THE ROLE OF NATURAL ORGANIC MATTER (NOM) IN THE SORPTION OF COPPER TO BRAZILIAN OXISOLS

by

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ABSTRACT

The inappropriate release of domestic and industrial wastes in Brazil is a severe environmental problem. Approximately three quarters of the domestic trash in Brazil is discarded without any attempt at mitigating the environmental hazards.

In Brasília, the capital of Brazil, the city's landfill has been in operation for the last 35 years without barriers for subsurface containment of leachate. Recently, studies by the University of Brasília have detected concentrations of Cd and Pb above the maximum contamination level (MCL) allowable for drinking water in leachate directly beneath the landfill. However, monitoring wells downgradient of the landfill have produced only low levels of these toxic metals, leading to the speculation that leachate-saturated soils have a high capacity for sorbing toxic trace metals.

For this study, a soil profile inside the Brasília National Park, which borders the landfill, was characterized macroscopically in the field and sampled. Ten soil horizons were chemically and physically characterized and, of these, three were chosen for more detail characterization and description using electron microscopy.

A series of sorption edges and isotherms for Cu^{2+} sorption was made before and after partial oxidation of soil natural organic matter (NOM). The results show a relatively small contribution of NOM to the adsorption of copper by soil. This result is in agreement with other studies of acidic soils. However, the apparently limited role of NOM in sequestering metals in soils is not generally true. The lack of significance of NOM in copper sorption in this system is hypothesized to be caused by the abundance of iron and aluminum in the system. It is concluded that, in acid soils, iron and aluminum effectively compete against copper for strong metal binding sites on NOM.

Two sets of sorption edges for copper on soil samples from the A_1 horizon, one after NOM extraction, and the other after different types of additional NOM had been sorbed to the soil, support this hypotheses. The first set confirms the minor role that NOM plays in the sorption of copper in this soil and the second strongly suggests that the Fe and Al are competing with copper for the same binding sites.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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Chapter 1

INTRODUCTION

Research background

The study of the adsorption of metals in natural sediments is important for many fields of environmental science: it helps us understand soil fertility, the capacity of soils and sediments for retaining toxic metals, and is a key component in regulating how fast a metal contaminant may travel in the subsurface (Stumm and Morgan, 1996; Bertsch and Seaman, 1999). Although 'adsorption' as a phenomena has been the subject of study for nearly half a century, a number of questions surrounding the behavior of metal ions in soils remain unanswered.

One area of research that has not yet adequately been explored is the role that soil organic matter plays in metal-ion retention by soils. NOM has long been know to be an important soil component for the sorption of metals (Nelson et al., 1985; Aringhieri et al., 1985; Tessier et al., 1996); however, a clear picture of the many facets of the soil NOM problem has yet to emerge. The main reason for the difficulty in clearly defining the many aspects of the chemistry of metal adsorption to soil natural organic matter is NOM's variability and close relationship with clay minerals and oxides as well as the many reactions that occur between NOM and metals and other organic molecules (Sparks, 1995).

To answer some basic questions about the role of NOM in nature in relation to sorption to minerals and complexation with metals, several laboratory studies have been conducted using more simple systems made up only of precipitated minerals and NOM (Davis and Leckie, 1978; Davis, 1982 and 19843; Schindler and Stumm, 1987, Zachara, 1994). However, due to the complexity of natural systems such as soil, direct extrapolations of results obtained in laboratory to the field may be erroneous (Bertsch and Seaman, 1999). To make a "bridge" between the laboratory systems and the natural system, the knowledge obtained in the former should be used with the understanding of the unique chemical characteristic of each class of natural system.

One of the goals of this study is to investigate the role of NOM in the adsorption of trace metals to oxisols, while observing the chemical characteristics of this soil system. This study will facilitate interpretation of the results obtained in laboratory as related to the sorption of copper to oxisols in the field.

The motivation for this study

Brasília National Park has an area of approximately 28,000 ha and is located between 15°35' – 15°45' South latitude and 48°05' – 47°53' West longitude in Brazil's Federal District (Ramos, 1995) (Fig. 1.1). It contains an important ecological reserve and contributes to the city's northern area water supply.

Brasília National Park has never been exposed to any agricultural or industrial activity. The soil formation present in the park is well-structured and well-drained with sporadic metric layers of lateritic material. These soils are Tertiary/Quarternary detritic sediments of 18 meters in average thickness, with very uniform particle size distribution and a composition dominated by clays. However, the clay minerals are commonly aggregated giving to soil a granular sandy texture. These soils have 63 to 65% porosity and an average permeability of 4.0 x 10^{-6} cm/sec (Santos, 1996). Therefore, these soils have significant potential as a ground water supply for the region (Barros, 1993). Soils sampled in the National Park, classified by the USDA system as Typic Acrustox and by the Brazilian system as Dark Red Latosol (DRL), represent the major soil formation that covers 38% of the park area (Ramos, 1995). The vegetation at the sample site is a Typic Ustic savanna with small to medium size trees that have 'tortuous' trunks. This type of vegetation is also very common in central areas of the country (Figure 1.1). The predominant climate in the park area is classified as Cwa by the Koppen system. The average annual precipitation is around 1200 mm/year, which is typical for areas that show a predominance of oxisols (Isbell, 1978).

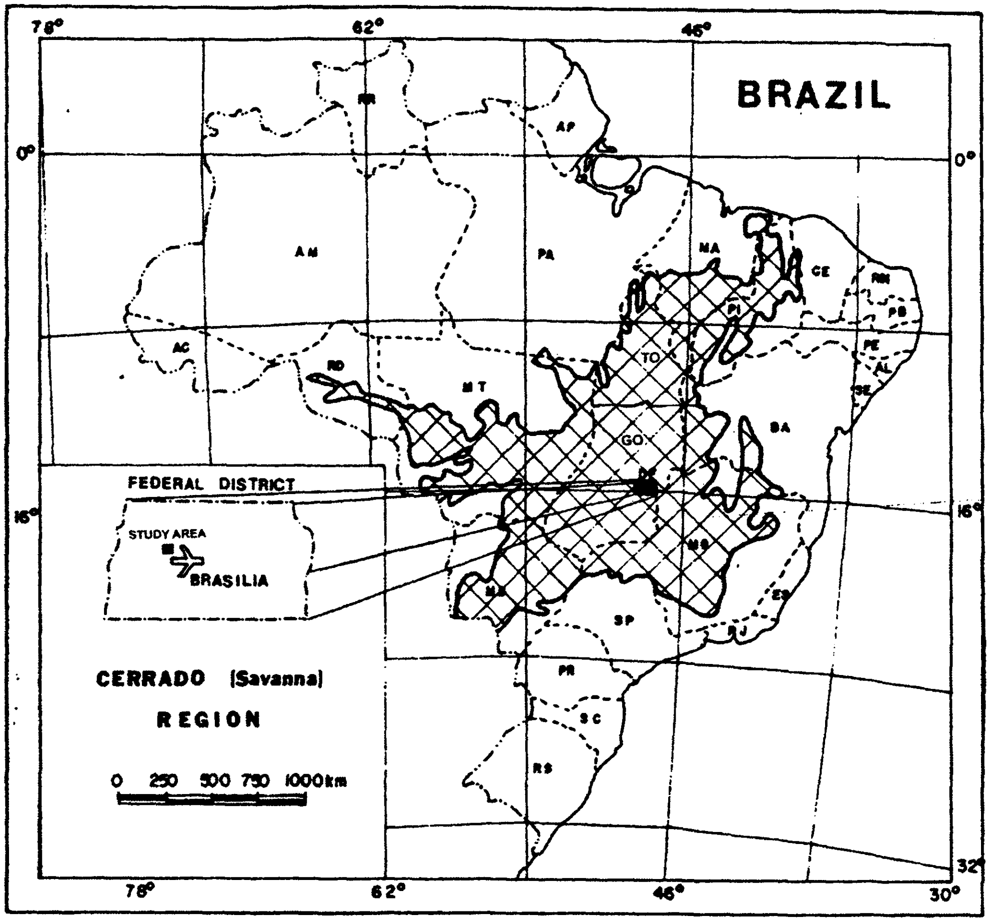


Figure 1.1 - Study area location and distribution of the cerrado (savanna) type of vegetation in Brazil (modified from Macedo and Bryant, 1987).

The Brasília National Park is located near the city's landfill, which has been in activity for over 35 years without any liners to retain the landfill leachate. Workers who are involved in recycling the garbage in the area have started to move into the old areas of the landfill and are establishing a village (Figure 1.2). There is no municipal infrastructure in the area. Therefore, families living in the village obtain their water from domestic wells. Studies developed by the University of Brasília established that while Cd and Pb inside the landfill are potential sources of ground water contamination (Santos, 1996), neither metal was detected in significant concentrations in the landfill plume.

The transport of pollutants in the subsurface is governed by various physical and chemical aspects of the system. These aspects include: the type of contaminant (inorganic or organic) and contaminant speciation, the characteristics of the medium in which the pollutant travels and 'general' chemical conditions (pH, redox etc) of the system of interest.

While passing through a medium, a contaminant may interact with the immobile phase. Because metal ions generally form relatively strong complexes with natural organic matter (NOM), the expectation exists that immobile-phase solids with significant concentrations of organic matter will retard metal-ion transport.

Previous studies have shown that oxisols have a great capacity to sorb, and thereby retard the transport, of toxic metals (Santos, 1996; Araújo, 1996; and Franco, 1996). However, no detailed study has been conducted to identify the soil component(s) that is (are) primarily responsible for the oxisol's sorptive characteristics.

This study

NOM has been reported by several researchers as an important trace metal binding agent, able to compete with oxyhydroxides for metal sorption (Davis and Leckie, 1978; Davis, 1984; Ali and Dzombak, 1996; Nowak and Sigg, 1996). Very little research has

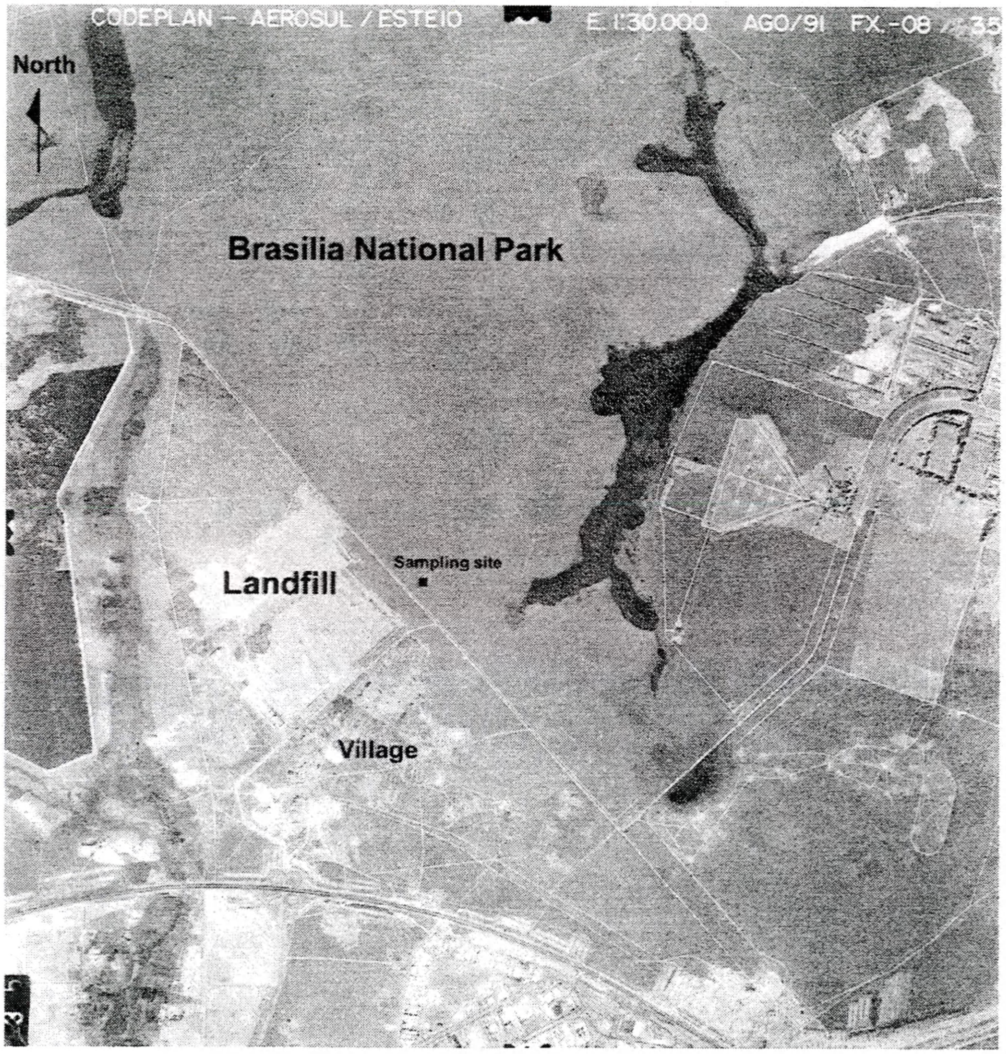


Figure 1.2 – Aerial photograph showing the location of the sampling site, at the border of the Brasília National Park, the landfill, and the village.

been done in natural systems to understand the role of NOM in binding trace metals (Davis et al., 1998) and even more rare are studies of this nature in oxisols. Therefore, this study has as the main goal to explore the role of NOM in the sorption of toxic trace metals to oxisols.

Copper was chosen for this research, as a representative toxic trace metal because of its strong affinity for oxyhydroxides and NOM (Davis, 1984). Considerable research has already been conducted on copper binding to soils (McLaren and Crawford, 1973; McLaren et al., 1983; Cavallaro and McBride; 1978 and 1984; Singh et al., 1988; Xing et al., 1995; Guilherme and Anderson, 1998) providing an ideal framework for evaluating the interaction of Cu with oxisols.

Since isotherm experiments performed at high copper concentrations will almost certainly result in some copper precipitation the term sorption will henceforth be used to refer to all reactions at the soil/solution interface. Sorption is a general term that does not distinguish between precipitation, adsorption and diffusion of copper through the soil or sediment structure (Spostio, 1986; Honeyman and Santschi, 1988). Also NOM in this study will be estimated by the amount of organic carbon measured in soil or extracted from soil. For more detailed calculation of the NOM capacity to sorb copper a conversion from organic carbon to NOM will be made.

The research described here was designed to test the hypothesis that NOM in oxisols does not play a significant role in the sorption of ionic copper. The research also has several related goals.

1- Physical, chemical and mineralogical characterization of the soil profile for the purpose of identification of the main trace metal sorbents and to know how they are arranged in the soil structure.
2- Evalutation of the role of soil NOM in the sorption of copper in different soil profiles by conducting sorption experiments before and after oxidation of soil NOM.

3- Investigation of the influence of the Fe and Al content of NOM on the sorption of copper to soil.

In order to investigate the role of NOM in the sorption of copper to soils, a detailed characterization of the soil medium is necessary. For this purpose a very detailed characterization of a soil profile was made. Then, three specific soil horizons were selected for more detailed studies on soil characterization and copper sorption to these soils.

Not many simple techniques are available to qualitatively estimate the importance of soil components during sorption of trace metals. A common technique is the use of sequential extractions of soil components. Despite the criticism by some researchers of the use of sequential extraction to study the significance of each soil component for metal sorption to sediments or soils (McCarty et al., 1998), it has been shown to be a reliable technique by various researchers (Tessier et al., 1979; Chao and Zhou, 1983; Yong et al., 1993). Sequential extractions of soil components, performed with well characterized soils or sediments, provide important information about the role of specific natural media components in metal adsorption (Griffioen and Broers, 1993).

This study is composed of five chapters that are strongly related to each other, and chapters 2, 3, and 4 are independent research work that can be published separately. This chapter is a presentation of the research background and the motivation for this study. The second chapter contains a characterization of a soil profile six meters deep in terms of chemical, physical and mineralogical composition. The soil profile evaluated was obtained deep inside the Brasília National Park (Figure 1.2). Ten soil horizons were characterized and sampled in the field. After 1) a macroscopic description of the profile was completed and 2) the physical, chemical and mineralogical properties of the clay sized fractions of these horizons were determined, then three soil horizons (A_1, Bw_2, and C_2) were selected for a more detailed analysis of their physical and chemical properties. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were used for characterization of soil structure.

The third chapter describes the results of analyses of Cu binding to representative fractions of the three soil horizons before and after oxidation of the NOM by NaOCl. Copper sorption is evaluated as a function of pH (3 to 6.5) and ionic strength (0.01 and 0.1 M $NaNO_3$). The maximum sorption capacity (Γ_{max}) of the soil for copper was determined as a function of NOM concentration.

The influence of the iron and aluminum on copper sorption by the A_1 oxisol horizon is described in the fourth chapter. NOM is extracted by 0.001 M NaOH and characterized by several analytical techniques, including fractionation into 'humic' and 'fuvic' acids. NOM was also treated with Chelex resins to exchange iron and aluminum and to evaluate the influence of these elements in copper sorption. Then, the influence of iron and aluminum in copper sorption is discussed.

The fifth chapter is a summary of the findings from the previous chapters and provides suggestions for future work in this field.

References

Araújo, R. N. G. 1996. Estudos geoquímicos da contaminação dos recursos hídricos e sua propagação nas adjacências do aterro de resíduos sólidos Jockey Club – D. F. - Master Thesis from Geoscience Institute University of Brasília, Brasília D.F. Brazil.

Aringhieri R., P. Carral., and G. Petruzzelli. 1985. Kinetics of Cu^{+2} and Cd^{+2} adsorption by an Italian soil. *Soil Science* 139 (3):197-205.

Barros, J. G. C. 1993. Caracterização geológica e hidrogeológica do Distrito Federal. In: *Cerrado: Caracterização, Ocupação e Perspectivas*. Edited by Novaes Pinto, M. University of Brasília , Brasília D.F. Brazil.

Bertsch, P. M. and Seaman, J. C. 1999. Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. *Proc. Natl. Acad. Sci. USA* 96:3350-3357.

Cavallaro N., and M. B. McBride. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal* 42:550-556.

Cavallaro N., and M.B. McBride. 1984. Zinc and copper sorption and fixations by an acid soil clay: Effect of selective dissolutions. *Soil Sci. Society of America Journal,* 48:1050-1054.

Chao, T. T. and Liyi Zhou. 1983. Extraction Techniques for Selective Dissolution of Amorphous Iron Oxides from Soils and Sediments. *Soil Science Society of America Journal* 47 (2):225-232.

Davis, J. A. and Leckie, J. O. 1978. Surface ionization and complexation at the oxide/water interface: II. Surface properties of amorphous iron oxyhydroxides and adsorption of metals ions. *Journal of Colloid and Interface Science* 67:90-107.

Davis, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosmochimica Acta* 46:2381-2393.

Davis, J. A. 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica Acta.* 48:679-691.

Davis, J. A.; J. A. Coston; D. B. Kent; C. C. Fuller. 1998. Application of the surface complexation concept to complex mineral assemblages. *Environmental Science and Technology* 32:2820-2828

Franco, H. A. 1996. Geofísica e química aquática aplicadas ao estudo da contaminação de recursos hídricos subterrâneos no aterro do Jockey Club Brasília D.F., Master Thesis Geociense Institute - University of Brasília, Brasília D.F. Brazil.

Griffioen J., H.P. Broers. 1993. Characterization of sediment reactivity: the feasibility of sequential extraction techniques. In *TNO Environmental and Energy Research, Netherlands, edd. TNO Institute of Applied Geoscience.* Delft The Netherlands.

Guilherme, L. R. G., and Anderson, S. J. 1998. Copper sorption kinetics and sorption hysteresis in two oxides-rich soils (oxisols): Effect of phosphate pretreatment. In: Adsorption of Metals by Geomedia edited by Jenne, E. A. Academic Press, San Diego CA.

Honeyman, B. D. and Santschi, P. H. 1988. Metals in aquatic systems. *Environmental Sciences and Technology* 22 (8):862-871.

Isbell, R. F.1978.Characteristics of Tropical and Sub-Tropical Soils. In: *Mineral Nutrition of Legumes in Tropical and Subtropical Soils.* Edited by Andrew, C. S., and Kanprath, E. J., Melbourne, Australia.

Macedo, J. and Bryant, R. B. 1987. Morphology, mineralogy, and genesis of a hydrosequence of oxisols in Brazil. *Soil Science Society of America Journal* 51:690-698.

McCarty, D. K., J. N. Moore, W. A. Marcus. 1998. Mineralogy and trace element in an acid mine drainage iron oxide precipitate; comparison of selective extractions. *Applied Geochemistry* 13:165-176.

McLaren, R. G. and Crawford, D. V. 1973. II. The specific adsorption of copper by soils. *Journal of Soil Science* 24: 443-452.

McLaren, R. G., Williams, J. G., Swift, R. S. 1983. Some observations on the desorption and distribution behavior of copper with soil components. *Journal of Soil Science* 34 325-331.

Nelson, D.M., W. R. Penrose, J. O. Karttunen and P. Mehlhaff. 1995. Effects of dissolved organic carbon on the adsorption properties of plutonium in natural waters. *Environmental Science and Technology* 19:127-131.

Ramos, P. C. M. 1985. Vegetation communities and soils in the National Park of Brasília. Ph.D., in Geography - University of Edinburgh, Edinburgh Scotland.

Santos, P. C. V. 1996. Estudos da contaminação de água subterrânea por percolação de aterro de resíduos sólidos – Caso Jockey Club – D. F. Master thesis. Civil Eng. University of Brasília, Brasília D. F. Brazil.

Schindler, P. and Stumm, W. 1987. The Surface Chemistry of Oxides, Hydroxides and Oxide Minerals. In *Aquatic Surface Chemistry.* Edited by W. Stumm. Wiley-Interscience. New York.

Sparks, D. L. 1995. *Environmental Soil Chemistry.* Academic Press Inc. San Diego CA.

Sposito, G. 1989. The chemistry of soil. Oxford University Press. New York.

Singh J.P., S.P.S. Karwasra, and Mahendra Singh. 1988. Distribution and forms of copper, iron, manganese, and zinc in calcareous soils of India. *Soil Science* 146 (5): 359-366.

Stumm, W and J. Morgan. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters.* 3rd Edition. Wiley Interscience, New York.

Tessier, A., P.G.C. Campbell, M. Bisson. 1979. Sequential extraction procedure for the speciation of particular trace metal. Analytical Chemistry 51 (7):844-851.

Tessier, A., Fortin, D., Belzie, N., DeVitre, R. R. and Leppard, G. G. 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: "narrowing the gap between field and laboratory measurements." *Geochemica et Cosmochimica Acta.* 60 (3): 387-404.

Xing, G. X., Xu, L. Y., and Hou, W. H. 1995. Role of amorphous Fe oxides in controlling retention of heavy metal elements in soils. In *Environmental Impact of Soil Component Interactions – Metals, Other Inorganic, and Microbial activities.* edited by P.M. Huang, J. Berthelin, J.M. Bollag, W.B. McGill, A.L. Page. Vol. II Chapter 6, 63-74.

Yong, R. N., Rosa G. Cloutier, Yuware Phadungchewit. 1993. Selective sequential extraction analysis of heavy-metal retention in soil. *Canadian Geothecnical Journal* 30:843-847.

Zachara, J.M, C.T. Resch, and S.C. Smith. 1994. Influence of humic substances on Co^{2+} sorption by a subsurface mineral separate and its mineralogical components. *Geochimica et Cosmochimica Acta* 58 (2): 553-566.

Chapter 2

CHARACTERIZATION OF CHANGES IN MINERALOGY AND NATURAL ORGANIC MATTER (NOM) IN AN OXISOL PROFILE BY CHEMICAL AND PHYSICAL ANALYSIS, AND BY ELECTRON MICROSCOPY

Abstract

Ten soil horizons, ranging from 20 cm to 590 cm in depth, were sampled from a topographically flat and high area inside of the Brasilia National Park, Brasilia D.F. Brazil. Sections from the soil horizons were characterized for their chemical and mineralogical composition. All soil horizons were classified as Typic Acrustox according to the USDA soil classification system and as Dark Red Latosol by the Brazilian soil classification system. All soil horizons exhibited markedly similar chemical and mineralogical compositions, with the exception of the natural organic matter (NOM) concentration. The percentage of organic carbon varied from 2.3% at the topsoil horizon (A_1) to 0.2% at the deepest horizon ($2C_3$). Three soil horizons (A_1= 20 cm, BW_2 = 197 cm, and C_2 = 540 cm) were chosen to be studied with respect to the influence of NOM on soil properties along the soil profile. Transmission electron microscopy (TEM) was used in this study to describe soil structure and to observe the abundance and physical arrangement of soil NOM among other soil components, before and after NOM extraction. The physical arrangement may lead to occlusion of soil NOM limiting the sites available to sorb metals. Using the concept of aggregate hierarchy (Oades and Water, 1991), TEM results with soil aggregates smaller than 53µm show that soil NOM is not primarly present as mineral coatings, but is part of the soil aggregates in discrete 'pockets'. The NOM soil surface area exposed and available for chemical reactions with metals in solution, on soil samples from the A_1 horizon, was estimated by TEM to be about 15-20% of the total NOM.

Introduction

Oxisols are an extremely weathered type of soil rich in iron and aluminum oxide and hydroxide minerals (oxyhydroxides) and 1:1 clay types (Boul et al., 1980). Oxisols commonly occur in the intertropic countries, and constitute about 30% of the soil area (Boul et al., 1980). In Brazil they represent approximately 40% of the surface soils (Neto et al., 1981). Oxisols are a common type of soil in rainforest and tropical savanna areas from South America and Africa (Charlet, 1986) and are formed in regions where the average rainfall is higher than 1000 mm/yr (Isbell, 1978). Due to the intense weathering processes that this type of soil experiences, most of the permanent-charge types of minerals (clay type 2:1) have already been leached from the soil matrix. The remaining predominant types of minerals exhibit variable surface charge (kaolinite, aluminum and iron oxyhydroxides) and organic matter contents. As a consequence of the intense leaching, oxisols are also nutrient-poor (Jacomine, 1969; Charlet, 1986). In addition, a typical oxisol does not show significant variation in chemical and mineralogical composition with depth (Jacomine, 1969; Van Raij, 1971; Souza, 1979; Macedo and Bryant, 1987), with the exception of variations in soil organic matter.

Natural organic matter (NOM) in soil systems is widely known to play an important role in regulating physical and chemical soil properties. Examples of the contributions of NOM to soil properties include buffer capacity, metal binding capacity, sorption of hydrophobic organic compounds, stability of soil particle aggregates, and water-holding capacity (Wershaw, 1993). The quantity of NOM in soil profiles is usually greatest in the upper layers and decreases with depth (Thurman, 1985). The greater concentration of NOM in the top layer is due to the abundance of plants in the surficial soil zone. Plants are the primary source of organic matter for NOM genesis. NOM plays an important role in oxisol fertility because it is the soil component that contributes most to the soil C.E.C.. The importance of NOM in soils is also directly related to its considerable ability to complex ions in solution and to sorb to mineral surfaces (Davis and Leckie 1978; Tisdall and Oades, 1982). The ability of NOM to chemically react in a soil system will depend on the availability of NOM functional groups to react with ions in solution, and on the physical exposure of these NOM functional groups to the soil/solution interface. With few exceptions (Vrdoljak, 1998; this study) little work has been done on understanding the physical arrangement of NOM in a soil with respect to the availability of NOM for binding metal ions.

Previous studies of oxisol micromorphology have found its most characteristic feature to be a strong microped structure (Stoops and Buol 1985) of sand or silt size aggregates. Oxisols contain practically no weatherable minerals in the coarse fraction (they have been removed by the intense leaching). The coarse fraction of an oxisol typically is composed predominantly of sand- or silt size quartz, rutile, magnetite and anatase minerals (Stoops and Buol, 1985). The micromorphology of oxisols has seldom been investigated (Stoops *et al.,* 1994) and then the emphasis has been on weathering and laterite formation; studies of the morphology of the A horizon of oxisols have rarely been published.

Transmission electron microscopy (TEM) is the method of choice for the analysis of soil structure because it provides high resolution for the imaging of soil materials ranging in size from 10 μm to below 1 nm (FitzPatrick,1993; Vrdoljak, 1998). Furthermore, techniques for the stabilization and identification of organic components in soils using TEM have been established by Foster and Martin (1981). Typically, oxisol structure is examined by concentrating on the less than 53 μm diameter aggregates because previous studies (Oades and Waters, 1991; Vrdoljak 1998) suggest that this fraction is representative of other stages in the aggregation hierarchy of oxisols. Cytochemical techniques are used to locate organic matter; electron diffraction is used to identify minerals.

This study has three objectives:

1. To conduct a physical, chemical and mineralogical characterization of an entire oxisol profile. Based on this analysis, three soil horizons were selected to observe the influence of soil NOM on soil physical and chemical properties.

2. To investigate, by TEM, the geometrical arrangement of NOM among other soil components in the three selected horizons. From this arrangement we can estimate the fraction of the soil NOM that is exposed for metal sorption from solution.
3. To characterize the soil structural changes after NOM removal from the topsoil horizon by NaOCl oxidation of the organic material, using the TEM technique.

Material and Methods

A series of chemical techniques was used for extraction and oxidation of soil NOM as well as for chemical characterization of soil samples. All experiments were conducted using reagent chemicals that meet or exceed the latest American Chemical Society (ACS) specifications for reagent grade chemicals. All solutions were made with Nanopure™ water.

All glassware used was first submersed in an acid bath (2% HNO_3) for a minimum period of 24 hours, followed by a triple rinse with de-ionized water and submersion in a Nanopure water bath. The glassware was then dried before use.

Soil Sampling:

For the purpose of this study, soil samples were collected from a soil profile located in an undisturbed, flat and very well drained soil area inside the Brasília National Park. A trench six meters deep was made for the development of soil horizon morphological description, identification, and sampling (Table 2.1). Ten soil horizons were described in the field and further characterized by their physical size, and chemical and mineralogical compositions (Tables 2.2 and 2.3). The soil horizons at the site were highly similar with respect to texture and color.

Composite soil samples from each horizon were sieved into fractions smaller than 2 mm and air-dried. Then sub-samples were selected for further physical, chemical and mineralogical analysis.

Table 2.1 - Morphological description of an oxisol profile in the Brasilia National Park – Brasília D.F. – Brazil.

Horizon	*Depth* (*cm*)	*Color* (*moist*)	*Soil Texture*
A_1	0 - 19	2.5 YR 4/4	Very fine granular
AB	19 - 47	2.5 YR 4/8	Very fine granular and fine granular
BA	47 - 73	2.5 YR 4/7	Very fine granular and fine granular
Bw_1	73 - 117	2.5 YR 4/7	Very fine and medium granular
Bw_2	117- 97	2.5 YR 4/6	Fine and medium granular
Bw_3	197-263	2.5 YR 4/4	Very fine granular
BC	263-350	2.5 YR 4/7	Heavy clay
C_1	350-480	1.0 YR 4/6	Heavy clay
C_2	480-540	10R 4/6	Heavy clay
$2C_3$	540-590	2.5 YR 4/4	Heavy clay

Soil physical and chemical characterization

The physical characterization of the air-dried soil samples was carried out in the Brazilian soil research institution (EMBRAPA) in Brasília D.F. Brazil. Particle size analysis was made by the pipette method (Forsythe, 1975) prior to breakdown of soil particles by 0.1 N sodium hydroxide. The degree of dispersion test (Table 2.3) provides an estimate of the percentage of clay that can be dispersed in water in relation to the total clay composition of the soil. This estimate indicates the fraction of clay that is dispersed; in other words, it indicates the degree of physical stability of these soil aggregates (EMBRAPA, 1997).

Soil chemical characterization was carried out at both EMBRAPA and the Colorado School of Mines (Table 2.2). The percentages of silica, aluminum, iron and titanium oxides were estimated by the digestion of 1 gram of soil sample in concentrated sulfuric acid diluted 1:1 with Nanopure™ water (EMBRAPA, 1997). This acid digestion procedure dissolves amorphous and poorly crystallized material but not pure crystalline phases.

After a half-hour digestion on a hot plate, with no evaporation, the soil solution was filtered and the remaining soil was analyzed for silica. The solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP – AES) (Thermo Jarrel Ash – model IRIS/AP) for aluminum, iron, and titanium. Soil residue that did not pass through the filter was dissolved by sodium hydroxide followed by the addition of ammonium molybdate, tartaric acid, and ascorbic acid solutions (Duriez, 1974). One aliquot of the final solution was analyzed for silica using the spectrophotometer at an absorbance wavelength of 695 nm. The cation exchange capacity (CEC) was estimated using ammonium acetate solution at pH 7 (Vettori, 1969). Soil pH was measured in water and 1N KCl solution at a soil: solution ratio of 1:2.5. The soil organic carbon percentage was estimated on a mass basis using a combustion method with coulometric detection of evolved CO_2 (UIC-Coulometric Model 5011 coulometer). This equipment is used to burn

Table 2.2 - Chemical characterization of the Typic Acrustox (oxisol) soil profile sampled in Brazil:

Horizon	*Depth (cm)*	*Al_2O_3 (%)*	*SiO_2 (%)*	*Fe_2O_3 (%)*	*TiO^*_2 (%)*	*Total** (%)*	*Org. Carbon (%)*	*C.E.C.$^+$ cmol/Kg*	*pH H_2O (1:2.5)*	*pH KCl (1:2.5)*
A_1	19	10.0	22.6	11.3	0.98	44.8	2.32	7.51	5.1	4.0
AB	47	11.0	24.4	11.1	0.96	47.5	1.87	5.39	5.3	4.2
BA	73	10.8	24.9	12.6	1.10	49.4	1.23	3.10	5.6	4.8
BW_1	117	9.5	24.6	12.0	1.10	47.2	1.02	3.04	5.4	5.2
BW_2	197	10.5	23.8	11.4	0.99	46.7	0.84	2.30	5.5	5.6
BW_3	263	8.6	24.6	11.6	1.06	45.9	0.70	1.45	5.6	6.1
BC	350	10.2	26.0	12.7	1.24	50.1	0.61	1.20	5.7	6.3
C_1	480	10.6	26.0	13.3	1.20	51.1	0.40	0.88	5.7	6.5
C_2	540	11.2	23.8	11.2	1.04	47.2	0.35	0.84	5.7	6.3
$2C_3$	590	10.6	16.2	12.6	0.80	40.2	0.23	0.59	5.8	6.9

+ C.E.C. = Cation Exchange Capacity

* Percentage of oxides extracted by soil dissolution by H_2SO_4.

** Total percentage of oxides extracted by soil dissolution by H_2SO_4.

Table 2.3 - Physical characterization of the Typic Acrustox (oxisol) soil profile.

Horizon	*Depth (cm)*	*Coarse Sand $g.kg^{-1}$*	*Fine Sand $g.kg^{-1}$*	*Silt $g.kg^{-1}$*	*Clay $g.kg^{-1}$*	*Total air dry soil < 2mm $g.kg^{-1}$*	*Degree of dispersion (%)*
A_1	19	100	210	100	590	1000	42
AB	47	90	210	80	620	1000	31
BA	73	80	200	70	650	1000	29
BW_1	117	70	200	70	660	1000	36
BW_2	197	60	260	50	630	1000	100
BW_3	263	60	240	70	630	1000	100
BC	350	50	200	60	690	1000	94
C_1	480	50	170	40	740	1000	100
C_2	540	60	250	40	650	1000	98
$2C_3$	590	270	200	40	490	1000	100

the soil sample at 910°C causing combustion of organic and inorganic carbon. The CO_2 produced is auto-titrated in a coulometer cell containing monoethanolamine as an indicator. Monoethanolamine plus CO_2 forms a titrable acid (hydroxyethylcarbamic acid) and causes the color in the cell to fade. A platinum cathode and silver anode is positioned in the cell and the assembly is positioned between a light source and a photodetector. As the coulometric titration proceeds, a change in cell solution color is registered by the photodetector and converted to mass of organic carbon. Each soil sample was analyzed in triplicate. The method for these analyses was obtained from the coulometer manual.

Soil characterization of the three horizons chosen to be studied in detail

Considerable similarity among the soil samples was observed during the soil characterization described above (Tables 2.2 and 2.3). Such consistency has been reported by other researchers (Van Raij and Peech, 1972; Macedo and Bryant, 1987; Santos et al., 1989; Fontes and Weed, 1991). To further evaluate the soil profiles in more detail, three soil horizons (A_1, BW_2, and C_2) were selected for extensive analysis. The following soil characterization techniques were applied only to samples from these soil horizons.

Soil XRD analysis

Clay and soil fractions smaller than 2.0 mm were analyzed by x-ray diffraction (XRD). Each mineral has a different ability to sorb metals; therefore, the identification of the whole suite of soil minerals is the first step in evaluating the soil potential for sorbing metals. Before the XRD analysis, the three soil horizons selected for this study had their clay fraction separated through centrifugation, after physical breakdown of soil aggregates. Soil and clay samples were ground in a porcelain mortar and pestle prior to XRD analysis on a Scintag X-1 diffractometer. Using a sample spinner, randomly oriented powder samples were subjected to Cu α radiation (45 kV, 35 mA). Sample parameters were as follows: scan range from 4° to 62° 2θ; step size of 0.02; and counting time of one second. The relative intensity of the diffracted peaks was used to estimate the relative abundance of the different minerals in the soil and clay samples (Table 2.4). This estimation was possible with the use of the software JADE + with s/m version 3.1 in conjunction with reference intensity ratios (RIR) of the phases present. X-ray analyses were made before and after soil treatment with sodium hypochlorite (NaOCl - 5% vol.) and ammonium oxalate, at pH 3 in the dark, to document changes in the crystalline soil phases as a result of chemical treatments (Figures 2.1, 2.2, and 2.3).

Extraction of non-crystalline material in soil by ammonium oxalate

Chemical extraction of noncrystalline or amorphous material in soil samples followed the procedure of Shwertmann (1964). Amorphous material may play an important role in metal sorption to soil due to its high specific surface area. Prior to the oxalate extraction, soil NOM was partially oxidized by a series of four treatments with NaOCl (5% vol.) at pH 9.5 (in 50 ml plastic centrifuge test tubes). The samples were subsequently oven dried at 110°C for 24 hours. Two 0.175 subsamples of the soil were put in 50 ml plastic centrifuge tubes, which were wrapped in aluminum foil, and mixed with 25 ml of 0.2 M ammonium oxalate at pH 3. The plastic centrifuge tubes were sonicated for 1 hour in a water bath to disaggregate soil particles. They were then gently shaken for 2 hours and subsequently centrifuged at 2,500 rpm (Fisher Scientific Marathon^{TM} model 12KBR) for 15 minutes.

The supernatant was saved for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Perkin Elmer model Optima 3000) of the extracted iron and aluminum. Table 2.4 presents the results of the extraction and provides the ratio of contribution of non-crystalline phases to the total soil mass.

Soil point of zero salt effect (pH_{pzse}) titration.

Evaluation of the soil point zero of charge (pH_{pzc}) was made by the point of zero salt effect (pH_{pzse}) titration method. As Sposito (1989) points out, the pH_{pzc} corresponds to the

pH_{pzse} when no constant-charge minerals are present. It is an important soil parameter for the interpretation of metal or organic matter sorption to soil.

Prior to the soil titration, soil samples were pretreated with lithium perchlorate to replace exchangeable cations (Charlet, 1986). Ten grams of dry soil were mixed with 42.86 ml of 0.5 M $LiClO_4$ at pH 6. The soil solution was stirred gently for 10 minutes and left to settle for 2 hours and fifteen minutes to allow the reaction to occur and to separate solid and liquid phases by settling. At this point, the supernatant liquid was carefully collected using a 20-ml glass pipette. The washing/settling/pipetting steps were repeated, producing a soil sample for which all exchangeable cations had been replaced by lithium.

Further preparation of the soil subsamples for the salt titration consisted of replacing the lithium with sodium through two 'washing' cycles (Charlet, 1986). In the first cycle, a solution of 0.5 M NaCl at pH 6 was mixed with soil at a ratio of 7 g of soil per 30 ml of solution, and stirred for 10 minutes, and then centrifuged at 2500 rpm for 10 minutes. The supernatant liquid was discarded and the washing and phase separation was repeated. In the second cycle, a solution of 0.01 M NaCl at pH 5.0 was applied, as described above, to reduce the salt concentration of the soil interstitial volume. The salt solution had a pH

Table 2.4 - Soil chemical, mineralogical and physical characterization of selected horizons from a Typic Acrustox (oxisol) profile.

Soil horizon:	A_1	Bw_2	C_2
Soil % Weight			
% Fe	7.4	7.7	7.9
(duplicate)	7.6	7.9	8.5
% Al	15.4	16.2	16.3
(duplicate)	16.2	17.2	16.9
% Organic C	2.32 (±0.01)	0.84 (±0.003)	0.35 (±0.003)
Soil Mineralogy*			
< 2.0mm	Q>K>G>H>A	K>Q>G>H>A	K>G>Q>H>A
Clay fraction	K>G>H	K>G>H	K>G>H
Amorphous Material**			
Fe (g/Kg)	2.0	1.1	0.7
(duplicate)	1.6	1.2	0.7
Al (g/Kg)	2.8	2.8	1.5
(duplicate)	3.4	2.8	2.1
P.Z.S.E.***	4.7	5.4	5.6
Surface Area (m^2/g)****			
Before	94.3 (±1.3)	118.6 (±2.3)	94.8 (±0.75)
After	114.8 (±0.1)	116.6 (±5.4)	94.9 (±1.9)

*Mineralogy: Q = Quartz, K = Kaolinite, G = Gibbsite, H = Hematite, A = Anatase.

**Amorphous material: Ammonium Oxalate at pH = 3.0 in the dark (Schwertmann, 1964).

***P.Z.S.E. = Point of Zero Salt Effect.

****Surface Area: B.E. T. method before and after soil treatment with NaOCl (5% vol.).

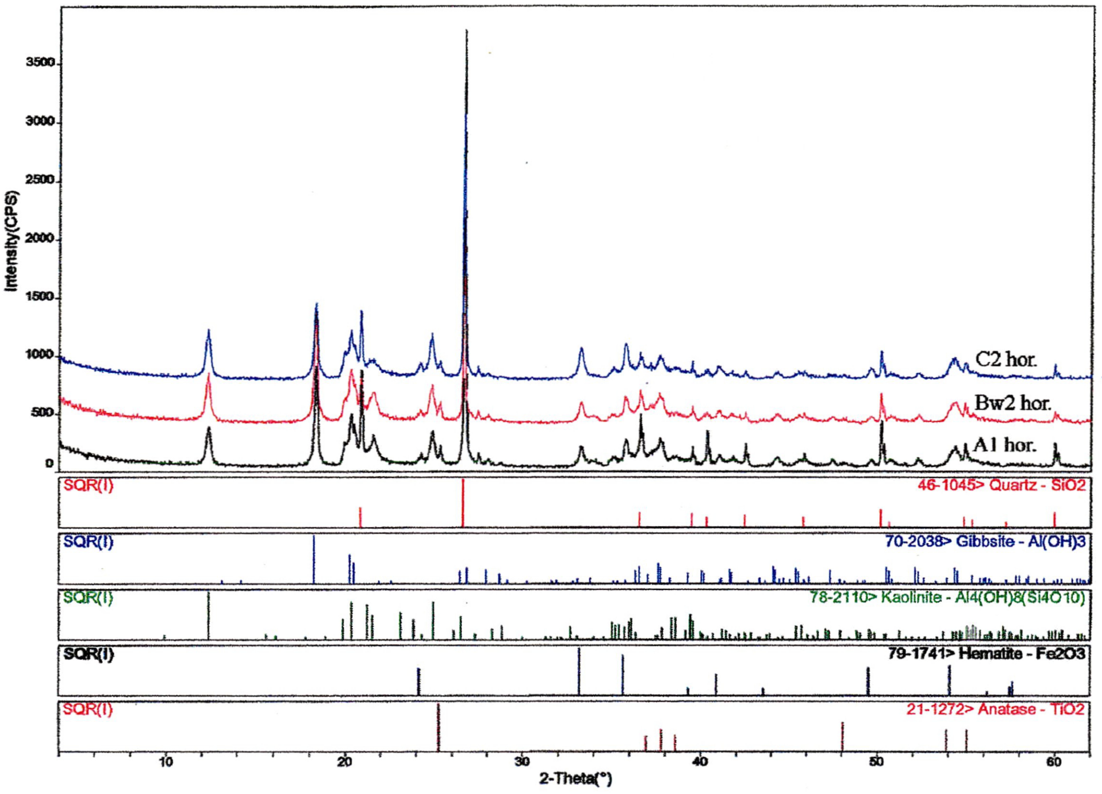


Figure 2.1 - X-ray diffraction of soil from untreated soil horizons. Colors: Black = A_1 horizon, Red = Bw_2 horizon, Blue = C_2 horizon. Diffractogram peaks overlay each other indicating the same soil mineralogy among the three soil horizons.

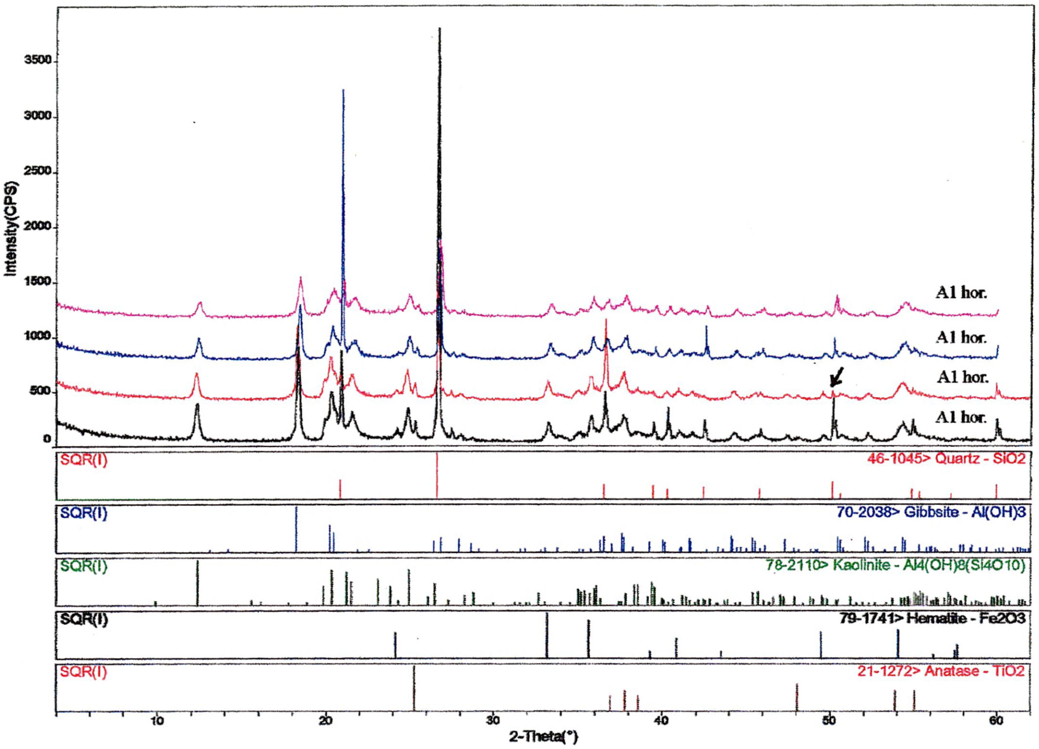


Figure 2.2- X-ray diffraction of soil from A_1 horizon before and after soil NOM oxidation and amorphous material extraction. Colors (from bottom to top) = Black (untreated soil), Red = (after NaOCl), and Blue and Purple = (after NH_4 Oxalate). The overlay of diffractogram peaks suggests that there was no change in soil mineralogy with the exception of some quartz dissolution after NaOCl treatment, indicated by the arrow.

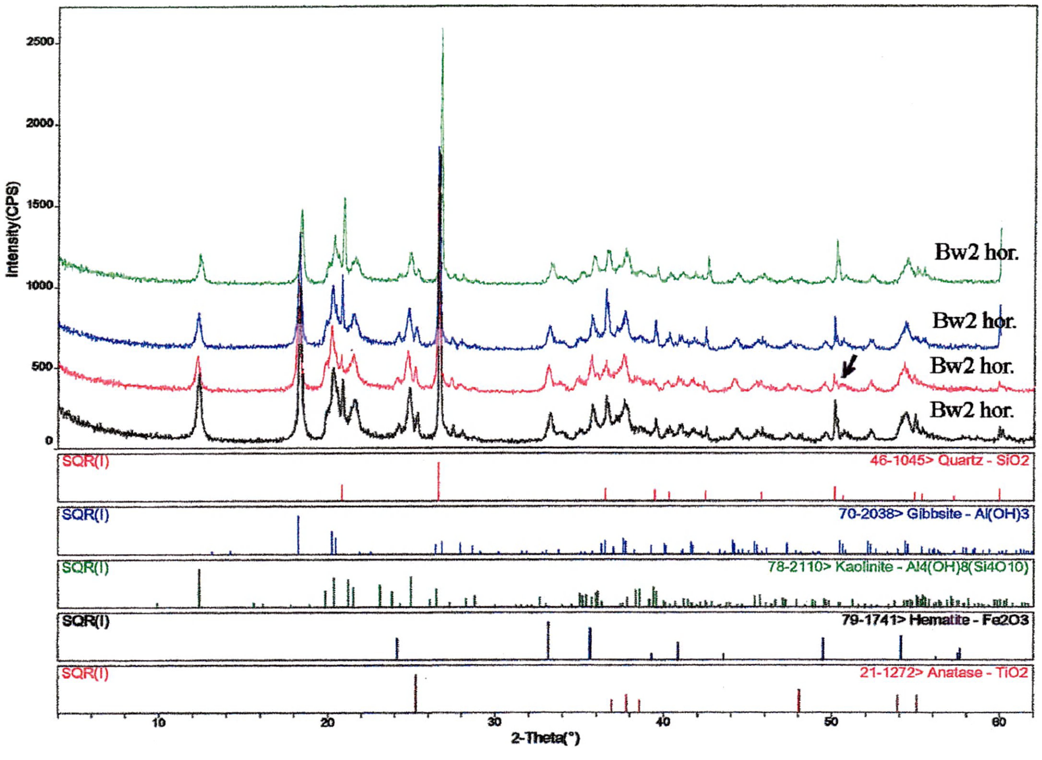


Figure 2.3- X-ray diffraction of soil from Bw_2 horizon before and after soil NOM oxidation and amorphous material extraction. Colors (from bottom to top) = Black (untreated soil), Red = (after NaOCl), and Blue and Green = (after NH_4 Oxalate). Difractogram peaks overlay suggests that there is no change in mineralogy after soil treatment, with the exception of some quartz dissolution after NaOCl treatment, indicated by the arrow.

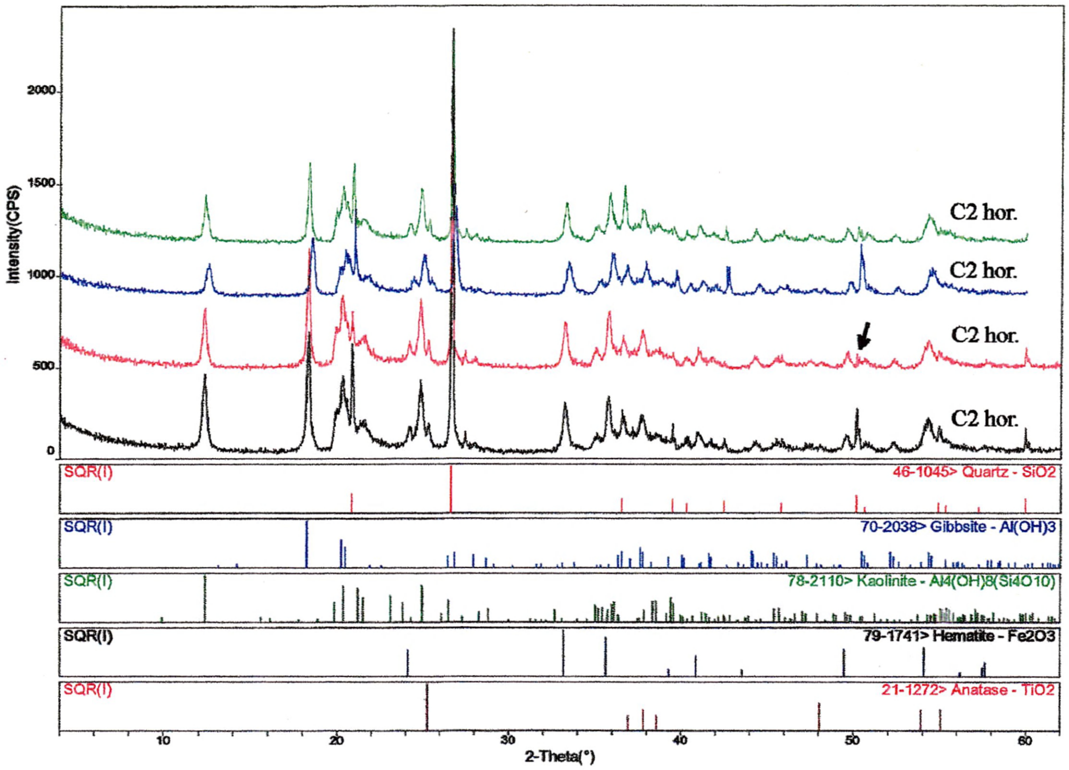


Figure 2.4- X-ray diffraction of soil from C_2 horizon before and after soil NOM oxidation and amorphous material extraction. Colors (from bottom to top) = Black (untreated soil), Red = (after NaOCl), and Blue and Green = (after NH_4 Oxalate). Overlay of diffractogram peaks suggests no change in soil mineralogy, with the exception of some quartz dissolution after NaOCl treatment, indicated by the arrow.

between 5.0 and 6.0 to avoid dissolution of any clay mineral or oxyhydroxides (Charlet, 1986; Shorter, 1993).

Three subsamples of less than one gram of the paste, produced from the operation above, were put in porcelain crucibles and then weighed to one milligram precision. The crucibles were then put into an oven at 110°C and the crucible weight was periodically measured over a 24 hour period. At this point, the soil moisture content was calculated. Knowing the soil moisture content, a soil paste was mixed with 0.001 M NaCl solution with a ratio of dry soil:solution of 1:100. The soil solution was placed in a 50 ml, jacketed, borosilicate glass titration cell (Wheaton) which had ports for the introduction of a pH electrode and an N_2 line. The cell temperature was regulated at 25°C ± 0.1°C using a VWR Scientific (Model 1141) circulating water bath.

The slurry pH was adjusted to a set pH through the addition of 0.1 M HCl. The ionic strength of the slurry was altered through addition of NaCl to increase the solution ionic strength by multiples of ten, from 0.001 M to 0.01 M, 0.01 to 0.1, and so on. Changes in pH during the 'jumps' in ionic strength were recorded. The procedure was repeated for selected pH values and the data set was plotted as ΔpH versus pH for the series of ionic strength values. The point of zero salt effect is the pH at which the $\Delta\text{pH} \approx 0$ for all solution ionic strength values. Each salt titration point was obtained in duplicate. The results for the PZSE analyses of the three horizons are listed on Table 2.4.

Total soil digestion by strong acids.

Total soil digestion by strong acids was performed using concentrated HNO_3, $HClO_4$ (70%), and HF (49%). To estimate the efficiency of this method to dissolve all the aluminum and iron present in the soil samples, three different masses of soil (0.1g, 0.25g, and 0.50g) were used for digestion. The method used for this soil digestion (Briggs, 1990) was obtained from the Quality Assurance Manual for the Branch of Geochemistry at the United States Geological Service (U.S.G.S.). The digested soil samples were analyzed with a Perkin Elmer model Optima 3000 - ICP-AES. The concentration of aluminum and iron in mg/l was plotted as a function of mass of soil, to verify the digestion efficiency (Figure 2.5).

Soil NOM removal by different extractants

Soil NOM was extracted by the following 'extractants': water at pH 5-11, sodium hydroxide (0.5 M NaOH at pH 13.7 and 55°C), sodium pyrophosphate ($Na_4P_2O_7$) at pH 9, sodium hypochlorite (NaOCl 5% by volume; pH 9.0), and hydrogen peroxide (H_2O_2 10%, 20%, and 30% by volume).

Water extraction at different pH's. The soil solution, composed of ten grams of soil (< 2 mm) and 200 ml solution at a specific pH (5, 7, 8, 9, 11 or 13.7), was gently shaken for 24 hours. The soil solution pH was occasionally adjusted with the addition of small amounts of 0.1 M NaOH. The soil slurry was centrifuged at 2500 rpm for 15 minutes and the supernatant liquid was carefully collected using a 20 ml glass pipette; the solution was immediately passed through a 0.45 μm filter. The filtrate was pH-adjusted to close to neutral by the addition of concentrated HNO_3 to minimize hydrolysis of NOM functional groups such as esters (Bowles et al., 1989). The soil and NOM samples were refrigerated at 4°C until further use.

Subsets of the NOM-enriched solutions were pH-adjusted to 4. Then the NOM was analyzed for total carbon concentration using a Shimadzu TOC 500. Before each analysis, each sample was bubbled with N_2 gas for a few minutes to purge CO_2. For the pH = 13.7 (0.5 M NaOH) extraction, there was no pH adjustment required during extraction, and the soil slurry was held at 55°C for 48 hours instead of 24 hours at room temperature.

Sodium pyrophosphate. Soil NOM extraction by sodium pyrophosphate at pH 9.0 was made using 200 ml of 0.1 M $Na_4P_2O_7$ mixed with ten grams of soil and shaken for 62

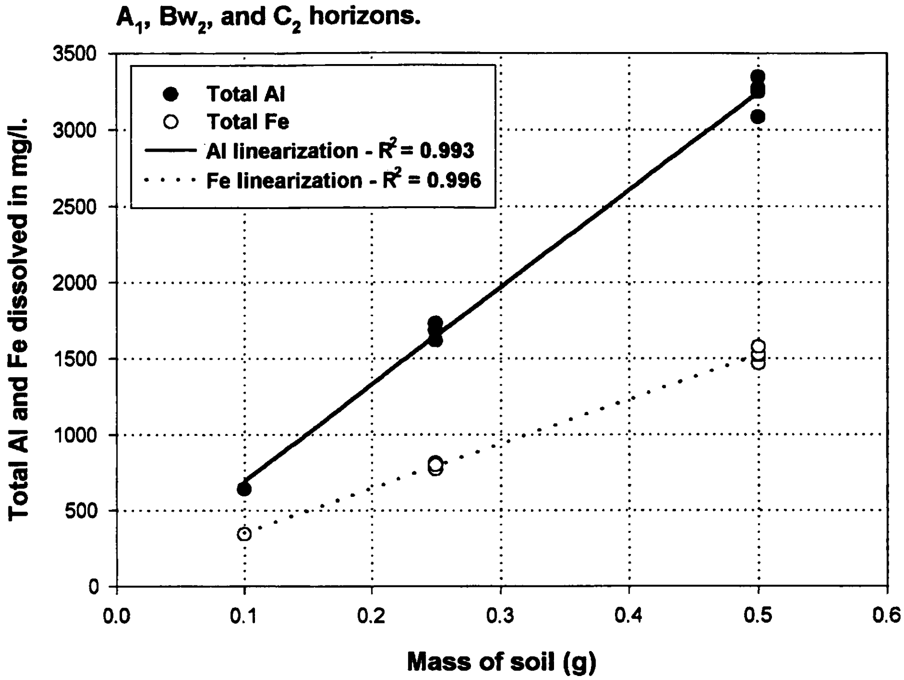


Figure 2.5- Total soil digestion plotted as mg/l of Fe and Al versus mass of soil.

hours. The soil solution pH was constantly adjusted by the addition of 0.1 M HCl. Subsequent steps were identical to those described above for the leaching of NOM by basic solutions.

Sodium hypochlorite. For NOM extraction by sodium hypochlorite the method of Papp et al. (1991) was used. One gram of soil was mixed with six milliliters of 5% NaOCl solution adjusted to pH 9.5 with 6N HCl prior to use. The soil solution was then put into a boiling water bath for 15 minutes. The soil solution was transferred to a centrifuge and spun at 2500 rpm for 15 minutes. The supernatant liquid was passed through a 0.45 μm filter and acidified by a solution of 1% by volume of concentrated HNO_3. The filtrate was analyzed for its elemental composition by Perkin Elmer model Optima 3000 - ICP-AES (data not shown).

This extraction procedure was repeated four times. At the conclusion of the washing step, an acid solution of HCl at pH 2 was added to the remaining soil and the mixture was shaken for few minutes to return the soil pH to near its initial pH value of 5.0. Sub-samples of the soil paste were dried in an oven at 110°C for 24 hours. These samples were analyzed for total carbon content as described above.

Hydrogen peroxide. Hydrogen peroxide oxidation of the soil NOM was attempted using 10%, 20% and 30% by volume hydrogen peroxide. Two grams of soil were mixed with 40 ml of H_2O_2 at different concentrations and gently shaken for 66 hours. Then the soil solution was centrifuged at 2500 rpm for 15 minutes. The supernatant liquid was discarded and sub-samples of the soil paste were dried in the oven at 110°C for 24 hrs. Then, the dried samples received the same treatments as the samples that were oxidized by NaOCl.

The results for all extractions and oxidations of the soil NOM by the different techniques are listed in Table 5.

Soil specific surface area (SA)

Specific surface areas of the soil subsamples were measured by the BET isotherm method using a Micromeritics Flow Sorb II 2300. This instrument is capable of the 'single point method'; its use range is 0.1 to 300 m^2/g. This method is based on the absorbency of a gas mixture (30% N_2 and 70% He) at one gas specific partial pressure (10 lb/in^2), forming one molecular monolayer of the gas on the surface of the adsorbent. The method used for the analysis is in the instrument manual. Soil specific surface areas, before and after NOM removal, are listed in Table 2.4.

Soil TEM and SEM analysis

TEM images were acquired for soil samples from the A_1, Bw_2, and C_2 horizons before NaOCl treatment, and for the A_1 horizon after treatment. Instruments used were JEOL S100, Philips 301, and JEOL 200CX. Soil sample preparation and sample analysis were done in the Electron Microscopy Laboratory at the University of California in Berkeley by the method described by Vrdoljak (1998). Scanning electron microscopy (SEM) was done for one sample from the A_1 horizon using a Hitachi S5000, also at the University of California in Berkeley. Dr. Vrodoljak kindly made all the TEM and SEM pictures presented in this chapter

Sample preparation

TEM: Aggregates less then 53 μm in diameter obtained by dry sieving were and transferred into a warm 2% agar solution. The agar with the aggregates was refrigerated overnight to gel. After solidification in agar, the samples were trimmed to approximately 1-3 mm-sized cubes for processing. The soil cubes were fixed in a 2% glutaraldehyde solution with a 0.1.M sodium cacodylate buffer at pH 7.2 (from this point on referred to only as buffer) for 1-2 hours with gentle rocking agitation. The soils were then rinsed three times for fifteen minutes in the buffer. Post fixation staining was done with 1% OsO_3 in the buffer for 1-2 hours. Samples were rinsed in the buffer three times for 5 minutes with agitation, and then rinsed three times for 10 minutes in distilled water. The samples were stained overnight at 4° C in the dark with 0.5% aqueous uranyl acetate, and then rinsed 15 minutes three times with distilled water. Samples were dehydrated by rinsing for 10 minutes with increasing concentrations of acetone:water mixtures (35%, 50%, 70%, 80%, 95%, 100% and 100%). After dehydration, the samples were infiltrated with Spurr's epoxy resin (Spurr, 1969) and acetone mixtures. Acetone:resin mixtures of 2:1, 1:1, and 1:2 were rinsed with the samples successively for 1 hour each. The samples were then rinsed with pure resin for 1 hour, and again overnight. An accelerator was added to the resin and the samples were rinsed with resin plus accelerator for 1-2 hours. Finally, the samples were placed into beam capsule molds with accelerator and resin and left for 2 days at 60° C to harden.

After curing, the samples were trimmed and ultrathin sections (> 60 nm) were prepared on a Sorval MT-6000-XL microtome utilizing diamond knifes with a cutting speed of 0.1 mm/sec. Sections were deposited onto copper or nylon TEM grids coated with a support film of formvar and carbon for ultimate use in the transmission electron microscope. Coated grids were made in the laboratory because those ordered from suppliers often contain contaminants.

SEM: SEM images were taken using a Hitachi S-5000 SEM. Randon aggregates were taken for SEM analysis. The aggregates were 'fixed' using a 2% glutaraldehyde in a 0.1M Sodium cacodylate buffer at pH 7.2 for 1-2 hours. The samples were rinsed with buffer three times for 15 min each time. After rinsing, the soil aggregates were again fixed with 1% OsO_3 in 0.1 M sodium cacodylate buffer at pH 7.2 for 1-2 hours. The aggregates again were rinsed in buffer three times for 5 minutes per rinse.

After the rinsing and fixation steps, the aggregates were dehydrated by washing with solution of increasing ethanol:water ratios: 35, 50, 70, 80, 95, 100 and 100% ethanol washes were used for 10 minutes at each step. The samples were then critical-point dried to replace the ethanol with CO_2. Specimens were mounted using carbon conductive tape onto SEM sample holders. The samples were then sputter coated with 30 nm of Au-Pd. After desiccating overnight, the samples were viewed at 10 KV in the SEM.

Results and Discussion

Soil characterization of the 10 soil horizons

The ten soil horizons classified in the field had markedly similar color and soil texture (Table 2.1). The reddish hues (2.5 YR) indicate an oxidizing environment and are typical for Typic Acrustox (USDA classification) or Dark Red Latosols (DRL) (Brazilian classification) (Mothci, 1977; Macedo and Bryant, 1987). The soil profile homogeneity is a consequence of the long period of weathering that these soils have undergone.

The annual precipitation in average is approximately 1500 mm, and the soil is located in a landscape classified as "neogenic chapada" which is related to a weathering process from the Pliopleistocene (Novaes, 1993) (Figure 2.6). Laterization is the geochemical process most responsible for the development of oxisols (Souza, 1979); it is caused by an intense weathering of the initial rock formation. During this process, dissolution of silica results in the leaching of Ca, Mg, K, and Na from the parent rock; consequently there is a depletion of these elements in the forming soils. As the laterization of the bed rock formation develops, secondary minerals are formed in the general sequence: kaolinite, gibbsite and metal oxides. Souza (1979) distinguishes between two types of oxisols: one rich in kaolinite and which is less leached, and the other rich in gibbsite and more leached in soil nutrients (Ca, Mg, K, Na). The pedon evaluated for this work is classified as a kaolinitic type of oxisol.

The soil profile texture and color homogeneity (Table 2.1) are reflected in the soil profile chemical and physical characterization (Tables 2.2 and 2.3). The percentage of aluminum, iron, titanium oxides and silica is constant along the soil profile (Table 2.2) as is the soil mineralogy. The order of mineral dominance is kaolinite > gibbsite > hematite > anatase. This percentage of minerals from the 50% H_2SO_4 dgestion is operationally

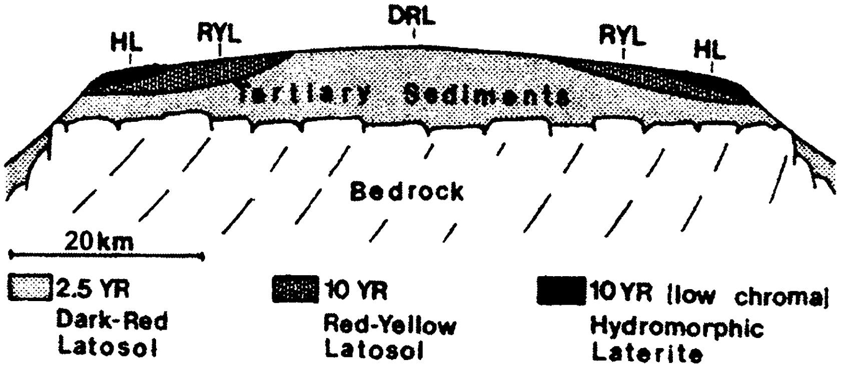


Figure 2.6 - Cross section of the landscape where the pedon was classified and the soil types nearby. DRL = Dark Red Latosol, RYL = Red Yellow Latosol, and Hydromorphic Laterite (modified from Macedo and Bryan, 1987).

defined as the percentage of diagenic clay-sized minerals (EMBRAPA, 1997). The sum of all percentages is relatively constant along the soil profile and is in the range of 45% to 51% (Table 2.2), which correlates to the percentage of poorly-crystalline minerals (size <0.05 μm) observed in TEM pictures (q.v.). This fraction of minerals is not amorphous, as can be seen quite well in the TEM pictures.

A direct relationship is observed between the percentage of organic carbon in the soil isolates and the soil cation exchange capacity (Figure 2.7). This correlation suggests the dominant role of soil organic matter in contributing to the soil cation exchange (Jacomine, 1969; Van Raij and Peech, 1972; Motchi, 1977). The values of CEC obtained in this study are within the range of CEC values expected for this category of soils inside the National Park (Ramos, 1995).

The soil pH was measured with soil isolates suspended in water or in 1N KCl solution. The difference in the pH values between the water pH and the 0.1 M KCl pH was negative for the top four horizons and positive for the lower horizons. The sign of the

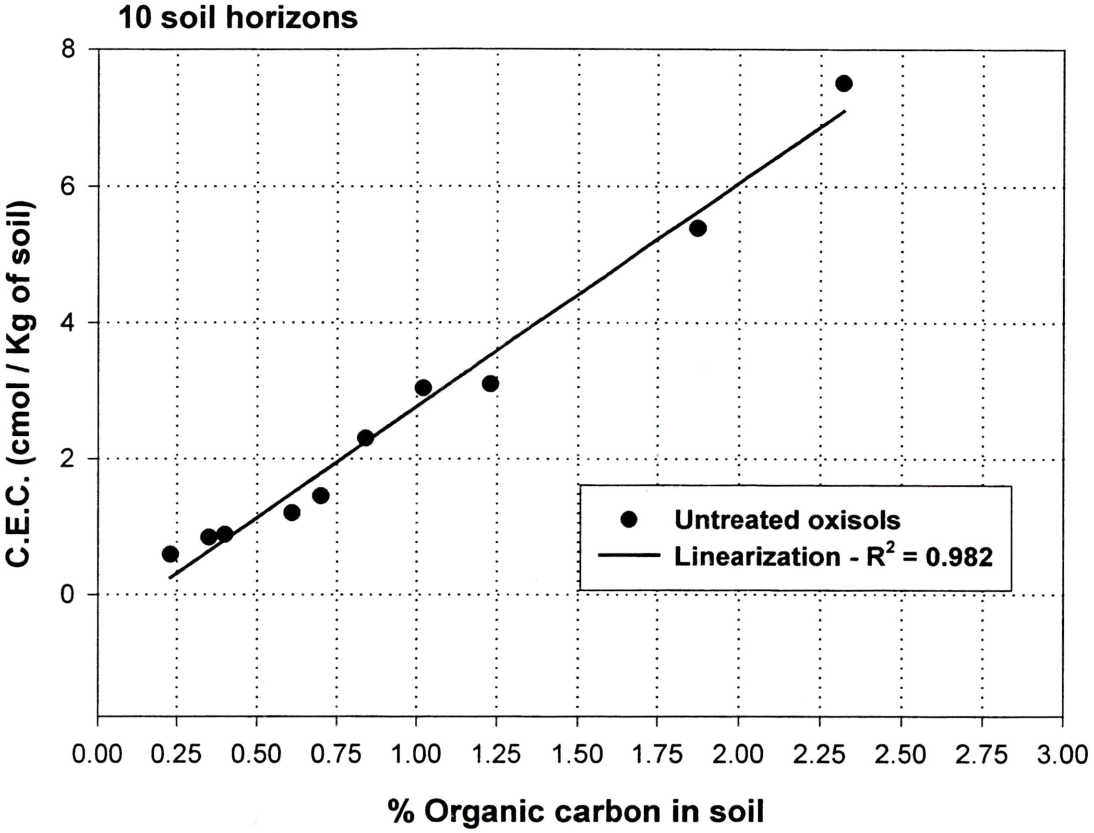


Figure 2.7 - Plot of Cation Exchange Capacity (CEC) versus the percentage of organic carbon in all soil horizons.

$pH_{water} - pH_{KCl}$ operation suggests a predominance of negative charge in the top four horizons which is probably due to the greater abundance of soil NOM at these horizons (see Van Raij, and Peech, 1972; Morais et al., 1976).

Soil physical characterization (size distribution, texture etc.) was accomplished after soil disaggregation through suspension in 0.1 M NaOH (EMBRAPA, 1997). Physical characterization determined a predominance of the clay size fractions followed by fine sand, coarse sand and silt. Therefore, these soils are a clay-type of soil, although they have a sandy texture (Table 2.1). The predominance of clay size particles could be related to the type of bedrock (slate) that created this pedon (Ker, 1995).

The degree of dispersion is a metric that relates the ration of the amount of clay that can be dispersed in water to the total clay in the soil (as a percentage). Since there is less clay dispersed in the top horizons, where the NOM is more abundant, than in the lower horizons, the results suggest that soil NOM is at least partially responsible for keeping soil particles together.

Soil characterization of the three chosen soil horizons

Mineralogy:

The diffractogram peaks of the three horizons are identical and indicate no differences in soil mineralogy (Figure 2.1). However, there is a slight difference in soil mineralogy when one compares the whole soil (<2.00 mm) to the clay size fraction. In the soil clay fraction, kaolinite ($Al_4(OH)_8(Si_4O_{10})$) is the predominant mineral followed by gibbsite ($Al(OH)_3$), hematite (Fe_2O_3), and anatase (a polymorph of rutile - TiO_2). In the soil fractions smaller than 2.0 mm, almost the same mineral predominance sequence is observed, with the exception of quartz (SiO_2), a silicate mineral, which is the predominant mineral species in the top horizon and the second most predominant in the intermediate horizon and the third most predominant in the deepest horizon. Anatase

(TiO_2) is a minor mineral (approximately 1%) present in all horizons of soil fractions smaller than 2 mm.

The mineralogical suite present in the soil horizons is the consequence of the intense weathering to which the bedrock (slate and quartzite), and secondary minerals, is subjected. All the feldspar minerals (from the slate rocks) and possible constant charge minerals, such as 2:1 clays, have been leached from the soil. The remaining minerals quartz, kaolinite, gibbsite, hematite and anatase have a lower solubility relative to the more leachable minerals mentioned above.

Non-crystalline or amorphous material:

Amorphous material is defined in this study as the solid phase that does not have a repeating structure (3 nm) based on a chemical formula (Sposito, 1989). Because this fraction of soil does not have a mineralogical structure it is not recognized by x-ray diffraction (XRD); it is observable by transmission electron microscopy (TEM).

Among the various methods suggested to extract iron and aluminum amorphous materials, ammonium oxalate at pH 3.0 in the dark (Schwertmann, 1964) and hydroxylamine hydrochloride 0.25 M at 50°C to 70°C, are the most common (Chao and Zhou, 1983; Griffioen and Broers, 1993). Hydroxylamine is able to reduce iron from crystalline minerals but it is unable to extract aluminum from solid phases (Martins et al., 1999). As a consequence, ammonium oxalate at pH 3.0 in the dark is the method of choice to remove iron and aluminum amorphous material from oxisol.

Before extraction of the non-crystalline material, soil NOM was partially oxidized by NaOCl. XRD analysis was made before and after 1) oxidation of the soil NOM and 2) extraction of amorphous material (Figures 2.2, 2.3, and 2.4). No change in soil mineralogy was observed after these soil treatments with the exception of some dissolution of quartz after soil NOM oxidation by NaOCl.

Results of the extraction experiments show that a trace amount (< 0.5%) of Fe- and Al-containing amorphous material exists in the soil profile (Table 2.4). These results are consistent with the finding of other oxisol researchers (Fey and Roux, 1977; Fontes and Weed, 1991; Lima and Anderson, 1997). The contributions of amorphous Fe and Al to the soil mass when converted to μmoles/g of soil, are 13.1 to 32.2 for Fe and 77.8 to 114.9 for Al. Amorphous Fe and Al oxyhydroxides can play an important role in the sorption of trace metals in soil solution even in trace amounts. For comparison, Davis et al. (1998) reported that 8 μmoles/ g of soil of amorphous Fe and 17 μmoles/ g of soil of amorphous Al were the main mineral sorbents of zinc in a quartz sandy aquifer in Cape Cod, MA.

The method used to estimate the amount of amorphous material is based on an operational definition, that most of the soil amorphous material would be extracted by ammonium oxalate in the dark at pH 3.0 (Schwertmann, 1964). Nevertherless, as will be seen below, the results are in agreement with the TEM analysis of these soil samples. In this soil profile, amorphous material is present in trace amounts. However, TEM analysis also shows that there are substantial percentages of poorly crystalline minerals that correlate to the soil percentage dissolved by sulfuric acids (Table 2.2).

Point of Zero Salt Effect (PZSE)

Mineral surface charge is caused by either isomorphic substitution between ions of different valence inside the mineral structure or by reactions of surface functional groups with adsorptive species in the solution (Sposito, 1989 and 1992). Salt titrations were performed to obtain the point of zero salt effect (PZSE) for the soil sample. Since there are no permanent charged minerals (2:1 clays) present in these soils, the PZSE is equal to the point of zero net charge (PZNC), which is equal to the point of zero net proton charge (PZNPC) (Sposito, 1984; Charlet, 1986; Chorover; 1993).

The pH_{PZSE} values for these soils show a constant increase from the top horizon (A_1) to the lowest horizon (C_2) (Table 2.4). This decrease in pH_{PZSE} is correlated with the decrease in organic carbon (Van Raij and Peech, 1972; Morais et al., 1976). The higher the concentration of organic carbon in a soil sample, the lower its pH_{PZSE}; this relationship is due to the negative charge associated with NOM (Morais et al., 1976; Bell and Gillman, 1978; Mendonça and Rowell, 1996). The effect of organic matter on soil surface charge can also be observed in the soil Δ pH between a salt solution and water. The negative values have a direct relationship to higher organic carbon content (Table 2.2). Another factor that could cause a decrease in the pH_{PZSE} for the topsoil horizons is the higher percentage of quartz found in these horizons. Quartz has low point of zero charge ($pH_{pzc} = 2.0$); therefore it can contribute to the negative surface charge of soil surface.

As described in the methods section, the pH_{PZSE} determined is the pH where a series of salt 'titration curves' intersect (Parker et al., 1979). For soil systems of low mineral solubility, and no constant-charge minerals, the application of the salt-titration procedure is relatively straightforward. However, in the soils examined here, aluminum solubility is significant.

The dissolution of aluminum (exchangeable aluminum, aluminum from solid and organic matter phases) is a common phenomenon observed for oxisols, as well as other soils (McBride, 1994; Chorover and Sposito, 1995; Malengreau and Sposito, 1997). The extent of aluminum dissolution as a function of pH is one factor responsible for inaccurate estimates of soil surface charge. Aluminum is a Lewis acid; in water (upon dissolution from the solid phase) it causes the release of protons from water through hydrolysis and the association of aluminum ions with hydroxyls. This problem can be solved by the estimation of protons produced by the hydrolysis of aluminum; this procedure was not used in the pH_{PZSE} estimation here. The results should be considered to be a semi-quantitative estimate of the soil point of zero charge (PZC). For a more accurate estimation of the soil PZC, aluminum dissolution should be accounted for.

Iron and aluminum bulk chemical composition

Total soil digestion by strong acids (HNO_3, $HCLO_4$, HF) was highly efficient in dissolving nearly all soil solid phases. After digestion, a residual, gray in color with nearly black submilimetric layer, remained. XRD analysis of this material (data not shown) revealed that the remaining material was mostly quartz.

Different masses of soil material, from different soil horizons, are plotted against the amount of iron and aluminum extracted (mg/l) from those samples. A plot of the data is a straight line whose intercept passes close to the origin (Figure 2.4). The linear regressions (R^2) of these plots are 0.993 for Al and 0.996 for Fe. These data suggest a high correlation between the mass of soil digested and the concentrations of Fe and Al obtained. Other information that can be obtained from this plot is about the homogeneous bulk chemical composition of iron and aluminum along the soil profile. Since samples from different horizons were used for the same elements the results indicate that the amount of iron and aluminum are still very similar.

NOM extractions

Table 2.5 contains the results of the series of experiments followed to remove NOM, through a sequence of increasingly harsher treatments, from the soil isolates. As Hayes (1985) points out, no ideal extracting protocol exists.

The maximum percentage of soil NOM that could be extracted by water and dilute base was 27%. For water at pH values between 5 and 7 less than 5% of soil NOM was released to solution. Above pH 7 (dilute base) there was a linear increase of NOM dissolution up to 27% of the total NOM released to solution. This extraction is considered to be mild; it causes a maximum aluminum and iron dissolution of approximately 10 mmols / kg of soil.

Table 2.5 - NOM extraction from A_1 soil horizon with different extractants:

NOM extractants	*% NOM extracted from oxisol*
H_2O pH = 5-11	0 - 27%
$Na_4P_2O_7$ pH= 9.0	33%
NaOH 0.5 M at 55°C	52%
NaOCl (5%)	87 %
H_2O_2 (10 – 30%)	70% - 76%

A solution of 0.5 M NaOH at 55°C was able to extract nearly twice the maximum amount of NOM removed in the experiments described above. While substantial NOM was removed from the soil, significant dissolution of aluminum and iron oxyhydroxides is likely.

Sodium pyrophosphate at pH 9 was able to remove one third of the soil organic carbon. Possibly in oxisols, as many other soils, iron and aluminum maintain organic matter in a flocculated and insoluble condition (Stevenson, 1982). Phosphate from sodium pyrophosphate is able to complex iron or aluminum causing the solubilization of soil NOM (Stevenson, 1982). The following reaction (2.1) has been used to illustrate the NOM extraction in this case. Although in the oxisols used in this research, since there is no abundance of calcium, it is less probable that soil NOM is associated with this element.

$$2[RCOOX(OH)_2](COO)_2Ca + Na_4P_2O_7 \leftrightarrow 2[RCOOX(OH)_2](COONa)_2 + Ca_2P_2O_7\downarrow \quad (2.1)$$

In this case X is a trivalent cation (Fe or Al) that can be either complexed with the NOM and not acting as a flocculating agent such as calcium, or it can be replacing calcium in the reaction above. This technique removed 5% more NOM than dilute base at pH 11.

Two additional methods were evaluated for the removal of organic carbon from the soil samples; both methods are based on the chemical oxidation of carbon. The first method involved suspending soil isolates in a sodium hypochlorite (5% by volume) solution at pH 9.5. This method was the most efficient in removing soil organic matter with the least deleterious affect on soil minerals. ICP-AES analysis of the sodium hypochlorite solution after extraction indicates that less than 3% of the total iron and aluminum mineral dissolved and less than 10% of the silicates. These results are similar to those of other researchers who used NaOCl (Anderson, 1963; Lavkulich and Wiens, 1970).

The second chemical oxidizer used to remove NOM was hydrogen peroxide. Concentrations used were 10%, 20%, and 30% by volume. The NOM removal was quite efficient with between 70% and 76% of the total soil NOM removed. A general drawback of this method is the likely dissolution of manganese oxides and oxidation of sulfide minerals (Papp et al., 1991). This method is suitable for this particular oxisol because of the absence of manganese oxides or sulfides. However, the extent of iron and aluminum dissolution during the application of this method was not evaluated.

Specific surface area of soil

Analyses of soil specific surface area were performed before and after organic matter oxidation by NaOCl (Table 2.4). Sodium hypochlorite was the most efficient chemical evaluated for the oxidation of soil NOM. It removed 87%, 67%, and 43% of the initial soil NOM present in horizons A_1, Bw_2, and C_2, respectively. These results suggest that the NOM in the deeper horizons is in a more advanced stage of humification, more decomposed, and therefore less easily oxidized.

In contrast with the efficiency of this oxidizer in removing soil NOM, the increase of soil specific surface area was not especially significant. Only in horizon A_1 was there a significant increase in soil specific surface area (approximately 22%) after the partial oxidation of soil NOM; and in the other horizons there were virtually no changes in soil surface area (Table 2.4). The lack of a change in the specific surface area of the soils upon NOM removal is likely the result of the key role that iron and aluminum oxyhydroxides are playing in this system in keeping soil particles together. At the natural soil pH of 5 to 5.5, the soil surface charge of kaolinite, and iron and aluminum oxyhydroxides (hematite and gibbsite), are opposite (Sposito, 1989), thereby fostering heterocoagulation. NOM is an important soil aggregation agent, but it is not the only agent in tropical soils (Foster, 1978; Tisdall and Oades, 1982; Bartoli et al., 1991).

If the NOM sites that bind solid particles are already occupied by trivalent ions (Fe^{3+} and Al^{3+}), the role of NOM as a soil aggregating agent will be minimized. The complexation of trivalent ions by NOM has been shown by several soil researchers (De Coninck, 1980; Schwertmann, 1985; McBride, 1994; Sparks, 1995).

Soil SEM and TEM pictures.

SEM analysis was made on samples from the A_1 horizon only (Figure 2.8). The magnification of these pictures ranges from 15,000 to 20,000 times the original grain size. SEM pictures allow the visualization of the surface of the whole microped shape, only. The soil samples from the A_1 horizon present a very coarse, sandy, porous structure, sometimes with soil particle aggregates in long structures lying over other minerals (Figure 2.8). The clearly visible long tubular shapes have been associated by some researchers with some sort of fungal structure such as hyphae. Previous researchers (Oades and Water, 1991; Vrdoljak, 1998) observed similar aggregate morphology in oxisols. The soil's porous structure is a reflection of the randomly aggregated kaolinite minerals bound together by iron and aluminum oxyhydroxides and NOM (Vrdoljak, 1998).

TEM analyses were performed on untreated samples from A_1, Bw_2, and C_2 horizons and for soil samples from the A_1 horizon after partial oxidation of soil NOM by NaOCl. TEM is the optimal microscopy method for observing soil structure (Vrdoljak, 1998) because the small thickness of the samples (60 nm) allows the electrons to pass through the samples. As a result, we can see the arrangement of minerals and organic material in the micropeds.

A staning technique was used in this study to distinguish soil NOM that had not been totally decomposed. It is a cytochemical staining technique, known in biological fields for many years, that has been used successfully in the characterization of organic material in soil structure (Foster and Martin, 1981; Santos et al., 1989; Vrdoljak, 1998). The staning technique is used to identify NOM *in situ* through the complexation of trace metals, in this case Os and U, with organic matter binding sites. As a consequence of

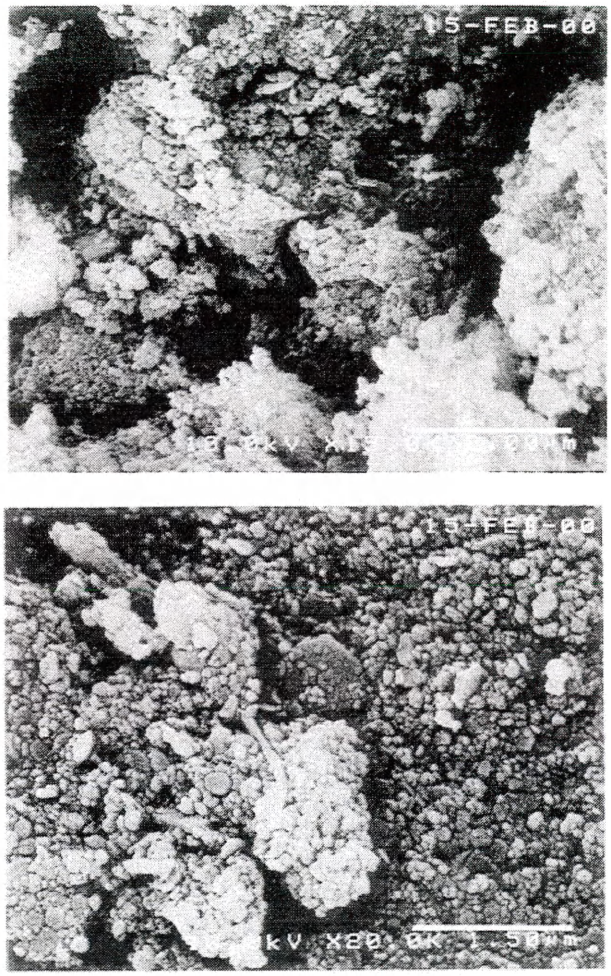


Figure 2.8- SEM micrographs of untreated soil from the A_1 horizon presenting a coarse granular texture of microaggregates.

staining of the NOM by OsO_3 and uranyl acetate, the organic materials are visualized as a slightly darker background color than the embedding resin.

The concept of soil aggregation hierarchy proposed by Tisdall and Oades (1982) was used in this study to separate the smaller aggregated soil unit (53 μm) and to describe the soil structure in the different horizons.

The identification of soil minerals using TEM is not always easy. In this particular case, kaolinite is the only mineral that could be identified by its geometrical shape. Neither gibbsite nor hematite appeared to be as well crystallized as kaolinite; they are present in the soil in poorly crystalline or microcrystalline, forms. Iron oxides have been located in kaolinitic oxisols in the size range of 20-60 nm, and distributed across kaolinite minerals of 150-400 nm (Vrdoljak, 1998). Iron oxides in these soils are believed to have the same range of size and to have the same relationship with kaolinite as described by Vrdoljak. Amorphous materials could also not be identified in the TEM micrographs due to their low concentration in these soils.

The following description of these oxisol samples will be based on the soil components easily identifiable in TEM (kaolinite and NOM). Other techniques such as elemental mapping (EDX – spectroscopy) should be used for identification of soil minerals other than kaolinite. Below is a description of the soil structure in the different soil horizons.

A_1 Horizon

The A_1 horizon is the horizon with the greatest percentage of soil NOM (2.32%). NOM represents 10% to 20% of the soil aggregate total area and is found disseminated among soil minerals, isolated in discrete sites, or in filling up long soil structures (Figures

2.9, 2.10, and 2.11). The NOM arrangement in soil, verified by TEM, is very important for answering some questions related to metal sorption to soil. The amount of soil NOM obtained from analytical techniques that measure the amount of organic carbon by the combustion of NOM does not give any information about how much of this NOM is available for chemical reactions. The A_1 horizon is the closest to the surface and consequently it is the horizon with most biological activity. Fungal hyphae are likely creating the observed long soil structures long structures (Figure 2.9). Cells of plants are quite often filled with poorly crystalline minerals (Figure 2.9). Circular structures present in these soils are identified as organelle membranes; however, it is not possible to identify the organism because of the high degree of humification (Figure 2.10). Small mineral grains usually surround discrete organic material; such occlusion of soil NOM by mineral phases may help to protect the organic material from degradation. NOM is frequently associated with minerals either by being surrounding by them (cell membranes, discrete moieties) or disseminated among them as an aggregating agent.

Kaolinite is the predominant mineral in this and the other soil horizons. It is randomly distributed and constitutes 70% to 80% of all the observable minerals in the soil. Kaolinite is formed in subhedral to anhedral shapes and is generally subdivided into two mineral size populations: one with crystals of basal section diameter from 0.1 to 0.4 μm (well crystallized) and other population with crystals of basal section diameter smaller than 0.05 μm. These two populations are evenly distributed (suggesting 50% by mass of each type) in this top soil horizon and they are present in all soil horizons analyzed by TEM. The smaller grain size material is considered to be poorly crystalline in this research and its percentage in TEM images of soil (~50%) correlates to the soil digestion by sulfuric acids (Table 2.2). In fact "poorly crystalline" as used here refers either to small particles sufficiently crystalline to appear in TEM micrographs, or to paritcles dissolved by 50% H_2SO_4. There is no evidence to verify the correspondence of these two definitions other than the strong circumstantial evidence highlighted here.

Bw_2 Horizon

This horizon contains significantly less NOM relative to horizon A_1 (Figures 2.12, 2.13, 2.14). NOM is predominantly disseminated among minerals. No microorganism shapes are observed and only a phytolith recently deposited in soil was present in one of the micrographs (Figure 2.14). Kaolinite is randomly present in two grain size populations as in the A_1 horizon; however, now the grain sizes smaller than 0.05 μm, the poorly crystalline group of minerals, is predominant (60% to 70%). Dark bands (Figures 2.12 and 2.14) are artifacts from overlapping of wrinkled areas of the sample.

C_2 Horizon

No obvious structures are visible related to microorganism activity nor to plant residuals. In this horizon, NOM is disseminated among minerals in the soil matrix (Figures 2.15, 2.16, 2.17, and 2.18). The distinction of NOM by the use of the cytochemical staining technique is not so evident in this horizon. This fact suggests that NOM in this horizon is in an advanced stage of decomposition. Kaolinite still is the predominant mineral phase (60% to 70%) and the larger particle-size population (0.1 to 0.4 μm) is predominant (60%) in this horizon, indicating a stage of less advanced weathering compared to the horizons above. Some euhedral shapes of kaolinite are observed in this horizon (Figure 2.18). Irregular porosity of the soil matrix is also observed (Figure 2.16).

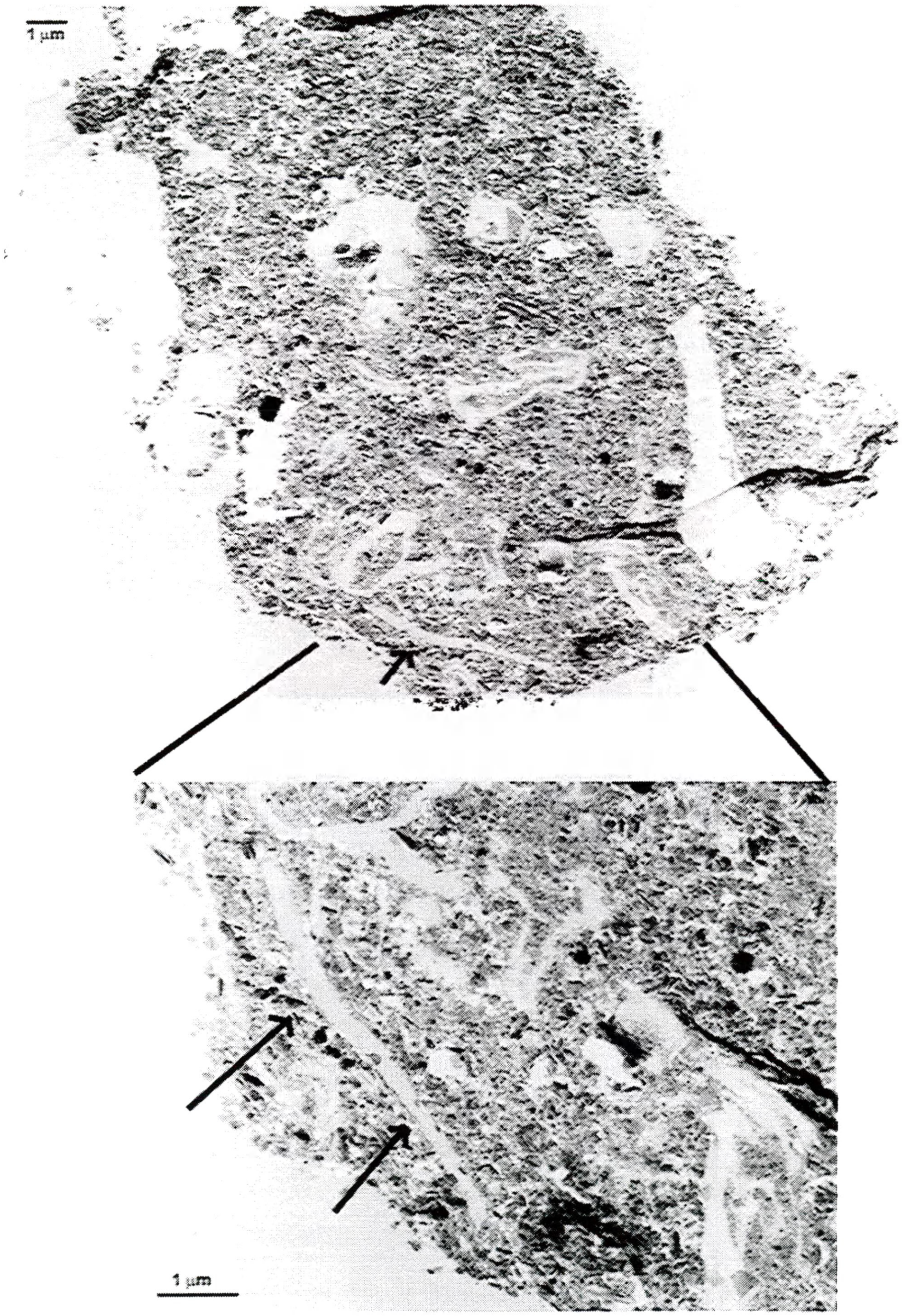


Figure 2.9 – TEM of apparent fungal hyphae (long structure, indicated by the arrows), in untreated soil from the A_1 horizon.

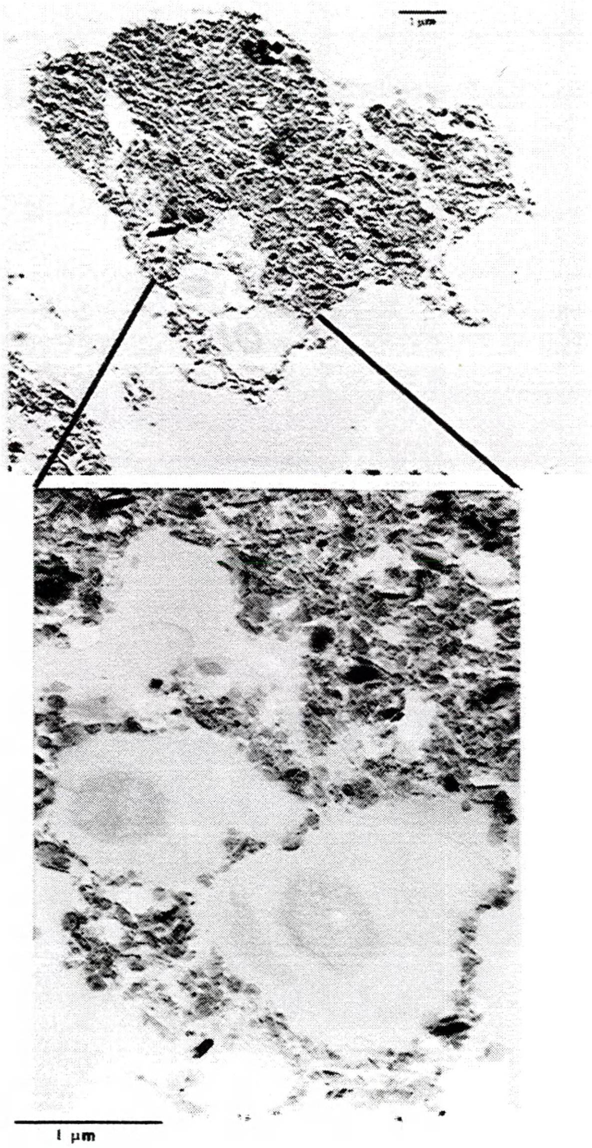


Figure 2.10 – TEM of organelle membranes surrounded by kaolinite mineral grains, untreated A_1 horizon oxisol.

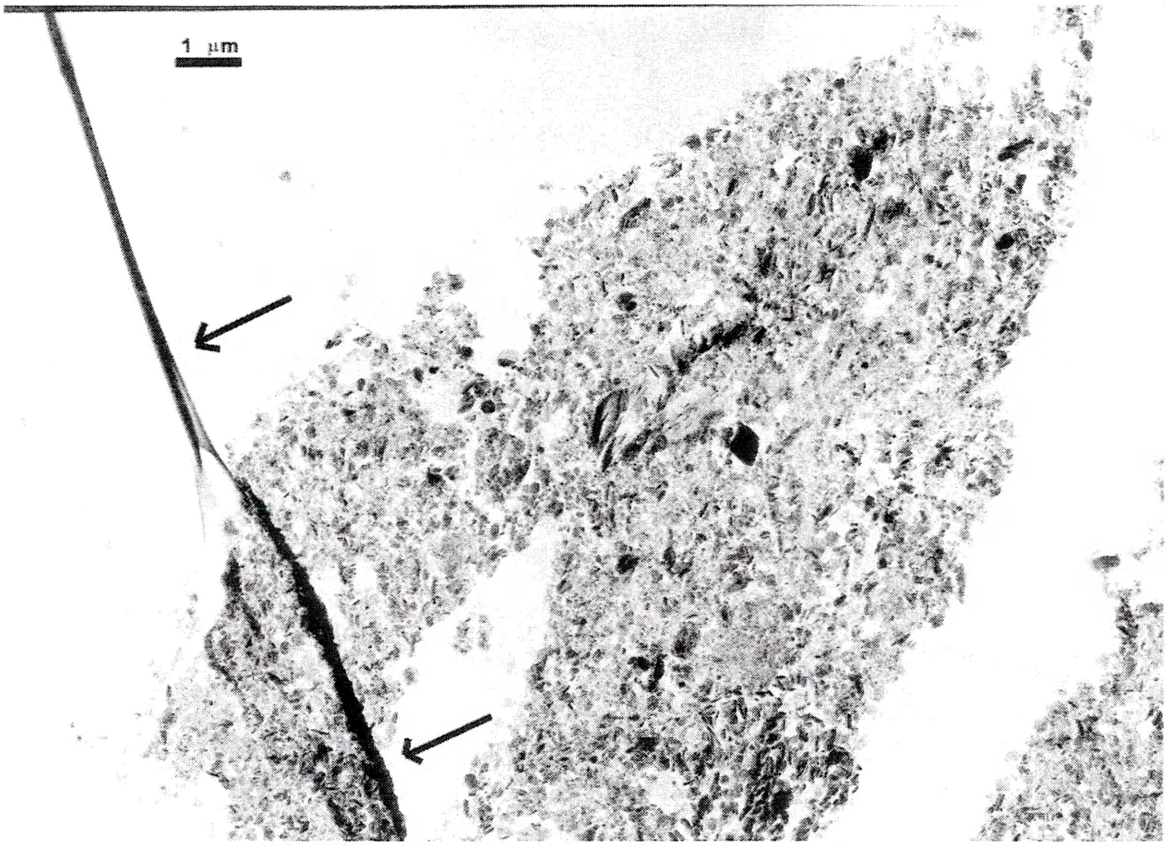


Figure 2.12 – TEM of soil microaggregates from Bw_2 horizon showing smaller grain sizes and a dark band, indicated by the arrows, formed because of overlapping of wrinkled areas of the sample.

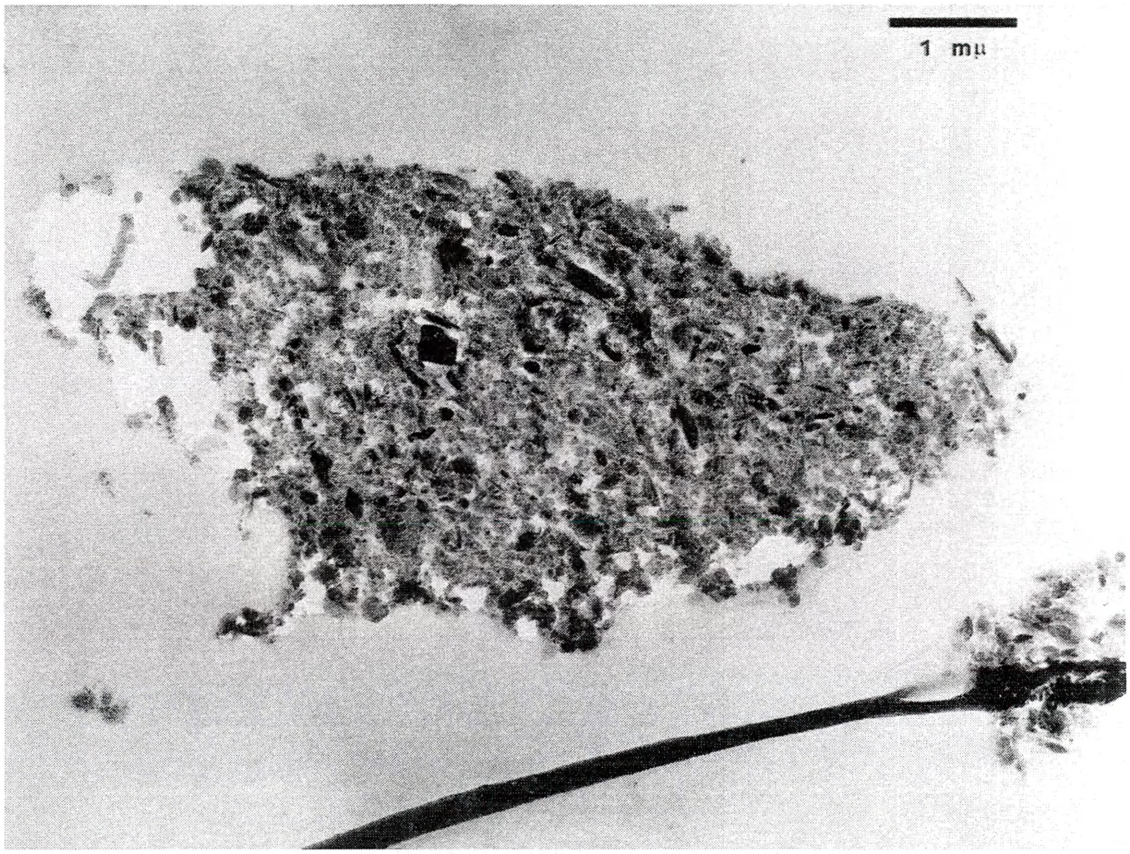


Figure 2.13 – TEM of oxisol aggregate from Bw_2 horizon with less soil NOM than soils from A_1 horizon. The micrograph shows a smaller amount of NOM disseminated among soil minerals.

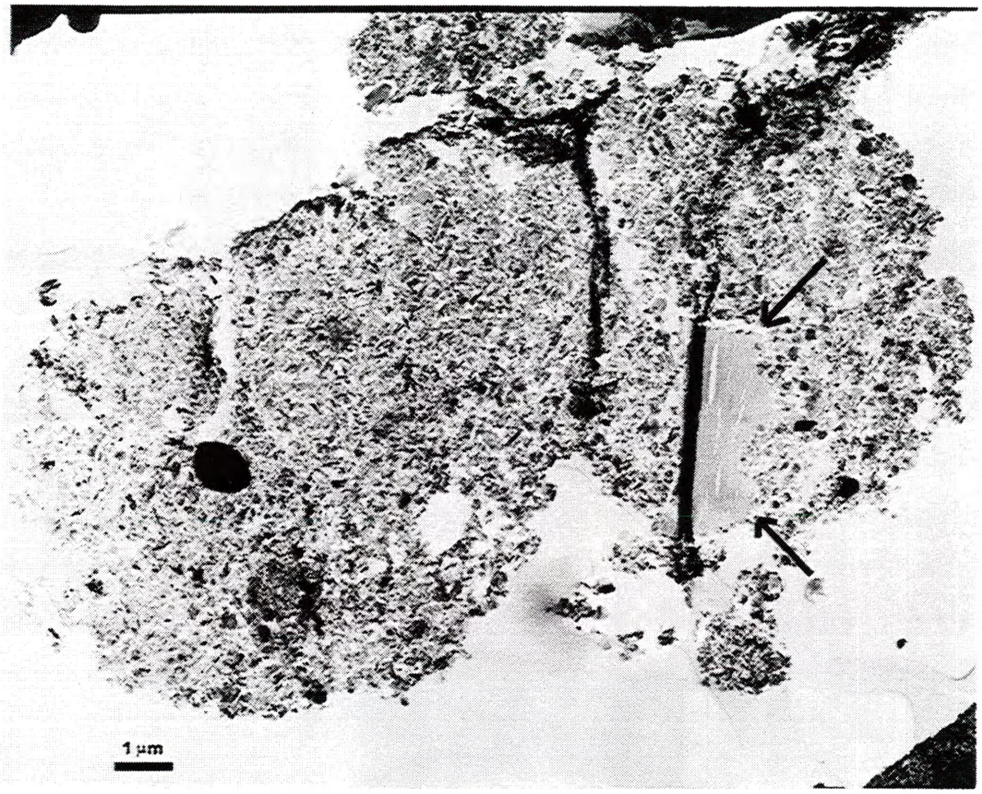


Figure 2.14 – TEM of a phytolith, indicated by the arrows, recently deposited in soil on the low right side of the micrograph. Artifacts caused by wrinkled areas are also present in this micrograph (BW_2 horizon).

A_1 Horizon after NaOCl treatment

A significant decrease in soil NOM and a relatively significant increase in soil porosity was observed after partial soil oxidation by NaOCl (5%) (Figures 2.19 and 2.20). No organic material related to cells of plant, fungi or bacteria was observed after oxidation, only a small phytolith is observe at the lower left corner of one micrograph (Figure 2.19). In addition, some NOM resistant to soil oxidation is observed in Figure 2.19.

Even with a relative increase in soil porosity, the microaggregates are still cohesive, preserving the soil structure. This fact indicates that iron and aluminum oxyhydroxides either in amorphous or poorly crystalline stages are very important soil aggregation agents. This suggests that poorly crystalline iron and aluminum oxyhydroxides retain a primary role in keeping kaolinite particles together. Such interactions also explain the relatively small increase in soil surface area even after 87% of the original NOM has been oxidized. The increase in soil porosity is probably responsible for the 22% increase in soil specific surface area.

Conclusions

A soil profile, classified as Typic Acrustox (USDA) and as Dark Red Latosol (Brazilian classification), was evaluated with respect to physical and chemical properties. The soil is remarkably homogeneous in terms of chemical and physical composition throughout its profile as a consequence of the intense weathering to which the soil has been exposed. Tables 2.1, 2.2 and 2.3 summarize the properties of the soil horizon as a function of depth. Soil NOM is one of the few soil components that vary in concentration along the soil profile. A positive relationship exists between the percentage of soil NOM and the soil CEC, indicating a dominant role of NOM in the cation exchange process (Figure 2.6).

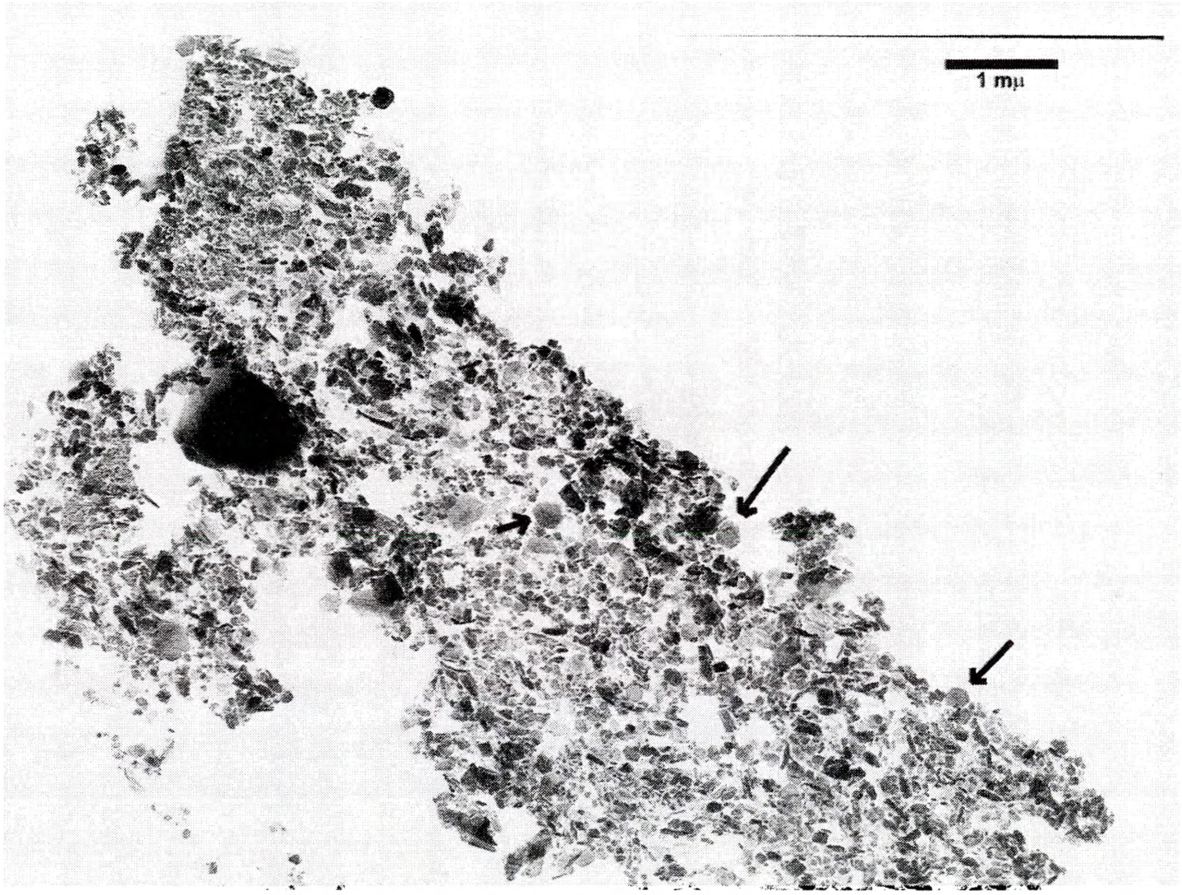


Figure 2.15 – TEM of soil from C_2 horizon with less NOM than in the other soil horizons. Kaolinite is present in a subhedral form, indicated by the arrows. Well-crystallized mineral grains are predominant in this soil horizon.

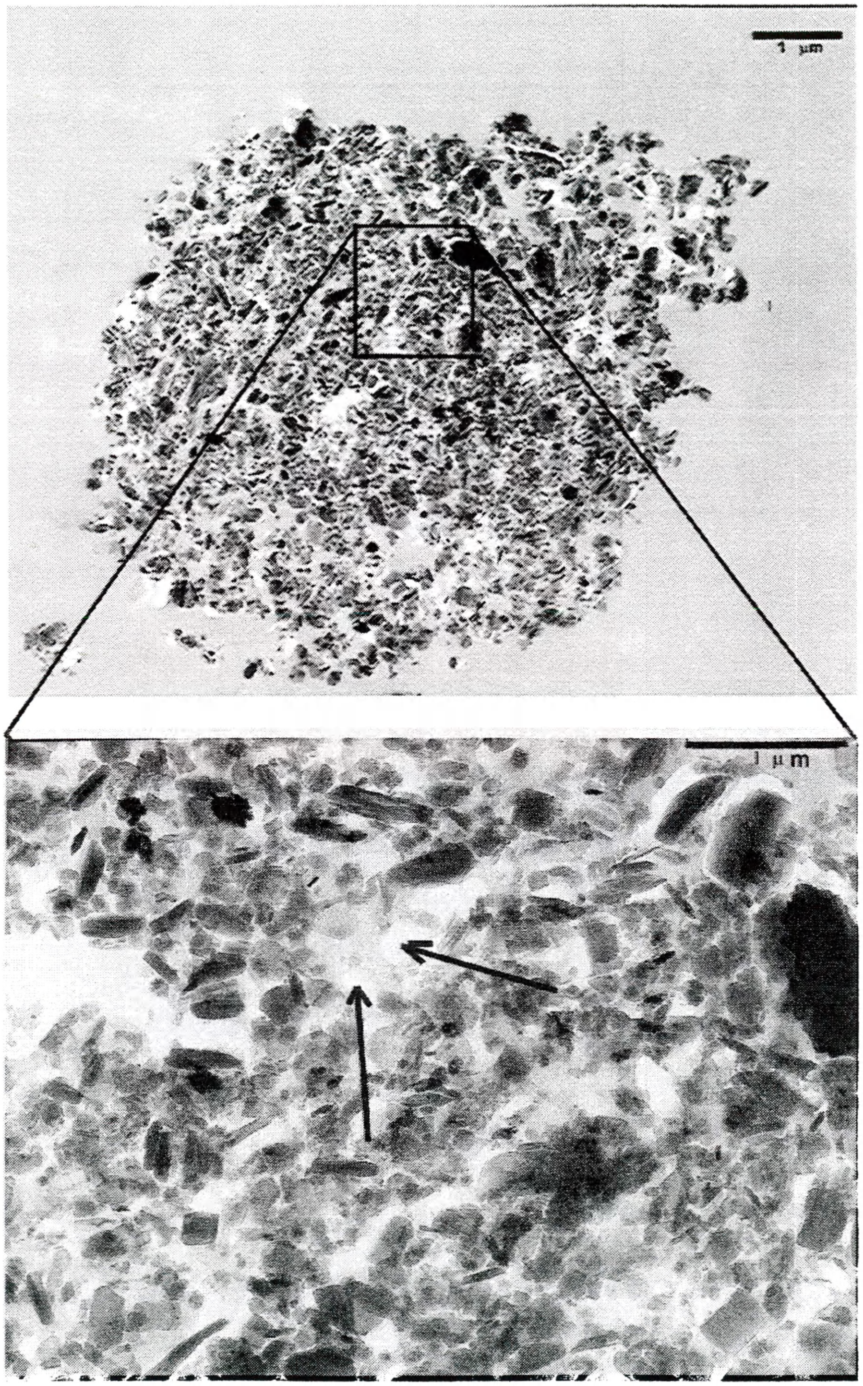


Figure 2.16 – TEM of the NOM disseminated among soil minerals, indicated by the arrow, in soil from C_2 horizon. Again note the larger crystal grain size in this horizon.

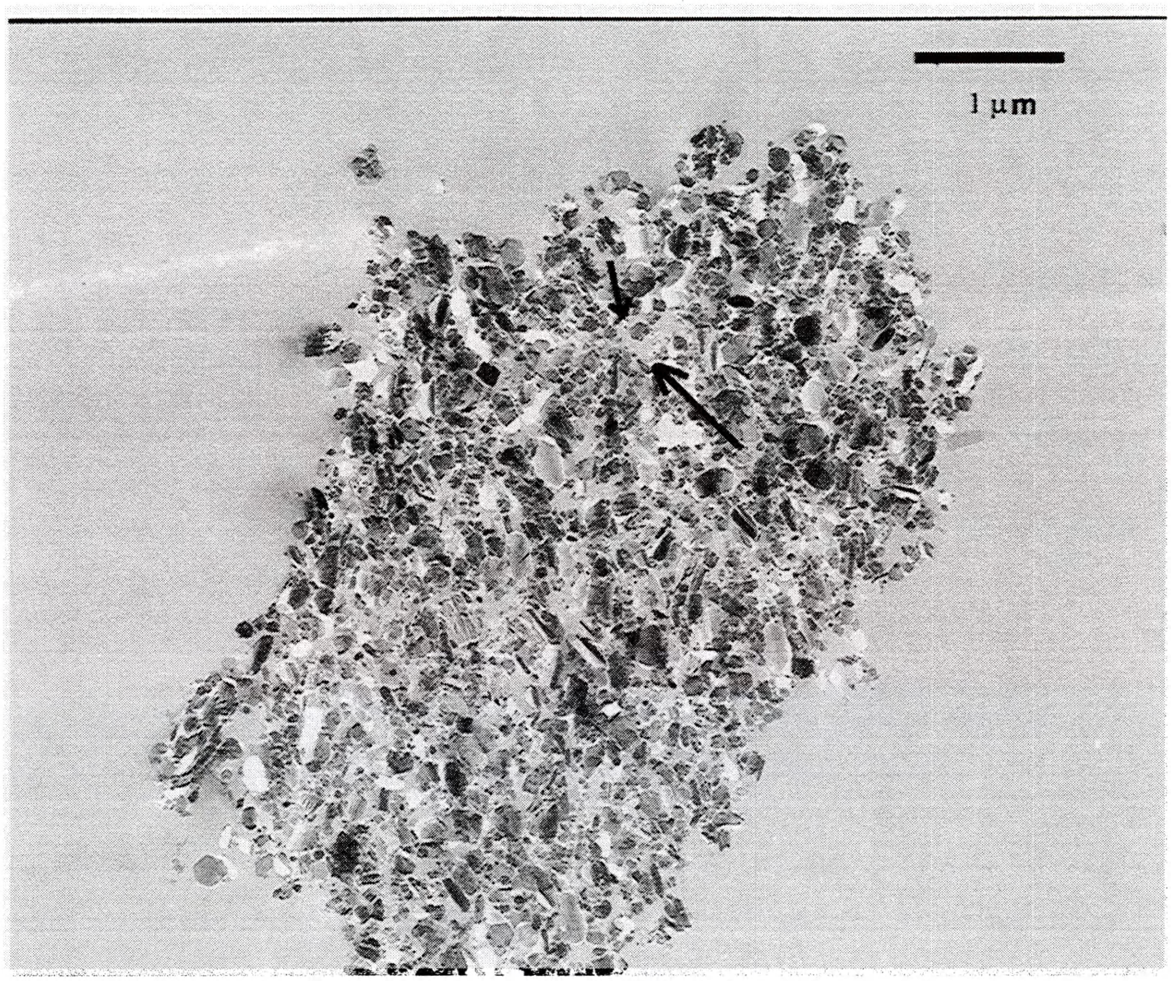


Figure 2.17 – TEM of NOM in advanced stage of decomposition, so as a consequence it is hard to distinguish between the color of the resin and the color of the NOM complexed with U and Os. The arrows indicate the NOM in soil to be compared with the color of the resin that surrounds the microaggregate (C_2 horizon).

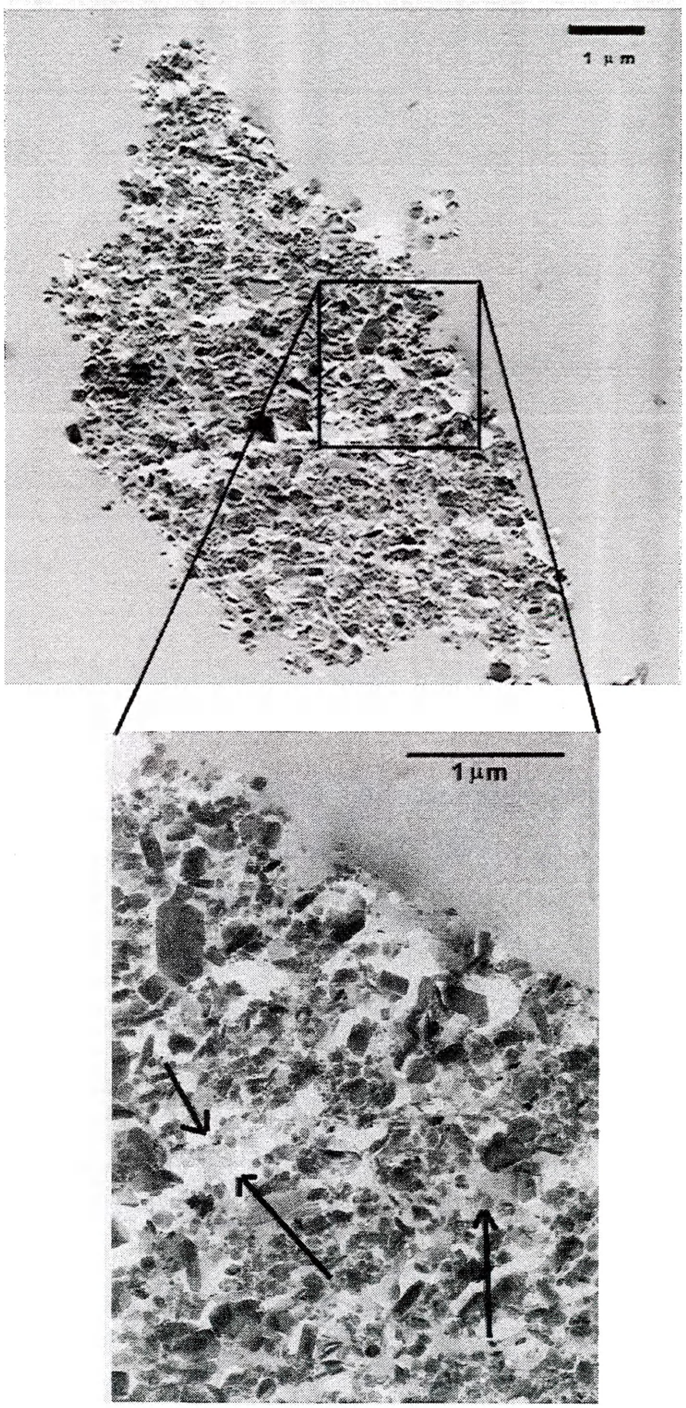


Figure 2.18 – TEM with a detailed micrograph showing the random orientation of kaolinite in the C_2 horizon. Arrows indicate NOM disseminated among soil minerals.

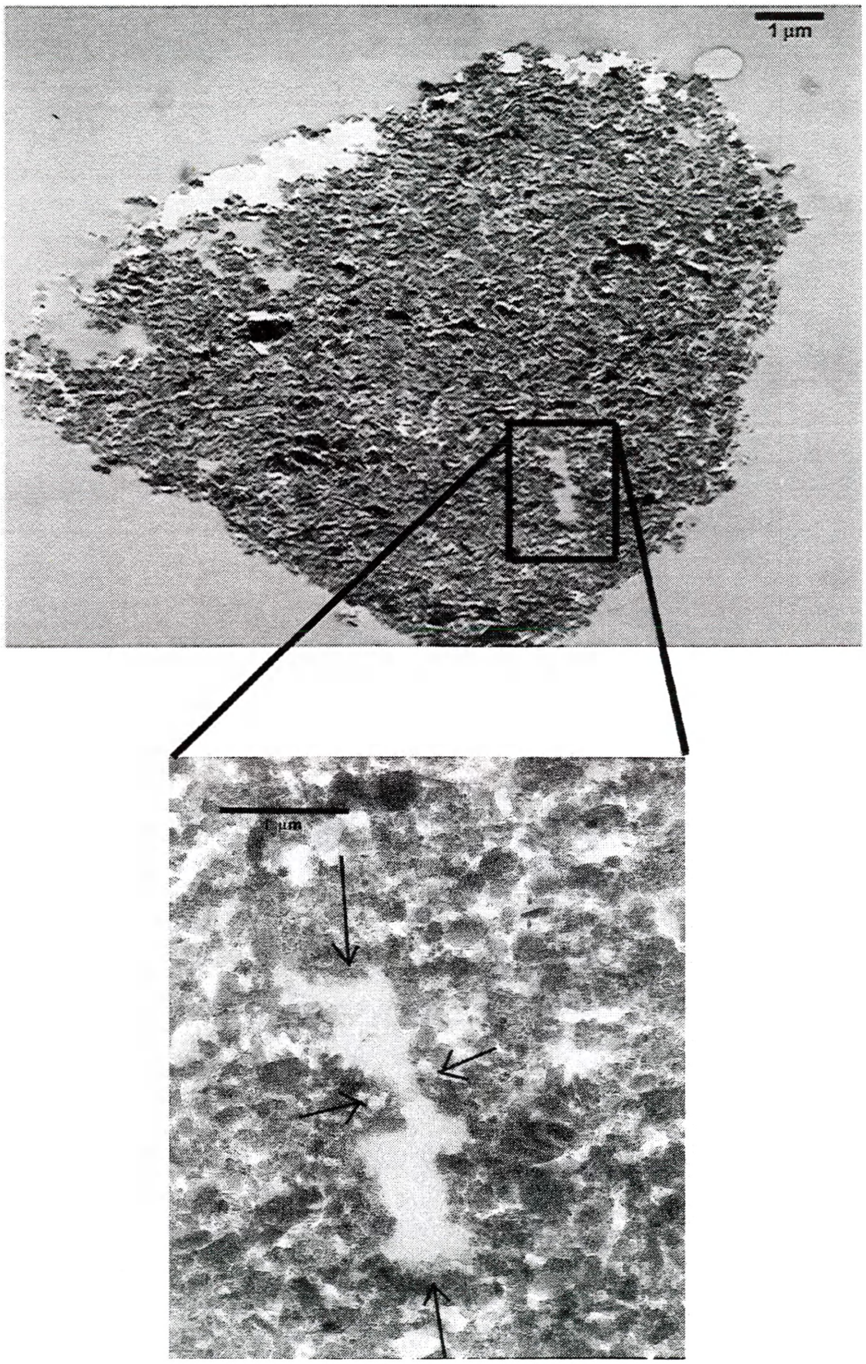


Figure 2.19 – TEM with a detailed micrograph of soil NOM from A_1 horizon resistant to NaOCl (5%) oxidation, indicated by the arrows, and increase in soil porosity around the NOM.

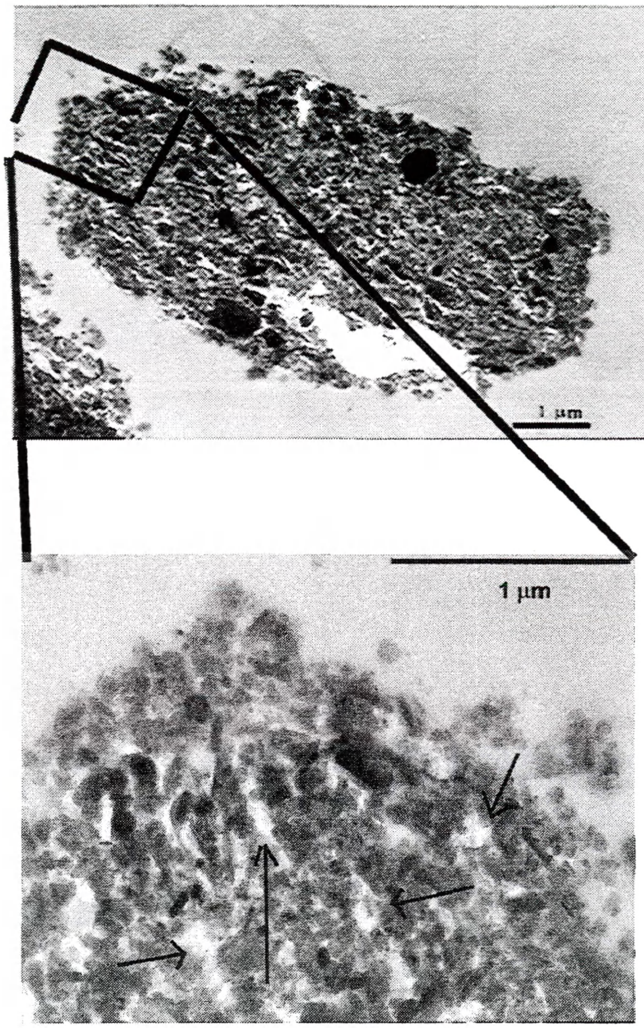


Figure 2.20 – TEM with a detailed micrograph illustrating the increase in soil porosity after NOM oxidation by NaOCl (5%). Arrows indicate the areas of increased soil porosity.

Three soil horizons (A_1, Bw_2, and C_2) werre chosen to be studied in more detail to further evaluate the physical and chemical properties of the soil with respect to NOM concentration and association with other soil constituents (Table 2.4). The results observed were:

1. The mineralogy of the soil's clay-size fraction is constant along the soil profile with the mineralogical predominance in the order: kaolinite > gibbsite > hematite.
2. The whole soil (<2.0 mm) has almost the same mineralogy but with the addition of quartz and anatase.
3. Quartz is the first, second and third most predominant mineral, respectively, in the three soil horizons evaluated from the top to the bottom; anatase is always the least predominant mineral.
4. A small amount of amorphous material is present in the soil horizons, as defined by the chemical extraction method described by Schwertmann (1964). Although the amorphous material is low in terms of relative mass, it may play an important role in the sorption of trace metal in soil systems.
5. The point of zero surface charge was estimated for the three soil horizons; the pH_{PZC} increased with depth in the soil horizon. The variation in pH_{PZC} with depth corresponds to changes in the quartz and NOM concentration in the soil profile.
6. The percentage of aluminum and iron, as determined by total soil digestion followed by ICP-AES analysis, remained constant with depth, at 16 and 8 %, respectively.
7. Sodium hypochlorite was determined to be the most efficient chemical for NOM extraction with the least impact on other minerals in the soil. Surface area was obtained in all three soil horizons before and after soil treatment with NaOCl. A small change (22%) in soil specific surface area was observed for the A_1 horizon; no changes in the specific surface area were detected for samples from the other soil horizons. These results may be explained by the central role that poorly crystalline iron and aluminum oxyhydroxides must be playing in soil aggregate maintenance.

8. TEM analysis indicates that the majority of the NOM in this soil is either a) disseminated among soil minerals, interconnecting them, b) localized in discrete areas, or c) filling up long soil structures. NOM localized in isolated areas may have been the consequence of microbial activities (fungi hyphae, bacteria). However, the relatively high degree of NOM decomposition makes it difficult to clearly identify possible microbiological origin.
9. NOM in the top soil horizon occupies 10% to 20% of the soil aggregate area observed by TEM. Oxidation of soil NOM from the A_l horizon caused a significant decrease in the concentration of soil NOM and some increase in soil porosity. The increase in soil porosity may be correlated to the 22% increase in soil surface area. The non-disruption of soil structure after oxidation by NaOCl, was attributed to the role that poorly crystallized iron and aluminum oxyhydroxides play in the maintenance of soil aggregates.
10. TEM results point out that NOM cannot be considered to exist only as a surface coating. It also exists as discrete particles that may be occluded in the soil aggregates. Thus the fraction of the NOM able to bind metals may be less than that indicated by total organic carbon analyses obtained by combustion techniques.

References

Anderson, J. U. 1963. An Improved Pretreatment for Mineralogical Analysis of Samples Containing Organic Matter. *Clays and Clay Minerals* 10:380-388.

Bell, L. C. and Gillman G. P. 1978. Surface charge characteristics and soil solution composition of highly weathered sols. In: Mineral Nutrition of Legumes in Tropical and Subtropical Soils. Ed. by Andrew, C. S. and Kamprath, E. J., Melbourne Australia.

Bartoli, F., G. Burtin and A.J. Herbillon. 1991. Disaggregation and clay dispersion of Oxisols: Na resin, a recommended methodology. *Geoderma*, 49:301-317.

Boul S. W., Hole F. D. and McCracken R. J. 1980. *Soil Genesis and Classification.* The Iowa State University Press. Ames Iowa.

Bowles, E.C., R.C. Antweiler, and P. MacCarthy. 1989. Acid-base titration and hydrolysis of fulvic acid from the Suwannee River. In: *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures.* U.S. Geological Survey. Open-File Report 87-557.

Briggs, P. 1990. Elemental analysis of geological material by Inducted copper plasma – Atomic Emmision Spectrometry. In: *Quality Assurance Manual for the Branch of Geochemistry.* U.S.G.S. edited by Belinda F. Arbogest. Open-file report 90-668.

Chorover, J. 1993. Surface charge and colloidal properties of benchmark Brazilian Oxisols. Ph.D. Thesis. University of California, Berkeley.

Chorover, J. and Garrison Sposito. 1995. Dissolution behavior of kaolinitic tropical soils. *Geochimica et Cosmochimica Acta* 59 (15):3109-3121.

Charlet, Laurent. 1986. Adsorption of some macronutrient ions on an oxisol. An application of the triple layer model. Ph.D in Soil Science. University of California, Riverside.

Chao, T. T. and Liyi Zhou. 1983. Extraction Techniques for Selective Dissolution of Amorphous Iron Oxides from Soils and Sediments. *Soil Science Society of America Journal* 47 (2):225-232.

Davis, J.A., and J.O.Leckie. 1978. Surface ionization and complexation at the oxide/water interface – II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67 (1):90-107.

Davis, J. A.; J. A. Coston; D. B. Kent; C. C. Fuller. 1998. Application of the surface complexation concept to complex mineral assemblages. *Environmental Science and Technology* 32:2820-2828

De Coninck, F 1980. Major Mechanisms in formation of spodic horizons. *Geoderma* 24:101-128.

Duriez, M.A. 1974. Método rápido papa determinação complexiométrica do ferro a alumínio em solos. PUC, Rio de Janeiro, Brazil.

EMPRAPA. 1997. *Manual de Métodos de Análise de Solo.* 2nd Ed. Ministério da Agricultura e do Abastecimento. Rio de Janeiro, Brazil.

Fey M.V., Roux J. Le. 1977. Properties and quantitative estimation of poorly crystalline components in sesquioxidic soil clays. *Clays and Clay Minerals* 25:285-294.

FitzPatrick, E.A. 1993. *Soil Microscopy and Micromorphology.* John Wiley & Sons, New York NY.

Fontes M.P.F., and S.B. Weed. 1991. Iron oxides in selected Brazilian oxisols: I. Mineralogy. *Soil Science Society of America Journal* 55:1143-1149.

Forsythe, W. 1975. *Física de Suelos: Manual de Laboratório.* Turrialba, IICA.

Foster, R.C. 1978. Ultramicromorphology of some South Australian soils. In *Modification of Soil Structure* (ed. by W. W. Emerson, R.D. bond and A.R. Dexter), Emerson-Wiley. 103-109.

Foster, R.C. and J.K Martin. 1981. In situ analysis of soil components of biological origin. (ed. By *E.A. Paul and J.N. Ladd) Soil biochemistry.* Marcel Dekker, New York. 5:75-111.

Griffioen J., H.P. Broers. 1993. Characterization of sediment reactivity: the feasibility of sequential extraction techniques. In: *TNO Environmental and Energy Research, Netherlands, ed. TNO Institute of Applied Geoscience.* Delft The Netherlands.

Hayes, M.H. 1985. Extraction of humic substances from soil. In: *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization.* Wiley-Interscience, New York.

Isbell, R. F.1978.Characteristics of tropical and sub-tropical soils. In: *Mineral nutrition of legumes in tropical and subtropical soils* edited by Andrew,C. S., and Kanprath, E. J., Melbourne, Australia.

Jacomine, Paulo. 1969. *Descrição das características morfológicas, físicas, químicas e mineralógicas de alguns perfis de solos sob vegetação de cerrado.* Boletim Técnico #11. Ministério da Agricultura, Rio de Janeiro, Brazil.

Ker, J.C. 1995. Mineralogia, sorção e dessorção de fosfato, magnetização e elementos traços de latossolos do Brasil. Ph.D. Soil Science. Viçosa, Minas Gerais, Brazil.

Lavkulich, L. M. and J.H. Wiens. 1970.Comparison of Organic Matter Destruction by Hydrogen Peroxide and Sodium Hypochlorite and Its Effects on Selected Mineral Constituents. *Soil Science Society of America Journal Proceedings* 34:755-758.

Lima, Jose M., and Sharon J. Anderson. 1997.Aggregation and Aggregate size Effects on Extractable Iron and Aluminum in Two Hapludoxs. *Soil Science Society of America Journal.* 6 (1):965-970.

Macedo, J. and Bryant, R. B. 1987. Morphology, mineralogy, and genesis of a hydrosequence of oxisols in Brazil. *Soil Science Society of America Journal* 51:690-698.

Malengreau, N. and Garrison Sposito. 1997. Short time dissolution mechanisms of kaolinitic tropical soils. *Geochimica et Cosmochimica Acta* 61 (20):4297-4307.

Martins, E. S.; G. R. Boaventura; W. M. Farias; J. C. Gaspar. 1998. Extração de fases de baixa cristalinidade de solos tropicais por oxalato de amônio-edta. Proc. XXVI Congresso Brasileiro de Ciências do Solo, Rio de Janeiro – Brazil.

McBride, M. 1994. *Environmental Chemistry of Soils.* Oxford University Press, New York.

Mendonça, E. S. and David L. Rowell. 1996. Mineral and organic fractions of two oxisols and their influence on effective cation-exchange capacity. *Soil Science Society of America Journal* 60:1888-1892.

Morais, F. I., A. L. Page, and L. J. Lund. 1976. The Effect of pH, Salt Concentration, and Nature of Electrolytes on the Charge Characteristics of Brazilian Tropical Soils.. *Soil Science Society of America Journal* 40:521-527

Mothci, E.P. 1977. Características, gênese e aptidão agrícola de uma sequência de solos no planalto central brasileiro. Ph.D in Soil Science. Universidade Federal do Rio Grande do Sul, Brazil.

Neto, J. S. M., Macedo, J. and Azevedo, L. G. 1981. *Brazilian Problems Soils: Distribution Characteristics and Utilization.* EMBRAPA, Planaltina, D. F., Brazil.

Novaes, P.M. 1993. Caracterização Geomorfológica do DF. In: *Cerrado: Caracterização, Ocupação e Perspectivas.* Edited by Novaes Pinto, M. Editora UnB, Brasília-DF Brazil.

Oades, J. M. and A. G. Waters. 1991. Aggregate Hierarchy in Soils. *Australian Journal of Soil Research* 29:815-829

Papp, C.S.E.; Lorraine H. Filipek, and Kathleen S. Smith. 1991. Selectivity and effectiveness of extractants used to release metals associated with organic matter. *Applied Geochemistry* 6:349-353.

Parker, J. C.; L.W. Zelazny, S. Sampath, and W. G. Harris. 1979. A critical evaluation of the extension of zero point of charge (ZPC) theory to soil systems. *Soil Science Society of America Journal* 43:668-674.

Ramos, P. C. M. 1985. Vegetation communities and soils in the National Park of Brasília. Ph.D., in Geography University of Edinburgh, Edinburgh Scotland.

Santos, M.C.D., A. R. Mermut, and M. R. Ribeiro. 1989. Submicroscopy of Clay Microaggregates in an Oxisol from Pernanbuco, Brazil. *Soil Science Society of America Journal* 53:1895-1901.

Schwertmann, V. 1964. Diflerenzierung der Eisenoxide des Bodens Durch. Extraktion. Mit Ammouriumoxalat-Lösung. Z. Pflanzwnarnähr. Düng. Bodenk. 105:194-102.

Schwertmann, U. 1985. The effect of environments on iron oxide minerals. *Advances in Soil Science* 1:172-200.

Souza, G. A. 1979. Estudo comparativo de Latosollos do Brasil. Ph.D. in Agriculture, Soil Science. Universidade Federal do Rio Grande do Sul, Brazil.

Sparks, D. L. 1995. *Environmental soil chemistry.* Academic Press Inc., San Diego CA.

Sposito, G. 1989. *The Chemistry of Soil.* Oxford University Press, New York NY.

Sposito G. 1992. Characterization of particle surface charge. In *Environmental Particles,* Vol.1, Chapter 7, edited by J.Buffle and H. Van Leeuwen Publ. Environmental Analytical Chemistry.

Sposito, G. 1984. *The Surface Chemistry of Soils.* Oxford University Press Inc., Riverside CA.

Spurr, A.R. 1969. A low-viscosity epoxy resin embedding medium for electron microscopy. *Journal of Ultrastructure Research.* 26:31-43.

Stevenson, F.J. 1982. *Humus Chemistry: Genesis, Composition, Reactions.* Wiley-Interscience, New York.

Stoops, G.J. and S.W. Buol. 1985. Micromorphology of Oxisols. L.A. Douglas and M.L. Thompson, (eds) Soil Micromorphology and Soil Classification, *Soil Science Society of America Special Publication* 15:105 – 119.

Stoops, G., Marcelino, G., Zauyah, S., and Maas, A. 1994. Micromorphology of soils of the humid tropics. Edited by A.J. Ringrose-Voase and G.S. Humphreys. Soil micromorphology studies in management and genesis, International Working-Meeting on Soil Micromorphology, *Developments in Soil Science* 22:1–15.

Thurman, E. W. 1985. *Organic Geochemistry of Natural Waters.* Martinus Nijhoff/ Dr W. Junk Publishers. Netherlands.

Tisdall, J.M., and J.M. Oades. 1982. Organic matter and water-stable aggregates in soils. *Journal of Soil Science* 33:141-163.

Van Raij, Bernado. 1971. Electrochemical properties of some Brazilian soils. Ph.D. in Agriculture, Soil Science. Cornell University.

Van Raij B., and M. Peech. 1972. Electrochemical properties of some oxisols and alfisols of the tropics. *Soil Science Society of America Journal* 36 (4):587-593.

Vettori, L. 1969. *Métodos de análise de solo*: Equipe de Pedologia e Fertilidade do Solo. Boletim Técnico 7. Rio de Janeiro, Brazil.

Vrdoljak, G.A. 1998. Ultramicroscopy of a Brazilian Oxisol. Ph.D. Thesis. University of California, Berkeley.

Wershaw, R. L. 1993. Model for Humus in Soil and Sediments. *Environmental Science and Technology* 27 (5):814-816.

Chapter 3

THE ROLE OF NATURAL ORGANIC MATTER (NOM) IN THE ADSORPTION OF COPPER IN AN OXISOL PROFILE.

Abstract

In the last few decades, many researchers have reported the influence of organic ligands in the sorption of ionic metals onto mineral surfaces (see for example: Davis and Leckie, 1978; Davis, 1984; Schindler and Stumm, 1987, Zachara et al., 1994). In most cases, organic ligands significantly increase or decrease the fraction of ionic metal adsorption onto metal oxide surfaces, depending on the mineral and the pH of the solution. The same behaviors are not always observed when the "ligand" is natural organic matter (NOM) and the sorption process involves trace metals and soils or sediments (Cavallaro and McBride, 1984; Singh et al., 1988; Xing et al., 1995; Smith, 1991). It seems that NOM, present in certain soils and sediments, does not always behave as it does in a simpler system, such as studies of monomineralic laboratory systems. To investigate the role of NOM in the adsorption process of Cu(II) onto an oxisol profile, three soil horizons were well characterized and had their NOM fraction partially removed by oxidation with NaOCl (5% by volume). Copper adsorption edges before and after NOM oxidation show that there are only insignificant changes in copper sorption after NOM oxidation. In addition, sorption isotherms before and after NOM oxidation suggest that NOM is responsible for a maximum of 30% of the Cu(II) adsorption onto soil from the uppermost horizon, A_1. This is a small contribution compared to other experiments of copper sorption on pure minerals in the presence of NOM. For the Bw_2 horizon, the oxidation of NOM actually increases copper sorption to the soil and for the C_2 horizon the oxidation has no measurable affect. The adsorption of Cu(II) was investigated over a pH range from 3.0 to 6.5, with one order of magnitude variation in the solution ionic strength. The results from sorption experiments suggest that the mechanism of the copper sorption to soil may have both inner-sphere and outer-sphere components.

Introduction

Natural organic matter (NOM) occurs in essentially all surficial environments including soils, fresh surface and groundwaters, and marine systems. NOM in soil systems is widely recognized for playing an important role in regulating physical and chemical soil properties. NOM can affect soil properties such as buffering capacity, sorption of inorganic and organic compounds, stability of soil particles, and water-holding capacity (Wershaw, 1993). From an environmental point of view, NOM can significantly affect the sorption of toxic trace metals and organic pollutants (Jenne, 1998; Chiou, 1989). A better understanding of the role of NOM in the sorption of pollutants in soils can improve our ability to make accurate predictions of the fate and transport of pollutants in the subsurface. It can also aid in better estimates of the bioavailability of toxic metals, since NOM is well known to be a strong sorbent of trace metals (Davis, 1984; Righetto et al., 1991; Ali and Dzombak, 1996).

The sorption of trace metals by minerals can be significantly affected by the presence of NOM. Several geochemists have reported the effects of NOM in the sorption of trace metals by different mineral sorbents (Table 3.1). The NOM generally affects the sorption of trace metals on minerals by increasing their sorption at low pH by complexing with organic functional groups attached to the mineral surfaces. And it reduces metals sorption at high pH due to complexation of metals with NOM that is not attached to mineral surfaces. Soil scientists and some geochemists who have worked with certain natural soils or sediments (Table 3.2) have observed different sorption behavior. NOM in these environments has been reported to play a limited role in the sorption of trace metals (Cavallaro and McBride, 1984; Singh et al., 1988; Smith, 1991). Soil mineral solubility, as well as their different abilities to sorb and compete with NOM for metals present in solution, makes the studies of metal sorption in natural systems a challenging one.

Oxisols are an acidic type of soil predominant in the tropical savannas of South America and Africa. They formed as the consequence of intense weathering processes for long periods of time. The oldest oxisol in Brazil dates back to the Pleistocene (White, 1978); therefore, most of the constant charge minerals (clays type 2:1) have already been leached. The most predominant minerals in these soils (i.e., those minerals remaining after the intense leaching) are quartz, kaolinite, hematite, and gibbsite. These minerals are rich in silicon, aluminum and iron and have a variable mineral surface charge (Van Raij and Peech, 1972; Charlet, 1986; Chorover, 1993).

The research reported herein is designed in part to test the hypothesis that oxisol NOM does not play a major role in the sorption of copper. Similar observations have been reported by other researchers who performed similar studies on acidic soils and sediments rich in iron and aluminum (Cavallaro and McBride, 1984; Singh et al., 1988; Smith, 1991). It is known that trivalent cations such as aluminum and iron bind strongly to humic substances (McBride, 1994) and can also compete with copper for the same binding sites (Stevenson, 1982).

The goal of this work is to estimate the role of NOM in the sorption of copper in three well-characterized oxisol horizons. A series of isotherms at pH 5.0 and sorption edges with pH ranging from 3.0 to 6.5 were performed before and after NOM oxidation by sodium hypochlorite (NaOCl) to quantitatively estimate the partitioning of copper to NOM. Two sets of sorption edges at different salt concentrations were performed to investigate the nature of copper complexation on oxisols (inner-sphere or outer-sphere complexation). The dissolution of aluminum and iron was monitored during the sorption experiments to evaluate the effect on copper sorption.

Table 3.1 - Summary of metal sorption research in metal ion/organic ligand/mineral systems.

Sorbent	*Metal ion*	*Ligand(s)*	*Result*	*Authors*
HFO	Cu(II), Ag(I)	model organic acids	Sorption behavior (e.g., orientation at particle surfaces) of organic ligands must be considered.	Davis and Leckie (1978)
γ-alumina	Cu(II) and Cd(II)	lake NOM	Cu complexation by sorbed NOM is stronger than Cu complexation by surface alumina groups; Cd not affected by sorbed NOM	Davis (1984)
natural sediments	Pu(III,IV)	lake and river DOC	Fractional metal sorption decreased as [NOM] increased	Nelson et al. (1985)
(am)-silica	Cu(II)	2,2′-bipyridine	Cu sorption is enhanced in the presence of the bipyridine; non-sorption of uncoordinated bipyridine.	Schindler and Stumm (1987)
γ-alumina, amorphous silica	Am, Th, Np, Pu	HA	Extent of actinide sorption depends on the extent of HA binding of the actinide on the surface and in solution.	Righetto et al. (1991)
HFO	Ni	EDTA	Fraction of Ni sorbed depends on the component addition sequence; EDTA sorption was independent of sequence.	Bryce et al. (1994)
gibbsite, Al-goethite, kaolinite	Co(II)	Leonardite humic acid	Mineral-bound LHA increased Co sorption.	Zachara et al. (1994)
quartz, hydrargillite and goethite	Zn(II)	fulvic acid	Zn sorption either enhanced or reduced in the presence of FA, depending on component ratios.	Duker et al. (1995)
goethite	Ca, Zn, Ni, Cu, Co(II), Pb	EDTA	Ligand-like sorption of M-EDTA complexes	Nowak and Sigg (1996)
α-alumina	Cd	citrate	Enhanced Cd sorption in the acid-pH range; reduced Cd sorption in the alkaline pH range.	Boily and Fein (1996)
goethite	Cu and Ca	phthalic and chelidamic acids	Enhancement of Cu sorption at low pH-values possibly due to the formation of Cu/acid 'ligand-like' surface complexes; Ca sorption unaffected by phthalic acid	Ali and Dzombak (1996)

Table 3.2 - Summary of researches demonstrating the non-predominance of natural organic matter in the sorption of transition metal ions in soil/sediment systems.

Sorbent	*Metal ion*	*Ligand(s)*	*Result*	*Author(s)*
Estuarine sediments	Cd(II) and Pb(II)	Natural organic matter	Natural organic matter did not affected the sorption of Pb(II) on estuarine sediments	Lion et. al. (1982)
Soils	Zn (II) and Cu (II)	Soil minerals and natural organic matter	Remove of natural organic matter by NaOCl either enhance or have little effect on sorption and fixation of Cu and Zn.	Cavallaro, N. and McBride M. B. (1984)
Soils	Cu(II), Fe(III), Mn(II), and Zn (II)	Soil minerals and natural organic matter	Less than 0.1% of the trace metals had their soil partitioning associated to natural organic matter.	Singh, et. al., (1988)
Soils	Al(III), Fe(III)	Clay minerals	Part of Al(III) and Fe(III) complex with humus and block ionized carboxyl groups of humus resulting in variable negative charges for humus, allowing sorption of phosphate.	K. Wada (1995)
Soils	Cu(II)	Mn oxides, organic matter	The extraction of organic matter represents no obvious effect on the quantity of Cu retained.	Xing et.al. (1995)
Acid mine drainage	Cu(II)	Fe oxides, natural organic matter	Substantial differences in organic matter content of stream sediments made no difference in Cu(II) sorption edges	Smith, K.S. et. al. (1998)

Material and Methods

Soil sampling and characterization

Soil samples for the experiments were collected from Brasília National Park in Brasília D.F. – Brazil. A 2.0-meter deep trench and a 3.90-meter hole made by an auger allowed us to describe and classify ten soil horizons in the vadose zone (Figure 3.1). Soil samples were air dried and sieved into fractions smaller than 2.00 mm. Three soil horizons (A_1, Bw_2, and C_2) were selected for further studies of copper sorption by batch experiments before and after oxidation of the soil natural organic matter (NOM).

Sodium hypochlorite at pH 9.5 was the method of choice for the oxidation of most oxisol NOM without destruction of the oxide and kaolinite phases (Lavkulich and Wiens, 1970). The method used here was the same as that described in Chapter 2, and now the treatement was also made on the other two soil horizons (Bw_2 and C_2). An acid solution of HCl at pH 2 was added to the remaining soil, after NaOCl treatment, and the mixture was shaken for a few minutes to lower the interstitial soil solution pH back to the natural soil acidic pH of 5.0.

Soil fractions were analyzed by x-ray diffraction (XRD). Soil samples were ground in a porcelain mortar and pestle prior to XRD analysis on a Scintag X-1 diffractometer. Using a sample spinner, random oriented powder samples were submitted to Cu α radiation (45 kV, 35 mA). Sample parameters were as follows: scan range from 4^o to 62^o 2θ step size of 0.02, and counting time of one second. The relative intensity of the diffracted peaks was used to estimate the relative abundance of the different minerals in the soil and clay samples (Table 3.1). This estimation was possible due to the use of the software JADE + with s/m version 3.1 in conjunction with reference intensity ratios (RIR) of the phases present. X-ray analyses were made before and after soil treatment with sodium hypochlorite (NaOCl - 5% vol.) (Figure 3.2) and ammonium oxalate at pH 3 in the dark to verify changes in the crystalline soil phases during chemical treatments.

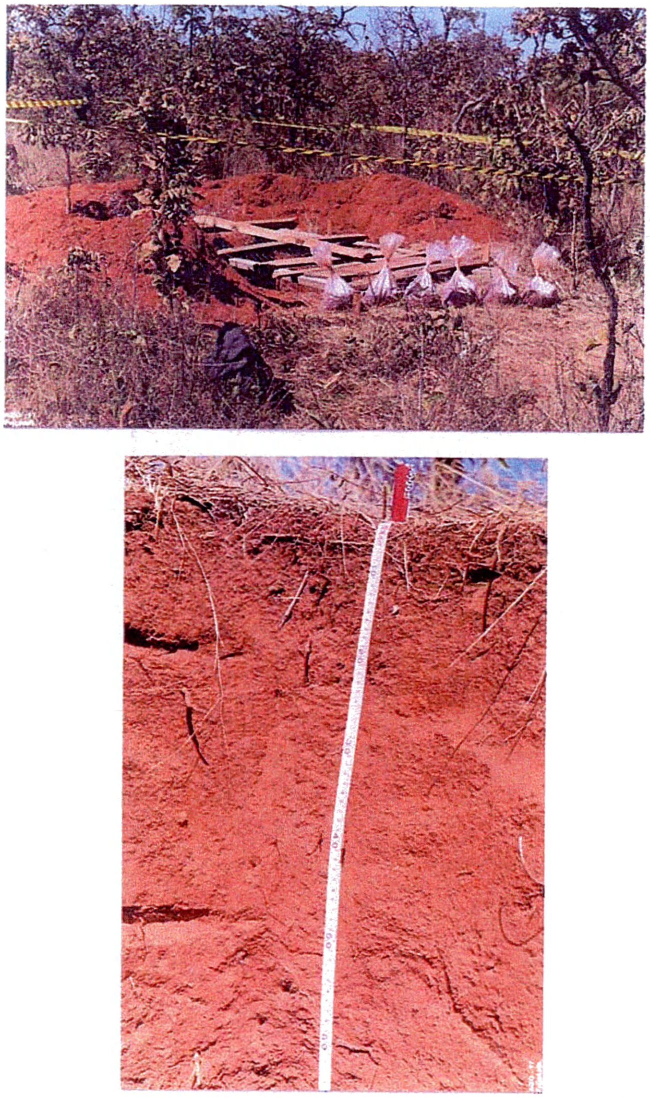


Figure 3.1 – Picture of the sampling site showing the dug trench and a detailed picture of the top soil horizons in field.

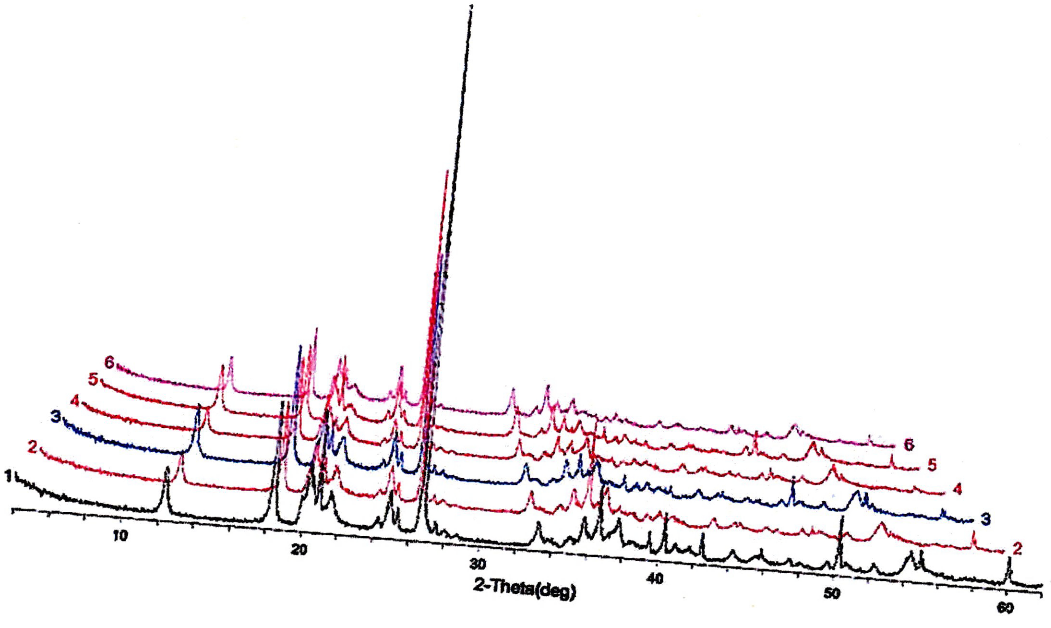


Figure 3.2 - X-ray diffractogram of all soil horizons before and after NaOCl treatment. 1 = Untreated A_1, 2 = Treated A_1, 3 = Untreated Bw_2, 4 = Treated Bw_2, 5 = Untreated C_2, 6 = Treated C_2.

Soil bulk iron and aluminum composition, organic matter content, amorphous material content, specific surface area, and point of zero salt effect (PZSE) were estimated using the soil characterization methods described in Chapter 2. An example plot for the determination of the pH_{PZSE} for soil from the A_1 horizon is presented in Figure 3.3.

Cu (II) sorption experiments

All soil samples used either for kinetic studies or for copper sorption experiments were treated with a series of $NaNO_3$ solutions of different concentrations to remove soil exchangeable ions. Ten grams of dry soil were mixed with 42.85 ml of 0.5 M $NaNO_3$ at pH 6.0 ±0.02 and gently shaken for ten minutes. The solution was then allowed to settle for one hour and the supernatant liquid was carefully collected by a 20-ml glass pipette. The remaining solid received the same treatment a second time. Then the same volume of $NaNO_3$ solution at the same pH, but now 0.1 M, was mixed with the same soil material and gently shaken for ten minutes. After this period the soil solution was centrifuged at 2500 rpm for 15 minutes and the supernatant liquid was carefully collected by a 20-ml glass pipette. This procedure was repeated once again. This last procedure was repeated once more, but now with 0.01 M $NaNO_3$ at pH 5.0 ±0.02. The range of pH used for the replacement of exchangeable ions was chosen to avoid a significant dissolution of low crystalline minerals and amorphous soil material (Charlet, 1986; Chorover, 1993). The remaining soil material was stored under refrigeration for further experiments, except for three sub-samples (< 0.5 g) that were placed in porcelain crucibles. The crucibles were weighed and then placed in an oven at $110^{o}C$ for a period of 24 hours. A series of readings of the weights of the crucibles with soil material were taken during this period and the soil moisture content was measured at the end.

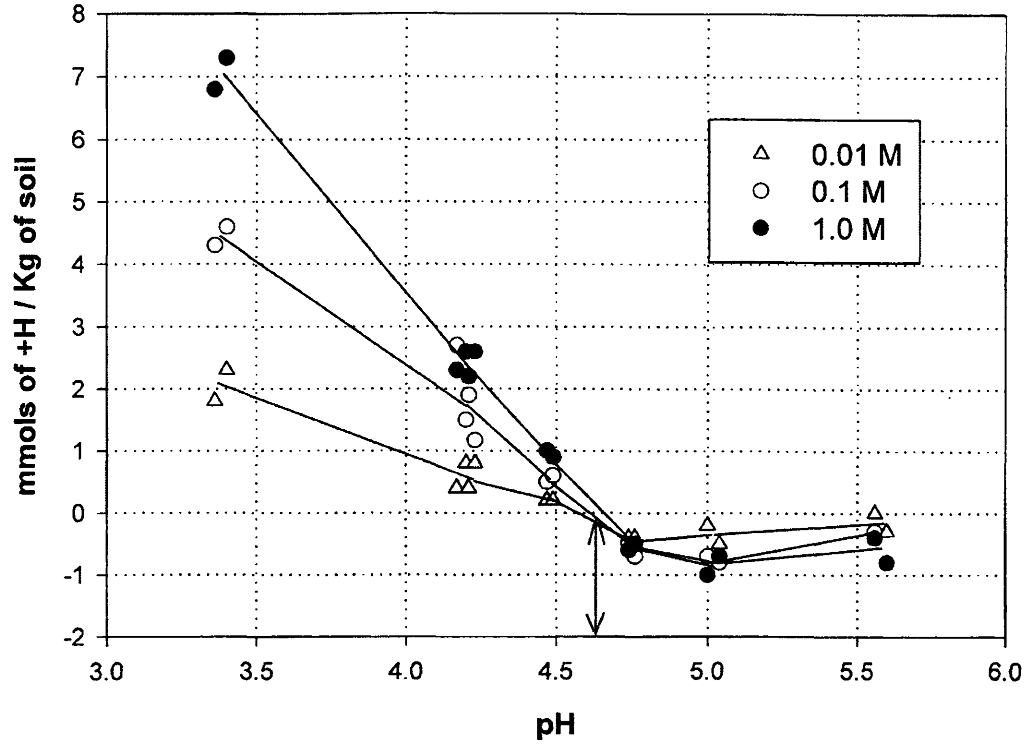


Figure 3.3 – Salt titration of untreated oxisol sample from A1 horizon. Point of zero salt effect = 4.7.

The time required for the copper equilibration with oxisol was previously established by batch experiments mixed for 6 to 72 hours. The experiments were performed with a soil solution ratio of 3.3g/l at pH 5. Copper sorption is characterized by a rapid uptake followed by a period of slower prolonged sorption (Figure 3.4). 'Equilibrium' was defined as reached at a constant time of 24 hours. Such a 'equilibrium' time is in agreement with other researchers who worked with trace metals sorption to natural media (Lion et al., 1982; Coston et al. 1995; Guilherme and Anderson, 1998).

Sorption experiments at various copper concentrations at a fixed pH of 5 (isotherms) and varying pH from 3 to 6.5 (sorption edges) were performed. For both experiments the ratio of soil to solution was kept at 3.3 g/l to facilitate comparison of results for different types of experiments. The copper solution concentration in the experiment varied from 5 to 125 μM for the isotherm experiments; it was fixed at 10 μM for the sorption edge experiments. Copper solutions for sorption experiments was made from a copper ICP standard solution (9,500mg/l) diluted by Nanopure™ water. A specific weight of solid $NaNO_3$ was added to the copper solution to make the electrolyte concentration either 0.01 or 0.1 moles/l.

Once soil material and the copper solution were combined in a clean 50-ml plastic centrifuge tube, the soil solution pH in each tube was adjusted by the addition of 0.1 moles/l HNO_3 or NaOH. Each set of experiments covered a pH range of 3.0 to 6.5. This is the natural pH range of oxisols in the field. The amount of acid and base added to the soil solution was less than 1% of the total copper soil solution volume, so this dilution was considered insignificant during the sorption experiment. Solution pH was occasionally adjusted for the first 12 hours, and then the solution was gently shaken for another 24 hours and a final pH reading was taken at the end. The soil solution was then centrifuged at 2500 for 10 minutes, 10 ml of the supernatant liquid was filtered with a 0.45 μm filter and acidified by adding 1% volume of concentrated HNO_3. This solution

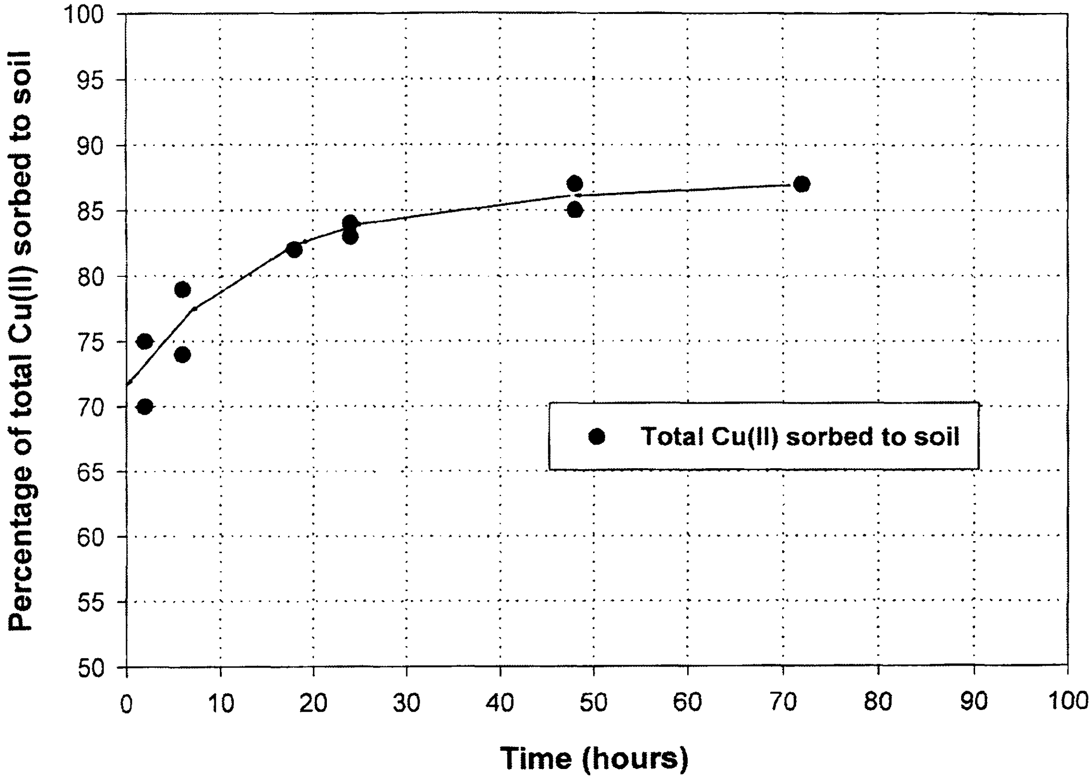


Figure 3.4 – Plot of total Cu (II) sorption to an oxisol sample at pH 5, I = 0.01 M NaNO3, and soil/solution = 3.3g/l.

was analyzed by the Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES - Perkin Elmer model Optima 3000). Quality control standards were analyzed before the sample analysis and an internal standard of scandium (1% of 500 ppm) was used to calibrate the instrument for fluctuations in plasma conditions.

Each ICP analysis gives the concentrations of 32 elements. In addition to copper concentration in the solution, iron and aluminum were also monitored to follow oxisol mineral dissolution. For each set of sorption experiments, three blank copper solutions, without soil material, were also measured for copper concentration at pHs 3.0, 5.0 and 6.5. Copper sorption to the soil was determined by the difference between the total copper added and the dissolved-phase copper after equilibration. Each sorption point was made in duplicate and have all the sorption points are plotted.

Results

Soil characterization

The oxisols characterized for this study are classified by the United States Department of Agriculture (USDA) method as Typic Acriustox. Table 3.3 presents a chemical, mineralogical, and physical characterization of the soil horizons. Both results are shown for soil analyses performed in duplicate. For soil analysis performed in triplicate, the mean and the standard error ( ) are shown.

Soil samples have a homogenous iron and aluminum bulk composition along the soil profile in a proportion of ≈ 2:1 aluminum to iron (Table 3.3). The constant iron and aluminum concentrations along the soil profile are reflected in the soil mineralogy. In the soil clay fraction, kaolinite, an aluminum silicate, is the predominant mineral. This is followed by gibbsite, an aluminum hydroxide, and hematite, an iron oxide. Almost the same mineral predominance is observed in the whole soil (<2 mm) with the exception of quartz, a silicate mineral, which is the predominant mineral species in the top horizon, and the second most predominant in the intermediate horizon and the third most predominant in the deepest horizon. Rutile, a titanium oxide, is a minor mineral (approximately 1%) present in all horizons in the whole soil (<2 mm). Besides the decrease in quartz along the soil profile, soil NOM has a constant decrease from 2.32% to 0.35% in weight percent carbon (Table 3.3).

Soil total digestion by strong acids also shows a uniform bulk composition of the soil profile in terms of iron and aluminum content. The results support the XRD analysis that showed a uniform chemical composition along the soil profile (Table 3.3).

To estimate the concentration of those portions of the iron and aluminum which are non-crystalline along the soil profile, extractions with ammonium oxalate at pH 3 in the dark (Schwertmann, 1964) were performed. The results show a small fraction of non-crystalline material in these soils (less than 1%). There is a predominance of amorphous aluminum material over iron. The method used is operationally defined and does not give absolute values of the concentration of amorphous material in these soils. However, the analyses of these soil samples via transmission electron microscopy (TEM) support these results (Chapter 2).

To estimate the soil surface charge, salt titrations were performed to obtain the point of zero salt effect (PZSE) (Figure 3.3). Since there are no permanently charged minerals (clays 2:1) in these soils, the pH at the PZSE is equal to the point of zero net charge (PZNC), which is equal to the point of zero net proton charge (PZNPC) (Sposito, 1984; Charlet, 1986; Chorover; 1993). The PZSE results for these soils show an increase in the pH value from the top horizon (A_1) to the lowest horizon (C_2) (Table 3.3). This increase in PZSE along the soil profile is correlated with the decrease in percentage of organic carbon (Van Raij and Peech, 1972). The higher the concentration of organic carbon in a soil sample, the lower its PZSE due to the negative charged associated with soil NOM (Morais et al., 1976; Bell and Gillman, 1978; Mendonça and Rowell, 1996).

Analyses of soil specific surface area were performed before and after soil organic matter oxidation by NaOCl (Table 3.3). The results show an increase by approximately

22% in soil surface area for the A_1 horizon after oxidation of soil NOM. The same increase in soil surface area is not observed in the other two soil horizons.

There was no significant change in soil mineralogy after oxidation of soil NOM by NaOCl. Only some decrease in the intensity of quartz peaks, on the XRD diffractrogram, was observed in samples from the A_1 horizon (Figure 3.2). No mineralogical change was observed by the XRD analysis after extraction of the amorphous material with ammonium oxalate.

Copper sorption experiments

A kinetic study was performed with batch experiments to find the time required for the copper sorption reaction to soil to reach equilibrium (Figure 3.4). Despite the fact that copper sorption to monomineralic oxides usually reaches equilibrium in a few minutes to a few hours (Davis and Leckie, 1978; Spark et al., 1995a), results obtained from these oxisol experiments show a longer time to reach equilibrium. In my kinetic studies, copper sorption to oxisol is characterized by an initial rapid uptake followed by an extended period of slow sorption (Figure 3.4). Because of the prolonged gradual uptake, 24 hours were chosen as our 'equlibrium' time. Guilherme and Anderson (1998) also found that at lest 24 hours was needed to investigate the role of phosphate in the sorption of copper to oxisols.

Once a standard time for copper reactions with oxisol was established, copper isotherms were developed. The sorption isotherms were established at pH 5 and under the same conditions of solution ionic strength and soil solution ratio as for the sorption edge experiments. The experiments were performed before and after partial removal of soil NOM by NaOCl (Figure 3.5). All the isotherms were classified as Freundlich type (Figure 3.6). The sorption isotherm data were plotted on logarithmic scales of copper in solution versus copper sorbed to a mass of soil. The raw data (Appendix A) were all fitted using linear least square regression and the slopes for all of the different isotherm experiments were significantly less than one.

Table 3.3 - Soil chemical, mineralogical and physical characterization.

Soil horizon:	A_1	Bw_2	C_2
Soil % Weight			
% Fe	7.4	7.7	7.9
(duplicate)	7.6	7.9	8.5
% Al	15.4	16.2	16.3
(duplicate)	16.2	17.2	16.9
% Organic C	2.32 (±0.01)	0.84 (±0.003)	0.35 (±0.003)
Soil Mineralogy*			
< 2.0mm	Q>K>G>H>A	K>Q>G>H>A	K>G>Q>H>A
Clay fraction	K>G>H	K>G>H	K>G>H
Amorphous Material**			
Fe (g/Kg)	2.0	1.1	0.7
(duplicate)	1.6	1.2	0.7
Al (g/Kg)	2.8	2.8	1.5
(duplicate)	3.4	2.8	2.1
P.Z.S.E.***	4.7	5.4	5.6
Surface Area (m^2/g)****			
Before	94.3 (±1.3)	118.6 (±2.3)	94.8 (±0.75)
After	114.8 (±0.1)	116.6 (±5.4)	94.9 (±1.9)

*Mineralogy: Q = Quartz, K = Kaolinite, G = Gibbsite, H = Hematite, A = Anatase.

**Amorphous material: Ammonium Oxalate at pH = 3.0 in the dark (Schwertmann, 1964).

***P.Z.S.E. = Point of Zero Salt Effect.

****Surface Area: B.E. T. method before and after soil treatment with NaOCl (5% vol.).

Dissolution of total aluminum and iron was evaluated during batch experiments for copper sorption to oxisols. The amount of total dissolved aluminum and iron per kilogram of soil before and after NaOCl treatment was plotted as a function of pH. (Figures 3.7 and 3.8). The results show different behavior for the unmodified and treated oxisols. The dissolution behavior is also different for each Fe and Al. For the aluminum dissolution from untreated soils, the maximum dissolution occurs at a low pH, decreasing with the increase of pH until pH 4.5. Then the aluminum dissolution increases from pH 4.5 to pH 6.5. The iron dissolution from untreated soils is also a function of pH, but not as intensely as aluminum, and it varies in the range of 0.1 to 2.0 mmols per kilogram of soil with minimum dissolution at pH close to 4.5 (Figure 3.7). Chorover (1993) and Malengreau and Sposito (1997) observed very similar aluminum dissolution as a function of pH for the oxisols. For the treated soils, aluminum dissolution has the same pattern as the untreated soils at pHs lower than 4.5, except that in this case aluminum dissolution was two to four times more than the untreated soils (Figure 3.8). However, at pH's higher than 4.5 the aluminum dissolution does not increase and remains at 2 to 5 mmols per kilogram of soil. For iron the same change in dissolution is also observed, but at less intensity. Iron dissolution for the treated soil samples reduces to values very close to zero in the pH range greater than 4.5.

Sorption edges were performed on soil samples from all three horizons before and after soil NOM oxidation by NaOCl at 0.01 and 0.1 M ionic strengths. All the sorption edges on untreated soil samples present a typical sigmoid shape of trace metals sorption to oxides (Davis and Leckie, 1978; Spark et al., 1995a) (Figure 3.9). The percentage of copper sorbed to the soil surface increases from approximately 10% at pH 3.0 to 90% at pH 5.0. No untreated sample at pH values more than 5.0 sorbed 100% of the copper in the solution. However, after oxidation of soil NOM by NaOCl, all soil horizons at pHs higher than 5.5 sorbed 100% of copper in solution (Figures 3.10, 3.11, and 3.12). Although copper sorbs to oxyhydroxides minerals in innersphere complexes (McBride, 1982), in oxisols copper, may have a non-specific sorption component due to the influence of kaolinite, which binds copper as an ion-pair (Schindler et al., 1987; Spark et al., 1995b). In these experiments, increasing solution ionic strength caused a shift of the sorption edge to higher pH (Figures 3.13 and 3.14).

Discussion

Soil characterization

The intense, extended weathering of the soil is the main reason for the homogeneous bulk chemical and mineralogical composition of any oxisol profile. All the feldspar minerals and possible constant charge minerals such as type 2:1 clays, have been leached from the soil. The remaining minerals, quartz, kaolinite, gibbsite, hematite, and anatase have a lower solubility constant than do the more leacheable minerals. Type 2:1 clays are also reported to be present in some tropical oxisols (Chorover 1993); however, they are not as abundant as kaolinite or oxyhydroxide minerals.

The results showing the amount of iron and aluminum in the studied oxisol profile reflect its soil mineralogy. Oxisols are typically clay types of soils that have their clay size minerals well structured in a very stable aggregate form (Chapter 2). The stable aggregates are formed because the soil net charge in oxisols (pH = 4.7 in this case) is zero at a pH very close to the natural soil pH (approximately 5.0-5.5), favoring attractive particle-particle interactions rather than repulsion (Lima, 1995). The clay-size fraction in the studied profile is predominately composed of kaolinite, gibbsite, and hematite (Table 3.3). The first two predominant minerals have aluminum in their mineral structure. Iron is present in hematite but not in kaolinite or gibbsite. Therefore, the aluminum predominance over iron can be explained by the clay-size mineralogy. The percentage of organic carbon along the soil profile significantly decreases from 2.3% in the A_1 horizon

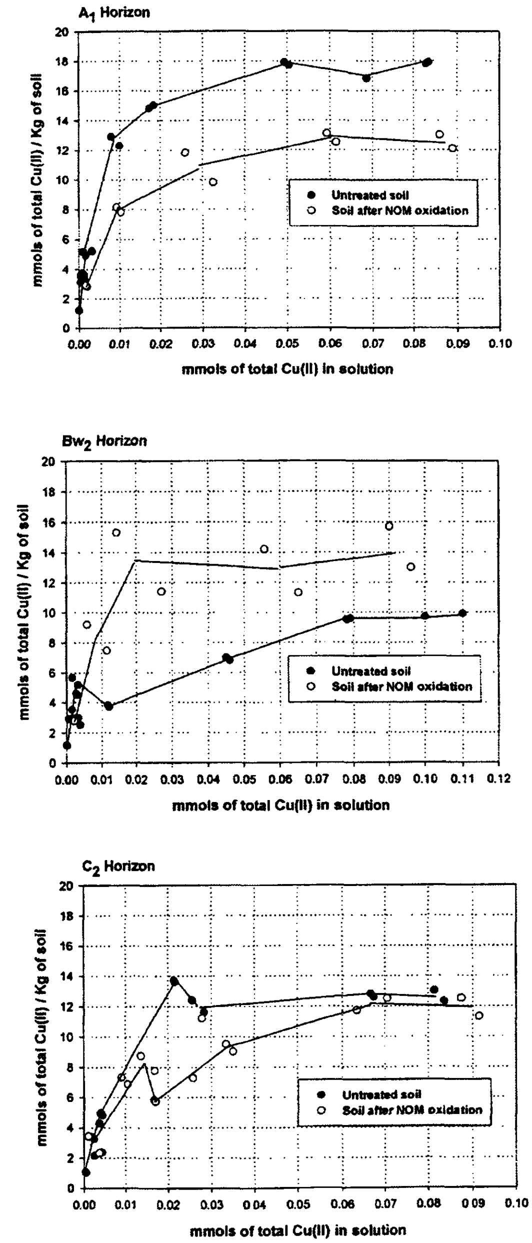


Figure 3.5 – Total Cu(II) sorption isotherm before and after oxidation of soil NOM by NaOCl. Soil solution pH = 5.0, Ionic strength = 0.01 M $NaNO_3$, and ratio of soil: solution = 3.3 g/l.

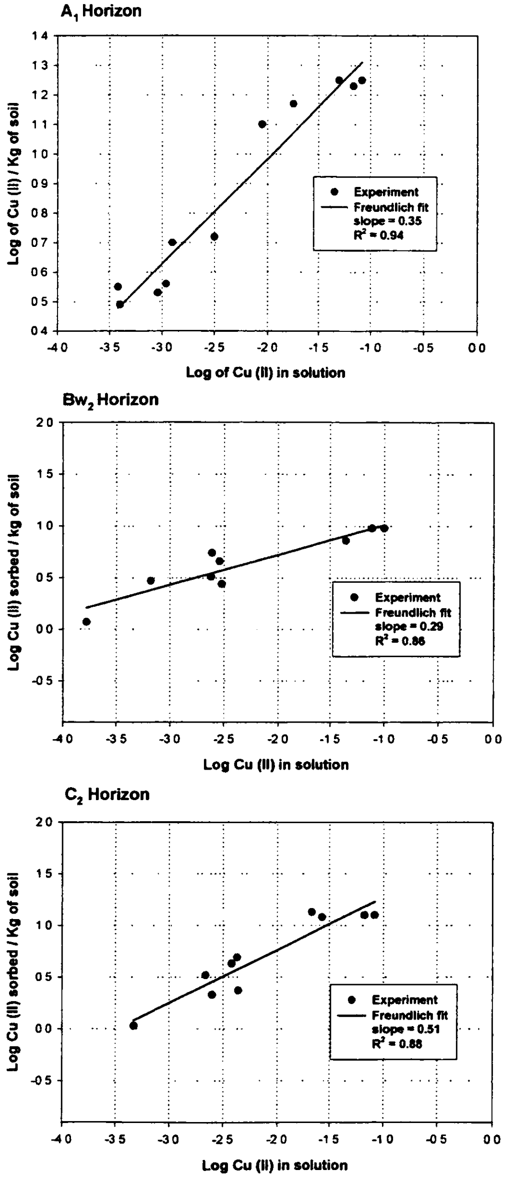
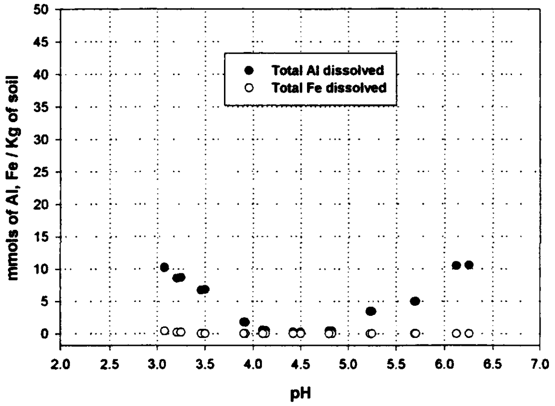
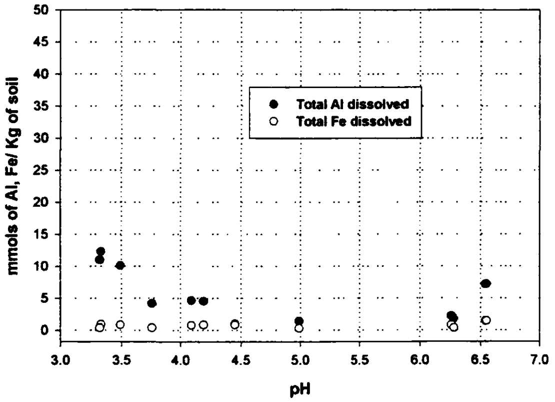


Figure 3.6 - Copper sorption isotherm on untreated soil horizons at pH 5.0 and ionic strength 0.01 M $NaNO_3$.

A_1 Horizon



Bw_2 Horizon



C_2 Horizon

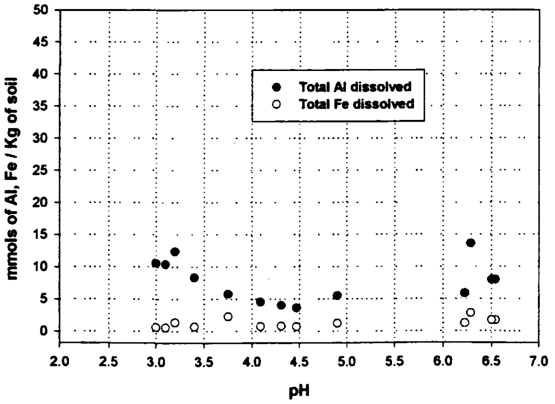


Figure 3.7 - Total Al and Fe dissolution on untreated soils during batch experiments

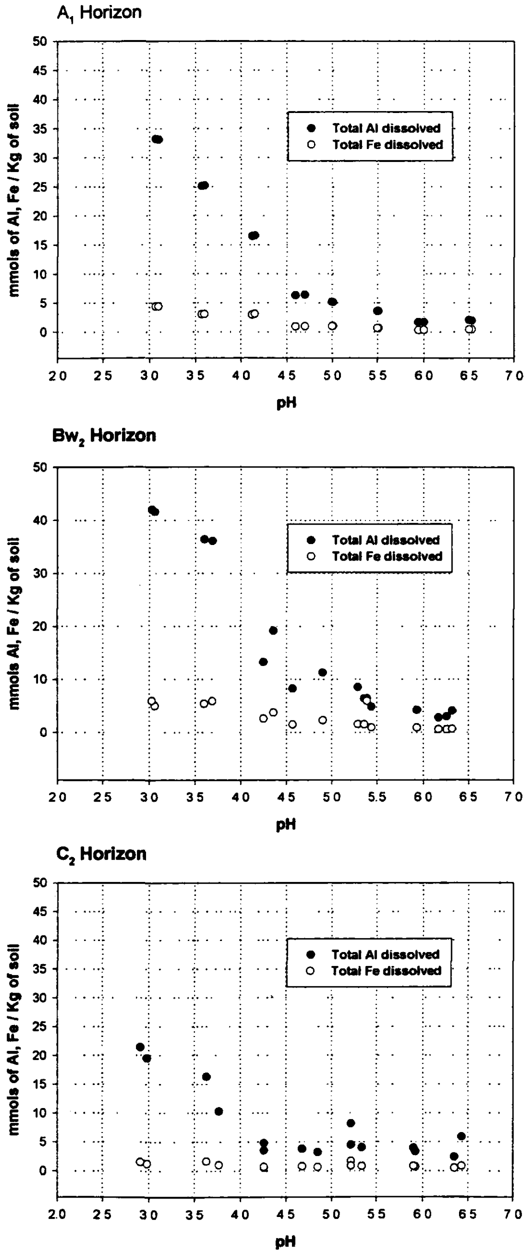


Figure 3.8 - Total Al and Fe dissolution on NaOCl treated soils during batch experiments.

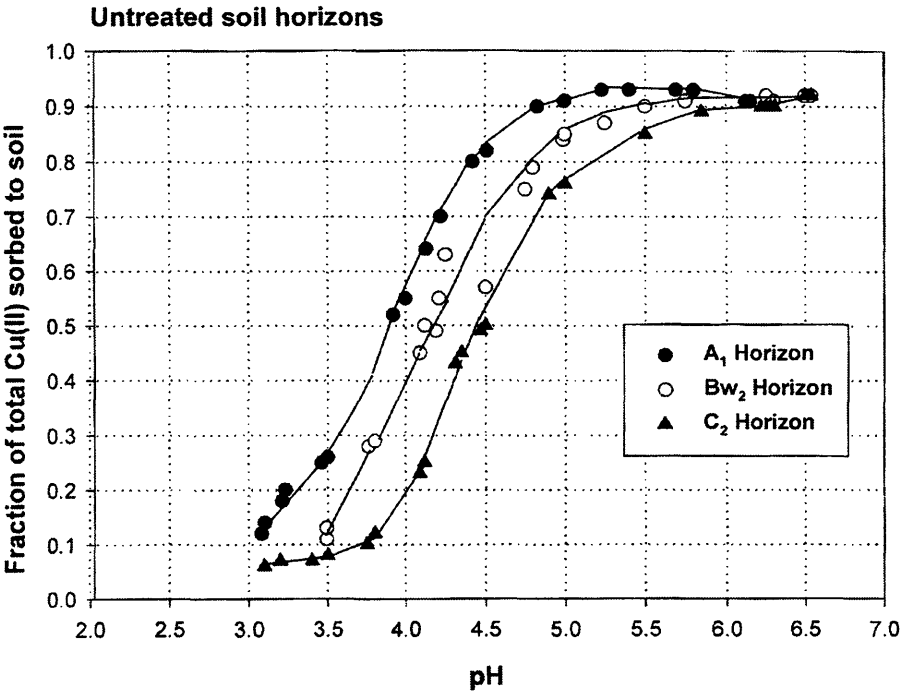


Figure 3.9- Copper sorption edge on untreated soil horizons. Total Cu(II) = 10 μM and Ionic strength = 0.01 M $NaNO_3$ Soil:solution ratio = 3.3g/l.

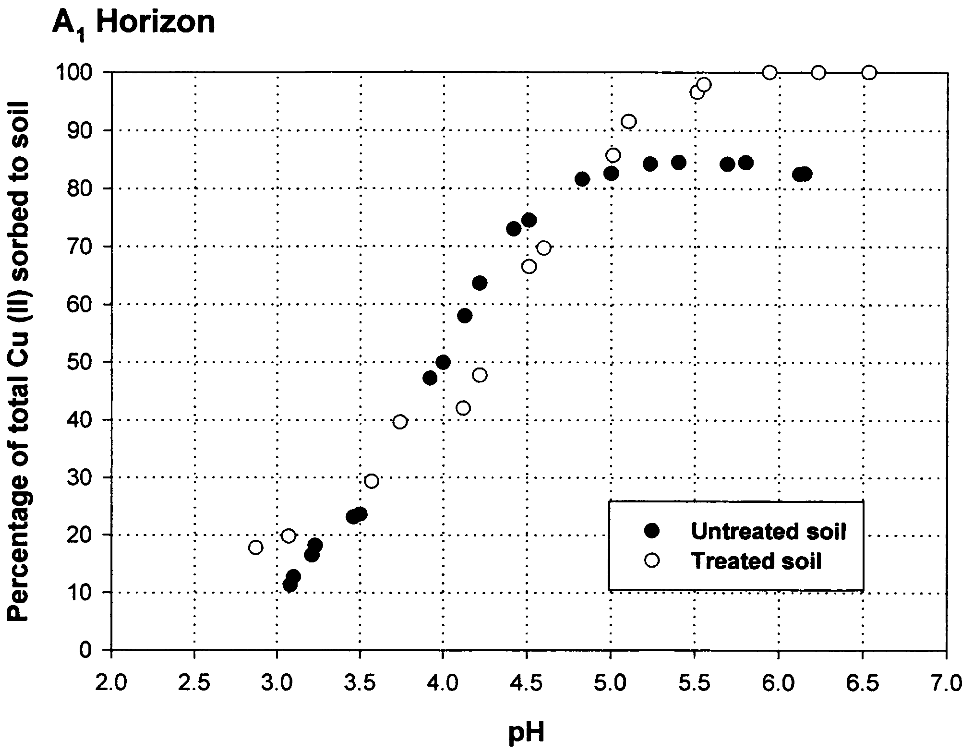


Figure 3.10- Copper sorption edge on A_1 soil samples untreated and treated with NaOCl. Total Cu (II) = 10 μM and Ionic strength = 0.01 M $NaNO_3$.

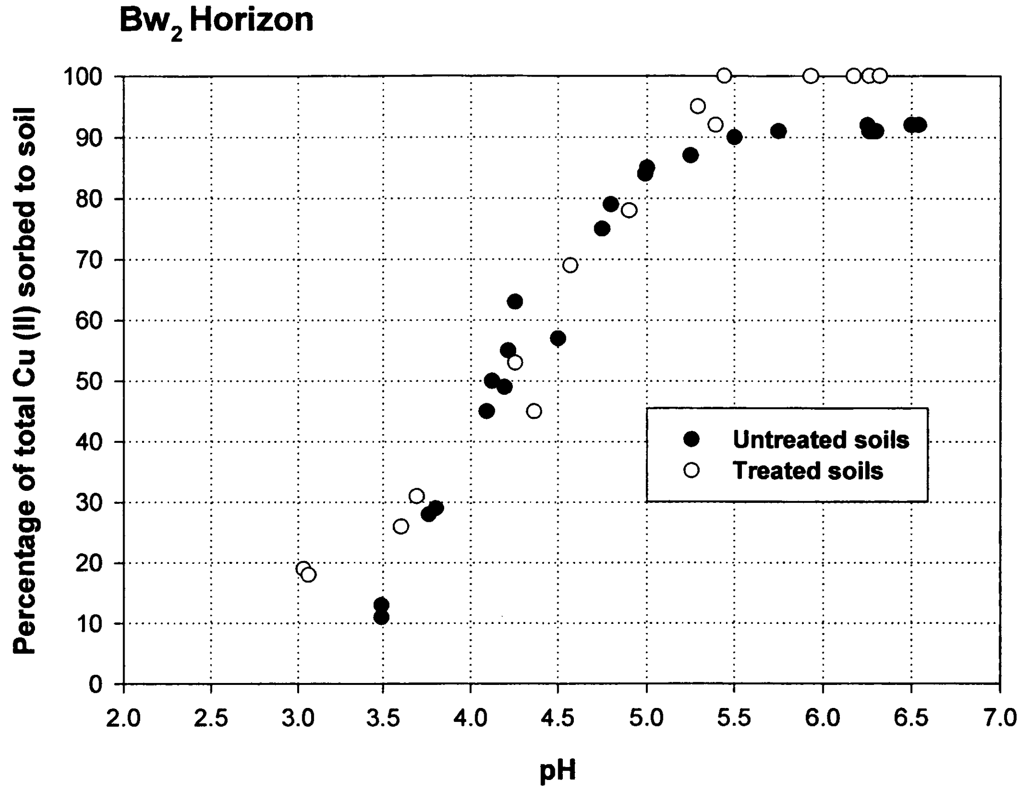


Figure 3.11 - Copper sorption edge on Bw_2 soil samples untreated and treated with NaOCl. Total Cu (II) = 10 μM and Ionic strength = 0.01 M $NaNO_3$.

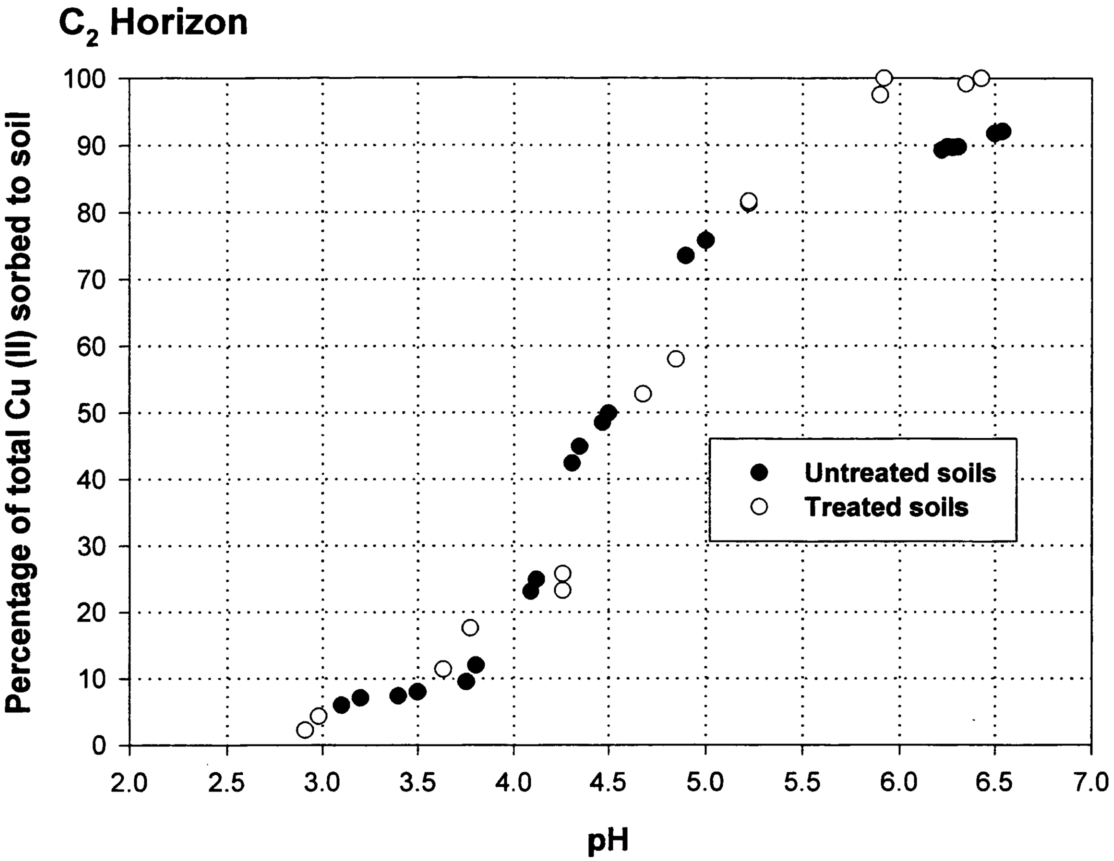


Figure 3.12 - Copper sorption edge on C_2 soil samples untreated and treated with NaOCl. Total Cu (II) = 10 μM and Ionic strength = 0.01 M $NaNO_3$.

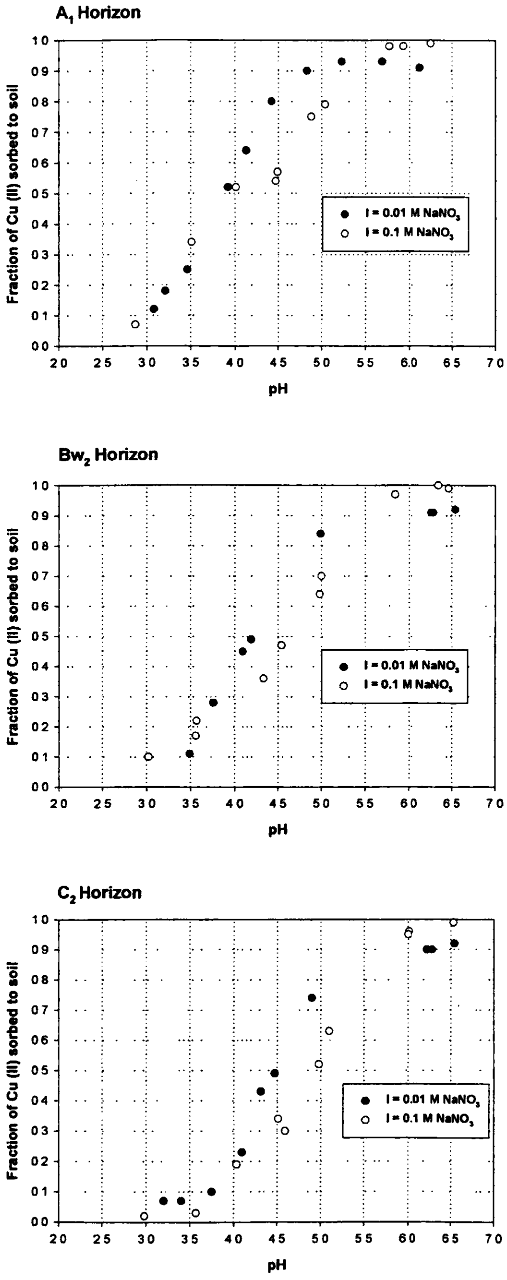


Figure 3.13- Copper sorption edges on untreated soil samples from different horizons. Total copper = 10 μM and Ionic strength = 0.01 and 0.1 M $NaNO_3$.

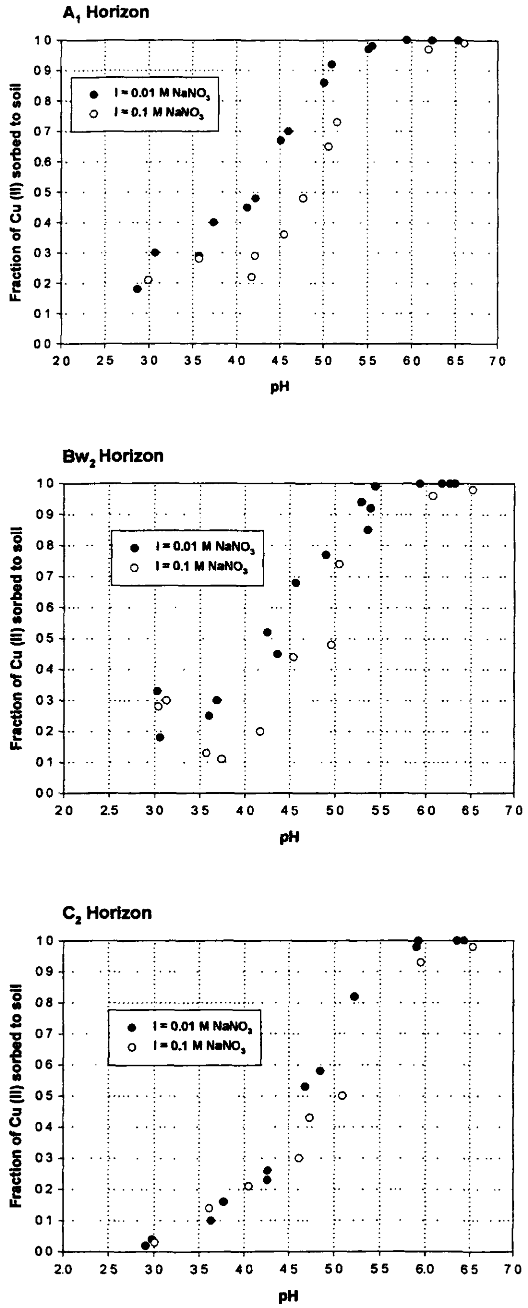


Figure 3.14- Copper sorption edges on treated soil samples from different horizons. Total copper = 10 μM and Ionic strength = 0.01 and 0.1 $NaNO_3$.

to 0.35% in the C_2 horizon (Table 3.3). In this oxisol profile, no inorganic carbon was detected. Hence, the carbon present in each soil horizon is entirely from natural organic matter. The origin and amount of NOM in each environment is determined by processes such as decomposition of plants and animals, micro-organism activity associated with physical factors (climate, vegetation, parent material and topography), and time (Thurman, 1985). Therefore, the main reason for the higher content of organic matter in the top horizon is related to the abundance of biomass in this horizon in comparison to the lower soil horizons.

Amorphous material was considered in this study as the fraction of soil that does not have a mineralogical structure; therefore, while it can not be recognized by x-ray diffraction (XRD) it is visible by transmission electron microscopy (TEM). Among the various methods suggested to extract amorphous iron and aluminum oxyhydroxides, ammonium oxalate at pH 3.0 in the dark (Schwertmann, 1964) and hydroxylamine hydrochloride 0.25 M at 50°C to 70°C are the most common (Chao and Zhou, 1983; Griffioen and Broers, 1993). Since hydroxylamine is able to reduce iron from crystalline minerals and it is not efficient at extracting aluminum from solid phases (Martins et al., 1998), the ammonium oxalate method was the method chosen for my experiments. Results show a low fraction of amorphous iron and aluminum material. Similar results were also observed by other researchers that characterized oxisol profiles (Fey and Roux, 1977; Fontes and Weed, 1991; Lima and Anderson, 1997). In spite of the fact that the method used to estimate the amount of amorphous material is based on an operational definition (Schuwertmann, 1964), the results seem to agree with observations on these soils made with TEM (Chapter 2). Trace amounts of amorphous material were found for this soil profile. However, there is a substantial percentage, roughly 50%, of poorly crystalline minerals that are not by definition amorphous (Chapter 2). This result has an important effect on the analysis of copper sorption to oxisol. Amorphous materials, as well as poorly crystalline minerals in natural systems, are well known to sorb large amounts of metals due to high surface areas and therefore high site density for metal binding (McBride, 1978a). The same observation is true for clay-size minerals. Consequently, some researchers conduct studies of metal sorption to soil using the soil clay-size fraction because this is the fraction that will sorb most of the metals due to high specific surface area (Charlet and Sposito, 1989). Since the soil studied here have a significant amount of poorly crystalline minerals, copper sorption is analyzed based on the clay size mineralogy.

To understand possible mechanisms of trace metal sorption to mineral surfaces, as well as other surface-related phenomena such as dissolution and colloidal reactions, a reliable estimation of mineral surface charge is required. Mineral surface charge is either caused by isomorphic substitution between ions of different valence inside the mineral structure or by reactions of surface functional groups with adsorptive species in the solution (Sposito, 1989 and 1992). In soil systems, the soil surface charge can be divided into four components, which should sum to a net per free surface charge σ_P (Sposito, 1989):

$$\sigma_P = \sigma_o + \sigma_H + \sigma_{IS} + \sigma_{OS} \tag{3.1}$$

σ_O is the soil structural charge created by isomorphic substitution in soil minerals like type 2:1 clays. The σ_H is the surface charge created by the difference between protons and hydroxyl groups adsorbed to the mineral surface. The σ_{IS} is the surface charge created by inner-sphere complexes, other than H^+ and OH^-, which are complexed with inner-sphere surface coordination. And finally, σ_{OS} is the surface charge created by outer-sphere complexes, which are complexed with outer-sphere surface coordination (Chorover and Sposito, 1995). In aquatic environmental systems, particle surface charges should balance out with ions that move freely in solution. These ions come from the diffuse layer, and the balance of the particle surface charge equation is:

$$\sigma_P + \sigma d = 0 \qquad (3.2)$$

Equation (3.2) is the general conservation law for the characterization of particle surface charge. σd is the diffuse-layer surface charge required to balance σ_P in order to maintain electrical neutrality (Sposito, 1992). The points of zero charge are the pH values where one or more of the components in equation (3.1) vanishes at fixed conditions of temperature, pressure, and aqueous solution composition. Sposito (1992) provides a succinct discussion of the meaning of the different points of zero charge.

For the soils studied here, the point of zero salt effect (PZSE) is the pH where a series of titration curves intersect (Parker et al., 1979) (Figure 3.3). In soil systems where constant charge minerals are not present, the pH where the cation exchange capacity (CEC) is equal to the anion exchange capacity (AEC) should be equal to the PZSE (Charlet and Sposito, 1987; Marcano-Martinez and McBride, 1989). However, dissolution of aluminum at low pHs may cause this surface charge relationship not to be true (Marcano-Martinez and McBride, 1989). The aluminum dissolution could cause water hydrolysis, creating more protons in the solution than the amount used for the surface titration. This problem could be solved by the estimation of protons produced by the hydrolysis with the use of thermodynamic constants for aluminum hydrolysis and measuring the amount of aluminum in solution (Chorover, 1993). Nordstrom and May (1989) averaged the hydrolysis constants for aluminum hydroxides species provided in the literature and obtained a pK of 5.00 ± 0.04 for the following reaction:

$$Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^{+} \qquad (3.3)$$

The formation of protons by the hydrolysis reaction written above could be corrected for in the calculation of the point of zero net charge (PZNC) for pHs lower than 4.0, where the amount of aluminum release can cause hydrolysis (Chorover, 1993). Charlet

(1986) did not measure the amount of aluminum in solution during titration and assumed that it was insignificant. From the results obtained in this study and the work developed by Chorover (1993) it is obvious that there is a significant release of aluminum in solutions of low pH (average 10 mmols/ kg of soil). The quantity of aluminum dissolution per mass of soil shows an average release of 3.3 x 10^{-5} M of aluminum in solution at low pH.

Here, constant charge soil minerals (type 2:1 clays) were not found by XRD analysis (Table 3.3) or by TEM analysis (Chapter 2). Therefore it can be assumed that there are no structural charges involved in these soils. In the case of soils composed of only variable-charge minerals, it is assumed that the PZSE is equal to the PZNC, which is equal to the soil point of zero charge (PZC) (Sposito, 1992). Since aluminum dissolution was not considered in the estimation of the PZSE, results here are a semi-quantitative estimation of the soil point of zero charge (PZC).

The results for soil PZSE in Table 3.3 show that the values of soil surface charge are greatest for the top horizon and increasing with depth. The higher concentration of NOM in the top horizon is the main cause of a lower surface charge in relation to the deeper horizons, since the soil mineralogy in the clay fraction does not change along the soil profile (Van Raij and Peech 1972). Another factor that could contribute to the drop of soil surface charge is the higher percentage of quartz in soil fractions smaller than 2.0 mm in the top horizon (Table 3.3). Quartz has a low PZC (2.0 – 3.0); its presence can cause the soil surface charge to decrease relative to a quartz-free system. The difference in the nature of NOM in the soil in the Bw_2 and C_2, as well as the low abundance of this organic material, may be the cause of a low variation of soil surface charge between these two horizons. NOM in the lower horizons is more decomposed (Chapter 2) and has lost important functional groups for copper binding through oxidation or binding to mineral surfaces. In fact, there is documented fractionation of NOM as it migrates to lower soil horizons (Mendonça and Rowell, 1996).

NOM has the ability to sorb to mineral surfaces by different mechanisms (Davis, 1982; Sposito, 1989; Gu et al., 1994). Mechanisms that could be involved during the sorption of NOM to mineral surfaces are: 1) anion exchange (electrostatic interaction); 2) ligand exchange-surface complexation; 3) hydrophobic interactions; 4) entropy effects; and 5) hydrogen bonding (Gu et al., 1994). Among these, ligand exchange is most commonly used to explain NOM sorption to iron and aluminum oxides (Tipping, 1981; Jardine et al., 1989; Gu et al., 1994 and 1995; Filius et al., 1997). By sorbing to mineral surfaces, NOM does not necessarily lose its ability to sorb to metals in solution or other mineral surfaces (Davis and Leckie, 1978; Tisdall and Oades, 1982). NOM in oxisols is present as discrete solid phases surrounded by minerals, filling up holes in the soil structure. Malengreau and Sposito (1997) performed diffuse reflectance spectroscopy before and after NOM extraction from oxisols and observed strong evidence that much of the NOM in oxisols is in the form of discrete solid phases. Santos et al. (1989) constructed ultrathin sections of undisturbed oxisol microaggregates and observed via TEM that the soil organic matter was not coating minerals but was locked-up in organo-iron complexes. Vrdoljak (1998) did a series of optical microscopy and TEM analyses of oxisols from uncultivated and cultivated areas in the Amazon rain forest. He observed the same arrangement of NOM inside the soil structure. In the TEM studies reported herein (Chapter 2) the same NOM arrangement in soil structure was observed. The estimated area occupied by NOM in the analyzed soil microaggregates from the A_1 horizon ranges from 15 to 20% of the microaggregate total surface area. Vrdoljak (1998) estimated in 20 to 42% the area that NOM occupies in his studied oxisols microaggregates. This area is filled up by different fractions of organic material with different ability to bind soil minerals.

Tisdall and Oades (1982) defined three organic binding agents: 1) transient (polysaccharides); 2) temporary (roots and fungal hyphae); and 3) persistent (resistant aromatic components associated with polyvalent metal cations, and strongly sorbed polymers). These three groups of natural organic binding agents were classified based on the age and degradation of the organic components. The first group is composed of organic materials that are decomposed rapidly by microorganisms. The most important aggregating agents in this group are the polysaccharides that are produced rapidly by microorganisms and associated with roots of plants. They are also decomposed rapidly and are usually associated with large stable aggregates (>250 μm). The second group of binding agents includes roots and hyphae. This group develops the ability to bind soil components in a few weeks to a few months. They persist in the field for months or even years, and the main aggregating agents in this group are roots, parts of plants, hyphae, saprophytic fungi, and vesicular-arbuscular mycrohizal fungi. This group is usually associated with young macroaggregates. The third and most important group of aggregating agents is also the most persistent group of binding agents. They consist of degraded, aromatic humic material associated with amorphous to poorly crystalline iron and aluminum oxyhydroxides and aluminosilicates. This association forms the large organo-mineral fraction of soil, which constitutes 52% to 98% of the total organic matter in soil (Turchenek and Oades, 1978; Tisdall and Oades, 1982). This group of aggregating agents is associated with clay size minerals between 1-20 μm and polyvalent cations such as aluminum, iron, and calcium.

NaOCl removed 87%, 67%, and 43% of the initial soil NOM present in horizons A_1, Bw_2, and C_2 respectively. Only in horizon A_1 was there a significant increase in soil specific surface area (approximately 22%) after the partial oxidation of soil NOM; for the other horizons basically there were no changes in soil surface area (Table 3.3). NOM is an important soil aggregating agent, but not the only agent in tropical soils (Foster, 1978; Tisdall and Oades, 1982; Bartoli et al., 1991). Amorphous material and poorly crystalline oxyhydroxides should also be considered as soil aggregating agents. At natural soil pH values, iron and aluminum oxyhydroxides have positive surface charges and kaolinite, the major mineral in this soil, a negative surface charge. These characteristics should contribute to the aggregation of kaolinite by having oxyhydroxide minerals working as bridges between clay particles.

In the A_1 horizon, a small fraction of the NOM (non-oxidized by 5% NaOCl) is apparently responsible, with the amorphous and poorly crystalline minerals, for a large amount of soil particle aggregation. The role of amorphous material and poorly crystalline minerals become more important for soil aggregation since the percentage of NOM is significantly reduced.

Copper sorption experiments:

All sorption experiments in this study were performed at a soil:solution mass ratio of 1:303 and a copper concentration of 10 μM. A simple copper sorption situation is assumed where all different soil sorbents (i.e., minerals, NOM, and amorphous material) are considered as only one soil sorbent. In this generalized composite (GC) sorption approach (Davis et al., 1998), an estimation of total site density for a complex mineral assemblage can be achieved by the multiplication of soil specific surface area by ferryhydrite site density (3.84 μM of site/m^2) (Dzombak and Morel, 1990). If this assumption is correct for the oxisol samples used in this study, I would have a range of site densities from 3.6×10^{-4} to 4.4×10^{-4} moles of site per gram of soil. The concentration of moles of sites per gram of soil is approximately two orders of magnitude higher than the concentration of copper in solution. Studies of copper sorption to monomineralic systems have the molar site concentrations three or four orders of magnitude higher than copper (Benjamin, 1978; Davis and Leckie, 1978; Leckie et al., 1980).

Kinetic studies at pH 5 were performed with the objective of estimating the minimum time required for the copper reactions to soil reach equilibrium (Figure 3.4). Initially the equilibration time was estimated to be 24 hours based on the work of Guilherme and Anderson (1998), who studied sorption of copper in kaolinitic and gibbsitic oxisols. For the first 24 hours of the reaction a first order reaction between soil and total copper was observed. This conclusion was obtained from a plot of the natural log of copper concentration in solution at certain time per total initial copper versus time in seconds (plot not shown). Experiments in this study used a constant soil/solution contact time of 24 hours. This time is probably not sufficient time for total equilibration.

Sorption isotherm experiments were performed on oxisol samples before and after soil NOM oxidation by NaOCl to investigate changes in soil maximum sorption capacity (Γ_{max}) (Figure 3.5). Figure 3.6 shows logarithmic plots of the data for the untreated soils. Before any analyses of the sorption isotherms are made, two things should be recalled. First, the oxidation of NOM by NaOCl was partial, removing 87%, 67%, and 43% of the total NOM from the soil horizons A_1, Bw_2, and C_2, respectively. Second, the oxidation did not cause any observable changes in soil mineralogy with the exception of some quartz dissolution (Figure 3.2). However, quartz is not a major sorbent of copper in oxisol, but rather hematite, gibbsite, and kaolinite. Hence, the sorption isotherms before and after oxidation of soil NOM give us direct information about the role of soil NOM in the sorption of copper. The changes in Γ_{max} for oxisols from different horizons before and after NOM oxidation are used to estimate the effect of NOM on copper sorption to oxisols.

For the A_1 soil horizon, the concentration of NOM is the highest in the soil profile. NOM functional groups (carboxyl, phenol, carbonyl etc) are presumably able to sorb copper and compete with oxyhydroxide minerals for copper complexation (Davis and Leckie, 1980; Tisdall and Oades, 1982). Luoma and Davis (1983) estimated based on a literature review, that total NOM functional groups that can complex metal have a site density of 0.001 moles/ g of organic carbon. In this oxisol, the A_1 horizon has an organic carbon percentage of 2.3% on a mass basis, which represents about 40-60 g NOM per kilogram of soil (since NOM is approximately 50%±10% C) (Thurman, 1985). Therefore, using the functional group density estimated by Luoma and Davis (1983), and assuming a complexation ratio of one metal ion per functional group, the NOM in one kilogram of A_1 horizon soil should be able to complex a maximum of 40-60 mmols of copper. After soil NOM oxidation, Γ_{max} drops by about 5.5 mmols per kilogram of soil

(Figure 3.5). Therefore, the decrease in Γ_{max} represents approximately 9-14% estimated maximum sorption capacity of the NOM. This supports the hypothesis that NOM plays only a minor role in copper sorption. This may be true because aluminum and iron are occupying the NOM sites that are favorable for copper complexation (McBride, 1994).

A second reality that could explain the minor importance of NOM in copper sorption in oxisols is the geometrical arrangement of the NOM in these soils. NOM may be serving as a binding agent for soil particles, filling gaps in the soil structure rather than as a coating on mineral surfaces. This does not by itself explain the small role of NOM in copper sorption, since TEM evidence shows that though, NOM in oxisols is not coating mineral particles, covering great amount of mineral surface, it is nevertheless occupying significant areas (15% to 20%) in soil that could sorb copper (Chapter 2).

In support of the first explanation, it is well known that aluminum and iron have high affinities for NOM carboxylic and phonemic groups attached to aromatic rings (Schnitzer, 1969; Gamble et al. 1970; De Coninck, 1980; Stevenson and Fitch, 1986; Senesi et al., 1989; McBride, 1994). Oxisol by definition is a type of soil that is rich in aluminum and iron (Table 3.3) (Macedo and Bryant, 1987; Chorover, 1993). It is also known that the toxicity of aluminum ions in soil solutions is attenuated by aluminum complexation with soil NOM (McBride, 1994).

Analysis of oxisol microaggregates by transmission electron microscopy (TEM) (Santos et al. 1989; Vroljak, 1998) and diffuse reflectance spectroscopy (Malengreau and Sposito, 1997) has shown that much of the soil NOM is not coating minerals. This supports the second explanation. Together, these realities explain why the role of NOM in copper sorption to oxisols is not so significant. To further evaluate this soil copper sorption capacity, a comparison should be made between the copper Γ_{max} values obtained from this soil and from soil minerals that make up this soil. Another good source for comparison would be with different types of soils.

The sorption isotherm from the Bw_2 horizon presents a reverse result from that of the A_1 horizon. NOM in this soil horizon seems to block mineral sites for copper sorption.

The Γ_{max} in this soil increases 42% for the oxidized in relation to the untreated soil (9.5 mmols of Cu (II)/ Kg of soil) (Figure 3.5).

The C_2 horizon has a substantially lower NOM content than either the A_1 or Bw_2 horizons. Oxidation of this NOM, which is probably predominantly decomposed and thus not reacting to a great extent with trace metals, produces little or no change in the Γ_{max} value. The NOM in the C_2 horizon is therefore probably not active in Cu^{2+} complexation or in blocking mineral sites otherwise available for Cu^{2+} binding.

For analysis purposes, the experimental data for the untreated soils were plotted logarithmically and fitted to adsorption isotherm equations (Figure 3.6). All the plots were classified as the Freundlich type of isotherm. The same isotherm classification was found by other researchers that studied copper sorption to acid soils (Cavallaro and McBride, 1978; Msaky and Calvet, 1990). However, this conclusion is probably valid only for the low ranges of copper concentrations used in these experiments (5 μM to 125 μM). The logarithmic sorption isotherms were fitted by linear regression (Kinniburgh, 1986). The mathematical explanation is presented below:

$$n = kc^{\beta} \qquad (3.4)$$

$$\text{Log}\, n = \beta\, \text{Log}\, k + \beta\, \text{Log}\, c \qquad (3.5)$$

Where n is the concentration of sorbed metal (e.g., mols/g), c is the concentration of metal in solution, k is an affinity parameter, and β is an empirical constant.

Evaluation of isotherms at different pH values may be useful for understanding the interface reaction stoichiometry (Honeyman and Leckie, 1986). This type of study would be helpful in the determination of more accurate postulated chemical reactions for modeling purposes.

It is not possible to accurately postulate chemical mechanism merely from the analysis of the sorption isotherm (Veith and Sposito, 1977). The only information obtained from this study is in relation to the slope of the plots. The slope values for the three horizons A_1, Bw_2, and C_2 are 0.35, 0.29, and 0.51, respectively. These values, less than one, are typical of heterogeneous systems such as soils (Sposito, 1984; Stumm, 1992).

Aluminum dissolution during sorption experiments before and after soil NOM oxidation was monitored by ICP-AES analysis. The results show the same pattern of aluminum and iron dissolution obtained by other researchers (Chorover, 1993; Malengreau and Sposito, 1997). Since $NaNO_3$ solutions supposedly removed all the exchangeable aluminum after sequential soil washings at different salt concentrations (Dahlgren and Walker, 1993), the soil NOM and the amorphous and crystalline mineral phases remain as the main sources for aluminum and iron dissolution. However, it is difficult to determine which of these sources is predominant.

Despite the difficulties in identification of the source of aluminum released from oxisols, some conclusions can be derived from analyses of these plots (Figures 3.7 and 3.8). First, the aluminum and iron dissolution is a phenomenon common in oxisols and varies significantly as a function of pH. The large release of aluminum at pH's above 5 (8 to 14 mmols / Kg of soil) supports the notion that aluminum may be blocking soil NOM complexation sites. This is also expected for other acidic soils but not as much for neutral pH soils. The main sources for aluminum and iron dissolution are oxides and silicates, where the solubility is controlled by the concentration of charged species at the mineral surfaces produced by adsorption of proton and hydroxyl ions (Stumm and Wollast, 1990). In the case of acidic soils, a higher concentration of protons in solution should enhance aluminum and iron dissolution. Second, the increase in aluminum and iron dissolution at pH's lower than 4.5 after NOM oxidation may be related to the unblocking of mineral sites that would release aluminum and iron at low pHs. Organic ligands (NOM) can enhance solid mineral dissolution, but can also inhibit it by complexing to bi- or multinuclear complexes or surface films and block surface groups that would otherwise be exposed to proton and hydroxyl ions (Stumm, 1992, McBride, 1994). Third, NOM could be strongly related to the release of aluminum and iron at pHs higher than 4.5, since the solubility drops drastically in this pH range after soil NOM oxidation. However, the reasons for this relation are not entirely clear.

The monitoring of aluminum dissolution is very important for soil surface charge modeling as well as for surface complexation modeling. For development of these types of studies using oxisols, sample dissolution of aluminum and iron must be accounted for or the result may be biased.

The sorption edges for copper on untreated soil horizons were performed in the same pH range, soil solution ratio, and salt and copper concentrations as the oxisol samples that were treated with NaOCl. The plots of copper sorption to the untreated soil horizons have shapes similar to copper sorption to oxyhydroxide minerals (Davis and Leckie, 1978; Dzombak and Morel, 1990; Spark et al., 1995a) (Figure 3.8). The sorption edges are also similar to those for the sorption of copper to kaolinite with the exception that, in general, 50% copper sorption (pH_{50}) occurs at pH 5.5-6.0 for kaolinite (Schindler et al., 1987; Holm and Zhu, 1994; Spark et al., 1995b) and for oxisols it occurs at pH 4.0-4.5. This fact may suggest kaolinite participation in copper sorption to oxisols, but this comparison should be made with experiments using the same mineral/solution ratio, and my data is not comparable to literature values in this regard.

Another sorption parameter should be used to suggest kaolinite participation on copper sorption. The slope of the copper sorption isotherms for oxisols is less steep than those for pure oxyhydroxide minerals. This difference is due to the heterogeneity of surface functional groups present in soil and sediments (Davis et al., 1998). Another important aspect to observe is the shift of the sorption edge with depth in soil profile. This shift is not related to decrease of soil NOM content with soil depth, since partial oxidation of soil NOM does not caused significant shift in sorption edges (Figures 3.10, 3.11, and 3.12). One reasonable explanation for this shift in sorption edges is the higher concentration of amorphous material in the top soil horizons than in the lower soil horizons (Table 3.3).

Higher iron and aluminum amorphous material will cause more sorption of trace metal than crystalline phases (Davis and Kent, 1990).

Soil NOM oxidation by NaOCl did not significantly affect copper sorption to the different oxisol horizons (Figures 3.10, 3.11, and 3.12), except at pH's higher than 5 where the treated soils sorbed more copper than the untreated soils. The sorption edge probably did not reach 100% copper sorption due to the relative small amount of soil used (3.3g/l) for the Cu concentration used (10 μM). However, the oxidation of soil NOM apparently made available some mineral sites that were not exposed for copper reactions in the natural soil. Since the most favorable sites for copper sorption were probably already occupied by aluminum and iron (untreated samples), soil NOM was not enhancing copper sorption to soil, but doing the opposite. The non-shift or change in sorption edge suggests that NOM is not important in the copper sorption on oxisols under these experimental conditions.

The sorption of copper to oxides or soils can be represented by chemical reactions that suggest an inner-sphere type of complexation mechanism:

$$\equiv SOH + Cu^{2+} \leftrightarrow \equiv SOCu^{+} + H^{+} \qquad K_{Cu2+} \tag{3.7}$$

$$K_{Cu^{2+}} = \frac{\{\equiv SOCu^{+}\}\{H^{+}\}}{\{\equiv SOH\}\{CuOH^{+}\}} \tag{3.8}$$

$$\equiv SOH + CuOH^{+} \leftrightarrow \equiv SOCuOH + H^{+} \qquad K_{CuOH+} \tag{3.9}$$

$$K_{CuOH^{+}} = \frac{\{\equiv SOCuOH\}\{H^{+}\}}{\{\equiv SOH\}\{CuOH^{+}\}} \tag{3.10}$$

Where:

Soil surface functional group = $\equiv SOH$

Surface complexes = $\equiv SOCu^+$ and $\equiv SOCuOH$

Sorbates = Cu^{2+} and $CuOH^+$

Proton released from surface = H^+

K_{Cu2+} = adsorption constant for reaction (3.7)

K_{CuOH+} = adsorption constant for reaction (3.9)

It is assumed in this case that hydrolysis is insignificant in the pH range used for copper sorption. Otherwise, soil hydrolysis reactions (equation 3.3) should also be postulated. Also, the adsorption constants have an electrostatic component that in certain cases should be taken into consideration for more accurate representation of the adsorption of metals to mineral surfaces (Davis and Leckie, 1978; Farley et al., 1985), and this was not done here.

These complexes do not have a water molecule interposed between the surface functional group and the bound molecule and are therefore classified as inner-sphere complexes, or specific sorption (Sposito, 1984). McBride (1978a) and (1982) studied the adsorption of copper to oxyhydroxide minerals using electron spin resonance and compared this non-labile sorption to the inability of these minerals to retain Mn^{2+}, Ca^{2+}, and Mn^{2+}. He concluded that copper sorbs specifically to oxyhydroxides. Spark et al. (1995a) reached the same conclusion by varying the solution ionic strength during copper sorption to oxyhydroxides. He observed no effect on copper sorption. Experiments made in different types of soils for investigating the nature of metal binding to soil samples present similar results for soils that are not acidic. The types of reactions with copper are classified as specific sorption and the time required for the reactions to reach equilibrium is in the range of minutes (McLaren and Crawford, 1973; Aringhieri et al., 1985). For acidic soils, and oxisols are in this soil category, there is a greater likelihood for the soil organic matter to have its sites blocked by aluminum and iron due to the release of these elements from mineral and amorphous phases. In addition, sorption of trace metals on kaolinite is a non-specific or outer-sphere type of complexation. Since NOM does not have available the important functional groups for copper complexation, copper will preferentially sorb to mineral phases. Kaolinite is the predominant mineral phase in these oxisols. Therefore, copper sorption, in this type of soil, can be classified as a mix of specific and non-specific sorption. The maximum amount of copper sorbed (Γ_{max}) to this type of soil is much less than the amount sorbed for neutral pH soils or organic soils (Misra and Tiwari, 1962 and 1966; Cavallaro and McBride, 1978 and 1984; Singh et al., 1988). A non-specific complexation between copper and soil surface is represented below:

$$\equiv SOH + Cu^{2+} + H^{+} \leftrightarrow \equiv SOH_2^{+}...Cu^{2+} \qquad (3.11)$$

Two sets of sorption edges for one order of magnitude difference in salt concentration were also performed. The results support what was observed by other researchers that studied copper sorption on acidic soils (Misra and Tiwari, 1962 and 1964; Cavallaro and McBride, 1978 and 1984). The sorption edges shift to a higher pH when the salt concentration is increased (Figures 3.13 and 3.14), but less than expected for a study of an outer-sphere complex (Spark et al., 1995b). This fact suggests that copper sorption on kaolinitic oxisols may have a non-specific sorption component. Therefore, if modeling of copper sorption to oxisols is performed, a non-specific type of complexation (equation 3.11) should be also considered as well as the inner-sphere type of complexation.

Conclusions

A series of sorption isotherms and sorption edges were performed on a well-characterized oxisol profile before and after partial oxidation of soil NOM by NaOCl (5% by volume). Soil samples from A_1, Bw_2, and C_2 horizons showed a uniform bulk composition of Fe and Al along the soil horizon. The homogeneous bulk chemical composition is a consequence of the homogeneous identical clay size mineralogy where kaolinite was the predominant mineral followed by gibbsite and hematite. In the whole soil (<2mm), quartz was the predominant mineral in the top soil horizon, the second most predominant in the intermediate soil horizon, and the third most predominant in the deepest soil horizon. There were trace amounts of amorphous Fe and Al along this soil horizon, which is similar to results found by other researchers who characterized oxisol profiles (Fey and Roux, 1977; Fontes and Weed, 1991; Lima and Anderson, 1997). The percentage of soil organic carbon decreased with depth from 2.32% at A_1 to 0.35% at C_2. The higher percentage of soil NOM in the top horizon was responsible for the low PZSE values of this horizon (Van Raij and Peech, 1972). Poorly crystalline and amorphous materials were able to aggregate a majority of the soil clay size particles since the increase in soil specific surface area after NOM oxidation was minor.

Partial oxidation of soil NOM by NaOCl did not affect the soil mineralogy with the exception of some dissolution of quartz. However, quartz is not an important sorbent for copper. Sorptive interactions between oxisol samples and copper solutions are kinetically slow, requiring more than 24 hours for equilibration (Figure 3.4). This is in agreement with other kinetic studies involving copper and oxisols (Msaky and Calvet, 1990; Guilherme and Anderson, 1998). During sorption experiments a significant amount of aluminum and iron is released from the soil into the solution. Aluminum concentration released is one order of magnitude higher than iron. However, patterns of metal release for both metals are the same, as a function of pH. They are high at pH 3, decrease between pH values 3 and 4.5, and rise back up from pH 4.5 to pH 6, at which point the metal release is the same as at pH 3. The relatively high concentrations of aluminum and iron in solution at natural soil pH's of 5 to 5.5 support the hypothesis that sites for copper sorption on soil NOM may already be occupied by aluminum and iron. Dissolution of aluminum to solution, after partial oxidation of soil

NOM, increases two to three times at pH's lower than four. This fact suggests that NOM was blocking mineral surface sites that were not exposed to dissolution by protons and hydroxyls in solution. At pHs higher than four, the aluminum dissolution decreases drastically.

Sorption isotherms for copper sorption to oxisols were classified as Freundlich isotherms with slopes less than one, which is expected for metal sorption to heterogeneous systems like soils (Sposito, 1984; Stumm, 1992). The partial oxidation of soil NOM caused ubiquitous results in soil isotherms. At the A_1 horizon the Γ_{max} reduces after oxidation of soil NOM, and at the Bw_2 horizon it increases and at C_2 soil horizon it is the same as before oxidation. This sort of behavior of Γ_{max} was attributed to the abundance of soil NOM at the topsoil horizon. Copper sorption edges showed no significant effect of soil NOM on copper complexation on oxisols, except at pH's higher than 5.0 where the oxidation increased the soil sorption capacity by about 10%. This fact confirms the minor role of NOM in the binding copper to oxisol's and suggests that the shifts in sorption edges at different soil depths are caused by the higher amount of amorphous material in the top soil horizon.

The increase in salt solution concentration, from 0.01 M to 0.1 M $NaNO_3$, in batch experiments shifted the copper sorption to higher pHs. This is not observed for copper sorption on iron or aluminum oxyhydroxides. However, copper sorption on kaolinite is dependent on solution ionic strength (Schindler et al., 1987; Spark et al., 1995b). This fact suggests that kaolinite mineral surfaces may be involved in copper sorption in kaolinitic oxisols. Since copper sorbs on kaolinite with a non-specific type of complexation mechanism, a mix of specific and non-specific sorption is probably operative in copper sorption to these oxisols.

References

Ali, M. A. and Dzombak, D. A. 1996. Interactions of copper, organic acids, and sulfates in suspensions. *Geochemica et Cosmochim. Acta* 60:5045-5053.

Aringhieri, R., P. Carral., and G. Petruzzelli. 1985. Kinetics of Cu^{+2} and Cd^{+2} adsorption by an italian soil. *Soil Science* 139 (3):197-205.

Bartoli, F., G. Burtin, and A. J. Herbillon. 1991. Disaggregation and clay dispersion of oxisols: Na resin, a recommended methodology. *Geoderma* 49:301-317.

Bell, L. C. and G. P. Gillman. 1978. Surface Charge Characteristics and Soil Solution Composition of Highly Weathered Soils. In: *Mineral Nutrition of Legumes in Tropical and Subtropical Soils*, edited by Andrew, C.S. and Kamprath, E.J., Melbourne, Australia.

Benjamin, M. M. 1978. Effects of competing metals and complexing ligands on trace metal adsorption at the oxide/solution interface. Ph. D. Thesis. Stanford University, Stanford CA.

Cavallaro N., and M. B. McBride. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal* 42:550-556.

Cavallaro N., and M.B. McBride. 1984. Zinc and copper sorption and fixations by an acid soil clay: Effect of selective dissolutions. *Soil Science Society of America Journal* 48:1050-1054.

Chao T.T., and L. Zhou. 1983. Extrasction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Science Society of America Journal* 47 (2):225-232.

Charlet, Laurent. 1986. Adsorption of some macronutrient ions on an oxisol. An application of the triple layer model. Ph.D in Soil Science. University of California, Riverside.

Charlet, L. and G. Sposito. 1987. Monovalent Ion Adsorption by Oxisoil. *Soil Science Society of America Journal* 51:1155-1160.

Charlet L., and Garret Sposito. 1989. Bivalent Ion Adsorption by an Oxisol. *Soil Science Society of America Journal* 53:691-695.

Chiou, C.T. 1989. Theoretical Considerations of the Partition Uptake of Nonionic Organic Compounds by Soil Organic Matter. *In Reactions and Movement of Organic Chemicals in Soils*, SSSA Special Publication no. 22.

Chorover, J. 1993. Surface charge and colloidal properties of benchmark Brazilian Oxisols. Ph.D. Thesis. University of California, Berkeley.

Chorover J., and Garrison Sposito. 1995. Surface charge characteristics of kaolinictic tropical soils. *Geochimica et Cosmochimica Acta* 59 (5):875-884.

Coston J. A., C. C. Fuller, and James A. Davis. 1995. Pb2+ and Zn+2 adsorption by a natural aluminum and iron bearing surface coating on an aquifer sand. *Geochimica et Cosmochimica* Acta 59 (17):3535-3347.

Dahlgren, R.A. and W.J. Walker. 1993. Aluminum release rates from selected Spodosol Bs Horizons: effect of pH and solid phase Al pools. *Geochim. Cosmochim. Acta* 57:57-66.

Davis J.A., and Leckie J. O. 1978. Surface ionization and complexation at the oxide/water interface – II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67(1):90-107.

Davis, J.A. and Leckie, J. O. 1980. Surface ionization and complexation at the oxide/water interface. III. Adsorption of anions. *Journal of Colloid Interface Science* 74:32-43.

Davis, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosdmochimica Acta.* 46:2381-2393.

Davis J.A. 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica*, Acta 48:679-691.

Davis, J.A. and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. In *Mineral-water interface geochemistry*, edited by M.F. Hochella and A.F. White. Mineralogical Society of America, Vol 23 Whashigton D.C..

Davis, J.A., J.A. Coston, D.B. Kent, and C.C. Fuller. 1998. Application of the surface complexation concept to complex mineral assemblages. *Environmental Science and Technology* 32:2820-2828

De Coninck, F. 1980. Major Mechanisms in formation of spodic horizons. *Geoderma*, 24: 101-128.

Dzombak, D.A. and Morel, F.M. 1990. *Surface Complexation Modeling*. Wiley-Interscience, New York.

Farley K.J., David A.D, and Francois M. M. Morel. 1985. A surface precipitation model for the sorption of cations on metal oxides. *Journal of Colloid and Interface Science* 106 (1):226-242.

Fey M.V., Roux J. Le. 1977. Properties and quantitative estimation of poorly crystalline components in sesquioxidic soil clays. *Clays and Clay Minerals* 25:285-294.

Filius, D. J., Tjisse Hiemstra, and Willem H. Van Riemsdijk. 1997. Adsortion of Small Weak Organic Acids on Goethite. Modeling of Mechanisms. *Journal of Colloid and Interface Science* 195:368-380

Fontes M.P.F., and S.B. Weed. 1991. Iron oxides in selected Brazilian oxisols: I. Mineralogy. *Soil Science Society of America Journal* 55:1143-1149.

Foster, R.C. 1978. Ultramicromorphology of some South Australian soils. In *Modification of Soil Structure* (eds W. W. Emerson, R.D. bond and A.R. Dexter), Emerson-Wiley. 103-109.

Gamble, D.S., M. Schnitzer, and I. Hoffman. 1970. Cu^{+2} fulvic acid chelation equilibrium in 0.1 m KCl at 25.0 Celsius. *Canadian Journal of Chemistry* 48:3197-3204.

Griffioen J., H.P. Broers. 1993. Characterization of sediment reactivity: the feasibility of sequential extraction techniques. TNO Environmental and Energy Research, Netherlands.

Gu, B., Jurgen Schmitt, Zhihong Chen, Liyuan Liang, and John F. McCarthy. 1994. Adsorption and Desorption of Natural Organic Matter on Iron Oxide: *Mechanisms and Models. Environmental Science and Technology* 28:38-46.

Guilherme, L. R. G., and Anderson, S. J. 1998. Copper sorption kinetics and sorption hysteresis in two oxides-rich soils (oxisols): Effect of phosphate pretreatment. In: *Adsorption of Metals by Geomedia.* Edited by Jenne, E. A. Academic Press, San Diego CA.

Holm T. R., Xiao-Feng Zhu. 1994. Sorption by kaolinite of Cd^{2+} and Cu^{2+} from landfill leachate-contaminated groundwater. *Journal of Contaminant Hydrology* 16:271-287.

Honeyman B.D., James O. Leckie. 1986. Macroscopic Partitioning Coefficients for Metal Ion Adsorption. In *Geochemical Processes at Mineral Surfaces*, Ed. by J.A. Davis and K.F. Hayes, ACS Symp. Sor. 323, Am. Checm. Soc.,Washington, D.C.

Jardine P. M., N L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Science Society of America Journal* 53:1378-1385.

Jenne, E.A. 1998. Adsorption of metals by geomedia: data analysis, modeling, controlling factors, and related issues. In: *Adsorption of Metals by Geomedia: Variables, Mechanisms, and Model Applications*, edited by Everett A. Jenne. Academic Press, San Diego.

Kinniburgh David G. 1986. General purpose adsorption isotherms. *Environmental Science and Technol*ogy 20:895-904

Lavkulich, L. M. and J.H. Wiens. 1970. Comparison of Organic Matter Destruction by Hydrogen Peroxide and Sodium Hypochlorite and Its Effects on Selected Mineral Constituents. *Soil Science Society of America Proceeding* 34:755-758.

Leckie, J.O., Benjamin, M.M., Hayes, K.F., Kaufmann, G. and Altmann, S. 1980. Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide. EPRI Rept. CS-1513, Electric Power Research Institute, Palo Alto, CA.

Lima, J.M. 1995. Relation between phosphate sorption and aggregation in oxisols from Brazil. Ph.D. in Crop and Soil Sciences. Michigan State University.

Lima Jose M., and Sharon J. Anderson. 1997.Aggregation and Aggregate size Effects on Extractable Iron and Aluminium in Two Hapludoxs. *Soil Science Society of America Journal* 6 (1):965-970.

Lion, L. W., Altmann R. S., and Leckie J. O. 1982. Trace Metal Absorption Characteristic of Estuarine Particulate Matter: Evaluation of Contributions of Fe/Mn Oxide and Organic Surface Coating. *Environmental Science and Technology* 16 (10):660-666.

Luoma, S.N. and Davis, J.A. 1983. Requirements for modeling trace metal partitioning in oxidized estuarine sediments. *Marine Chemistry* 12:159-181.

Macedo, J. and Bryant, R. B. 1987. Morphology, mineralogy, and genesis of a hydrosequence of oxisols in Brazil. *Soil Science Society of America Journal* 51:690-698.

Malengreau N., and Garrison Sposito. 1997. Short time dissolution mechanisms of kaolinitic tropical soils. *Geochimica et Cosmochimica Acta* 61 (20):4297-4307.

Marcano-Martinez E., and M.B. McBride. 1989. Comparison of the titration and ion adsorption methods for surface charge measurement in oxisols. *Soil Science Society of America Journal* 53:1040-1045.

Martins, E. S.; G. R. Boaventura; W. M. Farias; J. C. Gaspar. 1998. Extração de fases de baixa cristalinidade de solos tropicais por oxalato de amônio-edta. Proc. XXVI Congresso Brasileiro de Ciências do Solo, Rio de Janeiro – Brazil.

McBride M.B. 1978a. Retention of Cu^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} by Amorphous Alumina. *Soil Science Society of America Journal* 42:27-31.

McBride, M.B. 1978b. Copper(II) interactions with kaolinite: factors controlling adsorption. *Clays and Clay Minerology.*

McBride M.B. 1982. Cu+2 adsorption characteristics of aluminum hydroxide and oxyhydroxides. *Clays and Clay Minerals* 30 (1):21-28.

McBride, M. 1994. *Environmental Chemistry of Soils*. Oxford University Press, New York NY.

McLaren R.G., and D.V. Crawford. 1973. The specific adsorption of copper by soils. *Journal of Soil Science*, 24 (4):443-452.

Mendonca E. S., David L. Rowell. 1996. Mineral and organic fractions of two oxisols and their influence on effective cation-exchange capacity. *Soil Science Society of America Journal* 60:1888-1892.

Misra, S.G. and R.C. Tiwari. 1962. Studies on the adsorption and release of copper of soils. Effects of cations. *Soil Science and Plant Nutrition* 8:93-96.

Misra, S.G. and R.C. Tiwari. 1964. Retention and release of copper and zinc by some Indian soils. *Soil Science* 101:465-471.

Morais F.I., A.L. Page, and L.J.Lund. 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils *Soil Science Society of America Journal* 40:521-527.

Msaky J.J., and R. Calvet. 1990. Adsorption behavior of copper an zinc in soils: influence of pH on adsorption characteristics. *Soil Science* 150 (2):513-522.

Nordstrom, D.K. and H.M. May. 1989. Aqueous equilibrium data for mononuclear aluminum species. In: *The Environmental Chemistry of Aluminum.* Edited by G. Sposito. CRC Press, Boca Raton, FL.

Nowak, B. and Sigg L. 1996. Adsorption of EDTA and metal-EDTA complexes on goethite. *Journal of Colloid Interface Science* 177:106-121.

Papp Clara S. E., Lorraine H. Filipek and Kathleen S. Smith. 1991. Selectivity and effectiveness of extractants used to release metals associated with organic matter. *Applied Geochemistry* 6:349-352.

Parker J. C., L.W. Zelazny, S. Sampath, and W.G.Harris. 1979. A critical evaluation of the extension of zero point of charge (ZPC) theory to soil systems *Soil Science Society of America Journal* 43:668-674.

Righetto, L., Giovanni Bidoglio, Giovanna Azimonti, and Ignazio R. Bellobono. 1991. Competitive Actinide Interactions in Colloidal Humic Acid-Mineral Oxide Systems. *American Chemical Society. Environmental Science and Technology* 25 1913-1919.

Santos M.C.D, A.R. Mermut, and M.R. Ribeiro. 1989. Submicroscopy of Clay Microaggregates in an oxilol from Pernambuco, Brasil *Soil Science Society of America Journal* 53:1895-1901.

Schindler P.W., P; Liechti and J.C. Westall. 1987. Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface. *Netherlands Journal of Agricultural Science* 35:219-230.

Schindler, P. and Stumm, W. 1987. The surface chemistry of oxides, hydroxides and oxide minerals. In *Aquatic Surface Chemistry.* edited by W. Stumm. Wiley-Interscience. New York.

Schnitzer, M. 1969. Reaction between fulvic acid, a soil humic compound and inorganic soil constituents. *Soil Science Society of America Journal* 33:75-81.

Schwertmann, V. 1964. Differenzierung der Eisenoxide des Bodens durch. Extraktion. mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Düng. Bodenk.* 105:194-102.

Senesi N., Garrison Sposito, Gordon R. Bradford. 1989. Iron, Copper, and Manganese Complexation by Forest Leaf Litter. *Forest Science* 35 (4):1040-1057

Singh J.P., S.P.S. Karwasra, and Mahendra Singh. 1988. Distribuition and forms of copper, iron, manganese, and zinc in calcareous soils of India. *Soil Science* 146 (5):359-366.

Smith, K.S. 1991. Factors influencing metal sorption onto iron-rich sediment in acid-mine drainage. Ph.D. in Chemistry and Geochemistry. Colorado School of Mines, Golden, CO.

Spark K.M., B.B. Johnson, and J.D. Wells. 1995a. Characterizing heavy-metal adsorption on oxides and oxyhydroxides. *European Journal of Soil Science* 46:621-631.

Spark K.M., B.B. Johnson, and J.D. Wells. 1995b. Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Scienc* 46:633-640.

Sposito, G.. 1992. Characterization of particle surface charge. In *Environmental Particles.* (Chapter 7), ed. by J.Buffle and H. Van Leeuwen. Publ. Environ.Anal.Chem. Vol 1.

Sposito, G. 1984. *The Surface Chemistry of Soils.* Oxford University Press Inc., Riverside CA.

Sposito, G. 1989. *The Chemistry of Soil.* Oxford University Press. New York NY.

Stevenson, F.J. 1982. *Humus Chemistry: Genesis, Composition, Reactions.* Wiley-Interscience, New York.

Stevenson, F.J and Fitch, A.. 1986. Chemistry of complexation of metal ions with soil solution organics. In: *Interactions of Soil Minerals with Natural Organics and Microbes.* Soil Science Society of America Special Publication Number 17.

Stumm W., and R. Wollast. 1990. Coordination chemistry of weathering: kinetics of the surface-controlled dissolution of oxide minerals. *Reviews of Geophysics* 28 (1):53-69.

Stumm, W. 1992. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*. Wiley-Interscience, Canada.

Thurman, E. W. 1985. *Organic Geochemistry of Natural Waters*. Martinus Nijhoff/ Dr W. Junk Publishers. Netherlands.

Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. *Geochimica et Cosmochimica Acta* 45:191-199.

Tisdall J.M., and J.M. Oades. 1982. Organic matter and water-stable aggregates in soils. *Journal of Soil Science* 33:141-163.

Turchenek, L.W., and J.M. Oades. 1978. Organo-minero particles in soils. In: *Modification of Soil Structure*. edited by W.W. Emerson, R.D. Bond and A.R. Dexter. Wiley, London.

Van Raij B., and M. Peech. 1972. Electrochemical properties of some oxisols and alfisols of the tropics. *Soil Science Society of America Journal* 36 (4):587-593.

Veith J. A., and Garrison Sposito. 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. *Soil Science Society of America Journal* 41:697-702.

Vrdoljak, G.A. 1998. Ultramicroscopy of a Brazilian Oxisol. Ph.D. Thesis. University of California, Berkeley.

Wada, K. 1995. Role of aluminum and iron in the accumulation of organic matter in soils with variable charge. In Environmental Impact of Soil Component Interactions – Metals, Other Inorganic, and Microbial Activities. edited by P.M. Huang, J. Berthelin, J.M. Bollag, W.B. McGill, A.L. Page. Vol. I Chapter 3, 47-58.

Wershaw, R. L. 1993. Model for Humus in Soil and Sediments. *Environmental Science and Technology* 27 (5):814-816.

White, R.E. 1978. *Introduction to the principles and practice of soil science*. Blackwell Sci. Publ. New York NY.

Xing, G. X., Xu, L. Y., and Hou, W. H. 1995. Role of amorphous Fe oxides in controlling retention of heavy metal elements in soils. In *Environmental Impact of Soil Component Interactions – Metals, Other Inorganic, and Microbial activities.*

edited by P.M. Huang, J. Berthelin, J.M. Bollag, W.B. McGill, A.L. Page. Vol. II Chapter 6, 63-74.

Zachara, J.M, C.T. Resch, and S.C. Smith. 1994. Influence of humic substances on Co 2+ sorption by a subsurface mineral separate and its mineralogic components. *Geochimica et Cosmochimica Acta* 58 (2): 553-566.

Chapter 4

THE ROLE OF NATURAL ORGANIC MATTER (NOM) IN COPPER SORPTION TO OXISOLS. THE INFLUENCE OF HIGH FE AND AL CONTENT.

Abstract

In oxisols and other soils and sediments rich in Al and Fe oxyhydroxides, natural organic matter (NOM) is minimally involved in sorption processes of transition metals (Cavallaro and McBride, 1984; Smith, 1991). One hypothesized reason for this behavior is the abundance of non-NOM sites and the saturation of NOM binding sites by ferric and aluminum ions. Another is the geometrical arrangement of NOM in these natural systems, where NOM may not primarily occupy surface sites where it is available for chemical reactions. To investigate these hypotheses two sets of Cu (II) sorption edges were obtained on oxisol samples from the A_1 horizon (20cm) of a Brazilian oxisol. One set includes untreated soil samples plus soil samples that had NOM extracted and the other set includes untreated soil samples plus soil samples that had additional NOM fractions sorbed to them. Soil NOM was extracted by 0.001M NaOH, 0.5 M NaOH at 55°C, and removed by oxidation with 5% NaOCl. A portion of the NOM that was extracted by 0.001M NaOH was fractionated into 'humic' and 'fulvic' acids and these were later sorbed to soil to investigate their influence on Cu (II) sorption. Another sample of the NOM extracted by 0.001 M NaOH was exposed to a cation exchange resin (Chelex 100) to exchange ferric and aluminum ions. This ion-exchanged sample was also sorbed to the untreated soil to investigate the influence on the Cu (II) sorption. The modified and unmodified samples of NOM extracted from soil were characterized by several analytical techniques (total carbon concentration, UV-absorbance, and acid/base titration). Experimental results support the hypotheses stated above.

Introduction

It is universally recognized that natural organic matter (NOM) in natural systems is a strong binding agent for mineral surfaces and dissolved metal ions (see for example Davis and Leckie, 1978; Davis, 1982 and 1984; Righetto et al., 1991; Murphy et al., 1992; Zachara et al., 1994; Duker et al., 1995). NOM can bind to mineral surfaces by a variety of mechanisms (Sposito, 1989; Gu et al., 1994 and 1995) and change substantially the surface charge of minerals (Hunter, 1980; Tipping and Cooke, 1982; Davis, 1982 and 1984). Changes in the oxide mineral surface charge can enhance the sorption of some trace metals at low pH's and reduce sorption at pHs higher than five (Davis, 1984). Also NOM in solution can complex metals and change their speciation and availability to plants and microorganisms (Stevenson, 1976).

One of the difficulties in studying NOM complexation with metals or sorption to minerals is its complex chemical composition. There is no chemically defined composition for NOM. It is best defined as a general class of biogenic, refractory, yellow-black organic substances that are ubiquitous in all terrestrial and aquatic environments (Aiken et al., 1985). Another factor that complicates the study of NOM in natural systems is the complexity intrinsic to soils and sediments. Soils and sediments are made up of a suite of minerals with different degrees of crystallinity that are bound in clusters by amorphous material and organic matter. Each mineral has its own physical and chemical properties that will determine more or less its ability to complex metals or NOM from solution.

To avoid some of the complexities involved in studying the role of NOM in natural systems, a common approach is to extract NOM from a natural system, and then treat this NOM to remove impurities (e.g., minerals, complexed ions) and/or to fractionate it into operationally defined fractions (e.g. humic and fulvic acids) to reduce the chemical complexity intrinsic to the initial material. On the other hand, to investigate the role that each soil component might play in a natural system, single minerals are either prepared in the laboratory or purchased for the development of experiments.

Working with laboratory systems that include single pure minerals and protons and/or trace metals (Parks and DeBruyn, 1962; Stumm et al., 1970; Davis and Leckie, 1978; Honeyman, 1984; Dzomback and Morel, 1990) or single pure mineral and trace metals in the presence of NOM (Davis, 1984; Charandrakanth et al., 1996; Schoroth and Sposito, 1998; Lenhart and Honeyman, 1999), researchers answered some basic questions about the sorption relationships among pure oxide minerals, trace metals, and NOM.

However, application of such fundamental knowledge to studies of the role of NOM in the sorption of trace metals in natural systems rich in iron and aluminum is problematic. Cavallaro and McBride (1984) reported both enhancement and no effect in the sorption of copper and zinc to an acidic soil clay fraction after NOM oxidation by hypochlorite. Smith (1991) did a series of sorption edges with trace metals in systems contaminated with acid mine drainage and observed the same sorption shapes for more organic-rich sediments and sediments with low organic content.

NOM has also been shown to play a minimal role in the sorption of copper to soil samples from a Brazilian oxisol profile (Chapter 3), despite the fact that NOM is the predominant determinant of cation exchange capacity (CEC) in these soil samples (Chapter 2). The research described here is designed to test the following hypothesis concerning the interactions among soil minerals, NOM and copper sorption: The NOM bound to oxisol minerals is highly saturated with iron and aluminum, precluding the availability of sites for copper binding.

Materials and Methods

Materials

All reagents used in the experiments described below were conducted using reagent grade chemicals that meet or exceed the latest American Chemical Society (ACS) specifications for reagent grade chemicals. All solutions were made with Nanopure™ water. All glassware was submersed in an acid bath (2% HNO_3) for at least 24 hours followed by triplicate rinses with dionized water and submersion in a Nanopure™ water bath. The glassware was then dried before use.

Filtration was performed with GelmanScience™ Supor Acrodisc 45 μm filters, after copper sorption batch experiments were centrifuged in a Fisher Scientific Marathon™ model 12KBR. Acidification was done with a 1% volume of concentrated HNO_3. Then samples were analyzed for a suite of metals by Inductively Coupled Plasma Atomic Emmission Spectroscopy (ICP-AES) using a Perkin Elmer model Optima 3000 instrument (Boss and Fredeen, 1997) (see also Chapter 3).

Solutions were analyzed for organic compound concentration on a total carbon analyzer (Shimadzu TOC 500). Before each analysis samples were bubbled with N_2 gas for a few minutes to remove CO_2.

The surface areas (BET) of all the samples before and after the removal of soil organic carbon were measured. Soil specific surface area was determined using a Micromeritics – Flow Sorb II 2300™. This instrument can measure surface areas in the range of 0.1 to 300 m^2/g, using a single point method. This method is based on the absorbency of a gas mixture (30% N_2 and 70% He) at one specific partial pressure (10 lb/in^2), forming a molecular monolayer of the gas on the surface of the adsorbent. The method used for the analysis is in the instrument manual.

The soil material that had part of its organic matter oxidized or extracted by 0.001 or 0.5 M NaOH treatments had subsamples collected and placed in porcelain crucibles that were put in an oven at 110°C for 24 hours. After being dried these samples were analyzed for total carbon content in a total carbon analyzer (UIC-Coulometrics Model 5011 CO_2 Coulometer). The method used for this analysis was the method from the instrument manual. The results were used to determine the amount of organic carbon removed from soil for each technique (Chapter 2). Soil organic carbon percentage for untreated soil samples were determined using the same instrument and procedures.

Samples of NOM extracted from the A_1 soil horizon with 0.001 M NaOH treatments were subjected to several different treatments and were subsequently sorbed to untreated soil from the A_1 horizon. The types of NOM were: 1) unmodified extracted NOM; 2) NOM extracted and treated with a Chelex 100 resin; 3) NOM extracted and fractionated into 'humic' acid; and 4) NOM extracted and fractionated into 'fulvic' acid. All NOM samples were sorbed to soil in the batch experiments (see below).

Acid-base titration of the NOM was performed using an automated computer controlled titrator. It was equipped with a Ross Orion semimicro combination electrode. A 50-ml borosilicate glass titration cell (from Wheaton Scientific Glassware) had two outlets for the introduction of pH electrode, acid and base hoses, and an N_2 hose. The cell had double walls where water from the water bath, pumped by a VWR Scientific peristaltic pump model 1141, could circulate through the cell walls and keep the temperature constant at $25^{\circ}C \pm 0.1^{\circ}C$. Automatic injections of 0.1 M HCl or 0.1 M NaOH were performed by computer controlled Gilmont micro-burettes. The acid and base solutions used for all titrations were prepared with CO_2-free Nanopure™ water and were standardized using sodium carbonate ($NaCO_3$) and potassium hydrogen phthalate ($KOOCC_6H_4COOH$), respectively.

Cupric ion activity was monitored by the use of an ORION ion selective electrode Model 9629 ion**plus**™ with a built-in reference cell connected to an ORION RESEARCH microprocessor ionoanalyzer/901 voltmeter. Hydrogen ion activity was measured with an ORION combination pH electrode connected to a Beckman Φ45 pH meter. This type electrode was also used for measurement of soil solution pH from batch experiments.

The instrument used for the UV analyses was a Perkin Elmer Lambda 11 UV/VIS spectrometer. Triplicates of each sample were scanned four cycles with wavelength ranging from 250 to 290 nm. In this wavelength range, absorbency would represent a surrogate for aromatic moieties in the NOM sample (Skoog and Leary, 1992).

NOM extraction and oxidation

NOM was removed from A_l soil horizon samples by three different procedures of increasing severity:

1. Extraction with 0.001 M NaOH at ambient temperature.
2. Extraction with 0.5 M NaOH at 55°C.
3. Oxidation with a 5% NaOCl.

For the extractions, NaOH solutions were prepared from solid NaOH. A soil/solution ratio of 1:20 was used in all experiments. For the experiments using 0.001 M NaOH, the extraction was performed in 250-ml Erlenmeyer flasks with mild continuous agitation using a Teflon stir bar. Periodic dropwise additions of 5 M NaOH were used to maintain a constant pH of 11.0. Changes in pH were used as an indication of the progress of the extraction. Changes in pH generally ceased after 24 – 36 hours. Extractions were allowed to continue until 48 hours elapsed time to assure complete reaction.

For extractions with 0.5 M NaOH there were no pH adjustments. The soil solutions were contained in sealed glassware for the entire 48 hour period in an oven at 55°C. In both extractions the soil solution was separated from soil particles by centrifugation at 2500 rpm for 15 minutes. The supernatant was collected, filtered, and adjusted to near-neutral pH by the addition of concentrated HNO_3. This was done to minimize hydrolysis of NOM functional groups such as esters (Bowles et al., 1989) during subsequent storage. The separated soil and NOM samples were then refrigerated at 4^o until use. Extracted NOM solutions were diluted ten times with Nanopure™ water, and the solution pH reduced to less than four. These solutions were analyzed for total organic carbon (TOC).

Sodium hypochlorite at pH 9.5 was the method of choice for the oxidation of most oxisol NOM without destruction of the mineral phases (Lavkulich and Wiens, 1970). Most of soil organic carbon (87%) was removed without affecting the soil mineralogy (Chapter 2). Lavkulich and Wiens (1970) obtained similar results with respect to NaOCl selectivity. This oxidizer was first used for this purpose by Anderson (1963) and later by several others (Lavkulich and Wiens, 1970; Hoffman and Fletcher, 1981; Papp et al. 1991). The method used here is that of Papp et al. (1991). One gram of soil was mixed with six milliliters of 5% NaOCl solution adjusted to pH 9.5 with 6N HCl. The soil solution was then put into a boiling water bath for 15 minutes. The soil solution was then centrifuged at 2500 rpm for 15 minutes and the supernatants were filtered and acidified. This procedure was repeated four times. The supernatants were further analyzed by ICP-AES. Then an acid solution of HCl at pH 2 was added to the remaining soil and the mixture was shaken for few minutes to drop down the interstitial soil solution pH back to the natural acidic soil pH of 5.0. The soil material was kept under refrigeration prior to the execution of any experiment.

NOM characterization

NOM from the relatively mild extraction of A1 horizon oxisol samples was chosen for additional experiments. This NOM represents an easily-extracted portion of the soil NOM and remains in solution over the pH range used in subsequent experiments:

NOM was separated into fractions similar to classically defined humic and fulvic acids by dropping the pH of 100-ml of the NOM solution to 1.0 by the addition of 0.9 ml of concentrated HNO_3 (Thurman, 1985) in polycarbonate centrifuge bottles. The solutions were then centrifuged at 2500 rpm for 30 minutes. The supernatant was carefully removed using a pipette (Mohr) and the remaining (mostly solid) material in the bottle (i.e. humic acid) was diluted to 100 ml by the addition of Nanopure™ water. Then the pH was increased to 10.0 by the addition of 0.6 ml of 0.5 M NaOH to dissolve most of the humic acid fraction.

Chelex 100 chelating ion exchange resins (from BIO RAD, Inc.) were used in batch experiments to attempt to exchange hydrogen for ferric and aluminum ions, as well as other trace metals present in the unfractionated NOM from 0.001 M NaOH extraction of the A_1 horizon soil. One gram of Chelex resin was used for each 10 ml of NOM extract solution. A NOM/Chelex mixture of 170 ml was adjusted to 4.07 ± 0.02 by the addition of 0.375 ml of concentrated HNO_3 and gently shaken for 72 hours. The Chelex-NOM mixture was then centrifuged at 2500 rpm for 15 minutes and the supernatant was carefully collected. Then the solution was filtered to assure that no Chelex resin remained within the NOM solution.

Metal contents in the different samples of extracted NOM were measured after the organic matter was oxidized by 30% volume H_2O_2. A volume of 0.5 ml of a given NOM sample was mixed with 4.5-ml hydrogen peroxide and gently stirred for a period of 48 hrs. Then, prior to the ICP–AES analysis, this solution was acidified by concentrated HNO_3 at 1% of the solution volume and spiked with a 500-ppm scandium solution, also at 1% volume. Scadium is an element rarely found in natural systems; therefore, it is used in the ICP-AES protocol for quality control of the metal concentrations in solution. Oxidation of the organic carbon in solution was never complete. Hydrogen peroxide was able to oxidize approximately 72% (±1.9%) of the initial organic carbon. Therefore, when the oxidized solution was adjusted to pH approximately 1 for the ICP preparation, some sedimentation of colloidal humic acids was visible after the solution has been sitting for few hours. To obtain a uniform concentration of the NOM solution the tube was shaken for few seconds to cause the NOM dissolution and then this solution was analyzed on the ICP-AES.

Individual NOM samples for acid base titrations were made by dilution of the NOM stock solution to achieve an organic carbon concentration of 60 mg/L. The ionic strength was adjusted to 0.01 M by the addition of $NaNO_3$. After the first acid and base titrations, more salt was added to increase the ionic strength to 0.1M. Before the beginning of any acid or base titration, the NOM solutions were bubbled for 2 hours with N_2 gas in a sealed titration cell to create a CO_2-free solution. The solutions were kept sealed during titrations. Acid titrations were performed from pH 3.3 to 10.0 followed by basic titrations from pH 10.0 to 3.3. Blank acid and base titrations were also run with Nanopure™ water with the same conditions of pH , solution ionic strength , but with no NOM in solution.

Copper titrations of NOM solutions were performed in 100 ml glass beakers. The beakers were wrapped in aluminum foil to minimize light interference with the electrode surface (Skold, 1999). The titrations were performed at room temperature, 25 ^{o}C at pH 6.0 ± 0.02 with 50 mmoles/l KNO_3 as background electrolyte. At this salt concentration the slope of the blank copper titration is close to a Nerstian slope (e.g., 29.6 mV/ log Cu $^{2+}$) (Skold, 1999). NOM stock solutions were diluted with UV water to a concentration of 10 mg C/l for all titrations. The solution pH was reduced to 4.0 ± 0.02 using a few drops of 0.1 M HNO_3. Titrant solutions were bubbled with oxygen-free N_2 gas for a period of one hour before each titration, in order to produce a CO_2 free atmosphere before the titrations. After one hour, the solution pH was raised to 6.0 ± 0.02 by the addition of few drops of 0.1 M NaOH. A gentle stream of nitrogen gas was maintained inside the titrator during the titration. Small increments ($< 5\mu L$) of 0.1 M of HNO_3 or NaOH were added to the solution to keep the pH constant through out the titration. Before and after each titration, the cupric selective electrode and the pH electrode were rinsed in 0.01 mole/l HNO_3 for five minutes to dissolve any metals remaining on the electrode surface. After that, the cupric electrode surface was polished using a 3 μm aluminum oxide-coated sheet to fully clean the electrode surface. The electrodes were stored in a 0.1 M KNO_3 solution for at least fifteen minutes before each use for stabilization purposes. Blank copper titrations were initially conducted by the addition of copper ions obtained from the dissolution of $Cu(ClO_4)_2.6H_2O$. Calibrated mechanical pipettes were used to deliver 50, 100, 200, 500, and 1000 μl of copper solution of concentrations from 1×10^{-3} to 1×10^{-1} mole/l to a 100 ml titrant solution. Exactly the same procedure was performed for the NOM titations, so each point in the blank titration has a corresponding point in the NOM titration. Blank copper titration results produce a straight line, with slope close to 29.6 mV/ log free copper. This plot was used to calibrate the cupric electrode and to check its expected Nerstian response. During the titration, two electrode readings were taken after each copper addition. A stir bar inside the titrator mixed the solution until equilibrium was reached at which point the stir bar was stopped and the readings taken. Equilibrium was assumed when the change in e.m.f. was less than 0.2 mV/minute over two subsequent minutes. Duplicates of the Cu(II) titration with NOM before sorption to soil were performed and present an excellent reproducibility of the data with difference in e.m.f. from the first titration data smaller than 0.4 mV.

An ultra violet light adsorbance technique was used to characterize untreated NOM and NOM fractionated into humic and fulvic acids. The analysis was performed on liquid samples diluted from different types of NOM obtained from stock solution and then placed in quartz cells. The organic carbon concentration in solution was from 5 to 6 mg/L, so the absorbance in all the samples was less than one.

NOM sorption to soil

Soil samples were pretreated with different concentrations of $NaNO_3$ solutions to replace exchangeable soil cations with sodium before receiving the different types of NOM described above (Charlet, 1986). The soil solution was shaken for 42 hours with periodic pH adjustments. At the end of the sorption period, soil solutions were centrifuged at 2500 rpm for 30 minutes. The supernatant was carefully collected with a 25 ml glass pipette, and the remaining soil was washed a few times with 0.0001 M nitric acid to remove the interstitial NOM that was not sorbed to the soil. Three small subsamples of the remaining solid were collected in a porcelain crucible for measurement of the interstitial soil moisture content and also for later measurement of the organic carbon increase due to sorption. The remaining solid was stored under refrigeration at 4°C until further use.

The soil/solution ratios for the sorption experiments for the four different types of NOM (1- unmodified extracted NOM; 2- NOM extracted and treated with a Chelex 100 resin; 3- NOM extracted and fractionated into humic acid; and 4- NOM extracted and fractionated into fulvic acid) were 1:70, 1:90, 1:55, and 1:50 respectively. All sorption experiments were performed in clean centrifuge bottles at pH's 3.85, 4.06, 3.96, and 1.13

respectively. Aliquots of soil solution were collected after sorption to evaluate the amount of NOM sorbed to soil.

Cu (II) sorption to soil

All soil samples that were used for NOM and/or ionic copper sorption experiments were pretreated with $NaNO_3$ solutions to replace exchangeable cations. Charlet (1986) used a similar approach in experiments to measure the sorption of monovalent and divalent cations to oxisol samples.

Ten grams of dry soil were mixed with 42.85 ml of 0.5 M $NaNO_3$ at pH 6.00 ±0.02 and shaken gently for ten minutes. Then, the mixture was allowed to settle for one hour and the supernatant was carefully collected using a 20-ml glass pipette. The remaining soil received the same treatment once again. Then the same volume of 0.1 M $NaNO_3$ at the same pH was mixed with the soil material and gently shaken for ten minutes. After this period the soil solution was centrifuged at 2500 rpm for 15 minutes and the supernatant was carefully collected using a 20-ml glass pipette. This rinsing procedure was then repeated. Finally, an equal volume of 0.01 M $NaNO_3$ at $pH = 5.00 \pm 0.02$ was used as a rinse. The pH range used for the replacement of exchangeable cations was chosen to avoid significant dissolution of low crystalline minerals and amorphous soil material (Charlet, 1986; Chorover, 1993).

The treated soil was then placed in storage under refrigeration except for three sub-samples (< 0.5 g) that were placed in porcelain crucibles of known mass. The crucibles were weighed and placed in an oven at 110°C for 24 hours. A series of weighings of the crucibles with soil material were taken during this period and the soil moisture content was determined.

All copper sorption experiments were made using a dry soil/solution ratio of 3.3 g/l. The total copper concentration in the absorption vials (50-ml plastic centrifuge tubes) was always 1.0×10^{-5} M. Based on a previous kinetic experiment the copper sorption reaction with oxisols was allowed to proceed for 24 hours (Chapter 3). This equilibration time is in agreement with that used by other researchers who studied copper sorption to oxisols (Guilherme and Anderson, 1998). Copper solutions were made from dilution of an ICP standard solution for copper analysis. Then a specific weight of solid $NaNO_3$ was added to the copper solution to make the electrolyte concentration of 0.01 M. Once soil material and copper solution were mixed the soil solution pH in each tube was adjusted by the addition of 0.1 M HNO_3 or NaOH. Each set of experiments covers a pH range from 3.0 to 6.5. The soil solution was gently shaken for 24 hours, time necessary for copper sorption to soil reach the assumed equilibrium (Jarvis, 1981; McLaren et al., 1981 and 1983; Msaky and Calvet, 1990). The amount of acid and base added to soil solution was less than 1 % of the total copper soil solution volume, so this dilution was considered insignificant during the sorption experiment. Adjustment of solution pH was effectuated for the first 12 hours, then the solution was gently shaken for another 24 hours and a final pH reading of each sample was taken. Each sorption point was made in duplicate. Subsamples of soil solution were collected after copper sorption experiment to measure the amount of organic carbon in solution.

Results

NOM extraction and oxidation

Two NOM extractants and one oxidizing agent were used in efforts to remove the organic carbon material from A_1 horizon oxisol samples (Table 4.1). All extraction/oxidation experiments were performed in the open atmosphere with no added salt. In these experiments there was a reference sample also from the A_1 horizon that was used as a control sample to evaluate the efficiency of each NOM removal technique (Table 4.1). The purpose of the use of different extractants was to attempt to remove different fractions of the oxisol NOM. For extractions with basic solutions (0.001 or 0.5 M NaOH), material balance calculations revealed organic carbon losses less than 5% (Table 4.1). Measurements of the specific soil surface area were made by the BET method after each soil NOM extraction or oxidation to evaluate the importance of soil organic matter fractions as soil aggregation agents (Table 4.1). Basically no changes in soil specific surface area were observed except in the case where NaOCl oxidized most of the organic carbon present in soil. These results imply that a substantial fraction of the NOM in oxisols is deep inside the soil structure, since only after severe oxidation of the soil organic carbon do the particles start to break apart and consequently increase the surface area.

NOM characterization

As mentioned above, only the NOM extracted by 0.001 M NaOH was extensively characterized. The main reason for this choice was the fact that this NOM type would precipitate from solution only at pH's <~ 2.5. Thus, experiments with NOM sorption to soil could be conducted at pH's as low as 4.0 followed by copper sorption experiments at various pH's.

The first characterization of the extracted NOM was the measurement of the total organic carbon concentration (Table 4.1 and 4.2). Then a NOM sample was fractionated into fractions operationally similar to humic and fulvic acids by dropping the solution pH to 1.0 followed by careful collection of the solution supernatant with a glass pipette (Thurman, 1985). The remaining material was then re-dissolved and diluted to the same volume as the initial NOM solution. Both fractions were analyzed for organic carbon concentration. About one third of the NOM fractionated to 'humic acids' and two thirds into 'fulvic acids' (Table 4.2).

Table 4.1 - Extraction of NOM from A1 horizon Oxisol samples using various extractants and resulting soil surface areas.

Soil type	*% Org. C remaining*	*% Org. C removed*	*T.O.C.* mg/L*	*Soil (SA)** m^2/g*	*Material balance*
Untreated soil	2.32 (±0.01)	0%	-	94.30 (±1.3)	-
Soil after extraction by 0.001 M NaOH	1.69 (±0.04)	27.4%	275.6 (±19.1)	96.50 (±1.3)	96.6%
Soil after extraction by 0.5 M NaOH at 55 °C	1.01 (±0.04)	56.5%	606.6 (±41.1)	98.79 (±1.3)	95.8%
Soil after extraction by 5% vol. NaOCl	0.34 (±0.05)	85.3%		114.80 (±1.3)	

*T.O.C. = Total Organic Carbon

**Soil Surface Area (SA)

To investigate the influence of the native metal content of the extracted NOM on the ability of the NOM to complex copper in solution, the amount of iron and aluminum associated with the NOM was measured after oxidation of NOM samples by 30 volume percent H_2O_2. The results show high concentrations of iron and aluminum in the humic acid fraction (Table 4.2). This suggests that the iron and aluminum present in humic acids are strongly bound to NOM and are not released into solution even at the very acid pH used in the NOM fractionation.

Another experiment designed to investigate the role of native metals in the extracted NOM in determining the extent of copper sorption to soil was the use of Chelex 100 resin to exchange complexed metals, including iron and aluminum, with protons from the resin. The results, presented as the metal/carbon mass ratios, show a noticeable depletion of trace metals by treatment with the Chelex 100. However, the treatment was not very effective in the removal of metals from the NOM. For example, the ratio of iron and aluminum to organic carbon was only reduced by 50% and 43% respectively (Table 4.3). The resin remained in contact with the NOM at pH 4.0 for 72 hours. All measurements of trace metals in the fulvic and humic acid samples were below the ICP-AES detection limit; therefore it was not possible to measure the standard deviation for these measurements.

NOM sorption to soil

Three of the four types of NOM sorbed to untreated soil from the A_1 horizon caused a detectable increase in organic carbon percentage (Table 4.4). The only NOM sample that did not cause a significant change was the NOM-humic acid sample. However, there was a significant reduction of NOM concentration (from 73 mg/l to 40 mg/l) in the supernatant after the sorption to untreated soil (Table 4.4). If this depletion of NOM were attributed to its sorption to the untreated soil, it would represent an increase of 7.8 % of the soil organic carbon content after the sorption of NOM-humic acids.

The sorption of the NOM to soil caused a fractionation of the original NOM solution.

Table 4.2 - Fractionation of NOM extracted from A1 horizon Oxisol by 0.001 M NaOH.

	T.O.C. (mg/L)*	*% of total*	*Ratio: Mols of (Al/C) duplicates*	*Ratio: Mols of (Fe/C) duplicates*
Total extract	270 (±3)	100%	0.13 0.15	0.043 0.039
Humic Acids	73 (±8)	32% (±4)	0.34 0.33	0.09 0.10
Fulvic Acids	157 (±13)	68% (±4)	0.02 0.02	0.0007 0.0005

* T.O.C. = Total Organic Carbon

Table 4.3 - Metal content in duplicates (mg of metal / mg of C) in different types of NOM and after oxidation by H_2O_2 by 30% vol.

	NOM extracted by 0.001 M NaOH	*NOM treated by* Chelex	*NOM Humic Acids*	*NOM Fulvic Acids*
Cu	3.46 x 10^{-4}	3.10 x 10^{-4}	$<$ 1 x 10^{-4}	$<$ 1 x 10^{-4}
	3.54 x 10^{-4}	2.70 x 10^{-4}		
Cd	3.10 x 10^{-4}	2.90 x 10^{-4}	$<$ 1 x 10^{-4}	$<$ 1 x 10^{-4}
	3.50 x 10^{-4}	3.10 x 10^{-4}		
Pb	3.37 x 10^{-4}	$<$ 4 x 10^{-5}	$<$ 2 x 10^{-4}	$<$ 2 x 10^{-4}
	3.43 x 10^{-4}			
Zn	1.28 x 10^{-3}	1.70 x 10^{-3}	$<$ 1 x 10^{-4}	$<$ 1 x 10^{-4}
	1.32 x 10^{-3}	2.30 x 10^{-3}		
Ca	2.63x 10^{-3}	3.30x 10^{-3}	$<$ 7 x 10^{-4}	$<$ 7 x 10^{-4}
	2.77 x 10^{-3}	4.70 x 10^{-3}		
Mg	1.26 x 10^{-3}	0.90 x 10^{-3}	$<$ 1 x 10^{-4}	$<$ 1 x 10^{-4}
	1.34 x 10^{-3}	1.30 x 10^{-3}		
Fe	1.97 x 10^{-1}	0.10 x 10^{-1}	3.60 x 10^{-1}	2.20 x 10^{-3}
	2.03 x 10^{-1}	1.00 x 10^{-1}	4.60 x 10^{-1}	3.20 x 10^{-3}
Al	2.96 x 10^{-1}	1.60 x 10^{-1}	5.30 x 10^{-1}	3.98 x 10^{-2}
	3.04 x 10^{-1}	1.80 x 10^{-1}	6.70 x 10^{-1}	4.02 x 10^{-2}

This behavior was confirmed by three different analytical techniques representing different chemical signatures. The first technique used was acid base titrations. The results show a striking difference in NOM acidity before and after sorption to soil. The base titration shows that NOM after sorption to soil is consistently less acidic than before sorption by about 0.2 meq of OH^- / g C over the entire pH range (Figure 4.1). The same general behavior is observed in the NOM acid titration, but not as distinctly as the base titration. In the latter case the lines almost overlap and there is a little bit more hydrogen consumption by the whole NOM sample before the sorption to the soil (Figure 4.2). In both titrations the plots are straight lines due to the chemical heterogeneity of these samples, it was not possible to detect any end point along the titration. In other words, it was not possible to recognize any distinct functional groups such as carboxyl or phenol.

The second analytical technique used to characterize NOM before and after sorption to soil was copper titration. All such titrations were performed under identical conditions. The concentration of organic carbon used was 10 mg/l, and the concentration of the electrolyte (KNO_3) in solution was 50 mmoles/l. The same increments of copper were added to the NOM solutions and the blank solutions. The results are highly reproducible, showing differences of less than 0.4 mV for each point (Figure 4.3). The blank titrations produced straight lines with slopes of 28.42 and 27.93. Both results were considered within the Nerstian slope of 29.6 ± 2.0 mV/ log free copper. The blank titration was used as a standard curve for measuring the activity of the copper in solution during NOM titrations. The percentage of complexed copper was obtained from the difference between total copper and free copper. In each titration the plots of voltage vs. the log of free copper in the NOM titration reaches an asymptote value equal to those for the blank titration. This behavior is expected as the limited number of metal complexing sites on NOM are soon filled and the free copper approaches total copper. In addition, this behavior also indicates that possible NOM coatings on the electrode surface did not occur. A copper concentration of 1×10^{-5} M was selected to analyze the results of the

Table 4.4 - Sorption of different types of oxisol NOM to untreated A_1 soil horizon, based on the increase of organic carbon percentage in soil after NOM sorption (original % org. C = 2.32%).

NOM type	*% Org. C in soil after NOM sorption*	*% Org. C increase in soil*	*T.O.C.* (mg/L) before sorption*	*T.O.C. (mg/L) after sorption*
NOM extracted by 0.001 M NaOH	2.73 (±0.16)	17.7 %	270 (±3)	186 (±10)
NOM after Chelex resin	2.75 (±0.12)	18.5 %	210 (±5)	180 (±4)
NOM – Humic Acids	2.30 (±0.15)	7.8 %	73 (±8)	40 (±5)
NOM – Fulvic Acids	2.61 (±0.18)	14.3 %	157 (±13)	110 (±4)

*T.O.C. = Total Organic Carbon

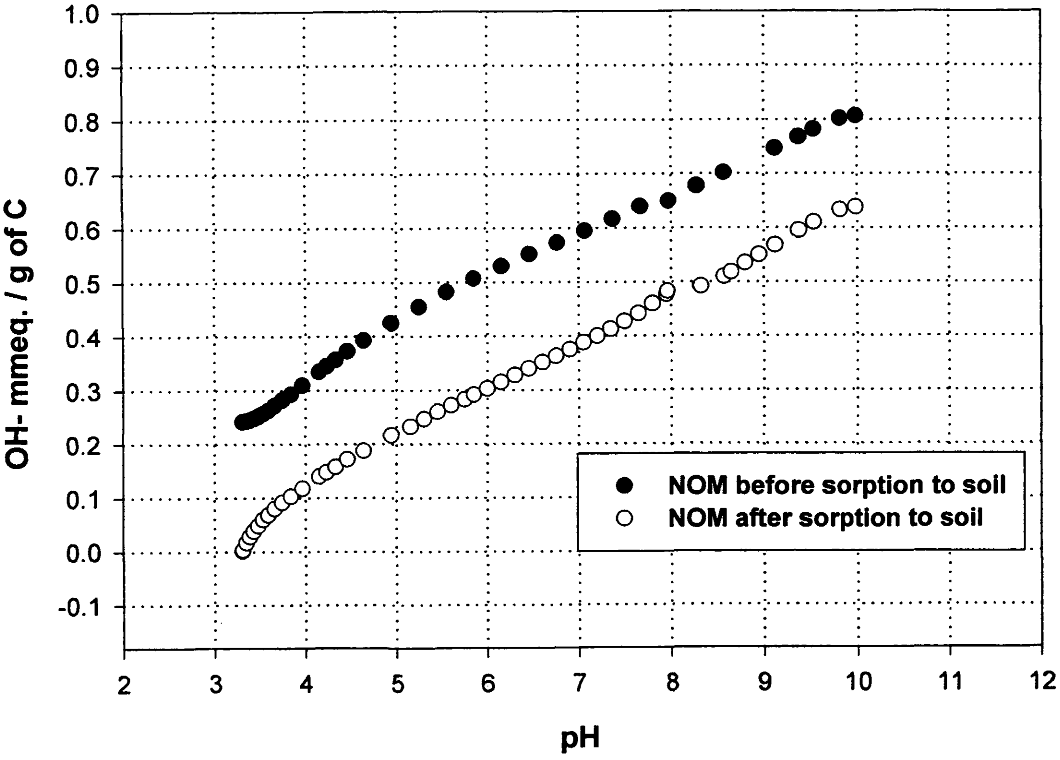


Figure 4.1 – Base titration of NOM extracted by 0.001 M NaOH before and after sorption to soil. I = 0.01 M $NaNO_3$ and NOM = 60 mg/l.

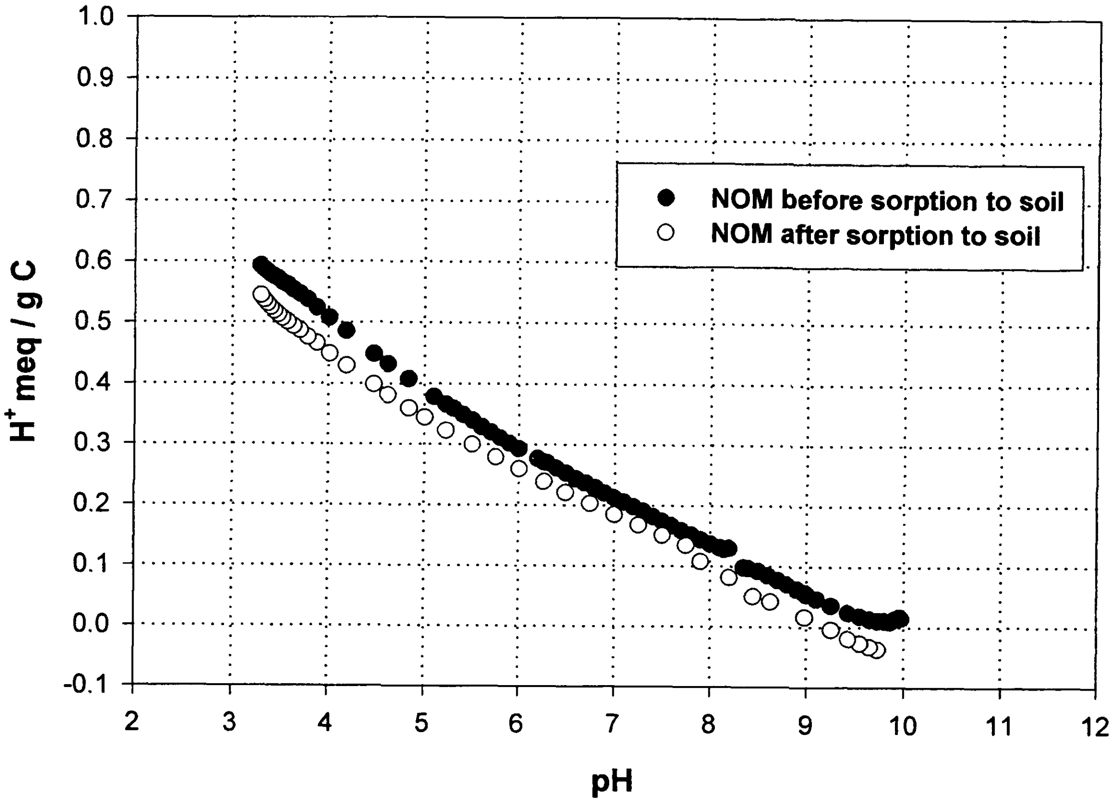


Figure 4.2 – Acid titration of NOM extracted by 0.001 M NaOH before and after sorption to soil. I = 0.01 M $NaNO_3$ and NOM = 60 mg/l.

copper titration, since this concentration was used for the copper soil sorption experiments.

Here again the signatures of NOM before and after sorption to soil are different. The NOM after sorption is less acidic and has less ability to complex copper in solution. There was a significant decrease in the percentage of complexed copper in solution from 89% to 74% when the NOM after sorption to soil was titrated (Figure 4.4). In other words, the more aliphatic NOM, that which did not sorb to the soil mineral phase, has a lessened ability to complex copper compared to the whole NOM, which is more aromatic. Some researchers that choose to work with the discrete ligand approach for modeling the NOM complexation of copper to NOM associate copper to carboxylic acid functional groups (Davis, 1984). However, carboxylate functional groups are predominant in the more aliphatic NOM fractions. Thus the notion of carboxylate dominated copper complexation by NOM contradicts the decrease of copper complexation to NOM after sorption to soil. Skold (1999) found similar results after a series of copper titrations with samples of different aquatic NOM, followed by potentiometric titration determination of NOM functional groups. He could not correlate complexation of copper and NOM with the predominance of carboxyl functional groups. The third characterization of NOM before and after sorption to soil was made with ultra violet light (UV) absorption. UV analysis is a relatively simple technique that can be used to broadly characterize molecular structures. Aromatic structures have their maximum UV absorption around 250 to 290 nm, while aliphatic structures have their maximum absorption at shorter wavelengths (Skoog and Leary, 1992). From UV measurements from 250 to 290 nm, the average of triplicate readings at 280 nm were obtained and normalized to the total organic carbon concentration. The data show that after untreated NOM was sorbed to soil there was a depletion of aromatic structures since the specific ultra violent absorption value is smaller than the value before sorption to soil. Comparing these results to the copper titration data, I conclude that there is a correlation between the decreased copper complexation in solution and the decrease in specific UV absorption

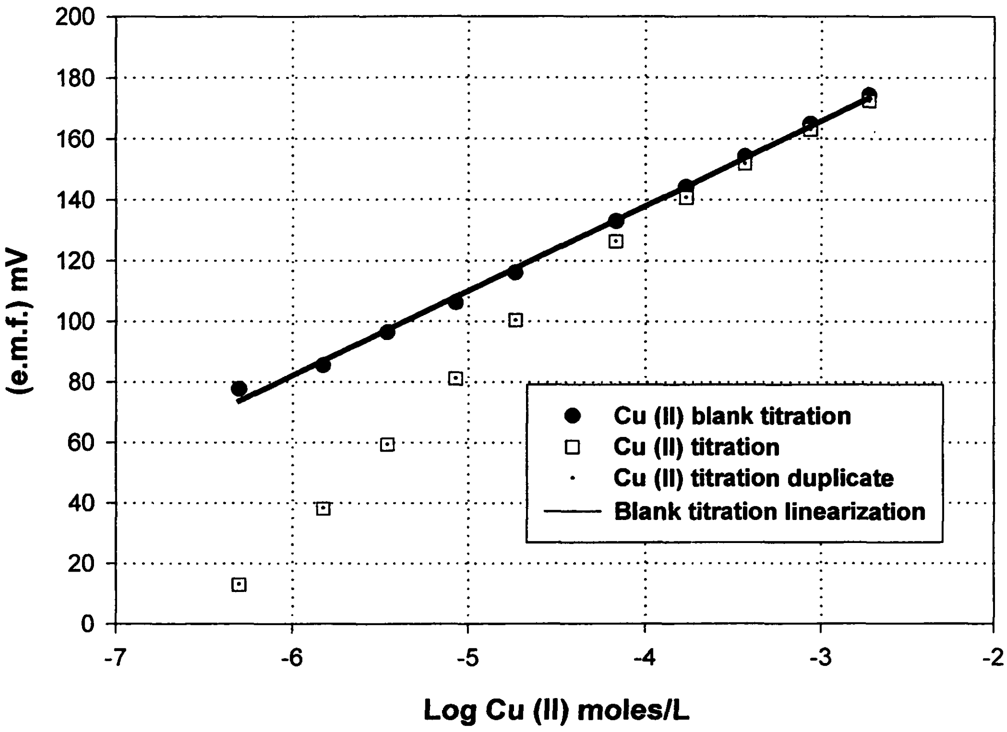


Figure 4.3 – Cu(II) titration of NOM extracted by 0.001 M NaOH. I = 0.05 M KNO_3 pH = 6.0.

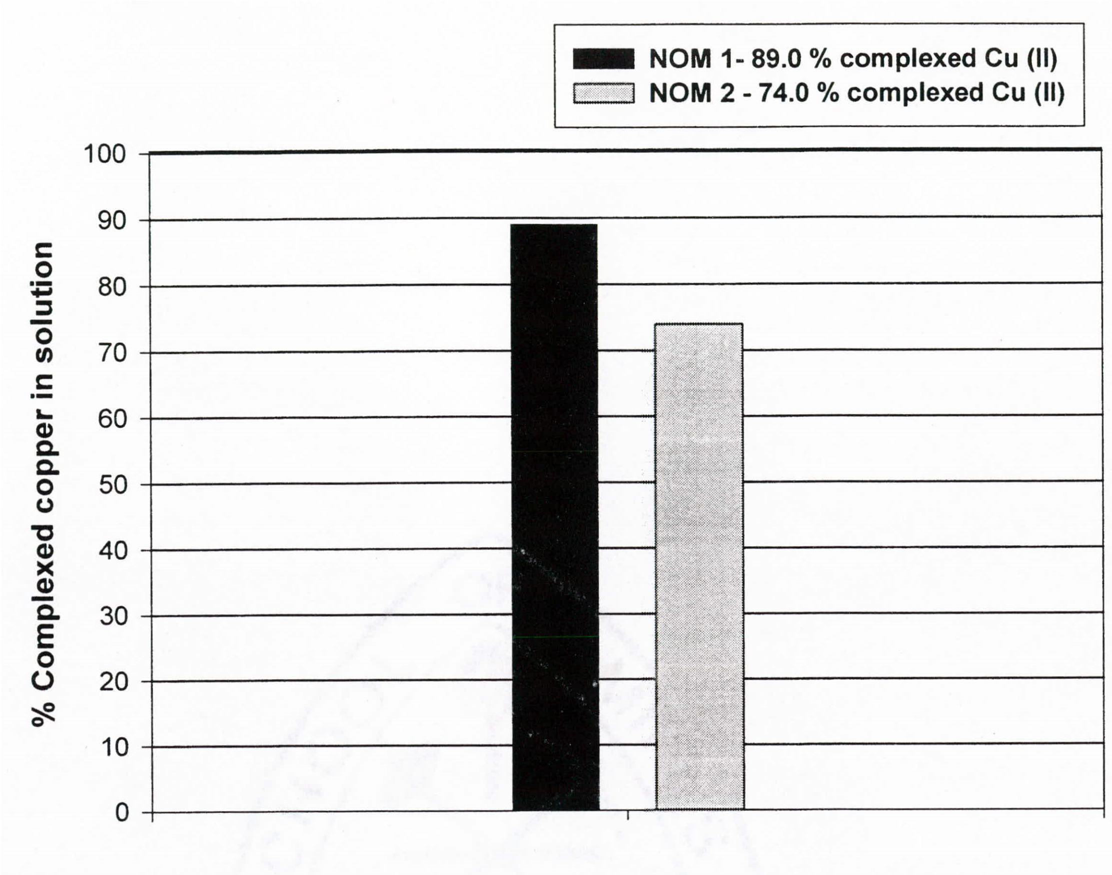


Figure 4.4 - Percentage of complexed copper in 10 mg of C/l NOM solution at pCu = 5.01. I = 0.05 M KNO3 and pH = 6.0. NOM 1= NOM extracted by 0.001 M NaOH from A_1 horizon soil. NOM 2 = NOM extracted by 0.001 M NaOH from A_1 horizon soil and re-exposed to untreated soil.

(Skold, 1999) (Table 4.5 and Figure 4.4). These results together provide strong evidence for the notion that the decrease of copper complexation in solution can be directly correlated with depletion in the aromatic NOM structures due to fractional sorption to soil.

Cu sorption to soil:

Two sets of experiments measuring the pH dependent copper sorption to oxisol samples from the A_1 horizon were performed. Both sets had similar conditions of pH, solution ionic strength, soil/solution mass ratio, and copper concentration. The difference between these two sets was only the fact that the first set used untreated samples plus samples that had NOM extracted or oxidized by different chemical compounds while the second one had untreated samples plus samples that had different types of additional NOM sorbed to them. The main goals of these experiments were: 1) to investigate how the removal of NOM from soil samples by different compounds would affect the copper sorption to soil; 2) to investigate whether or not the geometrical NOM arrangement in soil was related to the low influence of NOM on the sorption of copper to oxisol samples; and 3) to investigate whether or not iron and aluminum present in the soil NOM structure was blocking NOM sites that could be occupied by copper, also partially accounting for the lack of influence of NOM on copper complexation capacities of oxisols.

The first set of pH profiles for copper sorption to oxisol had the typical sigmoid shape of transition metal sorption to oxides (Figure 4.5). For typical metal oxides the fraction of metal sorbed to the oxide surface increases from a low fraction sorbed at low pH to an almost complete sorption in one and a half to two pH units (Davis and Leckie, 1978; Benjamin and Leckie, 1981; Kooner et al., 1995). After the removal or oxidation of the soil NOM (from 27.4% to 85.3% reduction in soil NOM) no significant difference was observed in the copper sorption edges. The only consistent change in the sorption edges after the removal of NOM was a 10% increase of copper sorption at pH higher than 5.5.

The second set of copper sorption edges for oxisol samples showed somewhat

Table 4.5 - UV analyses of NOM extracted by 0.001 M NaOH at 280 nm wave length before and after sorption to soil and NOM-Humic and Fulvic fractions.

NOM type:	*S.U.V.A.** *(abs./mg C)*	*% Cu Complexed in solution*
NOM before sorption to soil	0.045 (±0.002)	89.0 %
NOM after sorption to soil	0.028 (±0.001)	74.0 %
NOM-Humic	0.090 (±0.001)	
NOM-Fulvic	0.020 (±0.003)	-

*SUVA = Specific Ultra Violet Absorption.

different trends (Figure 4.6). The untreated soil sample sorption edge was repeated (Figure 4.5). The sigmoid shape continuously changed as different types of NOM were added to the soil. The soil that received additional NOM that had been extracted by 0.001 M NaOH from a similar soil sample showed an increase of approximately 17% in the copper sorbed at pH 3.0 to 3.5 (compared to the untreated soil). In contrast, this same treated soil sample showed approximately 2.5% less sorption at pH's greater than 5.5, again compared to untreated soils.

The soil sample that was treated with only the humic acid fraction of the NOM removed from a similar soil sample by 0.001 M NaOH showed a minor degree of enhanced sorption over the entire pH range. The sorption edge for soil that received NOM treated with Chelex 100 resin showed a significant increase in sorption to soil (from 0.1 to 0.5) over the untreated soil at pH 3.0. However, this difference decreases as the solution pH increases, and becomes essentially similar to the untreated soil at pH's above 5. Similar low pH sorption edge behavior was observed for the soil sample that had received NOM-fulvic acids. In this case, the enhancement of copper sorption at low pH is even higher than the samples that received NOM-Chelex treatment. At higher pH's, fulvic acid treated soil shows a measurable reduced ability to sorb copper (down by 15%) in comparison to the untreated soil (Figure 4.6).

In all of these copper sorption experiments to soil that had added NOM, some desorption of NOM from soil back into solution was observed. The NOM desorption always increased with the increasing pH. The observed NOM desorption to solution was in the range between 1.6×10^{-6} moles C/l at pH 3.0 to 3.5×10^{-5} moles C/l at pH 6.5. This range of concentrations represents 0.41% to 9.92% of the total additional NOM sorbed to the soil. This desorbed NOM in solution should compete with the soil mineral or NOM surface for ionic copper in solution. If the desorbed NOM complexed ionic copper during the experiment, this fraction of the complexed copper would be measured and reported as non-sorbed.

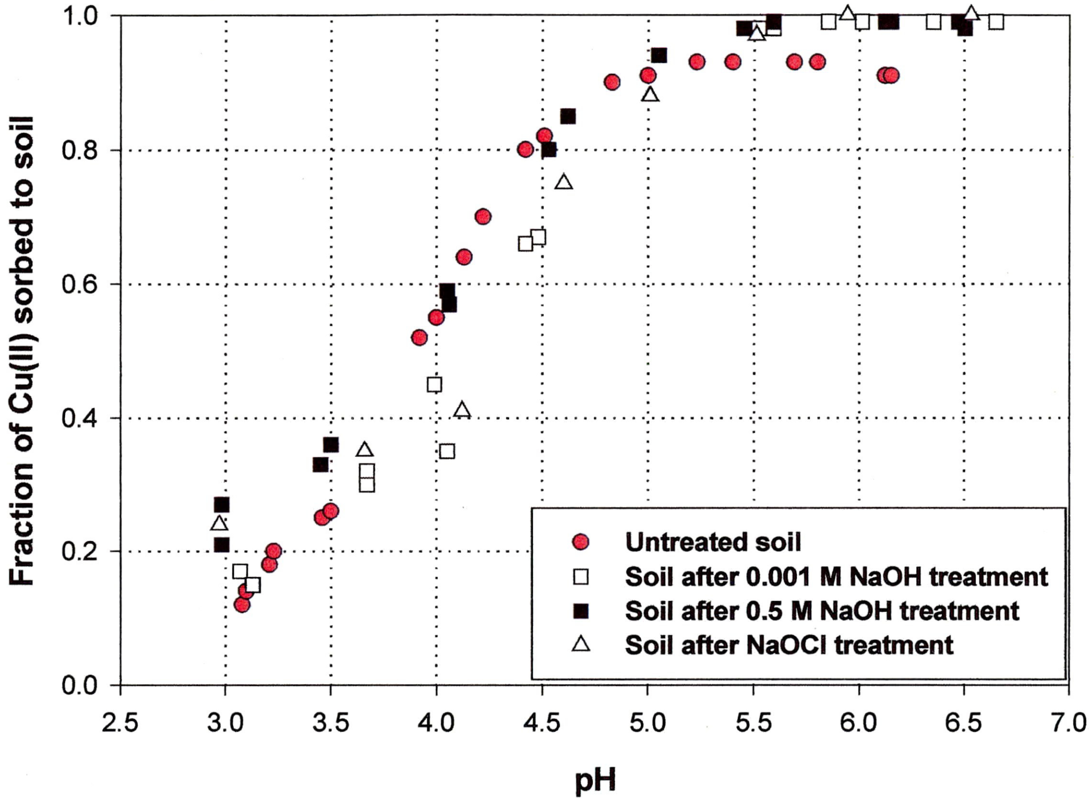


Figure 4.5 – Cu(II) sorption edges on untreated and treated oxisol from A1 horizon. Total Cu (II) = 10 μM, I = 0.01 M, and soil:solution = 3.3g/l.

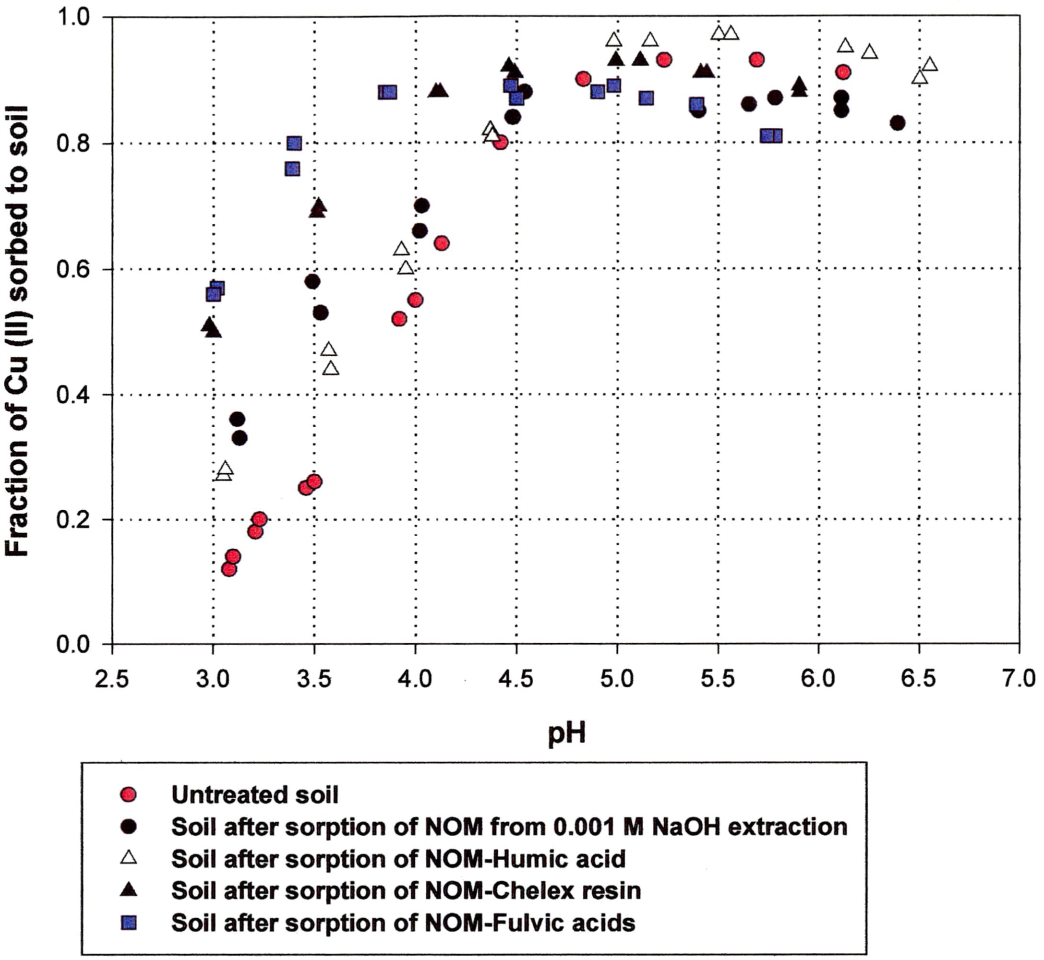


Figure 4.6 – Cu(II) sorption edge on untreated and soil with various type of additional NOM sorbed to the soil. Total Cu (II) = 10 μM, I = 0.01 M NaNO3 and soil:solution = 3.3 g/l.

Discussion

NOM extraction and oxidation:

The use of aqueous sodium hydroxide is a classical method and one of the most efficient ways of extracting soil NOM (Kononova, 1966; Stevenson, 1982; Hayes, 1985; Michaelson and Ping, 1997). Two aspects of the use of sodium hydroxide solution to extract soil NOM should be mentioned. One is the alteration of NOM molecules through hydrolysis and autooxidation (Stevenson, 1982; Bowles et al., 1989) and the other is the dissolution of iron and aluminum oxyhydroxides that are amorphous or poorly crystalline. To avoid the hydrolysis and autooxidation problem, the extracted NOM solution, after filtration, was neutralized with concentrated nitric acid. The possible dissolution of low crystalline mineral phases was investigated by XRD analysis following the alkaline extractions. The results showed no changes in soil mineralogy after NOM extraction (Chapter 2). The low crystalline phases in this particular type of soil represent a minor (less than 1%) of the total soil bulk chemical composition (Fontes and Weed, 1991; Chorover and Sposito, 1995; also see Chapter 2). Therefore, it was not a point of significant concern.

There is a significant correlation between the stability of soil aggregates and the humus material extracted by pyrophosphate followed by aqueous NaOH extraction (Chaney and Swift, 1984). This correlation between the organic matter extracted by these extractants and aggregate stability suggests that less oxidized and higher molecular weight substances are more strongly bound to inorganic particles. Consequently they are more important for soil aggregation than the lower molecular weight, more highly oxidized organic material extracted by pyrophosphate solutions. The same soil role of NOM is observed in my oxisol samples. The NaOH extractions presumably preferentially extracted the highly oxidized organic material that is closer to the soil surface. This organic matter, although abundant (27.4% to 56.5%) probably does not play a major role in soil aggregation, since the soil specific surface area after extraction did not change significantly (Table 4.1).

Another important aspect to be considered in the explanation of the small change in soil surface area is the role of iron and aluminum oxyhydroxides (poorly crystalline and amorphous material). At the conditions of natural soil pH (5.0-5.5) the surface charge of oxyhydroxides is predominantly positive and the surface charge of kaolinite, the major soil mineral, is negative. Hence, there is an electrostatic attraction between these minerals, allowing for a relative strong binding.

As mentioned before the soil organic matter oxidation by NaOCl did not affect the soil mineralogy and extracted a larger percentage of the soil organic material. ICP analyses of the supernatant solutions from the NaOCl oxidations revealed that less than 2.5% of the Si, Al, Fe, Mg, Ca, and K in the original soil bulk composition was dissolved. However, after this severe oxidation of soil organic material, a significant change in the soil specific surface area was observed. This fact supports the hypothesis that these different fractions of extracted and oxidized NOM have different roles in oxisol aggregation.

NOM characterization:

When the NOM extracted by 0.001 M NaOH was fractionated into 'humic' and 'fulvic' acids, the resulting proportion was one third 'humic' acids and two thirds 'fulvic' acids (Table 4.2). This result should not be compared with a typical fractionation of tropical soil NOM, because this fraction represents only 27% of the total soil NOM. Besides, the predominance of fulvic acids over the humic acids in this relatively easily extracted NOM is intuitively expected. Fulvic acids are more soluble than humic acids by definition (Gamble and Schnitzer, 1974; Stevenson, 1982); therefore, they should be more predominant than humic acids in more easily extracted NOM fractions.

The metal content in the NOM before and after its fractionation into 'humic' and 'fulvic' acids reveals some important results for the understanding of the ability of the oxisol organic material to complex ionic copper in solution. The first important result is the abundance of iron and aluminum associated with the soil NOM. It is well known that trivalent cations are bound to NOM in greater amounts than divalent cations at any given pH and ionic strength (Stevenson, 1986). Iron and aluminum are abundant elements in oxisols (Chorover, 1993) and probably can easily complex with more aromatic structures from soil NOM (Schnitzer and Skinner, 1965; Gamble et al., 1970; De Coninck, 1980). Humic acids have more aromatic organic molecules than fulvic acids (Stevenson, 1982 and 1985). The strength of this complexation is so high that even when there is a drop of the NOM solution pH to 1.0, the protons in the solution do not exchange for complexed iron and aluminum. These are probably the main reasons why, after the fractionation of oxisol NOM into 'humic' and 'fulvic' acids, a large fraction of the iron and aluminum ions resides in the humic fraction.

A second important observation is the ability of Chelex resin to extract approximately half of the iron and aluminum ions associated with extracted NOM (Table 4.3). The resin was also able to extract trace metals but these are two to three orders of magnitude lower than iron and aluminum content in the NOM from this type of soil. The significant depletion of iron and aluminum in the NOM solution, and the enhancement of copper sorption after the use of this NOM, support the hypothesis of the blocking of copper binding sites by iron and aluminum.

UV analysis of NOM humic and fulvic fractions at 280 nm indicates that the humic acid has a more aromatic structure than the fulvic acid fraction, since the specific ultra violet absorbancy value for the humic fraciton is bigger than the one for the fulvic fraction (Table 4.5).

NOM sorption to soil:

Four solutions of different types of NOM were sorbed to untreated soils from the A_1 horizon. The only NOM solution that was characterized before and after soil sorption was the NOM extracted by 0.001 M NaOH. However, the conclusions obtained can probably be extrapolated to the other types of NOM due to similarities in chemical composition.

The fractionation of NOM by sorption to the surface of minerals has been observed by various researchers (Parfitt et al., 1977; Davis and Gloor 1981; Tipping, 1981; Davis, 1982; Gu et al., 1995). The best pH for NOM sorption to oxide minerals is 5.0 (Tipping, 1981; Davis, 1982). At this pH for iron and aluminum oxides the mineral surface is positively charged (Point of Zero Charge = 8.0-9.0; Stumm, 1992), so the sorption of negatively charged NOM is enhanced by the electrostatic attraction between NOM and mineral surfaces. For the untreated oxisol samples used in this experiment the P.Z.C. is 4.7 (see chapter 2), so pH's lower than 5.0 would be most appropriate for enhanced NOM sorption to soil.

The sorption of NOM by iron and aluminum oxides decreases with increasing pH and can be influenced by other ions in solution such as Ca^{2+}, Mg^{2+}, and PO_4^{2-} (Davis and Gloor, 1981; Davis, 1982). It also depends on the soil to solution ratio and the nature of the solid sorbent (Davis, 1982). The higher the soil to solution ratio, the larger is the proportion of solution phase sorbed to the solid surface. This is due to the availability of more surface sites for NOM binding. Minerals with higher point of zero charge (P.Z.C.) will sorb more NOM at low pH.

NOM sorption to soil is analogous to the sorption of anions to these oxide minerals (Davis, 1982); however, NOM sorption will actually involve several functional groups. So, this type of reaction should consume protons. The consumption of protons can also be caused by other processes, such as: 1) The protonation of surface hydroxyls to form surfaces complexes; 2) disturbance of the surface equilibrium as compared to the surface charge before the sorption of organic carbon; and 3) proton consumption due to the formation of Al^{3+} complexes with NOM functional groups such as phthalic and salicylic acids (Davis, 1982).

The NOM functional groups involved in the sorption to mineral surfaces include carboxyl, phenol, hydroxyl, and aromatic moieties (Gu et al., 1995). Potentiometric titration of NOM can be used to investigate the fractionation of NOM during sorption to soil and to access possible functional groups involved in the sorption. Davis (1982) reported a depletion of weak acids after NOM sorption to alumina. He concluded that phenolic groups are the most involved in the sorption of NOM to alumina surfaces. Later, Gu et al. (1995) stated that carboxyl and hydroxyl functional groups of different NOM fractions are actively involved in the sorption reactions and also that the steric arrangement of these functional groups may play an important role in determining the adsorption of NOM fractions.

Here, a depletion of NOM acidity after sorption to oxisols was detected by potentiometric titration. However, it was not possible to access any specific functional groups predominantly involved in the sorption process. The base titration line dropped constantly by 0.2 meq/ g of C after sorption (Figure 4.1) not giving any information about predominance of any specific functional groups on the NOM sorption to soil. An elevation in solution pH was observed during NOM sorption to soil, since an average of 5 x 10^{-5} moles of nitric acid was added to the soil solution to keep the solution pH $\cong$ 4.0. The only solution that did not receive acid to control the solution pH was the fulvic acid soil solution that had pH of 1.13. The reasons for the consumption of protons during NOM sorption can be related to any of the reasons mentioned above. It is difficult to specify the predominant mechanism based only upon wet chemistry analyses.

Several mechanisms could be involved in the sorption of NOM to mineral surfaces: 1) anion exchange (electrostatic interaction); 2) ligand exchange-surface complexation; 3) hydrophobic interactions; 4) entropy effects; and 5) hydrogen bonding (Gu et al., 1994). Among these ligand exchange is most often used to explain NOM sorption to iron and aluminum oxides (Tipping, 1981; Jardine et al., 1989; Gu et al., 1994 and 1995; Filius et al., 1997). The following reactions are involved:

$$\equiv SOH_{(s)} + H^{+}_{(aq)} \leftrightarrow \equiv SOH_2{}^{+}_{(s)} \qquad (4.1)$$

$$\equiv SOH_2{}^{+}_{(s)} + R\text{-}COO^{-} \leftrightarrow \equiv SOOC\text{-}R_{(s)} + H_2O \qquad (4.2)$$

The reaction (4.1) represents the protonation of the soil surface. At a pH lower than the point of zero charge there is a net positive charge at the mineral surfaces which will enhance the ligand exchange mechanism. If the soil surface is positively charged, a carboxyl group from NOM can react with the mineral surface, exchanging a carboxyl ligand for a water molecule from the soil mineral surface (Sposito, 1989). In the oxisols experiments the soil solution pH was always below the soil P.Z.C., and there was always an increase in the pH of the soil solution during sorption of NOM.

During the copper sorption experiments, NOM desorption (from 0.41% to 9.92%) was low at lower pH's and relatively high at pH's above the soil P.Z.C. (4.7) (Figure 4.6). This desorption at pH's above soil P.Z.C. was probably caused by electrostatic repulsion of the negative soil surface and the negative NOM attached to soil. Based on the mechanisms involved in ligand exchange reactions and on the experimental conditions, as well as the type of soil used, it is reasonable to suggest that ligand exchange is probably the predominant mechanism of NOM sorption to oxisols. Based on potentiometric titrations I could not conclude that only the carboxyl groups were significantly depleted after sorption. In fact, it is probable that other acidic functional groups are also involved in the sorption reactions. Finally, electrostatic reactions must be involved in the NOM sorption NOM sorption to oxisol since a detectable desorption of NOM was observed at pH's above the P.Z.C. where the soil mineral surface had a predominantly negative charge.

To further characterize the sorption of NOM to soil surfaces, two more analytical techniques were used on NOM before and after sorption to soil. The first was copper titration. The results indicate that after sorption to soil, NOM has a diminished ability to complex copper from solution (by ca. 15% percent) (Figure 4.4). From the copper titration results I can estimate an apparent stability constant for the following complexation reaction:

$$L^{-x} + Cu^{2+} \leftrightarrow L\text{-}Cu^{2-x} \qquad K = \frac{[L - Cu^{2-x}]}{[L^{-x}][Cu^{2+}]} \quad (M^{-1}) \qquad (4.3)$$

The apparent stability constant between copper and NOM before sorption is 2.92. Some of the NOM is sorbed to soil; the remaining NOM shows a stability constant of 2.75. These values are not absolute and should be analyzed only by the fact that some fractionation of soil NOM occurred after sorption to soil and the cosequence of this to the ability of this soil NOM to bind copper. These values for conditional stability constants are much lower than typical NOM-Cu values (Skold, 1999). This is further indication that this NOM has the stronger Cu-binding sites occupied by Fe and/or Al ions.

The second technique use to characterize some types of NOM before and after sorption to soil is UV absorbence. The results show a measurable loss of aromatic organic NOM moieties, due to NOM sorption to soil. These two experiments provide strong evidence that aromatic moieties in NOM are primarily associated with NOM copper binding sites (Table 4.5). Several researchers (Schnitzer, 1969; Gamble et al. 1970; De Coninck, 1980) have postulated that complexation of metal ions by humic substances is associated with aromatic organic structures having attached carboxilic and phenolic groups (Figure 4.7). The order of strength of metal binding to aromatic carboxilic and phenolic functional groups is Fe > Al > Cu at a solution pH of 3.5, and Fe > Al = Cu when the solution pH is 5.0 (Schnitzer and Skinner, 1965). The reaction mechanisms shown in Figure 4.7 illustrate one of the ways that sesquioxides may be transported through a soil profile for the formation of spodic horizons when organic chelation sites are occupied by iron and aluminum (Stevenson, 1986).

Town and Powell (1993) also reported competition of Fe and Al for Cu binding sites in humic substances. They used a series of ion-selective electrode potentiometric titrations with soil derived humic and fulvic acids and copper. They found that when Cu was titrated into a fulvic acid solution in the presence of Al, displacement of copper from

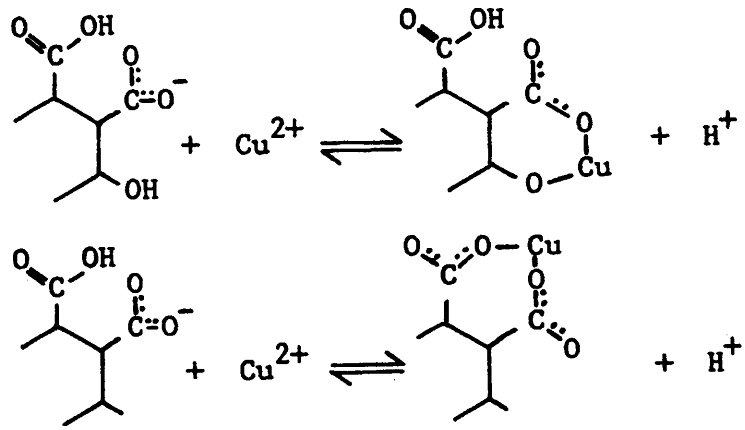


Figure 4.7- Two types of reactions involved in the sorption of copper as well as iron and aluminum (Stevenson, 1986).

fulvic acid sites was observed, indicating site competition between these ions. Cabaniss (1992) also detected a similar competition between Al and Cu for the same organic sites using synchronous fluorescence spectra of metal-fulvic acid complexes.

In this research, the average mole ratio between NOM-associated iron and aluminum and organic carbon is 0.18 (Table 4.2). At the same time, the mole ratio between bound copper and organic carbon is 0.01. This means that the sites occupied by copper are approximately 5.5 % of the sites occupied by iron and aluminum. This suggests that copper does not complex with NOM because iron and aluminum already occupy the binding sites.

In summary, the fractionation of NOM by sorption to soil involves several acidic functional groups present in NOM. After fractionation more aliphatic organic materials remain in solution. This type of material is not able to complex as much copper in solution. One reason for this depletion in copper complexation ability is that most of the sites associated with copper binding are located in aromatic NOM moieties and not in aliphatic. At most of these sites there are already ferric and aluminum ions since these elements are abundant in oxisols (Charlet, 1986; Chorover, 1993). One mechanism involved in NOM sorption to soil mineral surfaces is ligand exchange with some electrostatic influences. As a consequence of this sorption of NOM to soil, one can expect different soil mineral surface properties (Hunter, 1980). This new mineral surface can be expected to have altered sorption of ionic copper as a function of the type of NOM sorbed to soil.

Cu (II) sorption to soil

The first set of copper sorption experiments involved untreated soil and soil from which NOM was extracted or oxidized (Figure 4.5). The sorption edges have the typical shapes of sorption edges of copper to oxide minerals (e.g., hematite or alumina). These sorption edge shapes suggest a strong role of iron and aluminum oxyhydroxides in the copper sorption to oxisols. Even when a significant amount of NOM is removed (i.e., 27.4% to 85.3%) almost the same sorption pattern results. The only difference is a small increase in copper sorption above pH 5.5. There are at least two possible explanations for the non-influence of NOM on the sorption of copper: 1) NOM in this oxisol is not coating the surface of minerals and exposed for reactions with copper in solution. Instead NOM is filling up spaces in the soil structure, working as a cementing agent to keep soil aggregates physically stable; 2) The copper binding sites are already occupied by iron and aluminum, which are abundant elements in this type of soil and known competitors with copper for the same NOM binding sites. One or both of these mechanisms may justify the observed non-influence of NOM in copper sorption to oxisol.

The ability of NOM to sorb to mineral phases is well-known (Parfitt et al., 1977; Davis and Gloor 1981; Tipping, 1981; Davis, 1982; Gu et al., 1995). This sorption may alter mineral surface proprieties causing significant changes in the ability of minerals to complex metal ions from solution and also cause fractionation of the NOM (Hunter, 1980; Davis, 1982 and 1984). The concept of NOM coatings on mineral surfaces was verified in the laboratory and postulated to be valid under field conditions (Davis, 1982 and 1984; Murphy et al., 1992; Gu et al., 1994). At the same time other researchers concluded that NOM in soil systems was not primarly present as mineral surface coating but serving as soil aggregating agents (Tisdall and Oades, 1982; Santos et al., 1989; Bartoli et al., 1991). If NOM in soil systems is not coating but instead trapped among mineral grains, there will be fewer metal binding sites.

Santos et al., (1989) concluded that NOM in oxisols is not present as a mineral surface coating, but rather is filling up holes in the soil structure. At least some of the NOM in the soil used in this study has a similar type of arrangement (Chapter 2). Therefore, one of the reasons for the non-influence of NOM on copper sorption is the arrangement of the NOM in the oxisol. NOM is trapped among mineral grains rather than coating their surface. This is why in the first set of copper sorption isotherms, when NOM was removed; the sorption edges did not change much from the untreated soil. The abundance of mineral sites exposed for copper reactions dictates the copper sorption.

If these statements are correct the sorption of copper may increase, decrease or remain unchanged if NOM is sorbed to untreated soil. Sorption of additional NOM to soil could expose more NOM binding sites for copper complexation, and/or it could block mineral sites available for copper bindings. The consequences of added NOM are illustrated in Figure 4.6. In general, modifications in the sorption edges due to additional NOM were relatively minor except for fulvic acids and Chelex-treated NOM samples at low pH. Both of these NOM additions provided substantially increased copper sorption at pH's less than 5, with slightly reduced sorption above pH 5, where NOM-desorption may have complicated the interpretation. When the humic acid fraction of the NOM removed from the A_1 horizon oxisol was used as the additional NOM, a small increase in copper adsorption was observed over the entire pH range (3 – 6.5). Addition of untreated NOM from 0.0001 M NaOH extraction of soil from the same horizon showed slightly enhanced sorption at low pH and slightly reduced sorption above pH 5.

This second set of experiments using added NOM also helped to investigate the second hypothesis stated in the beginning of this section. The high abundance of iron and aluminum in oxisols and the fact that copper also binds to the same sites as the aforementioned elements would reduce the influence of NOM in copper sorption to oxisols. This hypothesis is confirmed by the experimental results (Figure 4.6). Thus when additional unfractionated NOM or humic acid were sorbed to the soil, there was an increase in copper sorption but not as dramatically as when NOM after Chelex 100 treatment or fulvic acids were sorbed. The first two types of NOM have high iron and aluminum content (Table 4.3), and are probably bound to the soil through the same types of aromatic carboxylate groups that contribute to strong metal-binding sites. Both suggest only minor increases in the Cu-binding ability of the soil.

The nature of NOM sites for metal binding can be conceptually considered in terms of two end-member types of sites. On the one end are the weaker, highly labile sites that are represented by the cation exchange capacity (CEC). These are generally considered to be dominated by aliphatic carboxylate groups in NOM. At the other end are the stronger, less labile sites that are associated here with binding of iron, aluminum and copper (McKnight et al., 1983). The first type of site would dominate those in the more aliphatic fulvic-like fractions, whereas the second would predominate in the more aromatic, humic-like fractions. Chelex resins would certainly exchange metal ions in the first type of site; those in the second type would be incompletely exchanged by the resin.

For the fulvic acids, it appears that the NOM-binding to the soil involves sites on the soil surfaces that are important for Cu binding at higher pH's. This causes a slight decrease in Cu binding at pH's above 5 when fulvic acid is added to the natural NOM in the soil sample. The same phenomenon is observed to a lesser extent for the Chelex-treated NOM. This notion of NOM blocking metal-binding sites can also explain why, in the first set of copper sorption experiments, the removal of NOM actually caused a 10% increase in copper sorption (Figure 4.5). NOM that had blocked the sites for metal binding was no longer a part of the soil structure; at this range of pH (5.0-6.5), this caused a slight increase of mineral binding sites for copper.

These types of NOM (NOM after Chelex 100 treatment and NOM Fulvic acids) have considerably less iron and aluminum (Table 4.3) and an abundance of strong metal binding sites. The exchange of iron and aluminum by protons from the Chelex resin and the NOM fractionation, respectively, frees sites for copper sorption and consequently increases the copper sorption to soil. At low pH's the weaker Cu(II) binding sites on NOM are more important. And here the fulvic acid and Chelex modified NOM soil additions produced enhanced Cu(II) sorption.

Conclusions:

Despite the great volume of literature stressing the importance of natural organic matter in the speciation and sorption of trace elements in various natural systems, some research has indicated the opposite in acidic soil systems and sediments rich in iron and aluminum. NOM in these systems can have minor to non-detectable influence on the sorption of trace metals.

Two sets of copper sorption experiments were performed to test the hypotheses that NOM was not playing a major role in copper sorption by the oxisol A_1 horizon. The results support the following two hypotheses: 1) iron and aluminum, abundant elements in oxisols, are irreversibly blocking copper binding sites on NOM and 2) NOM in oxisol systems is not primarily present as mineral coatings but rather trapped among minerals filling up holes in the soil structure.

Copper sorption after NOM removal with NaOH or oxidation with NaOCl showed little or no change in copper sorption to the oxisol. Also the sigmoid shape of the pH-sorption profile, typical of oxides, suggests that oxyhydroxide minerals are playing the major role in the copper sorption to untreated oxisol. The sorption of different types of NOM to an untreated oxisol samples does indeed increase the sorption of copper at pH's lower than 5.0. But the increase of copper sorption was inversely related to the amount of iron and aluminum in these organic solutions. In addition to the established fact that iron and aluminum can complex strongly to the same sites on NOM that bind copper, these experiments also suggest that copper binding sites are more associated with aromatic rings rather than aliphatic structures in NOM.

References

Aiken, G. R., D. M. McNight, R. L. Wershaw, and P. MacCarthy. 1985. An introduction to Humic Substances in Soil, Sediment, and Water. In *Humic Substances in Soil, Sediment, and Water. Geochemistry, Isolation, and Characterization*, edited by Aiken, G. R., D. M. McNight, R. L. Wershaw, and P. MacCarthy. Wiley Interscience.

Anderson, J. U. 1963. An Improved Pretreatment for Mineralogical Analysis of Samples Containing Organic Matter. *Clays and Clays Minerals* 10:380-388.

Bartoli, F., G.Burtin and A.J. Herbillon. 1991. Disaggregation and clay dispersion of Oxisols: Na resin, a recommended methodology. *Geoderma*, 49:301-317.

Benjamin, M. M., J. O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorhous iron oxyhydroxide. *Journal of Colloid and Interface Science* 79 (1):209-221.

Boss, C.B. and K. J. Fredeen. 1997. *Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry.* 2nd ed.,Perkin Elmer.

Bowles, E.C., R.C. Antweiler, and P. MacCarthy. 1989. Acid-base titration and hydrolysis of fulvic acid from the Suwannee River. In: *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures.* U.S. Geological Survey. Open-File Report 87-557.

Cabaniss, S. E. 1992. Synchronos Fluorescence Spectra of Metal-Fulvic Acid Complexes. *American Chemical Society. Environmental Science and Technology* 26 (6):1133-1139.

Cavallaro N., and M.B. McBride. 1984. Zinc and copper sorption and fixations by an acid soil clay: Effect of selective dissolutions. *Soil Science Society of America Journal* 48:1050-1054.

Chandrakanth, M. S., B.D. Honeyman, and G.L. Amy. 1996. Modeling the Interactions Between Ozone, Natural Organic Matter, and Particles in Water Treatment. *Colloids and Surfaces* 107:321-342.

Chaney K., and R. S. Swift. 1984. The influence of organic matter on aggregate stability in some British soils. *Journal of Soil Science* 35 (2):223-230.

Charlet, Laurent. 1986. Adsorption of some macronutrient ions on an oxisol. An application of the triple layer model. Ph.D in Soil Science. University of California, Riverside.

Chorover, J. 1993. Surface charge and colloidal properties of benchmark Brazilian Oxisols. Ph.D. Thesis. University of California, Berkeley.

Chorover, J. and G Sposito. 1995. Dissolution behavior of kaolinitic tropical soils. *Geochimica et Cosmochimica Acta* 59 (15):3109-3121.

Davis, J.A., and James O. Leckie. 1978. Surface Ionization and Complexation at the Oxide/Water Interface. II Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions. *Journal of Colloid and Interface Science*. 67:90-107.

Davis, J.A. and Rolf Gloor. 1981. Adsorption of Dissolved Organics in Lake Water by Aluminum Oxide. Effect of Molecular Weight. *American Chemical Society* 15 (10):1223-1229.

Davis, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosdmochimica Acta* 46:2381-2393.

Davis, J.A. 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica Acta* 48:679-691.

De Coninck, F. 1980. Major Mechanisms in formation of spodic horizons. *Geoderma* 24:101-128.

Duker, A., A. Ledin, S. Karlsson and A. Allard. 1995. Adsorption of Zn on colloidal (hydr)oxides of Si, Al and Fe in the presence of a fulvic acid. *Applied Geochemistry* 10:197-205.

Dzombak, D.A. and Morel, F.M. 1990. *Surface Complexation Modeling*. Wiley-Interscience, New York NY.

Filius, D. J., Tjisse Hiemstra, and Willem H. Van Riemsdijk. 1997. Adsortion of Small Weak Organic Acids on Goethite. Modeling of Mechanisms. *Journal of Colloid and Interface Science* 195:368-380

Fontes M.P.F., and S.B. Weed. 1991. Iron oxides in selected Brazilian oxisols: I. Mineralogy. *Soil Science Society of America Journal* 55:1143-1149.

Gamble, D.S., M. Schnitzer, and I. Hoffman. 1970. Cu^{+2} fulvic acid chelation equilibrium in 0.1 m KCl at 25.0 Celsius. *Canadian Journal of Chemistry* 48:3197-3204.

Gamble, D.S. and M. Schnitzer. 1974. The chemistry of fulvic acid and its reactions with metal ions. In: *Trace Metals and Metal-Organic Interactions in Natural Waters.* Edited by P.C. Singer. Ann Arbor Science, Ann Arbor, MI.

Gu, B., Jurgen Schmitt, Zhihong Chen, Liyuan Liang, and John F. McCarthy. 1994. Adsorption and Desorption of Natural Organic Matter on Iron Oxide: *Mechanisms and Models. Environmental Science and Technology* 28:38-46.

Gu, B., J. Schmitt, Z. Chen, L. Lian, and J.F. McCarthy. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochemica et Cosmochimica Acta* 59 (2):219-229.

Guilherme, L. R. G., and Anderson, S. J. 1998. Copper sorption kinetics and sorption hysteresis in two oxides-rich soils (oxisols): Effect of phosphate pretreatment. In: Adsorption of Metals by Geomedia edited by Jenne, E. A. Academic Press, San Diego California.

Hayes, M.H. 1985. Extraction of humic substances from soil. In: *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization.* Wiley-Interscience, New York.

Hoffman, S.J. and W.K. Fletcher. 1981. Organic matter scavenging of copper, zinc, molybdenum, iron, and manganese estimated by a sodium hypochlorite extraction (pH 9.5). *Journal of Geochemical Exploration* 15:549-562.

Honeyman, B. D. 1984. Cation and anion adsorption at the oxide/soltution interface in systems containing binary mixtures of adsorbents. Ph.D. Thesis, Standford University, Stanford, CA.

Hunter, K.A. 1980. Microelectrophoretic properties of natural surface-active organic matter in coastal seawater.*Limnol. Oceanogr*aphy 25 (5):807-822.

Jardine P. M., N L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Science Society of America Journal* 53:1378-1385.

Jarvis, S.C. 1981. Copper sorption by soils at low concentrations and relation to uptake by plants. *Journal of Soil Science* 32:257-269.

Kononova, M.M. 1966. *Soil Organic Matter.* Pergamon, Elmsford, NY.

Kooner, Z.S., Chris D. Cox, and James L. Smoot. 1995. Prediction of adsorption of divalent heavy metals at the goethite/water interface by surface complexation modeling. *Environmental Toxicology and Chemistry* 14 (12):2077-2083.

Lavkulich, L. M. and J.H. Wiens. 1970. Comparison of Organic Matter Destruction by Hydrogen Peroxide and Sodium Hypochlorite and Its Effects on Selected Mineral Constituents. *Soil Science Society of America Proceedings* 34:755-758.

Leckie, James O. 1981. Multiple-Site Adsorption of Cd, Zn, and Pb on Amorphous Iron Oxyhydroxide. *Journal of Colloid and Interface Science* 79 (1).

Lenhart, J.J. and Bruce D. Honeyman. 1999. Reactions at the solid/solution interface Fe-Oxides and Hydroxides. Uranium(VI) sorption to hematite in the presence of humic acid. *Geochimica et Cosmochimica Acta* 63 (19/20):2891-2901.

McKnight, D.M., Feder G.L., Thurman, E.M., Wershaw, R.L. and Westall, J.C. 1983. Complexation of copper by aquatic humic substances from different environments. *The Science of the Total Environment* 28:65-76.

Mclaren, R.G., R.S. Swift and J.G. Williams. 1981. The adsorption of copper by soil materials at low equilibrium solution concentrations. *Journal of Soil Science* 32:247-256.

Mclaren, R.G., J.G. Williams, and R.S. Swift. 1983. The adsorption of copper by soil samples from scotland at low equilibrium solution concentrations. *Geoderma* 30:97-106.

Michaelson, G. J., C. L. Ping. 1997. Comparison of 0.1N Sodium Hydroxide with 0.1M Sodium Pyrophosphate in the Extraction of Soil Organic Matter from Various Soil Horizons. *Commun. Soil Sci Plant Anal.* 28 (13&14):1141-1150.

Msaky, J.J., and R. Calvet. 1990. Adsorption behavior of copper an zinc in soils: influence of pH on adsorption characteristics. *Soil Science* 150 (2):513-522.

Murphy, E.M., John M. Zachara, Steven C. Smith and Jerry L. Phillips. 1992. The sorption of humic acids to mineral surfaces and their role in contaminant binding. *The Science of the Total Environment* 117/118:413-423.

Papp, C.S.E., Lorraine H. Filipek, and Kathleen S. Smith. 1991. Selectivity and effectiveness of extractants used to release metals associated with organic matter. *Applied Geochemistry* 6:349-353.

Parks, G.A. and P.L. de Bruyn. 1962. The zero point of charge of oxides. *Journal of Physical Chemistry* 66:967-973.

Parfitt, R.L., V.C. Farmer, and J.D. Russell. 1977. Adsorption on hydrous oxides 1. Oxalate on benzoate on goethite. *Journal of Soil Science* 28:29-39.

Righetto, L., Giovanni Bidoglio, Giovanna Azimonti, and Ignazio R. Bellobono. 1991. Competitive Actinide Interactions in Colloidal Humic Acid-Mineral Oxide Systems. *American Chemical Society. Environmental Science and Technology* 25 1913-1919.

Santos, M.C.D., A.R.Mermut, and M.R. Ribeiro. 1989. Submicroscopy of Clay Microaggergates in an Oxisol from Pernanbuco, Brazil. *Soil Science Society of America J*ournal 53:1895-1901.

Schnitzer, M. and S.I.M.Skinner. 1965. Organo-mettalic interactions in soils: 4. Carboxyl and hydroxyl groups in organic matter and metal retention. *Soil Science* 99 278-284.

Schnitzer, M. 1969. Reaction between fulvic acid, a soil humic compound and inorganic soil constituents. *Soil Science Society of America Journal* 33:75-81.

Schroth, B.K. and G. Sposito. 1998. Effect of Landfill Leachate Organic Acids on Trace Metal Adsorption by Kaolinite. *Environmental Science and Technology* 32:1404-1408.

Skold, Magnus. 1999. Copper complexation by natural organic matter (NOM) as related to sample origin. Master Thesis in Env. Sci. and Eng. - Colorado School of Mines, Golden, CO.

Skoog, D.A. and J.J. Leary. 1992. *Principles of Instrumental Analysis*. 4th ed. Sounders College Publishing.

Smith, K.S. 1991. Factors influencing metal sorption onto iron-rich sediment in acid-mine drainage. Ph.D. in Chemistry and Geochemistry. Colorado School of Mines, Golden, CO.

Sposito, G. 1989. *The Chemistry of Soil.* Oxford University Press. New York NY.

Stevenson, F. J. 1976. Stability Constants of Cu+2, Pb+2, and Cd+2 Complexes with Humic Acids. *Soil Science Society of America Journal* 40:665-672.

Stevenson, F.J. 1982. *Humus chemistry: Genesis, composition, reactions.* Wiley-Interscience, New York NY.

Stevenson, F.J. 1985. Geochemistry of Soil Humic Substances. In: *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization.* Wiley-Interscience, Canada.

Stevenson, F.J and Fitch, A.. 1986. Chemistry of complexation of metal ions with soil solution organics. In: *Interactions of Soil Minerals with Natural Organics and Microbes.* Soil Science Society of America Special Publication Number 17.

Stumm, W., W. Huang, C.P. and Jenkins, S.R. 1970. Specific chemical interactions affecting the stability of dispersed systems. *Croatica Chemica Acta* 42:223-244.

Stumm, W. 1992. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems.* Wiley-Interscience, Canada.

Thurman, E. W. 1985. *Organic Geochemistry of Natural Waters.* Martinus Nijhoff/ Dr W. Junk Publishers. Netherlands.

Tipping, E. and David Cooke. 1982. The effects of adsorbed humic substances on the surface charge of goethite (alpha-FeOOH) in freshwaters. *Geochimica et Cosmochimica Acta* 46:75-80.

Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. *Geochimica et Cosmochimica Acta* 45:191-199.

Tisdall, J.M., and J.M. Oades. 1982. Organic matter and water-stable aggregates in soils. *Journal of Soil Science* 33:141-163.

Town, R.M., H.Kipton J. Powell. 1993. Ion-selective electrode potentiometric studies on the complexation of copper(II) by soil-derived humic and fulvic acids. *Analytica Chimica Acta* 279:221-233.

Zachara, J.M, C.T. Resch, and S.C. Smith. 1994. Influence of humic substances on Co 2+ sorption by a subsurface mineral separate and its mineralogic components. *Geochimica et Cosmochimica Acta* 58 (2):553-566.

Chapter 5

SUMMARY AND CONCLUSIONS

Summary of results

The study of trace metal ion sorption to soil material still represents a challenge in environmental science due to the complexity intrinsic to soils and sediments. The role of natural organic matter (NOM) in the sorption of a representative trace metal ion, Cu^{2+}, to an oxisol was the main focus of this research. And yet, only some aspects of the importance of NOM in this process were investigated. More work is necessary to clarify questions raised in this study.

A landfill near the Brasília National Park located in Brasília D. F. Brazil has been in activity for the last 35 years without any environmental concern for its potential in the contamination of the soil and ground water of that region. Studies developed by the University of Brasília detected toxic trace metals (Cd and Pb) inside the landfill that are threatening to the health of those living nearby, as well as to the local ecological reserve (Brasília National Park) (Santos, 1996). Although there is great potential for development of a contaminant plume that could migrate to other areas hydrogeologically dowgradient, the landfill contaminant plume (identified by elevated ammonium, magnesium, chloride, nitrate, calcium, and phosphorous) is limited to areas near the landfill (Araújo, 1996; Franco, 1996) and does not present high concentrations of Cd or Pb. This suggests a high ability of this type of soil to sorb toxic trace metals.

A soil profile with ten soil horizons was characterized in the field and sampled inside the Brasília National Park. Due to the great chemical, physical, and mineralogical homogeneity of these soil horizons, three soil horizons (A_1, Bw_2, and C_2) were selected for further soil characterization. Transmission electron microscopy (TEM) showed the following features for the soil horizons described. The main mineral present is kaolinite

(70% to 80%) randomly distributed. There is only a trace amount of amorphous material in all soil horizons; however, roughly 50% is composed of poorly crystalline minerals. Soil NOM decreases in percentage from the top horizon to the bottom, and seems less decomposed and shows more microorganism structures in the top horizon (A_1). Most of the NOM is either disseminated among minerals or is occupying discrete areas inside the soil structure. It covers 15% to 20% of the soil aggregate area in the A_1 horizon. NOM is not the only aggregating agent; poorly crystalline iron and aluminum oxyhydroxides also play an important role in soil aggregation in this type of soil.

Sorption edges and isotherms for copper adsorption to the three selected soil horizons were performed before and after partial oxidation of NOM by NaOCl (5%). The results indicated a relatively small role for NOM in the sorption of copper. This result is in agreement with other researchers who investigated the role of NOM in the sorption of copper and other trace metals to soil or sediments from acidic environments rich in iron and aluminum (Cavallaro and McBride, 1978 and 1984; Smith, 1991; Xing et al., 1995). However, this result is in disagreement with researchers who have studied the role of organic matter in the sorption of trace metals in monomineralic systems (Davis and Leckie, 1978; Davis, 1984; Schindler and Stumm, 1987; Zachara et al., 1994; Ali and Dzombak, 1996). The sorption experiments for the deeper horizons showed the role of NOM in the sorption process to be even more negligible. This result supports the use of conditional equilibrium constants of iron and aluminum oxyhydroxide to estimate the partitioning of trace metals to soil in deeper soil horizons. There is a significant release of aluminum during the sorption experiments even at the natural soil pH. This fact suggests that aluminum hydrolysis should be considered for estimation of soil surface charges and any surface complexation modeling. In addition, it supports the hypothesis that aluminum and iron must have already saturated the NOM sites for complexation with trace metals.

To explain the relatively low influence of NOM on the sorption of copper to oxisols two sets of sorption experiments were performed on soil samples from the A_1 horizon. The first set had untreated soil and soil from which NOM was partially extracted by various extractants. All experiments in this group presented a consistent result showing that NOM affected the sorption of copper only at pH above 5.0 where NOM removal caused a small increase (10%) in copper sorption. The second set of sorption experiments was performed with untreated soils from the A_1 horizon that had different types of additional NOM sorbed to them. The types of NOM that had lower Fe and Al contents caused significant changes in the sorption edges. In contrast, the sorption edges for the types of NOM that had high concentrations of iron and aluminum did not differ much from those obtained from the untreated soil. This result indicates a competition among copper, iron and aluminum for the same sites on NOM (Schnitzer and Skinner, 1965; Gamble et al., 1970; De Coninck, 1980; McBride, 1994). UV absorbance studies indicate that the fraction of NOM remaining in solution after sorption to untreated A_1 horizon soil is more aliphatic and less aromatic. Copper titrations with this NOM fraction and with NOM prior to sorption show that the original, more aromatic NOM sample, complexes more copper. This result is in agreement with Skold (1999) who could not correlate copper complexation with NOM from rivers to their carboxilic functional groups, but found some relationship between aromatic content and copper complexation. In addition Lenhart (1998) also found that humic acid complexes more with uranium than fulvic acid.

Conclusions

A list of the conclusions is presented below.

1. Although oxisols have a great ability to sorb trace metals, there is a limited sorption capacity (Γ_{max} = 10 to 18 mmols of Cu(II) / Kg of soil). Once this capacity is reached the trace metals will become more mobile and ground water contamination may result.

2. There is great chemical, physical, and mineralogical homogeneity in the composition of the soil horizons due to the high rainfall and long weathering processes that this type of soil has experienced. NOM in this soil decreases with depth and it is either disseminated among soil minerals or located in discrete areas in the soil (15 to 20% of the soil aggregate area in the A_1 soil horizon).

3. NOM in oxisols does not play a significant role in the sorption of copper. The implications are that acidic soils and sediments rich in iron and aluminum will result in the saturation of NOM sites with iron and aluminum ions thereby reducing the ability of NOM to complex other trace metals.

4. NOM association with soil surfaces results in a blocking of copper complexation sites in soil. This hypothesis is supported by the 10% increase in copper complexation to an oxisol at a pH higher than 5 when the soil NOM was partially removed by oxidation.

5. There is a significant release of aluminum from NOM, poorly crystalline minerals or amorphous materials during copper sorption in the pH range of 3 to 6.5. Any studies to estimate soil surface charge or to model the sorption of copper to this type of soil should consider aluminum hydrolysis.

6. NOM fractions with more aluminum and iron in their chemical compositions do not affect copper sorption to the oxisol. In contrast, NOM fractions with less iron and aluminum significantly affect sorption of copper by an oxisol. This fact supports the hypothesis that NOM sites for complexation of copper may already be occupied by aluminum and iron.

7. Copper complexes more strongly with more aromatic fractions in soil NOM than with aliphatic fractions. This fact supports the chemical mechanism proposed by other researchers who suggest that carboxylic and phenolic functional groups attached to aromatic ring s are the main sites on NOM for copper complexation through chelation.

Future work

1. Extended work using elemental mapping by EDX spectroscopy is strongly recommended for chemical characterization of poorly crystalline minerals such as iron and aluminum oxyhydroxides.

2. Analysis of protons produced due to the aluminum hydrolysis should be made through comparison of experimental (titration) data and thermodynamic modeling. This estimation will help provide a more precise values for the soil surface charge and help to better model the sorption of trace metals to this type of soil through the use of surface complexation models.

3. Surface complexation modeling of copper before and after partial oxidation of NOM by NaOCl is recommended. This type of modeling can be considered a tool to support the data obtained in Chapter 3 and to test some possible sorption mechanisms involving copper and oxisols.

4. Copper titrations of the humic and fulvic acid obtained from the NOM extracted by 0.001 M NaOH would directly test the postulated that copper complexes more strongly with the humic acid fraction than the fulvic acid fraction.

5. Copper titrations of fulvic acid obtained from the NOM extracted by 0.001 M NaOH with the addition of some iron and aluminum salts during titration would further test the hypothesis of iron and aluminum competition with copper for the same NOM sites.

6. Development of projects is recommended to study the ability of these soils to sorb organic compounds that would have similar physical and chemical characteristics to those identified the landfill leachate. This type of work would greatly facilitate evaluation of the severity of the environmental impact of the landfill activities at that the Brasília site.

References

Ali, M.A. and D.A. Dzombak. 1996. Effects of simple organic acids on sorption of Cu^{2+} and Ca^{2+} on goethite. *Geochimica et Cosmochimica Acta* 60 (2):291-304.

Araújo, R. N. G. 1996. Estudos geoquímicos da contaminação dos recursos hídricos e sua propagação nas adjacências do aterro de resíduos sólidos Jockey Club – D. F. Master Thesis from Geoscience Institute University of Brasília, Brasília D.F. Brazil.

Cavallaro N., and M. B. McBride. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal* 42:550-556.

Cavallaro N., and M.B. McBride. 1984. Zinc and copper sorption and fixations by an acid soil clay: Effect of selective dissolutions. *Soil Science Society of America Journal* 48:1050-1054.

Davis J.A. 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica* Acta 48:679-691.

Davis J.A., and J.O.Lecki. 1978. Surface ionization and complexation at the oxide/water interface – II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67(1):90-107.

De Coninck, F. 1980. Major Mechanisms in formation of spodic horizons. *Geoderma* 24:101-128.

Franco, H. A. 1996. Geofísica e química aquática aplicadas ao estudo da contaminação de recursos hídricos subterrâneos no aterro do Jockey Club Brasília D.F.. Master Thesis from Geoscience Institute University of Brasília, Brasília D.F. Brazil.

Gamble, D.S., M. Schnitzer, and I. Hoffman. 1970. Cu^{+2} fulvic acid chelation equilibrium in 0.1 m KCl at 25.0 Celsius. *Canadian Journal of Chemistry* 48:3197.

Lenhart, J.J. 1998. The application of surface complexation modeling to the adsorption of uranium (VI) onto hematite in the presence of humic and fulvic acids. Ph.D. Thesis in Env. Sci. and Eng. - Colorado School of Mines, Golden, CO.

McBride, M. 1994. *Environmental Chemistry of Soils*. Oxford University Press, New York NY.

Santos, P. C. V. 1996. Estudos da contaminação de água subterrânea por percolação de aterro de resíduos sólidos – Caso Jockey Club – D. F. Master thesis. Civil Eng. Univeristy of Brasília, Brasília D. F. Brazil.

Schindler, P. and Stumm, W. 1987. The surface chemistry of oxides, hydroxides and oxide minerals. In *Aquatic Surface Chemistry.* edited by W. Stumm. Wiley-Interscience. New York NY.

Schnitzer, M. and S.I.M.Skinner. 1965. Organo-mettalic interactions in soils: 4. Carboxyl and hydroxyl groups in organic matter and metal retention. *Soil Science* 99 (4).

Skold, Magnus. 1999. Copper complexation by natural organic matter (NOM) as related to sample origin. Master Thesis in Env. Sci. and Eng. - Colorado School of Mines, Golden, CO.

Smith, K.S. 1991. Factors influencing metal sorption onto iron-rich sediment in acid-mine drainage. Ph.D. in Chemistry and Geochemistry. Colorado School of Mines, Golden, CO.

Xing, G. X., Xu, L. Y., and Hou, W. H. 1995. Role of amorphous Fe oxides in controlling retention of heavy metal elements in soils. In *Environmental Impact of Soil Component Interactions – Metals, Other Inorganic, and Microbial activities.* edited by P.M. Huang, J. Berthelin, J.M. Bollag, W.B. McGill, A.L. Page. Vol. II Chapter 6, 63-74.

Zachara, J.M, C.T. Resch, and S.C. Smith. 1994. Influence of humic substances on Co^{2+} sorption by a subsurface mineral separate and its mineralogic components. *Geochimica et Cosmochimica Acta* 58 (2):553-566.

APPENDIX A

This appendix contains raw data for Chapters 2 and 3. Experimental data for soil characterization (Chapter 2) made in the Brazilian soil research institution (EMBRAPA) is already presented within the chapter. For other experiments related to soil characterization and performed at the Colorado School of Mines, the raw data is presented here. The following are:

1- Soil total organic carbon.
2- Soil iron and aluminum amorphous material extraction.
3- Soil iron and aluminum bulk composition.
4- Soil point of zero salt effect (PZSE).
5- Kinetics of copper sorption to oxisol from A_1 horizon.
6- Isotherms of copper sorption to three soil horizons (A1, Bw2, and C2) before and after partial NOM oxidation by NaOCl
7- Copper sorption edge on three soil horizons, at 0.01 M $NaNO_3$, before and after partial NOM oxidation by NaOCl.
8- Copper sorption edge of untreated and treated soil horizons by NaOCl with 0.1 M $NaNO_3$.
9- Aluminum and iron dissolution during copper sorption to untreated and treated soil at 0.01 M $NaNO_3$.

1. Soil total organic carbon.

Soil horizon	*Depth(cm)*	*Total Carbon %*
A1	0	2.33
	0	2.31
	0	2.32
AB	19	2.04
	19	1.74
	19	1.83
BA	47	1.23
	47	1.25
	47	1.22
BW1	73	1
	73	1.03
	73	1
BW2	117	0.84
	117	0.83
	117	0.84
BW3	197	0.7
	197	0.68
	197	0.72
BC	263	0.61
	263	0.58
	263	0.64
C1	350	0.35
	350	0.41
	350	0.44
C2	480	0.35
	480	0.35
	480	0.36
2C3	590	0.2
	590	0.26
	590	0.23

2. Soil iron and aluminum amorphous extraction (Schwertmann, 1964).

		ICP-AES (mg/l)				*g/ Kg of soil*	
Horizon :	Dissolved soil (g)	Al	Fe	Dry soil (g)	Vol. (ml)	Al	Fe
A1	0.086	13.498	8.113	0.1829	36.58	2.70	1.62
A1	0.092	17.432	10.172	0.1787	35.74	3.49	2.03
BW2	0.095	14.238	5.440	0.1907	38.14	2.85	1.09
BW2	0.095	13.872	5.792	0.1932	38.04	2.77	1.16
C2	0.092	8.880	3.144	0.1801	36.02	1.78	0.63
C2	0.101	11.735	4.156	0.1723	34.46	2.35	0.83

3. Soil bulk iron and aluminum bulk composition.

Soil Fe and Al bulk composition:

Soil horizon:	*Mass of soil (g)*	*Al (mg/L)*	*Fe (mg/L)*	*Al %*	*Fe%*
A1	0.50	3086.7	1469.6	15.4	7.3
A1	0.25	1617.5	772.1	16.2	7.7
BW2	0.50	3250.0	1520.8	16.3	7.6
BW2	0.50	3275.7	1528.0	16.4	7.6
BW2	0.25	1732.0	814.1	17.3	8.1
C2	0.50	3348.0	1577.5	16.7	7.9
C2	0.25	1686.7	800.5	16.9	8.0
C2	0.10	642.9	345.2	16.1	8.6
Blank	0	0	0.06	0	0
Blank	0	0	0.017	0	0

4. Soil point of zero salt effect (PZSE):

A_1 Horizon:

NaCl (M)	pH	mmols H$^+$/ kg of soil	pH	mmols H$^+$/ kg of soil
0.01	3.36	1.8	3.40	2.3
0.1	3.36	4.3	3.40	4.6
1	3.36	6.8	3.40	7.3
0.01	4.17	0.4	4.20	0.8
0.1	4.17	2.7	4.20	1.5
1	4.17	2.3	4.20	2.6
0.01	4.21	0.4	4.23	0.8
0.1	4.21	1.9	4.23	1.17
1	4.21	1.2	4.23	2.6
0.01	4.47	0.2	4.49	0.2
0.1	4.47	0.5	4.49	0.6
1	4.47	1.0	4.49	0.7
0.01	4.74	-0.4	4.76	-0.4
0.1	4.74	-0.5	4.76	-0.7
1	4.74	-0.6	4.76	-0.5
0.01	5.04	-0.5	5.00	-0.2
0.1	5.04	-0.8	5.00	-0.7
1	5.04	-0.7	5.00	-1
0.01	5.56	0.0	5.60	-0.3
0.1	5.56	-0.3	5.60	-0.8
1	5.56	-0.4	5.60	-0.8

Bw2 Horizon:

NaCl (M)	pH	mmoles H^+/kg of soil	pH	mmoles H^+/kg of soil
0.01	3.29	5.01	3.5	5.50
0.1	3.29	13.22	3.5	13.80
1	3.29	16.74	3.5	17.20
0.01	4.34	1.35	4.5	1.90
0.1	4.34	2.45	4.5	2.90
1	4.34	3.05	4.5	3.70
0.01	5.38	0.16	5.49	0.10
0.1	5.38	0.23	5.49	0.25
1	5.38	0.26	5.49	0.32
0.01	6.76	0.00	6.9	0.00
0.1	6.76	0.00	6.9	0.00
1	6.76	0.00	6.9	0.00
0.01	9.08	-0.67	9	-0.67
0.1	9.08	-1.00	9	-1.01
1	9.08	-1.06	9	-1.06
0.01	10.24	-7.84	10.3	-7.86
0.1	10.24	-15.13	10.3	-15.13
1	10.24	-17.82	10.3	-17.82

C_2 Horizon:

NaCl (M)	pH	Mmoles H^+/kg of soil	pH	Mmoles H^+/kg of soil
0.01	3.318	5.661	3.287	6.90
0.1	3.318	14.844	3.287	17.2
1	3.318	17.013	3.287	21.0
0.01	4.470	1.267	4.449	1.70
0.1	4.470	2.592	4.449	2.70
1	4.470	3.148	4.449	3.30
0.01	5.528	0.155	5.558	0.20
0.1	5.528	0.251	5.558	0.20
1	5.528	0.273	5.558	0.30
0.01	7.013	-0.002	7.134	-0.002
0.1	7.013	-0.004	7.134	-0.004
1	7.013	-0.004	7.134	-0.003
0.01	8.451	-0.134	8.520	-0.136
0.1	8.451	-0.201	8.520	-0.203
1	8.451	-0.234	8.520	-0.236

5. Kinetics of copper sorption to an oxisol sample from the A_1 horizon.

Sample	*ID*	*Cu (mg/l)*
1	2hrs	0.194
2	2hrs	0.163
3	6hrs	0.164
4	6hrs	0.135
5	18 hrs	0.110
6	18 hrs	0.116
7	24hrs	0.093
8	24hrs	0.103
9	48hrs	0.081
10	48hrs	0.097
11	72hrs	0.082
12	72hrs	0.078
blank	2hr	0.644
blank	6hr	0.639
blank	18hrs	0.627
blank	24hs	0.623
blank	48hrs	0.530
blank	72 hrs	0.610

6. Isotherms of copper sorption to three soil horizons (A1, Bw2, and C2) before and after partial NOM oxidation by NaOCl.

A_1 Horizon untreated.

mmoles Cu(II) in solution	*mmoles Cu /Kg of soil*
0.00E+00	1.21E+00
0.00E+00	1.21E+00
4.00E-04	3.12E+00
3.78E-04	3.55E+00
3.71E-04	3.55E+00
1.44E-03	3.23E+00
1.31E-03	3.59E+00
8.61E-04	3.73E+00
3.23E-03	5.20E+00
3.13E-03	5.23E+00
1.69E-03	4.93E+00
8.50E-04	5.18E+00
7.87E-03	1.29E+01
9.92E-03	1.23E+01
1.73E-02	1.48E+01
1.84E-02	1.50E+01
4.96E-02	1.79E+01
5.06E-02	1.77E+01
6.85E-02	1.68E+01
6.87E-02	1.68E+01
8.30E-02	1.77E+01
8.32E-02	1.75E+01

A_1 Horizon treated with NaOCl.

mmoles Cu(II) in solution	*mmoles Cu /Kg of soil*
1.97E-03	2.82E+00
1.68E-03	2.90E+00
9.13E-03	8.17E+00
1.03E-02	7.81E+00
3.25E-02	9.80E+00
2.59E-02	1.18E+01
5.93E-02	1.31E+01
6.14E-02	1.25E+01
8.60E-02	1.30E+01
8.89E-02	1.21E+01

Bw_2 Horizon untreated.

mmoles C(II) in solution	*mmoles Cu/Kg of soil*
1.29E-04	1.18E+00
2.05E-04	1.16E+00
6.61E-04	2.92E+00
3.80E-03	2.52E+00
2.25E-03	2.98E+00
1.50E-03	3.54E+00
3.27E-03	3.00E+00
3.27E-03	5.19E+00
1.64E-03	5.68E+00
2.68E-03	4.63E+00
3.04E-03	4.52E+00
1.20E-02	3.72E+00
1.17E-02	3.82E+00
4.43E-02	7.21E+00
8.72E-02	6.54E+00
6.80E-02	1.24E+01
5.89E-02	1.98E+01

Bw2 Horizon treated with NaOCl.

mmoles Cu (II) in solution	*mmoles Cu /Kg of soil*
2.05E-03	2.79E+00
2.01E-03	2.80E+00
5.74E-03	9.19E+00
1.15E-02	7.46E+00
2.72E-02	1.14E+01
1.42E-02	1.53E+01
6.51E-02	1.13E+01
5.58E-02	1.42E+01
9.63E-02	9.83E+00
7.36E-02	1.67E+01

C_2 Horizon untreated.

mmoles Cu (II) in solution	*mmoles Cu /Kg of soil*
5.67E-04	1.05E+00
3.78E-04	1.10E+00
2.51E-03	2.14E+00
4.31E-03	2.36E+00
4.33E-03	2.35E+00
2.42E-03	3.26E+00
1.92E-03	3.41E+00
4.54E-03	4.81E+00
4.00E-03	4.97E+00
3.79E-03	4.29E+00
2.14E-02	1.37E+01
2.16E-02	1.36E+01
2.83E-02	1.16E+01
2.56E-02	1.24E+01
6.66E-02	1.28E+01
6.73E-02	1.26E+01
8.36E-02	1.23E+01
8.14E-02	1.30E+01

C_2 Horizon treated with NaOCl.

mmoles Cu(II) in solution	*mmoles Cu /Kg of soil*
3.62E-03	2.32E+00
3.63E-03	2.31E+00
1.69E-02	5.81E+00
1.72E-02	5.72E+00
3.27E-02	5.18E+00
2.58E-02	7.27E+00
4.21E-02	6.89E+00
3.51E-02	9.01E+00
9.15E-02	1.13E+01
8.74E-02	1.25E+01

7. Copper sorption edge for three soil horizons, at 0.01 M $NaNO_3$, before and after partial NOM oxidation by NaOCl.

A_l Horizon untreated:

pH	*% Cu (II) sorbed to soil*
3.08	12.5
3.10	14.0
3.21	18.2
3.23	20.0
3.46	25.4
3.50	26.0
3.92	52.0
4.00	55.0
4.13	63.9
4.22	70.0
4.42	80.4
4.51	82.0
4.83	89.9
5.00	91.0
5.23	92.7
5.40	93.0
5.69	92.6
5.80	93.0
6.12	90.9
6.15	91.0

A_1 Horizon treated

pH	*% Cu sorbed to soil*
2.87	18.1
3.07	29.5
3.57	29.4
3.74	40.0
4.12	35.0
4.22	47.8
4.51	66.7
4.6	69.8
5.01	85.9
5.1	91.7
5.51	96.9
5.55	98.1
5.94	100.0
6.23	100.0
6.53	100.0
6.53	100.0

Bw_2 Horizon untreated

pH	*% Cu (II) sorbed to soil*
3.49	11.4
3.49	13.0
3.76	28.2
4.09	44.8
4.19	49.0
4.25	63.0
4.75	75.0
4.80	79.0
4.99	84.2
5.25	87.0
5.50	90.0
5.75	91.0
6.26	90.9
6.28	90.5
6.54	91.5
3.49	13.0
3.80	29.0
4.12	50.0
4.21	55.0
4.50	57.0
5.00	85.0
6.25	92.0
6.30	91.0
6.50	92.0

Bw_2 Horizon after NaOCl treatment.

pH	*% Cu (II) sorbed to soil*
3.06	17.5
3.03	22.0
3.60	25.3
3.69	30.3
4.25	52.3
4.36	44.8
4.57	68.4
4.90	77.3
5.29	94.1
5.36	85.3
5.44	98.9
5.39	91.6
5.93	99.5
6.26	100.0
6.17	100.0
6.32	100.0

C_2 Horizon untreated.

pH	*% Cu (II) sorbed to soil*
3.10	6.0
3.20	7.2
3.40	7.4
3.50	8.0
3.75	9.6
3.80	12.0
4.09	23.2
4.12	25.0
4.31	42.5
4.35	45.0
4.47	48.6
4.50	50.0
4.90	73.7
5.00	76.0
5.85	89.0
6.22	89.6
6.25	90.0
6.28	89.9
6.31	90.0
6.50	92.0
6.54	92.4

C_2 Horizon treated with NaOCl.

pH	*% Cu (II) sorbed to soil*
2.98	3.8
2.91	2.0
3.63	10.1
3.77	15.5
4.26	25.8
4.26	23.3
4.68	52.9
4.85	58.2
5.22	81.6
5.22	81.8
5.9	97.6
5.92	100.0
6.35	99.6
6.43	100.0

8. Copper sorption edge for untreated and soil horizons treated with NaOCl with 0.1 M $NaNO_3$.

A_1 Horizon untreated.

pH	*Fraction of Cu sorbed*
2.87	0.07
3.51	0.34
4.01	0.52
4.49	0.57
4.88	0.75
5.04	0.79
5.77	0.98
5.93	0.98
6.25	0.99

A_1 Horizon treated.

pH	*Fraction of Cu sorbed*
2.99	0.21
3.57	0.28
4.21	0.29
4.55	0.36
4.77	0.48
5.16	0.73
6.19	0.97
6.60	0.99

Bw_2 Horizon untreated.

pH	*Fraction Cu sorbed*
3.02	0.10
3.56	0.17
4.33	0.36
4.54	0.47
4.98	0.64
5.00	0.70
5.84	0.97
6.34	1.00
6.46	0.99

Bw_2 Horizon treated with NaOCl

pH	*Fraction of Cu sorbed*
3.04	0.28
3.13	0.30
3.57	0.13
3.74	0.11
4.17	0.20
4.54	0.44
4.96	0.48
5.05	0.74
6.07	0.96
6.52	0.98

C_2 Horizon untreated.

pH	*Fraction of Cu sorbed*
2.98	0.02
3.57	0.03
4.03	0.19
4.51	0.34
4.98	0.47
5.1	0.63
6.01	0.96
6	0.95
6.53	0.99

C2 Horizon treated.

pH	*Fraction of Cu sorbed*
3.01	0.03
3.61	0.24
4.05	0.21
4.73	0.43
5.09	0.50
5.95	0.93
6.53	0.98

9. Aluminum and iron dissolution during copper sorption to untreated and treated soil at 0.01 M $NaNO_3$, soil (0.132 g) at 40 ml solution of 0.01 M $NaNO_3$.

A1 Horizon untreated

Samples	*pH*	*Al (mg/L)*	*Fe (mg/l)*
1	3.08	0.914	0.078
2	3.08	0.910	0.080
3	3.21	0.765	0.041
4	3.25	0.775	0.040
5	3.46	0.599	0.002
6	3.50	0.610	0.002
7	3.92	0.157	0.002
8	3.90	0.160	0.002
9	4.13	0.047	0.002
10	4.10	0.050	0.003
11	4.42	0.025	0.002
12	4.50	0.025	0.002
13	4.83	0.037	0.002
14	4.80	0.040	0.003
15	5.23	0.308	0.002
16	5.25	0.310	0.002
17	5.69	0.444	0.002
18	5.70	0.445	0.002
19	6.12	0.938	0.001
20	6.25	0.940	0.001

A1 Horizon treated with NaOCl.

Samples	*pH*	*Al (mg/L)*	*Fe (mg/l)*
1	3.07	2.955	0.805
2	3.57	2.233	0.552
3	4.12	1.473	0.544
4	4.6	0.559	0.169
5	5.01	0.455	0.181
6	5.51	0.318	0.116
7	5.94	0.148	0.054
8	6.53	0.173	0.076
9	3.1	2.95	0.807
10	3.6	2.24	0.56
11	4.15	1.475	0.57
12	4.7	0.57	0.17
13	5	0.46	0.18
14	5.5	0.32	0.12
15	6	0.15	0.06
16	6.5	0.18	0.077

Bw_2 Horizon untreated.

Sample	*pH*	*Al (mg/L)*	Fe (mg/l)
1	3.33	1.093	0.1689
2	3.32	0.981	0.0643
3	3.49	0.896	0.1521
4	3.76	0.372	0.0677
5	4.09	0.415	0.1385
6	4.19	0.404	0.1565
7	4.45	0.09	0.155
8	4.99	0.1246	0.0512
9	6.26	0.1948	0.1478
10	6.28	0.1615	0.066
11	6.54	0.637	0.2647
12	6.55	0.640	0.265

Bw_2 Horizon treated with NaOCl.

Samples	*pH*	*Al (mg/L)*	Fe (mg/l)
1	3.06	3.700	0.922
2	3.6	3.242	0.995
3	4.25	1.185	0.48
4	4.57	0.736	0.273
5	5.29	0.762	0.286
6	5.44	0.43	0.171
7	6.17	0.245	0.104
8	6.26	0.265	0.098
9	3.03	3.739	1.101
10	3.69	3.218	1.086
11	4.36	1.713	0.689
12	4.9	1.004	0.421
13	5.36	0.569	0.275
14	5.39	0.573	1.092
15	5.93	0.375	0.163
16	6.32	0.362	0.121

C2 Horizon untreated.

Samples	*pH*	*Al (mg/L)*	Fe (mg/l)
1	3.1	0.930	0.110
2	3	0.942	0.118
3	3.2	1.108	0.254
4	3.4	0.743	0.130
5	3.75	0.514	0.425
6	4.09	0.405	0.139
7	4.31	0.358	0.147
8	4.47	0.322	0.131
9	4.9	0.491	0.222
10	6.22	0.521	0.222
11	6.28	1.208	0.510
12	6.54	0.711	0.310
13	6.5	0.710	0.310

C_2 Horizon treated with NaOCl.

Samples	*pH*	*Al (mg/L)*	Fe (mg/l)
1	2.98	1.739	0.230
2	3.63	1.454	0.304
3	4.26	0.315	0.099
4	4.68	0.338	0.141
5	5.22	0.727	0.312
6	5.34	0.359	0.144
7	5.92	0.296	0.125
8	6.43	0.524	0.155
9	2.91	1.901	0.282
10	3.77	0.919	0.187
11	4.26	0.428	0.131
12	4.85	0.288	0.117
13	5.22	0.399	0.158
14	5.9	0.351	0.145
15	6.35	0.215	0.088

APPENDIX B

This appendix contains raw data for chapter 4. The experiments are made only on samples from A1 horizon. All experiments were made using 10μM copper solution at 0.01 M $NaNO_3$. The following are:

1- One set of copper sorption data for untreated soil samples and soil samples that had partial NOM removal by 0.001 NaOH, 0.5 M NaOH (at 55°C), (5% by vol.) NaOCl.

2- One set of copper sorption data for untreated soil samples and soil samples that had different types of additional NOM sorbed to the soil.

3- Acid and base titration of NOM extracted by 0.001 M NaOH before and after sorption to soil.

4- Copper titration of NOM extracted by 0.001 M NaOH before and after sorption to soil (10 mM of Cu(II) and 0.05 M KNO_3 and at pH = 6.0).

1- One set of copper sorption on untreated soil samples and soil samples that had partial NOM removal by 0.001 and 0.5 M NaOH, (5% by vol.) NaOCl.

a- Copper sorption on untreated soil samples.

pH	*Fraction of Cu (II) sorbed to soil*
3.08	0.125
3.10	0.140
3.21	0.182
3.23	0.200
3.46	0.254
3.50	0.260
3.92	0.520
4.00	0.550
4.13	0.639
4.22	0.700
4.42	0.804
4.51	0.820
4.83	0.899
5.00	0.910
5.23	0.927
5.40	0.930
5.69	0.926
5.80	0.930
6.12	0.909
6.15	0.910

b- Copper sorption on soil after NOM extractino by 0.001 M NaOH.

pH	*Fraction Cu sorbed*
3.07	0.17
3.13	0.15
3.67	0.32
3.67	0.21
3.99	0.45
4.05	0.27
4.48	0.67
4.42	0.66
5.52	0.98
5.59	0.98
6.01	0.99
5.85	0.99
6.35	0.99
6.65	0.99

c- Copper sorption to soil after NOM extraction by 0.5 M NaOH at 55°C.

pH	*Fraction Cu sorbed*
2.98	0.27
2.98	0.21
3.45	0.33
3.5	0.36
4.05	0.59
4.06	0.57
4.53	0.80
4.62	0.85
5.05	0.94
5.05	0.94
5.45	0.98
5.59	0.99
6.12	0.99
6.15	0.99
6.5	0.98
6.47	0.99

d- Copper sorption on soil after NOM oxidation by (5%) NaOCl.

pH	*% Cu sorbed to soil*
2.85	0.180
2.87	0.181
3.07	0.295
3.57	0.294
3.74	0.400
4.12	0.350
4.22	0.478
4.51	0.667
4.6	0.698
5.01	0.859
5.1	0.917
5.51	0.969
5.55	0.981
5.94	1.000
6.23	1.000
6.53	1.000
6.53	1.000

2- One set of copper sorption to untreated soil samples and soil samples that had different types of NOM sorbed to the soil.

a- Copper sorption to untreated soil samples.

pH	*Fraction of Cu(II) sorbed to soil*
3.08	0.125
3.10	0.140
3.21	0.182
3.23	0.200
3.46	0.254
3.50	0.260
3.92	0.520
4.00	0.550
4.13	0.639
4.22	0.700
4.42	0.804
4.51	0.820
4.83	0.899
5.00	0.910
5.23	0.927
5.40	0.930
5.69	0.926
5.80	0.930
6.12	0.909
6.15	0.910

b- Copper sorption to soil after sorption of NOM extracted by 0.001 M NaOH.

pH	*Fraction of Cu sorbed*
3.13	0.332
3.12	0.361
3.53	0.530
3.49	0.630
4.02	0.656
4.03	0.697
4.54	0.879
4.48	0.841
5.65	0.865
5.4	0.855
6.11	0.873
5.78	0.872
6.39	0.834
6.11	0.852
6.45	0.840

c- Copper sorption to soil after sorption of humic acid from NOM extracted by 0.001 M NaOH.

pH	*Fraction of Cu sorbed*
3.06	0.279
3.05	0.290
3.57	0.474
3.58	0.474
3.95	0.444
3.93	0.603
4.37	0.614
4.38	0.815
5.16	0.812
4.98	0.965
5.5	0.957
5.56	0.968
6.25	0.969
6.13	0.941
6.55	0.950
6.5	0.950

d- Copper sorption to soil after sorption of NOM extracted by 0.001 M NaOH treated with Chelex 100 resin.

pH	*Fraction Cu sorbed*
2.98	0.507
3.00	0.500
3.51	0.686
3.52	0.702
4.10	0.878
4.12	0.881
4.46	0.921
4.99	0.911
4.99	0.931
5.11	0.928
5.41	0.921
5.44	0.921
5.90	0.885
5.90	0.898
6.43	0.873
6.50	0.860

e-Copper sorption to soil after sorption of fulvic acid from NOM extracted by 0.001M NaOH.

pH	*Fraction of Cu sorbed*
2.98	0.507
3.00	0.500
3.51	0.686
3.52	0.702
4.10	0.878
4.12	0.881
4.46	0.921
4.99	0.911
4.99	0.931
5.11	0.928
5.41	0.921
5.44	0.921
5.90	0.885
5.90	0.898
6.43	0.873
6.50	0.860

3- Acid and base titration of NOM extracted by 0.001 M NaOH before and after sorption to soil.

a- NOM acid titration before sorption to soil.

pH	*meq H^+./ g C*
9.97	0.015
9.96	0.016
9.91	0.013
9.86	0.009
9.80	0.010
9.73	0.010
9.65	0.013
9.55	0.018
9.43	0.024
9.25	0.036
9.10	0.046
9.00	0.054
8.98	0.057
8.90	0.063
8.80	0.070
8.70	0.078
8.60	0.085
8.50	0.092
8.40	0.097
8.35	0.098
8.20	0.130
8.15	0.128

8.10	0.131
8.00	0.137
7.90	0.144
7.80	0.152
7.70	0.159
7.60	0.167
7.50	0.174
7.40	0.182
7.30	0.191
7.20	0.198
7.10	0.206
7.00	0.213
6.90	0.220
6.80	0.229
6.70	0.237
6.60	0.244
6.50	0.253
6.40	0.261
6.30	0.270
6.27	0.271
6.20	0.277
6.00	0.293
5.90	0.302
5.80	0.311
5.70	0.320
5.60	0.329
5.50	0.340

5.40	0.349
5.30	0.359
5.22	0.366
5.10	0.378
4.84	0.407
4.62	0.432
4.48	0.448
4.19	0.486
4.01	0.508
3.88	0.524
3.78	0.538
3.70	0.547
3.63	0.554
3.58	0.562
3.52	0.566
3.48	0.572
3.43	0.576
3.40	0.579
3.36	0.584
3.33	0.588
3.30	0.593

c- NOM acid titration after sorption to soil.

pH	*meq H+./ g C*
9.73	-0.037
9.65	-0.033
9.55	-0.027
9.43	-0.019
9.25	-0.004
8.98	0.016
8.63	0.042
8.45	0.050
8.20	0.082
7.90	0.108
7.75	0.135
7.50	0.151
7.25	0.168
7.00	0.185
6.75	0.203
6.50	0.221
6.27	0.239
6.00	0.260
5.75	0.279
5.50	0.300
5.22	0.323
5.00	0.344
4.84	0.359
4.62	0.381
4.48	0.398

4.19	0.429
4.01	0.449
3.88	0.466
3.78	0.476
3.70	0.487
3.63	0.494
3.58	0.501
3.52	0.507
3.48	0.513
3.43	0.519
3.40	0.525
3.36	0.531
3.33	0.537
3.30	0.544

d-NOM base titration before sorption to soil

pH	*meq* OH^-*./g C*
3.31	0.242
3.31	0.242
3.35	0.243
3.39	0.245
3.43	0.248
3.48	0.252
3.53	0.257
3.59	0.263
3.66	0.272
3.74	0.282
3.84	0.293
3.97	0.310
4.16	0.335
4.24	0.345
4.34	0.357
4.47	0.373
4.64	0.393
4.95	0.425
5.25	0.455
5.55	0.482
5.85	0.507
6.16	0.530
6.46	0.552
6.76	0.573
7.07	0.595

7.37	0.617
7.67	0.640
7.98	0.650
8.28	0.678
8.57	0.702
9.12	0.747
9.37	0.768
9.53	0.782
9.81	0.802
9.99	0.807

d-NOM base titration after sorption to soil

pH	*meq* OH^-*./g C*
3.31	0.002
3.31	0.003
3.35	0.017
3.39	0.028
3.43	0.038
3.48	0.048
3.53	0.060
3.59	0.068
3.66	0.080
3.74	0.092
3.84	0.103
3.97	0.118
4.16	0.140
4.24	0.148
4.34	0.158
4.47	0.172
4.64	0.188
4.95	0.217
5.15	0.233
5.30	0.247
5.45	0.260
5.60	0.272
5.75	0.283
5.85	0.292
6.00	0.303

6.15	0.315
6.30	0.328
6.45	0.340
6.60	0.352
6.75	0.363
6.90	0.375
7.05	0.388
7.20	0.400
7.35	0.413
7.50	0.427
7.65	0.442
7.80	0.460
7.95	0.477
7.96	0.483
8.32	0.492
8.57	0.510
8.65	0.518
8.80	0.535
8.95	0.550
9.12	0.568
9.37	0.595
9.53	0.610
9.81	0.633
9.99	0.638

4- Copper titration of NOM extracted by 0.001 M NaOH before and after sorption to soil.

a- Copper titration before NOM sorption to soil.

Blank titration:		Cu titration:		Cu titration (duplicate):	
Log Cu M	mV	Log Cu M	mV	Log Cu M	mV
-6.30206	77.6	-6.30204	12.9	-6.30204	13.1
-5.82494	85.4	-5.82492	38.1	-5.82492	38.3
-5.45696	96.4	-5.45694	59.3	-5.45694	59.4
-5.07161	106.1	-5.07159	81.1	-5.07159	81.2
-4.73386	116	-4.73383	100.3	-4.73383	100.4
-4.16534	132.9	-4.16532	126.3	-4.16532	126.4
-3.77443	144.2	-3.77441	140.7	-3.77441	140.8
-3.43459	154.2	-3.43457	151.9	-3.43457	151.9
-3.06226	164.9	-3.06224	163.1	-3.06224	163.1
-2.72953	174.2	-2.72951	172.4	-2.72951	172.4

b-Copper titration after NOM sorption to soil.

Blank titration:		Cu titration:	
LogCu(M)	emf(mV)	LogCu(M)	emf(mV)
-6.30	64.6	-6.30	35.8
-5.82	76.7	-5.82	49.2
-5.46	86.8	-5.46	64
-5.07	98	-5.07	81.9
-4.73	107.9	-4.73	97.5
-4.16	124.5	-4.16	120.6
-3.77	135.6	-3.77	133.7
-3.43	145.2	-3.43	144.6
-3.06	155.7	-3.06	155.6
-2.73	164.9	-2.73	164.8