

FACTORS AFFECTING MOBILITY OF COPPER IN SOIL-WATER MATRICES

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TABLE OF CONTENTS

<u>CHAPTER 1 INTRODUCTION</u>	1
<u>CHAPTER 2 SOIL DRYNESS AND ITS EFFECT ON COPPER MOBILITY</u>	3
<u>CHAPTER 3 FACTORS AFFECTING COPPER SORPTION AND MOBILITY THROUGH A AND B HORIZON SOILS FROM THE EASTERN SHORE OF VIRGINIA</u>	3
<u>CHAPTER 4 LITERATURE REVIEW</u>	60
4.2. <u>SOURCES OF COPPER CONTAMINATION:</u>	63
4.3. <u>FORMS OF COPPER PRESENT IN ENVIRONMENT:</u>	66
4.4. <u>MOBILITY OF HEAVY METALS:</u>	67
4.4.1. <i>Factors affecting heavy metals mobility:</i>	67
4.4.2. <i>Methods of copper mobility:</i>	68
4.4.2.1. <u>Complexation with inorganic compounds:</u>	69
4.4.2.2. <u>Effect of organic compounds:</u>	70
4.4.2.3. <u>Effect of colloids:</u>	73
4.5. <u>ADSORPTION OF METAL IONS BY SOILS:</u>	75
4.6. <u>SOIL NATURE AND CLASSIFICATION:</u>	77
4.6.1. <i>Soil phases:</i>	77
4.6.2. <i>Soil Classification (Rollings and Rollings, 1996):</i>	77
4.6.2.1. <u>USDA Textural Soil Classification:</u>	77
4.6.2.3. <u>AASHTO Classification System:</u>	79
4.6.3. <i>Soil Structure:</i>	79
4.7. <u>COLLOIDS:</u>	80
4.7.1. <i>General properties of colloids:</i>	80
4.7.2. <i>Types of soil colloids:</i>	81
4.7.3. <i>Humic Substances:</i>	83
4.7.3.1. <u>Colloidal characteristics of humic substances:</u>	83
4.8. <u>CHEMICAL BEHAVIOR OF COPPER IN SOIL:</u>	84
<u>REFERENCES</u>	86
<u>VITA</u>	96

List of Figures

	Page
CHAPTER 2	
Figure (1)	10
Figure (2)	13
Figure (3)	14
Figure (4)	15
Figure (5)	18
Figure (6)	18
Figure (7)	19
Figure (8)	19
Figure (9)	22
Figure (10)	23
Figure (11)	23
Figure (12)	24

preloaded with 0.25 mg/g copper nanopure water as eluant. For the oven dried column, the column was placed in oven at 70C for 2 hours, then eluant flow continued. For flow stopped column, the eluant flow as ceased but the soil did not dry. The arrows ▼ indicate the point in the experiment when either the flow was stopped or the column was dried.

CHAPTER 3

Figure (1)	Schematic Diagram of the Soil Column	38
Figure (2)	Freundlich Adsorption Isotherm on A-horizon soil (change of soil weight). The initial concentration of the copper solution was 247µg/l and its pH was 6. No filtration was applied. The soil solution was allowed to settle for ~48 hours to separate the soil.	44
Figure (3)	Freundlich adsorption isotherm (change of copper conc) at pH 6. The solution was either filtered through 0.45µm filters or allowed to settle prior to measurement of copper	44
Figure (4)	Column Study of copper mobility. The copper was applied as a pulse input with a conc. of 400µg/l and pH 6 to A-horizon soil. Replicate (1).	47
Figure (5)	Column Study of copper mobility. The copper was applied as a pulse input with a conc. of 400µg/l and pH 6 to A-horizon soil. Replicate (2).	47
Figure (6)	Relation between copper and TOC during copper mobility through A-horizon soil. Initial copper concentration was 400µg/l and its pH was 6. Replicate 1	48
Figure (7)	Relation between copper and TOC during copper mobility through A-horizon soil. Initial copper concentration was 400µg /l at pH 6, Replicate 2.	48
Figure (8)	Gel Chromatography of copper compounds from soil	49

column. Samples were obtained from the column depicted by the data in Figure (5)

Figure (9)	Kinetics of Humic substances-Copper Interaction at Different pHs. Initial copper concentration was 0.9mg/l. Initial humic and fulvic acids concentration was 10 mg/l as TOC	50
Figure (10)	Adsorption Isotherm of Copper on Soil Fulvic acids. Initial copper concentration was 0.8mg/l and its pH was 6. The fulvic acids concentration ranged from 1.5 to 19mg/l.	51
Figure (11)	Effect of pH change on mobility of copper through air-dried B-horizon soil. Initial copper conc. was 400µg/l and its pH was 6.	54
Figure (12)	Effect of pH change on mobility of TOC through air-dried B-horizon soil, initial copper conc. was 400µg/l, and its pH was 6.	54
Figure (13)	Mobility of Copper through columns containing different dried soil horizons. The concentration of the copper solution was 400µg/l and its pH was 6.	55
CHAPTER 4		
Figure (1)	USDA textural classification of soil	78

List of Tables

CHAPTER 1

Table (1)	Physical and Chemical Properties of the soil used	8
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CHAPTER 2

Table (1)	Chemical characteristics of the soils used	34
Table (2)	Equilibrium concentration of copper when reacting with different humic substances at different pHs	51

CHAPTER 1 Introduction

Copper provides a vital nutritional component for plants, animals and humans. A copper deficiency causes retardation of plant growth and in animals and man may cause many adverse effects on blood vessels, bone, central nervous system, kidney, liver and enzymes. High concentrations of copper in irrigated soils and ground water can also be a problem. Copper poses a threat to agricultural production and may impact the health of humans and animals (Owen, 1981; Zamuda and Sunda, 1982).

Agricultural practices can contribute important non-point sources of metals. The main sources of this type of pollution are impurities in fertilizers, pesticides, refuse derived compost, wood preservatives and corrosion of metal objects like metal roofs and fences (Alloway, 1995). Copper applied at high concentration to plasticulture tomato fields to protect against plant disease, was found to remain in the field sorbed to the soil following rainfall (Gallagher *et al.*, 2000). A comparison of aqueous and sediment copper concentrations in agriculture and non-agriculture watersheds showed that copper concentration was higher where agriculture was practiced (Dietrich *et al.* 2001). Sewage sludge and other wastes applied to agricultural lands represent another way for soil to become polluted with heavy metals. A typical copper content in sewage sludge is 850 mg/kg dry weight. A substantial amount of this copper can leach out of the soil during rain or irrigation. Copper movement is often associated with the movement of organics and inorganic constituents of soil (Reed, 1993).

Although copper movement has been observed in soils, the factors that are responsible for this movement are not well understood. In this study, the movement of copper in soils found on the Eastern Shore of Virginia where plasticulture is extensively used was studied.

Specific objectives of this research are:

- To determine the copper adsorption behavior of both A and B-horizon soils.
- To compare copper mobility between A-horizon and B-horizon soils.
- To study of factors that influence copper adsorption and mobility. Specific parameters to be investigated are pH, ionic strength, chlorides, and soil moisture changes.
- To study the kinetics and adsorption capacity of copper on humic and fulvic acids extracted from Bojac sandy loam soil.

CHAPTER 2: Soil Dryness and Its Effect on Copper Mobility

Abstract:

Copper is applied to many crops as a fungicide/bactericide, including plasticulture tomato growing operations. Field tests have shown that copper is sometimes found in ground water near these fields. Therefore, a laboratory study was undertaken to determine if this copper can result from plasticulture application and to determine the mechanisms that account for the movement through soil to the subsurface. From the factors that may affect this mobility process; TOC, dryness and its temperature cycle and water content of the soil were selected for study. These factors were investigated in both batch and continuous flow (column) processes. Copper mobility through soil columns was associated with TOC mobility, and soil drying had a major effect on both copper and TOC mobility. The concentration of copper eluted from columns containing dried soils was up to 20 times higher from those containing wet soils. The extent of dryness was found to affect mobility. First-flush-pattern for both copper and TOC from the columns was observed in all columns studies.

Introduction:

Many contaminants have been reported as sources of pollution of soil and ground water, e.g., exhaust, waste water and solid wastes from industrial production, fertilizers and pesticides. Agriculture practices constitute significant non-point sources of metals. The main sources of this type of pollution are impurities in fertilizers, pesticides, refuse derived compost, wood preservatives and corrosion of metal objects like metal roofs and fences (Alloway, 1995). A high concentration of copper applied to

plasticulture tomato fields was found to remain in the field sorbed to the soil following rainfall. “Following rainfall, 99% of the applied copper was found to remain on the field sorbed to the soil. Of the copper leaving the agricultural field, 82% was found in the runoff. The remaining copper, 18%, leached through the soil and entered the ground water. The average copper concentrations in ground water samples were $312 \pm 198 \mu\text{g/l}$ as total copper (Gallagher *et al.*, 2001). Aqueous and sediment copper concentrations were measured in agriculture and non-agriculture watersheds and was found higher for the former use. The dissolved copper concentrations in runoff from the agricultural land were $238 \mu\text{g/l}$ whereas the same concentrations from other land were $< 5 \mu\text{g/l}$ (Dietrich *et al.* 2001).

The mobility of heavy metals depends on their chemical speciation, which in turn is related to the chemical properties of soil. For example, in some types of soil the presence of carbonates effectively immobilizes Cd and Cu by providing an adsorbing surface or by buffering the pH (Dudley *et al.*, 1991). Soil parameters, such as pH, organic carbon content, iron and manganese oxide content and total metal content affect the distribution of copper and cadmium among different soil fractions (Fic and Schroter, 1989).

The mobility of heavy metals, including copper, may be enhanced by the formation of inorganic complexes. Chloride ions, for example, can form complexes with many cations such as Cd (II), Hg (II), Pb (II), Zn (II) and Cu (II). This complex formation mechanism is important, especially in saline soils. Salting of roads for deicing purposes is an important source of chloride ions in roadside environment (Doner, 1978).

Howell and Gawthorne (1987) discussed the important role of organic matter in the retention and behavior of copper. They reported both humic and fulvic acids as two ligands for copper (II) binding with the fulvic acids being the more soluble than humic acids. They reported also simple aliphatic acids, amino acids and aromatic acids as chelating agents for copper (II). The organic complexes of copper, according to their survey, account for more than 90% of the soil solution in the surface horizon. They reported that increases in pH of soils generally increases the amount of organic copper in solution.

Igloria *et al.* (1997) included the possibility of formation of complexes between heavy metals and organic matter colloids in solutions, as well as those attached to soil surfaces. Sposito (1986), on the other hand, claimed that the effect of these colloids might retard metals transport. Ma *et al.* (1997) suggested that the chemical speciation of the metals determined metal behavior and mobility in the environment.

Objectives:

Gallagher *et al.* (2001) found that copper from plasticulture systems entered groundwater and eventually impacted clam beds. The objective of this research was to determine the mechanism(s) of copper mobility through different soil horizons obtained from the Eastern Shore of Virginia. Identifying the major mechanism(s) helps in controlling copper mobility in these soils and reduces the potential for damage to clam beds in this region by changing agricultural practices.

Materials and Methods

The soil used for this study was a Bojac sandy loam. It was obtained from an undisturbed lot in Persley, VA. Grass and roots were removed from the top layer of the soil. A-horizon soil was obtained from depths ranging from 0 to 27 inches. The soil had a strong brown color and a sandy loam or loam texture. B-horizon soil was obtained from below the A-horizon. The B-horizon soil at this depth was obviously color differentiated from the A-horizon. The color of B-horizon soil was light brown compared with dark brown for the A-horizon soil. The soil was sieved and dried before being used for study; only the fraction < 2 mm was used. The moisture content for the wet soil was 13% unless otherwise mentioned. The moisture content after drying was 2%. In general air-dried soil was used through this research (2% moisture content) unless otherwise mentioned

All chemicals and reagents used for this study were analytical grade or trace metal grade. Nanopure® water was used for all reagent preparation and dilutions unless otherwise specified. The copper solutions were prepared by diluting copper reference solution (1 mg/ml) obtained from Fisher using Nanopure® water. All plastic ware and glassware used in experiments were soaked in 10% trace metal grade nitric acid for at least 8 hours, rinsed with distilled water three times followed by rinsing with Nanopure® water three times. The glassware (except for volumetric flasks) was oven dried at 102°C; plastic ware and volumetric glassware were air-dried. The containers used for batch adsorption processes were tested for copper adsorption by shaking copper solution in 8 glass conical flasks and 6 plastic bottles for 24 hours. Clear, rigid PVC columns used for continuous study were purchased from

United States Plastic Corp. They were not tested for copper adsorption but the information obtained from the manufacturer indicated that this material does not adsorb copper and it is not affected by acidity.

Total organic carbon (TOC) was measured on samples acidified with phosphoric acid to less than pH 2 and then purged with oxygen for five minutes. TOC was then measured by the UV assisted persulfate-oxidation method with infrared detection of the evolved carbon dioxide on a Dohrmann Carbon Analyzer DC-80.

The dissolved copper was measured according to Standard Methods for the Examination of Water and Wastewater, number 3030 B (APHA 1995) using a Perkin Elmer 703 Atomic absorption Spectrophotometer (Flame Atomic absorption). The wavelength used was 324.8nm with a 0.7nm slit setting; the range was 100-5000 µg/l copper. For copper concentrations below 100 µg/l, a Perkin Elmer Zeeman 5100 HGA Graphite furnace atomic absorption spectrophotometer was used. All the samples for copper analysis were acidified with 1:1 HNO₃ solution to less than pH 2 and stored at 4°C.

Dissolved copper losses during filtration were investigated. Three samples of copper nitrate solution (400 µg/l and pH 6) were passed through 0.45 µm membrane filters from different companies and through G6 filters. The initial and final concentrations of copper were measured. A minute amount of copper loss was measured for the 0.45 µm Gelman membrane filters whereas very high losses (65%) were detected for the G6 filters. Variable copper adsorption was noticed for other filters. For this reason Gelman 0.45 µm membrane filters were used for all filtration processes .

The soil used in this research was analyzed for organic matter (OM), pH, and selected metals (Ca, Mg, P, K, Zn, Mn and Fe) in the Soil Testing &

Plant Analysis Laboratory, Virginia Polytechnic Institute & State University.
Table (1) illustrates the soil analysis.

Table (1) Physical and Chemical Properties of the soil used

Sample	pH	%OM	Chemical Concentration (ppm)						
			P	K	Ca	Mg	Zn	MN	Fe
Sand	5.6	0.01	0.94	2.78	52.3	10.02	0.21	0.64	1.83
B-horizon	7.4	1.09	4.36	23	1335	40.48	1.08	21.89	6.32
A-horizon	6.7	3.29	10.3	57.3	1735	96.24	3.72	38.05	7.51

Some soil samples were preloaded with 0.25 mg Cu²⁺/g soil by adding 100 g of soil to a copper solution containing 25mg of Cu²⁺. The soil solution was stirred for 24 ours followed by drying at 106⁰C. The soil was crushed and sieved through 2mm sieves.

Effect of drying method on copper adsorption:

An experiment was conducted to study both the effect and method of soil drying on the adsorptive capacity of the soil. A-horizon of Bojac sandy loam soil samples were dried in three ways. The first sample was oven dried at 103⁰C for 2 hours. The second sample was placed in a tray at a thickness of about 2 cm, and then air dried in equilibration with room humidity for three days. The third sample was autoclave-dried for two hours in an Amsco Scientific SG-116 Autoclave (Eagle/century series). The temperature was adjusted to 132⁰C and the pressure was 30 psi. A 357µg/l and pH 6 copper solution was prepared. Duplicates of each type of soil (air-dried, oven dried

and autoclave dried) were used. A 100ml of copper solution was used with 2.1g soil sample for each test. The solutions were shaken for 24 hours, filtered through 0.45 μm filters and the final copper concentration was measured.

Copper desorption kinetics from B-horizon soil:

A batch system was used to study desorption kinetics from B-horizon soil that was preloaded with copper. A 150 g soil sample of B-horizon soil was placed in a 200ml solution containing 15mg of Cu^{2+} . The soil solution was stirred for 24 hour to reach equilibrium. The soil was then oven-dried at 103°C , crushed and then passed through a 2mm sieve. One hundred ml of Nanopure® water, adjusted at pH 6 with HNO_3 and NaOH , was placed in plastic bottles. The same weight of soil (1.11g) was added to each bottle. The bottles were shaken for different time interval (4 minutes up to 24 hours) followed by filtration though 0.45 μm membrane filter and analyzed for copper.

Effect of pulse input on copper desorption:

The purpose of this experiment was to study the possible copper desorption from B-horizon soil following the step addition of a copper nitrate solution. A mixture of dry B-horizon soil and sand was prepared to reach a ratio of 7:3, soil:sand respectively. Twenty grams of this soil mixture was placed into glass column (i.d. 3cm) to a height of 4 cm. A copper nitrate solution at pH 6 was added as a step input (100ml for each addition for a total amount of 6 litres). The volume of the copper solution added was equivalent to about 344 pore volumes. The amount of copper added was equivalent to 0.24mg/g, and should have exceeded the adsorption capacity of that type of soil based on adsorption isotherm data.

Comparison of copper mobility through both wet and dry A- and B-horizon soils:

This experiment was conducted to compare copper mobility through wet and dry soil. The first set of experiments was conducted using the wet (13% moisture content) fresh soil packed into stoppered polyethylene columns (see Figure (1)). Glass wool was placed over the stopper to prevent the loss of soil. Columns were packed with either 300g (wet weight) of fresh A-horizon soil or fresh B-horizon soil. The soil was added in small fractions (50g each) followed by tapping the column to achieve consolidation. The soil columns were stored at 4°C until the beginning of the experiment to minimize biological activity. A volume of 400ml of 500µg/l Cu²⁺ (pH 6) was added to each column as pulse input.

Two other columns with the same dimensions were filled with 300g of dry A- and B-horizon soils,

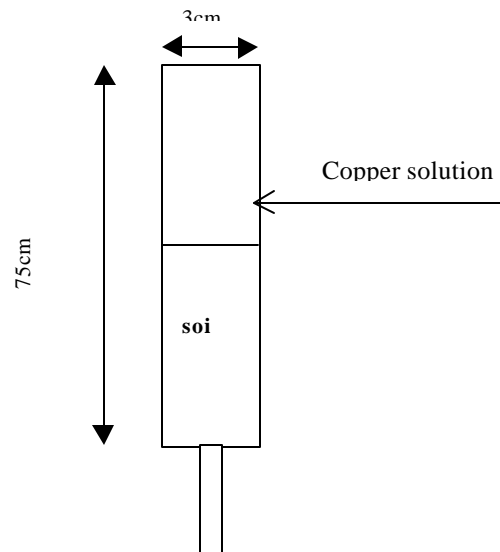


Figure (1) Schematic diagram of the column used for copper mobility study

respectively. The soil was air-dried for 2 weeks, crushed and passed through

2mm sieve, and loaded into the column. The soil column was tapped until no further consolidation was noticed. A volume of 400ml of the 500µg/l Cu²⁺ was added to the column. Effluent samples from all four columns were collected and analyzed for copper and TOC.

Effect of drying temperature on copper adsorption from soil:

Batch processes can provide a rapid indication of copper mobility under a variety of conditions. This batch experiment was conducted to study the effect of temperature on the possible sorption/desorption of copper on A-horizon soil. Four soil samples (preloaded with 0.25mg Cu²⁺/g) and having the same initial water content were oven dried at 38, 54, 64, 102°C until they no weight loss was measured. Each soil sample was placed in a plastic bottle containing 100ml of Nanopure® water (at pH 6). As a reference, a fifth sample from the same soil horizon that had been air-dried was placed in a different bottle with the same amount of soil and pH of Nanopure® water. The copper content of this sample was the same as for other samples (0.25mg Cu²⁺/g). The bottles were shaken for 24 hours at room temperature to reach equilibrium. Samples from each bottle were centrifuged at 10,000 rpm for 20 minutes. The supernatant was analyzed for copper using atomic absorption spectrophotometer.

Effect of soil moisture content on copper mobility:

It was observed during preliminary experiments that there was some difference in the mobility of copper in soil columns containing dried soil compared to wet soil. Therefore, an experiment was designed to study the effect of the soil water moisture content on copper mobility. Dry A-horizon soil was preloaded with 0.25mg/g copper using the method described previously. The soil was mixed with sand (7 parts soil to 3 parts sand) to

increase the rate of water flow. Water was added to provide water content of 13%, which was the percentage found in the fresh soil obtained from the field. The prepared wet soil was split into 20g fractions and either oven dried at 55°C or air-dried at room temperature to achieve different water contents. Glass columns (38cm length and 3cm i.d.) were packed to 4 cm soil height with these fractions. One hundred ml of Nanopure® water at pH 6 was added to each column. Effluent samples were collected and analyzed for copper and TOC.

Dry soil versus wet soil and the effect on copper desorption:

This experiment was designed to mimic seasonal variation from wet to dry soil and to determine the influence of moisture content on copper desorption from the soil preloaded with 0.25mg/g copper. Two columns were packed with 20g of a mixture of dry (2% moisture content) A-horizon soil and sand (7:3, weight ratio). The columns were tapped several times until the soil height in the columns became 4cm. One hundred ml aliquots of Nanopure® water (pH 6) were added to each column and effluent samples were collected. Water was allowed to gravity drain from the two columns, and then the columns were allowed to stand for 15 hours. One of the columns was also placed in an oven at 70°C for two hours to provide additional drying. After the drying periods, another 100ml portion of Nanopure® water was added to each column and effluent samples were collected. Another cycle of drying in the oven was applied to the same column that had been oven-dried previously while the other column was left in the open atmosphere. A third set of 100ml portions of Nanopure® water were applied to the columns. Effluent samples were collected and analyzed for copper.

Results and Discussion

Copper Adsorption on soils:

Effect of drying method on copper adsorption:

The goal of this portion of the study was to determine the effect of the different methods of drying on the sorption of copper on soil. The results of these experiments are illustrated in Figure (2).

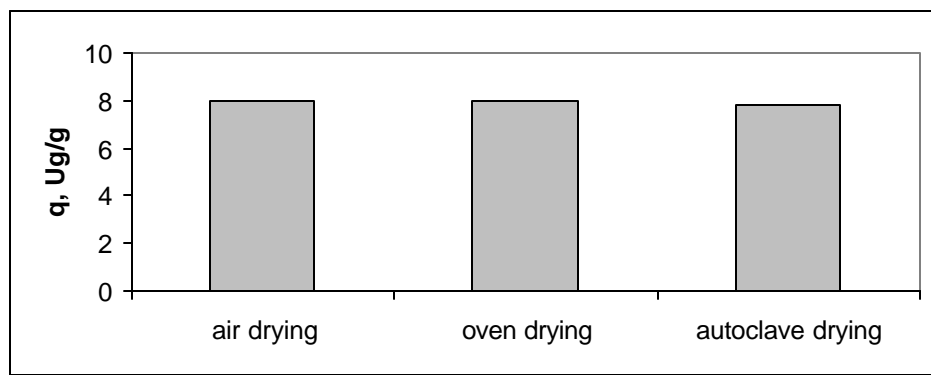


Figure 2 Effect of drying method on ability of A-horizon soil to sorb copper, initial copper solution used was 357 µg/l, at pH 6, 24 hour contact time.

It is clear from the data that the method of drying had minimal impact on the adsorptive capacity of the soil. Nevertheless, it has been reported (Newman *et al.*, 1993) that the rate of drying affected the adsorptive capacity and mobility of metals. The results of this study did not indicate any significant difference in the adsorption capacity, q , between the three methods of drying, a small decrease in the pH was measured for the autoclave-dried soil. The pH change was from 6.55 to 5.93. No change in pH was measured for the air-dried and oven dried soils.

Kinetics of copper desorption:

Desorption may result in mobilization of previously sorbed copper. Figure (3) shows the rate at which copper was transferred into solution from a soil preloaded with copper. About 60% of the copper desorbed within the first five minutes with equilibrium being achieved after 55 minutes. This equilibrium concentration was a function of the original copper content of the soil. When the copper content of the soil was 0.1mg/g the equilibrium concentration was found to be 9 μ g/l. When the copper content was increased to 0.25mg/g, the equilibrium concentration became 55 μ g/l.

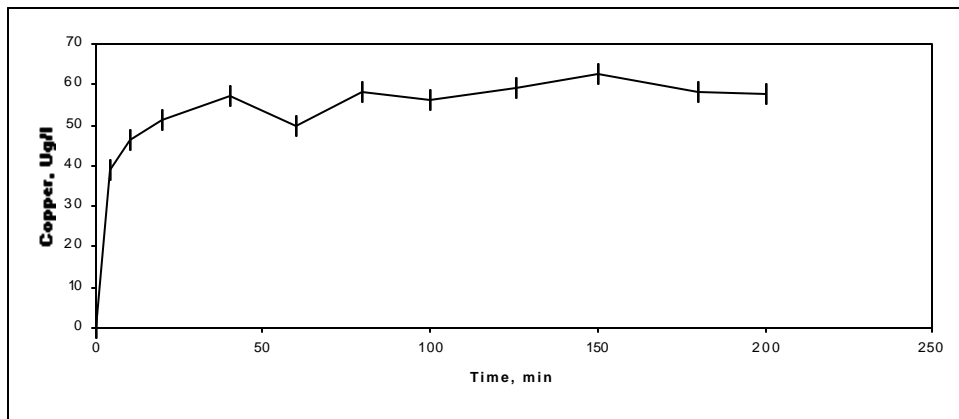


Figure (3) Desorption of copper from a batch test using B-horizon soil preloaded with copper (0.25mg/g) in nanopure water of pH 6.

Desorption of copper from soil preloaded with copper:

Based on the batch data, when adding a copper solution to a soil column, it was expected that little copper would elute from the column until saturation was reached and then the influent concentration would be equal to the effluent concentration. In this experiment, the copper concentration discharged from a column packed with dry B-horizon soil fed with a copper solution of 600 μ g/l was monitored to determine if the copper was retained by

the soil and to determine the capacity of the soil for copper under continuous loading conditions. The results in Figure (4) indicate that the saturation capacity of the soil for copper was not reached, even though the batch adsorption data suggested the system should have been at capacity. Because the addition of excess copper did not result in breakthrough, it is clear that the batch adsorption data was not indicative of the actual sorption capacity of the soil. The amount of copper applied to the column was 5 times the predicted batch capacity that was obtained in preliminary experiments.

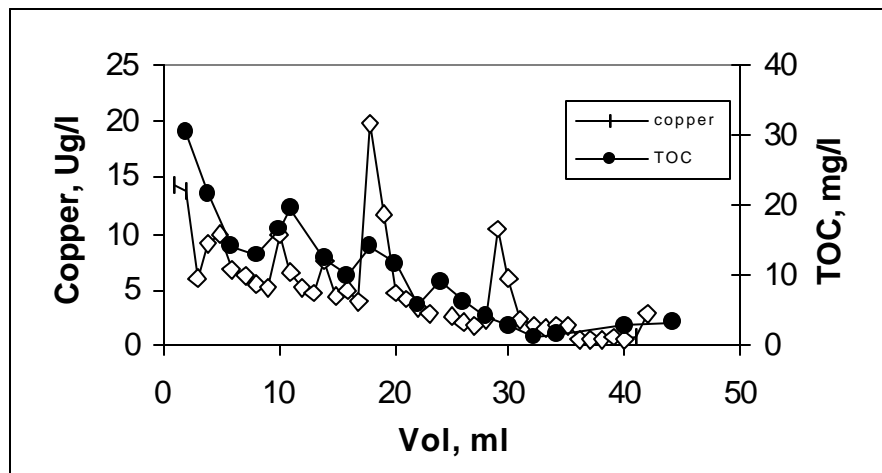


Figure (4) Copper mobility through B-horizon soil with excessive addition of copper nitrate solution of pH 6 and 600µg/l Cu.

A possible explanation of the copper behavior is its binding to the organic substances on the soil. Part of these organic substances were mobilized and flushed from the column. Data in Figure (4) indicate that the mobility of copper and TOC elution follow the same pattern. The organic matter that remained with the soil retained some of the copper thereby hindering its mobility. According to this mechanism, once the mobile TOC fraction has been flushed from the soil, the soil would have a very large

capacity for additional copper. This mechanism was suggested by batch isotherm data where the copper in solution was associated with solution TOC.

Another possibility is that physical filtration might be occurring. The copper combines with organic substances and possibly with other constituents of the soil. The fraction of these particles that has a size smaller than the interstitial positions will pass through the soil and will be washed out. Large particle sizes will be trapped throughout the soil column. This later scenario is strengthened by comparing the column results to those obtained from batch processes. When the soil solution from the batch isotherm studies was filtered after reaching equilibrium, the copper concentration was found to be low. When analyzing the solution without filtration (but with 2 days of settling) the concentration of the copper was found to be much higher, which indicates that copper is attached to organic particles in solution.

In a study of DOC mobility, Jardine *et al.*, (1990) noticed a higher mobility of DOC through large pores compared to small pores. They considered these small pores as a sink for DOC. In other studies (Jardine *et al.*; 1989; Jardine *et al.*; 1990), the high adsorption capacity of lower soil horizons for DOC compared with upper soil horizons was reported. Experimental results from this study indicate the high adsorption capacity of the B-horizon soil to copper. The reason may be an association of copper and organic substances followed by binding of the formed compounds to soil. Lehman and Mills (1994) results agree with these results. They found in their field study that one type of DOC enhanced the mobility of copper while the other type did not affect mobility. It is likely that the type of organic

matter that did not affect the mobility was sorbed on the soil surface or filtered out.

Mobility of copper:

Effect of soil dryness on copper mobility:

This portion of the study was conducted to study the effect of soil drying on copper mobility. Figures (5) and (6) show the results obtained from this experiment, and illustrate the effect of soil dryness on copper mobility. The maximum copper concentration in the effluent from the column containing wet B-horizon soil was $11\mu\text{g/l}$ and the average concentration was $1\mu\text{g/l}$. The copper concentration eluted from the dry-soil column reached a maximum of $70\mu\text{g/l}$ and an average concentration of $20\mu\text{g/l}$. The same effect was observed for TOC. The maximum TOC for the wet soil was around 15mg/l and the average value was around 7mg/l whereas for the dry soil the maximum TOC was 90mg/l and the average value was 30mg/l .

The copper and TOC values for A-horizon soils were higher than those for B-horizon. The average copper concentration eluted from the wet soil was $10\mu\text{g/l}$, whereas the maximum copper concentration eluted from dry A-horizon soil was $120\mu\text{g/l}$ with an average of $40\mu\text{g/l}$. The maximum TOC eluted from wet A-horizon soils was 15mg/l and the average was 10mg/l . The maximum TOC eluted from the dry soil was 150mg/l and the average was 50mg/l .

This suggests that the dryness of the soil increased the mobility of TOC. The relationship between copper mobility and TOC mobility can be clearly seen for both dry soil and wet soil. The data also shows that the soil with the highest organic matter content (A-horizon) was much more sensitive to drying than the lower organic content B-horizon soil.

The relationship between TOC and copper could be seen in all the studies. Every increase in the concentration of copper was associated with a corresponding

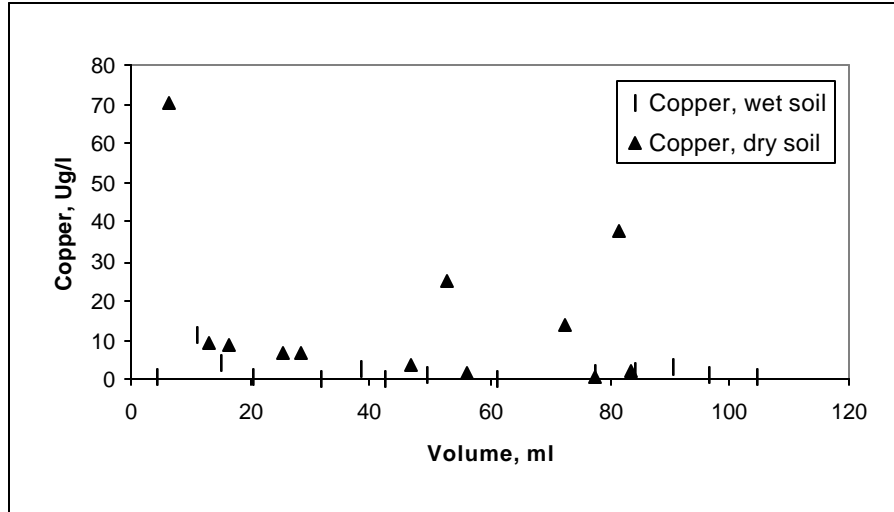


Figure (5) Mobility of copper through columns of wet and air-dried B-horizon soil. The concentration of copper solution used was 500µg/l and its pH was 6

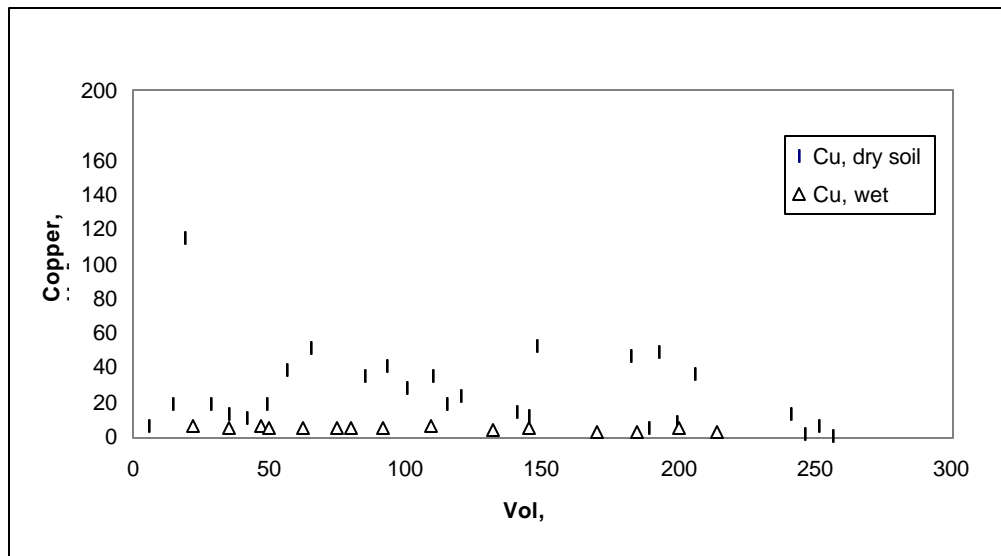


Figure (6) Mobility of copper through columns of wet and air-dried A-horizon soil. Cu solution=500Ug/l at pH 6

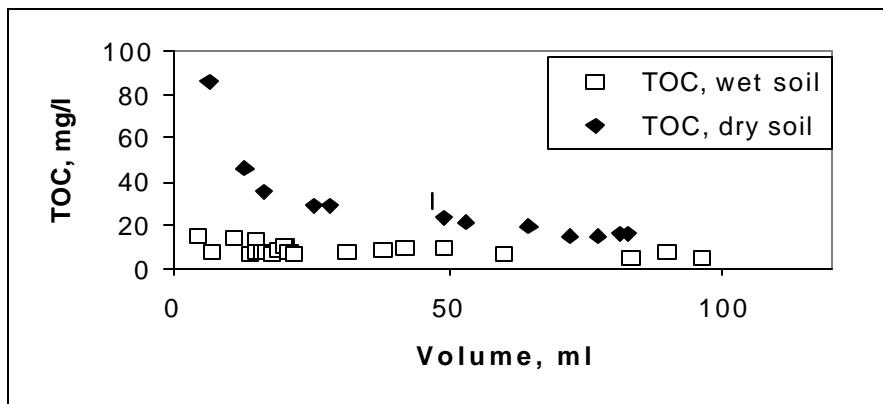


Figure (7) TOC mobility through wet and air-dried B-horizon soil. The copper nitrate solution was 500µg/l and its pH was 6

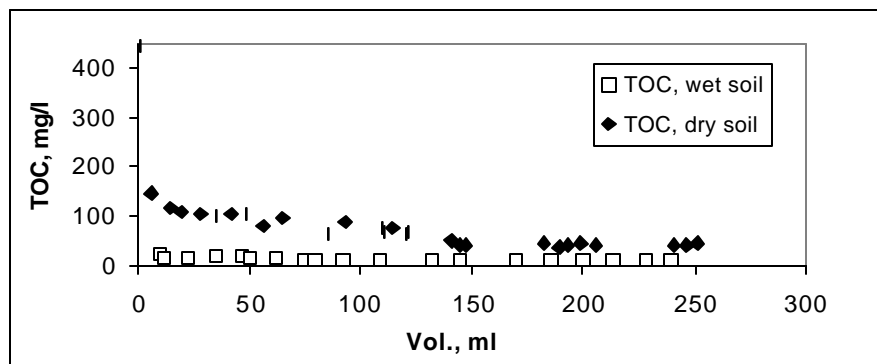


Figure (8) TOC mobility through wet and air-dried A-horizon soil, eluant was copper nitrate solution of concentration 500µg/l, pH6

increase in TOC. Research study results disagree as to the effect of soil dryness on organic carbon mobility. Jardine *et al.* (1990) indicated that the mobility of organic carbon in the form of DOC was greater during wet events. On the other hand, Borken *et al.* (1999) observed that the mobility of DOC increased after the soil was dried at different temperatures. They attributed this to modified microbial activity. The results of Noak *et al.* (2000) agree with Borken *et al.* (1999). They suggested that particle interaction due to dryness was a possible effect that enhanced the physical filtration of these particles. So in summary, both the moisture and organic content of the soil play an important role in organic carbon and copper mobility.

As illustrated in the soil analysis (Table (1)), the organic carbon content of A-horizon soil is higher than that of B-horizon soil. This organic carbon maybe the reasons for the higher copper concentration in the effluent from the A-horizon column even without drying of this soil. This argument is strengthened by the data observed in Figures (7) and (8). These two curves illustrate the mobility of TOC through dried A-horizon soil and dried B-horizon soil, respectively.

The concentration of TOC flushed out in dry A-horizon soil case is about twice that value for B-horizon. As indicated in the Figures (7) and (8), the base concentration of the flushed TOC from A-horizon is around 50mg/l where that of B-horizon is 20mg/l. The concentration of copper flushed from the A-horizon column is also more than twice the value for the B-horizon soil. As can be seen from Figure (4), whenever there was upward spike in the amount of copper eluted, this was accompanied by a spike in the TOC. These explanations agree with suggestion by Rigol *et al.* (1999) in a study of mobility of radio cesium in organic soil. They found that the soil drying changed the sorption capacity of the soil considerably. They reasoned that the increase in desorption capacity was due to structural change in the solid phase due to drying. On the other hand, Noak *et al.*

(2000) mentioned a filtration effect by the soil matrix but they claimed that dryness would increase colloidal particle interaction forming large particle size, thus increasing the filtration effect. Burcar *et al.* (1997) observed a similar effect for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$. They found that higher initial soil moisture resulted in the mobility of these two substances to greater soil depths.

Effect of soil moisture content on copper mobility:

The goal of this experiment was to investigate the effect of soil moisture content on copper mobility. Figures (9) and (10) illustrate the results of this experiment. The figures show that the water content of the soil primarily affects the early stages of the elution process. Both the 2.6% and 6.5% moisture content soils eluted similar concentration of copper and TOC. The method of drying had some impact on the elution pattern. This is clearly seen in Figure (10) where at 6.5% moisture, oven dried soil eluted more copper than the otherwise dried samples. Since the reason for these differences is not known, further studies are needed to determine the specific role of moisture content on the release of TOC from soil surface. Butkus and Grasso (1999), in their study of phosphate mobility, observed the effect of drying on copper mobility. They observed that the mobility of phosphate depends on the extent of dewatering of soil and its equilibrium pH. Also a first-flush-pattern appears clear in these experiments. Anderson *et al.* (1996) observed that the highest copper levels occur after rainfall following a long dry season. The first-flush-pattern is observed for both TOC and copper. After the first flush, the eluent concentration will be similar regardless of the initial soil water content. The reason may be that the soils become completely wet after the initial flush so the copper mobility is no longer influenced by prior moisture levels.

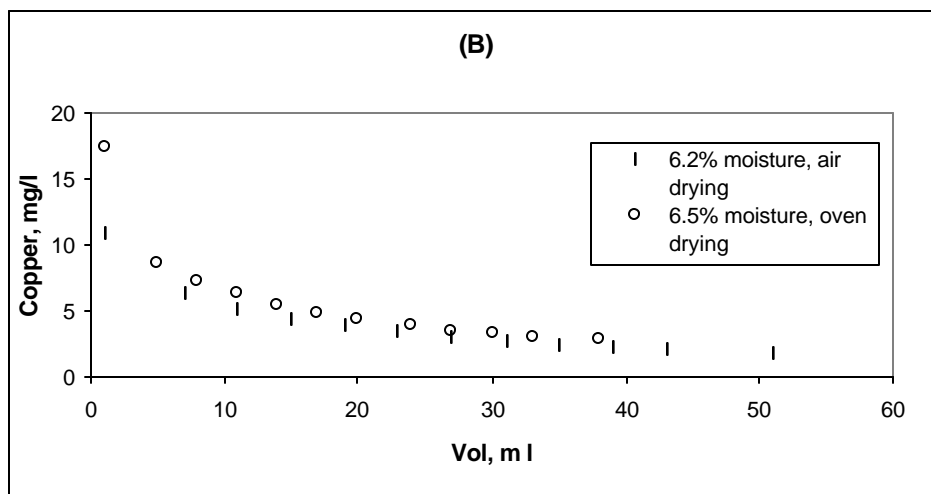
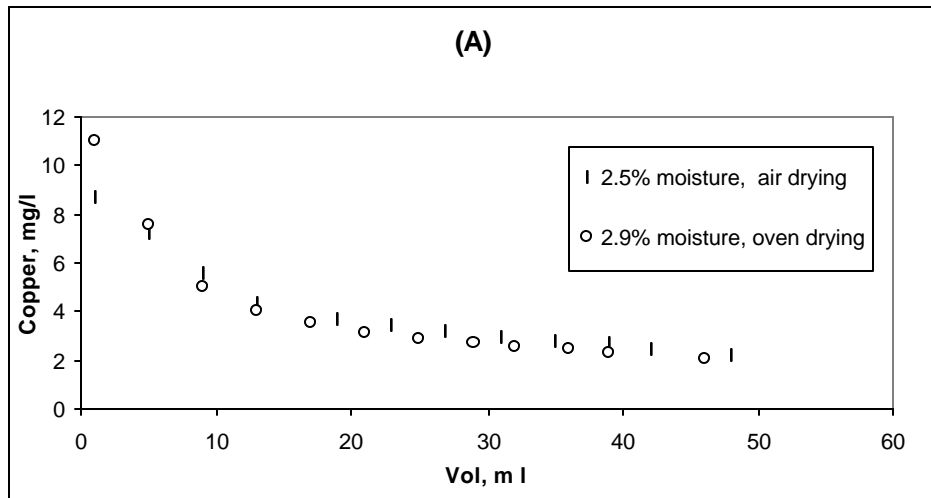


Figure (9) Effect of moisture content on copper mobility through A-horizon soil preloaded with 0.25 mg Cu/g soil dried at 55C. Figure (A) represents approximately 2.6 moisture and Figure (B) represents approximately 6.5 moisture

Plots of copper versus TOC eluted from columns having different moisture contents (Figure 10) show the relationship between moisture content, TOC and copper. The dryer soil produces both a Higher TOC concentration and copper concentration.

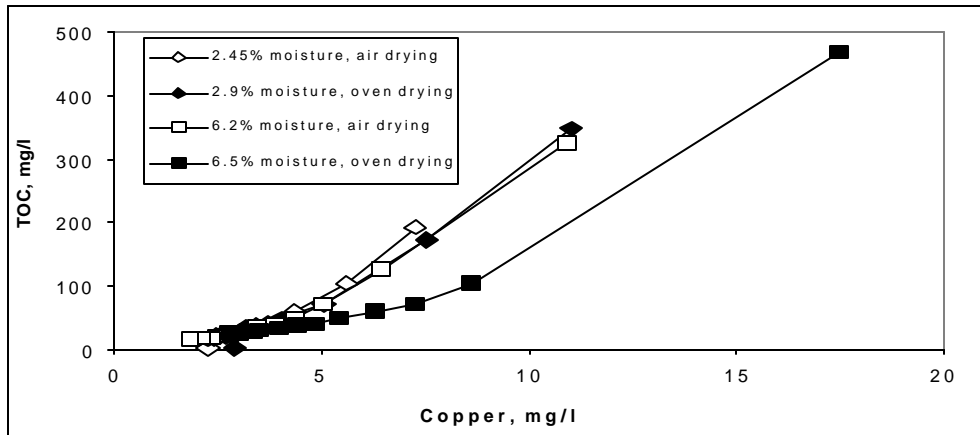


Figure (10) Effect of moisture content on copper and TOC mobility

Effect of drying temperature on copper desorption from soil:

This experiment was conducted to study the effect of drying temperature on the copper adsorption on soil. Results of this experiment are illustrated in Figure (11). Notice that, no significant effect on the adsorption capacity, q , was observed

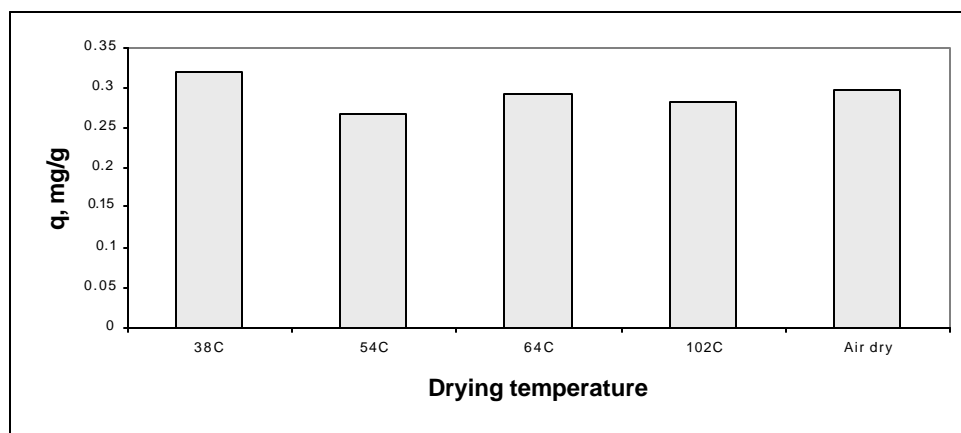


Figure (11) Effect of drying temp on copper desorption (batch process). Soil used was A-horizon preloaded with 0.25 mg Cu/g soil). Nanopure water at pH6 was used as liquid phase

due to drying temperature. These results agree with the results obtained from the experiment conducted to study the effect of method of drying (air, autoclave and oven drying). Therefore, we may conclude that the method or temperature of drying does not impact the copper sorption.

Alternate wet/dry cycles:

The purpose of this experiment was to investigate short term drying on copper mobility through soil. This was achieved by comparing the copper concentration eluted from column containing soil that was dried for 2 hours after every addition of copper solution versus a soil that was dried. The results of this experiment are depicted in Figure (12). The concentration of copper eluted after adding the first portion of copper solution was high. The second arrow indicates

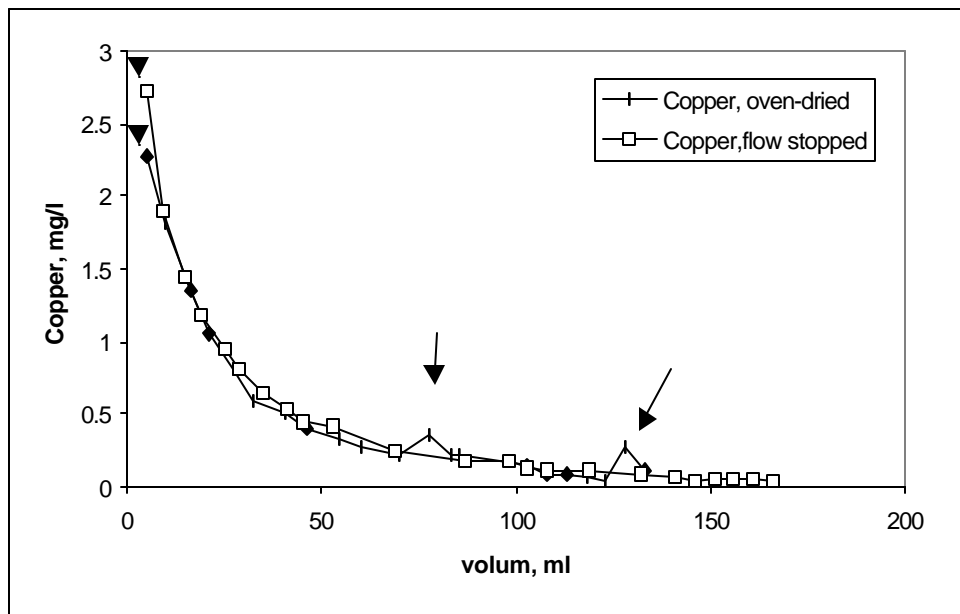


Figure (12) Effect of drying on TOC mobility. A-horizon soil preloaded with 0.25 mg/g copper nanopure water as eluant. For the oven dried column, the column was placed in oven at 70C for 2 hours, then eluant flow continued. For flow stopped column, the eluant flow as ceased but the soil did not dry. The arrows ▼ indicate thepoint in the experiment when either the flow was stopped or the column was dried.

where drying occurred and a second portion of the copper solution was added. The third arrow indicates where drying the column for the second time occurred and adding the third portion of the copper solution. The flow-stopped column did not show an increase in copper concentration after the flow was stopped but the column remained wet. The only difference between the two columns leading to these two curves was the drying cycle. Gallagher *et al.* (2001) demonstrated that application of rain to dried soil, to which copper based pesticides had been applied resulted in continued desorption of copper from the soil. Dietrich *et al.* (2001) demonstrated that dissolved copper continued to be present in runoff from copper-treated agricultural fields for months after the copper application and growing season ended. The data in Figure (12) suggests that even short periods of drying can increase copper desorption but that extended dryness will result in the discharge of larger amounts of TOC and sorbed copper.

Conclusion:

Copper mobility through soil is mainly associated with TOC mobility due to several factors. Of these, the water content of the soil or drying pattern is most important. Drying the soil will increase the copper and TOC mobility possibly due to change in the structure of the organic substances present in the soil. Therefore, peaks of copper after rain events should be expected, especially after an extended dry period. The drying cycle or the drying temperature does not affect copper mobility significantly. For vertical transport, the mobility of copper through A—horizon soil is greater than that through B-horizon soil. Part of the copper escaping the A-horizon soil, may be sorbed on B-horizon soil. Other factors such as channeling and horizontal mobility should be taken into account when assessing the overall copper mobility.

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CHAPTER 3: Factors Affecting Copper Sorption and Mobility Through A and B Horizon Soils from the Eastern Shore of Virginia

Abstract:

In this research the copper mobility through the A- and B-horizon of Bojac sandy loam from the Eastern Shore of Virginia was studied. This study included both batch and column processes. The effects of pH, TOC and humic substances were investigated. The mobility of copper was found to be higher through A-horizon soil. The pH was found to have a considerable effect on the mobility of copper and TOC. The highest mobility of copper was achieved at pH 6.24 and its mobility through both soil horizons was associated with the mobility of TOC. A study of the humic substances indicated that fulvic acids had 4 times higher adsorption capacity for copper than humic acids. The association between fulvic acids and copper, coupled with the mobility of TOC and fulvic acids in the soil, accounted for transport of copper through soil columns.

Introduction:

Agricultural practices constitute important non-point sources of heavy metals in soil, water and air. The main sources of this type of pollution are impurities in fertilizers, pesticides, refuse derived compost, wood preservatives and corrosion of metal objects like metal roofs and fences (Alloway, 1995). Copper applied at 3.8 kg Cu/ha to plasticulture tomato fields to protect against plant disease, remained in the field sorbed to the soil

following rainfall. Only 1% of the copper that was applied left the field. Of this 1%, 0.82% was in the runoff at concentrations of approximately 200 $\mu\text{g/l}$ total copper and 0.18% was in the ground water at a concentration of about 50 $\mu\text{g/l}$ dissolved copper (Gallagher *et al.*, 2001). A comparison of aqueous copper concentrations in agriculture and non-agriculture watersheds showed that the aqueous copper concentration was higher (up to 126 $\mu\text{g/l}$ dissolved copper) where agriculture was practiced (Dietrich *et al.* 2001). Heavy metal contamination of two Chesapeake Bay tributaries on the Eastern Shore of Maryland came from both points (sewage treatment plant) and non-point (agriculture runoff) sources (Gupta and Karuppiah, 1996). Copper is added to the diet of some growing animals at levels up to 250 ppm to increase their growth rate and promote feed conversion efficiency. Manure produced by these animals contains high concentrations of copper. The application of this manure to agriculture soils produces an increase in soil copper concentration (Mullins *et al.*, 1982).

Mobility of copper through soil:

The mobility of most heavy metals in the soil and subsoil depends on the physico-chemical properties of the solid and liquid phases (Fic and Schroter, 1989). Trace metals can be found in particulate, colloidal and truly dissolved phases. The fate and transport of metals in the environment depends on these phases and the interaction between them. Soil parameters, such as pH, organic carbon content, iron and manganese oxide content and total metal content affect the distribution of copper and cadmium between different soil fractions (Wilhelmy *et al.*, 1996).

Lazerte *et al.* (1989) reported two patterns of trace metal transport. One was related to the metal affinity for dissolved organic carbon and the

other was due to the metals solubility in dilute acid and mineral soils. Kuo and Parkin (1996) suggested that soluble microbial products have a role in heavy metal mobility through formation of metal complexes. Colloidal dissolved organic carbon (DOC) may play the same role. These organics are thought to transport the contaminants between particulate and dissolved phase (Huang *et al.*, 1998). Soil contaminants can travel for long distances through the soil due to the effect of colloidal substances. The mobility of natural colloids was proved by the presence of humic substances in deep aquifer (Thompson and Scharf, 1994). Borg and Johansson (1989) and Gallagher *et al.* (2001) reported that copper is largely retained in the soil. They reported that the mobility increased with the decrease of pH. They suggested that the mobility of copper was associated with the transport of organic material since the copper was highly adsorbed to organic matter rather than soil solids. Grout *et al.* (1999) reported silica as the main component of colloids during period of dry weather flow and at the maximum of the storm water flow. Carbon became the dominant component at the beginning and declining stages of the storm events.

The mobility of heavy metals, including copper, may be enhanced by the formation of inorganic complexes. Chloride for example can form complexes with many cations such as Cd (II), Hg (II), Pb (II), Zn (II) and Cu (II). This complex formation mechanism is important, especially in saline soils. Salting of roads for deicing purposes is an important source for chloride ions (Doner, 1978). The mobility of copper in the soil may also be enhanced by artificial organic compounds that serve as complexing agents for copper. An example of one of these compounds is nitriloacetic acid, which is used as a substitute of some detergents. Howell and Gawthorne

(1987) pointed out the important role that organic matter plays in the retention and behavior of copper. They reported that both humic and fulvic acids are ligands for binding of copper (II) and that the fulvic acids are the more soluble. Also simple aliphatic acids, amino acids and aromatic acids act as chelating agents for copper (II). The organic complexes of copper, according to their survey, accounted for more than 90% of the copper solution in the surface horizon.

Igloria *et al.* (1997) mentioned the possibility of forming complexes between heavy metals and organic matter colloids in solutions, as well as those attached to soil surfaces. This complex formation process increases the concentration of metals in the mobile phase, which allows their transport over long distances. Sposito (1986), on the other hand, claimed that the effect of these colloids might be the retardation of the transport of metals.

Brown *et al.* (1997) studied the effect of alkalinity on the metal mobility and found that the mobility of most metals increases with an increase in pH. The authors reasoned that these metals formed mobile fulvic acid metal complexes. When the soil pH increased the solubility of fulvic acids increased, thus promoting the formation of more fulvic acid complexes.

Objectives:

The goal of this research was to study copper mobility through different soil horizons obtained from the Eastern Shore of Virginia. The Bojac sandy loams in this region receive heavy doses of copper from pesticide and nutrients application to agricultural crops. Some of the copper is found in the ground water and the mechanisms for the release from and through the soil is not known. The goal of this study was to determine the mechanisms accounting for the movement of copper through this soil.

Materials and Methods

Soil used and its properties:

The soil used for this study was undisturbed Bojac sandy loam. It was obtained from either from the town of Exmore, Virginia or from Parksley, Virginia. The A-horizon soil was obtained from depth ranging from 0 to 27 inches. The A-horizon soil had a strong brown color, a sandy loam or loam texture and moderately rapid permeability. The soil excavated to a suitable depth to get the B-horizon soil samples. The B-horizon at this depth was obviously color differentiated from the A-horizon. The color of B-horizon soil was light brown compared with dark brown for the A-horizon soil. No special treatment was applied for this soil before use except for drying. The soil was sieved before adsorption processes. Only the fraction < 2 mm was used. The soil was not disturbed or tilled before.

Soil analysis:

The soil used in this research was analyzed for organic matter (OM), pH, and some elements (Ca, Mg, P, K, Zn, Mn and Fe) in the Soil Testing & Plant Analysis Laboratory, Virginia Polytechnic Institute & State University. The result of this analysis is presented in Table (2).

It is clear from the analysis the higher organic carbon content (OM) is in the A-horizon soil compared with the B-horizon soil. This may be the reason of the higher copper mobility through the A-horizon soil as will be illustrated in the following sections.

Table (1) Chemical characteristics of the soils used

Sample	pH	%OM	Chemical Concentration (ppm)						
			P	K	Ca	Mg	Zn	Mn	Fe
Sand	5.6	0.01	0.94	2.78	52.3	10.02	0.21	0.64	1.83
B-horizon	7.4	1.09	4.36	23	1335	40.48	1.08	21.89	6.32
A-horizon	6.7	3.29	10.3	57.3	1735	96.24	3.72	38.05	7.51

Chemicals and apparatus:

All chemicals and reagents used for this study were analytical grade or trace metal grade. Nanopure® water was used for all reagent preparation and subsequent dilution unless otherwise is mentioned. The copper solutions were prepared by diluting copper reference solution (1 mg/ml) obtained from Fisher using Nanopure® water. The containers, glassware, funnels and pipettes used in the analysis were soaked in 10% trace metal grade nitric acid for at least 8 hours, rinsed with distilled water three times followed by rinsing with Nanopure® water three times. The glassware (except for volumetric flasks) was oven dried at 102°C; plasticware and volumetric glassware were air-dried.

The containers used for batch adsorption processes were tested for copper adsorption by shaking copper solution in 8 glass conical flasks and 6 plastic bottles for 24 hours. The clear rigid PVC plastic columns used for continuous study were purchased from United States Plastic Corp. They were not tested for copper adsorption but the information obtained from the

manufacturer indicated that their material did not adsorb copper and it is not affected by the acidic solution.

Copper sorption by filtration paper:

During copper filtration studies, there was concern that copper was being retained on the filter paper. Therefore, copper losses during filtration were quantified for a variety of filter types. Three samples of copper solution of 400 $\mu\text{g/l}$ Cu^{2+} and pH 6 were passed through 0.45 μm membrane filters from different companies and through G6 filters. The initial and final concentrations of copper were measured. A minute amount of copper loss was noticed for the 0.45 μm Gelman membrane filters whereas very high loss (65%) was detected in the case of G6 filters. Variable copper adsorption was noticed for other filters. For this reason Gelman 0.45 μm membrane filters were used for all filtration processes.

Copper analysis:

The dissolved copper analysis was performed according to Standard Methods of for the Examination of Water and Wastewater, number 3030 B (APHA 1995). The device used was a Perkin Elmer 703 Atomic Absorption Spectrophotometer (Flame Atomic absorption), with a range of 100 to 5000 $\mu\text{g/l}$. The wavelength used was 324.8nm and slit setting was adjusted to 0.7nm. For copper concentration 100 $\mu\text{g/l}$ and lower, a Perkin Elmer Zeeman 5100 HGA Graphite furnace atomic absorption spectrophotometer was used. The samples were diluted with Nanopure® water when necessary. All the samples were acidified with a 1:1 HNO_3 solution to below pH 2 and stored at approximately 4°C.

Batch adsorption processes:

Two methods were used to perform the batch adsorption studies. In the first method, the weight of the adsorbent (air dried Bojac sandy loam soil) was changed and the concentration of the adsorbate (copper solution) was kept constant. In all the experiments the pH of the copper solution was adjusted to 6 using HNO_3 and NaOH . This was done by preparing a stock solution of the required concentration, adjusting its pH and then placing 100ml aliquots of this solution in acid-washed conical flasks. The stock solution was freshly prepared for each adsorption experiment. Different initial concentrations (23.6 and 247 $\mu\text{g/l}$) of the copper solution were used as the adsorbate. Each experiment included 10 different soil weights from 0.1 to 3g (weighed to the fourth decimal point). A volume of 100 ml of copper solutions was added to the flasks and then shaken on a reciprocal shaker for 24 hours at 20°C temperature, which was sufficient to achieve equilibrium (Biehn, 1999). To measure the final copper concentration of the solutions, approximately 10ml were taken from each flask, filtered through $0.45 \mu\text{m}$ membrane filters and analyzed for copper using an atomic absorption spectrophotometer. The rest of the solutions were allowed to settle for 2-5 days and samples were taken of the clear liquid and copper was measured.

The second batch test method involved the change of concentration of the copper solution with the weight of soil kept constant. The range of copper concentration of this set was from $47\mu\text{g/l}$ to $416\mu\text{g/l}$. The weight of soil was one gram (to the fourth decimal point). A volume of 100 ml was used and the pH values were adjusted to 6 using NaOH and HNO_3 . After shaking 24 hours on a rotary shaker at 20°C , a sample was taken, filtered through

0.45 μ m membrane filter, and analyzed for copper. The rest of the solution in each flask was left to settle for 2 days and then copper was measured in the clear liquid of each flask.

Soil organic matter:

The soil organic substances (fulvic acids humic acids and humin) were extracted by the method adopted from Page *et al.* (1982). This method involved the extraction of different organic materials according to their solubility in acids and alkalis.

The total organic carbon (TOC) was measured on acidified liquid samples that were purged with oxygen for five minutes to remove the inorganic carbon. TOC was then measured by the UV assisted persulfate-oxidation method with infrared detection of the evolved carbon dioxide. The instrument used was Dorham Carbon Analyzer DC-80.

Continuous Process:

Continuous flow column experiments were conducted to simulate the field conditions. Two columns were filled with Bojac loam soil (A horizon) and then loaded with copper by adding a copper nitrate solution at pH 6. Each column had three sections. The lower section was filled with graded gravel to prevent the soil from being washed out. The height of this section was about 6cm. The second section contained the soil that was air dried and sieved to be less than 2mm. A soil mass of 250g was used. After adding each fraction, the soil was pressed using a wooden rod covered with plastic sheet to avoid the contamination of the soil. This pressing process was continued until no further consolidation was observed. According to Newman *et al.* (1993), columns would have porosity of 30% (s.d. \pm 6%) if packed with this technique.

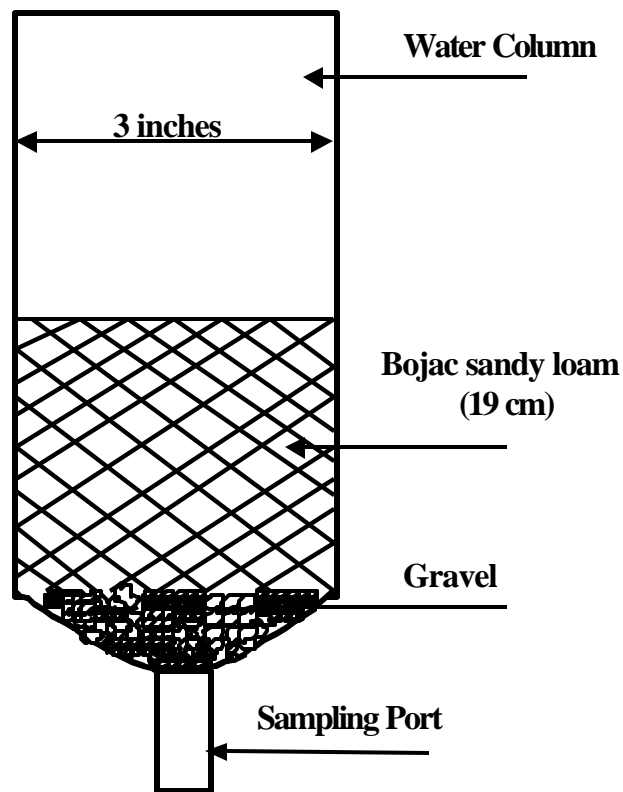


Figure (1) Schematic Diagram of the Soil Column

The height of this section was about 19cm. The third section served as a reservoir for the copper solution. No metal parts were used in the column to avoid any possible contamination. A schematic diagram of the used column is illustrated in Figure (4) The design of the column was adopted from the work of Igloria *et al.* (1997).

The column was fed with one volume of pH 4 copper solution, i.e. instantaneous pulse input. Effluent samples were collected from the bottom of the column at different time intervals; sampling continued until no significant copper was measured in the effluent. A freshly packed column was used for each run. The samples were analyzed for copper and TOC.

Effect of pH change on mobility of copper through B-horizon:

To accelerate the rate of copper mobility through the B-horizon soils, clean sand was mixed with the soil. Sand was first treated by washing several times with water. It was then placed in a muffle furnace for four hours to remove any organic substances. The sand was mixed with B-horizon soil in a ratio of 8:2 (soil:sand). Three columns were packed with 300g each of this mixture. The columns were tapped several times after addition of each portion to achieve consolidation. Three copper solutions (1200ml each) having the same copper concentration ($400\mu\text{g/l}$) and different pHs (4.24, 6.25, 7.25) were added to the three columns. Effluent samples were collected from the bottom of each column and analyzed for copper and TOC.

Mobility of copper through different soil layers:

The goal of this experiment was to study the mobility of copper through the combined A and B horizons and compare these to mobility through the separate A and B layers. Three columns were used for this experiment. The first one was packed with 300g of a mixture of A-horizon soil and sand (8:2 ratio, respectively). The second column was packed with 300g of mixture of B-horizon soil and sand (8:2). The third column consisted of both the A and B layers. The bottom layer was 150g of mixture of B-horizon soil and sand (8:2) and the upper layer was 150g of a mixture of A-horizon soil and sand (8:2). A volume of 300ml of copper solution ($400\mu\text{g/l}$ and pH6) was added to each column as pulse input. Effluent samples were collected from the bottom of each column and analyzed for copper and TOC.

Effect of ionic strength on copper mobility:

Both A- and B-horizon soils used for this experiment were air-dried, crushed and sieved through a 2mm sieve before usage. A copper nitrate solution was prepared with a concentration of 400 μ g/l and its pH was adjusted to 6. One hundred ml aliquots of this solution were placed in acid washed bottles. Sodium nitrate (solid form) was added to the bottles to reach sodium nitrate concentration ranging from 0.001 to 0.025 mole/l. The conductance of each solution was measured using YSI Model 32 Conductance Meter by Scientific Division, Yellow Springs Instrument Co., Inc. Approximately the same weight (1.200g) of either A- or B- horizon soil were added to each bottle. The bottles were shaken for 24 hours at 20°C. The final pH and the final conductance of each solution were measured. The solutions were filtered through 0.45 μ m membrane filter acidified to pH <2 with HNO₃ and the concentration of copper in the filtrate was measured.

Effect of chloride ions on copper mobility:

The same technique applied for studying the ionic strength effect was used to study the effect of chloride ions on copper mobility. A 400 μ g/l, pH 6 copper solution was also used. Similar weights of the A- and B-horizons were added to the copper solution (1.2g). The concentration range (0.001-0.025 mol/l) of sodium chloride salt that was applied to the copper solutions was similar to the concentrations of sodium nitrate that were used in the ionic strength experiment. That allowed a further comparison between the effect of ionic strength and chloride ions on the copper removal on both soil horizons.

Size of organic substances binding copper:

To further investigate the role of colloidal particles, gel chromatography was utilized to separate the different fractions contained in

the effluent samples from the soil/copper columns. About 1.5ml of the effluent samples from the soil columns were placed on a 25 cm x 1.2 cm (i.d.) column containing Sephadex (G-25). The samples were eluted with Nanopure® water until the copper concentration in the Sephadex column effluent was negligible. Both copper and TOC concentrations were measured for the eluted samples. The molecular weight range of the organic carbon was characterized by eluting 1.5 ml of Bovin Serum Albumin through the Sephadex G-25 column under the same conditions.

Gel chromatography of humic substances:

The column used for conducting this experiments was a volumetric burette fitted with a piece of glass wool at the bottom to prevent the Sephadex G-25 gel from escaping the column. The dimensions of this column were 25 cm x 1.2 cm i.d. The exclusion limit of such column is about 5000 Daltons (Kuiters and Mulders, 1989). Thirteen ml of aqueous gel solution (Sephadex G-25) was placed in the column and was allowed to settle until the two phases were separated and no noticeable decrease of the gel height was noticed. A 1:1 mixture of humic substances (humic or fulvic):copper nitrate was prepared and allowed to equilibrate for 24 hours. 2 ml of this mixture was placed on the gel surface using micropipette and Nanopure® water was added as eluent. The flow rate was approximately 0.5 ml/min. About 1.5 ml aliquots were collected from the bottom of the column using automatic collector. The collection of samples was continued until no further copper was detected in the effluent.

Kinetics of humics copper interaction:

The concentration of copper during reaction with humic substances was measured as free copper using copper selective electrode (Orion® cupric

electrode, Orion® D/junct. reference electrode and Beckman Φ 12 pH/ISE). The pH/ISE meter was calibrated with three copper nitrate standard solutions (0.1, 0.5 and 0.9 mg/l) before each set of measurements. Sodium nitrate solution (4 Molar) was added to the standard solution to achieve a concentration of 2mM in each standard. The role of sodium nitrate was to provide the electrolyte necessary for measurement. The pH of the standards was adjusted at six using NaOH and HNO₃. Fifty ml of copper nitrate solution of pH 6 and initial concentration of 0.9 mg/l were placed in acid-washed polyethylene bottles. 0.8 ml of the soil-extracted humic acids (613 mg/l) was added to the bottle to achieve humic acids concentration of 10 mg/l. The free copper concentration was measured over time using the copper selective electrode until equilibrium was reached (indicated by no further change of copper concentration). The free copper concentration was measured as mv and converted to mg/l using the calibration curve. The copper concentration was measured after 24 hours to be sure that equilibrium was reached. The same procedure was applied for measurement of copper-fulvic acids kinetics but the fulvic acids was added to reach concentration of 10 mg/l as TOC.

Adsorption isotherms for copper on humic substances:

A stock solution of copper nitrate was prepared and its pH was adjusted to 6. The initial concentration of this solution was 0.8 mg/l and this concentration was checked by the copper selective electrode. 50 ml aliquots of this solution were placed in acid-washed polyethylene bottles. Different volumes of fulvic acids were added to each bottle to achieve a concentration range from 1.5 to 19 mg/l as TOC. The bottles were capped and shaken for 24 hours at room temperature. The final copper concentration for each bottle

was measured using the copper selective electrode. The amount of copper adsorbed or reacted was calculated as the difference between the initial and final copper concentration. The same technique was applied for humic acids but its concentration was prepared as weight of humic acids per volume of solution. The experiment was performed in duplicate.

Results and Discussion

Batch adsorption:

The purpose of this experiment was to define the adsorption capacity of A-horizon soil for copper and attempt to evaluate the mechanism for this sorption. Some of batch adsorption results for A-horizon soil are shown in Figures (2) and (3). Based on literature results and the results of these experiments, the suggested mechanism is the attachment of copper ions to the organic substances contained in the soil. The basis of this proposed mechanism is explained below.

The first experimental approach for obtaining adsorption isotherms was to place a copper solution into several flasks at one concentration and vary the amount of soil added. Because of desorption of TOC from the soil surface, this resulted in an increase in the solution TOC as the soil mass increased. This was clearly observed by an increase in the color of the solution as the soil mass increased. When the soil mass was 3.05g , the solution TOC was 5.41 mg/l ; when the soil mass was 0.56 g , the TOC was 1.82 mg/l. The increased solution TOC resulted in a decrease in the amount of copper sorbed as the soil mass increased because most of the copper was associated with TOC in solution. This indicated that the copper was strongly associated with solution TOC and not the soil surface. Further, when these

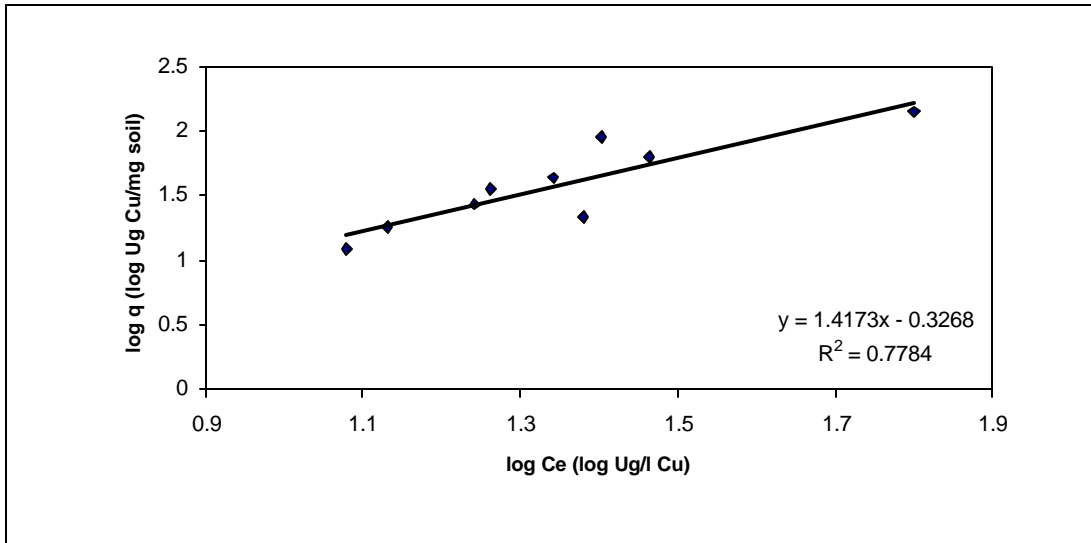


Figure (2) Freundlich Adsorption Isotherm on A-horizon soil (change of soil weight). The initial copper concentration was 247 μg/l and its pH was 6. No filtration was applied. The soil solution was allowed to settle for ~48 hours to separate the soil.

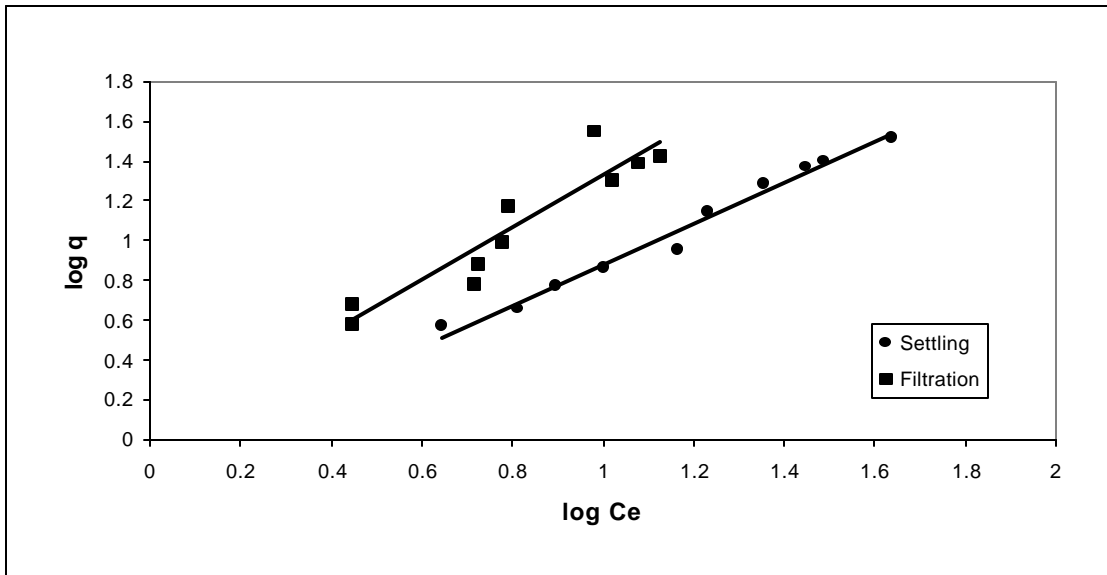


Figure (3) Freundlich adsorption isotherm (change of copper conc) at pH 6. The solution was either filtered through 0.45 μm filters or allowed to settle prior to measurement of copper.

data were plotted in the form of a Freundlich isotherm, the slope was negative rather than positive. The negative slope, indicating less adsorption as more soil was added, was evident even when the solution was filtered through a $0.45\mu\text{m}$ filter. The TOC associated copper could be removed from solution only after 48 hours of settling and even then, the removal of TOC associated copper was incomplete. An isotherm for copper is presented in Figure (2), where the soil mass was varied and the copper concentration held constant.

An alternative approach used in this study to obtaining an isotherm was to vary the copper concentration and hold the soil mass and TOC constant. Data for two such experiments are shown in Figure (3). In one case, the solution was filtered through a $0.45\mu\text{m}$ filter and in the other, the solution was allowed to settle for 48 hours before measuring the copper. It can be seen from these data that the greatest apparent sorption was for the solution filtered using the $0.45\mu\text{m}$ filter. A comparison to the isotherm data in Figure (2) indicates that the slope of the isotherm is different from the slope obtained for a constant soil mass.

The isotherm data showed that much of the copper is associated with soil organic matter and some of the soil organic matter that binds copper is easily desorbed from the soil. This desorbable organic matter contributes to the mobility of copper and might even be the major mechanism by which sorbed copper can move through soil. On the other hand, the ability to filter or settle the TOC-associated copper also suggests that as this material passes through soil, it may be removed. Both the mobilization of TOC-associated copper and the removal by filtration is expected to depend on the type of soil and composition of the TOC. The movement of TOC-associated

copper through soils from the Eastern Shore is the main focus of this research and will be dealt with in subsequent sections.

Column Studies:

The purpose of this portion of the study was to trace the mobility of copper through soil and to determine its association with organic substances. As illustrated in Figures (4) to (8) the copper that was eluted was associated with TOC. This association indicates the interaction of copper with organic substances present in soil. The copper solution added to these duplicate columns had the same concentration and pH (400 μ g/l and 6, respectively). Regression analysis for the data from the two columns indicated very high correlation between eluted copper and TOC ($p < 0.001$) for both columns. Borg and Johnson (1989) observed the same effect of organic material on the transport of copper. They suggested the adsorption of copper on these materials as a mechanism of interaction. Other researchers specified fulvic acids as the main organic substances responsible for this mobility (Lazerte *et al.* 1989; Howell and Gawthorne, 1987). On the other hand, others have a different opinion. McCarthy and Zachara (1989) concluded that natural organic matter did not facilitate the mobility of copper. Igloria *et al.* (1997) claimed that organic matter decreased the mobility of some heavy metals including copper. They attributed that to a high affinity of the organic substances to the soil, and in turn, the metals to the organic substances. The reason for the differences could be the different soil types and organic loadings that were used in these studies. This suggests that different soil properties and different organic substance structures and properties can give widely different metal mobilities. Data for the gel chromatography is shown in Figure (6). All the samples taken from the columns indicated the interaction

between copper and TOC. The peaks were broad, indicating high dispersion of molecular weight of the compounds eluted from the columns.

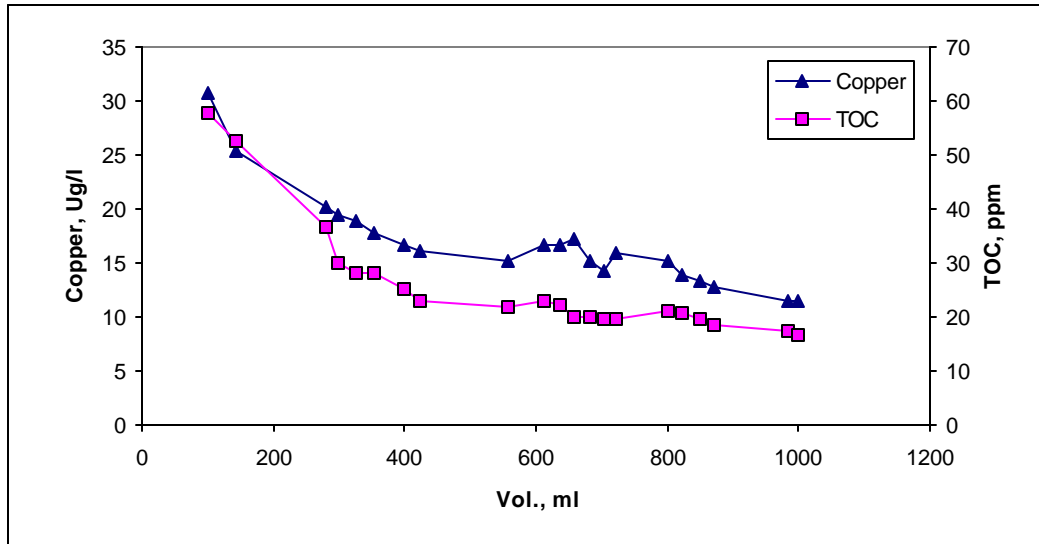


Figure (4) Column Study of copper mobility. The copper was applied as a pulse input with a conc. of 400 µg/l and pH 6 to A-horizon soil. Replicate (1).

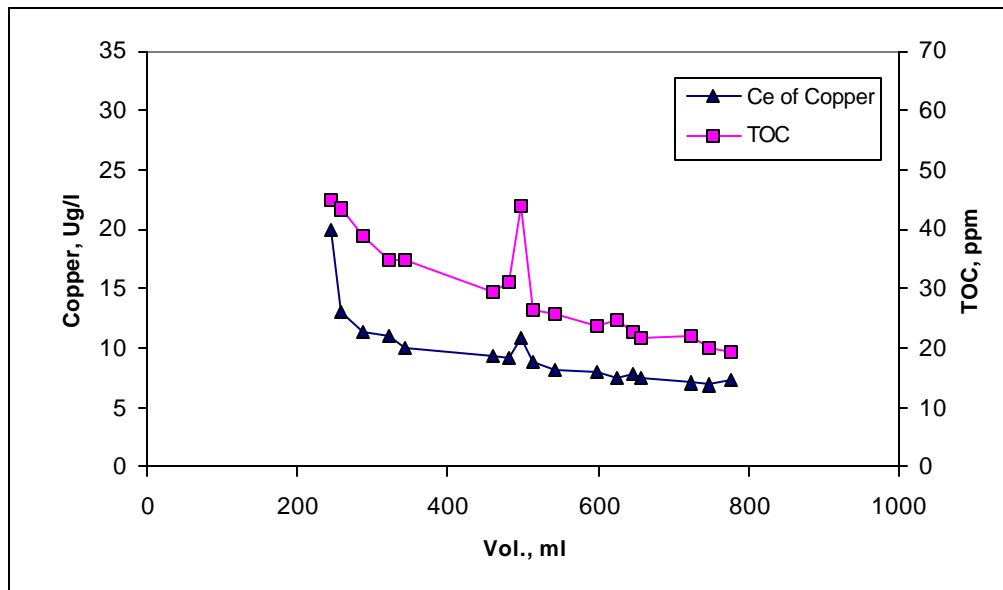


Figure (5) Column Study of copper mobility. The copper was applied as a pulse input with a conc. of 400 µg/l and pH 6 to A-horizon soil. Replicate (2).

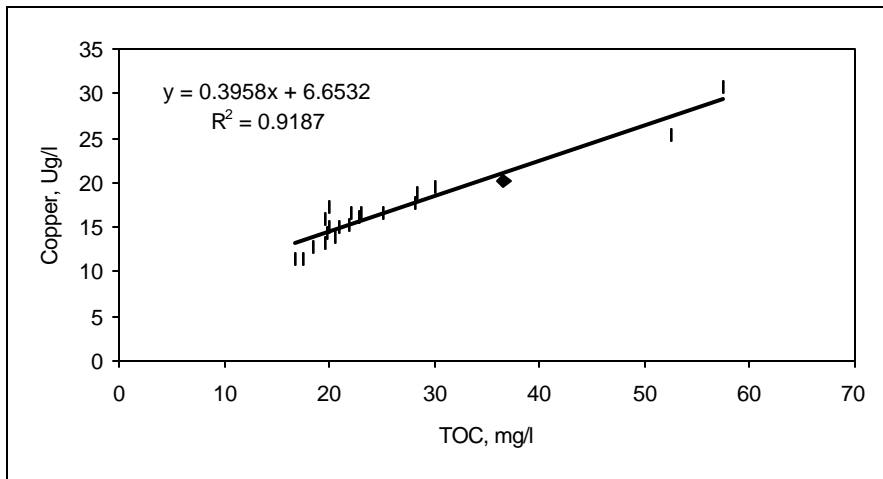


Figure (6) Relation between copper and TOC during copper mobility through A-horizon soil. Initial copper concentration was 400µg/l and its pH was 6. Replicate 1

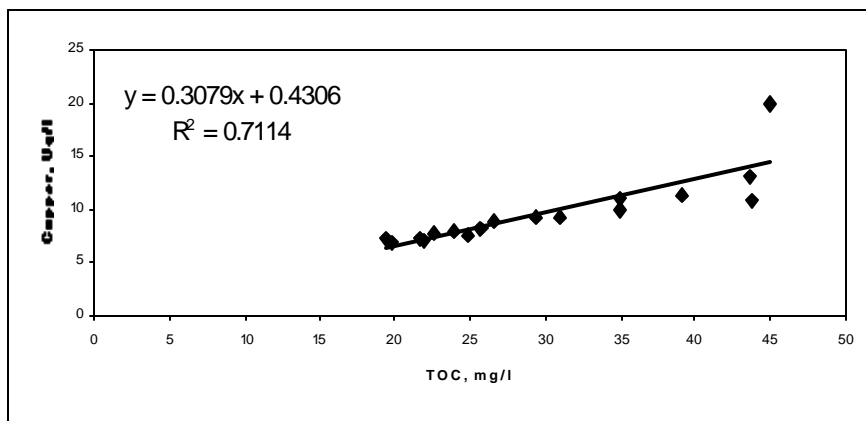


Figure (7) Relation between copper and TOC during copper mobility through A-horizon soil. Initial copper concentration was 400µg/l at pH 6, Replicate 2.

The copper and organic substances were eluted following a discharge of 7-9 ml, similar to the BSA marker used to identify the molecular size range as illustrated in Figure (8). Analyzing the data using Minitab indicated the high correlation between copper and TOC ($p < 0.001$ and <0.001). The exclusion limit of this column (5000 daltons) lies in the molecular weight range of both fulvic acids and humic acids. The results of the kinetics and adsorption isotherms of the humic substances suggest fulvic acids as the main substance responsible for the copper mobility. This phenomenon was further studied and will be addressed in the next section of the paper.

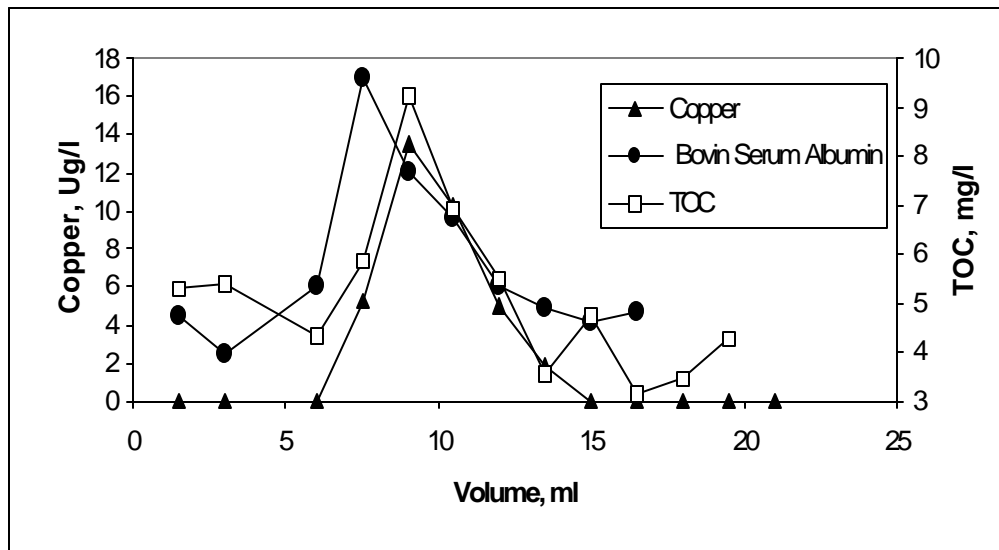


Figure (8) Gel Chromatography of copper compounds from soil column. Samples were obtained from the column depicted by the data in Figure (5)

Kinetics of humics-copper interaction:

As a further investigation of the role of humic substances on the copper binding and mobility, several kinetics experiments were conducted. As mentioned in the procedures section, the humic acids used were extracted from the A-horizon soil. The results of copper-humics interaction are

illustrated in Figure (9). The kinetics of fulvic acids reaction with copper indicates a fast rate with approximately 60% of the copper bound within the first 5 minutes. On the other hand, little change in copper concentration in the humic acids solution was observed even after 24 hours. Kramer and Duinker

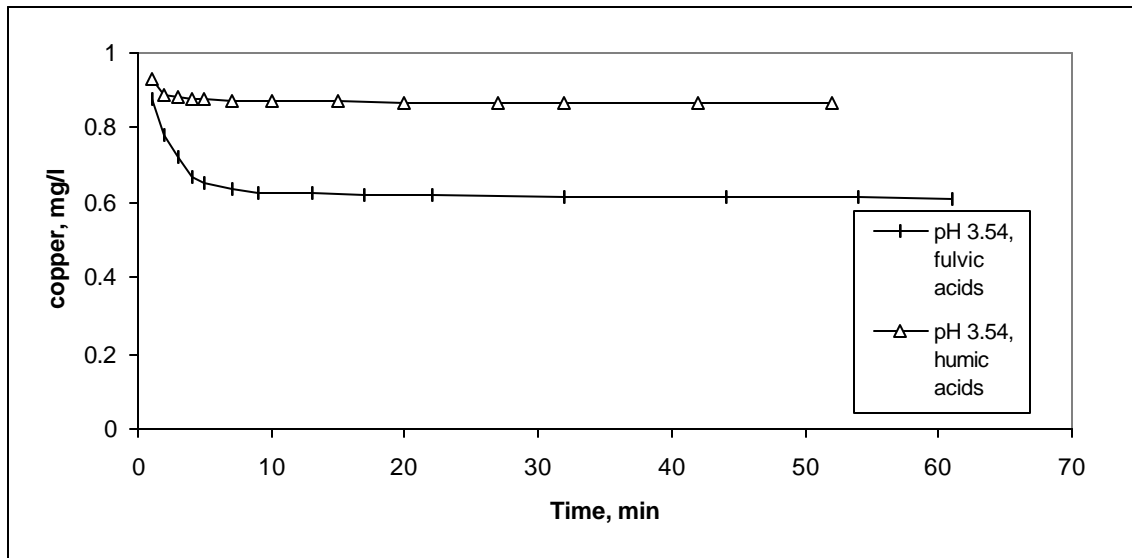


Figure (9) Kinetics of Humic substances-Copper Interaction at pH 3.54. Initial copper concentration was 0.9mg/l. Initial humic and fulvic acids concentration was 10 mg/l as TOC

(1980) observed the same results with humic and fulvic acids extracted from intertidal sediments. The fulvic acids fraction of their extract showed fast sorption whereas humic acids showed little if any sorption within the 3 hour measurement time. El-Sayed *et al.* (1991), on the other hand, found that the copper in humic acids was higher than that of fulvic acids extracted from the bottom sediments of Lake Edfu, Egypt. However, a study that was performed in another Egyptian Estuary (Mahakam Estuary) where the copper associated with fulvic acids was higher than that associated with humic acids. These differences may be due to several factors including differences in the chemical makeup or functional groups associated with these organics,

modification during transportation through different mediums and post depositional alterations.

Table (2) Equilibrium concentration of copper when reacting with different humic substances at different pHs

pH	Copper concentration, mg/l	
	3.54	6
fulvic acids	0.6	0.6
humic acids	0.85	.82

Adsorption isotherms of copper on organic matter:

The results of the adsorption isotherms, illustrated by Figure (10) agree with that of the kinetics experiments. The humic acids had very low adsorption (data not shown), if any, whereas the fulvic acids had a high adsorption capacity. Stevenson and Chen (1991) found that complexes formed between humic acids and copper were stronger than those formed between fulvic acids and copper. That means if the copper-humic complexes

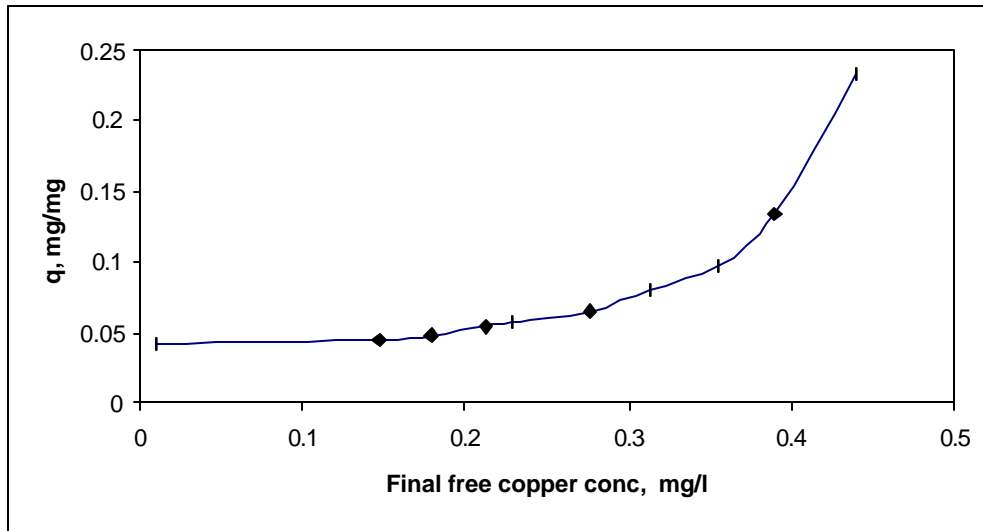


Figure (10) Adsorption Isotherm of Copper on Soil Fulvic acids. Initial copper concentration was 0.8mg/l and its pH was 6. The fulvic acids concentration ranged from 1.5 to 19mg/l.

are to be formed, then the copper will be less mobile. The results of this research indicated that fulvic acid was the possible chelating agent or adsorbing site of copper and that might describe the high mobility of copper.

Effect of conductivity on copper adsorption:

The conductivity change achieved by changing the concentration of sodium nitrate did not have a significant effect on the adsorption capacity of soil towards copper. The concentration range used was 100-2000 mg/l NaNO_3 corresponding to conductance in the range of 0.15-2.35 mmoh. The same result was noticed for both A- and B-horizon soil. The change in adsorption capacity due to change of conductance was negligible. A very slight increase in conductance was noticed after the equilibrium time for both soil horizons. Another observation was the increase of the pH of the solution from 6 to 8 in case of A-horizon and from 6 to 7.4 in case of B-horizon. This increase in pH was noticed in other experiments including column and batch studies. This increase of pH may be attributed to leaching of alkaline substances from the soil.

Effect of chloride ions on copper adsorption on both A- and B-horizon soils:

The chloride ion concentration did not have a major effect on the copper adsorption on either A- or B-horizon soils. Very slight difference in adsorption capacity of copper on these two horizons was noticed under the effect of chloride (the difference was in the range of $0.25\mu\text{g/g}$). That suggests that there is a minor effect of chloride ions on this type of soils and over the concentration range of 100 to 2000mg/l NaCl . These complexes would stay in the soluble form and will not adsorb on the soil surface, which may explain why the adsorption capacity did not increase with the increase of chloride ions concentration.

Effect of pH on copper mobility through B-horizon soil:

Three columns were run to study the effect of different pH levels on copper mobility through B-horizon soil. The results of this experiment are indicated in Figures (11) and (12). It is clear from the figures that changing the pH of the applied solution has a significant effect on the mobility of both copper and TOC. The lowest copper and TOC mobility was achieved at pH 4.24 whereas the highest mobility of copper was achieved at pH 6.24. These results agree well with that obtained for the A-horizon soil. The highest copper mobility is not in complete agreement with the highest TOC mobility. As seen from Figure (12), the highest TOC mobility was achieved at pH 7.25. Yet, the TOC and copper mobility at this particular pH (7.25) is clear to be in very good agreement. In general, the change pH has an effect on both TOC and copper mobility. The higher the pH, the higher is the mobility of copper and TOC. The effect of pH on this process is sometimes called variable charge effect. This effect of pH occurs on many components of the soil such as organic matter, oxides, hydroxides, oxyhydroxides and edges of phyllosilicates (Zelazny *et al.*, 1996). As the pH increases, deprotonation of the surface takes place and OH ions may cover the soil surface, which may result in the soil surface being negatively charged. The part of the organic substances (TOC) carrying a similar charge would be repelled from the soil surface, thus increasing the mobility of TOC. Another explanation of the effect of pH was given by Brown *et al.* (1997). They mentioned that when the soil pH increased the solubility of fulvic acids increased, thus giving chance for formation of more fulvic acids complexes. Borg and Johanson (1989) noticed the same effect of pH. They also suggested that the mobility of copper was associated with the mobility of organic materials because the copper was highly adsorbed on them.

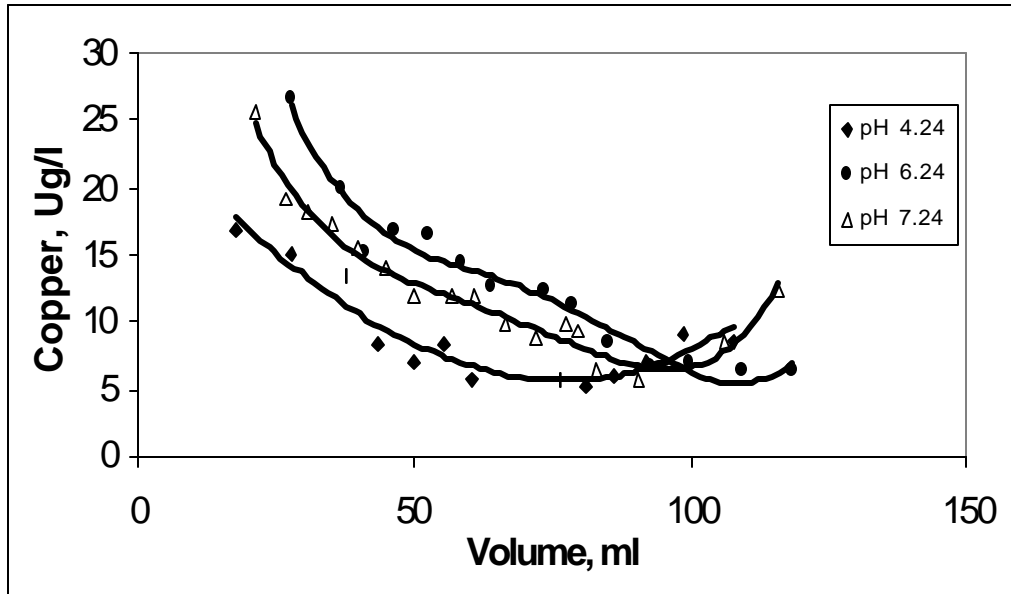


Figure (11) Effect of pH change on mobility of copper through air-dried B-horizon soil. Initial copper conc. was 400µg/l .

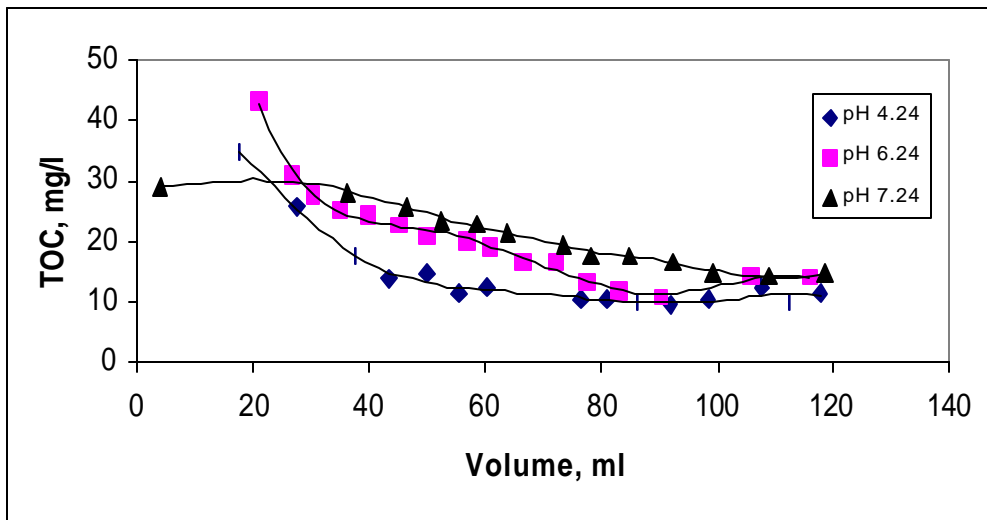


Figure (12) Effect of pH change on mobility of TOC through air-dried B-horizon soil. initial copper conc. was 400µg/l. and its pH

Column study of copper mobility through A and B horizons:

This experiment was conducted to study the vertical copper mobility through the different soil horizons. The results of this experiment are illustrated in Figure (13). As expected, the concentration of the copper eluted from the column containing the A-horizon soil mixture was much higher than that of the B-horizon (3 times) column and the combined A- and B- column (4 times).

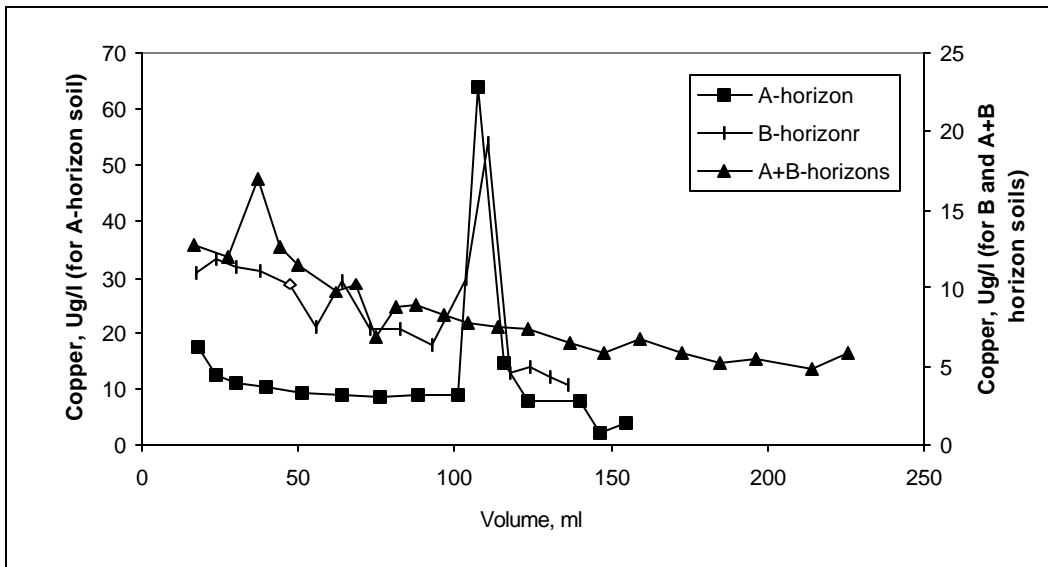


Figure (13) Mobility of Copper through columns containing different dried soil horizons. The concentration of the copper solution was $400\mu\text{g/l}$ and its pH was 6.

The major difference was that of TOC eluted from the double-layers column. The concentration of the TOC from the A- and B- column was lower than that of the A-horizon column. Two explanations may be suggested. First, the weight of A-horizon soil in the mono-layer column is double the weight of that soil in the two-layer column, which consequently might lead to this drop in TOC concentration. Second, the attenuation of TOC concentration might be due to sorption or filtration of TOC by the B-horizon layer. Under this scenario it is likely that the TOC flushed

out from the A-horizon layer was being retained by on the B-horizon layer as the solution penetrated the soil. This attenuation of TOC concentration did not have a considerable effect on the mobility of copper through these three columns as indicated in Figure (13). That might suggest that not all the mobile TOC could form complexes with copper. In a study of well tilled Bojac sandy loam, Gallagher *et al.* (2001) found similar results. That study indicated that for agricultural soil placed in a 2x4x7 ft soil bin, copper continued to leach through the soil for a 3 month period if rain water was applied to the soil. The continued migration of copper in that simulated study is similar to the results of this research for A-horizon soil.

Conclusions:

Copper mobility through A- and B-horizon soils from Bojac sandy loam from the Eastern Shore of Virginia is associated with the mobility of TOC. Fulvic acids are the main organic compounds responsible for copper mobility. The pH of the copper solution has a considerable effect on this mobility. The mobility of TOC and copper was least at pH 4 and greater at pH 6.24 and pH 7.24. The copper mobility through A-horizon soil is higher than through B-horizon soil. Ionic strength of the copper solution and the chloride ions do not have a considerable effect on the copper mobility.

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CHAPTER 4: Literature Review

4.1. COPPER TOXICITY:

All plants and animals require copper in their systems. In plants, copper is a component of certain enzyme complexes involved in oxidation reaction, lignin synthesis and other functions that influence plant metabolism. It also has a role in the control of DNA and RNA production and in the disease resistance mechanism (Anderson, 1997). A copper deficiency will cause retardation of plant growth. A deficiency of copper in animals may have adverse effects on blood, blood vessels, bone, central nervous system, fat, hair, kidney, liver, skin and enzymes (Owen, 1981; Zamuda and Sunda, 1982). Buck (1978) summarized the different effects of both a deficiency and excess of copper in mammals. He states; "A copper deficiency results in anemia, reduced hematopoiesis and cardiovascular lesions; defects in pigmentation, keratinization, bone formation, reproduction, myelination of the spinal cord, and connective tissue formation; and reduced growth. Chronic excess copper intake results in sudden release of copper from the hepatic storage sites into the blood stream causing hemolysis, icterus and anemia with accompanying hepatic renal necrosis".

Excess copper is also life threatening. Certain diseases of man and animals are due to increase in dietary copper levels. The basis for copper toxicity is diminished enzyme activity because copper inhibits a number of enzymes. Some of the substances that are affected by copper are adenosine triphosphate, aldolase, alkaline phosphodiesterase, aminoacyl t RNA, pepsin and lipase (Owen, 1981). There are two major categories of chronic copper toxicity in man. The first one is a primary form where copper damages the

liver and other organs. In the second form, excess copper either exacerbates or prolongs preexisting liver destruction (Howell and Gawthorne vol. II, 1987).

High concentration of metals in irrigated soils and ground water pose a threat to agricultural production and the health of human and animals. This can occur in four different ways: 1) metals can accumulate in plants to levels that cause phytotoxicity; 2) metals in plants have adverse effects on human and animals that consume these plants; 3) metals can enter surface water from agricultural drainage; and 4) metals can migrate into ground water and may re-emerge with subsurface drainage in surface water, thereby affecting wild life and human health. Some elements like Cu and Cd may cause adverse effects to aquatic life even at concentration slightly above natural background levels (Borg, 1989).

Copper is toxic to many plants including the potato, carrot and cauliflower. The toxic levels for some plants in water are 19 to 21 mg/l (Owen, 1981). Many aquatic organisms have been found sensitive to copper. Among these, are snails, fish and oysters (Owen, 1981). When comparing the toxicity of 17 metals on soil bacteria, fungi and actinomycetes, copper is the fifth highest behind silver, mercury, chromium and cadmium (Owen, 1981).

The forms of copper that cause toxic effects are the free ions and some inorganic complexes. The sorbed and organically complexed forms do not pose a toxic threat (Micheal, 1994). Complexation can reduce the toxicity of many pollutant metals to aquatic organisms (Bedsowrth and Sedlak, 1999). When water contains high concentration of organic pollutants, the availability of metals will be weak due to the reaction with these organic substances, which decreases the toxicity of the metals. Other characteristics

of sediments containing these metals such as oxidation-reduction may control the bioavailability of the majority of metals that are present (Burgess *et al.*, 1992). Humic substances are examples of substances that can affect copper availability. Humics can enhance the availability of Cu (II) to plants and other microorganisms and at the same time reduce the toxicity effects of free Cu (II) (Stevenson and Chen, 1991).

Soluble microbial products (SMP) have metal chelating properties. Typical chelating functional groups in SMP, such as hydroxyls, amines and phenols form complexes with metals. The complexation of the metals makes them less toxic but at the same time may also make them more or less available as micronutrients (Kuo and Parkin, 1996). The total concentrations of heavy metals in soil are of minor importance for nutrient acquisition by plants and metal toxicity to plant roots (Gerke, 1997). For example, aluminum toxicity to roots depends primarily on monomeric cationic Al in solution. Anionic Al species in solution are not toxic. The same can be said about Al complexes with low molecular weight organic acids and humic substances.

"The potential toxicity of heavy metals in the environment depends on their concentration in the soil and soil solution and dissociation kinetics of the dissolved species" (Castilho *et al.*, 1993). The total copper content of uncontaminated soil ranges from 6 to 60 mg Cu/Kg soil. Soil copper concentrations as high as 3500 mg/kg were detected in industrially polluted soils. Such high concentration has been reported to cause phytotoxicity in soils (Anderson, 1997).

4.2. Sources of copper contamination:

It is no longer a matter of argument that human activity has increased the concentration of heavy metals in soil, water and air. Sources of pollution of soil and ground water include automobile exhaust, waste water and solid wastes from industrial production, fertilizers and pesticides. Nearly all of these contain heavy metals (Fic and Schroter, 1989).

Copper has been widely utilized in many applications due to its malleability and heat of conductivity. It is included in many alloys such as brass, bronze, bell metal, gunmetal, German silver, aluminum-bronze, phosphor-bronze, silicon-bronze and beryllium-copper. The metal itself is employed in many industries such as casting, tubing, gas and water piping, chemical and pharmaceutical equipment and wire. Compounds such as copper acetoarsenite and cupric arsenite are used as pigments. It has been used also in some medical applications. As a result of these uses, copper contamination of the environment is widely reported (Nriagu, 1979).

Wood, intended for outdoor use is often treated with chemicals such as copper, chromium and arsenic compounds to withstand attack from fungi and bacteria. Soil contamination with these substances has been detected at wood-impregnation plants due to spills, deposition of sludge and dripping from newly impregnated wood (Andersen et al, 1996). Metal smelters have a large impact on air, soil and water pollution. In particular, the long-term ground water quality in the neighborhood of such sites is of main concern (Cernik *et al.*, 1994 and Jones *et al.*, 1991). Mine drainage is another source of pollution by heavy metals to soil and ground water (Dudley *et al.*, 1991). Borg and Johnson (1989) reported mining, non-ferrous smelters, burning of fossil fuels and vehicle exhaust as source of pollution of heavy metals

including copper. Fossil fuel combustion is another way of contamination of environment with heavy metals. The combustion of these fuels results in the dispersion of heavy metals over a large areas, polluting air, surface water, soil and consequently ground water (Alloway, 1995).

Warfare and military training may be a significant source of pollution with heavy metals including lead, copper and zinc. Battlefields were found to contain significant concentration of these heavy metals contained in bullets, cartridge and shell cases. These heavy metals may persist in soils for centuries (Alloway, 1995).

Landfilling and land application are used as methods of disposal of municipal and industrial wastewater and sludges. The rationale for land disposal or land application is the ability of soils to retain metals in a form not likely to leach. However, it has been found that copper and other metals may leach by several different mechanisms and contaminate ground water (King, 1988). Sewage sludge and other wastes applied to agriculture lands represent one way that soil becomes contaminated with heavy metals and other contaminants. These wastes contain high concentration of metals, organic and inorganic substances that aid in either the mobility or fixation the heavy metals. A typical sludge content of copper is 850 mg/kg dry weight (Reed, 1993). Given sufficient time and rainfall, a substantial amount of metals can leach out of the soil. This problem has become more serious as application of wastes to forest, rangelands as well as land reclamation sites has been more widely used. The reason of such wide utilization of this process is that it is a cost effective (Warwick *et al.*, 1989; Steenhuis *et al.*, 1999).

Salting of roads for deicing purposes may cause periodic high concentration of heavy metals in adjacent watershed areas due to

complexation with chloride ions and the mobilization of the complexed form (Doner, 1978, and Lehman and Mills, 1994). Navarro *et al.* (1991) monitored some heavy metals including copper in soil around a hazardous waste dump disposal site. Sulfate was found to form complexes with Cd, Cu and Pb in the soil. The complexes were thought to be responsible for the enhancement of the metal mobility (Newman and Elzerman, 1987). Carbonate minerals, on the other hand, were observed to effectively immobilize Cd and Cu by providing an adsorbing or nucleating surface and by buffering pH (Dudley *et al.*, 1991).

A serious source of pollution of surface water is the direct discharge of industrial and municipal wastewater to the rivers (Huang and Zhang, 1990). Barcan and Kohnatsky (1998) reasoned that the contamination of soil by copper and nickel near a smelter complex was due to the deposition of these heavy metals from smelter emissions.

Agricultural practices constitute very important non-point sources of metals. The main sources of this type of pollution are impurities in fertilizers, pesticides, refuse derived compost, wood preservatives and corrosion of metal objects such as metal roofs and fences (Alloway, 1995). Copper applied to plasticulture tomato fields to protect against plant disease was found to remain sorbed to soil following rainfall (Gallagher *et al.*, 2001).

Contamination of two Chesapeake Bay tributaries on the Eastern Shore of Maryland with heavy metals has been found and this contamination is due to the contributions of both point (sewage treatment plant) or non-point (agriculture runoff) sources (Gupta and Karuppiah, 1996). A study made by Karuppiah and Gupta (1998) in two Chesapeake Bay tributaries suggested

that the increase in toxicity and heavy metals appears to be related to an increase in industrial and agricultural activity around these two tributaries.

Copper is added to the diet of some growing animals at levels up to 250 ppm to increase their growth rate and promote feed efficiency. Manure produced by these animals has been found to contain high concentration of copper. The application of this manure to agriculture soils may lead to the increase of copper concentration in the soil (Mullins *et al.*, 1982).

4.3. Forms of copper present in environment:

Copper can be present in several insoluble forms; (1) adsorbed on surface of metal oxides, clay minerals, humic substances and organo-mineral complexes, (2) in structure of secondary minerals or in amorphous iron and manganese oxides; (3) or associated with authigenic sulfides (Hang, 1993).

According to Anderson, 1997, "other forms of copper in soils include soil solution and exchangeable copper, copper weakly bound to specific sites, organically bound copper, copper occluded in carbonates and hydrous oxides, and residual copper in clay lattice". Keller and Vedy (1994) adopted another classification of the forms of metals present in the environment. They classified these metals into six categories; water soluble, exchangeable, silicate bound, oxide bound (Mn and Fe), carbonate bound, and organic matter bound. They separated copper and cadmium into these fractions by applying sequential extraction technique. This sequential extraction technique indicated that the distribution of metals between different fractions depends on metal type.

Most of the dissolved copper found in the wastewater effluents and in the surface runoff is in the form of complex compounds. "Metals may be

found as labile metal species (metal cations, inorganic complexes and weak metal-organo complexes), moderately strong metal-organo complexes (metal complexes with humic substances) and strongly complexed metals (metals complexed by polydentate ligands)” Sedlak *et al.* (1997).

4.4. Mobility of heavy metals:

4.4.1. Factors affecting heavy metals mobility:

The mobility of heavy metals depends on their chemical forms, which in turn is related to the chemical properties of soil. For example in some types of soil the presence of carbonate effectively immobilized Cd and Cu by providing an adsorbing surface or by buffering the pH (Dudley *et al.*, 1991). Soil parameters, such as pH, organic carbon content, iron and manganese content and total metal content affect the distribution of copper and cadmium between different soil fractions.

Borg and Johansson (1989) reported that copper is largely retained in the soil. They noticed that the mobility increased with the decrease of pH. They suggested that the mobility of copper was associated with the transport of organic material since the copper was highly adsorbed on them.

The mobility of most heavy metals in the soil and subsoil depends on the physico-chemical properties of the solid and liquid phases. Many chemical changes may occur during the movement of water through the soil including dissolution/precipitation, adsorption/desorption, degradation, filtration and a variety of transport processes (Fic and Schroter, 1989). Trace metals can be found in different physical phases including particulate, colloidal and truly dissolved phases. The fate and transport of metals in the

environment depends on these phases and the interaction between them (Wilhelmy *et al.*, 1996).

In research conducted by Brown *et al.* (1997) to study the effect of alkalinity on the metal mobility, it was found that the mobility of most metals was enhanced with increase of pH. In this study, the soil was amended with lime-stabilized biosolids. The lime added might neutralize subsoil acidity to 70 cm below the soil surface. The concentration of Cu, Pb and Zn was measured at different depths and compared to control. The concentration of these metals at different depths was found to be high compared with control, which proved the mobility of these metals. The authors reasoned that the movement of these metals to the formation of fulvic acids metal complexes. When the soil pH increased the solubility of fulvic acids increased, thus giving chance for formation of more fulvic acid complexes (Brown *et al.*, 1997).

4.4.2. Methods of copper mobility:

Trace metals can be found in different forms or components of the soil or sediments. These forms are referred to as speciation. Chemical speciation determines the mobility and bioavailability of the trace metals. For example when using the sequential extraction technique to determine the concentration and partitioning of different heavy metals in soil, the highest concentration of copper was found in the residual fraction or organic matter fraction. Cadmium was found mainly in the carbonate fraction. Zinc and lead were found in the Fe-Mn oxide fraction. This speciation of metals on the different fractions suggested the effect of species type on the mobility of the metals (Ramos *et al.*, 1994).

Ma *et al.* (1997) suggested the chemical forms of the metals as the determinant of metal behavior and mobility in the environment. They classified heavy metals into five categories: (1) bound to carbonate; (2) bound to reducible phase (Fe and Mn oxides); (3) bound to organic substances and sulfides; (4) adsorptive and exchangeable; and (5) detrital or lattice metals. This classification was based on primary accumulation mechanisms in sediments. Therefore, it was important to determine the form and content of heavy metal in order to assess the environmental impact of contaminated soils. Their study indicated that the residual fraction contained a large fraction of all metals under the study (Zn, Cu, Cd, and Ni). Nevertheless, a significant fraction of total metals was associated with nonresidual fraction.

4.4.2.1. Complexation with inorganic compounds:

The mobility of heavy metals, including copper, may be enhanced by the formation of inorganic complexes. Chloride for example can form complexes with many cations such as Cd (II), Hg (II), Pb (II), Zn (II) and Cu (II). This complex formation mechanism is important, especially in saline soils. Salting of roads for deicing purposes is an important source for chloride ions (Doner, 1978).

The studies reported by Fic and Schroter (1989) indicated significant differences in mobility among heavy metals. They classified Zn and Cd as relatively mobile and Cu and Cr as relatively immobile. They attributed the mobility of heavy metals in the carbonate containing sediment water system to the dissolution/precipitation processes. These processes depend on the pH and the bicarbonate content of the water as well as the carbonate content of the material. They found also complexation with sulfates for Cd, Cu, Zn

and Cr. Under acid sediment/water conditions, they suggested adsorption/desorption as the main processes that control the mobility of these heavy metals.

In his survey, King (1988) reported that metal availability was controlled mainly by interaction of metals with hydrated oxides of Mn and Fe. He mentioned the opinion of Jenne (1968) that the important effect of organic matter was to promote the periodic reducing environment necessary to maintain Mn and Fe in a hydrous microcrystalline condition. He mentioned also that the pH had two effects; the exchange of hydrogen ions with heavy metals occluded by hydrous oxides and the dissolution–precipitation and oxidation of Fe and Mn oxides.

4.4.2.2. Effect of organic compounds:

Lazerte *et al.* (1989) reported two patterns of trace metal transport. One was explained by the metal affinity for dissolved organic carbon and the other was explained by the metals solubility in dilute acid and mineral soils. They found that the transport behavior of cadmium and zinc followed the transport of inorganic aluminum. They also mentioned that the transport of these two metals was correlated to the acidic deposition. They found that the transport of lead and copper was related to the behavior of dissolved organic carbon and organic aluminum. They suggested that these two metals move through the soil in the organic form. They reasoned the behavior of these two metals was related to their affinity for organic matter. They found that lead and copper had a high affinity for fulvic acids whereas cadmium and zinc had lower affinity.

In a study by Kuo and Parking (1996) on the role of soluble microbial products, they found this material included humic and fulvic acids, proteins,

enzymes, organic acids, aminoacids, polysaccharides and structural components of cells. These microbial products can chelate heavy metals, which can affect their toxicity, nutritional ability and transport.

Metal contaminants may be found in the interstitial water of soil associated with a filterable colloidal phase such as dissolved organic carbon (DOC). This DOC plays a certain role in the mobility of contaminants between the particulate and dissolved phase (Hwang *et al.*, 1998). Castilho *et al.* (1993) noticed that the concentration of metals in the soil solution increased with an increase of the concentration of the dissolved organic carbon (DOC) and that it was not affected by a change in pH. They also concluded that copper is associated with DOC. They performed cation exchange experiments with nine membrane filtered topsoil filtration extracts and found that copper was associated with low molecular weight complexes. Thirty to seventy percent of the copper was bound to fast-dissociating complexes which are the complexes formed with low molecular weight DOC.

The mobility of copper in the soil may be enhanced by some artificial organic compounds that serve as complexing agents for copper. Of these compounds, nitriloacetic acid, which is used as a substituent of some detergent constituent components, was found to have substantial effect on the mobility of copper. In contrast to other investigators' reports, Linn and Elliot (1988) found that the increase of the acidity of the soil decreased the mobility of copper. This was thought to be due to the competitive binding of nitriloacetic acid by protons and Fe released by hydrous oxides dissolution.

Howell and Gawthorne (1987) mentioned the important role of organic matter in the retention and behavior of copper. They reported both humic and fulvic acids as two ligands for binding of copper (II) with the fulvic acids

as the more soluble. They reported also simple aliphatic acids, amino acids and aromatic acids as chelating agents for copper (II). The organic complexes of copper, according to their survey, account for more than 90% of the soil solution in the surface horizon.

Newman and Elzerman (1987) suggested many mechanisms enhancing the mobility of metals in porous media. These mechanisms were associated with inorganic, organic ligands or with colloids, which might provide a faster transport mechanism. “The proposed mechanisms are: (1) macroscale non-homogeneities in the aquifer; (2) inappropriate application of K_d -based model (i.e. nonequilibrium reactions or nonlinear adsorption isotherms); (3) the presence of more than one mobile species of contaminant in solution; and (4) the presence of a mobile solid phase (e.g., colloidal phase) composed of contaminant or to which the contaminant is adsorbed”. They mentioned also that complexation and/or sorption of metals might result in mobility in excess of that predicted. Their results indicated that association of metal ions with the mobile colloids increased the mobility of these metals through the soil. They found also that pH together with ionic strength had important effect on this mobility.

The effect of dissolved organic carbon on leaching of copper from municipal solid waste incinerator (MSWI) was observed in a study by Meima *et al.* (1999). The dissolved organic carbon was found as a major component of MSWI bottom ash leachate. High molecular weight compounds (>10,000) were found in neutral extracts. In the absence of dissolved organic carbon, the copper leaching would decrease 2-3 orders of magnitude.

Kuiters and Mulder (1989) suggested the percolation of the soil solution as a mechanism for the transport of the soil organic matter through soil. This organic matter may form complexes with metal ions making them more mobile. They performed their experiments on a group of metals including aluminum, iron, copper, lead and zinc. A positive correlation was found between the concentration of soluble organic carbon and the concentration of Cu, Pb, Zn and Mn. They suggested the complexation of these ions with low-molecular weight compounds.

4.4.2.3. Effect of colloids:

Colloids can be responsible for the transport of pollutant from sediments to the aqueous phase. Both hydrophobic organic compounds and metal ions can be transported in this manner. The capacity of colloids for binding metals is very large. The distance reported for transporting these substances is also very large (Hiemenz and Rajagopalan, 1997). Beside inorganic and organic colloids, microbes play a role in metal movement. These microorganisms have high surface area to volume ratio that increases the possibility of their interaction with metal ions (Huang, 1993). Amrhein *et al.* (1993) reported the enhancement of metal mobility leachate from such soils was associated with colloidal particles. These colloidal particles were made up of organic matter and Fe oxides. They noticed that the mobility of these trace metals and colloidal particles increased when the salinity decreased. Stahr *et al.* (1980) reported the fixation of copper in most of the soils. They attributed this to irreversible adsorption on humus and iron oxide. On the other hand, Ramosa *et al.* (1994) found that most of the copper was present in the organic fraction and only small amounts were associated with the iron oxide fraction.

Mobile colloids may aid in transporting heavy metals in soils (Thompson and Scharf, 1994; and Amrhein *et al.*, 1993). The mobility of natural colloids was proved by the presence of humic substances in deep aquifer. Humics were also found as coatings of accumulated clays and organic matter in subsoil horizon of many soils. Colloids travel with water through soils (Thompson and Scharf, 1994). Colloidal particles have large surface area and so they are considered by some researchers to play a key role in metal mobility. They are thought to be responsible for both chemical fractionation occurring during estuarine mixing and for the downward transport of organic matter and many metals in coastal and open ocean water (Wilhelmy *et al.*, 1996).

Igloria *et al.* (1997) mentioned the possibility of formation of complexes between heavy metals and organic matter colloids in solutions, as well as those attached to soil surfaces. This complex formation process increases the concentration of metals in the mobile phase, which allows their transport over long distances. McCarthy and Zachara (1989) classified ground waters into three-phase systems. These phase systems are the traditional mobile phase (aqueous), immobile (solid) and mobile colloids (e.g. NOM) phases. They suggested that this mobile colloidal phase might enhance the transport of solute. Their conclusion was that natural organic matter (measured as TOC) did not facilitate the mobility of heavy metals including copper. They suggested that there was a high affinity of the NOMs to the soil and in turn, the metals to the NOMs.

Sposito (1986), on the other hand, claimed that the effect of these colloids might be the retardation of the transport of metals. “He mentioned five possible effects of organic ligands on the adsorption of heavy metals by

soil surfaces: (1) the ligand has a high affinity for the metal and the soluble complex formed has a high affinity for the sorbent, resulting in increased sorption; (2) the ligand has a high affinity for the sorbent and the sorbed ligand has a high affinity for the metal, resulting in increased sorption; (3) the ligand has a high affinity for the metals, but the soluble complex formed has low affinity for the sorbent, resulting in decreased sorption; (4) the ligand has a high affinity for the sorbent, but the sorbed ligand has a low affinity for the metal, resulting in decreased sorption; and (5) the ligand has a low affinity for both metal and sorbent, resulting in little effect on sorption. The first and second possibilities will increase sorption leading to greater effective retardation factors, while the third and fourth will result in just the opposite.”

4.5. Adsorption of metal ions by soils:

Adsorption is the most important process affecting the bioavailability of metals in soils. The reason is that it controls the concentration of metal ions and complexes in the soil solution. Different mechanisms may be involved in the adsorption process, namely, cation exchange, specific adsorption, coprecipitation and organic complexation.

In cation exchange, sometimes called nonspecific adsorption, heavy metals that exist as cations in the soil solution will exchange with counter ions on the negatively charged soil colloids. The cation exchange capacity (CEC) of mineral soils ranges from a few to 60 cmole/kg but in organic soils, it may exceed 200 cmole/kg. The organic substances in soil make a major contribution to the cation exchange capacity of soil due to their high adsorptive capacity at pHs above five. Specific adsorption involves the exchange of metal cations with surface ligand forming covalent bonds with

lattice ions. The adsorption is greater than the cation exchange capacity of a soil. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions. Heavy metals can also diffuse into minerals such as goethite, Mn oxides and some other minerals in a process that is also pH-dependent (Alloway, 1995).

Another way of interaction of heavy metals with soil is insoluble precipitation. This occurs whenever the physico-chemical conditions and concentration of metal are stable. Copper is more stable in adsorbed form (soil-Cu) than any copper minerals except under strongly reducing conditions. Coprecipitation involves the simultaneous precipitation of a chemical agent in conjunction with other elements. Many solids may be formed by this mechanism including clay minerals, hydrous Fe and Mn oxides and calcite for which isomorphous substitution has occurred.

Humic substances and other organic ligands can form chelate complexes with metals, causing them to be tightly adsorbed to the structure. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids (Alloway, 1995).

Some ions like Ca^{2+} are found to aid adsorption of copper on soil. This adsorption was found to take place on inorganic and organic colloids depending on the nature of the soil and is pH dependent. The reason for the dependence of copper adsorption on pH was attributed to adsorption of hydrolyzed species (CuOH^+). The desorption process was also found to depend on the pH of the solution. A decrease in pH will cause desorption of the copper initially adsorbed on the soil. The amount of copper desorbed depends on the type of the soil and the decrease in pH (Atanassova and Okaazaki, 1997). It was found in other studies that a substantial increase in

pH caused increase of copper sorption (Carey *et al.*, 1996 and Stahr et al, 1980).

Particle size of the adsorbent soil has a significant effect on the adsorption capacity. In a study by Huang and Zhang (1990), it was found that metals were highly concentrated on both coarse (sand size, $> 50\mu\text{m}$) and fine (clay size, $\leq 2\mu\text{m}$). They attributed this behavior to the association of clay minerals with these metals. They reasoned the low concentration on the moderate size fraction (silt size, $50\text{-}2\ \mu\text{m}$) to the presence of light minerals, such as quartz, in higher concentration than the other fractions.

4.6. Soil Nature and classification:

4.6.1. Soil phases:

Soil consists of three phases; solid mineral and organic matter, water and gas. Normally, air is the only gaseous phase but in some soils other gases like methane may exist. The moisture content of a soil is defined as the weight of the water in a sample divided by the dry weight of the soil sample.

2.6.2. Soil Classification (Rollings and Rollings, 1996):

There are three common systems for classifying soils; the U.S. Department of Agriculture (USDA) Textural system, the Unified Soil Classification System (USCS), and the American Association of State Highway and Transportation Official (AASHTO).

4.6.2.1. USDA Textural Soil Classification:

This system defines sands to be particles between 2.000 and 0.050mm, silts to be particles between .050 and 0.002 mm and clays to be smaller than .002 mm. The soil is classified according to its relative content

of these three components. This classification is widely used and is facilitated using the triangular textural classification chart in figure (1.1).

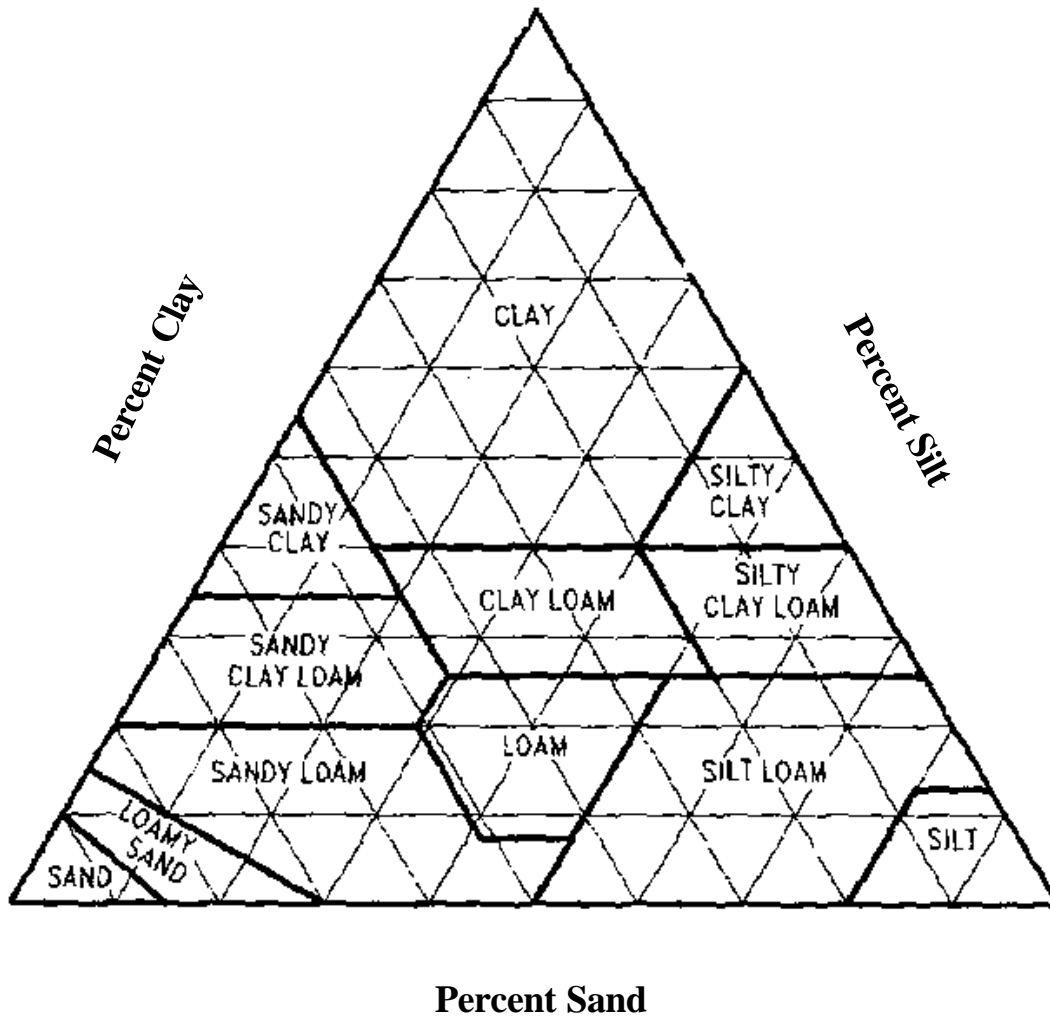


Figure 2.1 USDA TEXTURAL CLASSIFICATION OF SOIL

4.6.2.2. Unified Soil Classification System:

The soil is classified in this system into two types; coarse and fine-grained. The main criterion of classification is the percentage of particles passing through No. 200 sieve. If 50 percent or more of the soil is retained on the No. 200 sieve then the soil is classified coarse-grained. If 50 percent passes the No. 200 sieve, then the soil is classified fine-grained. The coarse-grained soils are classified into gravel if 50 percent or more of this fraction is retained on the No. 4 sieve, and sand if more than 50 percent of this fraction passes the No. 4 sieve. Fine-Grained soils are divided into silts or clays according to their plasticity characteristics.

4.6.2.3. AASHTO Classification System:

This system divides soils into eight groups A-1 through A-8. The first three groups, A-1 through A-3, comprise coarse-grained soils that have 35 percent or less of particles passing the No. 200 sieve. Soils with more than 35 percent passing the same sieve are considered fine-grained soils and are classified A-4 through A-7 depending on their liquid limit and plasticity. Group A-8 includes soils that have high organic content.

4.6.3. Soil Structure:

The soil profile is divided into layers. Every layer has a certain thickness and is called a horizon. The top level is called the O horizon and it has high content of organic substances due to plant decay. The next layer is called the A-horizon. This mineral layer is characterized by aerobic biological activity and high accumulation of humic substances. The thickness of this layer is between 2-50 cm. The B-horizon lies below the A-horizon. The salts and clays that leach from the A horizon may accumulate in the B-horizon. The characteristics of this layer include lower permeability and being the site

of denitrification. The subsequent layer is the C-horizon and it extends up to the top the parent bedrock. The organic content of this layer is low and it is made up of weathered parent rock. This layer is thought of as the region where ground water flows (Kupar, 1991).

4.7. Colloids:

Most of the chemical and physical properties of soils are controlled by colloidal materials. They serve as surfaces on which cation and anion exchange take place. Ions of essential mineral elements such as calcium, potassium and sulfur are held by these colloidal particles until taken up by plant roots. Soil colloids affect the soil structure, retention and movement of water and soil temperature.

4.7.1. General properties of colloids:

All types of colloids have a common feature, which is an extremely small size coupled with high charge. Most colloids are smaller than 2 μm . Colloids have a large external surface area per unit mass. Some colloids, especially some silicate clays, have very large internal surfaces. The surface area of clays ranges between 10 m^2/g and 800 m^2/g . Colloidal surfaces can carry negative and/or positive charges. Most soil colloids carry electronegative charges and some mineral colloids in very acidic soils have electropositive charge. Since the colloids carry a charge, they can attract ions of opposite charge from solution. Most of these particles are cations such as H^+ , Al^{3+} , Ca^{2+} and Mg^{2+} . This property can be responsible for the transport of contaminant through the soil or water column.

4.7.2. Types of soil colloids:

There are two types of colloids contained in the soils; inorganic (clays) and organic (humus) colloids. The inorganic colloids are subclassified into three classes; layer silicate clays, which consist of layers of oriented sheets of silicon, aluminum, magnesium and/or iron held together by oxygen and hydroxy groups. The second type of inorganic colloids is hydrous oxides of iron and aluminum. Examples of these oxides are gibbsite and goethite. The third type of inorganic colloids is allophane and other amorphous minerals. These colloids lack the ordered three-dimensional structure.

The original source of soil organic matter is plant tissue. The tops and roots of different plant supply large quantities of organic matter. During harvest, one-tenth to two-third of the aboveground part of the plant falls to the soil surface and is incorporated into the soil. Insects are a secondary source of organic matter. They attack the plant tissue and their dead bodies become part of the carbon supply to the soil (Brady and Weil, 1996).

Organic matter may affect both physical and chemical properties of soil. Humus give the surface horizon dark brown to black colors. Plasticity, cohesion and stickiness of soil are decreased with the increase of humus. The increase of organic content of water will lead to improvement the soil water retention. Humus affects the chemical properties of soil in many ways. It is responsible for the adsorption of most absorbable cations, keeping them in easily exchangeable form. Some components of humus form complexes with metal ions making them more available to plants (Brady and Weil, 1996). Both humus and nonhumus organic substances are important to the soil environment. The humic substances provide the long-term effect such as increasing the ability of soil to exchange ions due to their high specific

surface area. They also increase the pH buffering and the water-holding capacities. Nonhumus materials provide short-range effects such as providing food and energy for microorganisms and provide fertility for the soil (Bohn *et al.*, 1979).

All soils contain organic matter of different amounts and types. Colloidal soil organic matter is divided into non-humic and humic substances. The nonhumic substances include amino acids, carbohydrates, organic acids, fats and waxes. Humic substances are a continuum of compounds varying in molecular weights. They are formed by secondary synthesis reactions involving microorganisms and have different characteristics from any other compound contained in living organisms. They have a wide variety of functional groups, including phenolic, hydroxyl, carbonyl, ester, carboxyl and possibly quinone and methoxy groups. Humus are separated into three fractions: (1) humin, which is insoluble in alkalis and acids, (2) humic acids, which is soluble in alkalis and insoluble in acids, and (3) fulvic acids, which is soluble in both acids and alkalis (Alloway, 1995). The amount of organic matter in soils varies from trace amounts (sandy, desert soils) to as high as 20 or 30% (some forest A horizons). Some soils contain higher concentration of organic substances but these types of soils are not considered mineral soils, instead they are considered organic soils. The organic substances content of surface horizons are much lower than those of surface horizons. The reason is that most activities dealing with organic substances take place at the surface horizons (Brady and Weil, 1996). The organic matter content of soils can be determined by two ways. The first method include the determination of percentage loss in weight after ignition in furnace at 375° C for 16 hours or the oxidation of carbon by a

potassium dichromate followed by titration of excess dichromate (Alloway, 1995).

4.7.3. Humic Substances:

Humic materials comprise about 60-80% of the organic content of the soil. They are divided into three main groups, namely, humic acids, fulvic acids and humins. The exact structure and properties of these substances are still unknown. The suggested structure of humic substances is a skeleton of alkyl/aromatic units cross-linked by oxygen and nitrogen groups. The major functional groups of these substances are carboxylic acids, phenolic and alcoholic hydroxyls, ketones and quinone groups. Fulvic acids are richer in carboxylic acid, phenolic and ketonic groups which makes them more soluble at all pH values. The structure of fulvic acids is aliphatic with small number of aromatic groups. Humic acids are more aromatic and less soluble at low pH. The structure of humic substances below them to perform as surfactants with the ability to bind both hydrophilic and hydrophobic materials, which makes the humic substances play an important role in the transport of organic and inorganic contaminants in the environment (Gaffney *et al.*, 1996).

Humic substances were proved to be very stable and resistant to microbial attack, which helps in maintaining appropriate organic matter levels in the environment. Fulvic acids are most susceptible to microbial attack followed by humic acids with the humin as the most resistant to such attack (Brady and Weil, 1996).

4.7.3.1. Colloidal characteristics of humic substances:

The surface area of the humic substances per unit mass is very high and is negatively charged. The source of these negative charges is

carboxylic (-COOH) and phenolic (-OH) groups. Because the charge characteristics and high specific area, cation exchange capacity of humic substances is much higher than that of silicate clays. Cation exchange reactions take place by exchanging the cation adsorbed on the surface of humic substances with cations present in the soil solution. These exchange reactions are enhanced due to the colloidal properties of humic substances.

The suggested structure of colloidal humic substances is coiled, long-chain or three-dimensional crosslinked macromolecules with a molecular weight ranging from a few hundred to as much as several hundred thousand atomic mass unit. Humic substances vary in composition depending on their source, location and method of extraction. The most important factors that control the molecular conformation of humus are their concentration, pH and ionic strength of the system. At high concentration (> 3.5 g/l), low pH (< 3.5) and high electrolyte concentration (> 0.05 M), the humic substances are rigid, uncharged colloidal particles. As these factors convert, the humic substances become more flexible and linear (Brady and Weil, 1996 and Gaffney *et al.*, 1996).

4.8. Chemical behavior of copper in soil:

Chemical processes may affect the mobility of heavy metals like copper. Precipitation and dissolution are two mechanisms that affect the mobility and activity of copper in the soil. These reactions are described by the solubility product, which is the product of the two activities of the anion and cations forming the solid phase of the metal. If the solubility product has a high value then most likely the metal will be present in its dissociated form. Being in the dissociated form will facilitate the mobility of the metal through the soil.

Solution phase speciation is another process that affects the copper mobility and availability. The total concentration of copper or any other metal is the sum of the concentration of the all complexed and uncomplexed forms of copper. This total concentration depends on the ionic strength of the solution.

Adsorption reactions have a vital effect on the concentration of the bioavailable copper and on its mobility. If copper is adsorbed on mobile species then that will increase its mobility through the soil. If instead it is adsorbed on the surface of large particles that have low mobility, its mobility will decrease. Adsorption occurs mainly on the clay fraction of the soil. Two main models are used to describe the data of adsorption processes. These two are Langmuir and Freundlich adsorption isotherms. Langmuir model assumes that monolayer adsorption takes place on specific sites having the same adsorption energy. The adsorption equation is given as:

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad 4.1.$$

Where $X = x/m$, the amount of solute adsorbed, x , per unit weight of adsorbent, m ; C_e = equilibrium concentration of the solute; X_m = amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage (Faust and Aly, 1987). If the data of the adsorption process fit the Langmuir model, then plotting C_e against $1/X_m$ should result in a straight line. This straight line has $1/bX_m$ as its intercept and $1/X_m$ as its slope.

Freundlich adsorption isotherm is the most widely used equation to describe adsorption processes. Its theory depends on the monolayer formation of the adsorbate on the adsorbent surface. Its equation is given by:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \quad 4.2.$$

Where x = the amount of solute adsorbed; m = the weight of adsorbent; C_e = the solute equilibrium concentration, and K and $1/n$ = constants. Plotting $\log x/m$ against $\log C_e$ will result in a straight line with a slope $1/n$ and intercept $\log K$ (Faust and Aly, 1987).

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