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#### COPPER ADSORPTION/DESORPTION IN PHOSPHATE- AND SLUDGE-TREATED OXISOLS: KINETICS AND EFFECTS OF AGING AND pH

presented by

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has been accepted towards fulfillment of the requirements for

degree in Crop and Soil Sciences/ Environmental Toxicology Ph.D.

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### COPPER ADSORPTION/DESORPTION IN PHOSPHATE- AND SLUDGE-TREATED OXISOLS: KINETICS AND EFFECTS OF AGING AND pH

By

Luiz Roberto Guimarães Guilherme

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### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

### DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences Institute for Environmental Toxicology

#### ABSTRACT

### COPPER ADSORPTION/DESORPTION IN PHOSPHATE- AND SLUDGE-TREATED OXISOLS: KINETICS AND AGING AND pH EFFECTS

By

Luiz Roberto Guimarães Guilherme

Copper mobility in the environment typically is controlled by

adsorption/desorption reactions. This research studied the kinetics and the effects of aging and pH upon Cu adsorption/desorption in phosphate- and sludge-treated A and B horizons of two Brazilian Oxisols. Phosphate fertilization is nearly ubiquitous in Oxisols. Sewage sludge application to agricultural land is increasing in Brazil. The time-dependence of Cu adsorption/desorption revealed that initial adsorption rate constants were up to 45% greater in P-treated, and up to 70% greater in sludge-treated than control soils. In P-treated soils, the fraction of Cu desorbed  $(Cu_{der}/Cu_{ads})$  was half that in control soils, and smaller in B than A horizons. Sludge treatment affected Cu<sub>des</sub>/Cu<sub>ads</sub> somewhat less than did P treatment. Little Cu was desorbed from P-treated soils after 15 min, whereas desorption occurred up to 1 d for sludge-treated, and up to 18 d for control soils. Increasing adsorption reaction time (aging 1h to 54 d) increased Cu sorption distribution coefficients (K<sub>ads</sub> and K<sub>des</sub>); K<sub>ads</sub> was 2 to 8 times greater for 54-d than 1-h aging, whereas K<sub>des</sub> increased 2- to 4-fold over the same aging period. Aging caused up to an 80% decrease in Cu desorption. Samples aged 3 d or less exhibited rapid desorption followed by readsorption. Kads and Kdes values and aging effects on Kads and Kdes followed the trends Ptreated > sludge-treated > control,  $50 > 150 \mu M$  Cu, and A > B horizon. Increasing pH

from 4.5 to 6.5 increased adsorption up to 3-fold and decreased  $Cu_{des}/Cu_{ads}$  to < 0.01. At a given pH, more Cu was adsorbed on A than B horizons, and on pretreated than control samples. Copper desorption from aged soils can be overestimated more than 2-fold by measuring desorption after a 24- or 72-h adsorption reaction, as is typical in laboratory experiments. The large increase in initial Cu adsorption and the decrease in  $Cu_{des}/Cu_{ads}$  for P- or sludge-treated soils is noteworthy as this will affect Cu mobility and availability in Oxisols.

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#### Chapter 1

#### **GENERAL INTRODUCTION**

#### Rationale

Phosphate fertilization is nearly ubiquitous in Oxisols used for agriculture. High concentrations of Cu in some P fertilizers have been of concern in Brazil. Application of sewage sludge to agricultural land is also becoming an increasing practice in Brazil. Thus, there is a need for better understanding of the effects of such agricultural inputs on Cu sorption and transport in Oxisols. This research is proposed to determine the effects of phosphate and sludge treatment on Cu adsorption/desorption in A and B horizons of two Brazilian Oxisols with similar Fe oxides content but different kaolinite:gibbsite and goethite:hematite ratios. The kinetics of Cu adsorption/desorption, as well as the effects of aging and pH, on Cu adsorption and desorption were measured at initial Cu concentrations from 5 to  $150 \mu M$ .

### Origin of Cu in Oxisols

Average Cu concentrations in soils range from 20 to 30 mg kg<sup>-1</sup> (Baker, 1990), though Oxisols can contain much greater Cu concentrations (Baker, 1990; Kabata-Pendias and Pendias, 1992), mainly if the parent material originally has a high Cu concentration (Curi and Franzmeier, 1987). A total Cu content as high as 210 mg kg<sup>-1</sup> was reported for mafic-derived Oxisols from Brazil (Curi, 1983). Total Cu concentration in Brazilian soils has shown a close association with total Fe and clay contents (Pérez et al., 1995). Heavy metal additions to soils normally are regulated based on cation exchange capacity (CEC) and soil pH, but Mattiazzo and Glória (1995) have suggested that clay content and concentrations of Fe and Al oxides seem to be better criteria for Brazilian soils.

Anthropogenic inputs of Cu to soils are very diverse and include fungicides, fertilizers, lime, animal manures, sewage sludges, and atmospheric deposition (Baker, 1990). On a local scale, inputs from anthropogenic sources can greatly exceed natural Cu contents (Tiller and Merry, 1981). Copper concentrations (dry weight basis) in some agricultural sources of Cu are: fungicides = 12000 to 50000 mg kg<sup>-1</sup>; sewage sludges = 50to 17000 mg kg<sup>-1</sup>; P fertilizers = 1 to 300 mg kg<sup>-1</sup>; farmyard manure = 2 to 172 mg kg<sup>-1</sup>; lime = 2 to 125 mg kg<sup>-1</sup>; N fertilizers = <1 to 15 mg kg<sup>-1</sup>(Alloway, 1990; Baker, 1990; Kabata-Pendias and Pendias, 1992). Annual additions of Cu from P fertilizers in Brazil are estimated at 213 t per year (Malavolta, 1994), which adds on average 2.25 µg Cu kg soil<sup>-1</sup> year<sup>-1</sup> to Brazilian agricultural soils. Annual additions from lime and phosphogypsum represent 302 t Cu per year, and contributions from sewage sludge can be even greater. Copper concentrations of 1455 mg kg<sup>-1</sup> have been reported for sewage sludges in Brazil (Berton et al., 1989). Applications of only 10 t ha<sup>-1</sup> y<sup>-1</sup> of this sludge could double, in three years, the concentration of Cu in soils having an initial concentration of 20 mg Cu kg<sup>-1</sup> soil.

#### Reactions of Cu in Oxisols

Reactions controlling availability of Cu in soil solutions include adsorption/desorption, precipitation/dissolution, and soluble complex formation. At Cu

concentrations typically found in soils, Cu is removed from solution by adsorption rather than precipitation (Ellis and Knezek, 1972; James and Barrow, 1981). This is especially true for most Oxisols, since the low solution concentration as well as the low pH do not allow precipitation to occur easily. Oxisols, which are highly weathered, acid soils with low to medium organic matter content and variable clay content, represent about 60 % of the Brazilian territory (Figure 1.1). The mineralogy of the clay fraction is characterized by the predominance of Fe and Al oxides and kaolinite (Oliveira et al., 1992), all of which have low CEC. Goethite ( $\alpha$ -FeOOH) and hematite ( $\alpha$ -Fe2O<sub>3</sub>) are the most common Fe oxides, whereas gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>) is the main Al oxide present in these soils. These oxides have points of zero charge (PZC) in the range 7.5 - 9.0, which means that they will be positively charged at the natural soil pH of most Oxisols. Organic matter decreases the PZC to near 4.0, so Oxisol A horizons are negatively charged.



Figure 1.1. Oxisol distribution in Brazil indicated by dark shading (EMBRAPA, 1981) (Brazil's area = 8,511,965 km2)

The relative importance of a particular mineral for cation and anion sorption depends on the surface area and on the surface charge density (sites per unit area), both of which depend on crystallinity as well as on crystal structure. Specific surface area and crystallographic estimates of maximum moles of complexed proton charge per unit area  $(q_{\rm H}/{\rm S})$  and of complexed hydroxyl charge per unit area  $(q_{\rm OH}/{\rm S})$  on proton-selective surface functional groups of minerals in the clay fraction of Oxisols are presented in Table 1.1.

Table 1.1. Specific surface area (SSA) and crystallographic estimates of maximum values of  $q_{\rm H}$ /S and  $q_{\rm OH}$ /S for selected soil minerals presented in Oxisols

Mineral	SSA <sup>(1)</sup>	$q_{\rm H}/{\rm S}^{(2)}$	$q_{\rm OH}/{\rm S}^{(2)}$
	<b>m</b> <sup>2</sup> g <sup>-1</sup>	$\ \mu mol_c m^{-2}$	
Goethite	30-120 (avg.= 104)	4.4	6.7
Gibbsite	20	2.8	5.6
Kaolinite	10-150 (avg.= 52)	0.35	1.0
Hematite	10-150 (avg.= 64)		
<sup>(1)</sup> Source: Resende et al. (1988)			

<sup>(2)</sup> Source: Sposito (1984)

Copper concentrations in natural soil solutions are controlled by adsorption on oxides and organic materials to a far greater extent than by adsorption on clay minerals, the influence of which may be negligible in some soils (McLaren et al., 1981). In addition, Cu desorption from organic matter and Fe and Al oxides is very small (McLaren et al., 1983), because activation energies are large for desorption of inner-sphere complexes (McBride, 1989). Adsorption equilibria involving Fe and Al oxide (and silicate) surfaces can be illustrated by reactions of Table 1.2.

One important effect of  $Cu^{2+}$  adsorption (and also proton transfer, and ligand adsorption), as shown by Table 1.2, is the change in surface charge upon adsorption.

Specifically adsorbed cations like  $Cu^{2+}$  increase the pH of the point of zero charge (pH<sub>PZC</sub>), also known as the isoeletric point, but lower the pH of the point of zero net proton charge (pH<sub>PZNPC</sub>) (Stumm, 1992). The pH<sub>PZC</sub> increases upon  $Cu^{2+}$  adsorption because the fixed surface charge becomes zero only at higher pH values (higher OH<sup>-</sup> solution concentration). Conversely, the pH<sub>PZNPC</sub> is shifted toward lower pH because protons are released as a consequence of  $Cu^{2+}$  adsorption.

Acid base equilibria			
S-OH + H <sup>+</sup>	⇔	$S-OH_2^+(1)$	
S-OH + OH <sup>-</sup>	⇔	$S-O^{-} + H_2O(2)$	
Metal (Cu <sup>2+</sup> ) binding			
$S-OH + Cu^{2+}$	⇔	$S-OCu^{+} + H^{+}$ (3)	
$2 \text{ S-OH} + \text{Cu}^{2+}$	⇔	$(S-O)_2Cu + 2 H^+ (4)$	
$S-OH + Cu^{2+} + H_2O$	⇔	$S-OCuOH + 2 H^{+} (5)$	
<b>T</b> · · <b>J</b> · <b>J</b> · <b>J</b> · · · J			
Ligand exchange $(L = ligand)$	, e.g. $H_2PO_4$ or $HPO_4^{(*)}$		
$S-OH + L^{-}$	⇔	$S-L+OH^{-}(6)$	
$2 \text{ S-OH} + L^{-}$	⇔	$S_2-L^+ + 2 OH^-(7)$	
$S-OH + L^{2-}$	⇔	$S-L^{-} + OH^{-}(8)$	
$2 \text{ S-OH} + L^{2}$	⇔	$S_2-L+2 OH^-(9)$	
Termany surface complex formation (metal = $C_{12}^{2+}$ )			
$S_{-}OH + I^{-} + Cu^{2+}$	$\overline{\mathbf{a}}$	$S_{-}I_{-}C_{1}u^{2+} + OH^{-}(11)$	
$S - OII + L^{2} + Cu^{2+}$		$S = L - Cu^{+} + OH^{-}(11)$	
$5-0H + L^{-} + Cu^{-}$	\$	S-L-Cu + OH (11)	
$2 \text{ S-OH} + L^2 + Cu^2$	⇔	$2 \text{ S-L-Cu} + 2 \text{ OH}^{-}(12)$	

Table 1.2. Adsorption equilibria on Fe and Al oxide (and silicate) surfaces

 $S = Fe \text{ or } Al \text{ (or } Si). Modified from Stumm (1992)}$ 

Specifically adsorbed anions such as  $H_2PO_4^{-}$  or  $HPO_4^{-2}^{-}$ , cause the opposite effects on  $pH_{PZC}$  and  $pH_{PZNPC}$  of variable-charge mineral surfaces. Some agricultural inputs such as lime, fertilizers, manures, and sewage sludge, which are potential sources of Cu to soils, can modify Cu sorption behavior in soils by changing the net surface charge or generating mobile organic and inorganic colloids, which can enhance Cu transport throughout the soil profile (McCarthy and Zachara, 1989).

#### Kinetics of Soil Reactions

Most soil reactions are described as heterogeneous solid-liquid reactions that take place by a multistep mechanism comprising transport processes as well as chemical reactions (Aharoni and Sparks, 1991) (Figure 1.2). Rates of ion exchange processes are especially likely to be transport controlled in the case of readily exchangeable ions, whereas specifically adsorbed ions (e.g. Cu<sup>2+</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>-2</sup>) may participate in reactions that are surface controlled (Sposito, 1994), although effects of transport and chemical processes are often experimentally inseparable (Sparks, 1989).



Figure 1.2. Transport processes in solid-liquid soil reactions - Nonactivated processes: 1. Transport in the soil solution, 2. Transport across a liquid film at the solid-liquid interface, 3. Transport in a liquid filled micropore; Activated processes: 4. Difussion of a sorbate at the surface of the solid, 5. Diffusion of a sorbate occluded in a micropore, 6. Diffusion in the bulk of the solid (from Aharoni and Sparks, 1991).

The difficulty of separating the effects of transport phenomena and chemical reaction, and the heterogeneous character of soil ion exchangers restrict the use of simple kinetic models such as first- or second-order rate equations in studies concerning soil reactions kinetics (Sparks, 1989). However, attempts have been made to treat adsorption as a simple reaction in which the surface and the sorbing solute are reactants and the sorbed solute a product (Aharoni and Sparks, 1991).

The objectives of this research were to:

- a) study the time-dependence of Cu adsorption/desorption in A and B horizon samples of two Oxisols as affected by phosphate (P) or sludge pretreatment (Chapter 2);
- b) determine the effect of aging upon Cu desorption from untreated and P- or sludge-treated A and B-horizon samples of two Oxisols (Chapter 3);
- c) determine the effect of pH upon Cu adsorption/desorption in untreated and P- or sludge-treated A and B-horizon samples of two Oxisols (Chapter 4).

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#### Chapter 2

#### COPPER ADSORPTION/DESORPTION KINETICS IN PHOSPHATE- AND SLUDGE-TREATED OXISOLS

#### Abstract

Phosphate fertilization is nearly ubiquitous in Oxisols used for agriculture, and the application of sewage sludge to agricultural land is increasing in Brazil and elsewhere. This study measured the effects of phosphate and sludge pretreatment on Cu sorption kinetics and Cu availability in A and B horizon samples of two Oxisols at pH 5.5. Initial rate constants for Cu adsorption were up to 45% greater in P-treated than control soils, and up to 70% greater in sludge-treated than control soils. The large increase in the initial sorption rate for P- and sludge-treated soils may be caused by an increase in the number of sites with low activation energy, or by a decrease in the activation energy for sorption at either surface-organo or surface-phosphate groups compared with surface-OH groups. Phosphate treatment caused a marked decrease in the initial fractional Cu desorption. In Ptreated soils, the fraction of Cu desorbed was about half that in control soils, and smaller in B than A horizons. Sludge treatment affected fractional desorption in a similar way, but the effects were not as remarkable as those for P treatment. Little Cu was desorbed from P-treated soils after the initial 15-min reaction time, whereas Cu desorption increased with increasing reaction times up to 1 d for sludge-treated soils and up to 18 d for control soils. The large increase in initial Cu adsorption and the decrease in fractional desorption for Por sludge-treated soils is noteworthy because of its implications for the mobility and availibility of Cu in Oxisols.

#### Introduction

Adsorption/desorption reactions are among the most important controls on the mobility of Cu in the environment (James and Barrow, 1981). Copper concentrations in natural soil solutions and sediment-water systems typically are controlled by adsorption on surface hydroxyl groups of metal oxides and organic matter (McLaren et al., 1981; Piccolo and Stevenson, 1982; Wang and Chen, 1997). Soil organic matter can provide high concentrations of sites for metal sorption (Logan, 1990; Stumm, 1992; Harter and Naidu, 1995; Spark et al., 1997a; Temminghoff et al., 1997). The increase in heavy metal adsorption in sandy soils amended with sludge has been attributed to an increase in the number of sites for metal adsorption from the solid organic matter added (Petruzzelli et al., 1994). Among divalent first-row transition metals, Cu has the greatest affinity for organic matter (Stevenson and Arkadani, 1972). The high degree of selectivity shown by organic matter for Cu is caused by the formation of inner-sphere complexes, often referred to as chemisorption or specific adsorption. Iron and aluminum oxides are also recognized to have a high affinity for Cu (Jenne, 1968; Forbes et al., 1976; Schwertmann and Taylor, 1977; McBride, 1982; Spark et al., 1995a). Electron spin resonance studies have shown that Al-OH groups sorb Cu mainly in inner-sphere complexes (McBride, 1982; Harsh and Doner, 1984). For kaolinite, ion exchange (outer-sphere complexes) may be important at low pH and low ionic strength, whereas an increase in both ionic strength and pH favor chemisorption at amphoteric surface hydroxyls (Schindler et al., 1987; Spark et al., 1995b). Copper desorption from organic matter and Fe and Al oxides is limited (McLaren

et al., 1983) because activation energies are large for desorption of inner-sphere complexes (McBride, 1989).

Oxyanions such as phosphate, sulfate, and organic acids can cause either an increase or a decrease in metal sorption by soils, metal oxides, and layersilicates (McBride, 1994; Guilherme et al., 1995; Murphy and Zachara, 1995; Ali and Dzombak, 1996a; 1996b; Spark et al., 1997c). When an anion and a metal are added to a soil simultaneously, the effect of the anion on metal sorption depends on a) the net surface charge of the soil; b) the affinity of the soil for the metal, anion, and metal-anion complexes; and c) the tendency of the metal and anion to form soluble complexes. The latter depends in part upon the anion:metal charge ratio. A large excess of the anion generally suppresses metal adsorption, while charge parity (or less) with the metal generally favors adsorption by ternary complex formation (McBride, 1994). Increased Cu sorption by goethite in the presence of organic acids at low pH has been attributed to a) a decrease in positive surface charge in the low pH region due to sorption of an organic acid anion, resulting in a more favorable electrostatic environment for Cu sorption or b) the sorption of Cu-organic acid complexes, i.e., the formation of "Cu-organic acid-mineral" ternary surface complexes (Ali and Dzombak, 1996a).

If an anion is added to a soil or mineral before a metal is added (for example, phosphate fertilization followed later by Cu fungicide application), the anion will affect metal sorption principally by converting  $M^{3+}$ -OH groups into  $M^{3+}$ -anion surface functional groups, possibly altering the net surface charge, and promoting the formation of  $M^{3+}$ anion-Cu surface ternary complexes (M = Al or Fe). Beneficial effects of phosphate for reducing injury from Cu fungicide applications have been reported (Chaney and

Giordano, 1977) and may be due to Cu sorption by M<sup>3+</sup>-phosphate surface functional groups. Copper sorption by humate-treated minerals has also been attributed to M<sup>3+</sup>-humate-Cu ternary surface complexes (Spark et al., 1997c).

Pretreatment with oxyanions may also affect trace metal sorption kinetics. The time-dependence of trace-metal sorption on goethite indicates that the adsorption reaction initially involves adsorption on external surface sites, with subsequent diffusion to internal sorption sites (Brüemmer et al., 1988). Benjamin and Leckie (1981) reported a rapid initial (1 h) adsorption of Cd followed by a much slower second step, possibly related to solid-state diffusion in amorphous Fe oxyhydroxide. Diffusional processes can contribute to desorption hysteresis and reaction irreversibility (Padmanabham, 1983a, 1983b; Barrow, 1985).

Most soil reactions can be described as heterogeneous solid-liquid reactions that take place by a multistep mechanism comprising transport processes as well as chemical reactions (Aharoni and Sparks, 1991). In a practical sense, the effects of transport and chemical processes are often experimentally inseparable (Sparks, 1989). The difficulty of separating the effects of transport phenomena and chemical reaction kinetics, along with the heterogeneous character of surface functional groups in soils, often restrict the use of simple kinetic models in soils (Sparks, 1989). However, attempts have been made to treat adsorption as a simple reaction in which the surface and the sorbing solute are reactants and the sorbed solute a product (Aringhieri et al., 1985; Aharoni and Sparks, 1991). In one study, Cu desorption data for a Cu-contaminated soil were fit very well by a first-order kinetics equation in which sorbed Cu was considered the reactant (Jopony and Young, 1987). Aringhieri et al. (1985) found that Cu adsorption kinetics for an organic soil could

be described by a model wherein the reaction is first-order with respect to both Cu and substrate concentration (second-order overall) and exhibits a dependence on internal diffusion. Long-term sorption reaction rates are probably mass-transfer limited for metal oxides (Van der Zee and Van Riemsdijk, 1991; Brüemmer et al., 1988) and for highly aggregated Oxisols (Nkedi-Kizza et al., 1982), although batch-shake methods may eliminate much of the mass-transfer control normally found in aggregated soils (Lima, 1995).

The objective of this work was to determine the effect of phosphate or sludge pretreatment on Cu adsorption/desorption kinetics and Cu availability in Oxisols that differ in mineralogy and organic carbon (OC) concentration. Batch-shake methods were used so that mass transfer limitations due to differences in aggregation would be minimized or eliminated and the resulting initial reaction rates would reflect differences in the surface chemistry of control, P-treated, and sludge-treated soils.

#### **Materials and Methods**

#### Soil Material

Samples of A and B horizons from two uncultivated Oxisols were collected near S. João Del Rei in the Campos das Vertentes region of Minas Gerais, Brazil (latitude 21° 20' S; longitude 44° 30' W). Both soils were vegetated with semi-deciduous tropical cerrado (tortuous trees and shrubs scattered above grass and herbaceous plants) and were underlain by mica schists of the Andrelândia group. The first soil, a Dark-Red Latosol (very fine, allitic, isothermic Typic Hapludox), formed on steeply inclined strata and was

very well drained. The second soil, a Yellow-Red Latosol (very fine, allitic, isothermic Typic Hapludox), developed in nearly horizontal strata and was relatively poorly drained. Both soils have pH near 4.5 in the A horizon and 5.5 in the B horizon. Although both soils have similar clay contents (about 700 g kg<sup>-1</sup>) and total Fe oxide contents (165 g kg<sup>-1</sup>), differences in drainage have caused the Yellow-Red Latosol to have greater kaolinite:gibbsite and goethite:hematite ratios than the Dark-Red Latosol (Table 2.1).

Horizon	Clay	OC†	Fe <sub>d</sub> <sup>‡</sup>	Fe <sub>o</sub> ‡	Kt <sup>s</sup>	Gb⁵	Gt:Hm <sup>1</sup>	SSA <sup>#</sup>
		g kg <sup>-1</sup> so	il		g kg <sup>-1</sup>	clay		cm <sup>2</sup> g <sup>-1</sup>
		1	Dark-Rea	Latosol (C	<u>GbHm)</u>			
Α	691	25.3±0.0	99	1.88	350	510	5.0	59±3
В	753	9.9±0.1	114	0.65	350	510	4.1	61±3
		נ	Yellow-R	ed Latosol	(KtGt)			
Α	711	23.6±0.3	101	1.20	480	375	10.2	53±4
В	721	8.0±0.1	114	0.59	480	400	8.3	58±3

Table 2.1. Selected properties of A and B horizons of two Oxisols from Brazil.

<sup>†</sup> OC is organic carbon measured by the Walkley-Black method.

<sup>‡</sup>  $F_d$  and  $Fe_o$ , respectively, are Fe extracted by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) and ammonium oxalate (pH 3.1) in the dark (Schwertmann, 1964). <sup>§</sup> Kt and Gb, respectively, are kaolinite and gibbsite measured by differential thermal analysis in dithionite-treated clay samples (but expressed on a total-clay basis).

<sup>1</sup> Gt:Hm is the goethite:hematite ratio in the clay fraction, measured by X-ray diffraction of NaOH-treated samples (Kämpf and Schwertmann, 1982a; 1982b).

\* Specific surface area determined by  $N_2$  adsorption isotherms (BET).

The A and B horizons of each soil differ in OC content as well as in the relative

proportions of amorphous and crystalline Fe (estimated as the ratio of oxalate-extractable

to dithionite-extractable Fe). Soil samples were gently crushed to break large aggregates

and then were sieved to obtain the <2-mm fraction, which was used in all of the experiments described below. Relevant soil properties are summarized in Table 2.1; additional details concerning soil characterization may be found in Lima and Anderson (1997).

#### Phosphate and Sludge Pretreatment

To assess the effect of phosphate pretreatment (hereafter termed P treatment) on Cu sorption kinetics, samples of each soil material were reacted with 10.75 mM  $Ca(H_2PO_4)_2$ ;  $H_2O(21.5 \text{ mmol P L}^{-1})$  at a soil:solution ratio of 2:3 to give a P addition rate of 1 g P kg<sup>-1</sup> soil. The samples were shaken for 48 h on a reciprocating shaker (120 cycles min<sup>-1</sup>) and centrifuged for 10 min at 9000 rpm. Excess solution was removed, and the P concentration was measured colorimetrically. The samples were centrifuge-washed once with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> (2:1 solution:soil) to remove entrained and readily desorbed P. The P concentration of the supernatant wash solution was measured. Adsorbed P was near 30 mmol kg<sup>-1</sup> for all samples. Sludge pretreatment consisted of reacting each soil material with air-dried, <0.5-mm lime-stabilized sludge at a rate of 5 g kg<sup>-1</sup>. Samples treated with sludge were incubated for 30 d (until constant pH) at 37 °C at a moisture content of 60% of saturation. The dry sludge had an OC content of  $276 \pm 8 \text{ mg kg}^{-1}$ ; other sludge properties are reported in Appendix A1. The sludge-treated soils contained about 2 g kg<sup>-1</sup> more OC (Appendix A2) than the control soils. Phosphate- and sludge-treated soils were air dried and crushed to pass a 2-mm sieve. The pH<sub>PZSE</sub>, and DTPA-extractable Cu measured in subsamples of control and P- or sludge-treated soils are reported in Table 2.2.

		pH <sub>PZSE</sub> '		UIF	A-EXITACIA016	Cu.	Cu	sorpuon Lapa	city
Hor.	Ctrl	d	Sludge	Ctrl	Ч	Sludge	CHI	<u>а</u>	Sludge
					µmol kg <sup>-l</sup>			mmol kg <sup>-1</sup>	
				Dark-Rec	l Latosol (GbH	(m)			
V	4.35	4.00	4.35	28.2±0.0	39.6±1.7	<b>38.9±0.2</b>	54±4	70±0	60±2
В	6.10	5.85	6.10	6.3±0.1	12.2±0.2	10.3±0.1	<b>44</b> ±0	<b>5</b> 0.±0	47±2
				Yellow-R	ed Latosol (Ku	GU			
A	4.30	3.75	4.20	24.5±0.1	<b>39.3±1.4</b>	34.7±0.5	53±3	62 ±2	54±1
В	6.25	5.35	5.75	<b>2.6±0.2</b>	5.5±0.1	<b>4</b> .8±0.2	47±3	49±1	<b>43</b> ±3

Table 2.2. Chemical properties of control (Ctrl) and P- or sludge-treated soil samples.

? . 2 D <sup>‡</sup>Cu extractable by DTPA (Baker and Amacher, 1982).

Prior to measuring Cu sorption capacity or Cu sorption kinetics, suspensions of the twelve soil samples (control and P- or sludge-treated samples from A and B horizons of two Oxisols) were adjusted to pH 5.5 using the following procedure. For each set of experimental conditions (described below), triplicate 2.5-g subsamples of each soil material were suspended in 167 mL of 5 mM Ca(NO<sub>3</sub>), (pH 5.5) and stirred continuously with a TPFE-coated stirring bar. The pH was measured and readjusted to 5.5 with either saturated Ca(OH), or 7 mM HNO<sub>3</sub>. All samples were shaken for 24 h on a reciprocating shaker (120 cycles min<sup>-1</sup>), suspension pH was measured again, and acid or base was added as needed to readjust to pH 5.5. Samples were shaken again for 24 h and pH was readjusted as necessary before the samples were shaken again for 24 h. During the third 24-h shaking period, suspension pH changed less than 0.05 pH units, so pH was considered to be stable after 72 h. This 72-h shaking time during pH adjustment effectively disaggregates all samples (Lima, 1995). Consequently, the sorption kinetics experiments described below are unaffected by the original degree of aggregation of the soils and are not confounded by initial differences in aggregation between P- or sludgetreated and control samples. The pH-adjusted soil suspensions were used in the Cu sorption capacity and kinetics experiments described below and were prepared fresh immediately before each experiment.

#### Copper Sorption Capacity

Copper sorption capacity at pH 5.5 was measured by repeated reaction with 500  $\mu M$  Cu. This "repeated reaction" approach is preferable to a single reaction at a high Cu

concentration because Cu concentrations >500  $\mu$ M could cause Cu precipitation at pH 5.5 (Allison et al., 1990). After suspension pH was adjusted as described above, appropriate amounts of Cu(NO<sub>3</sub>)<sub>2</sub> in Ca(NO<sub>3</sub>)<sub>2</sub> (pH 5.5; I=15 mM) were added to each soil suspension to give initial total Cu concentrations of 500  $\mu$ M and a solution:soil ratio of 100:1. Triplicate soil suspensions were shaken with 500  $\mu$ M Cu(NO<sub>3</sub>)<sub>2</sub> in 4.5 mM Ca(NO<sub>3</sub>)<sub>2</sub> (pH 5.5; I=15 mM) for 72 h, then centrifuged. The supernatant solutions were decanted and saved for Cu analysis, and the mass of entrained solution was recorded. Each soil paste was reacted again with fresh 500  $\mu$ M Cu in Ca(NO<sub>3</sub>)<sub>2</sub>, and centrifuged as described above. This Cu reaction-centrifugation-decantation-Cu analysis procedure was repeated until negligible additional Cu was sorbed. Ten such sorption cycles were required, and the supernatant pH was readjusted to 5.5 after every two cycles. The Cu sorption capacities of control and P- or sludge-treated soils are reported in Table 2.2.

#### Adsorption/Desorption Kinetics

After pH adjustment, appropriate amounts of Cu(NO<sub>3</sub>)<sub>2</sub> in Ca(NO<sub>3</sub>)<sub>2</sub> (pH 5.5; I=15 m*M*) were added to each soil suspension to give initial total Cu concentrations of 50 and 150  $\mu$ *M* and a solution:soil ratio of 100:1. Samples were shaken at 120 cycles min<sup>-1</sup> on a reciprocating shaker for 10 min and then were centrifuged for 10 min at 9000 rpm. A 1.5- mL aliquot of supernatant solution was withdrawn from each bottle and saved for Cu analysis by flame atomic absorption spectroscopy. The soils were resuspended and shaken as described above. The centrifuging and subsampling procedure was repeated later for

total shaking times of 1 h, 6 h, 24 h, 3 d, 6 d, and 18 d. After 18 d, the supernatant solution was decanted carefully to minimize the amount of entrained solution.

The soil pastes that remained in the bottles after centrifuging and decanting the adsorption solution were weighed to determine the mass of entrained solution. Copper desorption from these soil pastes was measured by adding 250 mL of 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> to each soil paste. Samples were shaken, centrifuged, and subsampled at the same time intervals used for adsorption kinetics. Total Cu desorbed by 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> at each reaction time was corrected for the amount of Cu entrained at the start of the desorption reaction.

#### Initial Rate Constants

Rate constants for Cu adsorption  $(k_{ads})$  were calculated by considering adsorption to be first-order with respect to both total solution-phase Cu,  $[Cu_i]$  and the concentration of adsorption sites, [S]. Using the initial rate method and making the assumption that the desorption reaction makes a negligible contribution to the overall reaction rate during the initial 15-min reaction time,  $k_{ads}$  may be calculated as

$$-\Delta[\mathbf{C}\mathbf{u}_{t}]/\Delta t = \mathbf{k}_{\mathsf{ads}} [\mathbf{C}\mathbf{u}_{t}]_{0} [\mathbf{S}]_{0}$$
<sup>[1]</sup>

where  $\Delta$ [Cu<sub>1</sub>] is the change in [Cu<sub>1</sub>] during the initial 15-min reaction, [Cu<sub>1</sub>]<sub>0</sub> is the initial solution-phase Cu concentration, and [S]<sub>0</sub> is the Cu adsorption capacity. Because the speciation of solution-phase and sorbed Cu is unknown, all concentrations are expressed as m*M* total Cu, so Eq. [1] is an apparent rate expression. We used 15-min as the time interval for the initial reaction time because the reaction stops when soil is separated from solution, and 15 min represents a 10-min shaking time plus half the centrifugation time. These rate constants are precise in that each sample was reacted for exactly the same amount of time prior to centrifugation. However, because of differential settling during centrifugation and the impossibility of determining exactly when the "average" soil particle was no longer in contact with the bulk solution, the initial rate constants may not be appropriate for comparison with other studies that have used other methods and time scales. Nevertheless, these rate constants are suitable for determining the effects of P and sludge treatment and soil composition on  $k_{ads}$ . Desorption rate constants are not calculated here because the net desorption during the initial 15-min desorption was affected by Cu readsorption, and extensive irreversibility precluded using the relation  $K_{eq} = k_{ads}/k_{des}$ , as was previously suggested by Aringhieri et al. (1985).

#### Results

#### Soil Chemical Properties

Pretreatment with P caused Cu adsorption capacity to increase by as much as 30%and pH<sub>PZSE</sub> to decrease by 0.25 to 0.9 pH units compared with the control soils (Table 2.2). Phosphate treatment had a greater effect on pH<sub>PZSE</sub> in the KtGt than GbHm soil. Sludge pretreatment, on the other hand, had no effect on pH<sub>PZSE</sub> except in the B horizon of the KtGt soil and did not have a statistically significant effect on Cu adsorption capacity (Table 2.2), even though the OC contents of sludge-treated soils were about 2 g kg<sup>-1</sup> greater than for control soils (Appendix A2). Both P and sludge treatment caused increases in DTPA-extractable Cu (Table 2.2), although DTPA-extractable Cu was at least 1000 times less than the Cu sorption capacity and thus should have little effect on the Cu adsorption experiments described below.

#### Adsorption Kinetics

Rate constants for Cu adsorption ( $k_{ads}$ ) measured during the initial 15-min reaction were up to 45% greater for P-treated than control soils and up to 70% greater for sludgetreated than control soils (Figure 2.1). Adsorption rate constants were greater for 50  $\mu M$ than 150  $\mu M$  Cu for any given sample.

The time-dependence of Cu adsorption is plotted both in terms of the fraction adsorbed (*i.e.*, Cu<sub>ads</sub>/Cu<sub>added</sub>) and the adsorbed Cu concentration (mmol kg<sup>-1</sup>) on the left and right axes, respectively, of Figure 2.2. For 50  $\mu$ M Cu (Figures 2.2a-c), Cu adsorption by sludge-treated samples approached steady-state after 6 h, whereas P-treated samples required about 24 h, and control samples did not reach a plateau within the 18-d reaction time. For 150  $\mu$ M Cu, Cu adsorption again was fastest in sludge-treated soils and slowest in control soils, although Cu adsorption did not reach steady state within the 18-d reaction time for any of the soils (Figures 2.2d-f).

Pretreatment with P and sludge had much less effect on Cu adsorption after 18 d (i.e.,  $Cu_{ads,18d}$ ) than on either the concentration of Cu adsorbed during the initial 15-min reaction or on the time-dependence of Cu adsorption. For soils reacted with 50  $\mu$ M Cu, sludge treatment caused up to a 70% increase in initial (15-min) Cu adsorption but only a 10% increase in  $Cu_{ads,18d}$ . Phosphate treatment caused a smaller increase in initial Cu adsorption (up to 60%) but a 30% increase in  $Cu_{ads,18d}$ . For soils reacted with 150  $\mu$ M Cu, sludge treatment caused a 40 to 75% increase in initial Cu adsorption but only a 25% increase in  $Cu_{ads,18d}$ ; P treatment caused a 30 to 65% increase in initial Cu adsorption and a 10 to 45% increase in  $Cu_{ads,18d}$ .



Figure 2.1. Initial rate constants for Cu adsorption  $(k_{ads})$  in control and P- or sludge-treated A and B horizon samples of two Oxisols (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).


Figure 2.2. Time-dependence of Cu adsorption in control and P- or sludge-treated A and B horizon samples of two Oxisols (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol). Left axis is Cuasoned/Cuasted; right axis is adsorbed Cu.

### **Desorption Kinetics**

Concentrations of Cu desorbed during the initial 15-min desorption reaction are shown in Figure 2.3. For 50  $\mu$ M Cu, P and sludge treatment caused initial Cu desorption to decrease by about 50% (Figure 2.3a), even though the adsorbed Cu concentration was greater for P-treated and sludge-treated soils than for control soils (Figures 2.2a-c). For 150  $\mu$ M Cu, P treatment caused a 4 to 16% decrease in initial Cu desorption, and sludge treatment a 16 to 30% decrease in initial Cu desorption compared to control soils (Figure 2.3b). For both Cu concentrations, adsorbed Cu was greater and desorbed Cu less in GbHm than KtGt soils. For 50  $\mu$ M Cu, desorbed Cu was less in A than B horizons, although sludge and P treatment minimized the differences in initial Cu desorption between A and B horizons.

These effects of soil type and pretreatment on fractional desorption can be seen more clearly in Figure 2.4. For soils initially reacted with 50  $\mu$ M Cu, only 2 to 9% of sorbed Cu was desorbed during the 18-d desorption reaction (Figures 2.4a-c), whereas soils reacted with 150  $\mu$ M Cu released 8 to 18% of adsorbed Cu (Figures 2.4d-f). For both Cu concentrations, the fraction of Cu initially desorbed from P-treated and sludgetreated soils was about half that desorbed from control soils. Fractional Cu desorption generally was smaller in A than B horizons and in the GbHm than KtGt soil, although Ptreatment greatly diminished the differences among soils, and both P and sludge treatment had greater effects on fractional desorption than did soil properties.

Both P and sludge treatment had notable effects on the time dependence of Cu desorption (Figure 2.4). At both Cu concentrations, Cu desorption from control soils increased steadily throughout the 18-d reaction time (Figures 2.4a and d), whereas Cu desorption from P-treated soils was nearly complete after the initial 15-min desorption reaction (Figures 2.4b and e). Net Cu desorption from sludge-treated soils increased





Figure 2.3. Copper desorbed during initial 15-min desorption reaction for control and Por sludge-treated A and B horizon samples of two Oxisols (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).



Figure 2.4. Time-dependence of fraction of Cu desorbed (Cude/Cude/18d) in control and P- or sludge-treated A and B horizon sample of two Oxisols (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).

#### Discussion

The decrease in  $pH_{PZSE}$  and the increase in Cu adsorption capacity caused by P pretreatment are consistent with prior studies wherein phosphate adsorption in innersphere complexes on metal oxides and Oxisols causes a decrease in  $pH_{pzc}$ . The very small or negligible effects of sludge pretreatment on pH<sub>PZSE</sub> and on Cu adsorption capacity, however, are unexpected, particularly since the sludge-treated soils contained 2 g kg<sup>-1</sup> more OC than did control soils. Other researchers have shown that humic acid adsorption on metal oxides and kaolinite causes pH<sub>PZC</sub> to decrease (Kretzschmar et al., 1997; Spark et al., 1997b). Further, an increase in Cu adsorption has been reported for goethite in the presence of organic acids (Ali and Dzombak, 1996a) and humic acid (Spark et al., 1997c) and attributed to M3+-organo surface functional groups. Increased Cu adsorption by sandy soils after sludge treatment, on the other hand, has been attributed to adsorption by sites on solid organic matter that is not adsorbed by soil minerals (Petruzzelli et al., 1994). The negligible effect of sludge pretreatment on pH<sub>PZSE</sub> in the present study may simply reflect the fact that pH<sub>PZSE</sub> is not a true zero point of charge and cannot be assumed equal to pH<sub>PZC</sub> in a system as complex as a soil amended with lime-stabilized sludge. Prior to pH<sub>PZSE</sub> measurements (but not before Cu adsorption experiments) the sludge-treated soils were washed with dilute acid to remove CaCO<sub>3</sub> because pH<sub>PZSE</sub> for unwashed sludge-treated soils were greater than those for control soils. Thus, the pH<sub>PZSE</sub> values for the sludgetreated soils cannot be interpreted as true zero points of charge.

Both P and sludge treatment had much greater effects on  $k_{ads}$  and on initially adsorbed Cu than on either Cu adsorption capacity or  $Cu_{ads,18d}$ . Further, sludge had a greater effect than P on  $k_{ads}$ , whereas P had a greater effect than sludge on Cu adsorption capacity and  $pH_{PZSE}$ . Thus, P and sludge treatment must affect Cu adsorption kinetics by increasing the proportion of sites with low activation energies for Cu adsorption, not simply by increasing the total number of Cu adsorption sites. It is not likely that Cu adsorption kinetics were affected by solution-phase complex formation between Cu and either dissolved phosphate or organic matter, because the solution-phase P and organic C concentrations during the batch adsorption reaction were too low to promote significant complex formation (unpublished data, 1996).

The slow Cu sorption reaction that occurs between 15 min and 18 d may be caused by adsorption on sites with greater activation energies or by slow diffusion of Cu to internal adsorption sites in metal oxides. Initial Cu adsorption was greater, and slow reaction less important, in P- and sludge-treated than control soils. This suggests that the concentration of readily accessible, highly reactive sites was greater in the P- and sludgetreated soils, even though the Cu adsorption capacities differed little between treatments. Phosphate and sludge treatment convert M<sup>3+</sup>-OH groups into M<sup>3+</sup>-phosphate and M<sup>3+</sup>organo functional groups, thereby modifying the reactivity of the site toward Cu but not increasing the number of surface  $M^{3+}$  sites, which exert overall control on the Cu adsorption capacity. Fast metal adsorption on Fe oxide has been attributed to adsorption on doubly coordinated (bridging) OH groups, and slower adsorption to terminal OH groups (Grossl and Sparks, 1995). In contrast, oxyanions more readily form surface complexes at terminal OH groups, particularly protonated OH groups (Sposito, 1984; Hiemstra et al., 1989). Thus, P or organic matter adsorption on positively charged (or neutral) terminal OH groups would decrease the activation energy for Cu adsorption on that site by decreasing the electrostatic repulsion (increasing the electrostatic attraction) between Cu and the site while having little effect on the Cu adsorption capacity. This modification of the native  $M^{3+}$ -OH groups also explains why P and sludge treatment tended to diminish any differences between A and B horizons of GbHm and KtGt soils that were pronounced in the control soil.

The fact that  $k_{ads}$  was greater for 50  $\mu M$  than 150  $\mu M$  Cu indicates either that it was inappropriate to make the assumption that the reverse (desorption) reaction made a negligible contribution to the reaction rate during the initial 15-min reaction, or else that

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the initial reaction was influenced by transport processes such as diffusion. Aringhieri et al. (1985) found that Cd adsorption was influenced by diffusion at high concentrations and short reaction times. In addition, Cu adsorption kinetics may depend on the concentration of CuOH<sup>+</sup> or some other species, not [Cu<sub>1</sub>], which is used to calculate  $k_{ads}$  in Eq. [1]. If the proportionality between [CuOH<sup>+</sup>] and [Cu<sub>1</sub>] differs greatly between 50 and 150  $\mu$ M, then formulating the rate expression in terms of [Cu<sub>1</sub>] is inappropriate. However, because the identity of the rate-controlling Cu species is unknown, Eq. [1] is as suitable as any other formulation of the rate expression.

The marked decrease in Cu fractional desorption observed in this study is typical for trace metal adsorption/desorption by organic matter and oxides (McLaren et al., 1983) and soils (Sparks, 1985). The smaller fractional desorption caused by P and sludge treatment, especially in B horizons, is also consistent with the explanation that these treatments change surface M<sup>3+</sup>-OH groups into M<sup>3+</sup>-phosphate and M<sup>3+</sup>-organo surface functional groups that have greater affinity for Cu than do the normal  $M^{3+}$ -OH groups. The smaller fractional desorption for samples reacted with 50  $\mu$ M Cu than 150  $\mu$ M Cu is also consistent with the hypothesis that there are a limited number of sites with very great affinity for Cu. The smaller fractional desorption in A than B horizons is consistent with the generally observed decrease in metal desorption as OC content increases (Sparks, 1985). In addition, A horizons had 2.5 to 3 times more oxalate-extractable Fe (Fe.) than did B horizons, and other researchers have reported that isotopically exchangeable Cd and Zn decreases with increasing Fe, (Fujii and Corey, 1986). The smaller fractional desorption for the GbHm than KtGt soil may be attributed to the formation of stronger bonds between Cu and gibbsite compared with Cu-kaolinite bonds or to the greater Fe<sub>0</sub> concentrations in the GbHm than KtGt soils.

In summary, phosphate and sludge pretreatments have much greater effects on Cu sorption kinetics and fractional desorption than on net Cu adsorption after 18 d or on Cu adsorption capacity. In a transient system such as a soil with alternating leaching and

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drying events, the initial rates of adsorption and desorption may have greater impacts on Cu mobility and availability than would the Cu adsorption capacity. Thus, the 45 to 70% increase in initial Cu adsorption in P and sludge-treated soils, combined with the roughly 50% decrease in initial Cu desorption, suggest that sludge and P treatment will greatly decrease the mobility of Cu in Oxisols.

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### **Chapter 3**

# AGING EFFECTS ON COPPER ADSORPTION AND DESORPTION IN PHOSPHATE- OR SLUDGE-TREATED OXISOLS.

#### Abstract

Copper mobility in soils is influenced by soil properties, solution composition, and the Cu residence time in soil. This study evaluated the effects of adsorption reaction time (aging 1 h to 54 d) on Cu adsorption and desorption distribution coefficients (K<sub>ads</sub> and K<sub>des</sub>) and on Cu desorption from phosphate- and sludge-treated Oxisols at pH 5.5 for 50 and 150  $\mu$ M Cu. Copper desorption for each adsorption aging time was measured at desorption times from 0.25 h to 18 d. Values of K<sub>ads</sub> were 2 to 8 times greater for 54-d than 1-h aging, whereas K<sub>des</sub> values increased only 2- to 4-fold over the same aging period. Aging caused Cu desorption to decrease by as much as 81%. Samples that were aged 3 d or less exhibited rapid Cu desorption followed by readsorption, probably because 3 d was insufficient for Cu adsorption to reach steady state. Values of Kads and Kdes and the effects of aging followed the trends P-treated > sludge-treated > control soils,  $50 > 150 \mu M Cu$ , and A > B horizon. This work showed that Cu desorption from aged soils can be overestimated more than two-fold by measuring desorption after a 24- or 72-h adsorption reaction, as is typically done in laboratory experiments. Both P and sludge treatment caused decreased Cu desorption, and such treatments might be used to control the availability and mobility of Cu in Oxisols.

### Introduction

The availability and mobility of Cu in the environment is greatly influenced by adsorption/desorption reactions. The importance of organic matter for Cu adsorption in soils and sediments has been discussed by several authors (Stevenson and Arkadani, 1972; McLaren et al., 1981; Petruzzelli et al., 1994; Spark et al., 1997a ; Temminghoff et al. 1997). Numerous studies have reported Cu adsorption characteristics of variable-charge soils (Barrow et al., 1981; James and Barrow, 1981; Barrow; 1985), as well Fe oxides (Jenne, 1968; Forbes et al., 1976; Schwertmann and Taylor, 1977; Benjamin and Leckie, 1981), Al oxides (McBride, 1982; Harsh and Doner, 1984; Spark et al., 1995a), and kaolinite (Schindler et al., 1987; Spark et al., 1995b). Additional attention has been given to the effects of anions on Cu adsorption in variable-charge soils or pure sorbents (Guilherme et al., 1995; Harter and Naidu, 1995; Murphy and Zachara, 1995; Ali and Dzombak, 1996a; 1996b; Spark et al., 1997b; Chapter 2, this dissertation).

In contrast, relatively fewer studies have addressed Cu desorption and the effects of aging on Cu adsorption and desorption. Copper desorption from organic matter and Fe and Al oxides is often limited (McLaren et al., 1983), and aging causes Cu desorption to decrease (Padmanabham, 1983a; Lehmann and Harter, 1984; Schultz et al., 1987; Hogg et al., 1993). Brennan et al. (1980) reported that incubation of soils up to 120 d with Cu caused Cu availability to plants to decrease by up to 70% compared to freshly applied Cu; the observed decreases in Cu availability were generally greatest for soils with the highest OC and Fe and Al oxide contents. Decreased Cu availability due to aging has been attributed to (i) movement of Cu ions from low energy sites to higher energy sites, (ii) alteration of site energy under the influence of the Cu ion, (iii) movement of Cu ions to internal sites less accessible to solution phase, or (iv) formation of a separate solid phase (Lehmann and Harter , 1984). Padmanabham (1983a) suggested that monodentate Cusurface complexes are readily desorbed from goethite, whereas Cu in bidentate surface complexes is less readily desorbed. Sorption hysteresis is greater for  $Cu^{2+}$ ,  $Co^{2+}$ , and  $Zn^{2+}$  than for the much larger  $Pb^{2+}$  ion, which led Padmanabham (1983b) to conclude that the smaller ions could be incorporated into the goethite lattice by forming a bridge with two surface Fe atoms on the oxide surface, whereas  $Pb^{2+}$  is too large to be accommodated.

Other authors have attributed slow adsorption and desorption of heavy metals to diffusion either into the crystal matrix or into surface sites between aggregates of crystals (Barrow, 1985; 1986b; 1989; Van der Zee and Van Riemsdijk, 1991). Benjamin and Leckie (1981) reported a rapid initial (1 h) adsorption of Cd followed by a much slower second step, possibly related to solid-state diffusion in amorphous Fe hydrous oxide. Aringhieri et al. (1985) also found that Cu sorption kinetics in an organic soil were consistent with a dependence on internal diffusion. The time-dependence of heavy metal sorption on goethite has been attributed to initial adsorption on external surface sites, with subsequent diffusion to internal sorption sites (Brüemmer et al., 1988). Intraparticle diffusion coefficients are reported to be at least one order of magnitude smaller than bulk-solution mass transfer coefficients (Lo and Leckie, 1993; Michard et al., 1996). Intraparticle diffusion is less affected by variables such as pH and particle size, but more affected by pore-size distribution than is external mass transfer (Michard et al., 1996).

Differences in mesopore shapes have been used to explain the much slower phosphate desorption from lepidocrocite, with has cylindrical mesopores that are considered less accessible to solution, than from hematite, which has a mixture of cylindrical and slit-shaped mesopores (Madrid and Arambarri, 1985). In highly aggregated Oxisols, long-term sorption rates might be limited by intra-aggregate rather than intraparticle mass-transfer (Nkedi-Kizza et al., 1982). Although batch-shake methods eliminate much intra-aggregate mass-transfer control normally found in aggregated Oxisols (Lima, 1995; Lima and Anderson, 1997), intraparticle diffusion may still be important in batch-shake systems.

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The objectives of this study were to test the hypothesis that the effect of aging on Cu sorption and desorption differs between P-treated, sludge-treated, and untreated Oxisols, and also depends on soil mineralogy and OC content. A previous experiment has shown that P and sludge treatment in Oxisols cause Cu adsorption kinetics to increase but Cu availability (desorption) to decrease (Chapter 2), but the effect of aging on Cu sorption reversibility in P- and sludge-treated soils has not been studied previously.

## **Materials and Methods**

## Soil Material

Samples of A and B horizons from two uncultivated Oxisols, a Dark-Red Latosol and a Yellow-Red Latosol, were used in this study. Both soils have pH near 4.5 in the A horizon and 5.5 in the B horizon. Although both soils are classified as very fine, allitic, isothermic Typic Hapludox, differences in drainage have caused one soil (a Yellow-Red Latosol) to have greater kaolinite:gibbsite and goethite:hematite ratios than the other (a Dark-Red Latosol) (Table 3.1). The A and B horizons of each soil differ in OC content as well as in the relative proportions of amorphous and crystalline Fe, estimated as the ratio of oxalate-extractable to dithionite-extractable Fe. Additional details concerning soil characterization have been described elsewhere (Lima and Anderson, 1997).

Porosity was calculated from  $N_2$  adsorption isotherms (Appendix A4). Total porosity was taken from the experimental isotherms at a partial pressure of 0.99, as suggested by Lippens and de Boer (1964). Micropore ( $r_p < 20$  Å) volume was calculated by the method of Horváth and Kawazoe (1983) and accounted for 15 to 18% of the total pore volume in all samples. Mesopores ( $r_p > 20$  Å) accounted for the remaining pore volume (82 to 85%) and could be classified as slit-shaped pores (de Boer and Lippens, 1964). No macroporosity was detected in any case, as the soil samples showed no steep gradient at partial pressure values near 1.0. Differences in percent micro and mesoporosity between soil samples were not significant (P > 0.05).

Horizon	Clay	OC <sup>†</sup>	Fed‡	Fe <sub>o</sub> ‡	Kt⁵	Gb⁵	Gt:Hn	n SSA <sup>#</sup>	Total porosity
	————g kg <sup>-1</sup> soil ———				g kg <sup>-1</sup> clay			m <sup>2</sup> g <sup>-1</sup>	cm <sup>3</sup> g <sup>-1</sup>
	Dark-Red Latosol (GbHm)								
Α	691	25.3±0.0	99	1.88	350	510	5.0	59±3	0.154±0.019
В	753	9.9±0.1	114	0.65	350	510	4.1	61±3	0.137±0.016
	<u>Yellow-Red Latosol (KtGt)</u>								
Α	711	23.6±0.3	101	1.20	480	375	10.2	53±4	0.128±0.019
В	721	8.0±0.1	114	0.59	480	400	8.3	58±3	0.143±0.024

Table 3.1. Selected properties of A and B horizons of two Oxisols from Brazil.

<sup>†</sup> OC is organic carbon measured by the Walkley-Black method.

<sup>t</sup> F<sub>d</sub> and Fe<sub>o</sub>, respectively, are Fe extracted by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) and ammonium oxalate (pH 3.1) in the dark (Schwertmann, 1964). <sup>8</sup> Kt and Gb, respectively, are kaolinite and gibbsite measured by differential thermal analysis in dithionite-treated clay samples (but expressed on a total-clay basis). <sup>1</sup> Gt:Hm is the goethite:hematite ratio in the clay fraction, measured by X-ray diffraction of NaOH-treated samples (Kämpf and Schwertmann, 1982a; 1982b).

<sup>\*</sup> Specific surface area determined by  $N_2$  adsorption isotherms (BET).

#### Soil Pretreatment

Soils were pretreated with phosphate (P) by reacting samples of each soil material with 10.75 mM Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (21.5 mmol P L<sup>-1</sup>) at a soil:solution ratio of 2:3 to give a P addition rate of 1 g P kg<sup>-1</sup> soil, then washing with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> to remove excess P. The adsorbed P content of all P-treated soils was near 30 mmol kg<sup>-1</sup>. For sludge pretreatment, soils were reacted for 30 d with air-dried, <0.5-mm lime-stabilized sludge at a rate of 5 g kg<sup>-1</sup> soil and a moisture content of 60% of saturation. The dry sludge had an OC content of 276 ± 8 mg kg<sup>-1</sup>; other sludge properties are reported in Appendix A1. The sludge-treated soils contained about 2 g kg<sup>-1</sup> more OC (Appendix A2) than the control soils. Although P- and sludge-treatent caused moderate increases in DTPA-extractable Cu (Chapter 2), the DTPA-extractable Cu concentrations were about three orders of magnitude less than the Cu concentrations adsorbed in the experiments described below. The P- and sludge-treated soils were air-dried and gently crushed to pass a 2-mm sieve.

### Cu Sorption

Copper sorption was measured in batch-shake experiments. Prior to Cu sorption experiments, all soil suspensions were adjusted to pH 5.5 as described in Chapter 2. Copper sorption capacity at pH 5.5 was measured by repeated reaction with 500  $\mu M$ Cu(NO<sub>3</sub>)<sub>2</sub> in a Ca(NO<sub>3</sub>)<sub>2</sub> background electrolyte (I=15 mM) at a soil:solution ratio of 1:100. Suspension pH was readjusted to 5.5 after every two adsorption cycles. Adsorption was complete after nine reactions with 500  $\mu M$  Cu.

To assess the effect of aging upon Cu adsorption and desorption, triplicate samples of untreated and P- or sludge-treated soils were reacted at pH 5.5 for 1 h, 3 d, 18 d, and 54 d with 50 and 150  $\mu M$  Cu(NO<sub>3</sub>)<sub>2</sub> in Ca(NO<sub>3</sub>)<sub>2</sub> (I = 15 mM; 1:100 soil:solution). After the specified adsorption reaction time, the suspensions were centrifuged, the supernatant solutions were decanted, and the centrifuge bottles were weighed to determine the mass of entrained solution. The Cu concentrations in the supernatant solutions were measured by flame atomic absorption spectroscopy. The soil pastes that remained in the centrifuge bottles were then reacted with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> at pH 5.5. Copper desorption was measured after 0.25 h, 1 h, 6 h, 24 h, 3 d, 6 d, and 18 d. The concentration of Cu desorbed at each successive desorption reaction time was corrected for the amount of copper in the entrained solution.

Distribution coefficients for Cu adsorption at each of the four aging times  $(K_{ads})$  were calculated with the equation

$$\mathbf{K}_{ads} = \{\mathbf{C}\mathbf{u}_{ads}\} / [\mathbf{C}\mathbf{u}_{T}]$$
[1]

where  $\{Cu_{ads}\}\$  is the adsorbed Cu concentration (mmol kg<sup>-1</sup>), and  $[Cu_T]$  is the total solution-phase Cu concentration (mmol L<sup>-1</sup>) at each aging time. Distribution coefficients for Cu desorption (K<sub>des</sub>) after each of the four aging times were calculated for the 1-h desorption reaction period with the equation

$$K_{des} = \{Cu_{ads}\}/[Cu_{T}]$$
<sup>[2]</sup>

where  $\{Cu_{ads}\}\$  is calculated here as the difference between the adsorbed Cu concentration at the end of the aging period and the concentration of Cu desorbed after 1-h reaction with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub>.

### Results

## Adsorption Distribution Coefficient

The effect of increased adsorption reaction (aging) time on  $K_{ads}$  is shown in Figure 3.1. Values of  $K_{ads}$  ranged from about 50 in control B horizons at 150  $\mu$ M Cu to 9000 in P-treated A horizons at 50  $\mu$ M Cu. Both the  $K_{ads}$  values and the effect of aging on  $K_{ads}$  followed the general trends P-treated > sludge-treated > control soils, 50 > 150  $\mu$ M Cu,

and A > B horizons, though aging effects in sludge-treated soils at 50  $\mu M$  Cu were greater for B than A horizons. Although aging effects differed slightly between the GbHm and KtGt soils, there were no consistent trends, and the effect of aging on K<sub>ads</sub> depended much less on soil mineralogy and horizon than on soil pretreatment and initial Cu concentration.

The overall increases in  $K_{ads}$  as aging time increased from 1 h to 54 d ranged from less than two-fold for control samples reacted with 150  $\mu$ M Cu to eight-fold for P-treated A-horizon samples reacted with 50  $\mu$ M Cu (Figure 3.1). As aging time increased from 1 h to 18 d,  $K_{ads}$  always increased. However, a further increase in aging time from 18 to 54 d caused little or no additional increase in  $K_{ads}$  in many of the samples. Only P-treated Ahorizon samples exhibited a consistently large increase in  $K_{ads}$  as aging time increased from 18 to 54 d, whereas  $K_{ads}$  for P-treated B-horizon samples actually decreased over that time period. The  $K_{ads}$  values plotted in Figure 3.1 show that it is not possible to predict *a priori* whether the largest increases in  $K_{ads}$  occur between 1 and 3 d, 3 and 18 d, or between 18 and 54 d.

## Fraction of Copper Desorbed

To show the effect of aging on the time-dependence of Cu desorption, Cu desorption is plotted as the fraction of Cu desorbed (i.e., Cu desorbed after the specified desorption time / Cu adsorbed at the end of the specified aging time, hereafter  $Cu_{des}/Cu_{ads}$ ). The time-dependence and the effects of soil type and pretreatment were the same for both Cu concentrations, even though  $Cu_{des}/Cu_{ads}$  for 150  $\mu$ M Cu (Figure 3.2) was about twice that for 50  $\mu$ M Cu (Figure 3.3). Copper desorption is least for the samples aged 18 and 54 d, and greatest for samples aged 1 h. The effects of pretreatment, initial Cu concentration, and soil type and horizon on  $Cu_{des}/Cu_{ads}$  and on the time dependence of  $Cu_{des}/Cu_{ads}$  for

[Cu]<sub>initial</sub> 150µM [Cu] initial 50 µM 10000 4 GbHm<sub>A hor</sub>. 1000 3 100 2 GbHm<sub>B hor.</sub> 1 h 2////// 3 d IN 18 d 1000 54 d  $K_{ads}$  (L kg<sup>-1</sup>) E Kades (L kg<sup>-1</sup> 100 KtGt<sub>A hor.</sub> 1000 100 2 KtGt B hor. 1000 3 100 2 **Control Phosphate Sludge Control Phosphate Sludge** 

samples aged 18 d have been discussed in Chapter 2, so only the effects of aging will be emphasized here.

Figure 3.1. Distribution coefficients (Cu adsorbed/Cu supernatant) for Cu adsorption in control and P- and sludge-treated A and B horizon samples of two Oxisols reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).



Figure 3.2. Time-dependence of fraction of Cu desorbed from control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 150  $\mu M$  Cu for 1h, 3 d, 18 d, and 54 d (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).





The time-dependence of  $Cu_{des}/Cu_{ads}$  and the effect of aging on the time-dependence of Cu desorption differ greatly between control, P-treated, and sludge-treated soils, as well as between A and B horizons. For samples aged 18 or 54 d, Cu desorption from all A horizon samples and from P-treated B horizons was complete after 1 h, whereas control and sludge-treated B horizons required 6 to 24 h to reach desorption steady-state. For the 1-h and 3-d adsorption aging times,  $Cu_{des}/Cu_{ads}$  reached a maximum after 0.25 to 24 h desorption, with subsequent readsorption at longer desorption times. Readsorption always commenced sooner for samples aged 1 h than for samples aged 3 d. Increasing the aging time from 1h to 54 d cause a 40 to 80% decline in values of  $Cu_{ads}/Cu_{des}$  measured after a 1-h desorption reaction. The 1-h desorption time was chosen because it is relevant for understanding Cu remobilization in soil during a heavy rain. The effect of aging on  $Cu_{des,1h}/Cu_{ads}$  at 1 h was not consistently greater in P-treated than sludgetreated and control soils, nor in A than B horizons (Figures 3.2 and 3.3).

### Desorption Distribution Coefficient

Values of  $K_{des}$  calculated for a 1-h desorption time increased as aging increased from 1 to 54 d (Figure 3.4), although aging effects on  $K_{des}$  were only about half those on  $K_{ads}$  (Figure 3.1).  $K_{des}$  values ranged from about 350 for control B-horizon samples aged 1 h with 150  $\mu$ M Cu to 9000 for P-treated A-horizon samples aged 54 d with 50  $\mu$ M Cu. As aging time increased from 1 to 54 d, the increase in  $K_{des}$  ranged from two-fold for control and sludge B horizons at 150  $\mu$ M Cu to four-fold for P-treated A horizons at 50  $\mu$ M Cu. Both the  $K_{des}$  values and the effect of aging on  $K_{des}$  followed the general trend P-treated >sludge > control soil and 50 > 150  $\mu$ M Cu, as previously noted for  $K_{ads}$ . However, the effects of aging on  $K_{des}$  differed less among the different soil pretreatments and initial Cu concentrations (Figure 3.4) than was noted previously for  $K_{ads}$  (Figure 3.1).



Figure 3.4. Distribution coefficients of Cu (Cu remaining adsorbed/Cu supernatant) after 1 h of Cu desorption from control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).

Except for P- and sludge-treated samples reacted with 50  $\mu$ M Cu, the effects of aging on K<sub>des</sub> were similar in A and B horizons, and there was no effect of soil mineralogy. In general, K<sub>des</sub> (Figure 3.4) was greater than K<sub>ads</sub> (Figure 3.1), except for Pand sludge-treated soils at 50  $\mu$ M Cu, where the ratio K<sub>des</sub>/K<sub>ads</sub> was near unity (Figure 3.5). The ratio K<sub>des</sub>/K<sub>ads</sub> decreases with aging time and was greater for control than P- or sludgetreated soils, for 150  $\mu$ M than 50  $\mu$ M Cu, and for B than A horizons. The ratio of K<sub>des</sub>/K<sub>ads</sub> ranged from 1 to 2 for P- and sludge-treated samples at 50  $\mu$ M Cu to 5 or 6 for control B samples at 150  $\mu$ M.

To evaluate whether  $K_{der}/K_{uds}$  values greater than unity are evidence for sorption hysteresis or simply a result of isotherm nonlinearity (i.e., greater K values at lesser sorbed Cu concentrations), the sorbed Cu concentrations are plotted as a function of solution-phase Cu concentration (Figures 3.6-3.8). Although the shape of the adsorption and desorption isotherms is not well defined, because only two initial Cu concentrations were used in this study, it generally is apparent that the adsorption and desorption data do not fall on the same smooth curve, and that sorption exhibits hysteresis. Based on the extent to which desorption points lie above the adsorption data points, hysteresis is greatest for control soils and least for P-treated soils, and is much great for B than A horizons. For most samples, hysteresis is most evident for samples aged 1 h and least evident for samples aged 54 d. Strictly speaking, however, hysteresis cannot be evaluated unless adsorption and desorption times are the same, so it is not possible to use 1-h desorption data to ascertain aging effects on sorption hysteresis.



Figure 3.5. Ratio of  $K_{des, 1}/K_{ads}$  in control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d.



Figure 3.6. Sorbed Cu concentration as a function of solution-phase Cu concentration in control Oxisols samples reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d.



Figure 3.7. Sorbed Cu concentration as a function of solution-phase Cu concentration in P-treated Oxisols reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d.



Figure 3.8. Sorbed Cu concentration as a function of solution-phase Cu concentration in sludge-treated Oxisols reacted with 150 and 50  $\mu$ M Cu for 1 h, 3 d, 18 d, and 54 d.

### Discussion

The effect of P treatment on both  $K_{ads}$  and  $K_{des}$  was greater than the effect of sludge treatment and of soil OC content (A vs. B horizon) or soil mineralogy (KtGt vs. GbHm). However, the effects of initial Cu concentration and aging time were at least as great as the effect of P treatment. The decrease in  $K_{ads}$  and  $K_{des}$  as initial Cu concentration increases indicates that sorption sites differ in their affinity for Cu, with high-affinity sites occupied at low surface coverage. The pronounced effect of P treatment on  $K_{ads}$  and  $K_{des}$ suggests that inner-sphere complexes of P with metal oxides increases the affinity of the surface for Cu, and that this effect is enhanced by aging. An increase in  $K_{ads}$  and  $K_{des}$ caused by sludge treatment might be related to the high affinity of humic substances for Cu (McLaren at al., 1981), and has been reported previously by Petruzzelli et al. (1994). Similarly, the higher  $K_{ads}$  observed for A than B horizons is likely caused by the higher OC content of the A horizon compared with the B horizon. The smaller  $K_{ads}$  observed for the KtGt soil compared with the GbHm soil is consistent with the very low value of Cu distribution coefficient reported for kaolinite by McLaren et al. (1981).

The marked effects of aging upon  $K_{ads}$  and  $K_{des}$  have not been formally reported in the literature. However, based on the original data of Padmanabham (1983a) (Figs. 1 and 2, pages 313 and 314) one could estimate a small increase (about 5 to 10%) in  $K_{ads}$  for Cu in goethite due to aging from 12 to 19 d. The increases in  $K_{ads}$  and  $K_{des}$  indicate that shortterm adsorption experiments underestimate Cu adsorption and overestimate the solutionphase Cu concentration in aged soils.

The fact that samples reacted for either 1 h or 3 d showed Cu readsorption during the desorption period is additional evidence that adsorption does not reach steady-state in 3 d . Similar results have been reported for P adsorption onto Fe oxides (Cabrera et al., 1981; Madrid and Arambarri, 1985). The 80% decrease in Cu desorption with increasing aging time corroborates the results of Brennan et al. (1980), who found that Cu availability to plants decreased up to 70% with increased aging. In that study, aging caused Cu availability to decrease more in samples with higher OC content (Brennan et al. (1980). However, in the present study, aging effects on  $Cu_{des}/Cu_{ads}$  did not differ between A and B horizons nor between sludge-treated and control soils (Figures 3.2 and 3.3). The increases in  $K_{des}$  with increasing aging time, together with the decrease in  $K_{des}/K_{ads}$  for longer aging times indicates that although Cu desorption decreases with aging time, the reaction may approach steady state after 54 d.

Decreased solution-phase ion concentrations with increased aging has been attributed to either diffusional processes (Madrid and Arambarri, 1985; Barrow, 1986a; Strauss et al., 1997) or to changes in sorption mechanism (surface speciation) (Padmanabham, 1983a; 1983b; Lehmann and Harter, 1984). The aging effects observed in the present study may be caused by both changes in surface speciation and by diffusion. Mesopores with radii greater than 20 Å compose over 80% of the total porosity in these soils, and internal diffusion of hydrated  $Cu^{2+}$  (radius ~ 3.5 Å) would not be restricted by pore size. However, micro/mesoporosity and pore shape did not vary significantly (P >0.05) between soil samples, so the differences in aging effects between control and P- or sludge-treated soils, and between A vs. B horizon cannot be explained solely on the basis of diffusion. Therefore, specific chemical interactions between Cu and surface functional groups, and changes from monodentate to bidentate complexes are likely to be a more important cause for the greater aging effect in P-treated samples compared with either control or sludge-treated samples, and in A horizon compared with B horizon. In addition, aging likely causes changes in the surface-phosphate and surface-sludge interactions, so aging effects are more difficult to explain precisely in P- and sludge-treated soils.

In conclusion, this study suggests that aging effects upon Cu desorption and Cu adsorption and desorption distribution coefficients in Oxisols are likely to be caused mainly by time-dependent changes in surface speciation, though by diffusional processes may also play a role. However, the fact that aging has a greater effect on  $K_{ads}$  than on  $K_{des}$ 

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has implications for the use or misuse of distribution coefficients for modeling purposes. Models that ignore this will certainly overestimate Cu availability in Oxisols. Copper desorption from aged Oxisols can be overestimated as much as two-fold if desorption is measured after 1- or 3-d adsorption reactions, as is typically done in laboratory experiments. Both P and sludge treatment caused decreased Cu desorption and increased the effect of aging on Cu sorption reactions

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## **Chapter 4**

## COPPER ADSORPTION/DESORPTION IN PHOSPHATE- OR SLUDGE-TREATED OXISOLS AS AFFECTED BY pH

#### Abstract

Adsorption/desorption reactions of Cu in soils are affected by surface chemistry and solution composition. This study evaluated the effects of pH upon Cu adsorption/desorption by P-treated, sludge-treated, and control A- and B-horizon samples of two Oxisols reacted with 0, 5, 50, and 150 µM Cu. Sorption isotherms changed from a L-type at pH 4.5 to a H-type at pH 6.5. Increasing pH from 4.5 to 6.5 generally caused Cu adsorption to increase more in control than pretreated samples, and in B than A horizons. At a given pH, more Cu was adsorbed by (and generally less Cu was desorbed from) Pand sludge-treated than control samples, and by A than B horizons. Copper adsorption increased by as much as 3.2 times as pH increased from 4.5 to 6.5, with the greatest increase in the B horizon of a Yellow-Red Latosol reacted with 150  $\mu M$  Cu and least increase in the A horizon of a Dark-Red Latosol reacted with 5  $\mu$ M Cu. Increasing preequilibration pH caused the fraction of Cu desorbed to decrease from as much as 0.35 to less than 0.01 (Cu desorbed/Cu adsorbed < 1%) in all A-horizon samples. The fact that a considerable fraction of Cu still remained adsorbed at a preequilibration pH of 4.5 is noteworthy as this may reduce the availability of Cu in Oxisols even at low pH.

#### Introduction

Copper concentrations in natural soil solutions and sediment-water systems typically are controlled by adsorption/desorption reactions (Ellis and Knezek, 1972; James and Barrow, 1981), particularly with surface hydroxyl groups of metal oxides and organic matter (McLaren et al., 1981; Piccolo and Stevenson, 1982; Wang and Chen, 1997). The retention of Cu by selective bonding processes at variable-charge mineral surfaces and layer silicate particle edges is a pH-dependent process usually termed chemisorption or specific adsorption (formation of inner-sphere complexes) (Forbes et al., 1976; McBride, 1994). The free energy of adsorption comprises both an intrinsic term that describes the chemical interaction between the metal and the surface and a Coulombic term for the electrostatic attraction at the surface, which may vary as a function of pH and surface coverage (Stumm and Morgan, 1996). Changes in pH affect not only the surface charge but also Cu speciation (Ritchie and Jarvis, 1986). Specifically adsorbed anions might complicate the effects of pH, because inner-sphere complexes of anions with variablecharge surfaces cause net surface charge to become less positive (more negative) and pH<sub>P7C</sub> to decrease (Sposito, 1989; Stumm, 1992; Kretzschmar et al., 1997; Lima and Anderson, 1997; Spark et al., 1997a).

Copper adsorption by soils (Harter, 1983; Barrow, 1985; Basta and Tabatabai, 1992; Carey et al., 1996), Al oxides (McBride, 1982; Hsu, 1989, Spark et al., 1995a), Fe oxides (McKenzie, 1980, Benjamin and Leckie, 1981, Padmanabham, 1983; Wang and Stumm, 1987; Spark et al., 1995a) and organic matter (Kabata-Pendias and Pendias, 1992) increases as pH increases. Copper adsorption increases with increasing pH for two reasons

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(Barrow, 1989). First, OH groups at variable-charge surfaces deprotonate at high pH, which decreases the electrostatic repulsion between Cu and the surface. Second, CuOH<sup>+</sup> is apparently more strongly sorbed than is Cu<sup>2+</sup> (Barrow et al., 1981). The pK<sub>a</sub> for solutionphase hydrolysis of Cu<sup>2+</sup> to CuOH<sup>+</sup> is 7.7 (Lindsay, 1979). Chemisorption of Cu by metal oxides occurs mainly in the pH range 4.5-6.5 (McBride, 1994). Copper sorption by humic acid is greatest between pH 4 to 5, whereas Cu sorption by fulvic acid is greatest at pH 6 to 7 (Kabata-Pendias and Pendias, 1992). For kaolinite, ion exchange (outer-sphere complexes) is reported to be important at low pH and low ionic strength, whereas an increase in both ionic strength and pH favors chemisorption at amphoteric surface hydroxyls (Schindler et al., 1987; Spark et al., 1995b).

Metal hydrolysis and formation of metal oxides or hydroxides are all favored at high pH. Because metal precipitation might occur even before adsorption sites are occupied by the trace metal of interest, and even when bulk solution is undersaturated with respect to the metal hydroxide, the distinction between chemisorption and precipitation is not always clear (James and Healy, 1972; McBride, 1994; Sparks, 1995). However, electron spin resonance (ESR) studies (McBride, 1982) have shown that most Cu sorbed on noncrystalline alumina at pH 5 to 6 was chemisorbed on Al-OH groups (which may be the dominant surface functional group in Oxisol B horizons). Yet, the ESR signal for Cu chemisorption on goethite decreased as pH was raised from 4.8 to 7.6, which indicated that Cu likely sorbed as a surface precipitate at the higher pH (McBride, 1982). A surface precipitation model (which considers the formation of a surface phase whose composition varies continuously between that of the original solid and a pure

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precipitate of the sorbing material) has been used to describe Cu sorption on amorphous Fe(OH)<sub>3</sub> at pH 5.1 (Farley et al., 1985).

The increase in Cu adsorption with increasing pH corresponds to a decrease in desorption as pH increases (Schultz et al., 1987; McBride, 1994; Temminghoff et al., 1994; Coughlin and Stone, 1995), probably in part because chemisorbed metals are more readily displaced by H<sup>+</sup> ions than by other cations (McBride, 1989). However, even when acidic solutions are used for desorption, metal sorption becomes increasingly less reversible as the pH during adsorption increases (Padmanabham, 1983; Coughlin and Stone, 1995). Liming Oxisols to higher pH has been proved to be an efficient way to control Cu toxicity in coffee seedlings (Gimenez et al., 1992).

The objective of this study is to test the hypothesis that the effect of pH on Cu adsorption and desorption will differ between P-treated, sludge-treated, and untreated Oxisols and between A and B horizons because the affinity for Cu of surface functional groups in each soil material will differ in pH-dependence. A previous study has shown that Cu adsorption at pH 5.5 was greater and the fractional Cu desorption was smaller in P- and sludge-treated than untreated Oxisols, and in A than B horizons (Chapter 2), but the effect of pH on Cu adsorption/desorption in P- and sludge-treated soils has not been studied previously.

#### **Materials and Methods**

## Soil Material

Samples of A and B horizons from two uncultivated Oxisols, a Dark-Red Latosol and a Yellow-Red Latosol, were used in this study. Both soils have pH near 4.5 in the A horizon and 5.5 in the B horizon. Although both soils are classified as very fine, allitic, isothermic Typic Hapludox, the Yellow-Red Latosol has a greater kaolinite:gibbsite and goethite:hematite ratios than the Dark-Red Latosol. Soil properties are reported in Chapter 2; additional details concerning soil characterization have been described elsewhere (Lima and Anderson, 1997).

Soils were pretreated with sludge or P as described in Chapter 2. Properties of the control, P-treated, and sludge-treated soils are reported in Appendix A2.

## Cu Sorption

Replicate 0.45-g subsamples of each soil material were suspended in 30 mL of 5  $mM \operatorname{Ca(NO_3)_2}$  and the pH was adjusted to 4.5, 5.5, and 6.5 (I = 15 mM) with either saturated  $\operatorname{Ca(OH)_2}$  or 7 mM HNO<sub>3</sub>. This pH range was selected because the natural pH in the A and B horizons of these soils respectively is 4.5 and 5.5; the soils typically are limed to a maximum pH of 6.5 when used for agriculture. All samples then were shaken for 24 h on a reciprocating shaker (120 cycles min<sup>-1</sup>), and acid or base was added as needed to readjust pH to the desired value. Samples were shaken again for 24 h and pH was readjusted as necessary before the samples were shaken again for a third 24-h period.

During the third 24-h shaking period, suspension pH changed less than 0.1 pH units, so pH was considered to be stable.

Copper adsorption capacity at pH 4.5, 5.5, and 6.5 was measured by repeatedly reacting the pH-adjusted soil suspensions with sufficient  $Cu(NO_3)_2$  in a  $Ca(NO_3)_2$ background electrolyte (I = 15 mM) to give an initial Cu concentration of 500  $\mu$ M Cu. Because Cu adsorption caused a decrease in pH, especially at pH 6.5, suspension pH was readjusted to 4.5, 5.5, or 6.5 with saturated Ca(OH)<sub>2</sub> after every two adsorption cycles, though little or no pH adjustment was needed for the pH 4.5 samples. Adsorption was considered complete when the increment in Cu adsorption was < 2% of the total Cu previously adsorbed, which corresponded to 6 reactions with 500  $\mu$ M, for pH 4.5 and 5.5, and 8 reactions with 500  $\mu$ M, for pH 6.5. However, all samples were reacted 9 times with 500  $\mu$ M Cu. This "repeated reaction" approach is preferable to a single reaction at a high Cu concentration because Cu concentrations >500  $\mu$ M could cause Cu precipitation in solution either at pH 5.5 or 6.5 (Allison et al., 1990). Although Cu precipitation cannot be ruled out at pH 6.5, the fact that sorption reached a clearly defined plateau is evidence that nearly all sorbed Cu was adsorbed, not precipitated.

To assess the effect of pH on Cu adsorption and desorption at lower initial concentrations, appropriate amounts of Cu(NO<sub>3</sub>)<sub>2</sub> in Ca(NO<sub>3</sub>)<sub>2</sub> (pH 4.5, 5.5, and 6.5; I = 15 mM) were added to each pH-adjusted soil suspension to give initial total Cu concentrations of 0, 5, 50, and 150  $\mu$ M and a solution:soil ratio of 100:1. Triplicate untreated and P- or sludge treated samples were reacted with Cu for 72 h. After adsorption, the suspensions were centrifuged, the supernatant solutions were decanted and saved for Cu analysis, and the centrifuge tubes were weighed to determine the mass of entrained solution. The soil pastes that remained in the centrifuge tubes were then reacted with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> at pH 5.5. Copper desorption was measured after 72 h. The concentration of Cu desorbed at each successive desorption reaction time was corrected for the amount of copper in the entrained solution. The 72-h reaction time was chosen because the amount of Cu adsorbed at 72 h was at least 80% of the total adsorbed after 54 d, and desorption was always at least 95% complete after 72 h (Chapter 3). Total solutionphase Cu concentration (supernatant [Cu<sub>T</sub>]) was analyzed by either electrothermal or flame atomic absorption spectroscopy.

Distribution coefficients for Cu adsorption (K<sub>d</sub>) at each pH were calculated as

$$\mathbf{K}_{d} = \{\mathbf{C}\mathbf{u}_{ads}\}/[\mathbf{C}\mathbf{u}]$$
<sup>[1]</sup>

where { $Cu_{ads}$ } is the adsorbed Cu concentration (mmol kg<sup>-1</sup>), and [Cu] is the final solutionphase Cu concentration (mmol L<sup>-1</sup>) after the 72-h adsorption reaction. Distribution coefficients for Cu desorption were calculated according to equation [1], except that for desorption, { $Cu_{ads}$ } was calculated as the difference between the adsorbed Cu concentration at the end of adsorption and the concentration of Cu desorbed after a 72-h reaction with 5 mM Ca(NO<sub>3</sub>)<sub>2</sub>.

## Results

## Copper Adsorption Capacity

Copper adsorption capacity increased with increasing pH (Table 4.1). As pH increased from 4.5 to 5.5 the Cu adsorption capacity increased 2.7- to 3.0-fold in A-

horizon samples, and was 3.3 to 3.9 times greater at 5.5 than 4.5 in B-horizon samples, with P-treated samples exhibiting the greatest increase. As pH increased from 5.5 to 6.5, Cu sorption capacity increased 2.8- to 3.6-fold in the A horizon, and 3.3 to 3.9 times in the B horizon, with the greatest increase for control samples. Thus, pH always had a greater effect in B than A horizons, but P-treated samples exhibited the greatest increase from pH 4.5 to 5.5, and control samples from pH 5.5 to 6.5.

Table 4.1. Copper adsorption capacity ( $Cu_{ads. max.}$ ) at pH 4.5, 5.5, and 6.5 of control and Por sludge-treated soil samples.

	Cu	<sub>ds. max.</sub> pH	4.5	C	u <sub>ads. max.</sub> pH	H 5.5	C	u <sub>ads. max.</sub> pH	6.5
Hor.	Control	Р	Sludge	Control	Р	Sludge	Control	Р	Sludge
	·				mmol k	g <sup>-1</sup>			
			D	ark-Red	Latosol	(GbHm)			
Α	19±0	24±1	22+1	54±4	70±0	60±2	192+5	193±2	168±1
В	12±0	15±0	14+0	44±0	50±0	47±2	173±6	167±4	160±3
			Y	ellow-Red	d Latoso	l (KtGt)			
Α	19±0	21±1	20+0	53±3	62 ±2	54±1	184±0	180±6	171±12
В	12+0	14±1	12+0	47±3	49±1	43±3	167±3	183±10	160±4

Pretreatment with P caused Cu adsorption capacity to increase by as much as 25% compared with control soils at pH 4.5 and 30% at pH 5.5, but had little effect at pH 6.5. At pH 4.5 and 5.5, the Cu adsorption capacity of sludge-treated soils generally was intermediate between control and P-treated soils, whereas sludge-treated soils have the smallest Cu adsorption capacity at pH 6.5.

## Copper Adsorption

Adsorption isotherms at pH 4.5, 5.5, and 6.5, are shown in Figure 4.1. The shape of the isotherms (Giles et al., 1960) changed from low to high affinity as pH increases. Based on the shape of the adsorption isotherms, a high-affinity type isotherm is observed for all A-horizon samples as well as all P-treated samples at pH 6.5. Adsorption isotherms for untreated and pretreated samples of both the Dark-Red Latosol (hereafter GbHm) and the Yellow-Red Latosol (hereafter KtGt) were quite similar in shape, except for control and sludge-treated B-horizon samples at pH 6.5. For B-horizon samples, considerable adsorption occurred at pH values below the pH<sub>PZSE</sub> (Appendix A2). This can be better seen when the fraction of Cu adsorbed (Cu<sub>nds</sub>/Cu<sub>added</sub>) is plotted as a function of pH (Figure 4.2).

The higher the initial  $[Cu_T]$ , the greater the increase in  $Cu_{ads}/Cu_{added}$  caused by an increase in pH from 4.5 to 6.5. For all initial  $[Cu_T]$ , the increase in  $Cu_{ads}/Cu_{added}$  upon increasing pH was always greater in the B than the A horizon. There is also a trend for  $Cu_{ads}/Cu_{added}$  to increase more in untreated than pretreated samples, and in the KtGt soil than the GbHm soil, as pH increased from 4.5 to 6.5 (Figure 4.2). Specifically, for samples reacted with 5  $\mu$ M Cu, increasing pH from 4.5 to 6.5 caused  $Cu_{ads}/Cu_{added}$  in control samples of the GbHm soil to increase about 1.2 times in the A horizon and 1.4 times in the B horizon.



Figure 4.1. Copper adsorption isotherms in control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with Cu at pH 4.5, 5.5, and 6.5 (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).



Figure 4.2. Fraction of Cu adsorbed as a function of pH in control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 5, 50, and 150  $\mu M$  Cu (1:100 soil:solution) (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).

Compared with the GbHm soil, the KtGt soil reacted with 5  $\mu$ M Cu exhibited a similar trend with respect to soil horizon, but Cu<sub>ads</sub>/Cu<sub>added</sub> values were 0.03 to 0.06 units smaller for the KtGt than the GbHm soil at pH 4.5 (Figure 4.2). Pretreated samples showed a greater Cu<sub>ads</sub>/Cu<sub>added</sub> than control samples at pH 4.5, but adsorption was almost complete at either pH 5.5 or 6.5, so little differences could be seen between untreated and pretreated samples with respect to Cu<sub>ads</sub>/Cu<sub>added</sub> at either pH 5.5 or 6.5. For samples reacted with 50  $\mu$ M Cu, increasing pH from 4.5 to 6.5 caused Cu<sub>ads</sub>/Cu<sub>added</sub> in control samples of the GbHm soil to increase almost 1.5 times in the A horizon, and 2.2 times in the B horizon. Pretreated B-horizon samples showed a greater Cu<sub>ads</sub>/Cu<sub>added</sub> than control Bhorizon samples at pH 5.5, but little or no differences at either pH 4.5 or 6.5. Again the GbHm and the KtGt soils reacted with 50  $\mu$ M Cu exhibited a similar trend with respect to pretreatment and soil horizon, but Cu<sub>ads</sub>/Cu<sub>added</sub> values were 0.06 to 0.09 units smaller for the KtGt soil than the GbHm soil. For 150 µM Cu, increasing pH from 4.5 to 6.5 caused Cu<sub>ads</sub>/Cu<sub>added</sub> in control samples of the GbHm soil to increase about 2.3 times in the A horizon, and 2.8 times in the B horizon; for the KtGt soil, Cu<sub>ads</sub>/Cu<sub>added</sub> in control samples increased almost 2.5 times in the A horizon, and 3.2 times in the B horizon.

Pretreatment generally had a greater effect on  $Cu_{ads}/Cu_{added}$  for samples reacted with 150  $\mu$ M Cu than for samples reacted with either 5 or 50  $\mu$ M Cu. The pH at a given fraction of adsorbed Cu (with no apparent saturation) increased with increasing [Cu<sub>T</sub>]. This increase is greater in control than either P- or sludge-treated soils, and in B than A horizon. Another way of seen the effects of soil pretreatment is that, despite the [Cu<sub>T</sub>], for a given fraction of adsorbed Cu, the pH tends to be higher for control than for either P- or sludge-treated samples.

## Copper Desorption

Copper desorption decreased remarkably as preequilibration pH increased. For a given pH, there was a trend of decreasing the fraction of Cu desorbed ( $Cu_{des}/Cu_{ads}$ ) as [ $Cu_T$ ] decreased. There is also a trend of  $Cu_{des}/Cu_{ads}$  being smaller in A than B horizon, and in the GbHm soil than in the KtGt soil, though little differences regarding both OC content or mineralogy occurred at pH 6.5 (Figure 4.3). As [ $Cu_T$ ] increases, much more Cu tends to desorb at either pH 5.5 or 6.5, so that increasing preequilibration pH from 4.5 to 6.5 caused the shape of the curves to change from exponential, at low [ $Cu_T$ ], to almost linear, at high [ $Cu_T$ ]. Soil pretreatment generally decreased  $Cu_{des}/Cu_{ads}$  and its effects were greater in B than A horizons.

Except for B-horizon samples reacted with 150  $\mu$ M Cu, for any other sample Cu<sub>des</sub>/Cu<sub>ads</sub> values at pH 6.5 were always smaller than 0.01, so that differences in Cu<sub>des</sub>/Cu<sub>ads</sub> caused by OC content, mineralogy or soil pretreatment are difficult to be seen. For samples reacted with 5  $\mu$ M Cu, Cu<sub>des</sub>/Cu<sub>ads</sub> at pH 4.5 in control samples were about 2.3 times smaller in the A horizon than in the B horizon of the GbHm soil. In the KtGt soil, Cu<sub>des</sub>/Cu<sub>ads</sub> in control samples was about 1.8 times smaller in the A horizon than in the B horizon. Pretreatment showed little effect in the GbHm soil, but caused Cu<sub>des</sub>/Cu<sub>ads</sub> at pH 4.5 to decrease as much as 1.6 times in the KtGt soil. For 50  $\mu$ M Cu, Cu<sub>des</sub>/Cu<sub>ads</sub> was about 1.4 times smaller in the A than in the B horizon of both soils at pH 4.5, and about 3 times smaller in the A than in the B horizon of both soils at pH 5.5.



Figure 4.3. Fraction of Cu desorbed in 5 mM Ca(NO<sub>3</sub>)<sub>2</sub> (pH 5.5) from control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 5, 50, and 150 µM Cu (1:100 soil:solution) at pH 4.5, 5.5, and 6.5 (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol).

Pretreated B-horizon samples from both soils desorbed up to 3 times less Cu (on a fractional basis) than control B-horizon samples at pH 5.5, and sludge pretreatment affected  $Cu_{des}/Cu_{ads}$  somewhat less than did P treatment. Little or no differences in the  $Cu_{des}/Cu_{ads}$  values between untreated and pretreated samples were observed at either pH 4.5 or 6.5. For samples reacted with 150  $\mu$ M, soil pretreatment also decreased  $Cu_{des}/Cu_{ads}$  at pH 5.5 (up to 2 times), but had little effect at either pH 4.5 or 6.5. Differences between soil horizons with respect to  $Cu_{des}/Cu_{ads}$  were smaller for samples reacted with 150  $\mu$ M Cu than for samples reacted with either 5 or 50  $\mu$ M Cu. As for  $Cu_{ads}/Cu_{added}$  (Figure 4.2), pretreatment generally had a greater effect on  $Cu_{des}/Cu_{ads}$  for samples reacted with 150  $\mu$ M Cu (Figure 4.3).

#### Distribution Coefficients

The effects of pH on the adsorption and desorption distribution coefficient of Cu  $(K_d)$  in control and P- or sludge-treated samples reacted with 150  $\mu$ M are presented in (Figure 4.4). For adsorption, increasing pH from 4.5 to 5.5 caused  $K_d$  to increase up to 3.4 times in control, up to 3.9 times in sludge-treated, and up to 6.2 times in P-treated samples. For desorption, the same increase in pH caused  $K_d$  to increase up to 2.2 times in control, up to 2.9 times in sludge-treated, and up to 3.1 times in P-treated samples. For both adsorption and desorption  $K_d$ , the pH effect was greater in the A than B horizon. Adsorption  $K_d$  at pH 6.5 were at least one order of magnitude greater in the B horizon and two orders of magnitude greater in the A horizon than adsorption  $K_d$  at pH 4.5. The same trend regarding soil horizon was observed for desorption  $K_d$ , but again the effects of pH

were smaller for desorption  $K_d$  than for adsorption  $K_d$ . Except for the B horizon of the KtGt soil, increasing pH up to 6.5 had a similar effect in adsorption and desorption  $K_d$  for both soils.



Figure 4.4. Adsorption and desorption distribution coefficients of Cu in control and P- or sludge-treated A and B horizon samples of two Oxisols reacted with 150  $\mu$ M Cu (1:100 soil:solution) at pH 4.5, 5.5, and 6.5 (GbHm = Dark-Red Latosol; KtGt = Yellow-Red Latosol)

Desorption  $K_d$  (Figure 4.4, right) was always greater than adsorption  $K_d$  (Figure 4.4, left). This difference decreased with increasing preequilibration pH, and is smaller for A compared with B horizons. At pH 6.5, little difference was observed between adsorption and desorption  $K_d$  for A-horizon samples ( $K_d$  adsorption/ $K_d$  desorption ~ 1.0).

#### Discussion

A change in the shape of the isotherms from low to high affinity (Figure 4.1) suggests a change in site affinity as pH increases, which may be associated with an increase in the Coulombic energy of attraction (Stumm and Morgan, 1996). Isotherms of the L-type have been associated with chemisorption (McBride, 1994), and are explained by a high affinity of the adsorbent for the adsorbate at low concentration, which then decreases as concentration increases (Sparks, 1995). An H-type isotherm indicates a very strong adsorbate-adsorbent interaction such as inner-sphere complexes (i.e., chemisorption), and is an extreme case of the L-type isotherm (McBride, 1994; Sparks, 1995). At pH 4.5, there is possibly a limited number of sites with high affinity for Cu, because the Coulombic energy of attraction is very small (solution  $pH \le pH_{PZSE}$ ). As pH increases to 5.5, the number of sites with great affinity for Cu increases, but are still limited, since the slope of the isotherm decreases markedly at high concentrations. This increase is greater in the A horizon compared with B horizon, and in P- and sludge-treated samples compared with control samples. Such observations are reported in a previous study, and have been attributed to the fact that P and sludge treatment might convert M<sup>3+</sup>-OH groups into M<sup>3+</sup>-phosphate and M<sup>3+</sup>-organo functional groups, thereby modifying the

reactivity of the site toward Cu but not increasing the number of surface M<sup>3+</sup> sites, which exert overall control on the Cu adsorption capacity (Chapter 2). A further increase in pH from 5.5 to 6.5 results in a remarkable increase in the number of sites with very great affinity for Cu. A greater increase occurred in the A horizon compared with the B horizon , and in P-treated compared with either sludge-treated or control samples. For P-treated samples, this occur despite of the fact that at high pH, the affinity of the surface for the pre-adsorbed phosphate tends to decrease, particularly in the A horizon.

The increase in Cu adsorption as pH increases (Figure 4.2) has been reported by several authors for either soils or pure sorbents. A greater adsorption for surface horizons compared with subsurface horizons has also been reported (Carey et al., 1996), and could be attributed to the very strong interaction between Cu and soil organic matter (McBride, 1989). This and the different behavior of control samples compared with either P- or sludge-treated samples (especially at high  $[Cu_T]$ ) suggests that the charge of the surface is of great importance for Cu adsorption.

Part of the increase in Cu adsorption with increasing pH has been attributed to an increase in the concentration of CuOH<sup>+</sup> species as pH increases (Barrow et al., 1981). However, at pH 6.5, most of the Cu species in solution would still be present as Cu<sup>2+</sup> (Table 4.2). These observations all questioned the hypothesis that the identity of the adsorbing ion is much more important for adsorption equilibria than is the surface charge (Spark et al., 1995a), at least within the pH range of this study.

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ncentration, [Cur] as simulated by MINTEQA2 (All

		$Cu_{\rm T}$ ] = 5 $\mu M$			$u_{\rm T}$ ] = 50 $\mu M$			u <sub>T</sub> ] =150 μM	
Cu species	4.5	5.5	6.5	4.5	5.5	6.5 <sup>‡</sup>	4.5	5.5	6.5 <sup>\$</sup>
					%				
Cu⁺²	100.00	<b>09</b> .60	86.06	100.00	99.58	84.60	100.00	99.53	81.67
CuOH⁺	·	0.22	1.87	·	0.22	1.84	•	0.22	1.77
Cu(OH) <sub>2 AQ</sub>	·	0.13	10.94	ı	0.13	10.70	•	0.13	10.31
Cu <sub>2</sub> (OH) <sup>2+</sup> 2	·	ı	0.10	·	0.01	0.95	•	0.04	2.66
CuHCO,⁺	·	0.05	0.39		0.04	0.38	·	0.04	0.37
CuCO <sub>3 AQ</sub>	I	ı	0.58	•	0.01	0.57	ı	0.01	0.55

re too 1 p low to promote significant complex formation (unpublished data, 1996). 0

<sup>‡</sup> Cu species do not account for all Cu because formation of the solid phases CuO, and CuCO<sub>3</sub>. Cu(OH)<sub>2</sub> is thermodynamically possible. <sup>4</sup> Cu species do not account for all Cu because formation of the solid phases Cu(OH)<sub>2</sub>, CuO, CuCO<sub>3</sub>. Cu(OH)<sub>2</sub>, and 2CuCO<sub>3</sub>. Cu(OH)<sub>2</sub> is thermodynamically possible. Even though surface charge might play an important role in Cu adsorption, it is noteworthy to mention that a considerable fraction of Cu in B-horizon, control samples was adsorbed at pH values below the  $pH_{PZSE}$  (Appendix A2) (especially at low [Cu<sub>T</sub>]), which is a typical behavior of chemisorbed cations (Padmanabham, 1983).

The shift in the adsorption curves toward a more alkaline region as  $[Cu_{\tau}]$  increases (Figure 4.2) has been reported elsewhere (Benjamin and Leckie, 1981; Farley et al., 1985). This arises from the effect of a high degree of occupancy of adsorption sites in lowering the tendency of further Cu chemisorption (McBride, 1994). However, such effects appear to be of less importance in P- and sludge-treated soils, possibly because of a greater affinity of either P- or sludge-treated soils for Cu. This is consistent with the fact that at a given fraction of adsorbed Cu and despite the  $[Cu_{\tau}]$ , the pH tends to be higher for control than for either P- or sludge-treated samples, a behavior that has been reported also for trace metal adsorption in combined goethite- and silica-humic acid systems (Spark et al., 1997b).

The smaller fractional desorption as preequilibration (adsorption) pH increases (Figure 4.3) has been reported elsewhere (Padmanabham, 1983; Coughlin and Stone, 1995) and may arise from the fact that a monodentate complexation reaction should give way to a bidentate reaction at higher pH, which requires a large activation energy for the desorption (McBride, 1994). A small fractional desorption of Cu in either soils or pure sorbents as observed in this study has been reported also by McLaren and Crawford (1974) and McLaren et al. (1983). According to McLaren et al. (1983), this suggests that some reactions involved in the adsorption processes are irreversible, very slowly reversible, or require a high activation energy for desorption, or involve a combination of all three. A high activation energy for desorption has been hypothesized to explain a smaller fractional Cu desorption at pH 5.5 in P- or sludge-treated samples of Oxisols compared with untreated ones (Chapter 2). Furthermore, the fact that a considerable fraction of Cu in Oxisols remains adsorbed even if a short adsorption time (e.g., 1 h) is followed by a long desorption period (e.g., 54 d) (Chapter 3) indicates that a somehow irreversible, or very slowly reversible reaction, occurs at the very beginning of Cu adsorption.

The large increase in the adsorption  $K_d$  upon increasing pH (Figure 4.4) has been reported elsewhere (Basta and Tabatabai, 1992) and is consistent with the hypothesis that site affinity increases as pH increases (isotherms change from L-type to H-type, Figure 4.1). Yet, the great difference between desorption and adsorption  $K_d$  at pH 4.5 (markedly in B-horizon samples) suggests that sites with great affinity for Cu exist even at pH values below the pH<sub>PZSE</sub>, *i.e.*, the "intrinsic" term, as described by Stumm and Morgan (1996), is an important component of the free energy of adsorption of Cu in Oxisols, and might be responsible for the small fractional Cu desorption (Cu adsorbed/Cu desorbed < 0.45) observed even at pH 4.5. The greater increase in adsorption  $K_d$  for A compared with B horizon, and for P- and sludge-treated soils compared with control soils (at pH 5.5) is also consistent with the hypothesis that, for the pH range and the soil samples used in this study, surface charge is much more important for adsorption equilibria than is ion speciation.

In conclusion, this study suggests that in the pH range 4.5 to 6.5, Cu availability in Oxisols is likely to be controlled by the surface chemistry rather than Cu speciation in solution. Increasing preequilibration pH from 4.5 to 6.5 caused Cu adsorption to go

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almost to completion and desorption to decrease markedly. However, the fact that a considerable fraction of Cu still remained adsorbed at pH values below the  $pH_{PZSE}$  is noteworthy as this will reduce greatly the availability of Cu in Oxisols.

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**APPENDICES** 

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Sludge characterization<sup>†</sup>

Constituent	g kg <sup>-1</sup> dry sludge
Al	5.88±0.70
В	0.03±0.01
Ca	153.37±18.57
Cu	0.24±0.01
Fe	14.05±1.61
К	19.02±2.88
Mg	8.92±1.18
Mn	0.22±0.02
Мо	0.05±0.01
Na	4.62±0.59
Р	31.77±3.96
Zn	0.48±0.07
Organic C <sup>‡</sup>	275.75±8.28
Total C <sup>§</sup>	313.40±2.53

<sup>†</sup>Elemental analysis done by ICP after extraction of oven-dried (550 °C for 8 h), < 0.5-mm sludge with 6 M HNO<sub>3</sub>.

<sup>†</sup>Organic C measured by the Walkley-Black method.

<sup>§</sup> Total C determined by high-temperature combustion.

Sludge 6.10 4.35 4.20 5.75 Chemical properties of control (Ctrl) and P- or sludge-treated A- and B-horizon samples of two Brazilian Oxisols. pH<sub>PZSE</sub> 4.00 5.85 3.75 5.35 ሲ 6.10 4.30 4.35 6.25 CEI 10±1 6.3±0.1 12.2±0.2 10.3±0.1 19±1 28.2±0.0 39.6±1.7 38.9±0.2 20±0 24.5±0.1 39.3±1.4 34.7±0.5 **4.8±0.2** Sludge **DTPA-Extractable Cu 5.5±0.1** – µmol kg<sup>-1</sup> പ Dark-Red Latosol (GbHm) <u> Yellow-Red Latosol (KtGt)</u> **2.6±0.2** GEI Sludge 13±1 469±1 2330<del>1</del>69 1779±21 Pmehlich --μmol kg<sup>-1</sup> 341±20 10±0 10±1 5±0 6±1 CH 25.3±0.0 26.7±0.1 25.7±0.5 11.8±0.6 **9.6±0.8** Crtl and P Sludge g kg<sup>-l</sup> 8 9.9<del>1</del>0.1 **23.6±0.3** 8.0±0.1 Hor. ш A ◄ B



Titration curves for the determination of the  $pH_{PZSE}$  of control, P-treated, and sludge-treated A- and B-horizon samples of two Brazilian Oxisols.

Specific surface area, total porosity, and pore distribution (micro and mesoporosity) of control (Ctrl) and P- or sludge-treated A- and Owinals ...... Å ţ -• ם איט

	Microporosity Mesoporosity	Sludge Ctrl P Sludge Ctrl P Sludge	%	tosol (GbHm)	).171±0.010 17±1 16±3 14±1 83±1 84±3 86±1	).143±0.008 21±4 16±1 15±1 79±4 84±1 85±1	atosol (KtGt)	0.136±0.001 15±2 15±2 16±0 85±2 85±2 84±0	).138±0.009 20±1 13±1 16±1 80±1 87±1 84±1	
	Total porosity	P Slud	-cm <sup>3</sup> g <sup>-1</sup>	Dark-Red Latosol	155±0.027 0.171±	149±0.014 0.143±	Yellow-Red Latoso	135±0.019 0.136±	174±0.013 0.138±	
azılıan Oxisols.		CHI			0.130±0.017 0.	0.120±0.024 0.		0.140±0.010 0.	0.105±0.010 0.	
of two Br	SSA	Sludge				60±1	57±1		56±1	58±1
umples o		Ч	m <sup>2</sup> g <sup>-1</sup>		60±4	63±1		53±3	62±2	
s nozno		E			64±5	63±2		54±3	54±2	
B-hc		Hor.			¥	B		¥	В	

