COPPER ADSORPTION/DESORPTION CHARACTERISTICS ON COPPER AMENDED SOILS

by

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(ABSTRACT)

Laboratory tests were conducted to determine Cu availability of three Virginia soils amended with Cu as either Cu-rich pig manure or $CuSO_4$ with the same Cu content as that in manure. The study also assessed the capability of Mehlich-3 to estimate deficient and toxic Cu levels in soil. Application of Cu as manure or $CuSO_4$ did not affect grain yield or grain Cu concentration in corn grown at each site. Young corn plant height was reduced by $CuSO_4$ application on the Bertie sandy loam, an indication of greater toxicity from inorganic than organic Cu.

Very little exchangeable or solution Cu was present in any of the three soils. The vast majority of Cu was distributed between the organic and soil oxide fractions. The ratio of soil oxide to organic matter determines the relative distribution of Cu among these fractions. Most organically bound Cu was held by specific adsorption mechanisms and Mehlich-3 strongly extracts this fraction. Mehlich-3 extraction patterns were indicative of Cu binding strength in the different soils. Since Mehlich-3 strongly extracts specifically bound Cu and only poorly removes oxide Cu, this test may underestimate Cu availability on sandy soils with low organic matter content. However, Mehlich-3 provides an acceptable test for soil Cu.

Soil sorption characteristics were studied for Cu, Pb, and Zn added, both alone and simultaneously. Copper sorption energy was higher than both Pb or Zn, however, sorption capacity followed the order Pb > Zn > Cu. High Pb and Zn sorption was in part due to precipitation reactions especially at high initial solution concentrations. Zinc was bound to soil mostly by weak electrostatic forces. Copper and Pb were bound at specific sorption sites and by complex multi-site bonding mechanisms possibly involving organic substances. These specific and multi-site mechanisms account for metal ions removed from solution at low concentration. Even at low metal concentration, Cu and Pb sorption results in concurrent release of H^+ and Ca^{2+} at a greater than one to one charge basis.

Soils adjusted to various pH levels were equilibrated with Cu solution and then extracted with a series of dilute acid extractions to determine Cu adsorption and fixation capacities. Copper adsorption and more importantly Cu fixation increased with an increase in soil pH. Soil with a high organic matter content as a result of manure applications adsorbed and fixed more Cu at all pH levels than the control and $CuSO_4$ soil. The presence of organic matter may have a greater effect on metal sorption characteristics than maintenance of pH $\geq$ 6.5. Heavy metal sorption was accompanied by concurrent release of H^+ and Ca^{2+} which represents exchangeable and specifically bound cation nutrients. Soils which receive heavy metal applications from sewage sludge or animal manure would have a short-term increase in plant available nutrients at the expense of long-term reserve capacity. Soil tests for cation nutrient availability on soils receiving heavy metal applications should be adopted to account for these responses.

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Dedication

I dedicate this work to my parents Sidney T. and Hazel H. Reed for all their love and support. And to my brother Joseph C. and my sisters Jayne D. and Cynthia M. Reed I thank you for not being jealous because Mom likes me best. And to my son Nicolas A. Reed I hope your career is filled with more happiness and success than mine, Love Dad.

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Chapter 1

Introduction

Background Information on Copper Usage

There are 7,500 Virginia farms with some 400,000 swine (*Sus scrofu domesticus*), making swine production in Virginia a major agricultural enterprise (Virginia Agricultural Statistics Service, 1989). Copper sulfate ($CuSO_4$) is commonly used as a feed additive for swine and also poultry (*Gallus gallus domesticus*) to promote weight gain and feed efficiency (Stahly et al., 1980; Lexmond and de Haan, 1977). As much as 250 mg Cu kg^{-1} of feed are fed to weanling pigs. Originally Cu was thought to have an antibiotic affect in the gastrointestinal tract but new evidence suggests that Cu may have a biochemical influence on growth control systems (Zhou et al., 1992; Zhou et al., 1992). Although a portion of Cu ingested by pigs may accumulate in certain tissue most is excreted in manure. Copper excreted in manure is in high concentrations of up to 1000 mg kg^{-1} (Miller et al., 1986). The high Cu concentrations have led to concerns about the long-term environmental effects of land application of these Cu rich manures. Research herein addresses environmental effects from long-term Cu rich manure application.

Long-term Field Research

In 1978 field plots were established to determine long-term affects of Cu applications as either Cu rich manure or $CuSO_4$ to agricultural soils. Sites were chosen in the Atlantic Coastal Plain, Limestone Valley, and Piedmont regions of Virginia. The experimental design was a randomized complete block with four replications of each of the following treatments:

1. A control,
2. 357 kg Cu ha^{-1} as $CuSO_4$ application over 14 years from 1978 through 1991, and
3. 357 kg Cu ha^{-1} as wet Cu rich pig-manure (1210 t ha^{-1}) application over 14 years from 1978 through 1991.

The inclusion of the $CuSO_4$ treatment was to assess the effect of organic matter on Cu retention.

Plots 3.66 x 6.10 m with 0.9 m (0.76 at Piedmont) row widths were designed with large borders and appropriate tillage procedures were used to minimize lateral movement of soil during the long-term field research. Corn was planted at recommended rates on each site during each year of the long-term research. Weed and pest control, and supplementary fertilization were applied each year as necessary. Annual soil and plant tissue analysis were used to determine field management procedures to maintain soil fertility for high yield corn production. Limestone was periodically applied to maintain soil pH ≥ 6.5. The broadcast amendments were then disced into the soil.

Height and mass of young corn plants were measured to determine the effect of treatments on corn growth. Concentration of selected elements in corn ear leaf samples (taken shortly after emergence of the ear) and corn grain (samples taken at harvest) plus grain yield (at black layer) were also determined annually to assess treatment effects. Surface and subsurface soil samples, taken yearly before application of each treatment, were analyzed for DTPA extractable Cu and other selected metals to evaluate accumulation and mobility of Cu. Surface soil samples were used to examine Cu, Pb, and Zn retention characteristics, and subsurface samples were used to determine effects of Cu rich manure and $CuSO_4$ application on downward movement of Cu in soil.

Site Characteristics

Sites were chosen to represent diverse climatic and soil characteristics within Virginia to ensure wide applicability of the experimental results. The first soil, a Bertie fine sandy loam (fine-loamy, mixed, mesic Aquic Hapludults) was located on the Tidewater Research Station in the Atlantic Coastal Plain region of Virginia. The site is at an elevation of 24 m and at approximately 36°41″ latitude and 76°47″ longitude. Annual precipitation (Table 1) for the growing season (April through August) at this site averages 56.4 cm with no monthly average below 8.2 cm. Average monthly temperature ranged between 14°C in April to 26°C in July.

A second site was located in Blacksburg, elevation 622 m, 37°14″ latitude, and 80°25″ longitude. The soil was a Guernsey silt loam (fine, mixed, mesic Aquic Hapludalfs) located in the Limestone Valley region. Average temperatures in Blacksburg are slightly cooler than that at Holland and growing season precipitation (May through October) is 52.2 cm (Table 1).

The third site was located on the Northern Piedmont Research Station, elevation 153 m and at approximately latitude 38°13″ and longitude 78°06″. The growing season

Table 1. Mean annual precipitation (cm) and daily maximum and minimum temperatures (°C) by month for the years 1961 through 1990 at the Holland (Tidewater), Blacksburg, and Piedmont locations.

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
						Holland						
char . Precipitation	10.4	9.0	10.3	8.2	10.4	11.2	13.4	13.2	10.4	9.2	7.6	8.9
Mean Daily Maximum	8.9	10.4	15.6	20.9	25.3	29.2	31.0	31.0	30.4	27.6	22.1	17.3
Mean Daily Minimum	-2.7	-1.4	2.8	7.1	12.4	17.0	19.4	18.8	15.2	8.5	4.11	-0.5
						Blacksburg						
Precipitation	7.0	7.3	9.0	9.2	10.3	8.7	10.2	9.6	8.9	4.5	7.3	7.2
Mean Daily Maximum	4.6	6.4	12.1	17.3	22.2	26.0	27.9	27.4	24.1	18.5	12.9	6.9
Mean Daily Minimum	-7.2	-6.0	-1.3	3.3	8.1	12.6	14.9	14.3	10.4	3.6	-0.5	-4.9
						Piedmont						
Precipitation	7.1	6.9	8.7	7.9	11.3	8.7	11.4	10.9	9.0	10.2	9.2	7.8
Mean Daily Maximum	5.8	7.6	13.3	19.0	23.8	28.2	30.2	29.4	26.0	20.1	14.4	8.2
Mean Daily Minimum	-5.6	-4.1	0.7	5.8	11.2	15.9	18.3	17.7	13.8	6.9	2.2	-2.9

for corn in the Piedmont region begins in late April and lasts through September. Temperatures at Piedmont are intermediate between Holland and Blacksburg and precipitation is 59.2 cm during the growing season (Table 1). Two soils were used at this site, a Starr-Dyke clay loam (fine-loamy, mixed, thermic Fluventic Dystochrept-clayey, mixed, mesic Typic Rhodudult) and a Davidson clay loam (clayey, kaolinitic, thermic Rhodic Paleudults).

The overall objectives of this research were as follows:

1. to determine the effect of Cu applications to agricultural soils, as either Cu-rich manure or $CuSO_4$, on corn yield,
2. to determine the fraction of soil Cu extracted by the Mehlich-3 soil tests and assess the suitability of Mehlich-3 as a test for predicting both deficient and toxic Cu levels in diverse Virginia soils,
3. to describe adsorption characteristics of Cu, Pb, and Zn added to soil either individually or simultaneously, and
4. to evaluate the effect of Cu-rich manure or $CuSO_4$ applications and pH adjustment to soil on subsequent Cu adsorption and desorption by soils.

This research is reported in three sections entitled, "Relationships Among Plant Response, Cu Fractions, and Mehlich-3 Extractable Cu for Soils Amended with Either $CuSO_4$ or Copper Rich Pig Manure", "The Effect of pH on Copper Adsorption/Desorption by Soils Amended with Pig Manure or Copper Sulfate", and "The Effect of Competing Ions on Metal Retention by Soil". Results of this research are expected to aid soil testing laboratory personnel adopt Mehlich-3 as a soil test for adequacy as well as deficiency of Cu on diverse soils. Adsorption data may aid in the determination of maximum metal loading levels on soils used for disposal of waste which contain more than one metals. Desorption data will aid in the prediction of long-term metal availability to plants.

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Chapter 2

RELATIONSHIPS AMONG PLANT RESPONSE, COPPER FRACTIONS, AND MEHLICH-3 EXTRACTABLE COPPER FOR SOILS AMENDED WITH EITHER COPPER SULFATE OR COPPER RICH PIG MANURE

Introduction

Plant available cations are held by several different mechanisms in the various soil fractions. An acceptable soil test should solubilize an amount of soil nutrient proportional to its availability to plants (Martens and Lindsay, 1990). A dilute acid extractant solubilizes labile cations complexed by organic matter and adsorbed by mineral surfaces. In addition, a portion of non-labile cations are solubilized from precipitated and occluded sites. The amount of metal extracted increases with an increase in acid concentration. A chelating agent extracts cations by decreasing their activity in soil solution which causes a release of adsorbed soil cations as the soil system moves toward equilibrium (Lindsay and Norvell, 1978). The amount extracted is determined by the solution concentration and by the ability of soil to replenish the solution. Extractants of varying acid concentrations and/or chelating agents may solubilize different amounts of soil cations. Therefore a new soil test requires both laboratory and greenhouse evaluation before field calibration (Martens and Lindsay, 1990).

Certain soil extractants are used for their ability to selectively solublize elements from particular soil fractions. Neutral salts are used to replace readily exchangeable cations in soil. However, Cu, Zn, and other heavy metals are largely held by mechanisms not subject to exchange reactions (Shuman, 1985; McLaren and Crawford, 1973a). Acetic acid is used to extract specifically adsorbed in addition to exchangeable cations held by both inorganic and organic soil fractions (McLaren and Crawford, 1973b). These metal fractions, exchangeable and specifically adsorbed, are defined by their method of extraction. Other procedures solubilize individual solid phase minerals. Chao (1972) reported that acidified hydroxylamine hydrochloride selectively dissolved Mn-oxides with little affect on Fe-oxides or organo-metal complexes. Once Cu associated with Mn-oxides is removed, organically bound metal can be selectively released by extraction with potassium pyrophosphate (McLaren and Crawford, 1973b; Miller et al., 1986). Ammonium oxalate can then be used to remove metals bound by Fe-oxides.

In 1984, Mehlich (1984) combined dilute acids and salt with EDTA to form a new soil extractant designated as Mehlich-3. This test had the advantage of simultaneous extraction of P as well as macronutrient and micronutrient cations (Cu included) and, because of its versatility, has replaced the double acid (DA) method (0.05 M HCl-0.0125 M H_2SO_4) as a measure for the adequacy of nutrients in many soil testing laboratories. Eventually the Mehlich-3 procedure is expected to replace the double acid method in other laboratories (Martens and Lindsay, 1990).

Soil test results from the Mehlich-3 procedure have been compared to those from other commonly used soil extractants (Sims, 1989; Sims et al., 1991). Mehlich-3 and double acid extractable Ca, Cu, K, Mg, Mn, P, and Zn were highly correlated for 400 soils from Delaware. However, for soils testing less than high, where no response to added nutrients would be expected, r^2 values were lower than those for all soils tested. Inclusion of organic matter or pH factors into regression equations improved correlation coefficients for only Cu and Mn. Mulchi et al. (1991) found that, on soils amended with sewage sludge, the relative ranking for amounts of Mehlich-1, Mehlich-3, and DTPA extractable Cu varied across different sludges. Hence, soils which have been amended with sewage sludge (or manure) may release a different Cu proportion from each fraction during extraction by Mehlich-3 than by other commonly used extractants. Levesque and Mathur (1986) concluded that forms of extractable Cu decreased with time in Cu amended histosols. Mullins et al. (1982) also found that a portion of Cu in soil amended with either $CuSO_4$ or Cu-rich pig manure reverted to unavailable forms with time.

There is much interest in adapting Mehlich-3 as the standard soil test in southeastern United States. It would be desirable if this procedure could be used to estimate both deficient and toxic Cu levels in soils. In this research, the level of Cu extracted by Mehlich-3 solution was compared with levels extracted by other soil tests commonly used in the U.S. Since individual soil extractants solubilize different soil Cu fractions and the form of applied Cu in soil will change with time, research was also conducted to determine the forms of soil Cu most readily extracted by the Mehlich-3 procedure.

MATERIALS AND METHODS

Field Experiments

Three soils with a wide range of chemical and physical properties were selected for this research. They were a Bertie fine sandy loam, Guernsey silt loam, and Starr-Dyke clay loam. The following three treatments were replicated four times in a randomized complete block design on each soil: 1) a control, 2) a 13 year cumulative total of 356, 360, and 351 kg Cu ha^{-1} as Cu rich pig manure on the Bertie, Guernsey, and Starr-Dyke soils, respectively, and 3) Cu as $CuSO_4$ applied annually at levels equivalent to that in the pig manure. Each year wet manure was applied and worked into the soils. Annual application rates varied from 1978 through 1990, but the average annual rate of wet Cu rich pig manure applied was 93 mt ha^{-1}. Data from only two of the four replicates from 1991 on the Guernsey soil were included herein due to bird damage to corn in several plots.

Nutrient concentrations in both pig feed and manure are listed in Table 2. The concentrations of Ca, Cu, Fe, K, Mg, Mn, Na, and Zn in feed and manure were determined by atomic absorption spectrophotometry from 1 g samples dry ashed at 450 °C for 3 hours and leached with acidic solution. Boron was determined by an Azomethine-H procedure (Parker and Gardner, 1981), P by a molybdivanadophosphoric acid method (Kitson and Mellon, 1944), and N by a micro-Kjeldahl technique (McKenzie and Wallace, 1954). Copper, Fe, and Zn concentrations in the feed were high from supplementation as sulfates and were concentrated in the manure.

Table 2. Nutrient concentrations in pig feed and manure in 1990 and for the 13-year average from 1978 through 1990.

	Pig Feed		Pig Manure	
Element	1990	13-Year Ave.	1990	13-Year Ave.
	---------------%	---------------		
Ca	0.73†	0.93	4.6	4.1
K	0.97	0.83	1.6	1.7
Mg	0.19	0.17	0.90	0.82
N	2.8	2.7	4.8	4.5
Na	0.38	0.16	0.47	0.45
P	0.68	0.61	2.6	2.3
	---------------mg kg^{-1}	---------------		
B	10	10	20	20
Cu	310	260	1400	1320
Fe	280	180	1430	1180
Mn	170	52	580	290
Zn	240	80	1110	420

† Each value is the average of triplicate analyses for two subsamples.

Soil Tests

Soil samples collected from a 0 to 15 cm depth of Ap horizons of the three treatments in each soil were air dried and ground to pass a 1-mm sieve. Copper was determined in these samples by extraction with 0.1 M HCl, 0.05 M HCl-0.0125 M H_2SO_4 (Baker and Amacher, 1982), DTPA (0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M triethanolamine) (Lindsay and Norvell, 1978), and Mehlich-3 (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.15 M NH_4F, 0.013 M HNO_3, and 0.001 M EDTA) (Mehlich 1984). The DA and Mehlich-3 procedures were calculated on a weight basis. A bulk density of 1.25 g cm^{-3} was used to convert sample volume to sample weight.

Soil Fractionation

In preparation for fractionation, one set of soil samples was pre-extracted with the Mehlich-3 solution and another set was not pre-treated. For the pre-extraction, soils were shaken as described above by the Mehlich-3 procedure except that, to decrease soil loss, samples were centrifuged for 5 min before filtering the supernatant through Whatman #42 filter paper. The soil was in contact with extractant for 10 min resulting in a somewhat greater concentration of Cu extracted than with a conventional 5 min extraction time (Mehlich 1984).

Samples were then sequentially extracted as described by Mullins et al. (1982) to determine exchangeable Cu by extraction with 0.05 M $CaCl_2$, specifically adsorbed Cu with 2.5% acetic acid, organically bound Cu with 0.1 M potassium pyrophosphate, and oxide occluded Cu with 0.1 M oxalic acid-0.175 M ammonium oxalate under ultraviolet light. The percent Cu of a given fraction remaining after the Mehlich-3 extraction was calculated by dividing the amount in the pre-extracted soil by the amount in the soil that was not pre-extracted. Each extraction was replicated four times.

Statistical Analysis

Yield and nutrient concentration data were evaluated by analyses of variance. Mean separation was accomplished by Fisher's LSD test at the 0.05 level of significance (Ott, 1977).

RESULTS AND DISCUSSION

High Cu diets increase both rate of weight gain and feed efficiency of young pigs (Aviotti et al., 1980; Braude, 1981; Cromwell et al. 1982). Copper accumulates in surface soil from application of manure from pigs fed high Cu diets. This research addresses the detection of soils with potentially phytotoxic Cu levels though soil test procedure.

Copper Status of Soils

The cation exchange capacities (CEC) of the soils under study were 5.0, 10.4, and 12.3 $\text{cmol}_c\ \text{kg}^{-1}$ for the Bertie, Guernsey, and Starr-Dyke soils, respectively (Table 3). The USEPA (U.S. Environmental Protection Agency) has set the maximum safe Cu

Table 3. Selected properties of the surface horizon of three soils that received three annual applications of Cu as either copper rich manure or $CuSO_4$.

Soil series	pH (H_2O)	Organic matter	CEC	Free Fe	Free Mn	Mineral suite of < .002-mm clay fraction†
		%	cmol kg^{-1}	%	ppm	
Bertie fsl	6.2	1.7	5.0	0.3	20	I_1‡, K_2, Q_3, M_4
Guernsey sil	5.7	1.8	10.4	1.6	1620	S_1, I_2, M_3, K_3, Q_4, F_4
Starr-Dyke cl	5.9	1.4	12.3	5.7	3510	K_1, I_1, M_2, Q_2, F_3, G_3

†S = smectite; I = 14 A intergrade; M = mica; K = kaolinite; Q = quartz; F = feldspar; G = gibbsite.

‡Subscript 1 = most abundant; 4 = least abundant.

loading rate of 280 kg ha^{-1} for these soils with a CEC of 5 to 15 $cmol_c$ kg^{-1} and pH levels ≥ 6.5 (U.S. Environmental Protection Agency, 1983). Soil pH was below 6.5 in 1978 (Table 3) (Mullins et al., 1982). Dolomitic limestone has been periodically applied to maintain pH of these soils at ≥ 6.5. Percent organic matter in 1978 was 1.7, 1.8, and 1.4 for the Bertie, Guernsey, and Starr-Dyke soils, respectively. By 1990 percent organic matter in the control treatment was 2.4 for the Bertie, 1.9 for the Guernsey, and 2.0 for the Starr-Dyke soils, thus increases ranged from 30 to 70 percent by application of 1210 mt wet Cu rich manure ha^{-1} to the three soils.

Copper Uptake and Grain Yield

Continuous corn has been planted on these soils since 1978. The cumulative amount of Cu applied to each of the three soils as Cu rich pig manure or $CuSO_4$ exceeded the maximum safe Cu loading rate as set by the USEPA. The Cu rich manure treatment increased early season growth on the Starr-Dyke and Bertie soils (Table 4). However, grain yield was not increased by the manure application on any of the three soils. The height of young corn plants on the Bertie soil was decreased by the high level of Cu application as $CuSO_4$, but not as Cu rich manure. These results are similar to the findings of Cunningham et al. (1975) that inorganic metal salts are more toxic than an equivalent amount of metal in organic form. Corn grain yields during the 1989 and 1990 growing seasons were unaffected by the high level of Cu application and averaged 9670, 10,520, and 9930 kg ha^{-1} on the Guernsey, Bertie, and Starr-Dyke soils, respectively (Table 4). These relatively high corn grain yields reflect satisfactory growing conditions and adequate nutrients (data not shown) as indicated by the sufficiency ranges for corn ear leaves reported by Jones et al. (1990). Although Cu application exceeded the

USEPA limits of 280 kg Cu ha^{-1} (USEPA, 1983) for these three soils, the high amounts of Cu application did not decrease corn grain yield or increase grain Cu concentration.

Corn ear leaf Cu concentrations were similar for the control and either Cu rich pig manure or $CuSO_4$ treatment on the Guernsey and Starr-Dyke soils, but there was a trend toward higher Cu concentration with applied Cu on the Guernsey soil (Table 4). There was an increase in Cu concentration from both Cu treatments on the Bertie soil which reflects the low Cu fixing ability of this sandy loam soil. Ear leaf Cu concentrations were in the normal range of 5 to 15 mg kg^{-1} (Jones et al., 1990) for all treatments on the three soils. Copper concentrations in grain also were within the normal range of 1 to 5 mg kg^{-1}, and were not influenced by treatments.

Comparison of Soil Tests

Total soil Cu levels determined by Miller et al., (1987) were 14 for the Bertie, 29 for the Guernsey, and 68 mg kg^{-1} soil for the Starr-Dyke control treatments. Addition of Cu as both Cu-rich manure and $CuSO_4$ did not result in a change in the order of soil Cu content from Starr-Dyke > Guernsey > Bertie. Extractable soil Cu levels determined by four commonly used soil tests were increased with Cu-rich manure and $CuSO_4$ application for all three soil types (Table 5). Plots amended with manure tended to release more Cu than those with $CuSO_4$, when extracted by Mehlich-3 (M3), DTPA, and HCl. Copper extracted by DA was highest in $CuSO_4$ amended plots only for the Bertie and Starr-Dyke soil. The comparatively low Cu content extracted from $CuSO_4$ and manure plots was a result of an initially lower total Cu content in these plots. For the control treatment where Cu was not added, the extractable Cu levels were highest in the Starr-Dyke soil. Variation in levels of Cu extracted from the control and plus Cu

Table 4. Effect of 13 annual applications of copper on young corn plant height, on copper concentrations in corn grain and ear leaves, and on the 12th and 13th growing season average of corn grain yields.

Copper Treatment			Plant Copper Concentration		
Total Applied	Source	Plant Height	Grain	Leaf	Grain Yield
kg Cu ha^{-1}		cm	-----mg kg^{-1}-----		kg ha^{-1}
		Guernsey silt loam			
0	Control	45.3a†	2.5a	9.5a	9,670a
360	Pig Manure	49.0a	1.7a	12.5a	10,570a
360	$CuSO_4$	45.3a	2.0a	11.5a	9,590a
		Bertie fine sandy loam			
0	Control	63.3b	2.1a	8.8b	10,520a
356	Pig Manure	80.3a	2.4a	10.8a	10,830a
356	$CuSO_4$	57.3c	2.3a	10.3a	9,815a
		Starr-Dyke clay loam			
0	Control	50.3b	2.6a	8.0a	9,930a
351	Pig Manure	61.3a	2.8a	7.8a	10,400a
351	$CuSO_4$	45.3b	2.1a	8.0a	10,090a

†Column means for each experiment followed by different letters are significantly different at the 0.05 probability level.

treatments indicate that the procedures extract different amounts from various Cu fractions in these soils.

No one test extracted the highest Cu concentration from controls on all soils, however, soil Cu levels indicated M3 extracted Cu in amounts less than 0.1 M HCl similar to DTPA, and greater than DA. Mehlich-3 extracted greater amounts of Cu than DTPA from the sandier, high organic matter content Bertie soil. However, as clay content increased from Bertie to Guernsey to Starr-Dyke and organic matter decreased from 2.4 to 2.0% in the Bertie and Starr-Dyke respectively, M3 extracted significantly less Cu than DTPA in all treatments.

Although Mehlich-3 soil test values were as high as 47.3 mg kg^{-1}, the ear leaf Cu concentrations were within the normal range (Jones et al., 1990) and yields were not decreased on the three soils. High amounts of added Cu combined with normal ear leaf concentration agrees with the contention that Cu accumulates in the roots with little translocation (Miller et al., 1985; Loneragan, 1981; Kabata-Pendias and Pendias, 1991). Reversion of applied Cu to less available forms with time (Mullins et al., 1982; Levesque and Mathur, 1986) also would decrease uptake and, hence translocation of Cu by plants.

Fractionation of Soil Copper

Soils were sequentially extracted to determine the amounts of Cu in the $CaCl_2$ exchangeable (CACL-Cu), specifically adsorbed (HOAC-Cu), organically bound (PYR-Cu), and oxide occluded (OX-Cu) fractions remaining after extraction by M3. Combined, these fractions will be referred to as nonstructural Cu. McLaren and Crawford (1973a) considered Cu in the exchangeable, specifically adsorbed, and a portion of the organically bound fractions to be in equilibrium and to constitute the ma-

Table 5. Effect of 13 annual applications of copper as copper rich pig manure and $CuSO_4$ on Mehlich-3 (M3), DTPA, HCl, and Double Acid (DA) extractable Cu in three soils.

Copper Treatment		Extractable Cu			
Amount	Source	M3	DTPA	HCl	DA
kg Cu ha^{-1}		-------------------------mgkg^{-1}-------------------------			
		Guernsey silt loam			
0	Control	2.8C/a†	2.4C/ab	2.0C/bc	1.5B/c
360	Pig Manure	42.1A/b	40.9A/b	52.1A/a	35.4A/c
360	$CuSO_4$	37.3B/b	37.0B/b	42.8B/a	33.0A/c
		Bertie fine sandy loam			
0	Control	2.6B/a	2.0B/b	2.2B/ab	2.0B/b
356	Pig Manure	25.6A/a	20.6A/b	28.0A/a	14.5A/b
356	$CuSO_4$	23.2A/b	19.5A/d	26.1A/a	20.8A/c
		Starr-Dyke clay loam			
0	Control	7.2C/b	10.3C/a	10.2C/a	7.7C/b
351	Pig Manure	47.3A/c	59.3A/b	69.8A/a	28.3B/d
351	$CuSO_4$	35.1B/d	46.6B/b	59.1B/a	41.5A/c

†Column means for each experiment followed by different capital letters are significantly different at the 0.05 probability level.
Row means followed by different lower case letters are significantly different at the 0.05 probability level.

jority of plant available Cu. Manure application creates zones with reducing conditions, which solubilizes certain oxides with release of a portion of oxide occluded Cu (Payne et al., 1988). Under field conditions sites temporarily exposed to low pe/pH conditions provide small amounts of oxide occluded Cu for plant uptake. Copper associated with soil mineral structure, (residual Cu) is not affected by either Cu treatment and remains essentially unchanged (Mullins et al., 1982; Payne et al., 1988). Since residual Cu is unavailable to plants this fraction was not determined in this research.

Mehlich-3 Extractable Copper

In preparation for fractionation, soil samples were extracted with M3. Since these samples were to be preserved soil/solution separation was accomplished by centrifugation. This resulted in a 10 min extraction time and hence different extraction characteristics than with the conventional 5 min extraction time (Table 6). Although experimental error cannot be ruled out (the Starr-Dyke manure and $CuSO_4$ samples yielded 78.3 and 83.8 mg M3 extractable Cu kg^{-1} soil respectively when the experiment was repeated) the general trends were reproducible. Mehlich-3 extractable Cu in the control soil was greatest in the Starr-Dyke followed by the Bertie and Guernsey soils (Table 6). Addition of Cu as either Cu rich manure or $CuSO_4$ resulted in a greater increase in soil Cu concentration on the Guernsey than either the Bertie or Starr-Dyke soils. There was no difference between either $CuSO_4$ or Cu rich manure treatments for the Mehlich-3 extractable Cu from the Guernsey; however, more Cu was extracted from the manure treatment for the Bertie and from the $CuSO_4$ treatment for the Starr-Dyke soils.

Table 6. Effect of 13 annual applications of Cu as Cu rich manure and $CuSO_4$ on nonstructural Cu, Mehlich-3 extractable Cu, and percentage of nonstructural Cu extracted by Mehlich-3 in three soils.

Soil	Nonstructural Cu	Mehlich 3 Extractable Cu	Percent of Nonstructural Cu
	mg kg^{-1}	mg kg^{-1}	%
		Control	
Starr-Dyke cl	58.6	9.5a†	16.2
Bertie sl	11.2	3.8b	34.0
Guernsey sil	14.5	3.0c	20.7
		Manure	
Starr-Dyke cl	219.1	59.6c	27.2
Bertie sl	103.9	69.2b	66.6
Guernsey sil	152.9	86.1a	56.3
		$CuSO_4$	
Starr-Dyke cl	238.1	71.2b	29.9
Bertie sl	86.0	54.5c	63.4
Guernsey sil	160.1	87.6a	54.7

†Column means for each experiment followed by different letters are significantly different at the 0.05 probability level.

Extraction patterns for Mehlich-3 reflect the strength of Cu binding by the different soils. The total nonstructural Cu was much higher in the Starr-Dyke, followed by the Guernsey and Bertie respectively (Table 6). The higher Mehlich-3 extractable Cu concentration from the control in the Starr-Dyke reflects the high soil Cu levels. Although the Guernsey and Bertie had low nonstructural Cu the higher M3 Cu level from the Bertie is a function of a higher percentage of Cu held in a more readily extractable form.

Mehlich-3 extracted a similar percentage of nonstructural Cu from $CuSO_4$ and manure treatments for each soil tested (Table 6). The percentage extracted was highest in the Bertie followed by the Guernsey and Starr-Dyke, respectively. In the control, M3 extracted between 16 and 34% of nonstructural Cu and between 27 and 66% in Cu amended treatments.

The Guernsey retained added Cu in a readily extractable form regardless of the source of Cu. While a greater percentage of M3 extractable Cu was found in the manure than $CuSO_4$ treatment for the Bertie soil, just the opposite was true for the Starr-Dyke. Fewer potential Cu binding sites on the Bertie sandy loam made Cu binding more dependent on readily extractable sites resulting from an increase in organic matter with applied manure. Copper bound from $CuSO_4$ on the Bertie soil may involve some form of precipitation, shielding Cu at the mineral surface from extraction under the experimental conditions. McBride (1982) found clay mineral surfaces can act as sites of nucleation for $Cu(OH)_2$ precipitation and some Cu, bound at the surface, resists desorption. The Starr-Dyke clay loam with more native binding sites might have a shift in partitioning away from the organic fraction to less extractable sites. With more available native sites for nucleation Cu precipitated at the surface might be dilute and shielding would be limited. Therefore more Cu may be extracted from $CuSO_4$ treatments than those that received manure.

$CaCl_2$ Extractable Copper

Levels of CACL-Cu were initially very low for all soils with all treatments. After extraction by Mehlich 3, CACL-Cu was increased in all soils, except Bertie manure and $CuSO_4$ treatments (Table 7). The percentage increase in CACL-Cu was greatest in the Starr-Dyke followed by Guernsey and then Bertie soils. For the Bertie, the increase in CACL-Cu percentage in the control was more than 2.7 times that of either Cu treatment. In the remaining two soils, Cu amendments resulted in greater CACL-Cu levels with $CuSO_4$ treatments retaining a slightly higher percentage. Exchangeable Cu levels increased by more than 1.6 times in the Guernsey and 1.8 times in the Starr-Dyke over the control, respectively.

Several explanations for this increase in CACL-Cu are plausible. Copper may have been readsorbed from solution during M3 extraction however, some Cu redistribution from other fractions may also have occurred. Conditions created by M3 extraction might liberate occluded Cu binding sites and, thereby, increase the potential for redistribution of Cu among the fractions. Removal of trivalent Al by M3 extraction may have created new exchange sites on both organic and inorganic soil constituents. This would also increase the potential for Cu binding to exchange sites.

Acetic Acid Extractable Copper

From the nonstructural fractions the smallest percentage of its original Cu content remaining after M3 extraction was HOAC-Cu. Less Cu remained in the control for the Starr-Dyke than either of the other soils. Treatment comparisons indicate that more HOAC-Cu remained in the control than manure and $CuSO_4$ treatments for the Bertie

Table 7. Percentage of copper fractions remaining in three soils after extraction by the Mehlich-3 procedure.

Soil	Control	Manure†	$CuSO_4$
	--------%	--------	--------
	Exchangeable		
Bertie sl	190	67	70
Guernsey sil	270	430	470
Starr-Dyke cl	1410	2350	2600
	Specifically Adsorbed		
Bertie sl	20	5	4
Guernsey sil	20	7	7
Starr-Dyke cl	10	14	15
	Organically Bound		
Bertie sl	67	44	46
Guernsey sil	80	56	54
Starr-Dyke cl	79	80	73
	Oxide Occluded		
Bertie sl	45	53	47
Guernsey sil	60	72	70
Starr-Dyke cl	46	60	46

†The three soils were treated with 13 annual applications of copper as copper rich manure and $CuSO_4$.

and Guernsey soils. On these soils, HOAC-Cu comprised the highest portion of any fraction before extraction by M-3. More HOAC-Cu remained in the $CuSO_4$ followed by manure and then control treatments in the Starr-Dyke.

Pyrophosphate and Oxalate Soluble Copper

Between 43 and 81% of the PYR-Cu originally present for all treatments on all soils remained after extraction with M3 (Table 7). On the Bertie and Guernsey soils, a higher percentage of PYR-Cu remained in the control than either manure or $CuSO_4$ treatment. Copper added to soil as manure or $CuSO_4$ is originally readily available and only with time reverts to unavailable forms (Mullins et al., 1982). Native Cu concentrations however, are comparatively small and less available to plants. Both PYR-Cu and HOAC-Cu would be extracted to a greater degree from Cu treated soil. In the Starr-Dyke a high native Cu concentration and a low number of potential binding sites (Zhu et al., 1991) can explain roughly similar PYR-Cu concentration for all treatments. Oxalate-Cu remaining after M3 extraction for control and $CuSO_4$ treatments on the Bertie and Starr-Dyke soils ranged between 44 and 47% of total OX-Cu originally present. The manure treatment retained 53 to 60% OX-Cu on these soils.

General Trends

Patterns of Cu distribution among different soil fractions for the Starr-Dyke soil can be seen in Figure 1. Each bar represents the mean of four soil samples from the field treatments listed below the bar; whereas, each bar segment represents the percentage of total nonstructural Cu extracted by a given extractant. The black bar segment represents a portion of Cu not extracted from that sample. No Cu fraction can be considered a discrete independent fraction. There is a degree of overlap in the Cu solubilized by each extractant. For example acetic acid may release organically bound Cu considered a part of PYR-Cu as well as some inorganically bound Cu considered a part of OX-Cu.

In control plots where no Cu was applied in the field, there was very little exchangeable Cu present. Pyrophosphate extractable Cu which is assumed to include $CaCl_2$ exchangeable, acetic acid extractable specifically adsorbed fraction, and organically bound Cu (McLaren and Crawford 1973a) contained 23.1% of nonstructural Cu present. Copper organically bound by mechanisms other than specific adsorption (PYR-Cu minus HOAC-Cu) was small, 0.6% and specific binding sites held 22.5% of extracted Cu. The greatest nonstructural Cu fraction, 76.9% was held in oxalic acid extractable oxide occluded forms. Addition of Cu as either manure or $CuSO_4$ increased the PYR-Cu fraction by partitioning more of the added Cu into specifically adsorbed organically bound than to oxide occluded sites. The ratio of PYR-Cu to OX-Cu in Cu amended soils approached 1:1. Miller et al. (1987) found a greater increase in HOAC-Cu in manure treated than $CuSO_4$ treated soil. In their study specific adsorption was defined as Pb displaceable [by 0.1 M $Pb(NO_3)_2$] or acetic acid soluble Cu. Copper displaced by Pb is generally assumed to be covalently bound to oxidic or organic functional groups. Acetic acid soluble Cu is a general extraction of all specifically adsorbed Cu. Miller and others in there 1987 study found a larger increase in Pb displaceable Cu over the control where soils were treated with $CuSO_4$ than when manured. They attributed this relationship to Cu strongly bound in the manure, and not accessible to Pb exchange. In either manure or $CuSO_4$ treatments, however, a high portion of HOAC-Cu, specifically adsorbed Cu, is associated with organic fractions in soil.

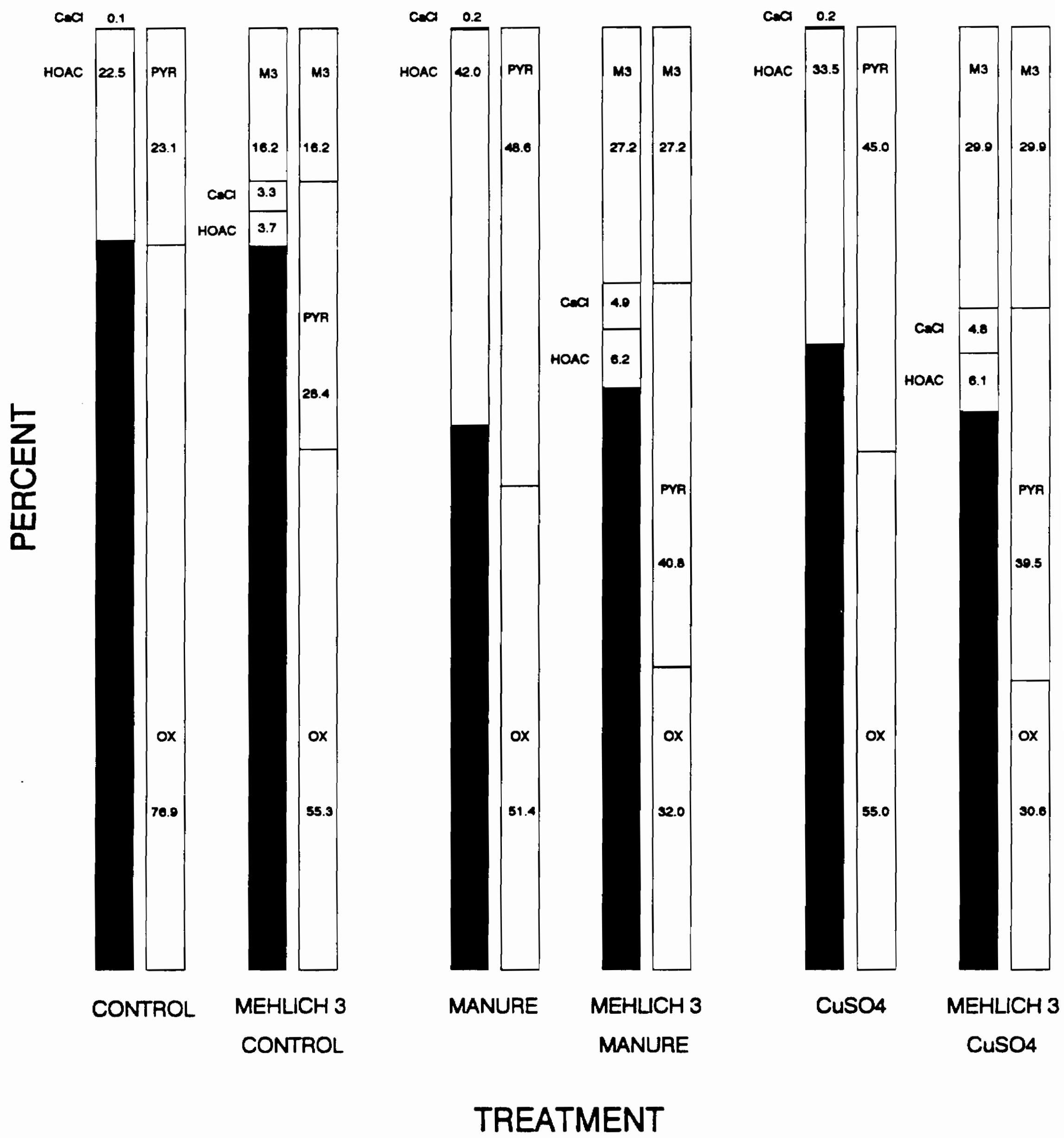

Figure 1. Percentage of available Cu in Mehlich-3 (M3), $CaCl_2$, pyrophosphate (PYR), acetic acid (HOAC), and oxalic acid (OX) fraction of a Starr-Dyke soil.

Pretreatment of soil with M3 extractant causes a redistribution of Cu between various soil fractions for all treatments (Fig. 1). Mehlich-3 solution extracts a large portion of specifically adsorbed, most likely held in organic forms, and exchangeable Cu. The high portion of PYR-Cu found after M3 extraction is attributed to oxide occluded Cu exposed by the pretreatment and subsequent extraction of the poorly crystalline metal oxide Cu fraction.

Distribution patterns on the Bertie soil were similar to those of the Starr-Dyke (Fig. 2). However, a greater portion of Cu was specifically adsorbed at organic sites and consequently M3 extracted a greater percentage of nonstructural Cu in the Bertie. Control treatments retained a large portion of HOAC-Cu after extraction by M3. In the control native Cu is more tightly held than that applied in either treatment possibly by multiple bond formation with organic functional groups or by occlusion. As discussed above, pretreatment with M3 may render these sites more susceptible to attack. A low oxide content with a greater percentage of surface sites resulted in a larger fraction of OX-Cu released than in the Starr-Dyke. The Guernsey soil (Fig. 3) had a large HOAC-Cu and PYR-Cu fraction resulting in a large portion of nonstructural Cu extracted by M3. Unlike the other soils OX-Cu was not affected by M3 pretreatment.

A portion of the organically bound Cu fraction in these soils appears to be readily extracted by Mehlich-3. The high portion of organically bound Cu found after Mehlich-3 extraction is partially attributed to oxide occluded Cu exposed by the pretreatment and subsequent extraction of the poorly crystalline metal oxide Cu fraction by potassium pyrophosphate. Despite the redistribution of Cu between soil fractions, oxide occluded Cu and remained high after Mehlich-3 extraction. Hence, Mehlich-3 is a weak extractant of the oxide as compared with the exchangeable and specifically adsorbed Cu fractions. Since Mehlich-3 strongly extracts Cu specifically bound to organic compounds and only poorly removes Cu associated with the oxide fraction, this

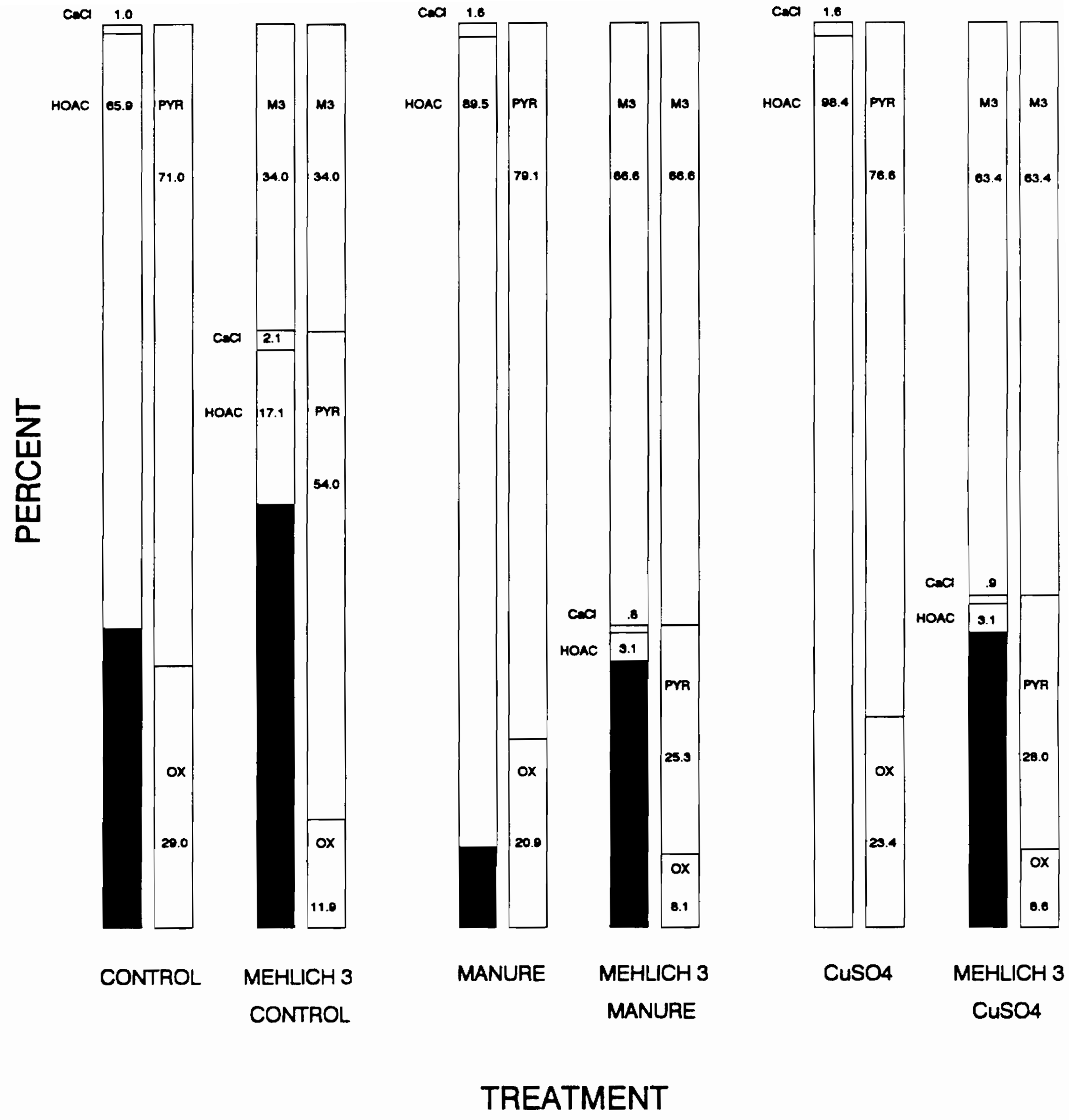

Figure 2. Percentage of available Cu in Mehlich-3 (M3), $CaCl_2$, pyrophosphate (PYR), acetic acid (HOAC), and oxalic acid (OX) fraction of a Bertie soil.

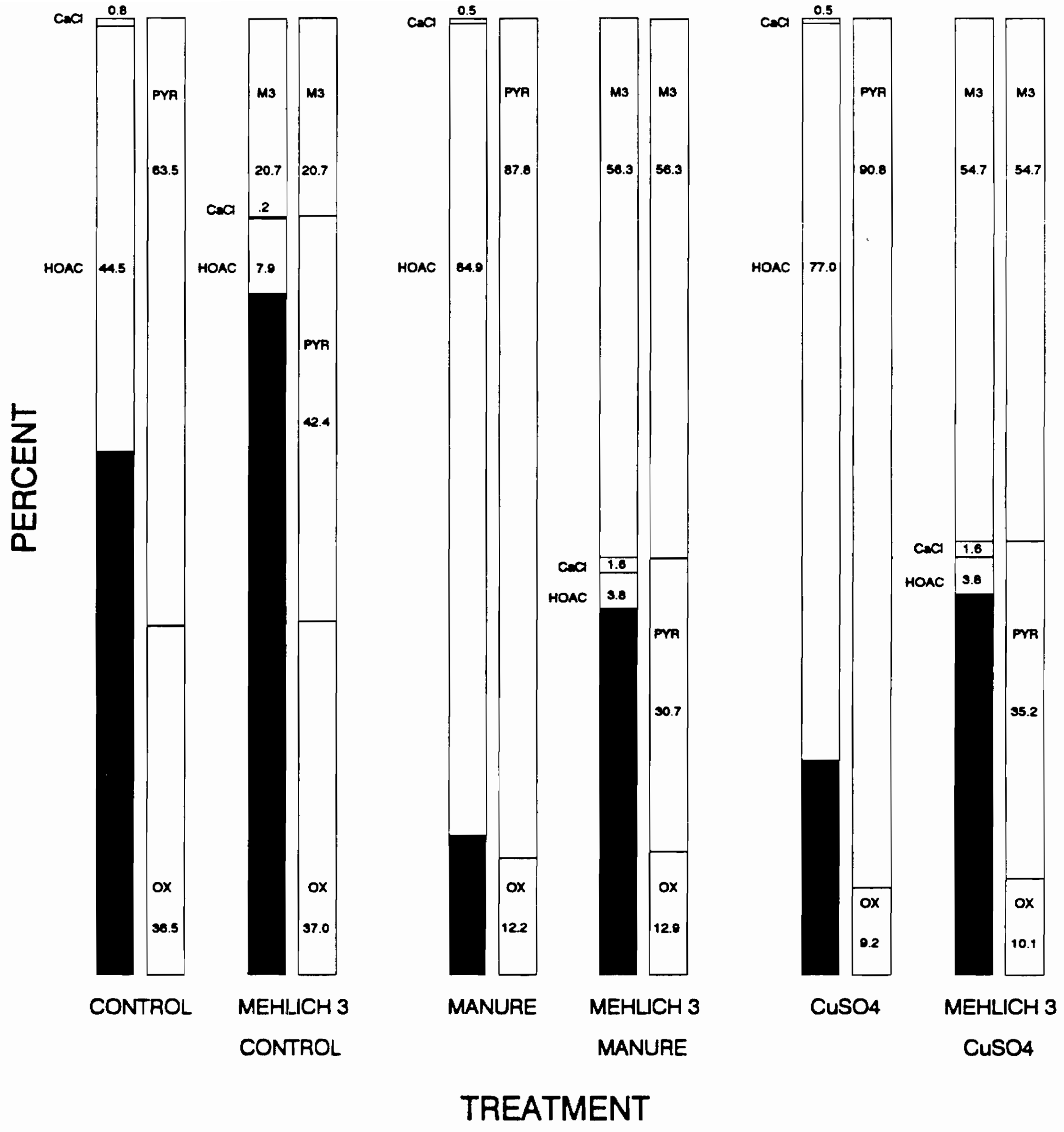

Figure 3. Percentage of available Cu in Mehlich-3 (M3), $CaCl_2$, pyrophosphate (PYR), acetic acid (HOAC), and oxalic acid (OX) fraction of a Guernsey soil.

test may under estimate Cu availability on sandy soils with low organic mat

However, Mehlich-3 should provide an acceptable Cu soil test on Virginia sc

CONCLUSIONS

Copper application exceeded the USEPA maximum safe Cu loading rate of 280 kg ha^{-1} for these soils. The pig manure and $CuSO_4$ treatments did not affect corn grain yield or Cu concentration, however, there was a trend toward reduced early season growth on one of the three soils (i.e., on the Bertie soil). Mehlich-3 extractant solubilizes a higher percentage of specifically adsorbed Cu than other fractions. It undoubtedly also solubilizes exchangeable and a high portion of organically bound Cu. The amount of Mehlich-3 extractable Cu was a function of total applied Cu, and the amount of Mehlich-3 extracted from the manure treatment was greater than or equal to that extracted from the $CuSO_4$ treatment. Although Cu applications to these soils surpassed the USEPA maximum safe loading rate the Mehlich-3 procedure, in spite of the high soil Cu content, solubilized Cu predominantly from soil Cu fractions considered available to plants. The Mehlich-3 procedure extracted mainly the exchangeable and specifically absorbed Cu at both relatively high and low levels of Cu in the three soils. Therefore, the Mehlich-3 procedure shows promise as a soil test for detection of both deficient and toxic Cu levels.

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Chapter 3

THE EFFECT OF COMPETING METAL IONS ON RETENTION BY SOIL

Introduction

Municipal and industrial waste may contain large concentrations of heavy metals. A typical sludge can contain 850 mg Cu, 500 mg Pb, and 1,740 mg Zn kg^{-1} dry weight as well as various amounts of Cd, Cr, and Ni (USEPA, 1983). Certain animal wastes may also contain a high content of metals. Copper and Zn are common additives to swine (*Sus Scrofu domesticus*) and poultry (*Gallus gallus domesticus*) feed. Zinc is added to eliminate antagonistic interactions with Ca, Cu, and Fe that may occur with marginally Zn deficient diets and Cu to improve feed conversion efficiency and weight gain (Lexmond and de Haan, 1977). The manure produced contains elevated levels of Cu and Zn. These manures and sludges are often applied to soil and consequently there are concerns about the agricultural and environmental effects from their application.

Land disposal of municipal and agricultural waste relies on the ability of soil to remove metals from solution and bind them in a form not likely to leach and unavailable for plant uptake. Heavy metals applied to soil may be held by a variety of mechanisms. They include the following: 1) free or complexed ions in soil solution, 2) nonspecific or specific adsorption to soil organic and inorganic fractions, 3) occlusion by carbonates and hydrous oxides, and 4) precipitation (McLaren and Crawford, 1973; Iyengar et al., 1981; Hickey and Kittrick, 1984; McBride, 1985; Neilsen et al., 1986; Liang et al., 1991).

Metal ions are nonspecifically adsorbed by electrostatic attraction which arises from isomorphous substitution in silicate minerals (Sposito, 1981). Nonspecifically adsorbed ions are bound by electrostatic interactions, retain their hydration water, and are readily exchanged by neutral salts. Specific adsorption of metal ions to soil is characterized by partial loss of hydration water and covalent bond formation. Ions are specifically adsorbed by soil carbonates, organic matter, phyllosilicates, and hydrous oxides (Kabata-Pendias and Pendias, 1991; Schnitzer, 1978; Udo et., 1970). Occlusion results from precipitation of an Al, Fe, or Mn hydrous oxide or Ca carbonate mineral layer over the adsorbed metal. The occlusion reactions isolate the metal from soil solution. Metal ions may also precipitate at the surface of hydrous oxides or as discrete mineral phases.

Literature Review

Adsorption Processes

Characterization of metal sorption mechanisms has generally involved removal of a single metal from solution by a whole soil or soil separate, for example adsorption of Zn^{+2} by gibbsite. An adsorption study by Harter (1979) showed that a portion of Cu adsorbed to soil was not labile and, hence, was not controlled by cation exchange reactions. Lead and possibly Cu retention involve both exchange and precipitation processes. Shuman (1979) used a fractionation procedure including oxidation of organic matter with H_2O_2 to determine Cu, Mn, and Zn distribution in soil separates. Zinc was bound mainly by clay sized particles and by the iron oxide fraction. Clay-sized particles and the organic matter fraction held the majority of soil Cu.

Kiekens et al. (1982) reported that a portion of adsorbed Cu could not be desorbed with Ca^{2+}. In addition, Cu adsorption curves followed a different pattern than desorption curves. They concluded that exchange reactions were not fully reversible and specific adsorption reactions predominate at low Cu occupancy. Copper was first bound at specific sites and as these sites became saturated, Cu binding was at less specific sites. Initial sorption was rapid and dependent on soil clay content and pH and was followed by a slower sorption mechanism associated with humic acid.

Cavallaro and McBride (1978) studied Cu and Cd adsorption in the presence of 0.01 M $CaCl_2$ and found that both adsorption maxima were reduced by Ca^{2+} competition. A high Cd-Ca selectivity coefficient and a high soil solution Cd^{2+} content led these authors to suggest that Cd was mobile in soil. Copper, however, was tightly held at adsorption sites. In their study, ion exchange reactions controlled Cu^{2+} and at low concentration Cd^{2+} activities in soil solution. Precipitation controlled solution Cd^{2+} at high concentrations. Cation binding was in the order $Cu > Cd = Ca$ on both acid and calcareous soils. Exchange mechanisms were the dominant forces for Ca, Cd, and Zn retention while Cu and Pb were tightly bound by other forces.

Nickel adsorption characteristics appeared to be dependent on equilibrium solution concentration and exhibited a slow kinetic reaction (Harter, 1983). Metal ions were adsorbed to soil in the order $Pb > Cu > Zn > Ni$, however, if the slow Ni adsorption reactions were included, there was more retention of Ni than Zn. Metal retention increased with soil pH for Pb, Cu, Zn, and Ni. Zinc was held on exchange sites, Pb fixation may have involved precipitation, and Cu sorption was assumed to be by a combination of adsorption and precipitation reactions. Nickel retention mechanisms were too complex to identify.

Adsorption kinetics for Cd and Cu were rapid and equilibration time was independent of suspension pH (Inskeep and Baham, 1983a). At low surface coverage, Cu and Cd adsorption occurred first at constant potential (pH dependent) sites. Once these sites were saturated adsorption isotherms began to resemble those of constant charge sites.

Soil may bind a given metals by a variety of different mechanisms. Any individual ion however, may be fixed by more than one mechanism. Copper, Cd, and Pb adsorption by kaolinite is postulated to be at two types of binding sites (Schindler et al., 1987), i.e., by a nonspecific ion exchange site and by an ampholytic surface Al-hydroxyl through formation of inner sphere complexes. Humic acid binds Cu by two unidentate complexes with a carboxylic group and a second carboxylic or phenolic group (Boyd et al., 1981). Additional Cu amide complexes may form without dissociation of either unidentate complex (Boyd et al., 1981).

Effect of Organic Matter on Adsorption

Soil organic substances may have a high affinity for heavy metals. In a study of metal complexes with humic acid, Stevenson (1976) found that, at a low metal/humic acid ratio, metal ions were bound by two functional groups and a portion of the H^+ released was due to non KOH titratable groups. At higher pH levels, additional H^+ dissociation probably occurred from metal ion hydration water. They reported that stability constants with soil organic matter followed the order Cu > Pb > > Cd.

Inskeep and Baham (1983b) reported that Cd and Cu adsorption to a Na-montmorillonite increased with increases in soil pH. With addition of a water soluble forest litter extract, soluble metal-organic complexes reduced adsorption of Cd, and to a greater extent Cu. Formation of these metal-organic complexes increased with pH and, therefore, decreased adsorption occurred at sites associated with water insoluble organic matter. These authors suggested that formation of Cu-organic complexes are important in control of Cu adsorption. However, with time, soluble organo-metal complexes would be converted to more insoluble forms and thus, become immobile in soil (Mullins et al., 1982; Levesque and Mathur, 1986).

Effect of pH on Adsorption

Although certain metals are not primarily held by simple exchange mechanisms, their adsorption is accompanied by a release of H^+ and therefore soil pH would affect their retention. Copper chemisorbed by Al hydroxides at low pH occurred at sites with OH^- in single coordination with Al and with a concomitant release of H^+ (McBride, 1982). At high pH surface precipitation may have also occurred. These reactions depended on the degree of crystallinity and type of mineral present.

The order of heavy metal adsorption on goethite, as pH increased, was $Cu > Pb > Zn > Co > Cd$ (Forbes et al., 1976). As surface charge increased Pb, Co, Zn, and Cd adsorption increased relative to H^+ but Cu adsorption had only a small comparative dependence on surface charge. Surface coverage increased with adsorption energy in the order $Cu < Pb = Zn = Co < Cd$. These authors suggested that hydrolysis reactions should be considered in metal adsorption models.

Kurdi and Doner (1983) reported that both Zn and Cu sorption resulted in a drop in soil pH and a release in Mn^{2+}. At high concentrations of added Zn, the pH was stabilized, and Mn release did not occur. They did not determine a reason for this observation; however, they did note that Cu effectively removes sorbed Zn whereas Zn does not effectively remove sorbed Cu.

Both Zn and Cu sorption increased with pH on acid clay (Cavallaro and McBride, 1978; Harsh and Doner, 1984). Adsorption by metal oxides seemed to be the most important cause of this pH dependency. Sorption by crystalline oxides was a more significant mechanism for Zn fixation than for Cu.

Zinc and Cd adsorption was depressed by Cu at pH levels below neutrality; however, Cu sorption was not affected by the presence of Zn or Cd (Kuo and Baker, 1980). Copper and Zn sorption occurred at a pH below the soil zero point of charge (ZPC). However, since ZPC represents a net charge, there still might be considerable negative charge on soil particles. Metal adsorption may also occur via an anionic bridge.

Effect of Anions on Adsorption

In the presence of phosphate, Cu was bound to Al hydroxide by two mechanisms (McBride, 1985). At low levels of phosphate, enhanced Cu adsorption can occur through ion pair formation. However, at high concentrations phosphate bound to sorption sites may partially block Cu access to these sites. Polymeric forms of Cu hydroxide can also precipitate on Al hydroxide surfaces. In contrast Cd and Zn sorption by a ferric hydrous oxide was not affected by phosphate (Kuo, 1986).

In an adsorption study of Zn by Fe and Al oxides, Kalbassi et al. (1978) determined the molar ratios of Zn^{2+} or Cl^{-} adsorbed and H^{+} released and indicated that there were two mechanisms for Zn^{2+} adsorption, one with and one without Cl^-. The first mechanism likely involved adsorption of $ZnCl^+$ (or perhaps Zn^{2+} and Cl^-) along with the release of one H^+ for each $ZnCl^+$. Zinc adsorption with Cl^- decreased as pH increased. The second mechanism likely involved adsorption of Zn^{2+} and release of two H^+ for each Zn^{2+}. Since this adsorption probably took place despite an unfavorable electrical potential, it can be reasoned that Zn^{2+} is held irreversibly.

Effect of Competing Ions

Ionic strength affects metal adsorption. Observations by Zhu and Alva (1993) showed that there was a decrease in Zn adsorption by sandy soils when Ca, Mg, or K was added to the equilibration solution. Copper adsorption was also reduced but to a much smaller extent. This reduction in adsorption was attributed to increased competition for exchange sites with increased ionic strength and was greatest on soils with low pH.

Most sorption research involves adsorption of a single metal to soil and relatively few studies use multiple metal solutions. Sidle and Kardos (1977) added Cu, Zn, and Cd simultaneously with common soil cations to a forest soil and found that Cu was instantaneously adsorbed while Zn and Cd adsorption were more time dependent. Benjamin and Leckie (1981a) demonstrated that amorphous Fe oxyhydroxide adsorption of heavy metals was consistent with a multiple site model. At very low metal ion concentration adsorption occurred concurrently at all sites and was independent of metal concentration. As specific sorption sites approached saturation, the average equilibrium binding constant decreased despite the fact that a high total number of sites remained available. On a Fe oxyhydroxide surface, specific binding for Cd, Zn, Cu, and Pb was at mostly unique sites with little competition between different ions for the same sites (Benjamin and Leckie, 1981b). These sites may differ in number, proximity to nearest neighbor, crystal defects, local electrical field strength, and physical characteristics (i.e., pore size, microcrystallinity, etc.). Metal adsorption to a whole soil, which has diverse constituents each subject to the same variations as Fe oxyhydroxides, is more complex.

Harter (1992) simultaneously added Co, Cu, and Ni to a Ca saturated soil. He discovered that Ni was bound to sites previously occupied by Ca; whereas a portion of Co and Cu adsorption did not require Ca release. Specific Cu adsorption without concomitant Ca release was attributed to H^+ exchange at carboxylic plus phenolic multiple binding sites and by $CuOH^+$ sorption. Adsorption of Co involved oxidation/reduction reactions with Mn oxides. A portion of Co, Cu, and Ni was adsorbed at unique sites.

Past research has revealed useful information about individual metal ion reactions with soil. However, interactions between different metal ions during adsorption are not thoroughly understood. This study will explore the affects of simultaneous additions of Cu, Pb, and Zn on adsorption characteristics of a Ca-saturated soil. Research will include a determination of individual ion adsorption maxima, adsorption characteristics with simultaneously additions of ions, and desorption of exchangeable and specifically adsorbed ions.

Materials and Methods

Ca-Saturation

Soil used for this study, a Davidson clay loam, was air dried and ground to pass through a 1 mm sieve. A Ca-saturation procedure adopted from Harter (1992) is described below. Several 2-g subsamples were added to 100 mL test tubes with 60 mL of 0.1 M $CaCl_2$ adjusted to pH 6.0. The suspensions were agitated for 1 hr and centrifuged until clear. The supernatants were discarded and the procedure was repeated a second time. Then, samples were washed with 60.0 mL of 6.7 mM $CaCl_2$ until electrical conductivity measurements indicated suspensions had returned to their original salt content. Finally, the washed samples were capped and weighed to determine the amount of entrained solution.

Metal Titration

Thirty milliliters of deionized distilled water was added to several tubes containing 1.0 g of Ca-saturated soil, and tubes were agitated and allowed to equilibrate for 1 hr. Suspensions were transferred to a beaker, soil pH was recorded, and samples were titrated to 1.0 pH unit change with either 2.0 mM $Cu(ClO_4)_2$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2$, or $HClO_4$ (Forbes et al., 1976). Suspensions were allowed to stand for 24 hr and then readjusted to 1.0 pH unit change. All solutions were added at a rate of 0.75 mL min^{-1} to a continually stirred suspension.

Metal Adsorption

The amount for each metal adsorbed per H^+ released was used to calculate the Pb to Cu to Zn ratio for multimetal solution initial concentrations. Samples were also equilibrated with single metal solutions from 50 μM (Cu) or 0.5 mM (Pb and Zn) to 2.0 mM to determine an adsorption maximum. Bimetal competition between Cu and either Pb or Zn was determined with 0.5 mM $Cu(ClO_4)_2$ and a range of concentrations from 0.1 to 2.0 mM $Pb(ClO_4)_2$ or $Zn(ClO_4)_2$. Lead and Zn competition was determined with 2.0 mM $Zn(ClO_4)_2$ and from 0.1 to 3.0 mM $Pb(ClO_4)_2$ solutions. Two grams of Ca-saturated soil were suspended in 60 mL of the appropriate metal solution and equilibrated for 24 hrs at 25°C with constant agitation for the adsorption determinations. All suspensions were agitated in a Precision shaking water bath at 100 oscillations per minute. Ionic strengths were fixed at 0.02 M and pH was recorded for all solutions. Suspensions were centrifuged, pH was recorded, and supernatant collected after filtration through Whatman # 42 filter paper.

Metal Desorption

Selected soil samples from metal adsorption equilibrations were sequentially extracted with 30 mL of 0.5 M $Mg(NO_3)_2$ and either 30 mL of 0.05 M $Pb(NO_3)_2$-0.1 M $Ca(NO_3)_2$ or 20 mL of 2.5% acetic acid (Mullins et al., 1982). Magnesium and $Pb(NO_3)_2$ extracts were shaken as described above for 16 hr and acetic acid extract for 8 hr at 25°C. Calcium, Cu, Pb, Zn, and other selected ions in solution were determined by atomic absorption spectrophotometry. Content of metal adsorbed was the difference between the original solution concentration and that detected in solution after equilibration.

Results and Discussion

Titration

Heavy metals are commonly applied to soil with agricultural and industrial wastes. Metal adsorption may be influenced by complicated interactions with organic and inorganic soil materials as well as with other constituents of the waste stream. This research was initiated to determine certain adsorption and desorption characteristics of soil.

Calcium saturated soil was titrated with $HClO_4$ or metal perchlorate solution to a 1 unit pH change. Micromoles of ions added, Ca released, and H^+ adsorbed (H^+ added - H^+ solution) are given in Table 8. Titration of soil with $Zn(ClO_4)_2$ released H^+ ions at a constant rate for 0.5 pH units change. Then further addition of $Zn(ClO_4)_2$ in amounts greater than the initial suspension volume produced only a slight decrease in pH. A 0.5 pH unit change was therefore chosen to determine ratios for metal competition experiments.

Micromoles of Zn^{2+} added were comparable to that of Ca^{2+} released to solution (Table 8). Perchloric acid titration yielded a ratio of 1.16 mole H^+ added to 1.0 mole Ca^{2+}, or 1.16 moles$^+$ added to 2 moles$^+$ released. Both Cu^{2+} and Pb^{2+} titration also released more micromoles of Ca^{2+} than metal added. A single Cu ion is known to form complexes with two independent carboxyl and an additional amide group (Boyd et al., 1981). Therefore, a single Cu^{2+} may neutralize more than two negative charges. If individual Ca^{2+} ions are held by the same sites on a one to one charge basis, at high concentrations, Cu exchange could cause Ca release in amounts greater than would be expected by exchange on an equivalent basis. A reduction in electronegativity, distributed over the soil surface, as a result of Cu replacement of Ca could cause additional Ca release from the surface. Similar mechanisms can account for non-equivalent Ca release with H and Pb addition.

Adsorption Maximum

Soil samples were equilibrated with 60 mL of a single metal ion solution with from zero to 120 μmol (or 2.0 mM) for Cu and to 300.0 μmol (or 5.0 mM) for Pb and Zn (Table 9). Equilibrium soil suspension pH ranged from 6.1, with no metal added to 4.2 for Cu, 4.2 for Pb, and 5.2 for Zn at the highest concentration of added metal. Speciation analysis performed using the Minteqa2 program (Allison et al., 1990) indicated metal hydrous oxides would not form a precipitate in solution. At initial solution content below 30 μmol (or 0.0005 M) the soil had a similar affinity for each metal. Adsorption sites were undersaturated and essentially all ions were removed from solution. No concentration effect was apparent. As initial concentration was increased, the soil adsorbs metals in the order Cu > Pb > Zn. Soil adsorbed 64.98 μmol Cu from an initial solution content of 90 μmol, which was nearly equivalent to the amount of Pb or Zn adsorbed from 120 μmol metal solution. A greater removal of Cu from solution than either Pb or Zn implies a higher bonding energy for Cu. Forbes et al. (1976) found that, with increased surface coverage on goethite, the energy of adsorption for Pb and

Table 8. Moles of Cu, Pb, Zn, and H^+ adsorbed (H^+ added - H^+ solution) and Ca released by a Davidson clay loam during titration to 0.5 pH unit change.

Ion	Moles added	Ca Released
Copper	7.956×10^{-6}	1.054×10^{-5}
Lead	9.482×10^{-6}	1.180×10^{-5}
Zinc	1.220×10^{-5}	1.217×10^{-5}
Hydrogen	7.439×10^{-6}	7.276×10^{-6}

Zn had a larger increase than for Cu. Stevenson (1976) determined humic acid also forms more stable complexes with Cu than Pb. These results are consistent with a high bond energy for Cu to soil. At low concentrations a greater fraction of solution Cu will be adsorbed than either Pb or Zn added at the same initial concentration.

Total sorption capacity follows the order Pb > Zn > Cu (Table 9). The Davidson soil used in this study was also found to adsorb more total Pb than Cu by King (1988). Apparently Pb has access to more sorption sites than Cu. Lead is either able to diffuse into sites inaccessible to Cu or expose and/or create additional sorption sites. It is likely that surface precipitation reactions with Pb may have occurred in the Davidson soil understudy.

Where metal was not present in the initial solution 27.8 μmol Ca was released as a result of exchange with Na. Calcium exchange increased with an increase in metal adsorbed for Cu and Zn. A portion of the sorbed heavy metal occurred at sites not previously occupied by Ca. A 2-g soil sample adsorbed 130 μmol Ca and equilibration with each metal used did not completely remove Ca even at concentrations of maximum metal adsorption. Lead exchange with Ca peaked at 65.7 μmol Pb adsorbed per 86.9 μmol Ca released. As Pb sorption increased above this point Ca released decreased slightly. Heavy metal exchange with Ca is an indication of a type of site occupied by the metal but does not necessarily yield information about bond strength for a given metal. The majority of labile soil Ca is likely held by electrostatic forces on exchange sites with some covalently bonded ions. It is held by comparatively weak forces and is readily exchanged by other ions. However, other ions may bind to the site previously occupied by Ca with different bond energies. Although Ca is readily exchangeable, heavy metals bound to the same site may not be as easily removed.

Soil equilibrated with metal ions resulted in an adsorption maximum for Cu of 33.8 μmol g^{-1} and 40.6 μmol g^{-1} for Pb (Fig. 4). Soil equilibrated with 0.005 M Zn adsorbed

Table 9. Initial solution content (M_0), metal adsorbed (M), and Ca released (Ca) in micromoles from Davidson clay loam samples separately equilibrated with Cu, Pb, or Zn

Cu_0	Cu	Ca	Zn_0	Zn	Ca	Pb_0	Pb	Ca
0.00	0.00	27.80	0.00	0.00	27.80	0.00	0.00	27.80
3.00	3.00	35.40	6.00	6.00	30.40	30.00	30.00	54.30
6.00	6.00	37.60	30.00	25.55	43.80	60.00	52.76	74.00
30.00	29.72	55.40	60.00	42.93	56.00	120.00	65.70	86.90
60.00	52.01	70.30	120.00	61.00	66.00	180.00	72.71	86.20
90.00	64.98	76.90	240.00	76.63	82.80	240.00	75.52	84.30
120.00	67.69	78.80	300.00	79.83	86.70	300.00	81.23	80.60

39.9 μmol g^{-1} from solution. The plot for Zn and to a lesser extent for Pb adsorption tended to reach a plateau with a slight increase in slope.

Adsorption Models

Langmuir isotherms have been used to model adsorption of ions to soil (Adamson, 1990). This isotherm has the general form

$$x/m = V_m \frac{KC}{1 + KC} \qquad (1)$$

where x/m is the concentration of adsorbed ion, μmol g^{-1}

V_m is the adsorption maximum, μmol g^{-1}

C is equilibrium solution concentration, μmol L^{-1}, and

K is a unitless function of the rate of adsorption divided by rate of desorption.

Equation (1) can be rearranged in the form $y = mx + b$ to give

$$\frac{C}{x/m} = \frac{1}{KV_m} + \frac{C}{V_m} \qquad (2)$$

or

$$\frac{1}{x/m} = \frac{1}{V_m} + \frac{1}{KV_m} \bullet \frac{1}{C} \qquad (3)$$

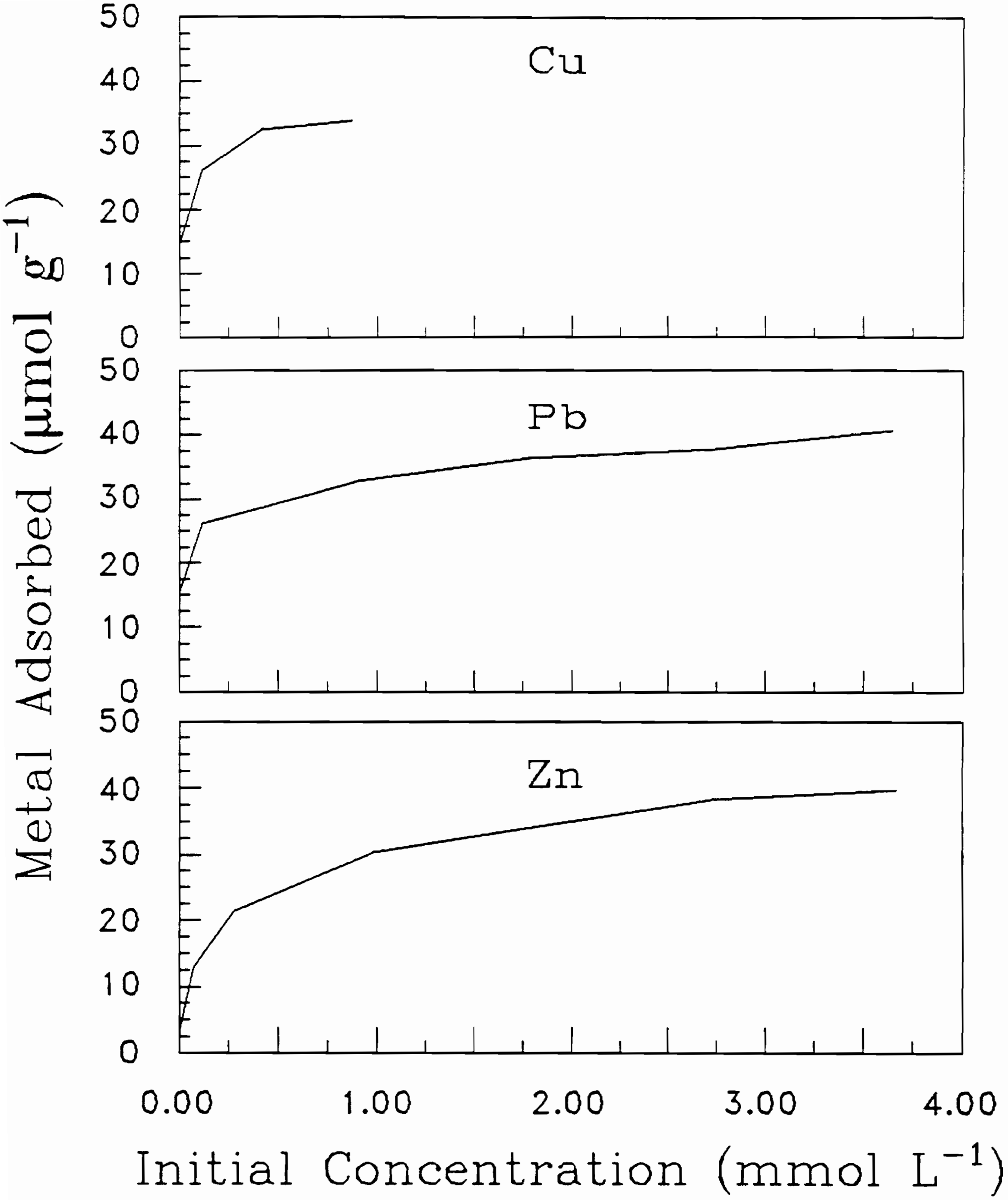

Figure 4. Metal adsorption to a Davidson clay loam as a function of Initial solution concentration.

and a plot of $\frac{C}{x/m}$ vs C from equation (2) and $\frac{1}{x/m}$ vs $\frac{1}{C}$ from equation (3) yields a straight line. The terms V_m and K can be obtained from the slope and intercept of the equation.

Langmuir type adsorption assumes no lateral interactions between adsorbate particles, a monolayer surface coverage, and uniform energy of adsorption for the entire adsorbant surface. Since metal ions can be adsorbed to soil by a variety of mechanisms a physical interpretation of K is difficult. However, V_m is an acceptable estimate of a soils adsorption capacity. Langmuir isotherms may be expanded to accommodate simultaneous adsorption of several ions from solution. For multiple adsorbate ions the general formula is as follows

$$x/m = \frac{V_m K_i C_i}{1 + \Sigma K_j C_j} . \qquad (4)$$

At low solution concentration where $KC_j << x/m_j << V_m$, equation (4) simplifies to

$$x/m_i = K_i C_i V_m \qquad (5)$$

and competition between metal ions is slight (Murali and Aylmore, 1983). In a binary system at high concentration equation (4) becomes

$$\frac{C_1/C_2}{x/m_1} = \frac{1}{(K_1/K_2)V_m} + \frac{C_1/C_2}{V_m} . \qquad (6)$$

Freundlich isotherms are similar to Langmuir except they allow for heterogeneous site energies of adsorption with a logarithmic decrease in energy with increased surface coverage. A linearized form of the Freundlich equation is

$$\log(x/m) = \log K + \frac{1}{V_m} \log C . \qquad (7)$$

A plot of log (x/m) vs log C should yield a straight line.

Adsorption data for Cu, Pb, and Zn were used to construct Langmuir, double reciprocal Langmuir, and Freundlich type isotherms. The data best fit Langmuir type adsorption, with r^2 values listed in Table 10. Plots were constructed from the data by equation 2 (Fig. 5). Points that represent complete removal of metal from solution were omitted (i.e., 3 μmol Cu_0 from Table 9). As discussed above a physical interpretation of K is difficult, however, a low intercept $\frac{1}{KV_m}$ indicates the relative ease with which ions are removed from solution. The Cu plot has an intercept of 0.64, Pb 4.20, and Zn 6.32, and as mentioned above, Cu is indeed more efficiently adsorbed at low initial solution concentration than either Pb or Zn. The low intercept especially in the case of Cu and Pb may be a function of negligible desorption at low surface coverage. These data seem reasonable because K is k adsorption/k desorption and both Cu and Pb are known to form strong complexes in soil (Kiekens et al., 1982; Cavallaro and McBride, 1978).

Maximum adsorption of Cu, Pb, and Zn as predicted by Langmuir equations compare favorably with observed values (Fig. 4 and 5). Agreement with observed data should not be interpreted as verification of Langmuir type adsorption. A lack of equivalent Ca release with metal addition indicates at least two different adsorption energies. Despite different site energies adsorption may mimic that of homogeneous sites when certain conditions exist (Benjamin and Leckie, 1981a;). If adsorption energies are similar for different sites, or adsorption is dominated by a few sites with similar energies then plots constructed with a wide range of solution concentrations would appear linear. High energy preferred sites dominate at low concentration but as these sites become saturated adsorption at less specific sites prevail. With a wide range of initial metal

Table 10. Langmuir, double reciprocal Langmuir, and Freundlich isotherm plots r^2 values for Cu, Pb, and Zn.

Equation	Cu	Pb	Zn
Langmuir	0.999	0.998	0.997
Double Reciprocal Langmuir	0.983	0.947	0.986
Freundlich	0.995	0.988	0.992

solution concentrations the change in slope may not be apparent. Copper, Pb, and Zn plots have a slight change in slope at very low concentration and another for Pb and Zn exists near saturation. At the resolution of this study three different sorption energies are observed (Fig 5).

Competition in Binary Systems

Cu vs Zn: Soil was equilibrated with various solutions that contained 0.5 mM Cu and a range of Zn concentrations between 0.1 to 2.0 mM. In a 0.5 mM Cu solution, the soil adsorbed 14.9 μmol Cu g^{-1}. From a solution that contained only 2.0 mM Zn soil adsorbed 30.5 μmol Zn g^{-1}. Additions of Zn had little affect on Cu adsorption (Fig. 6). The slight reduction in Cu sorption with an increase in Zn indicates these metals are held at mostly unique sites. Zinc adsorption was reduced by the presence of Cu. Although the Cu concentration chosen provided a high surface coverage, it did not saturate the soil. At Cu saturation there would undoubtedly be an additional reduction in Zn adsorption.

Cu vs Pb: Competitive adsorption of Cu vs Pb was determined in solution concentrations of 0.5 mM Cu and a range from 0.1 to 2.0 mM Pb. The effects of Pb additions on Cu adsorption was greater than that of Zn (Fig. 7). Copper adsorption in the presence of Pb was reduced to 6.8 μmol g^{-1}. Less than half of the 14.9 μmol Cu adsorbed from solution containing no Pb was held at sites unique to Cu. Lead sorption in the presence of Cu was greater than that from solution without Cu. Soil equilibrated with 0.002 M Pb alone adsorbed 32.9 μmol Pb g^{-1} compared with 40.6 μmol Pb g^{-1} adsorbed from additions of the same Pb concentration with 2.0 mM Cu.

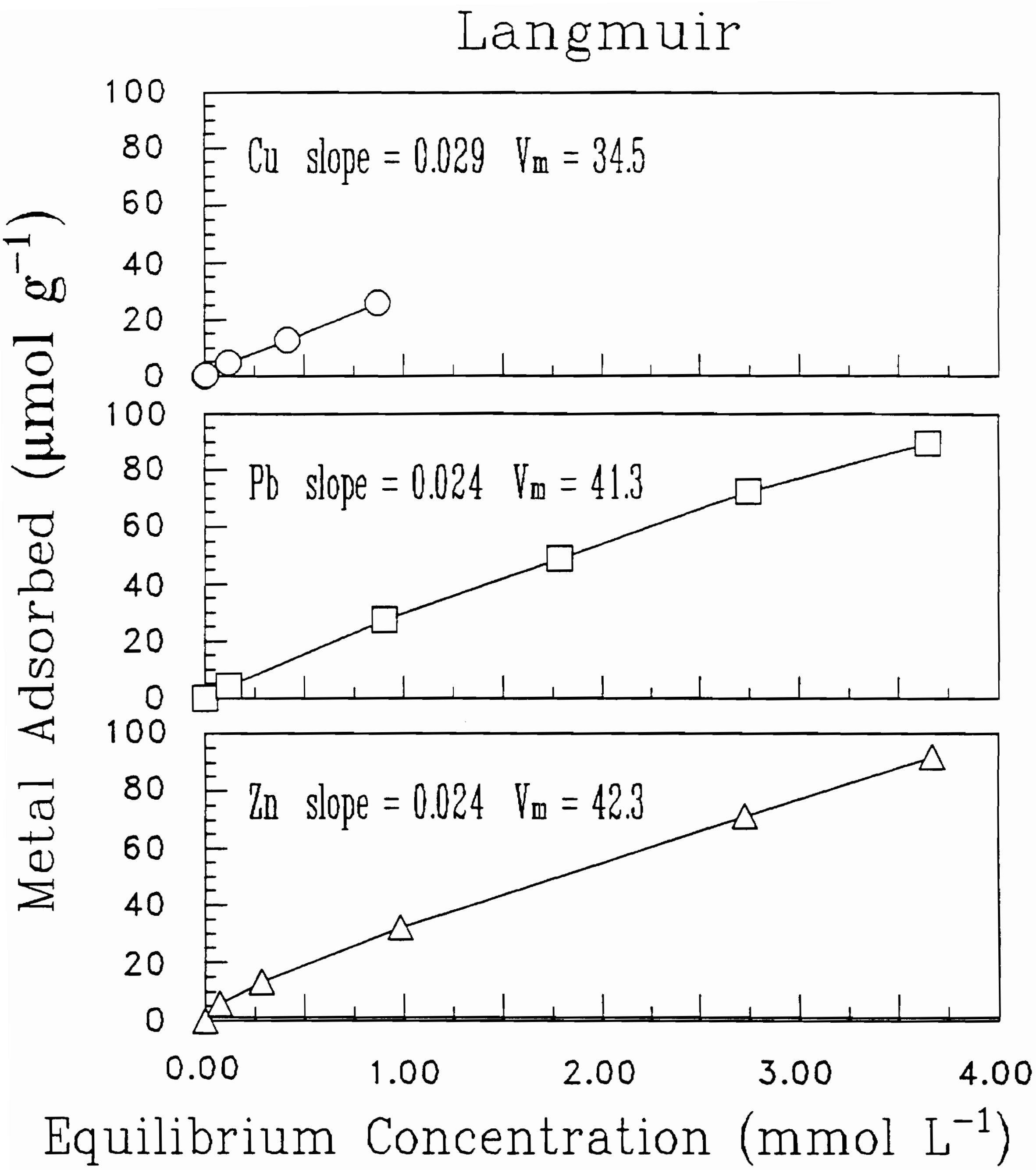

Figure 5. Linearized Langmuir plots for adsorption of Cu, Pb, and Zn to a Davidson clay loam.

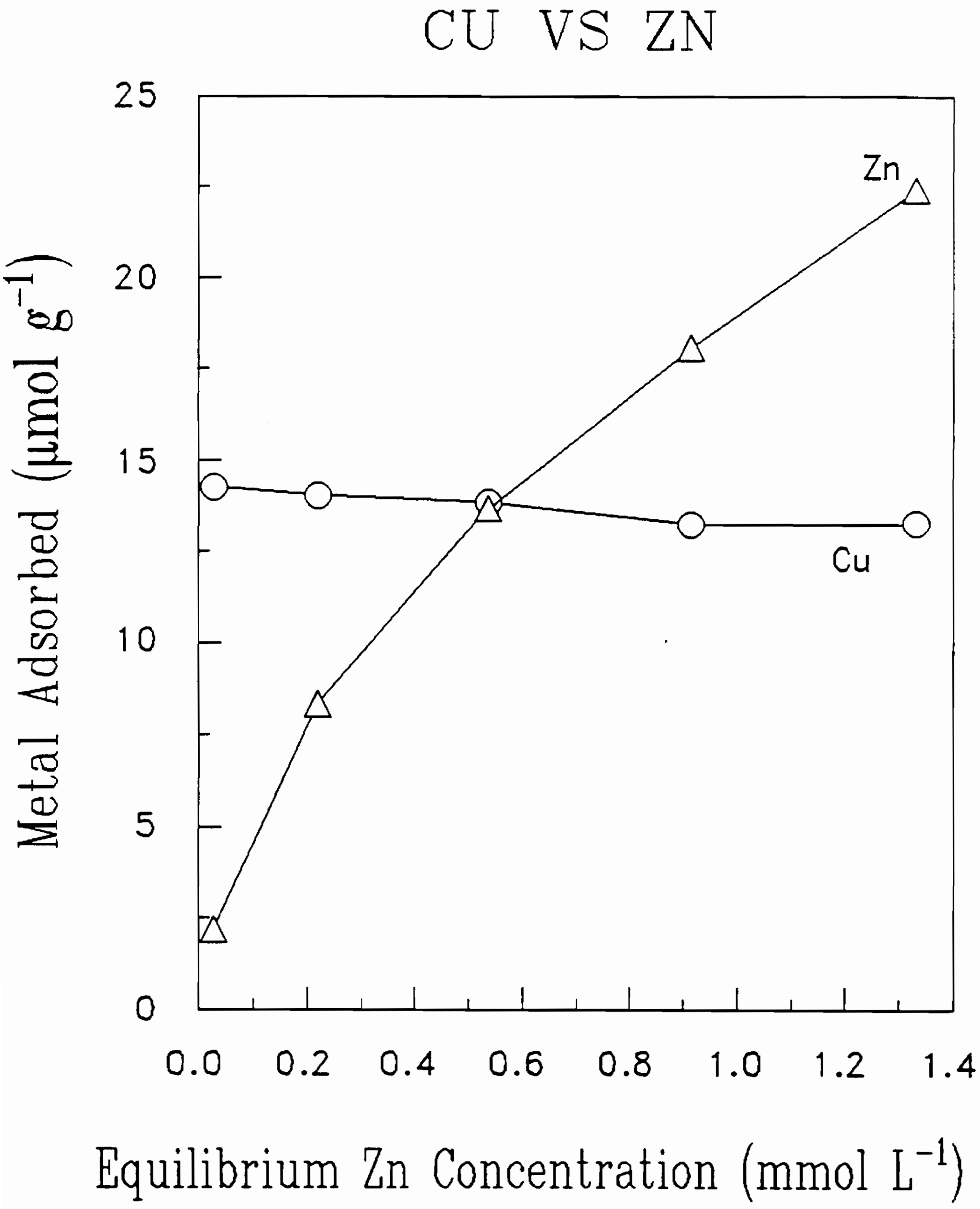

Figure 6. Simultaneous adsorption of Cu and Zn to a Davidson clay loam as a function of equilibrium solution concentration.

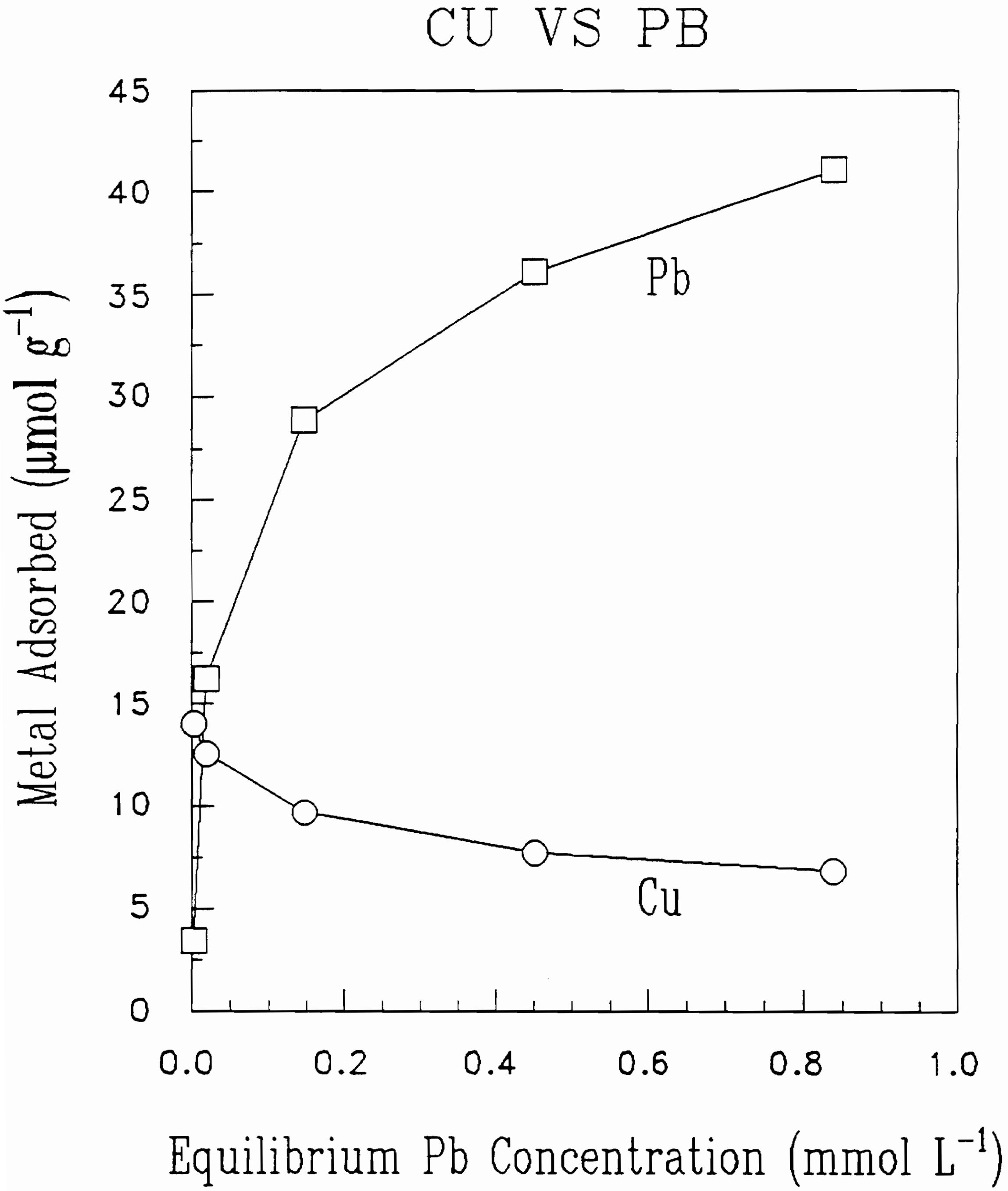

Figure 7. Simultaneous adsorption of Cu and Pb to a Davidson clay loam as a function of equilibrium solution concentration.

Zn vs Pb: Zinc vs Pb competitive adsorption determined by equilibration of 2.0 mM $Zn(ClO_4)_2$ with 0.1 to 3.0 mM $Pb(ClO_4)_2$ resulted in a decrease in Zn adsorption with an increase in Pb additions (Fig. 8). As Pb adsorption increased beyond 400 μmol, Zn displacement reached a minimum of 5.0 μmol. Adsorption of Zn in the presence of a high concentration of Pb indicates not only unique sorption sites for Zn but also that these sites are not subject to exchange reactions.

Lead adsorption, however, was enhanced by the presence of Zn and reached a maximum value of 46.7 μmol g^{-1} in comparison with 36.4 μmol g^{-1} adsorbed in the absence of Zn. Several explanations for enhanced Pb sorption are plausible. Co-precipitation of Pb with Zn (or Cu) on oxide surfaces may account for enhanced sorption, although suspension pH was lower than in research where Huang and Rhoads (1989) reported surface precipitation of Zn to hydrous aluminosilicates. Several authors observed surface precipitation of Cu or Zn in clay suspension at a lower pH than that of the metal hydroxide solution alone (Farrah and Pickering, 1976; McBride and Blasiak, 1979; Cavallaro and McBride, 1980; McBride, 1982; Harsh and Doner, 1984; Masky and Calvet, 1990). Where there is a greater OH^- concentration at the surface than in bulk solution, clay minerals or Fe, Al, and Mn hydrous oxides can act as nucleation sites for Cu and Zn precipitation. Co-precipitation of Pb with Cu or Zn on mineral surfaces at pH $\geq$ 4.0 cannot be discounted in this soil.

In the presence of Cu or Zn there may be a reduction in solubility of Pb complexed with humic acid. Metals can form a bridge between two separate humic acid molecules and at a high metal per humic acid ratio long chains form and the compound precipitates. Addition of a second metal with Pb may reduce the solubility of these complexes. Increased precipitation of Pb as an organic complex with another metal may account for enhanced Pb fixation. Finally, titration data indicate a greater release of Al, Fe, and Mn with Zn (and greater Mn release with Cu) than with Pb adsorption. Zinc adsorbed

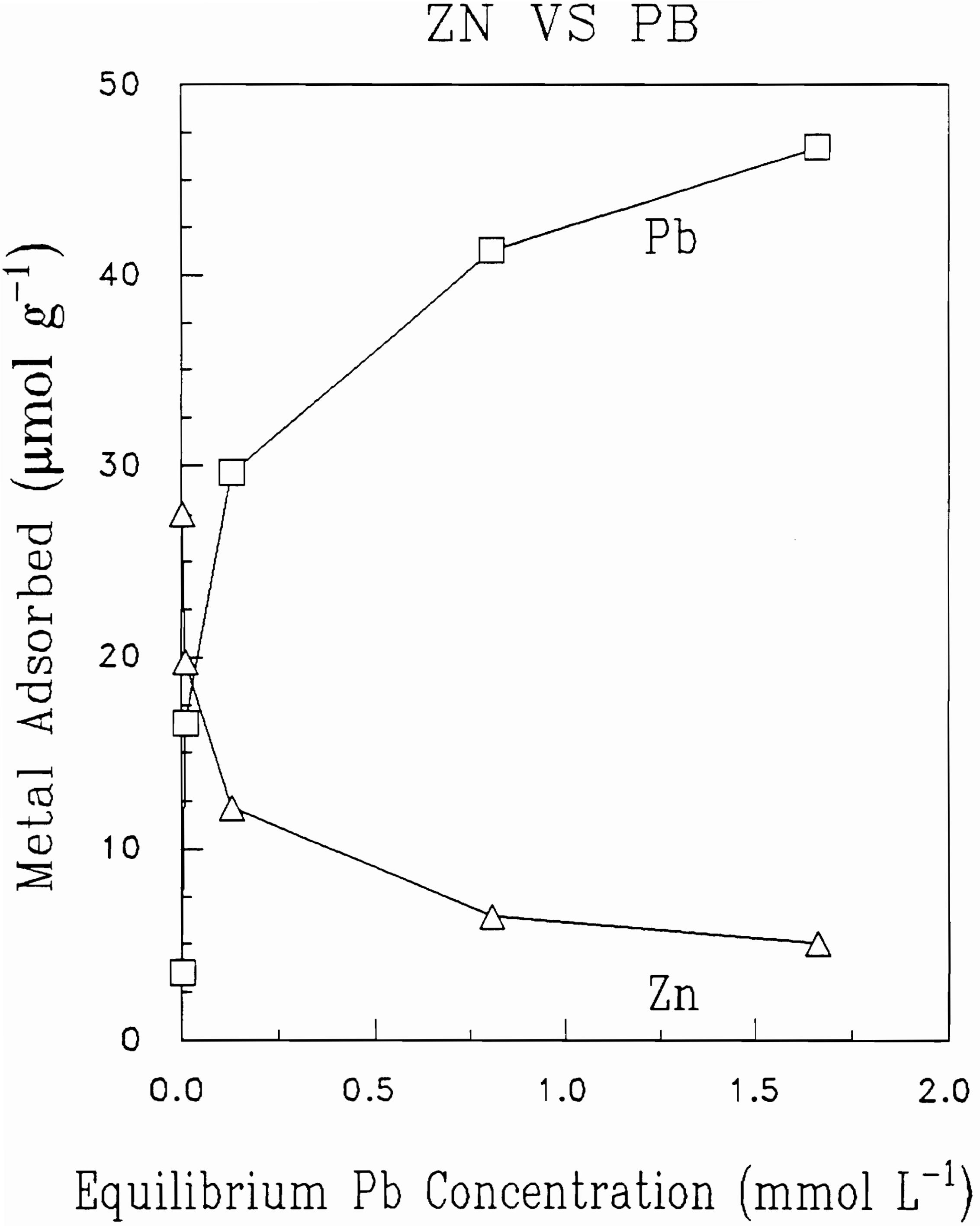

Figure 8. Simultaneous adsorption of Zn and Pb to a Davidson clay loam soil as a function of equilibrium solution concentration.

at sites formally occupied by Al, Fe, and Mn may participate in additional Pb exchange reactions which would not occur if the original ions remained in place.

Langmuir Isotherms in Binary Systems

Assuming that solution concentrations are high enough to saturate adsorption sites and V_m is the sum of maximum adsorption for each metal, if Langmuir type single metal isotherms reasonably fit adsorption data, equation 6 may be used to model competitive adsorption in binary systems. A plot of $\frac{C_1/C_2}{x/m}$ vs C_1/C_2 should yield a straight line for the binary system. Linearized plots of the binary system adsorption data are shown in figure 9a-c. Plots are of metals with varying concentration only (i.e., only Zn with Cu vs Zn data was plotted) since initial Cu concentration did not change. Each plot had a break in slope and maximum adsorption predicted from the slope did not fit the data. Elimination of points before the break in slope improved predicted V_m values for Pb in competition with Cu or Zn, but not for Zn with Cu where competition was weak. Ritchie and Jarvis (1986) found that a Freundlich isotherm for Cu adsorption was curvilinear; which they described as being composed of two straight lines. They attributed this to speciation of inorganic ligand complexes above pH 6. Below pH 6, they suggested involvement with organic complexes.

An alternative explanation for the change in slope would be to consider it to reflect a decrease in the average sorption energy of unoccupied sites. Since the metal ion held constant (Cu in competition with Zn or Pb, and Zn with Pb) was added at less than saturation concentrations, initially high energy sites would be available for sorption of the competing ion, C_1. As these sites fill, adsorption would occur at sites with a very weak affinity for the ion held constant, C_2. Finally, as the concentration of metal added

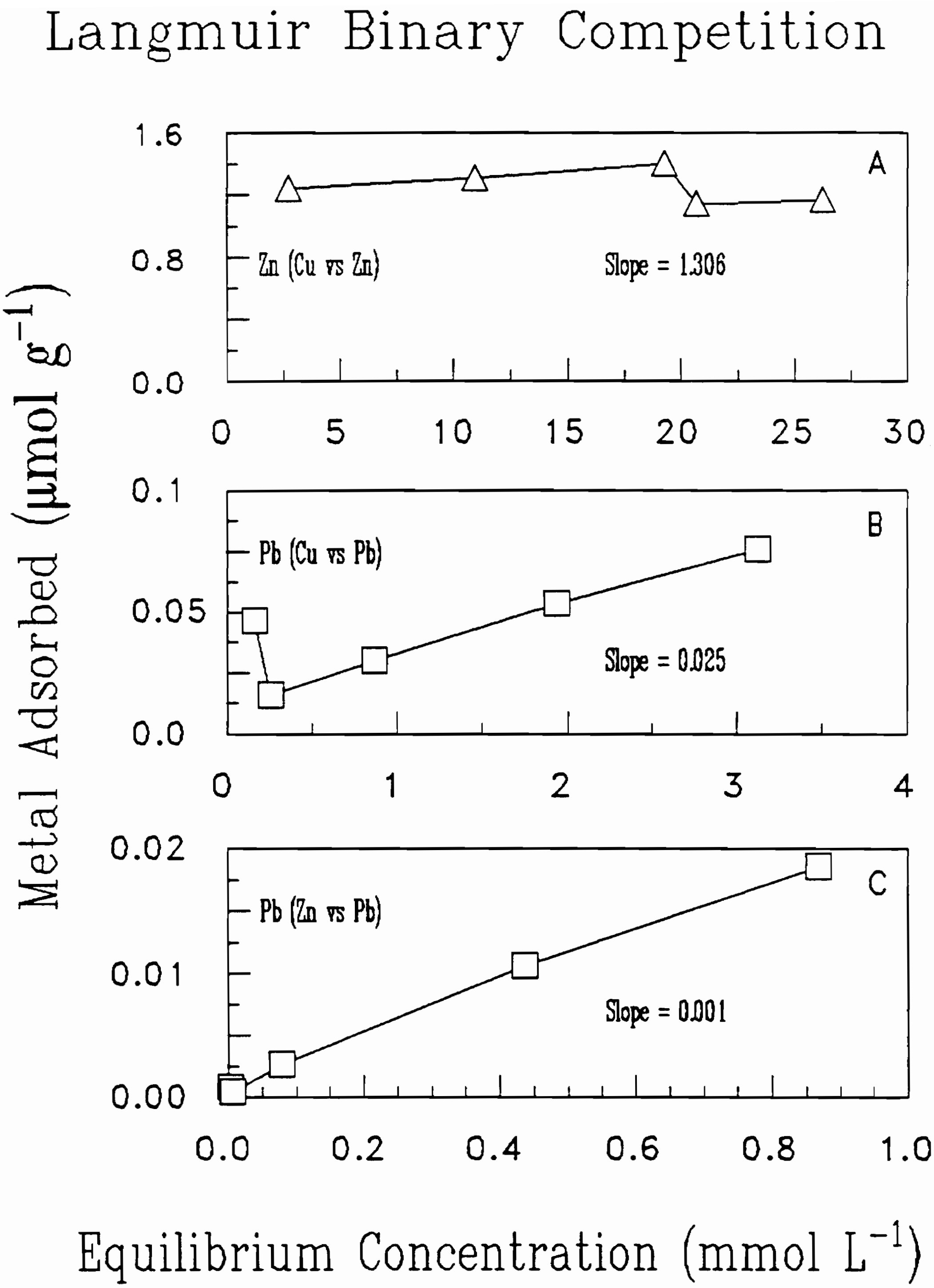

Figure 9. Linearized Langmuir plots for adsorption of Pb, with Cu or Zn, and Zn, with Pb to a Davidson clay loam ($\frac{C_1/C_2}{x/m_1}$ vs C_1/C_2).

increases, C_1 must adsorb to sites with a strong affinity for C_2. These sites would also require a lower bond energy than C_1 specific sites. This adsorption results in a drop in the ratio of C_1 to C_2 in equilibrium solution and, hence, in a break in slope. The point at which the break in slope occurs should be related to the concentration ratio of metal ions added and the number of high energy sites. However, a relationship between Ca release and the break in slope was not apparent, possibly because Ca release is not related to sites from which the different added metal ions will compete. The change in slope in Fig. 9a-c does correspond to the point where the ion held constant is not affected by the competing metal (Fig. 6-8). This occurs between 0.5 and 0.9 mmol equilibrium Zn (Fig. 6), 0.02 and 0.15 mmol equilibrium Pb (Fig. 7), and 16.5 and 30.0 mmol L^{-1} equilibrium Pb (Fig. 8).

Simultaneous Adsorption of Cu, Pb, and Zn

Two-gram samples of Ca-saturated soil were equilibrated simultaneously with Cu, Pb, and $Zn(ClO_4)_2$ at a metal ion ratio of 0.9 to 1.0 to 1.4, respectively. Solution concentration, in terms of Pb ranged from 5 x 10^{-6} to 0.002 M with Cu and Zn added at the appropriate ratio (Table 11). Ionic strength was fixed at 0.02 M with $NaClO_4$. Equilibrium soil pH decreased from 6.3 with no metal added to 4.1 at the high concentration of added metal. Copper adsorption maximum in the presence of Pb and Zn was reduced from 33.8 to 14.1 μmol g^{-1} (Fig. 10). Zinc adsorption was similarly inhibited by competition. At the highest metal concentration used, Zn sorption was reduced from 39.9 to 9.45 μmol g^{-1}. At the highest Zn levels used the adsorption curve exhibited a slight increase in slope above the plateau attained at an equilibrium concentration of 0.5μmol L^{-1}. Adsorption of $ZnOH^+$ or surface precipitation may account for the increase in slope. Although Pb adsorption did not reach a maximum in this study, at higher concentrations of Pb added, Zn replacement would increase to a maximum and then Cu displacement would occur.

There were similar adsorption curves for Pb added alone and Pb in the presence of Cu and Zn (Fig. 10); an enhancement of Pb adsorption did not occur. Compared to bimetal competition where the initial concentration of one metal was fixed, in this study there were incrementally increases in all metals. The higher combined concentrations where all three metals were added apparently inhibited Pb interaction with other metals.

Metal Desorption

Soil samples equilibrated with all three metals were sequentially extracted with $Mg(NO_3)_2$ and either $Pb(NO_3)_2$ or acetic acid to determine non-specific and specific adsorption, respectively. Since similar amounts of Cu and Zn were extracted by acetic acid and $Pb(NO_3)_2$, specific adsorption of Pb was determined by acetic acid extraction. Sorption of Cu at low initial solution concentration was by specific adsorption and only after these sites were saturated did non-specific sorption occur (Table 12). Sixty percent of adsorbed Cu remained after extraction with $Pb(NO_3)_2$.

Metals are generally fixed by soil first at high bonding energy sites and only after these are saturated do low energy bonds form. However, when the number of high energy sites are small compared to that of low energy sites, bond formation is controlled by the concentration of metal ions in solution. Then there is a similar probability of a metal ion coming in contact with either a low or high energy site. Due to a low number of specific sites for Zn, adsorption occurred simultaneously at specific and non-specific sites. As initial concentration of added metal increased, Zn displacement occurred pre-

Table 11. Initial solution content (M_0) and metal adsorbed (M), in micromoles and equilibrium pH from a Davidson clay loam simultaneously equilibrated with Cu, Pb, and Zn.

Cu_0†	Cu	Pb_0	Pb	Zn_0	Zn	pH
0.00	0.00	0.00	0.00	0.00	0.00	6.3
0.27	0.27	0.30	0.30	0.42	0.42	6.3
2.70	2.70	3.00	3.00	4.20	4.14	6.1
5.40	5.40	6.00	6.00	8.40	7.64	5.7
27.00	22.14	30.00	29.11	42.00	12.48	4.8
54.00	27.16	60.00	49.00	84.00	13.41	4.4
108.00	28.24	120.00	67.20	168.00	18.89	4.1

† Soil was equilibrated with 60 mL of metal solution.

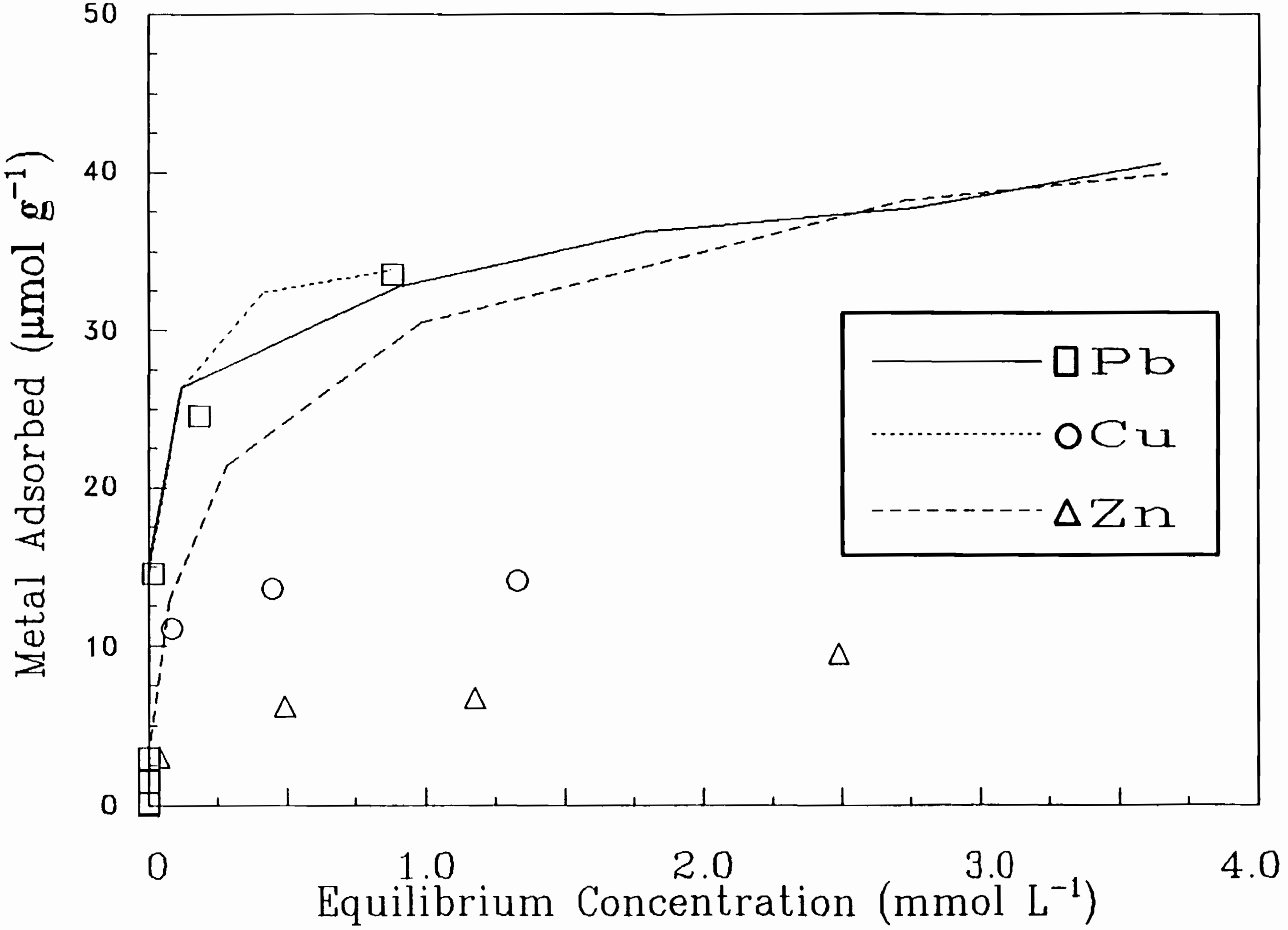

Figure 10. Simultaneous adsorption of Cu, Pb, and Zn (symbols) and single metal adsorption maximum (lines) to a Davidson clay loam as a function of equilibrium solution concentration.

Table 12. Micromoles metal adsorbed and sequentially extracted with $Mg(NO_3)_2$ then $Pb(NO_3)_2$ or acetic acid (Pb) from Davidson clay loam.

Cu_{ad}	Cu_{Mg}	Cu_{Pb}	Zn_{ad}	Zn_{Mg}	Zn_{Pb}	Pb_{ad}	Pb_{Mg}	Pb_{HOAC}
0.00	0.00	0.02	0.00	0.01	0.18	0.00	0.00	0.22
0.27	0.00	0.09	0.42	0.05	0.39	0.30	0.00	0.20
2.70	0.01	1.13	4.14	0.86	2.40	3.00	0.00	0.27
5.40	0.08	2.71	7.64	3.87	3.05	6.00	0.01	0.49
22.14	3.67	10.33	12.48	10.71	1.61	29.11	2.65	0.71
27.16	6.21	10.28	13.41	10.09	0.99	49.00	9.17	7.23
28.24	6.50	10.36	18.89	8.69	0.74	67.20	15.28	10.11

dominantly at specific sites, however, Zn sorption at non-specific sites continued to increase. An additional increase in initial metal concentration resulted in displacement at non-specific sites. There was an increase in Zn sorption to sites not subject to $Pb(NO_3)_2$ extraction at the highest metal concentration.

A small portion of the Pb adsorbed at low concentration was desorbed by either $Mg(NO_3)_2$ and acetic acid. Only after sites not subject to acetic acid extraction became saturated did simultaneous adsorption by non-specific and specific sites begin. There was greater adsorption to non-specific than specific sites at high metal concentration. Acetic acid extraction at $pH < 2.0$ would presumably solubilize most of the Pb fixed by inorganic sites. Since a high portion of Pb remained sorbed by soil, strong organo-metallic complexes may be responsible for Pb fixation.

Conclusions

Specifically adsorbed Zn was small compared to that electrostatic bound, and binding occurred concurrently at all sites. Copper was fixed at specific covalent bonding sites and electrostatically bound only when these were full. Both Cu and Pb were tightly fixed at sites not amenable to extraction by $Pb(NO_3)_2$ or acetic acid. Complexation by organic bond formation, possibly at a greater than 1 to 1 charge equivalence, may control Cu and Pb sorption. Precipitation of Pb and Zn may also occur.

Metals added simultaneously to soil may undergo complex interactions. Low concentrations of either Zn or Cu can enhance Pb adsorption, most likely by co-precipitation reactions with inorganic or organic materials. Metals added individually to a Davidson clay loam were bound in the order Pb > Zn > Cu. However, when metals were added simultaneously sorption was effectively reduced for Zn and to a lesser extent Cu. The order of retention shifted to Pb > Cu > Zn. The amount of an individual metal retained during competition is an indication of the number of unique binding sites for that metal.

Standards for cumulative metal application set by the USEPA are at the lower end of the adsorption curve. In this area individual metals are bound at unique sites and resist desorption in dilute acid solution. Application of mixed metal solutions to soil within USEPA guidelines should not pose a risk to groundwater quality or crop growth. However, even at these low concentrations, metal additions are still accompanied by concurrent release of H^+ and Ca^{2+} ions. These ions presumably occupied low energy bond sites before their release, and therefore, represent a portion of the soil nutrient reserve. In this study the soil was Ca-saturated, in the field Fe, Al, Mn, or other micronutrients would be held at these sites. Application of heavy metals to soil should result in a short-term increase in these constituents in soil solution at the expense of the reserve capacity. In addition, the affect of heavy metal adsorption on monovalent K^+ may be as great as that on divalent Mg^{2+} and Ca^{2+} (Yang and Skogley, 1989). Heavy metal additions may have to be factored into nutrient availability predictions.

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Chapter 4

THE EFFECT OF pH ON COPPER ADSORPTION/DESORPTION BY SOILS AMENDED WITH PIG MANURE OR COPPER SULFATE

Introduction

Copper is commonly added to swine feed to improve feed conversion and weight gain (Lexmond and de Haan, 1977). The resultant manure may contain high concentrations of Cu, Zn, and P as well as N and other plant nutrients. Consequently, many farmers apply manure to agricultural fields as a supplemental fertilizer. This practice has the added benefit of an increase in soil organic matter with a subsequent improvement in soil physical conditions. However, annual applications of manure result in an accumulation of Cu which has led to major concerns about the agricultural and environmental effects of applying this manure to soil.

Literature Review

Adsorption by Organic Components

Hodgson et al. (1965; 1966) found that Cu in soil solution may exist as complex organic forms. Organo-Cu complexes were associated with the soluble organic fraction and bore no relation to total organic matter. The influences of organic matter on metal complexation are to enhance, to inhibit or to have no effect on the adsorption of metals. Actual trends depend on the type and amount of complexes formed and on the solid surfaces present (Inskeep and Baham, 1983a). Adsorption of Cu from a coniferous forest litter layer extract decreased with increased pH values in comparison with adsorption in the absence of the extract, which increased with increasing pH. Long-term applications of Cu-rich manure to soils increased their adsorption capacity (Zhu et al., 1991). An increase in the ability of manure amended soil to adsorb Cu was related to an increase in organic matter content of these soils.

Effects of pH on Cu sorption by soil organic substances are due to both metal hydrolysis and the weak acid nature of exchange sites (Cavallaro and McBride, 1984). A low soil pH increases the fraction of soil organic functional groups that are associated with H^+ or Al^{3+}, thereby reducing their ability to adsorb Cu (Cavallaro and McBride, 1978). Kuo and Baker (1980) titrated Cu-saturated soil with either HCl or NaOH. Copper adsorption increased as suspension pH increased below pH 6. However, there was substantial Cu sorption at pH levels below the soil ZPC. They attributed adsorption at low pH to specific bond formation between metal and soil particles. There was a reduction in Cu sorption as suspension pH was raised above neutrality. At high pH levels soluble organo-Cu complexes reduced Cu competition for sorption sites.

Adsorption by Mineral Components

Retention of Cu by soil was mainly at sites, or by processes, other than normal exchange reactions (McLaren and Crawford, 1973). This phenomenon of specific adsorption was shown to depend primarily on organic matter and free Mn oxide content in soil. However, total organic matter and free Mn oxide content in a mineral soil may be low enough that their gross contribution to Cu sorption may be minimized by other more abundant constituents. Copper adsorption was characterized by release of both H and Mn (Kurdi and Doner, 1983). Adsorption behavior of Cu as influenced by pH reflected surface complexation, adsorption of monohydrated species, and formation of organo-Cu compounds (Msaky and Calvet, 1990).

Farrah and Pickering (1976a) reported clay suspensions in alkaline media act as a nucleation center for formation of hydroxy-bridged Cu species. Ligands in aqueous solution prevent formation of hydroxy species and 'mask' precipitation reactions. Copper adsorption by kaolinite was only found with charged complex species, certain uncharged and negatively charged complex species were not sorbed to any measurable extent. Greater adsorption occurred if hydrated Cu ions made contact with clay prior to addition of ligand than if initial Cu contact was with a ligand.

In a companion paper, Farrah and Pickering (1976b) found that montmorillonite clays have a greater affinity for protonated ligands than kaolinite or illite. Adsorption behavior on montmorillonite was influenced by competition between all positively charged species. For illite and kaolinite, formation of polymeric hydroxy species attached to particular sites on the clay appeared to control sorption processes.

Adsorption pH Dependency

Sorption of Cu in soil was reported to be pH dependent and the amount of metal fixed increased with pH (Forbes et al., 1976; McBride and Blasiak, 1979; Kuo and Baker, 1980). This pH dependence was believed to be due primarily to the tendency of clays to preferentially sorb hydrolyzed species (McLaren and Crawford, 1973; Cavallaro and McBride, 1984; Harsh and Doner, 1984). Increased metal adsorption corresponded to pH conditions where significant hydrolysis of metal ions began. Hydrolysis may have led to surface precipitation and nucleation further enhancing metal sorption. Copper adsorption curves for all but highly calcareous soils can commonly be divided into two straight lines with an increase in slope at low solution concentrations (Ritchie and Jarvis, 1986). The change in slope was attributed to a change in Cu hydrolysis species at pH 6 to 7.

Inskeep and Baham (1983b) noted that, at low concentration Cu was primarily adsorbed by a Na-montmorillonite at pH dependent sites. As Cu concentration approached edge site saturation, there was an increase in pH dependent adsorption. Harsh and Doner (1984) found that Cu sorption to a hydroxy-aluminum-montmorillonite increased with increases in pH and that metal oxides also seemed to be an important cause of pH dependency. Copper was bound both electrostatically and chemically. There was an initial rapid adsorption followed by a slow adsorption and a portion of the sorbed Cu became nonlabile with time.

A portion of Cu adsorbed to soil tends to be specifically adsorbed and fixed irreversibly. This portion is rapidly adsorbed, associated with constant potential edge sites, and more important at low Cu concentration than at high (Kiekens et al., 1982; Inskeep and Baham, 1983b; Forbes et al., 1976; Bunzl et al., 1976). At low Cu levels, sites highly selective for Cu will be occupied first. At high Cu levels amounts of specifically adsorbed Cu decrease proportionally so that larger amounts of exchangeable Cu are present.

Desorption

Although Cu adsorption characteristics are well documented there are relatively few studies on desorption. A portion of the adsorbed Cu was not removed by dilute acid and desorption was independent of pH (Harter, 1983). At pH values between 4 and 8 the same fraction of Cu adsorbed was released with an extractant for plant available metal. This fraction included a large portion of sorbed Cu. Bunzl et al. (1976) found that Cu desorption from partially saturated peat was rapid and that the amount desorbed increased with HNO_3 concentration. The rate of desorption declined as equilibrium was approached with release of $< 25\%$ of adsorbed Cu. Desorption rates were a function of total metal retained plus its binding strength. Desorption kinetics did not exhibit the same characteristics as adsorption. Apparently a portion of Cu adsorbed to soil was held by mechanisms not subject to simple exchange reactions or solubilized by dilute acid. Kinetics of Cu desorption from soil were consistent with a multi-site system complicated by diffusion (Jopony and Young, 1987).

Copper adsorption on montmorillonite and soil oxides increased with soil pH, however, adsorption to humic acid had the opposite effect (McLaren et al., 1983). Very little Cu sorbed by soil components was desorbed by 0.05 M $CaCl_2$. A small amount of the adsorbed Cu may have redistributed among soil components that were in intimate contact with one another.

Copper desorbed from soil (after a 30 min incubation time) by Na-citrate appeared to be held by weak bonding mechanisms (Lehmann and Harter, 1984). The amount of weakly bonded Cu, and subsequent Cu desorption, decreased with time. Padmanabham (1983a) believed Cu was sorbed to goethite by two mechanisms, one composed of monodentate bonds and a second by hydrolysis promoted bidentate bond formation. The fraction of Cu desorbed in acid solution was equivalent to that held by monodentate bonds. Desorption decreased with an increase in initial suspension pH or with an increase in equilibration time.

In most desorption studies, Cu is removed by a single extraction with acid. Release characteristics may be different with several extractions where soil is allowed to equilibrate between each extraction. This equilibration would characterize long-term Cu release from soils, such as those periodically amended with manure. A laboratory study was conducted to determine the effects of pH on adsorption and desorption of Cu from soils previously amended with either Cu as Cu-rich manure or applied as $CuSO_4$ at the same rate as that in the manure.

Materials and Methods

Adjustment of pH

Soil samples from control treatments and from treatments which had previously received 14 annual applications of Cu (357 kg Cu ha^{-1}) as Cu-rich manure and $CuSO_4$ on a Bertie sandy loam and a Guernsey silt loam were air dried and ground to pass a 2 mm sieve. Four-gram soil samples were titrated with either dilute HCl or NaOH to five pH levels from 4 to 8. Suspensions were allowed to equilibrated for 24 h and then re-adjusted to the appropriate pH levels. This procedure was repeated until the pH was stable. Results of these titrations were used to calculate milliequivalents of acid or base required to adjust larger soil samples to the required pH.

Subsamples of each soil and each treatment were adjusted to pH 4 through 8 by an adaptation of the procedure of Harter (1983). The appropriate amount of $Ca(OH)_2$ or H_2SO_4 was added to sufficient deionized distilled H_2O to saturate approximately 60 g of a given subsample. Soil was allowed to air dry and then resaturated with H_2O, this procedure was repeated for a total of 5 wet dry cycles. Final soil pH was determined in a 1:5 soil to solution ratio.

Adsorption/Desorption

Two grams of pH adjusted soil from each site and treatment were suspended in 30 mL of 2 mM $Cu(ClO_4)_2$ in a background solution of 20 mM $NaClO_4$ and agitated at 27°C for 24 h. An additional sample from each site, pH, and treatment was equilibrated in $NaClO_4$ solution without Cu. These samples were used to determine native Cu content. Samples were centrifuged, filtered, and the supernatant collected for Cu analysis. Soils were then washed with 30 mL deionized H_2O to remove entrapped solution. Adsorbed Cu was the difference between Cu in the initial solution and Cu remaining after equilibration with soil.

Copper was subsequently desorbed by a series of extractions with dilute HCl (pH 3.3) at 27° C for 1 h. Soils were washed with 30 mL deionized H_2O after each extraction to remove entrapped solution. Extractions continued until measurable amounts of Cu were no longer found in solution. Fixed Cu was the difference between Cu adsorbed and the sum of Cu removed by dilute acid extraction. Water wash pH was periodically monitored and solution Cu concentration was determined by flame atomic absorption spectophotometry.

Statistical Analysis

Each treatment was replicated 4 times. Analysis of variance was accomplished using the GLM procedure of SAS (SAS Institute, 1985). Means separation were accomplished by Fisher's LSD test, $P \geq 0.05$ level of significance (Ott, 1977).

Results and Discussion

Preliminary Experiments

Each soil and treatment was titrated with either HCl or NaOH to determine milliequivalents of charge necessary to adjust pH to a given level between 4 and 8 (Table 13). Beginning soil pH for the Bertie was 6.5 for all treatments. Beginning soil pH for the Guernsey was 6.8 for control, 6.5 for manure, and 6.6 for $CuSO_4$ treated plots. A greater amount of charge was required to adjust pH of manure than for control and $CuSO_4$ treated plots for both soils. An increase in organic matter (from 2.8% to 3.1% above the control for the Bertie and 2.4% to 2.9% for the Guernsey) as a result of annual applications of pig manure improved soil pH buffering capacity. There were only slight changes in milliequivalents of charge consumed by the Bertie control and $CuSO_4$ treatments, however, the Guernsey control required larger volumes of HCl to reduce pH to given levels than corresponding $CuSO_4$ treatments. This was the result of a higher initial pH in the control. Within a given soil and treatment milliequivalents of charge required to change soil pH one unit were roughly similar for pH 5 through 8. Excess H^+ was needed to reduce pH from 5 to 4 and this amount was greater in the Guernsey than Bertie soil. Between pH 4 and 5 there likely exists a pKa of some soil constituent, probably kaolinite or an amorphous Fe oxide or hydroxide which buffered soil against pH changes.

Copper perchlorate solution was equilibrated with soil from Bertie manured plots in the following treatments: 1) three different soil masses, 2, 5, and 10 g, 2) soil/solution

Table 13. Milliequivalents of charge (+) needed to adjust pH of a Bertie sandy loam and a Guernsey silt loam to 5 pH levels from 4 to 8.

pH	Control	Manure	$CuSO_4$
		Bertie sandy loam	
4	0.069	0.098	0.073
5	0.022	0.035	0.028
6	0.005	0.004	0.003
7	-0.019	-0.026	-0.017
8	-0.046	-0.059	-0.050
		Guernsey silt loam	
4	0.124	0.170	0.113
5	0.073	0.082	0.039
6	0.025	0.031	0.016
7	-0.013	-0.018	-0.015
8	-0.060	-0.073	-0.059

Table 14. Copper adsored from solution to a Bertie sandy loam manure treatment at 3 different soil masses, 2 soil/solution ratios, and 2 equilibration times.

Soil Mass	Soil/Solution Ratio	Equilibration Time	Cu Adsorbed
g		h	μg mL^{-1}
2	1:10	48	106.1
5	1:10	48	106.3
10	1:10	48	105.8
2	1:15	48	83.7
5	1:15	48	79.1
10	1:15	48	82.5
2	1:10	24	103.7
5	1:10	24	102.8
10	1:10	24	102.8
2	1:15	24	78.6
5	1:15	24	79.4
10	1:15	24	79.3

ratios of 1 to 10 and 1 to 15, and 3) equilibration times of 24 and 48 h (Table 14). There was only a slight increase in adsorption after 24 h and reproducibility was not improved by increasing soil mass above 2 g. Therefore, a 1 to 15 ratio, containing 2 g soil in 30 mL of 2 mM $Cu(ClO_4)_2$ in 20 mM $NaClO_4$ solution equilibrated for 24 h, was used for all adsorption determinations.

Adsorption vs pH

Copper adsorbed from solution by a Bertie soil increased with pH level from 13.6 μmol g^{-1} at pH 4 to 34.7 at pH 8 (Fig. 11). The rate of increase was greatest between pH 4 and 5 and was related to a low pH buffering capacity noted during pH adjustment. There were generally no difference between adsorption at a given pH for the control or $CuSO_4$ treated samples. However, manured soil samples adsorbed significantly more Cu at pH levels 4 to 7 than either control or $CuSO_4$ samples. At pH 8 control and $CuSO_4$ treatments adsorbed the most Cu. Two factors can account for this reversal of Cu sorption characteristics by the treatments. First, at high soil pH soluble organic Cu complexes reduced the amount of Cu available for sorption (Farrah and Pickering, 1976a; Kuo and Baker, 1980). This affect would have a greater influence on manured, which have a higher organic matter content, than control and $CuSO_4$ samples. Second, with more Cu available for sorption reactions in the control and $CuSO_4$ samples, precipitation of Cu to soil surfaces or as a separate mineral phase would be favored at pH 8. The combination of greater inorganic precipitation in samples which did not receive manure and greater inhibition of adsorption reactions by soluble organo-Cu complexes in manured samples resulted in the reversal of Cu sorption characteristics.

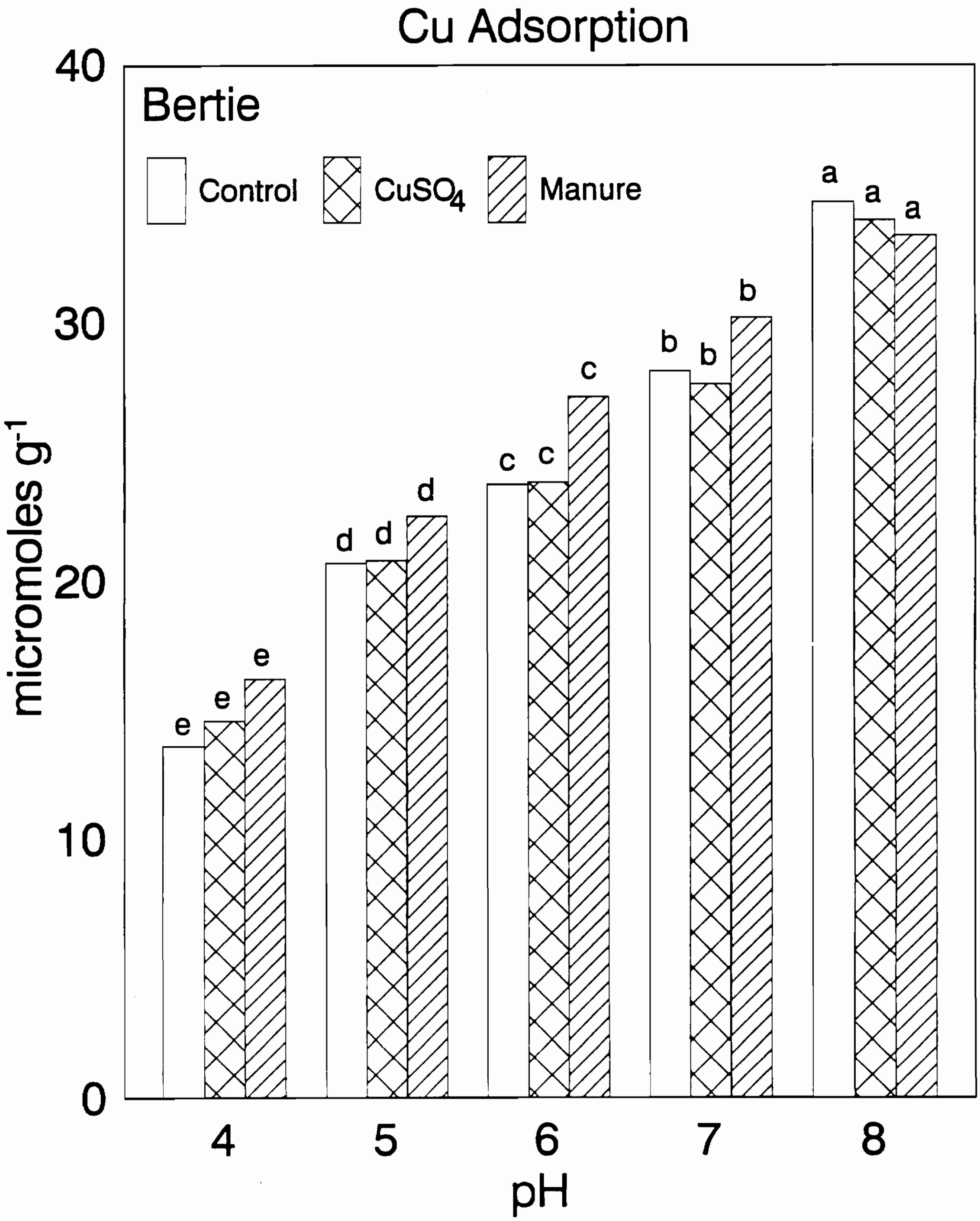


Figure 11. Copper adsorbed to a Bertie sandy loam adjusted to pH levels between 4 and 8 which received no Cu, Cu-rich manure, and $CuSO_4$ as field treatments. Means within treatments followed by the same letter are not different by Fisher's LSD test ($P > 0.05$).

Copper adsorbed by the Guernsey increased with pH for all treatments at pH levels 4 through 8 (Fig. 12). At pH 8, greater than 90% of the initial Cu was removed from solution during equilibration. Previous work by Zhu et al., (1991) revealed 2 mM $Cu(ClO_4)_2$ solution was sufficient to saturate Cu adsorption sites in this soil. Nevertheless, both control and $CuSO_4$ samples were suspended in Cu solution a second time. This resulted in a very large increase in Cu sorption. Unlike the Bertie, more Cu was adsorbed by Guernsey manure than $CuSO_4$ treated soil at pH 8. Increased adsorption at pH 8 was attributed to a concentration effect since sorption sites were already near saturation from the first equilibration. A Guernsey soil sample, pH 6, equilibrated with 3 successive 2 mM $Cu(ClO_4)_2$ suspensions adsorbed 27.2 μmol g^{-1} after the first, an additional 14.5 after the second, and released 0.8 for a total of 40.8 μmol Cu adsorbed g^{-1} soil after 3 equilibrations. The magnitude of this increase was consistent with concentration effect demonstrated during soil/solution ratio determination. Precipitation likely occurred to a small extent in all samples above pH 6, the greater Cu sorption at pH 8 by manured above $CuSO_4$ treated samples indicates either precipitation was a minor factor or the difference in organic matter between manured and $CuSO_4$ samples was inconsequential. In any event, total Cu adsorbed by a given treatment at a given pH is the result of complex interactions between the number of soil mineral verses organic sorption sites, formation of soluble organo-Cu complexes, and the rate of precipitation reactions.

Copper sulfate samples consistently sorbed less Cu, below pH 8, than either control or manured samples (Fig. 12). Given a finite number of sorption sites, and a lack of significant precipitation reactions, low adsorption by $CuSO_4$ samples was due to a limited number of available sites. Copper from field applications was likely sorbed in large clusters, occupying certain individual sites while limiting access to adjacent sites. Subsequent sorption during laboratory equilibration was then limited by site availability.

Below pH 8, there was no difference between Cu sorption by control and manured samples. The Guernsey soil has a high smectite content and Cu may have had greater access to interlayer space in the control soil. High organic matter content in manured samples may have reduced access to interlayer space to a point that ample unblocked interlayer sites in the control could offset any increase in sorption due to organic matter in manured samples. At pH 6 and above more Cu was sorbed by the Guernsey than Bertie soil. As pH decreased Cu sorption by the Bertie surpassed that of the Guernsey due to a higher organic matter content.

Cu Fixation vs pH

Soil samples were subjected to a series of dilute acid extractions for Cu fixation determinations. Copper fixation was the difference between total Cu adsorbed and total Cu removed by extractions. On the Bertie soil Cu fixation had a tendency toward increased Cu binding at higher pH (Fig. 13). Fixation was generally greater in manured than control and $CuSO_4$ samples. Where there were no differences in Cu adsorption between control and $CuSO_4$ treatments, fixation was generally greater in the control. As was mentioned above Cu sorption from field applied $CuSO_4$ was likely adsorbed as large poorly crystallized clusters, blocking access to near-by sites. Copper sorbed from equilibration solution by control samples would have greater access to strong binding sites, greater surface coverage, and better crystal formation. This would lead to a greater portion of Cu sorbed by the control fixed against solubilization in dilute acid.

The Guernsey tended to fix more Cu at higher soil pH levels in manure and $CuSO_4$ treatments (Fig. 14). Manured samples fixed more Cu than $CuSO_4$ treated soil,

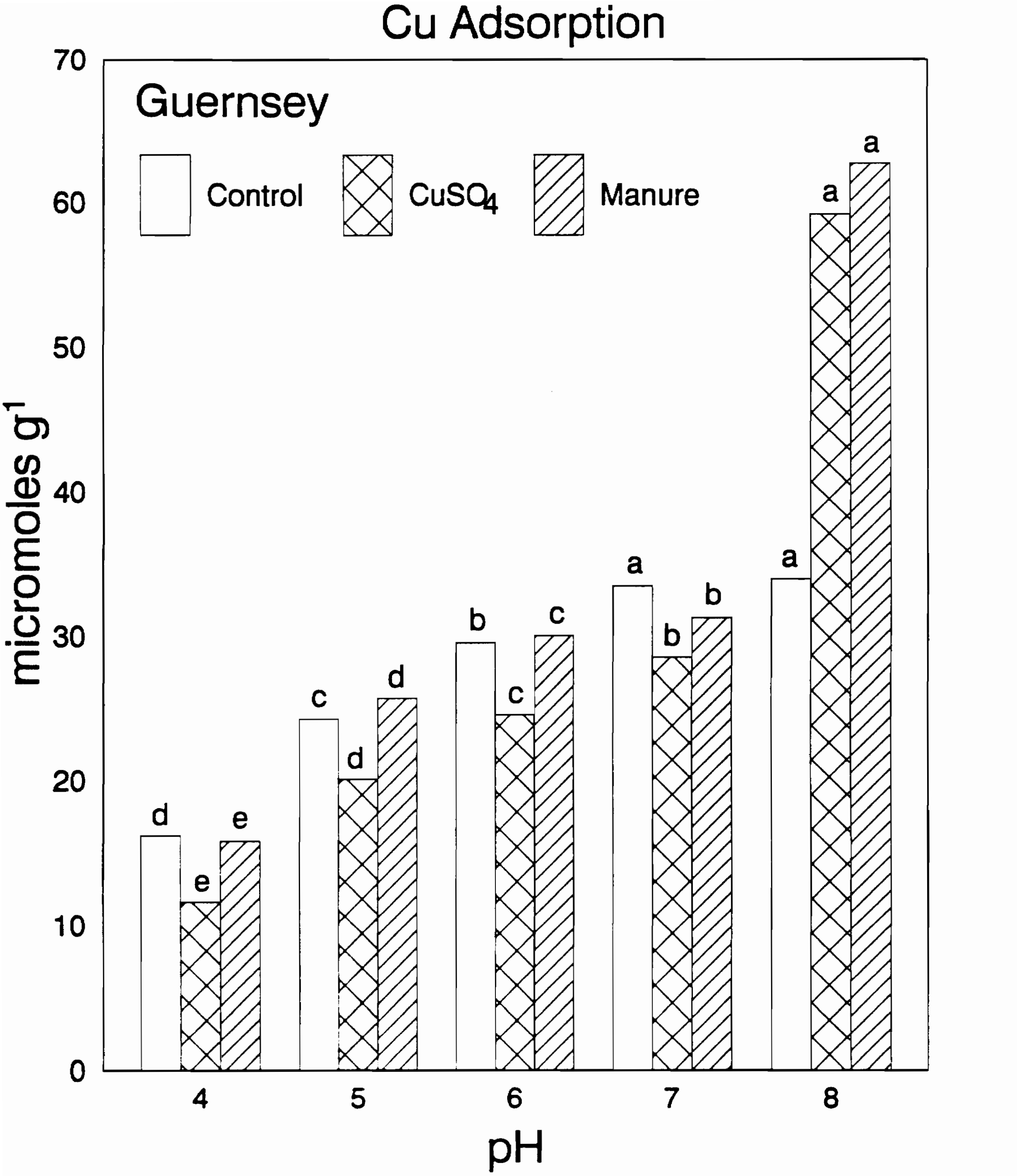


Figure 12. Copper adsorbed to a Guernsey silt loam adjusted to pH levels between 4 and 8 which received no Cu, Cu-rich manure, and $CuSO_4$ as field treatments. Means within treatments followed by the same letter are not different by Fisher's LSD test ($P > 0.05$).

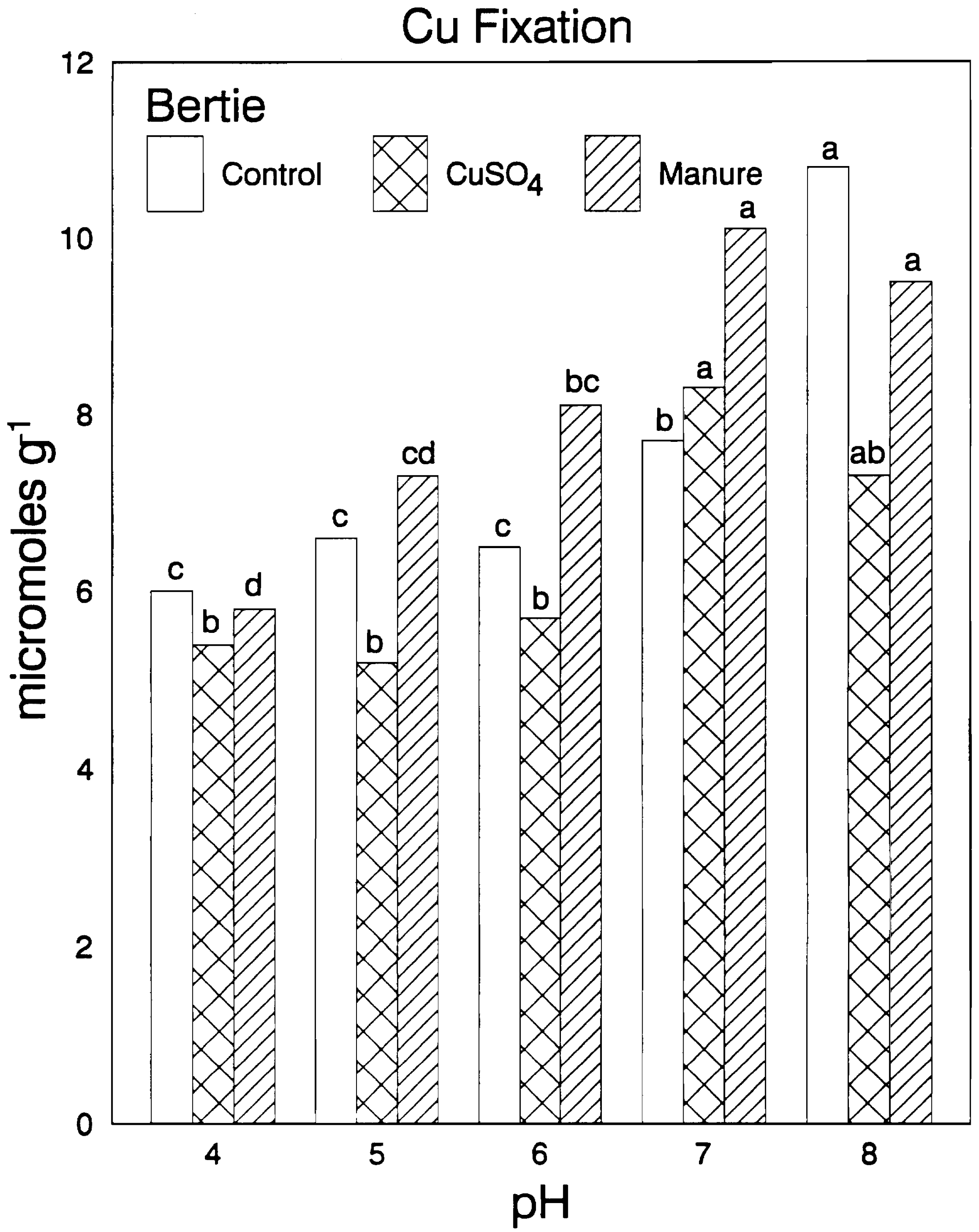


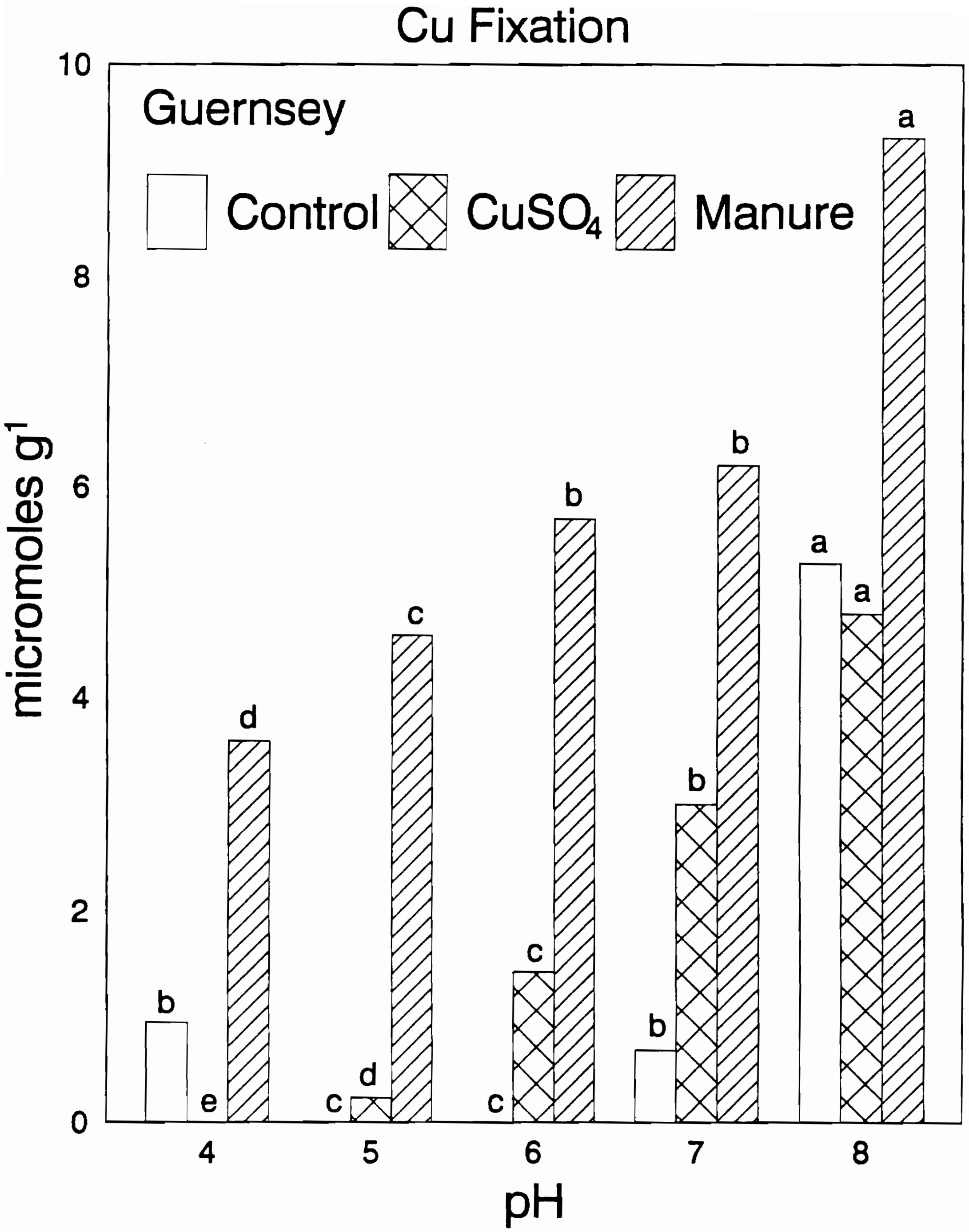
Figure 13. Adsorbed Cu held against desorption with dilute acid by a Bertie sandy loam adjusted to pH levels 4 through 8. Means within treatments followed by the same letter are not different by Fisher's LSD test ($P > 0.05$).

which generally fixed more than controls. Fixation in the control and $CuSO_4$ treated samples was highly inconsistent. The Guernsey had a high smectite clay content, high Fe and Mn oxide content, and a low percent organic matter compared with the Bertie. Thus, it also had more surface area and more mechanisms for Cu binding than the Bertie. With a high number of surface sorption sites, including interlayer sites, the potential for desorption was also high since a greater fraction of sorbed Cu was in direct contact with extraction solution. At pH $\leq$ 6 all added Cu and a portion of native Cu was removed by dilute acid extractions from certain non-manured samples.

Fixed Cu represents Cu which was either occluded from solution or bound by very strong forces. This fixed Cu also represent the first Cu ions removed from solution. An increase in organic matter as a result of manure applications led to a greater fixation capacity in both soils. Although there was a much lower clay and Mn oxide content, soil constituents related to Cu sorption, the Bertie soil with a higher organic matter content fixed more Cu than the Guernsey (Fig. 13 and 14). Although the general trend was to increase fixation at higher pH this did not hold true at all pH levels for the control and CuSO$sub4. samples. Organic matter seemed to have a greater impact on Cu fixation than pH.

Desorption Rates

Adsorbed Cu was desorbed by a series of dilute acid extractions. Desorption kinetics were similar for Bertie control and $CuSO_4$ samples (Figs. 15 and 16). Copper desorption was rapid with a majority of sorbed Cu removed after one extraction, with only small amounts removed thereafter. Desorption curves for pH $\leq$ 6 tended to merge after the third extraction. Copper fixation by soil seems to be affected most at a pH



Figuer 14. Adsorbed Cu held against desorption with dilute acid by a Guernsey silt loam adjusted to pH levels 4 through 8. Means within treatments followed by the same letter are not different by Fisher's LSD test ($P > 0.05$).

above 7. This finding is consistent with an adsorption study by Harter (1983) in which he stated pH management for retention of Cu had little benefits below pH 7, a pH too high for most commonly grown crops.

In contrast to the control and $CuSO_4$, desorption kinetics for manured samples were initially very slow, and desorption rates decreased as pH increased (Fig. 17). After the first 4 extractions desorption increased rapidly then returned to a very slow rate. The increase in desorption rate was greater for pH 8 and consequently Cu removal surpassed that removed at pH 7 by extraction number 10. More extractions were required to remove Cu at pH 7 and 8 than at lower pH levels. The influence of organic matter from manure was to enhance differences between Cu desorption curves at each pH.

Desorption kinetics for the Guernsey were similar to those of the Bertie (Fig. 18 and 19). Below pH 8 desorptions from control treatments were initially very rapid and then slowed considerably. From $CuSO_4$ treatments and control at pH 8 desorption rates were initially moderately fast, then increased before finally becoming reduced to a very low level. The number of extractions necessary to remove sorbed Cu increased with pH. Significant Cu fixation below pH 7 did not occur with the Guernsey.

Desorption from manured samples was initially very slow with only a modest increase in rate with continued extractions (Fig. 20). Manured samples required more extractions to remove Cu than that required by the control and CuSO&sub4,treated samples. A higher organic matter content from manure applications resulted in Cu fixation at all pH levels.

Two observations were noted in conjunction with the initiation of rapid decline in desorption curves. After each extraction, soils were washed with water to remove entrapped solution and water wash pH was monitored periodically. Soil pH changed from the initial values to near 4.5 before pH became stable. Although final pH was not related to initial pH, manured samples consistently maintained higher pH levels. The pH drop to 4.5 corresponded to rapid desorption sections of any given curve. In addition light brown 'globules', probably organic substances, were found floating on the surface of extraction solutions after each of the first few extractions. Appearance of these 'globules' ceased with the onset of rapid desorption rates. These observations bolster the arguments for a strong influence of organic matter on soil Cu desorption kinetics.

Conclusions

Although there are relatively few desorption studies involving soil Cu several facts about Cu adsorption and desorption seem clear. Copper is initially adsorbed by a number of high energy sites and then by a number of weak energy sites. Readily desorbed Cu is limited to that held by weak sites (Padmanabham, 1983a,b; Lehmann and Harter, 1984). However, with time, a portion of readily desorbed Cu becomes irreversibly or only slowly reversibly bound to soil (McLaren et al., 1983).

Soil pH management to improve Cu binding capabilities may be effective on very acid soils, but a large increase in sorption with pH does not occur until pH 7 and above. However, when organic matter is increased Cu sorption increases and more importantly Cu desorption decreases. Hogg et al. (1993) found Cu desorption kinetics from various soils [Cu desorbed by sequential extractions with $Ca(NO_3)_2$] to be initially rapid, in-

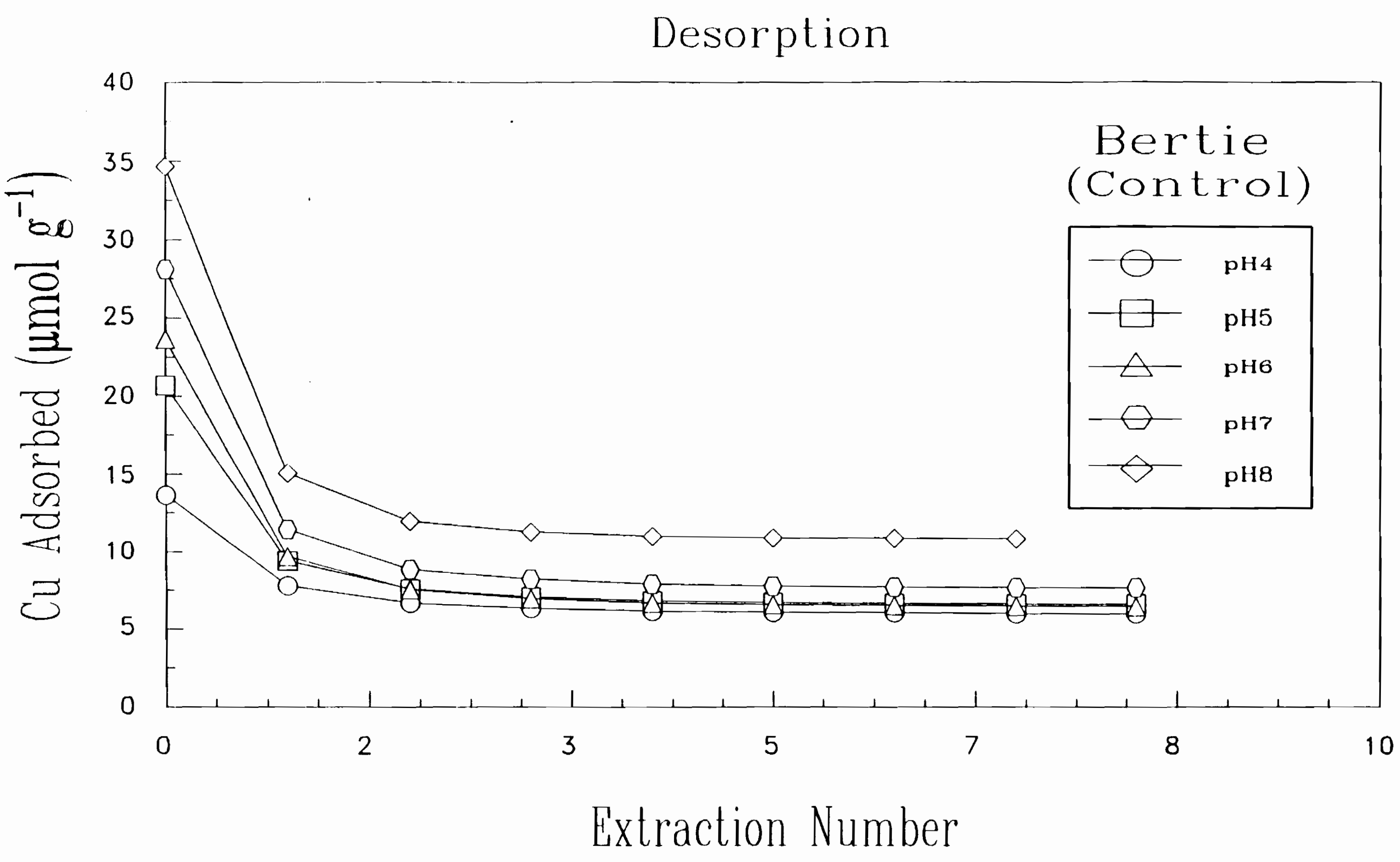


Figure 15. Copper adsorbed by a Bertie sandy loam control treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

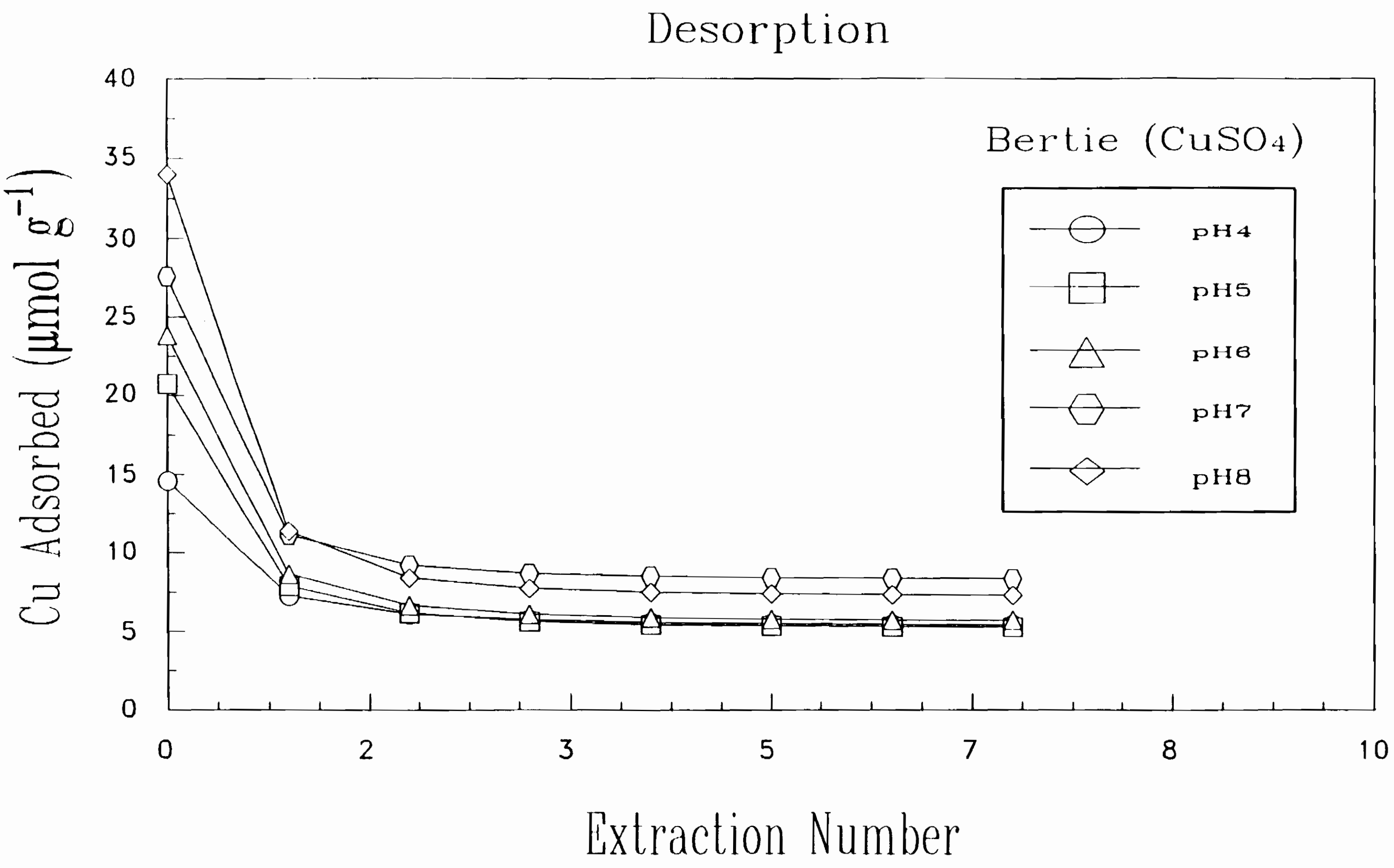


Figure 16. Copper adsorbed by a Bertie sandy loam $CuSO_4$ treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

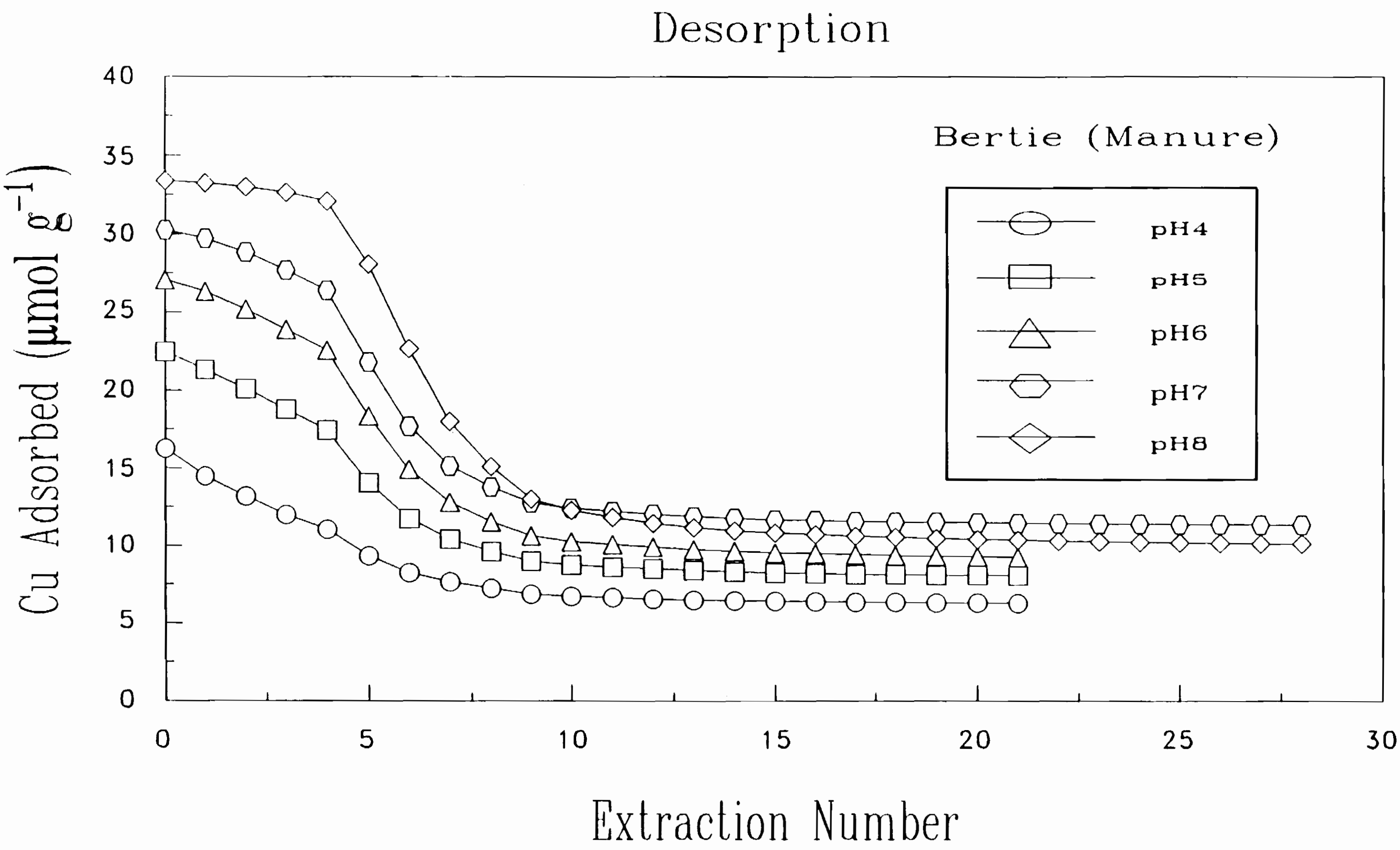


Figure 17. Copper adsorbed by a Bertie sandy loam manure treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

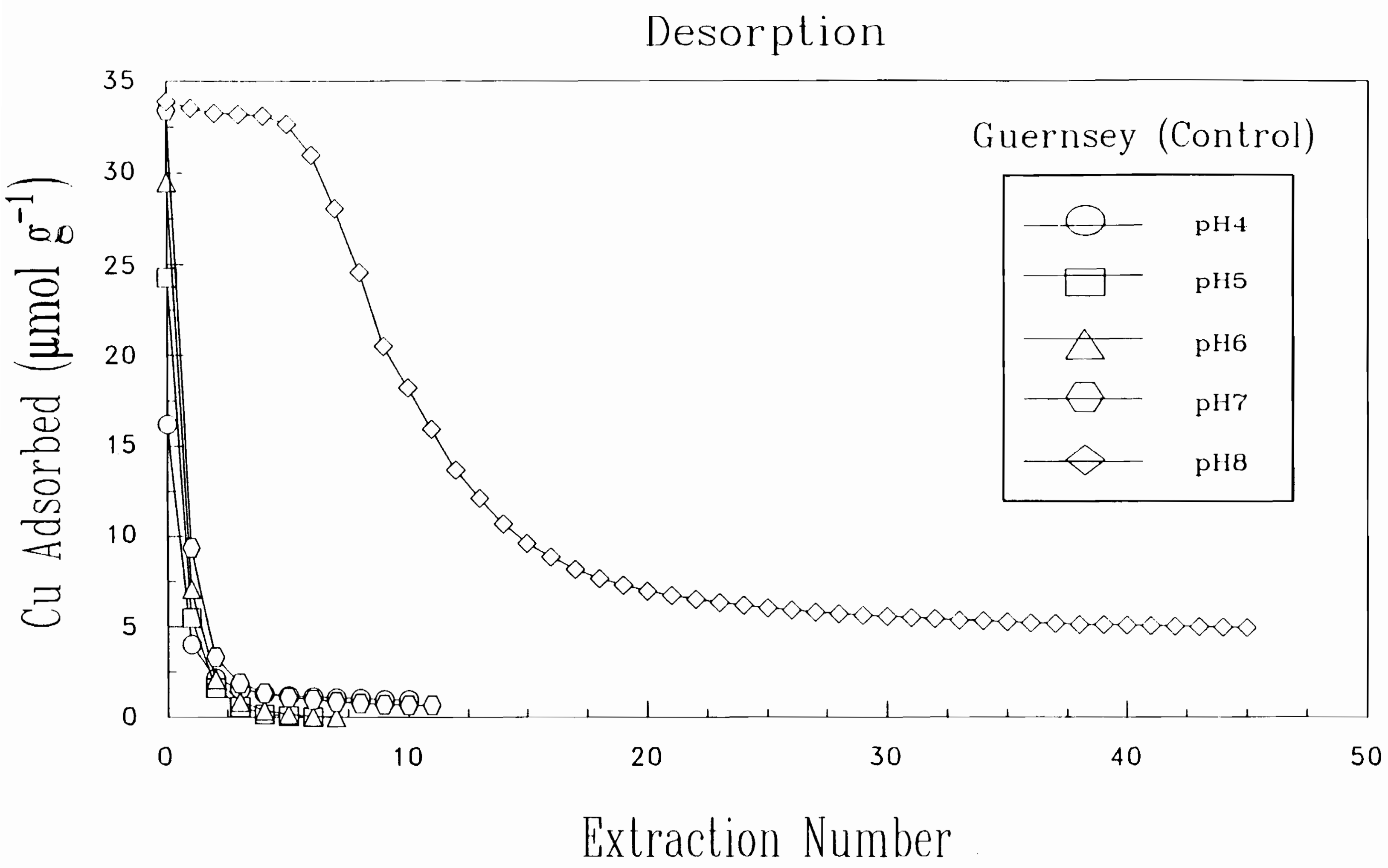


Figure 18. Copper adsorbed by a Guernsey silt loam control treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

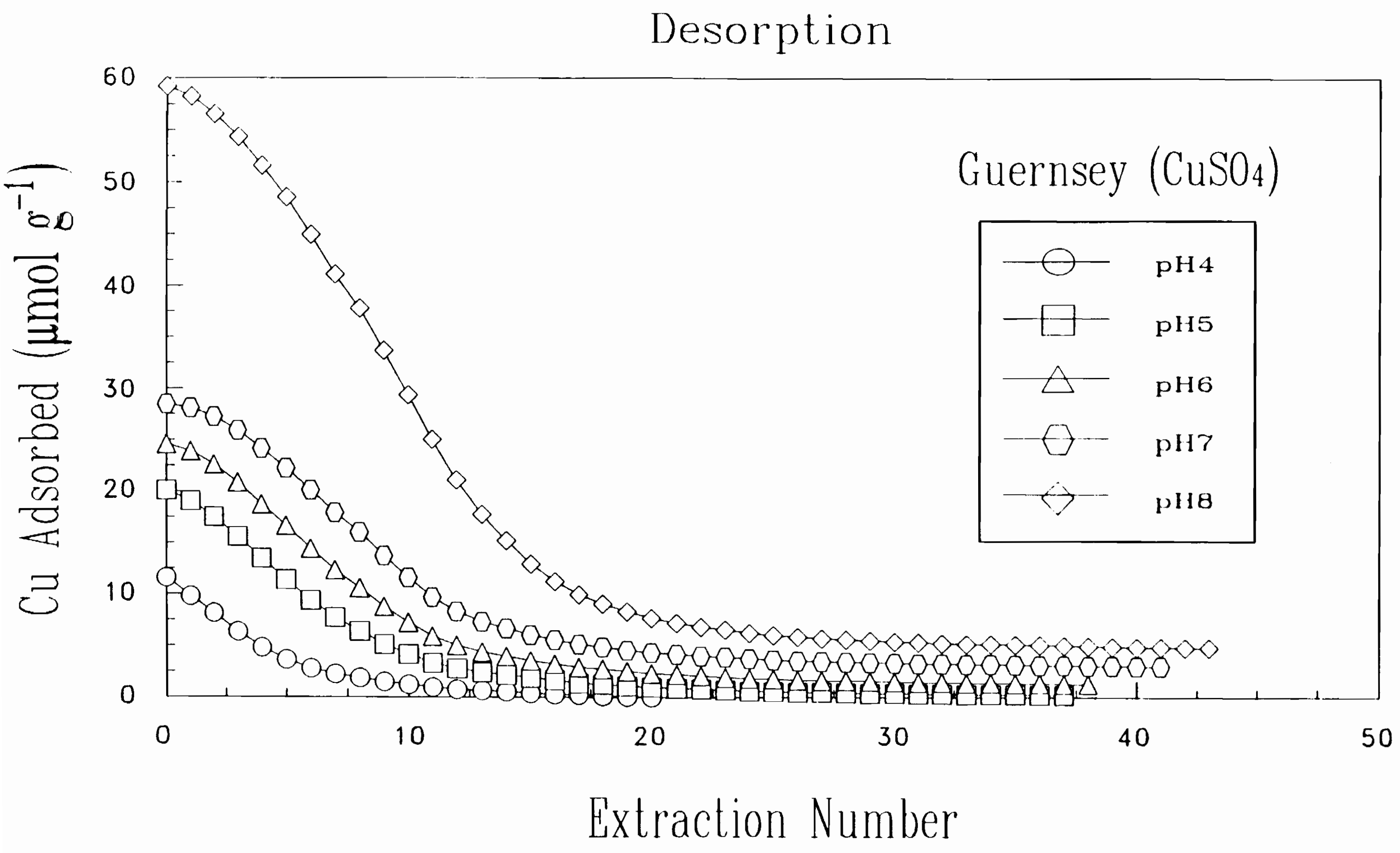


Figure 19. Copper adsorbed by a Guernsey silt loam $CuSO_4$ treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

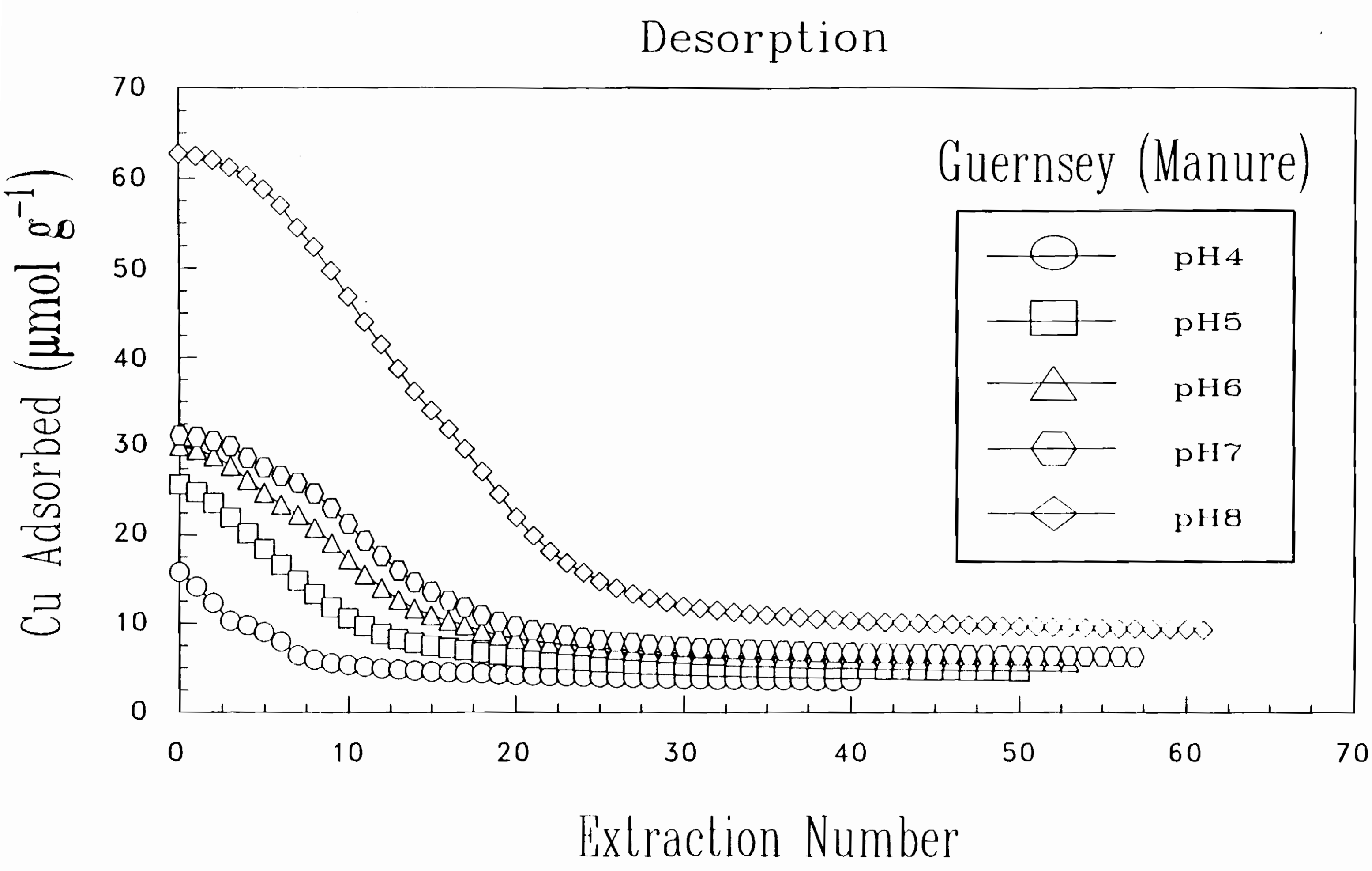


Figure 20. Copper adsorbed by a Guernsey silt loam manure treatment after sequential extractions with dilute acid. Extraction number zero represents the initial adsorbed Cu concentration.

creasing linearly until finally reaching a plateau. In the current study desorption rates were slowed by an increase in organic matter. The presence of organic matter not only buffers pH against rapid change but also retards Cu release from soil. Therefore, it is likely that maintenance of soil organic matter has a more significant effect on both initial Cu adsorption and strong Cu fixation than traditional pH control.

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Summary

Field and laboratory studies were conducted to characterize soil/copper interactions with objectives as follows: 1) to evaluate the effect of Cu applications to agricultural soils, as either Cu-rich manure or $CuSO_4$, on corn yield, 2) to study what fraction of soil Cu is extracted by the Mehlich-3 soil test and to assess the suitability of Mehlich-3 as a test for both deficient and toxic levels of soil Cu, 3) to describe adsorption characteristics of Cu, Pb, and Zn added to soil either individually or simultaneously, and 4) to determine the effects of Cu-rich manure or $CuSO_4$ applications and pH adjustment to soil on subsequent Cu adsorption.

The Mehlich-3 procedure is being adapted as a general soil test in the southeastern U.S. because it has the advantage of simultaneous extraction of P, macronutrient and micronutrient cations, as well as an improved ability to extract Cu over that of the double acid soil test. Since it would be desirable if this procedure could be used to estimate both deficient and toxic Cu levels, soil were examined for Cu extraction patterns of Mehlich-3. Soils used were a Bertie fine sandy loam, Guernsey silt loam, and a Starr-Dyke clay loam from the Atlantic Coastal Plain, Appalachian, and Piedmont regions of Virginia, respectively. Copper was applied to field plots at an average 13-year cumulative level of 365 kg ha^{-1} as either Cu rich pig manure or $CuSO_4$. Although Cu application exceeded the USEPA maximum safe Cu loading rate of 280 kg ha^{-1} for these soils, the pig manure and $CuSO_4$ treatments had no affect on yield or Cu concentration of corn grain, however, there was a trend toward reduced early season growth on one of the three soils (i.e., on the Bertie soil). Applied Cu was held by the three soils

in largely unavailable forms. Soils were obtained for laboratory experiments from the control and treatments that received either Cu rich manure or $CuSO_4$. Soil samples were divided into two groups; one was pre-extracted by the Mehlich-3 procedure and the other was not pre-extracted. Samples were then sequentially extracted to determine exchangeable, specifically adsorbed, organically bound, and oxide occluded Cu fractions remaining in the soil.

Mehlich-3 extractant solubilizes a higher percentage of specifically adsorbed Cu than other fractions and only poorly removes Cu associated with soil oxides. It undoubtable also solubilizes exchangeable and a high portion of organically bound Cu. The amount of Mehlich-3 extractable Cu was a function of total applied Cu, and the amount of Cu Mehlich-3 extracted from the manure treatment was greater than or equal to that extracted from the $CuSO_4$ treatment. Although Cu applications to these soils surpassed the USEPA maximum safe loading rate, the Mehlich-3 procedure, in spite of the high soil Cu content, solubilized Cu predominantly from soil Cu fractions considered available to plants. Since Mehlich-3 strongly extracts specifically bound Cu and only poorly removes oxide Cu, this test may under estimate Cu availability on sandy soils with low organic matter content. However, Mehlich-3 extracted mainly the exchangeable and specifically absorbed Cu at both relatively high and low levels of Cu in the three soils. These are the main sources of plant available Cu. Therefore, the Mehlich-3 procedure shows promise as a soil test for detection of both deficient and toxic Cu levels.

Since heavy metals are seldom applied to soil as a single metal waste, competitive adsorption characteristics of Cu, Pb, and Zn were studied. Soil samples from a Davidson clay loam were Ca-saturated and readjusted to their original ionic strength. Samples were equilibrated with single metal solutions of various concentrations to determine adsorption isotherms. Additional soil samples were equilibrated with a binary metal solution where one metal was held constant at below sorption capacity while a second metal concentration was varied. A third equilibration contained all three metals at a constant metal to metal to metal ratio added in increasing total concentrations. Finally soils were extracted with $Mg(NO_3)_2$ to determine readily exchangeable and with $Pb(NO_3)_2$, to determine specifically adsorbed metal.

The Cu adsorption curve had a steeper slope than either Pb or Zn adsorption curves, an indication of a higher sorption energy for Cu. Sorption capacity followed the order Pb > Zn > Cu in part due to precipitation reactions with Pb and Zn. There was significant Ca release associated with metal adsorption even at very low initial solution concentration, however, a portion of soil Ca could not be removed by any metal concentration understudy.

Copper and Pb were sorbed to soil by specific sorption reactions and complex multi-site mechanisms. Both were adsorbed with a concurrent release of H^+ and Ca^{2+} in amounts greater than that of a one to one charge exchange. Lead competed with Cu for slightly more than half of the Cu sorption sites. Zinc was sorbed to soil by weak electrostatic forces at largely unique sites. The presence of a second metal inhibited Zn sorption by reducing the net electrostatic attraction.

Standards for cumulative metal application set by the USEPA are at the lower end of adsorption curves. In this area individual metals are bound at unique sites by strong forces. However, even at these low concentrations metal additions are accompanied by release of both H^+ Ca^{2+} ions. Application of heavy metals to soil would result in a short-term increase in nutrient cation availability at the expense of long-term reserve capacity. These effects should be factored into nutrient availability predictions.

Soil samples were taken prior to application of treatments in the spring of 1990 from the 0 to 15-cm layer (Ap horizon) of the Bertie and Guernsey soils. In preparation for the Cu adsorption/desorption study soil pH was adjusted by adding an appropriate amount of either $Ca(OH)_2$ or H_2SO_4 solution. Soils were then subjected to five cycles of wetting to field capacity and air drying. Final soil pH measured in a 1:5 weight to volume ratio ranged from 4.0 to 8.0. To a 2 g subsample of each pH adjusted soil 30 ml of 0.002 M $Cu(ClO_4)_2$ in 0.02 M $NaClO_4$ were added and shaken for 24 h at 27° C. Soil suspensions were centrifuged and Cu concentration in the supernatant determined by atomic absorption spectrophotometry. Copper adsorption was considered to be the difference between Cu in the original solution and Cu remaining in the supernatant. Soils were then successively desorbed with dilute HCl, pH 3.3, until Cu was no longer extracted.

Copper adsorbed by both soils increased with pH in the control, manure, and $CuSO_4$ treatments. The rate of increase in Cu adsorbed with pH was greatest between pH 4 and 5 and again between pH 7 and 8 in the control and $CuSO_4$ treatments. This increase was only observed on the Guernsey manure treatment at pH 8. An increase in rate was also found with fixation between pH 7 and 8, however, the increase was small compared to that of adsorption. The excess Cu adsorbed at $pH > 7$ was apparently not strongly bound. Copper adsorption was greater on the manure treated soil than in the control or the $CuSO_4$ treated soil. The amount of adsorbed Cu retained after desorption with a weak acid increased with an increase in pH.

Copper desorption kinetics in the control and $CuSO_4$ treatment were initially very rapid then slowed with only small amounts extracted thereafter. In the manure treated soil, Cu desorption kinetics were slow with much less Cu removed in the initial extractions than in the other treatments. This relationship reflects the ability of organic substances to strongly complex Cu. The presence of organic matter not only buffers soil pH against rapid change but also retards Cu release.

Addition of manure increased soil adsorption capacity above that of either the control or $CuSO_4$ treatment. A portion of this Cu was not desorbed. The USEPA requires a pH $\geq$ 6.5 be maintained on soils receiving high Cu applications. However, maintaining a constant organic matter content may be equally important in limiting Cu availability.

Vita

Stewart T. Reed was born in New York City on June 20, 1950 the second of four children of Sidney T. and Hazel H. Reed. He attended Cardinal Spellman High School between 1964 and 1967, where he participated in football and track, and Seward Park High School from 1967 to 1968.

From 1968 to 1974 he attended Colorado State University majoring in microbiology and participating in the Black Students Association and broadcasting news and sports events on KCSU-FM. In 1974 he completed an internship with the U.S. Geological Survey.

He attended Rocky Mountain Business College in 1975 studying accounting and then managed the Home Improvement Department at K-Mart. Returning to Colorado State University in 1980 he received his B.S. in Soil and Water Conservation in 1985. He completed an internship with the Soil Conservation Service in Yuma, Colorado as a Conservation Assistant. While in Yuma he performed several community service functions including coaching a girls little league softball team to an undefeated record and the county championship.

He received a Minority Merit Fellowship at Texas A&M where he taught Introduction to Soils and Soil Fertility and Chemistry laboratories, and was elected Secretary of the Students Over Traditional Age Organization. He received his M.S. in Agronomy from Texas A&M in 1990.

Since leaving Texas A&M he has worked toward earning a Ph.D. degree in Soil Chemistry at Virginia Tech. He was awarded a State Graduate Deans Fellowship and a Commonwealth Graduate Fellowship on the basis of his academic and teaching success. At Virginia Tech he has taught Introduction to Soils and Soil Fertility laboratories and has acted as a research advisor to four undergraduate students. His work with students resulted in two published abstracts and two published refereed journal articles.

Among his research interests are the fate of heavy metals in soil and the final remediation of metal contaminated soil. Other areas of interest are soil analysis and hazardous waste disposal. His teaching interests include soil chemistry, fertility, and the application of hazardous wastes on agricultural soil.

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