
Churn Farm	(C-0)	60.2	17.0	22.8	7.88	7.58	58.0	10.15	1.34	0.46
Chrun Farm	(C-1)	70.0	17.3	12.7	8.04	7.63	78.0	4.74	0.44	0.10
Chrun Farm	(C-2)	50.8	19.4	29.8	8.03	7.65	74.0	6.12	1.08	0.31
Churn Farm	(C-3)	76.2	9.8	14.0	8.12	7.75	48.0	5.22	0.59	0.15

Table 2. Solution composition for soil P-31 (Tandojam soils) by the variable mole fraction method (XAD-2 resin treated and open system)

Initial mole fraction of Cu-EDTA	pH	EDTA	Cu	Zn	Fe	Mn	Cu	Zn	Fe	Mn ($\times 10^{-3}$)	Ca	Mg	Na	K
		µM	µM	µM	µM	µM	Final mole fraction	Final mole fraction	Final mole fraction	Final mole fraction	mM	mM	mM	mM
0.000	8.57	99.2	1.84	3.24	1.81	0.063	0.018	0.032	0.018	0.64	0.56	0.16	0.96	0.11
0.062	8.56	98.8	3.24	3.54	1.76	0.065	0.032	0.036	0.017	0.66	0.58	0.17	0.98	0.13
0.125	8.55	97.4	5.66	3.88	1.73	0.072	0.058	0.039	0.017	0.74	0.61	0.19	1.14	0.14
0.250	8.58	97.7	10.56	4.29	1.52	0.145	0.108	0.043	0.015	1.48	0.67	0.20	1.13	0.15
0.375	8.52	97.5	15.77	3.18	1.46	0.165	0.162	0.032	0.015	1.69	0.65	0.18	1.12	0.13
0.500	8.49	95.3	18.77	2.81	1.37	0.182	0.197	0.029	0.014	1.91	0.64	0.19	1.15	0.12
0.750	8.54	97.3	25.15	2.61	1.34	0.164	0.258	0.027	0.014	1.68	0.66	0.21	1.13	0.16
1.000	8.41	97.3	25.95	1.68	1.09	0.182	0.266	0.017	0.011	1.87	0.64	0.20	0.12	

Table 3. Composition of soil solution after 14 days equilibrium of soils with Cu-EDTA of graded mole fractions (H_2O preequilibirated and XAD-2 resin treated open system)

Soil type	pH (suspension)	Total Ca	10^3 Ca^{2+}	Equilibrium mole fraction of metal complexes				Negative logarithm of metal ion activities				
				Ca	Cu	Zn	Fe	Mn	pCu^{2+}	pZn^{2+}	pFe^{3+}	pMn^{2+}
(A-1)	8.08	1.81	1.778	0.319	0.0035	0.014	0.033	0.53	12.95	10.08	18.94	5.88
(B-5)	8.36	1.67	1.639	0.336	0.0030	0.019	0.020	0.52	13.06	10.00	19.19	5.93
(C-7)	8.14	1.80	1.778	0.215	0.0040	0.018	0.190	0.35	12.73	9.82	18.04	5.90
(D-10)	8.17	2.15	2.121	0.294	0.0019	0.011	0.110	0.38	13.11	10.09	18.33	5.92
(E-13)	8.18	2.89	2.887	0.021	0.0039	0.016	0.310	0.27	11.51	8.62	16.57	4.78
(F-17)	8.23	2.41	2.397	0.098	0.0035	0.009	0.099	0.66	12.30	9.63	17.80	5.13
(G-20)	8.31	1.67	1.665	0.044	0.0020	0.012	0.300	0.49	12.34	9.31	17.12	5.07
(P-31)	8.53	0.63	0.542	0.896	0.0250	0.035	0.018	0.0013	13.02	10.62	20.10	9.42
(C-0)	8.22	2.66	2.630	0.300	0.0024	0.009	0.080	0.52	12.91	10.07	18.34	5.68
(C-1)	8.18	1.57	1.504	0.660	0.0017	0.140	0.105	0.046	13.62	9.45	18.78	7.30
(C-2)	8.12	1.83	1.756	0.737	0.0012	0.071	0.068	0.068	13.77	9.74	18.98	7.13
(C-3)	8.04	1.54	1.454	0.860	0.0017	0.100	0.013	0.0017	13.74	9.72	19.80	8.84

correlation with metal ion activities, whereas organic matter showed a negative correlation only for Cu^{2+}, Fe^{3+} and Mn^{2+} ion activities (Table 4). The Cu^{2+} ion activities were influenced more by organic matter contents than that by the pH while the opposite trend was observed for Zn^{2+} ion activities. It seems that in an alkaline medium both the factors (pH and organic matter) counter each other's effect. A positive correlation between $CaCO_3$ contents and Cu^{2+} ion activities was also observed.

Table 4. Correlation coefficients among soil properties and metal ion activities

Soil property	pH	Organic matter	$CaCO_3$	Fe_2O_3	MnO_2	Cu^{2+}	Zn^{2+}	Fe^{3+}
Organic matter	-0.339							
$CaCO_3$	-0.275	-0.256						
Fe_2O_3	-0.038	0.121	-0.431					
MnO_2	-0.057	0.218	-0.243	0.259				
Cu^{2+}	-0.218	-0.391	0.617*	-0.795**	-0.335			
Zn^{2+}	0.354	-0.102	-0.093	-0.715**	0.008	0.520		
Fe^{3+}	0.150	-0.540	0.137	-0.680*	-0.276	0.806**	0.767**	
Mn^{2+}	0.181	-0.555	0.225	-0.468	-0.504	0.691**	0.511	0.859***

*, **, *** significant at 5%, 1% and 0.1% levels of probability, respectively.

Iron oxide (ammonium oxalate extractable Fe_2O_3) was significantly related to the metal ion activities (Table 4). This showed that particularly for Cu and Zn, solubility in calcareous soils is very much dependent on the nature and amount of extractable iron oxides. Associations between copper and iron oxides have commonly been observed in soils (McKenzie, 1975; Childs and Lslie (1977), although no evidence was found for copper-manganese associations in these soils. On the other hand, McLaren and Crawford (1973 a) observed correlation between the quantities of Cu and Mn dissolved by the treatment of soil with oxalate which suggested that Cu associates more strongly with manganese oxides than iron oxides. Thus, the data regarding Cu-Mn and Cu-Fe associations often appear to be contradictory. However, the abundance of iron relative to manganese may give Cu a better opportunity to associate with iron rich secondary mineral phases in soils despite a very strong affinity of manganese oxides for Cu.

Oxides of Fe or Mn may show enhanced as well as inhibited adsorption for Cu^{2+} in the presence of soluble organics. Because of the ability of oxides to adsorb organic acids, including fulvic and humic acids by ligand exchange reactions (Parfitt *et al.*, 1977 a, 1977 b), the presence of these organics on oxides surfaces may enhance adsorption of Cu^{2+} if only a portion of functional groups are involved in bonds to the surface.

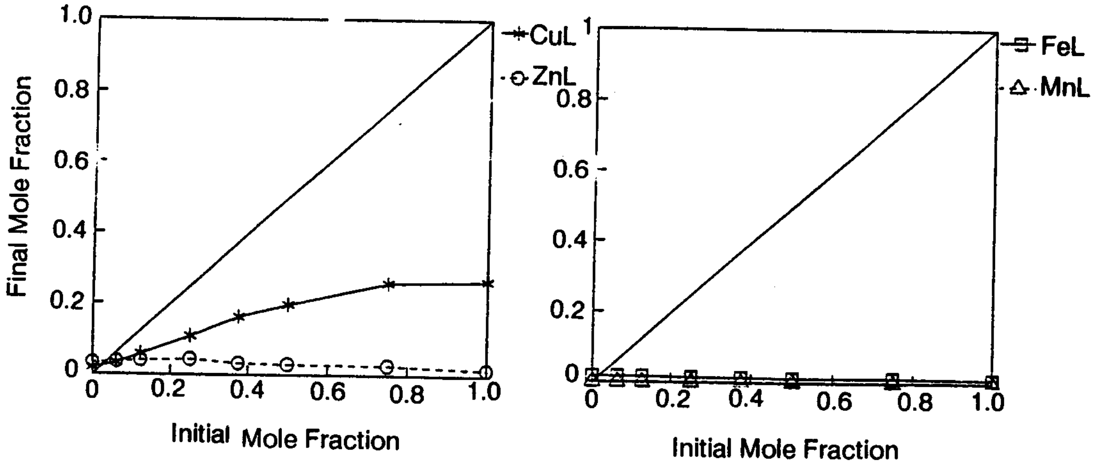

Fig. 1. Graphical method for estimating the equilibrium mole fractions of Cu, Zn, Fe and Mn for the Cu-EDTA (H_2O-preequilibrated open system). Data for Soil (P-31).

It would appear from these results that there are two opposing mechanisms controlling the solubility of copper in these soils. On the other hand, adsorption of copper by soil colloids tends to reduce its concentration in solution (i.e. less than 1% of the copper added to these soils remained in solution). On the other hand, soluble complexing agents compete with adsorption sites for free Cu^{2+} and thereby prevent its adsorption. Hence complexing is thought to be responsible for maintaining, or even increasing the total concentration of copper in the soil at pH values that would normally favour the removal of free Cu^{2+} ions from solution by precipitation or adsorption.

The effect of pH on Cu^{2+} ion activity in these soils is not clear, that is, correlation relationships are not significant (Table 4). One reason might be the narrow range of pH of equilibrium soil solution observed for these soils. Perhaps a difference of 0.5 pH would not significantly affect the Cu^{2+} ion activity in this high pH range. The other reason put forward for such a trend by several research workers (e.g. Hodgson *et al.*, 1966; McBride and Blasiak, 1979; Jarvis, 1981) is that any effect of pH on extractable copper is probably being masked by the larger contribution to copper in solution resulting from a fairly constant (i.e. irrespective of pH) part of the organically complexed copper pool.

Another dominant factor which emerged during the present investigation was that the solubility of Cu^{2+} in these soils was very much influenced by the solubility of Fe^{3+}. A significant positive correlation of 0.80 between Cu^{2+} and Fe^{3+} activities was observed. In an earlier investigation, Jahiruddin *et al.* (1986) reported that soils with a higher level of DTPA-extractable Fe tended to contain more DTPA-extractable Cu. The results suggest that either copper and iron are concurrently increasingly adsorbed or complexed by existing soil compo-

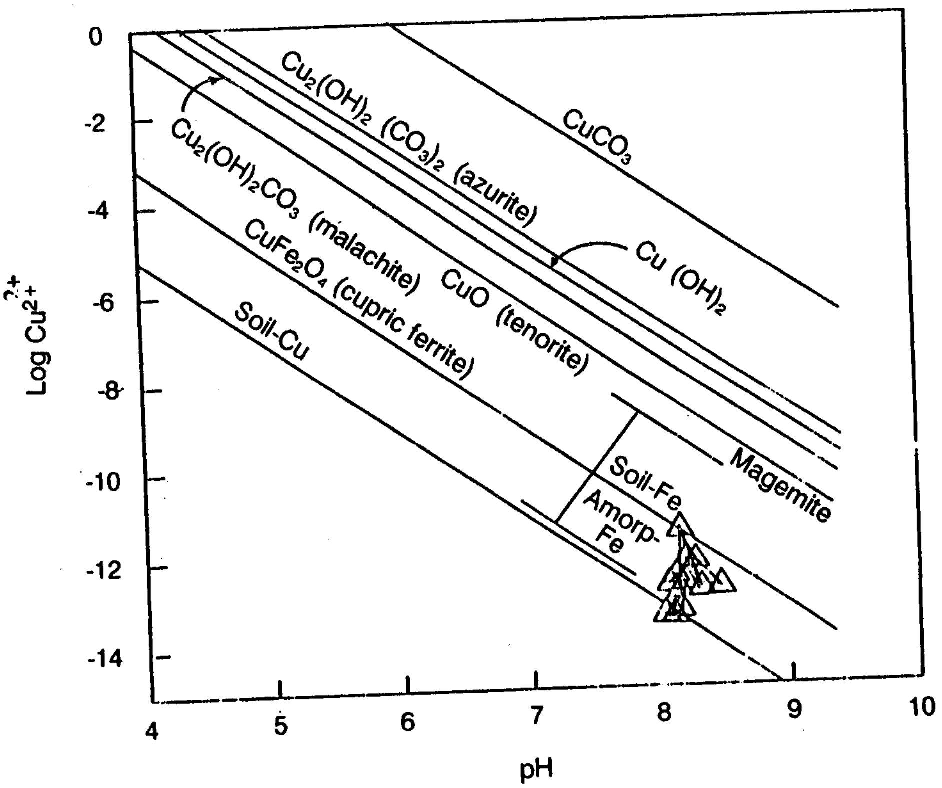

Fig. 2. Cu^{2+} activity in solution compared to solubility of various Cu-minerals and Soil-Cu. Data from 12 calcareous soils (Adapted from Lindsay, 1979).

nents with increasing pH. Precipitation-dissolution mechanisms are usually not considered to operate as controls on the concentrations of copper in soil solution as the solubilities of the common solid phase copper compounds are too high at the pH value of most soils.

The copper solubility data have also been plotted as a function of pH in Figure 2. Experimentally determined solubility lines of copper in soil solutions or in soil suspensions, usually lie below those of oxides, hydroxides and carbonate (McBride and Blasiak, 1979). Lindsay (1979) suggested that cupric ferrite ($CuFe_2O_4$) in equilibrium with iron oxides may control the solubility of Cu^{2+} ions in soil solution. The exact position of the cupric ferrite line depends on the form of iron oxide which is controlling the ferric ion concentration. Amorphous iron oxides are associated with higher levels of ferric ion in solution and at a given pH will result in the formation of cupric ferrite at a lower Cu concentration than will be by well-crystallised iron oxide, such as geothite, which results in a lower ferric ion concentration and hence a higher copper concentration. All of the cupric ferrite solubility lines lie in the region where control of Cu^{2+} in solution of alkaline and calcareous soils is possible by precipitation of the solid phase. The pCu values versus pH for the 12 calcareous soils studied are scattered within the area bounded by the lines of cupric ferrite and soil-Cu in equilibrium with amorphous iron oxide and soil-Fe (Fig. 2). If precipitation as the oxide etc. is dismissed because experimental data lie below their solubility lines, it can be argued that precipitation as a ferrite is feasible if the data lie below their solubility lines. Supporting evidence for some interaction between copper and iron comes from the observed correlation between copper and iron activities in solution.

The solubility diagram in Figure 2 shows that though the values for Cu^{2+} in these calcareous soils are scattered above the soil-Cu line, the formation of any discrete solid phase under the present experimental conditions is unlikely because of high organic matter contents, high pH and the low level (10^{-4} M) of copper addition. Similar results about other elements in soils show that solution concentrations of these elements cannot be explained by solubility isotherms (Vlek and Lindsay, 1977; Brummer *et al.*, 1983). Thus, it can safely be assumed that surface adsorption through ligand exchange controls the solubility of copper in these soils. Our data for Cu^{2+} activity (Table 4) produced using the chelate equilibria method support the above hypothesis and agree with others (Norvell and Lindsay, 1969, 1972; Hodgson *et al.*, 1966; Sinha *et al.*, 1978).

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