TRACE METALS PARTITIONING AND (RE)DISTRIBUTION IN
MODEL SOIL SYSTEMS

A Dissertation in
Soil Science

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2008
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**ABSTRACT**

Metal (re)distribution among ferrihydrite, leaf compost, and montmorillonite was studied over 8 months in systems that emulate a natural soil where different solid phases in compartmentalized batch reactors compete for metals through a common solution. All experiments were conducted at room temperature (~25°C), at pH between 6.0 and 6.5, at an ionic strength of 0.01 M using KNO₃, at a solid to liquid ratio of 1.5 g of solids in 1000 ml of solution, and at a concentration of metal(s) of 0.15 mg l⁻¹ in a volume basis or 100 mg kg⁻¹ in a mass basis. Metal speciation in solution (total dissolved, labile, and free) and exchangeable and total metals in individual solid phases were determined. Dissolved organic carbon in solution (DOC) and that retained by the mineral phases were also determined. The results are reported in three chapters titled:

2. Copper Redistribution in Multicomponent Systems Containing Ferrihydrite, Organic Matter, and Montmorillonite.

Copper sorption reached steady-state after 4 months and was incomplete due to increasing complexation of Cu in solution by DOC. Non-labile Cu-DOC complexes accounted for 82.8% of the total Cu remaining in solution after 8 months of equilibration. Sorption of DOC onto ferrihydrite was another factor accounting for the incomplete sorption of Cu observed in this study. The sorption of Cu was mostly specific (>90%) and followed the order: leaf compost (86 mg kg⁻¹) > montmorillonite (62 mg kg⁻¹) > ferrihydrite (15 mg kg⁻¹). Furthermore, Cu sorbed on ferrihydrite, leaf compost, and montmorillonite showed to be sensitive to perturbations caused by addition of other solid phases to the multicomponent system and resulted in significant desorption of Cu from ferrihydrite (81%), leaf compost (86%), and montmorillonite (66%). Desorbed Cu tended to redistribute between leaf compost and montmorillonite. Copper did not redistribute to ferrihydrite due to blockage of its surface by DOC sorbed therein. The initial composition of a multicomponent system was highly influential on the distribution and redistribution of Cu. Incomplete sorption was also observed for Cd (90%), Ni (82%), Cu (71%), and Cr (56%) due to the formation of metal-DOC complexes with different degrees of lability (Cd > Ni > Cu > Cr), Cd being the most labile metal and Cr the least labile metal according to speciation calculations using Visual Minteq. Initial formation of non-labile soluble complexes hindered metal sorption while the progressive formation of non-labile species over time resulted in incomplete metal sorption by the solid phases. Leaf Compost effectively sorbed all four metals early in the experiments and continued sorbing Cd, Cu, Cr, and Ni over time. Montmorillonite sorbed all four metals initially but Cd and Ni desorption occurred over time. Ferrihydrite sorbed small quantities of metals only indirectly through the sorption of DOC-metal complexes. The use of compartmentalized batch reactors in this study allowed to follow the dynamics of metal partitioning and redistribution among iron oxides, organic matter, and silicate clays in a simulated, competitive soil environment. It was established that soil organic matter (both colloidal and dissolved constituents) controls the retention of metals in multicomponent systems.
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ACKNOWLEDGMENTS

Research in this dissertation was funded by the NRI-USDA (Grant No 2003-35107-13650). Nadia Valentina Martínez Villegas was partially supported by CONACyT under Fellowship No 154889. Magaly Resto Roldán helped with some of the laboratory analyses for Chapter 2.
Para Guillermo, Mi Loco:

Basta, basta de llamarme así
Ya voy a ir, voy a subir
Cuando me toque a mi...
Mientras te canto esta canción
En tu voz, en tu honor o en la voz
De los que estén durmiendo aquí.
Y juro, que la cara voy a dar
Cada vez, cada vez que alguien te nombre
Aquí o allá.

Basta, basta de llamarme así
Ya voy a ir, voy subir
Cuando me toque a mi
Mientras te canto esta canción,
En tu voz, en tu honor, en la voz
De los que estén durmiendo allá
Y juro, que la cara voy a dar
Cada vez, cada vez que alguien te nombre
Aquí o allá.

Vicentico

¡Basta ya!
¡Ya basta!
☺

“Cálmese Monigota…”

A 29 de febrero del 2008.
Chapter 1
Perspective, hypothesis, and objectives

Perspective

Soils act as a barrier or filter that can prevent contamination of surface and ground waters as well as the transfer of trace metals to biota by sorbing metals on its solid constituents (i.e., layer silicate clays, oxides of iron and aluminium, and organic matter). Metal sorption is known to be highly dependent on soil properties (e.g., pH, organic matter, texture, mineral species, etc.) as well as on heavy metal properties (e.g., charge, coordination chemistry, solubility, and redox reactions). It has been traditionally accepted that metal sorption by soil solids follows the order of affinity organic matter > Al or Fe oxides > silicate clays. On the other hand, long term field studies in metal contaminated soils show organic matter and iron oxides amendments often result in higher metal mobility than in nonamended soils (1,2), raising the question of whether, and why, the application of highly reactive amendments increases metal mobility.

If we are to understand metal accumulation (either retention or mobility) in soils, we must be able to describe the rates of the sorption processes of metals in soils. In general, the overall sorption of a metal in a soil system consists of a series of steps that result in the net accumulation of that metal in the system (Figure 1.1). Such steps can include:

1. mass transfer from the bulk solution to the surfaces,

2. non-specific sorption reactions at the surfaces,
3. specific (chemical) sorption reactions preceding or following non-specific reactions, and

4. other surface reactions (e.g., precipitation, oxidation-reduction).

![Figure 1.1. Ideal pathway of a metal sorption process by a soil surface.](image)

The simplest metal sorption reactions in soils are those occurring at the interface between, for example, an iron oxide and cations present in the soil solution (Figure 1.1), where the concentration of dissolved and sorbed metal are in thermodynamic equilibrium and can be described by mass law equations (3). Assuming the rates of all the associated chemical reactions in soils are very rapid compared to mass transfer processes, the rate at which the metal is brought to the surface will be the rate-limiting step, thus governing the rate of sorption (Figure 1.1). Sorption reactions in soils are, however, more complicated. This is due to the fact that soils are open biogeochemical systems and are therefore driven
by a complex web of simultaneous biological and chemical processes, where a
temporally and spatially dynamic soil solution plays a major role. More complex sorption
reactions involve a series of processes (e.g., ligand complexation, splitting mechanisms,
and parallel pathways), are affected by the surface (e.g., site heterogeneity, changes in
surface charge, and non-uniform morphology) and by modifications to the surface (e.g.,
precipitation of other solids, crystallization, formation of ternary complexes) (Figure 1.2).

Figure 1.2. Metal sorption by a soil surface and competing processes. The ideal pathway
for metal sorption by soil solid surfaces (a) can be disrupted by metal complexation in
solution (b) and by sorption of DOC onto the surface (d). Simultaneous metal sorption (a)
and complexation (b) processes can cause metals to remain in solution (b) or to undergo
parallel sorption as a different metal species (c).
The rates of the processes described in Figure 1.2 dictate the net accumulation of metals in soil systems. Net accumulation can increase, reach a maximum, and decline to zero as a steady state condition is established. At steady-state the rates of all reaction steps in a series are the same. Although the extent of sorption of metals in soils can be mostly limited by mass transfer, it can also be limited by the inherent sluggishness of one or more sorption and/or desorption reactions. The systematic study of the dynamic behavior that drives overall metal sorption in soil systems might provide the explanation for why the application of highly reactive amendments increases metal mobility.

Hypothesis

Based on the argument above, I hypothesize that mass transfer, complexation in solution, and desorption processes determine metal sorption among soil solids.

Objectives

The aim of this research was to characterize the solution- and solid- phase dynamic behaviour of metals in model soil environments containing ferrihydrite, organic matter, and montmorillonite. The specific objectives of the proposed research were:

1. To determine the relative affinities of ferrihydrite, organic matter, and montmorillonite for Cu in a competitive environment.
2. To determine the solid phase that sorbs the most Cu.
3. To determine the extent of redistribution of Cu among solid phases after initial sorption on one solid phase.
4. To determine whether desorption hysteresis occurs and prevents or retards metal redistribution.

5. To determine whether desorption hysteresis is related to ion-exchange, specific sorption, and/or to the formation of ternary complexes.

6. To identify common and/or distinctive processes driving overall sorption and distribution of Cd, Cr, Cu, and Ni among soil solid phases.

The hypothesis of this dissertation was tested and the objectives were attained by conducting sorption studies using compartmentalized batch reactors equilibrated for 8 months. The experimental model used was derived from a mass balance in a soil column (Appendix A) that represented competition among diverse soil components for the sorption of metallic cations through a common solution.

References


Chapter 2

Solid- and Solution- Phase Organics Dictate Copper Distribution and Speciation in Multi-Component Systems Containing Ferrihydrite, Organic Matter, and Montmorillonite.

Abstract

Copper retention by ferrihydrite, leaf compost, and montmorillonite was studied over 8 months in systems that emulate a natural soil where different solid phases compete for Cu through a common solution in a compartmentalized batch reactor. Copper speciation in solution (total dissolved, labile, and free) and exchangeable and total Cu in individual solid phases were determined. Organic carbon in solution (DOC) and that retained by the mineral phases were also determined. Cu sorption reached steady-state after 4 months and accounted for 80% of the Cu initially added to the system (0.15 mg l⁻¹). The remaining 20% stayed in solution as non-labile (82.8%), labile (17%), and free (0.2%) Cu species. Copper sorption followed the order: organic matter > silicate clays > iron oxides. Within each solid phase, exchangeable Cu was ≤10% of the total Cu sorbed. DOC reached steady-state (22 mg l⁻¹) after 4 months and seemed to control Cu solubility and sorption behavior by the formation of soluble Cu-DOC complexes and by sorbing onto the mineral phases. DOC sorption onto ferrihydrite prevented Cu retention by this solid phase. Using a multi-component system and 8 months equilibrations, we were able to capture some of the more important aspects of the complexity of soil environments by taking into account diffusion processes and competition among solid- and solution- phase soil constituents in the retention of a metal cation.

Introduction

Soils are complex systems that contain iron oxides, layer silicate clays, and organic matter. These solid phases have a high affinity for trace metals and high sorptive capacities. The presence of multiple and mixed phases in soils makes the identification of their individual contributions for metal retention difficult. Such identification is, however, important to understand which solid phase(s) in soils could potentially limit metal solubility, bio-availability, and mobility.

The mechanisms involved in metal retention have been extensively studied and are known to depend on soil (e.g. pH, organic matter content, texture, mineralogy) as well as on metal (e.g. charge, coordination chemistry, redox potential) properties. Ion exchange, chemisorption and complexation reactions, for example, are likely mechanisms involved in the retention of low levels of metals. At higher loadings and pH, metals can precipitate as discrete (hydr)oxide phases or become part of ternary and mixed cation hydroxide complexes on solid surfaces.

It is generally accepted that Cu retention by soil solids follows the order: organic matter > Al or Fe oxides > clays (1). Although soil organic matter can be the largest sink for Cu retention, it is also a source of dissolved organic carbon (DOC). DOC is paradoxically a major controlling factor in trace metal transport in soils (2-6). DOC originates from plant litter, soil humus, microbial biomass, or root exudates and its chemical reactivity is influenced by pH, ionic strength, and water/soil ratio (7). DOC partitions between soil solution and soil solid phases (7). In solution, DOC can increase Cu solubility (3-6,8,9) by forming stable Cu-DOC soluble complexes (10,11). On solid phases, DOC can change mineral surface properties (12) and mineral reactivity towards metals (3). For example, humic acids sorbed on goethite can increase
the retention of Cu due to the creation of additional sorption sites (13). The sorption of negatively charged organics by positively charged iron oxides can increase the number of negatively charged surfaces (12), thus increasing Cu retention by iron oxides. However, sorption of organics onto mineral phases can in some cases block sites otherwise available for metal retention (14-16). Hence, sorbed organic compounds may impede rather than increase metal sorption. For example, the increased mobility of metals in sludge-amended soils when compared to non-amended soils can be attributed to complexation of metals by DOC and to modification of the sorptive properties of the mineral phases that are a direct consequence of the addition of organic amendments (17,18).

This work evaluates individual contributions of iron oxides, organic matter, and silicate clays for the retention of low levels of Cu (≈10^{-6} M) in a competitive soil environment simulated by a multi-component system. The system is equilibrated for 8 months, a period of time long enough to permit the simultaneous assessment of several soil chemical processes. We show iron oxides are not good competitors for Cu retention in the presence of DOC and additional solid phases.

**Materials and Methods**

**Solid Phases.** The solid phases used as model soil components were ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (SWy2). A 2-line ferrihydrite was synthesized in the laboratory by dissolving 40 g of Fe(NO₃)₃.9H₂O in 500 ml of deionized water (to yield a 0.2 M solution) and slowly (0.875 ml min⁻¹) adding 0.2 M KOH to bring the pH to 7-8 using a pH-stat device (Cole Parmer Eutech Instruments differential pH/ORP controller pH 200 and Master Flex C/L pumps) (19). The precipitate was washed three times with deionized water, dialyzed
(Spectra / Por 7 MWCO 10000) until free from electrolytes (final water conductivity < 3µS cm⁻¹), and freeze-dried (Thermo Savant ModulyoD-115). A sugar maple leaf compost was used in this study as a surrogate for soil organic matter. Details about its preparation and chemical characteristics can be found in Sauvé et al., 1998 (20) and 2000 (9) and Martínez and McBride, 1999 (8). Wyoming montmorillonite (SWy2) was purchased from the Clay Minerals Society-Source Clay Repository and treated to remove carbonates and exchangeable divalent cations using 1 N sodium acetate buffered with acetic acid to pH 5 according to Jackson, 1956 (21).

Particles smaller than 2 µm were separated using sodium phosphate and ultrasound. The < 2 µm fraction was collected and saturated with K⁺ using 1 M KCl (K-SWy2) and lyophilized (22).

The freeze-dried solid phases were characterized for particle size, effective cation exchange capacity (ECEC), specific surface area, mineralogy, and Cu and C concentrations as described below. Particle size distribution was estimated by light scattering of wet samples dispersed in water using a Mastersizer “S” with a QS small sample dispersion unit. The ECEC was determined using BaCl₂ according to Hendershot et al., 1993 (23). Specific surface area was determined by five-point N₂ adsorption measurements after a 45 min outgas procedure with N₂ at room temperature using a Micromeritics Gemini 2370 BET. X-ray diffraction (XRD) patterns of powdered samples were collected using a SCINTAG PAD V theta-2theta diffractometer with a liquid nitrogen cooled germanium solid state detector and CuKα radiation. Native Cu concentrations were determined after acid digestion with Aqua Regia (3:1 mixture of concentrated HCl and HNO₃) and native concentrations of C by combustion.

**Sorption Studies.** Sorption studies were carried out in a multi-component system. The multi-component system consisted of a batch reactor with three solid phases contained within different compartments (dialysis bags) that shared the same external solution and thus permitted...
competition among the solid phases for metal (Cu) retention (24) (Figure 2.1). The compartments were made from 0.01 µm polycarbonate membrane layers (STERLITECH Corporation) by sealing two 3.5 x 10 cm rectangles along the sides and clamping one end with a weighted closure. A given amount (0.5 g) of an individual solid phase and 5 ml of 0.01 M KNO₃ were placed in a dialysis bag and a second closure was used to seal the bag. Three dialysis bags, each containing Fe-Ox, LC, or K-SWy2, were placed together in a 1000 ml polypropylene container with 975 ml of 0.01 M KNO₃ (Figure 2.1). After equilibration for 24 h, a 1.5 ml aliquot of a 100 mg l⁻¹ Cu(NO₃)₂ solution was added to the reactor to yield a concentration of 100 mg Cu kg⁻¹ solids. The pH in the reactor was kept between 6 and 6.5 by addition of small amounts of 0.01 M HNO₃ or 0.01 M KOH using a pH-stat device. Eight reactors were prepared initially and at specific time intervals (1 and 15 days and 1, 2, 3, 4, 6, and 8 months), the experiments were stopped and the reactors disassembled for analyses of the solution and solid phases as described below. The rate of Cu diffusion through the membrane was tested and indicated that Cu diffusion was complete within 2 hours. Experiments were conducted to show that Cu was not sorbed by the container or by the membrane. All the chemicals used were ultra pure.

**Analyses of the Solution Phase.** Solutions were analyzed for free, labile, and total dissolved Cu. Free Cu (\(Cu^{2+} \cdot 6H₂O\)) was determined using a Cu ion selective electrode (Cu–ISE; Thermo Electron Corporation Orion-94-29 vs Thermo Electron Corporation Ag/AgCl Orion 90-02). Labile concentrations of Cu were determined by differential pulse anodic stripping voltammetry (DPASV) using a Metrohm 797 VA Computrace with 813 Autosampler \((E_d = 0.02Vs.Ag/AgCl(satKCl), t_d = 120s, v = 15mVs^{-1})\). Labile concentrations are often assumed to represent the fraction of the total dissolved metal that is bio-available (25). Total dissolved Cu was determined in acidified solutions (pH ≤ 2.0) by DPASV. Non-labile
concentrations of Cu were estimated as the difference of total minus labile Cu. Copper concentrations are reported as $- \log[Cu]$, where $[Cu]$ is in mol L$^{-1}$. DOC was determined using a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

**Analyses of the Solid Phases.** After equilibration, the solid phases were analyzed for exchangeable and total Cu. Exchangeable Cu was determined by mixing 0.1 g of freeze-dried solid phase with 30 ml of 0.01 M Ca(NO$_3$)$_2$ for 2 h at 25 °C in an end to end shaker. The suspension was centrifuged (10 min at 5000 rpm), and the supernatant filtered through a 0.2 µm membrane, acidified to a pH < 2 with HNO$_3$, and stored at 4 °C until analysis by DPASV. The concentration of total Cu in each solid phase was determined by digestion with Aqua Regia at near boiling temperature using 0.1 g of freeze-dried solid and 10 ml of Aqua Regia. Suspensions were allowed to evaporate to near dryness and the residues were re-dissolved in 5 ml of 2 N HNO$_3$, transferred quantitatively to 50 ml volumetric flasks, made to volume with deionized water, and mixed. Solutions were filtered (0.2 µm membrane) and stored at 4 °C until analysis by inductively coupled plasma mass spectrometry (ICP-MS) for Fe-Ox or by DPASV for LC and K-SWy2. Specifically adsorbed (chemisorbed or complexed) Cu concentrations were estimated as the difference between total and exchangeable Cu. The concentration of total organic carbon (TOC) on the solid phases was determined by combustion using a soil solid module (SSM-5000) coupled with a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

**Results and Discussion**

Ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (SWy2) were used as representatives of natural colloids from the fine fraction of soils, having high reactivity as indicated by particle size, ECEC, and surface area analyses (Table 2.1). These properties were
consistent with those reported in the literature (19,22,26,27). The cumulative native concentration of Cu in the system (39.3 mg kg\(^{-1}\)) was within the worldwide mean of 6 to 80 mg kg\(^{-1}\) (26). In addition to Cu, carbon was detected in Fe-Ox and K-SWy2; the source of carbon might have been (at least partially) the reagents used to prepare or treat the samples or cellulosic material from the dialysis bags used to desalt Fe-Ox and K-SWy2 during their preparation. After the multi-component system was spiked with Cu (simulating an anthropogenic input), the total concentration of Cu increased to 126.2 mg Cu kg\(^{-1}\).

Copper sorption by the solid phases present in the multi-component system was characterized by an initial sharp slope that decreased with time (Figure 2.2). Most of the Cu (60%) was removed from solution during the first 15 days of equilibration. However, sorption processes continued with a monotone decreasing slope and asymptotically approached a quasi steady state (80% Cu sorption) after 4 months. Thereafter, the curve suggests that Fe-Ox, LC, and K-SWy2 were no longer capable of removing Cu from the solution phase. This behavior indicates a strong initial affinity of the solids for Cu that decreases after longer equilibration times. The slow (4 months) sorption of Cu contrasts with fast equilibrations (within 24 h) commonly reached in conventional batch studies (28). This is partially due to differences in experimental setups. While in conventional batch studies the adsorbent and adsorbate are homogeneously mixed, in the multi-component system the solid phases are contained and thus metal retention includes diffusion controlled processes similar to those occurring in natural soil environments. Furthermore, the use of multi-component systems permits the analysis of slow kinetic processes and the determination of the concentration and speciation of Cu retained by each adsorbent, and thus the assessment of their efficacy in Cu retention. Compartmentalized systems have been used previously to study desorption and redistribution of Cu among humic
acid, iron-manganese oxides, and montmorillonite (24). Similar to our results, McLaren et al., 1983 (24) reported slower kinetics in Cu retention (17 days) compared to conventional batch studies.

**Speciation of Cu in solution.** Dissolved Cu species in the multi-component system decreased with time (Figure 2.3a). However, a large fraction (20%) of the Cu initially added to the system remained in the solution phase as non-labile, labile, and free Cu species (Figures 2.2 and 2.3a). The concentration of non-labile, labile, and free Cu species showed a logarithmic decay that stabilized after 4 months of equilibration; however, labile and free Cu species decreased at a faster rate than non-labile Cu species (Figure 2.3a). For example, the difference between total and labile species, which accounts for non-labile species, is smaller after one day than after equilibration for 8 months. Thus, the concentration of non-labile Cu species increased with time. Similar results have been reported elsewhere (8). After 8 months of equilibration, 82.8 % of the total dissolved Cu exists as non-labile complexes while labile species account for 17 % and free Cu accounts for 0.2% of the total dissolved Cu. Hence, a relatively small percentage of the total Cu in solution (17.2%) is potentially bio-available while most of the Cu is non-labile. While non-labile species may not represent a direct threat to living organisms, they are potentially mobile.

Opposite to the behavior of dissolved Cu species (Figure 2.3a), the generation of DOC increased sharply during the first 15 days and reached steady-state after 4 months of equilibration (Figure 2.3b). DOC was generated from dissolution, hydrolysis, and decomposition of LC (Figure 2.1). During equilibration, the solution phase presented a gradual increase in coloration that prevailed after filtration. The solution changed from a transparent colorless solution initially to a transparent yellow solution after 4 months and remained approximately the same for up to 8
months. Low molecular weight organic compounds that do not produce color (such as aliphatic compounds) must have been released to the solution phase initially, while higher molecular weight organics with conjugated double-bonds that produce characteristic yellow colors (i.e., fulvic and humic acids) must have been released after longer equilibration times. Furthermore, the concentration of total dissolved, labile, and free Cu species showed a linear decrease with DOC (Figure 2.3c), yet DOC produced during the experiment complexed Cu forming mostly non-labile and labile soluble species. As will be discussed below, soluble organics were sorbed by the mineral phases present in the multi-component system. It is therefore likely that decreases in total dissolved and labile Cu species observed with increases in DOC were due to sorption of Cu-organic soluble complexes onto ferrihydrite and montmorillonite.

**Speciation of Cu in the solid phases.** Figure 2.4a (see also Figure 2.6) shows the distribution of Cu among Fe-Ox, LC, and K-SWu2 as a function of time and indicates LC was the most effective solid phase in Cu retention followed by K-SWu2. Fe-Ox was the least effective competitor for Cu retention, accounting for 15 mg kg⁻¹ after equilibration for 8 months. Our results differ from those reported by McLaren et al., 1983 (24), where Cu retention after equilibration for 21 days followed the order humic acid>oxide>montmorillonite. This discrepancy is likely a result of the longer equilibrations used in our study (8 months) that permitted the dissolution of DOC and its sorption onto the mineral phases (see discussion below).

The concentration of dilute-salt extractable (exchangeable) Cu was only a small fraction of the total Cu retained by the solid phases (Figure 2.4b), thus suggesting most of the metal is held by stronger interactions such as complexation and chemisorption. Exchangeable Cu in LC was 2 %, while 98% was retained by complexation. Exchangeable Cu in Fe-Ox was 3%, while
97% was retained by chemisorption. Although ion exchange is the expected mechanism for the retention of trace metals by montmorillonite, exchangeable Cu accounted for only 10% of the total Cu retained by this mineral. Ion exchange processes in montmorillonite are presumed to be dominant due to the large internal surface areas with negative charges resulting from isomorphous substitution. However, chemisorption at mineral edges is also a plausible mechanism, especially when the concentration of trace metals in the system is low. In this study, the concentration of Cu is relatively low and the amount of K-SWy2 used in the experiment provides enough edge sites to sorb the total concentration of Cu in the system. Using the literature value of 847 m² g⁻¹ for total surface area and the ECEC of K-SWy2 (70 cmol(+).kg⁻¹), we estimated the concentration of edge charges to be 1.07 cmol(+).kg⁻¹. This value is much higher than the concentration of positive charges given by the total concentration of Cu (5.6×10⁻² cmol(+).kg⁻¹) in the multi-component system. Furthermore, metals react more strongly with pH-dependent sites such as broken edges in clays than with permanently charged sites in the interlayer space of clays. Since the concentration of Cu used in the experiment was rather low precipitation of Cu is not expected in this study.

Despite the well known capacity of iron oxides to sorb metals (29), we found Fe-Ox was the least effective competitor for Cu retention in multi-component systems. We explain this low contribution as a result of both the blockage of Fe-Ox sites by sorbed DOC (see below) and by a likely higher affinity between Cu and DOC than between Cu and iron oxides. The affinity of iron oxides for Cu (LogK_{int} = 2.89) (29) is lower than the affinity of fulvic (LogK_{Cu–bidentate} = 6.7) and humic (LogK_{Cu–bidentate} = 6.2) (30) acids for Cu, suggesting sorption of Cu by iron oxides is unlikely to occur in the presence of humic and fulvic acids (Figure 2.1). Although these constants (Table 2.2) are not strictly comparable, they provide insight regarding the relative
affinities of the different soil constituents. Indeed, a simple estimation of the competition
between organic matter and iron oxides for Cu using Visual MINTEQ (31) predicted bidentate
complexation of Cu by dissolved fulvic acids (7.0 %) was significantly higher than Cu sorption
by iron oxides (0.1 %); the remaining Cu was predicted to occur as bidentate complexes with
solid-phase organic matter (92.3 %) and monodentate complexes with solid (0.5 %) and liquid
(0.01 %) phases. Hence, the formation of Cu-DOC complexes in the multi-component system
seems to have contributed to the low effectiveness of Fe-Ox in Cu retention. The results from our
experiments suggest the contribution of iron oxides to Cu retention in soils would be negligible;
however, this has not been always observed. In fact, iron oxides are generally recognized as the
second largest pool (organic matter > oxides of Al and Fe > clays) (1) for metal retention in soils.
One reason might be the use of (sequential) chemical extractions to determine the speciation of
trace metals in soils. Such speciation may not represent the actual allocation of metals among
soil constituents. For example, sequential extractions have failed to correctly identify some metal
chemical species identified by synchrotron-based spectro-microscopy (32). While spectroscopic
techniques accurately represent chemical environments of trace metals in soils, operationally
defined chemical extractions may not do so since the reagents used in the extraction procedures
are often not selective enough and likely to dissolve solid phases in addition to the ones intended.
This can result in an erroneous attribution of Cu retention to iron oxides when chemical
extraction procedures are used to determine speciation of metals in soils. Furthermore, the
solubility of Zn, Pb, Cu, and Cd has been successfully reproduced in soils using mechanistically
based models where humic substances are considered the most important component (along with
clays for a few soils) and where contributions from iron oxides are neglected (33). The
contribution of iron oxides to Cu retention in natural soil environments might be overstated and
should therefore be reevaluated using experimental, theoretical, and analytical approaches that reflect Cu distribution in soils more accurately, such as reactors with compartments, spectroscopic studies, and modeling.

**Sorption of organic compounds onto the mineral phases.** As mentioned above and shown schematically in Figure 2.1, LC released soluble organic compounds that remained in solution and formed soluble Cu-DOC complexes (Figure 2.3). In addition, DOC underwent sorption onto the mineral phases (Figures 2.1 and 2.5). Sorption of DOC by Fe-Ox (Figure 2.5a), as determined by TOC measurements, increased with increasing DOC (Figure 2.3b), and reached a steady-state value of 6000 mg kg\(^{-1}\) after 4 months. Apart from the possibility that steady state was reached because of the steady-state of DOC in solution, pseudo-saturation of the Fe-Ox surface with organic molecules could have occurred. Pseudo-saturation can occur when sorbed organic molecules reduce the chance of other molecules to bind due to steric factors and electrostatic repulsion (12). Although a similar trend was observed for K-SWy2, the increase in TOC started after equilibration for two months and reached a steady state value of 3500 mg kg\(^{-1}\) (Figure 2.5a). The difference in sorption behavior of Fe-Ox and K-SWy2 for DOC was likely due to differences in predominant mineral surface charge and the negative charge of DOC. While Fe-Ox has a positively charged surface that can bind DOC strongly, K-SWy2 has negatively charged surfaces that are less likely to interact with DOC. The carbon isotherms presented in Figure 2.5b are a clear depiction of the higher affinity of DOC for Fe-Ox and show the existence of a threshold and a saturation DOC concentration as well. After this saturation concentration is reached, the Fe-Ox surface might be blocked by sorbed organic compounds thus preventing further sorption. Fulvic acids can form strong complexes with iron oxides (\(1.26 < \log K_f < 5.21\)) (Table 2.2) (34) and are therefore likely to outcompete Cu (\(\log K_{1\text{int}} = 2.89\)) (29) for sorption.
sites available on iron oxides (Figure 2.1). As shown in Figure 2.5b, detectable increases in TOC were not observed for K-SWy2 until the concentration of DOC was greater than 15 mg l⁻¹ and no saturation concentration was observed. In contrast to Fe-Ox, the surface of K-SWy2 was active in Cu retention early in the experiment (Figure 2.4), when DOC sorption on K-SWy2 was minimal (Figure 2.5). It is therefore possible that Cu sorbed by K-SWy2 served as a bridge for the retention of DOC via the formation of ternary complexes (K-SWy2 -Cu-DOC) after longer equilibration times. This conjecture is also supported by a dark yellow coloration observed on K-SWy2 samples older than two months.

**Environmental implications.** Besides soil solids and metal properties, metal retention in soils is influenced by DOC released from soil organic matter. DOC can increase Cu mobility in soils by the formation of soluble Cu-DOC complexes. DOC can also modify the properties of mineral surfaces (i.e., Fe-Ox) thus reducing Cu retention. At the same time, Cu retention can promote DOC sorption by the formation of ternary complexes (i.e., K-SWy2). The individual benefits of adding organic and mineral amendments to reduce metal mobility in soils could cancel each other when mixed in natural soils. Our findings advance the knowledge of the most basic interactions among trace metals and soil phases. This knowledge is important in order to successfully decrease metal mobility and solubility when using amendments to remediate metal contaminated soils.
Table 2.1. Properties of 2-line ferrihydrite (Fe-Ox), leaf compost (LC), and potassium-saturated montmorillonite (K-SWy2).

<table>
<thead>
<tr>
<th></th>
<th>Fe-Ox</th>
<th>LC</th>
<th>K-SWy2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle or aggregate size (µm)</td>
<td>26</td>
<td>245</td>
<td>1.2</td>
</tr>
<tr>
<td>ECEC (cmol(+)c kg⁻¹)</td>
<td>ND</td>
<td>142</td>
<td>70</td>
</tr>
<tr>
<td>Specific surface area (m² g⁻¹)</td>
<td>264</td>
<td>ND</td>
<td>13</td>
</tr>
<tr>
<td>Native Cu (mg kg⁻¹)</td>
<td>6.9</td>
<td>25.4</td>
<td>46.3</td>
</tr>
<tr>
<td>Native C (mg kg⁻¹)</td>
<td>2290</td>
<td>394400</td>
<td>&lt; 500</td>
</tr>
</tbody>
</table>

ND: Not determined
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log $K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$- \text{FeOH} + \text{Cu}^{2+} \leftrightarrow -\text{FeOCu}^+ + \text{H}^+$</td>
<td>2.89</td>
<td>(29)</td>
</tr>
<tr>
<td>$\text{FAH} + \text{Cu}^{2+} \leftrightarrow \text{FACu}^+ + \text{H}^+$</td>
<td>0.5</td>
<td>(30)</td>
</tr>
<tr>
<td>$2\text{FAH} + \text{Cu}^{2+} \leftrightarrow \text{FA}_2\text{Cu} + 2\text{H}^+$</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>$\text{HAH} + \text{Cu}^{2+} \leftrightarrow \text{HACu}^+ + \text{H}^+$</td>
<td>0.0</td>
<td>(30)</td>
</tr>
<tr>
<td>$2\text{HAH} + \text{Cu}^{2+} \leftrightarrow \text{HA}_2\text{Cu} + 2\text{H}^+$</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>$- \text{FeOH}^{0.5-} + \text{H}^+ + \text{RCOO}^- \leftrightarrow -\text{FeOH}_2\cdots\text{OCR}^{/0.5-} \text{ and}$</td>
<td>1.26</td>
<td>(34)</td>
</tr>
<tr>
<td>$- \text{Fe}_3\text{O}^{0.5-} + \text{H}^+ + \text{RCOO}^- \leftrightarrow -\text{Fe}_3\text{OH} \cdots\text{OCR}^{/0.5-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$- \text{FeOH}^{0.5-} + \text{H}^+ + \text{RCO}^- \leftrightarrow -\text{FeOH}_2\cdots\text{OCR}^{/0.5-} \text{ and}$</td>
<td>5.21</td>
<td>(34)</td>
</tr>
<tr>
<td>$- \text{Fe}_3\text{O}^{0.5-} + \text{H}^+ + \text{RCO}^- \leftrightarrow -\text{Fe}_3\text{OH} \cdots\text{OCR}^{/0.5-}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Affinity constant between hydrous ferric oxides ($-\text{FeOH}$) and Cu was calculated using the generalized two-layer model; between fulvic (FAH) and humic (HAH) acids and Cu were calculated using the Stockholm Humic Model; and between dissolved fulvic acids having carboxylic ($\text{RCOO}^-$) and phenolic ($\text{RCO}^-$) groups and goethite ($-\text{FeOH}^{0.5-}$ or $-\text{Fe}_3\text{O}^{0.5-}$) were calculated using the CD-MUSIC model.
Figure 2.1. Schematic diagram representing potential interactions in a multi-component system containing ferrihydrite (Fe-Ox), leaf compost (LC) and montmorillonite (K-SWy2). Equilibrium constants are not strictly comparable (see equilibrium reactions in Table 2.2).
Figure 2.2. Partitioning of Cu between the solution and solid phases (Fe-Ox + LC + K-SWy2) as a function of time.
Figure 2.3. Dissolved Cu species (a) and DOC generation (b) as a function of time and their relationship (c).
Figure 2.4. Total Cu (a) and exchangeable Cu (b) associated with each solid phase as a function of time.
Figure 2.5. Total organic carbon (TOC) on ferrihydrite (Fe-Ox) and montmorillonite (K-SWy2) as a function of time (a) and DOC (b).
Figure 2.6. Total Cu sorbed on ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) as a function of time expressed in mg of Cu per square meter of solid phase. Normalization by specific surface area was carried out using properties in Table 2.1 and from the literature (35).
References


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Chapter 3

Copper redistribution in multicomponent systems containing ferrihydrite, organic matter, and montmorillonite.

Abstract

Copper redistribution among ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) was studied using compartmentalized batch reactors. Copper was added to three reactors containing one single solid phase each (labeled iron oxide system, organic matter system, or smectitic system), and the systems were equilibrated for 30 days (1st equilibration), after which the other two phases were added to each system equilibrated for 8 additional months (2nd equilibration). The sequence of solid phase addition was varied to test whether Cu removal from solution and the concentration of Cu in each solid phase depended on initial system conditions. Total dissolved Cu and total and exchangeable Cu in individual solid phases were determined. Organic carbon in solution (DOC) and that retained by the mineral phases (TOC) were also determined. Final sorption of Cu was highly influenced by the initial composition of each system and followed the trend smectitic system > iron oxide system > organic system with 94%, 90%, and 80% of the Cu initially added to each system (0.05 mg l⁻¹) removed from solution, respectively. Compared to results from the 1st equilibration, the solid phases added in the 2nd equilibration caused Cu removal from solution to increase (76 to 80% in the organic system), to remain approximately constant (93 to 90% in the iron oxide system), and to decrease (99 to 94% in the smectitic system). Furthermore, perturbation of the system (caused by the addition of the other two solid phases) resulted in significant
desorption of Cu from the Fe-Ox (from 76 to 15 mg kg\(^{-1}\), 81%), LC (from 51 to 8 mg kg\(^{-1}\), 86%), and K-SWy2 (from 99 to 33 mg kg\(^{-1}\), 66%) phases, indicating limited desorption hysteresis. Copper remaining in solution at the end of the 1\(^{st}\) equilibration and that one desorbed during the addition of the other two phases tended to redistribute between the LC and K-SWy2 phases. The Fe-Ox phase competed less effectively for Cu retention due to sorption of DOC. DOC reached a concentration of 20 mg l\(^{-1}\) in each system and seemed to control Cu solubility and sorption behavior by the formation of Cu-DOC soluble complexes and by sorbing onto the mineral phases. Using compartmentalized batch reactors we were able to follow the dynamics of Cu partitioning and redistribution among iron oxides, organic matter, and silicate clays. We find system perturbation can cause Cu mobilization and does not always result in increased Cu sorption. We also highlight the importance of comparing metal sorption at steady state conditions for the evaluation of the effectiveness of amendment application to soils.

**Introduction**

Remediation of metal-contaminated soils often involves *in situ* application of oxides and hydroxides of Mn and Fe, clay layer silicates, and organic materials, among others. These materials are capable of reducing the mobility or bioavailability of metals through chemisorption, complexation, and/or ion exchange reactions. Field and laboratory experiments, however, often show metal mobility increases in amended soils (1-4), thus indicating the application of amendments does not always reduce metal mobility. It is therefore important to examine and explain the different outcomes resulting from the application of amendments.
The application of amendments to metal contaminated soils can cause metal sorption to increase, to remain constant, or to decrease (Figure 3.1a). In general, as sorption reactions proceed (Figure 3.1a), metal accumulation would increase, reach a maximum, and decline to zero as a steady state is approached (Figure 3.1b). This behavior is expected after initial addition of metals to a system as well as after the application of additional solid phases (amendments). Because sorption depends on metal and soil properties, accumulation paths can be as high as the capacity of the system to sorb a given metal and skewed to the right or to the left depending on the affinity of the metal-sorbent interaction. Furthermore, due to the perturbations caused by the application of amendments, desorption and negative accumulation (metal mobility) might occur at the onset of amendment application (Figure 3.1). Research is needed to determine whether metal (re)distribution in amended soils drive different sorption outcomes and the pathways of such (re)distribution.

Although several studies on the redistribution of metals have been carried out (5-13), a general conclusion can not be drawn yet. While some studies report redistribution occurs from readily available operationally defined fractions toward more stable fractions (8-12), others report the opposite (6,10,13). It has been reported that soils tend to return to their original pattern of fractionation at low metal contamination levels (7). Despite these inconsistencies, most of these studies report metals tend to accumulate in organic matter. However, there is concern that organically bound metals could undergo mobilization with the eventual decomposition of organic matter. In addition, as organic matter decomposes in soils, it generates dissolved organic carbon (DOC) that can form stable, soluble metal–DOC complexes (16,17). DOC can also sorb onto mineral phases,
changing their surface properties and preventing metal sorption (18). Metal complexation by DOC as well as DOC sorption onto mineral phases are processes that occur in natural soils and might explain the various sorption outcomes resulting from the application of amendments to metal–contaminated soils.

This work investigates the partitioning and redistribution of Cu in compartmentalized batch reactors containing iron oxides, organic matter, and silicate clays. Copper is allowed to react with a single solid phase during a 30 day equilibration (1st equilibration) after which the other two phases are added to the system and equilibrated for 8 additional months (2nd equilibration). The solid phases added in the 2nd equilibration are expected to provide reactive surfaces for the retention of dissolved and presorbed Cu. We show that Cu partitioning between the solution and solid phases depends on initial system conditions and that Cu redistribution occurs among the solid phases.

Materials and Methods

Experimental Design. Copper redistribution among ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) was studied using compartmentalized batch reactors. Copper was added to three reactors containing one single solid phase each (labeled iron oxide system, organic matter system, or smectitic system), and the systems were equilibrated for 30 days (1st equilibration), after which the other two phases were added to each system equilibrated for 8 additional months (2nd equilibration) (Figure 3.2). The preparation and physical and chemical characteristics of the solid phases as well as the assemblage of the reactors are detailed in Chapter 2. Briefly, a given
amount (0.5 g) of an individual solid phase (Fe-Ox, LC, or K-SWy2) and 5 ml of 0.01 M KNO₃ were added to a compartment (dialysis bag) and placed in a 1000 ml polypropylene container with 975 ml of 0.01 M KNO₃. After 24 h, a 0.5 ml aliquot of a 100 mg l⁻¹ Cu(NO₃)₂ solution was added to each reactor to yield a concentration of 100 mg Cu kg⁻¹ solids. The systems were equilibrated for 30 days (1st equilibration) and the other two solid phases (0.5 g each, in separate dialysis bags) were introduced to each reactor for the 2nd equilibration. A schematic of the experimental design is shown in Figure 3.2. The experimental design permitted the study of the partitioning and redistribution processes of Cu among the three main solid phases present in natural soils (iron oxides, organic matter, and silicate clays) while testing the influence of an initial sorbent on the final sorption. Seven reactors per system were prepared initially (a total of 21 reactors). Three reactors (one per system) were stopped and disassembled at specific time intervals (1 day before the addition of the other two solid phases and then after equilibration for 1 day, 15 days, and 1, 2, 4, and 8 months) for analyses of the solution and solid phases as described below. The pH was kept between 6 and 6.5 by addition of small amounts of 0.01 M HNO₃ or 0.01 M KOH using a pH-stat device. The rate of Cu diffusion through the dialysis bag was tested and indicated that Cu diffusion was complete within 2 hours. Preliminary experiments also showed that Cu was not sorbed by the container or by the membrane. All chemicals used were trace grade.

**Analyses of the Solution and Solid Phases.** The free Cu activity \( [Cu^{2+} \cdot 6H_2O] \) was analyzed during the first equilibration in the three reactors stopped 1 day before the addition of the other two solid phases using a Cu ion selective electrode (Cu–ISE; Thermo Electron Corporation Orion-94-29 vs Thermo Electron Corporation Ag/AgCl
Orion 90-02). Free Cu data was used to estimate total dissolved Cu concentrations. For the iron oxide and smectitic systems, total dissolved Cu concentrations were obtained by multiplying the free Cu activity by a factor of 1.02 as 97.5 % of the total dissolved Cu accounted for free Cu as determined by speciation calculations using Visual MINTEQ (19) and the experimental conditions of this study. For the organic system, total dissolved Cu concentrations were interpolated from an experimental correlation between total dissolved and free Cu obtained previously in the laboratory in solutions containing also DOC. Total dissolved Cu concentrations were then used to calculate Cu removal from solution (and interpreted as sorption) during the first equilibration.

The reactors stopped 1 day, 15 days, and 1, 2, 4, and 8 months after the addition of the other two solid phases (18 reactors) were analyzed for Cu species in solution (free, labile, and total dissolved) and dissolved organic carbon (DOC). Exchangeable Cu, total Cu, and total organic carbon (TOC) in individual solid phases were also determined. Free Cu (\(Cu^{2+} \cdot 6H_2O\)) was determined using a Cu ion selective electrode (Cu–ISE). Labile concentrations of Cu were determined by differential pulse anodic stripping voltammetry (DPASV) using a Metrohm 797 VA Computrace with 813 Autosampler

\(E_d = 0.02 \text{V}_{\text{Ag/AgCl(satKCl)}} \text{V}_{\text{Ag/AgCl(satKCl)}} \text{, } t_d = 120 \text{s, } v = 15 \text{mVs}^{-1}\). Labile concentrations are often assumed to represent the fraction of the total dissolved metal that is bio-available (20). Total dissolved Cu was determined in acidified solutions by DPASV. Total dissolved Cu concentrations were used to calculate Cu removal from solution during the second equilibration. Non-labile concentrations of Cu were estimated as the difference between total dissolved and labile Cu. DOC was determined using a Shimadzu TOC-5000A Total Organic Carbon Analyzer. Exchangeable Cu was determined by mixing 0.1
g of freeze-dried solid phase with 30 ml of 0.01 M Ca(NO₃)₂ for 2 h at 25 °C in an end to end shaker. The suspension was centrifuged (10 min at 5000 rpm) and the supernatant filtered through a 0.2 µm membrane, acidified to a pH < 2 with HNO₃, and stored at 4 °C until analysis by DPASV. The concentration of Cu in each solid phase was determined by digestion with Aqua Regia (3:1 mixture of concentrated HCl and HNO₃) at near boiling temperature using 0.1 g of freeze-dried solid and 10 ml of Aqua Regia. Suspensions were allowed to evaporate to near dryness and the residues were re-dissolved in 5 ml of 2 N HNO₃, transferred quantitatively to 50 ml volumetric flasks, made to volume with deionized water, and mixed. Solutions were filtered (0.2 µm membrane) and stored at 4 °C until analysis for Cu by inductively coupled plasma mass spectrometry (ICP-MS) in the case of Fe-Ox or by DPASV in the case of LC and K-SWy2. The concentration of total organic carbon (TOC) on the mineral phases was determined by combustion using a soil solid module (SSM-5000) coupled with a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

**Calculation of Cu Removal and Cu Accumulation.** Copper removed from solution (\( \Delta[Cu] \)) was calculated from the difference between the concentration of Cu initially added to the system (\( [Cu]₀ \)) and the final concentration of Cu in solution (\( [Cu]ₜ \)) at a time \( t \) as \( \Delta[Cu]ₜ = [Cu]₀ - [Cu]ₜ \). The concentration of Cu removed from solution, \( \Delta[Cu]ₜ \), was fitted as a function of the time \( t \) by equations of the type \( \Delta[Cu] = A + Be^{-t/C} \), where \( A, B, \) and \( C \) are fitting parameters for any time \( t > 1(\text{day}) \). The rate of Cu removal, interpreted as accumulation on the solid phases, was calculated as the slope of the sorption curve versus time as \( \frac{\Delta[Cu]}{\Delta t} \) for any time.
$0 \leq t \leq 1\text{(day)}$ and as the time derivative of the removal of Cu ($\frac{d(\Delta[Cu])}{dt} = -\frac{B}{C} e^{-t/C}$) for any time $t > 1\text{(day)}$ during the 1\textsuperscript{st} and 2\textsuperscript{nd} equilibrations. Copper removal from solution and sorption rates are reported as percentages of the initial Cu added to the system (i.e., mg of Cu removed per each 100 mg of Cu added) in Figure 3.3.

**Results and Discussion**

**Copper Removal from Solution: 1\textsuperscript{st} Equilibration.** The removal of Cu by the iron oxide system, the organic system, and the smectitic system during the 1\textsuperscript{st} equilibration is shown in Figure 3.3a and the fitting parameters ($A$, $B$, and $C$) and correlation coefficients ($r^2$) are shown in Table 1. Although the three single solid phases (Fe-Ox, LC, or K-SWy2) comprising each system have large surface area and high effective cation exchange capacity (18), clear differences in Cu removal behavior are observed. The smectitic system removed the most Cu (99% after 30 days of equilibration) followed by the iron oxide system (76%). The organic system presented the lowest removal of Cu (57%). Incomplete Cu removal by the iron oxide and organic systems was likely due to mass transport control, slow sorption kinetics, and dissolution of organic matter.

Different from conventional batch reactors where the effects of mass transport control and slow kinetics are overlooked by continuous and homogenous mixing, compartmentalized reactors take these effects into account, and therefore represent a more accurate model of natural soil environments. Compartmentalized reactors allow for competition and interaction among different components through a common solution whose composition may vary over time. In this study, for example, diffusion of Cu to bulk solid phases, sorption processes, as well as dissolution of organic matter are all
occurring in parallel. Yet, diffusion-limited kinetics might have ceased to exist within the first 30 days as demonstrated by the nearly 100 % Cu removal in at least one of the systems. In contrast, slow sorption (and desorption) reactions and DOC generation might have a longer lasting effect on the sorption of Cu. Compartmentalized reactors have been used previously to study desorption and distribution of Cu among oxides, organic matter, and silicate clays (5,18). Similar to our results, these studies reported slow kinetics when compared to conventional batch studies.

Copper accumulations in each system during the 1st equilibration are shown in Figure 3.3b. In general, Cu accumulation was highest early in the experiments and decayed asymptotically to zero as removal of Cu approached steady state in the three systems (Figure 3.3a). Accumulation maxima skewed toward short times indicate a high affinity of each single solid phase for Cu. The smectitic system showed the fastest removal kinetics with a maximum of accumulation of 49 mg Cu per each 100 mg Cu added per day and reached equilibrium within 30 days. The iron oxide (34 mg Cu per each 100 mg Cu added per day) and organic (9 mg Cu per each 100 mg Cu added per day) systems showed slower removal rates. Based on extrapolation calculations, zero accumulation (and therefore a steady state condition) will be reached after four months with 93 % of Cu removal in the iron oxide system and 76 % of Cu removal in the organic system.

It is interesting to note that the trend of sorption observed among the different systems (smectitic > iron oxide > organic) contrasts with the most widely observed trend of Cu sorption by soil solid phases (organic matter > iron oxides > silicate clays) obtained from conventional batch reactor studies (14). Because organic matter can be the largest
sink for Cu sorption in soils, it was unexpected that the organic system sorbed the least Cu (Figure 3.3a). We explain this finding based on the slower accumulation of Cu observed for the organic system (Figure 3.3b); which allowed for other competing mechanisms to emerge. In this particular case, DOC was being generated from the LC (see results below) thus resulting in the formation of Cu–DOC soluble complexes and decreased sorption by the solid phase. In contrast, Cu sorption in the iron oxide and smectitic systems was not affected by competing mechanisms (i.e., soluble organic ligands) and therefore Cu accumulation was faster in a given period of time than for the organic system. Our results suggest sorption trends have limited value for predicting bulk sorption patterns unless the associated sorption kinetics are known. This is particularly relevant in natural soils where a variety of inorganic and organic ligands that can complex metals are present and it would therefore be fortuitous if soil processes favoring Cu mobility had slower kinetics than sorption processes.

**Copper Removal from Solution: 2nd Equilibration.** Figure 3.3c presents the percentage of Cu removed from solution after addition of organic matter (LC) and silicate clays (K-SWy2) to the iron oxide system (Fe-Ox); iron oxides (Fe-Ox) and silicate clays (K-SWy2) to the organic system (LC); and iron oxides (Fe-Ox) and organic matter (LC) to the smectitic system (K-SWy2) (Figure 3.2). The removal of Cu during the 2nd equilibration followed the trend smectitic system > iron oxide system > organic system (Figure 3.3c). Similar removal trends during the 1st (Figure 3.3a) and 2nd (Figure 3.3c) equilibrations suggest Cu removal from solution was largely influenced by the initial composition of the systems. Since strictly speaking the iron oxide, organic, and smectitic systems had the same properties at the end of the experiment, removal of Cu should have
been similar among the systems. However, after the 2nd equilibration, Cu removal increased in the organic system (from 76 % to 80 %), was nearly equal (from 93 % to 90 %) in the iron oxide system, and decreased (from 100 % to 94 %) in the smectitic system (Figure 3.3a and c). Hence, different initial compositions led to different sorption outcomes that were not necessarily higher than during the 1st equilibration, neither straightforward to predict. In a similar two-step equilibration (21 days each) study, McLaren et al. (5) reported Cu sorption increased in a humic acid system during the second equilibration. In contrast, they found Cu sorption decreased in the oxide system and increased in the montmorillonite system (5). Different equilibration times (21 days vs 8 months) might account for the difference in our results. Evaluation of the effectiveness of solid phases in metal retention is done properly only at steady state conditions.

The accumulation of Cu during the 2nd equilibration was characterized by a pulse that decreased to zero over time with a negative accumulation at the onset of the addition of the other two phases (Figure 3.3d). Negative accumulation (-23, -25, and -28 mg Cu (100 mg Cu added)^-1 day^-1 for the smectitic, organic, and iron oxide systems, respectively) was likely due to Cu desorption from the initial sorbent and/or of native, easily exchangeable Cu present in the solids recently introduced to each system. Negative accumulation is a necessary condition for the redistribution of Cu to occur. On the other hand, negative accumulation highlights the potential for Cu to mobilize as soil systems are disturbed by the application of additional solids. Metal mobility in sludge amended soils, for example, is known to be highest during the first 3–4 years (21). In our systems, Cu sorption processes continued to dominate immediately after Cu mobilization; albeit more slowly (< 45 mg Cu (100 mg Cu added)^-1 month^-1 = 1.5 mg Cu (100 mg Cu added)^-1
day\(^{-1}\) in each system) than in the 1\(^{st}\) equilibration (Figures 3b and d). As the systems progressed toward a second equilibrium (reached within 8 months for the three systems), Cu accumulation decayed at different rates, suggesting the 2\(^{nd}\) equilibrium was reached through different paths in the iron oxide, organic, and smectitic systems. These paths might be a function of the relative contributions of the Fe-Ox, LC, and K-SWy2 phases for Cu sorption. McLaren et al. (5) concluded the final sorption was highly influenced by the identity of the initial sorbent.

**Copper Redistribution among Soil Solids.** Figure 3.4 shows the distribution of Cu among the Fe-Ox, LC, and K-SWy2 phases as a function of time during the 2\(^{nd}\) equilibration for the iron oxide, organic, and smectitic systems. Desorption of Cu from the initial solid phase occurred in all systems (Figure 3.4, left panels). In the iron oxide system, the Fe-Ox phase retained only 15 mg kg\(^{-1}\) of the 76 mg kg\(^{-1}\) initially sorbed (Figure 3.4a). The Cu desorbed redistributed towards the LC and K-SWy2 phases and reached 40 and 29 mg Cu kg\(^{-1}\) solid, respectively (Figure 3.4d). The LC sorbed more Cu than the K-SWy2 (Figure 3.4d). In the organic system, the desorbed Cu (from 57 to 8 mg kg\(^{-1}\)) was redistributed between the LC (31 mg Cu kg\(^{-1}\)) and K-SWy2 (47 mg Cu kg\(^{-1}\)) phases (Figure 3.4b and e). A small concentration of Cu (< 2 mg Cu kg\(^{-1}\)) redistributed to the Fe-Ox phase during the 2\(^{nd}\) equilibration (Figure 3.4e). The smectitic system retained about 30% of its Cu after system perturbation, and the desorbed Cu (from 99 to 33 mg kg\(^{-1}\)) was redistributed between the K-SWy2 (50 mg Cu kg\(^{-1}\)) and LC (54 mg Cu kg\(^{-1}\)) phases (Figure 3.4c and f). Total Cu on K-SWy2 varied between 33 and 66 mg kg\(^{-1}\) with no clear trend (Figure 3.4c). Again, no Cu redistribution towards the Fe-Ox phase occurred (Figure 3.4f). Our results are in accordance with those of McLaren et al. (5) in
that we also observed Cu redistribution toward the organic phase (humic acids or leaf compost). Our results, however, differ from those of McLaren et al. (5) because they observed the initial phase remained the predominant sorbent, presumably due to strong sorption leading to desorption hysteresis. As shown in Figure 3.4 (left panels), limited desorption hysteresis was observed in our systems. Besides revealing the relative contribution of each solid phase to bulk sorption, the results of Figure 3.4 support the hypothesis that Cu sorption can be attained through different paths.

Despite the well known capacity of iron oxides to sorb metals (22), redistribution of Cu to Fe-Ox was not observed in this study. We explain this finding by blockage of the Fe-Ox surface by DOC which impeded Cu sorption (see discussion below). In addition, more than a sink for Cu, added Fe-Ox seemed to contribute to Cu desorption in the organic and smectitic systems (Figures 3.3c, 3.3d, 3.4b, and 3.4c). Furthermore, although metals are presumed to form inner-sphere surface complexes with aluminum and iron oxides (23-26), a significant amount of Cu was desorbed (81 %) from the Fe-Ox in this study (Figure 3.4a). This unexpected behavior suggests iron oxides are sensitive to perturbations caused by the addition of LC and K-SWy2 (Figure 3.4a). In general, the results of this investigation suggest the use of iron oxides for the remediation of metal contaminated soils can be detrimental as in some cases the magnitude of the perturbation (mobilization or desorption of Cu) might not be compensated by sorption of Cu by other solid phases present in the system (see for example Figures 3.3a, 3.3c, and 3.4c). Our results contrast with a number of studies that, using sequential chemical extractions, find iron oxides are a major sink for Cu and that Cu redistribution occurs toward amorphous and/or crystalline iron oxides (8,11,12). However, there is increasing chemical,
Theoretical, and spectroscopic evidence suggesting that metal solubility in soil systems is controlled by organic matter and silicate clays rather than by iron oxides (18,27-30).

The concentration of dilute-salt extractable (exchangeable) Cu was a small fraction of the total Cu sorbed by each phase (Figure 3.6) suggesting Cu was mostly chemisorbed, complexed, or formed ternary complexes with the solid phases (see discussion below). In the iron oxide system, exchangeable Cu decreased in the Fe-Ox phase (from 0.87 to 0.32 mg kg⁻¹), varied in the LC phase (between <0.15 and 0.66 mg kg⁻¹), and increased in the K-SWy2 phase (from 0.64 to 1.72 mg kg⁻¹) (Figures 3.6a and d). In the organic system, exchangeable Cu increased in the LC (from <0.15 to 0.67 mg kg⁻¹) and K-SWy2 (from 0.45 to 3.04 mg kg⁻¹) phases (Figures 3.6b and e). In the smectitic system, exchangeable Cu decreased in the K-SWy2 phase (from 4.30 to 2.11 mg kg⁻¹) and increased in the LC phase (from < 0.15 to 2.50 mg kg⁻¹) (Figures 3.6c and f). Exchangeable Cu was low (< 0.15 mg kg⁻¹) in the Fe-Ox phase of the organic and smectitic systems. Exchangeable Cu concentrations were below 5% of the total Cu retained by each solid phase independent of initial system.

**DOC and sorption of organic compounds onto the mineral phases.** Hydrolysis and decomposition of LC in the iron oxide, organic, and smectitic systems generated DOC over time, reaching a concentration of 20 mg l⁻¹ after 8 months (Figure 3.7). Dissolved Cu species decreased with time and presented an inverse relationship with DOC (Figure 3.8). In general, non-labile species were significantly higher than labile and free Cu species, indicating the Cu remaining in solution formed mostly non–labile Cu–DOC complexes (Figure 3.8). The presence of soluble non–labile Cu–DOC complexes might account for the incomplete sorption of Cu observed in Figures 3.3a and 3.3c.
Similar to the organic system, incomplete Cu sorption (80%) was reported for a system where all three solid phases (Fe-Ox, LC, and K-SWy2) were equilibrated together for 8 months \( (18) \), suggesting LC (and therefore DOC) largely control Cu solubility. It is recognized that DOC can increase Cu solubility \((31-34)\) and/or prevent Cu sorption \((18)\) by forming stable Cu–DOC soluble complexes \((35,36)\).

In addition, DOC underwent sorption onto the mineral solid phases (Fe-Ox and K-SWy2) during the second equilibration period (Figure 3.5). Sorbed DOC (as determined by TOC measurements) increased sigmoidally with increasing DOC. Initial TOC was 2290 mg kg\(^{-1}\) in the Fe-Ox phase and < 500 mg kg\(^{-1}\) in the K-SWy2 phase. TOC reached average values of 7500 mg TOC kg\(^{-1}\) Fe-Ox and 3050 mg TOC kg\(^{-1}\) K-SWy2 (Figure 3.5). These values suggest a higher affinity of DOC for Fe-Ox than for K-SWy2, likely a consequence of the positive surface of Fe-Ox and the predominantly negative character of DOC. K-SWy2 has a negative surface and is therefore less likely to interact with DOC. The sorption of DOC on Fe-Ox might block surface sites thus impeding Cu redistribution toward Fe-Ox. In contrast, Cu redistribution toward K-WSy2 was not impeded and Cu sorption may even be a necessary step for DOC sorption on the K-SWy2 surface, promoting the formation of ternary complexes. The formation of K-SWy2-Cu-DOC ternary complexes provides a reasonable explanation to the presence of both Cu and DOC on K-SWy2 samples.

In agreement with results reported previously \((18)\), we find organic matter controlled Cu solubility in our model soil systems by two rather bipolar means. On one hand, organic matter effectively sorbed Cu in competitive environments. On the other hand, juxtaposed to Cu sorption, organic matter generated DOC that hindered the
sorption processes by complexing Cu strongly in solution and by modifying the surface properties of mineral phases. Modification of mineral phase surface properties included blockage of reactive Cu surfaces and/or protection of sorbed Cu by the formation of ternary complexes.

**System Disturbance and the Attainment of Steady-State Conditions.** Our results show amendments can disturb soil systems causing increased Cu mobility after their application. As a result, Cu sorption can increase, remain constant, or decrease (Figure 3.1) due to its redistribution towards organic matter or silicate clays, but not towards iron oxides. Final sorption outcomes are highly influenced by the composition of the original system. Due to the complexity of soil environments, sorption outcomes resulting from the application of amendments to metal-contaminated systems are not straightforward to predict. Furthermore, the evaluation of the effectiveness of any amendment must be carried out by comparing sorption before and after amendment application at steady state conditions, where no net accumulation occurs because sorption processes equal desorption processes or because metal inputs equal metal outputs in the soil system. Failure to do so can lead to erroneous conclusions, where sorption appears to increase. In the iron oxide system, for example, sorption of Cu after amendment application (90%) would be erroneously diagnosed supra-additive when compared to a 76% (non steady state) sorption of Cu at one month of 1st equilibration. A better understanding of the dynamic behavior of the most basic interactions between mineral and organic (solid- and solution-phase) soil constituents will help to determine the dominant mechanisms involved in the retention of Cu in soils and ultimately help decrease Cu mobility after amendment application to metal contaminated soils.
Table 3.1. Fitting parameters and correlation coefficients for experimental data on Cu removal\textsuperscript{a} from solution over time (Figure 3.3).

<table>
<thead>
<tr>
<th>System</th>
<th>1\textsuperscript{st} Equilibration</th>
<th>2\textsuperscript{nd} Equilibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (%)</td>
<td>B (%)</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>93.24</td>
<td>-61.66</td>
</tr>
<tr>
<td>Organic</td>
<td>77.81</td>
<td>-71.58</td>
</tr>
<tr>
<td>Smectitic</td>
<td>100.04</td>
<td>-57.65</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\Delta[Cu] = A + Be^{-c/t}$
Figure 3.1. Schematic diagram representing potential sorption (a) and accumulation (b) behavior of a metal (Me) in soil before and after system disturbance (i.e., amendment application, indicated by a star). a) System disturbance can cause sorption ($q_{Me,1}$) to increase ($q_{Me,2} > q_{Me,1}$), to remain constant ($q_{Me,2} = q_{Me,1}$), or to decrease ($q_{Me,2} < q_{Me,1}$). b) Metal accumulation increases simultaneously with sorption, reaches a maximum, and declines to zero as steady state is approached.
<table>
<thead>
<tr>
<th>System Identification</th>
<th>Solid Phase in 1st Equilibration</th>
<th>Solid Phases added in 2nd Equilibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Oxide</td>
<td>Fe-Ox</td>
<td>LC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-SWy2</td>
</tr>
<tr>
<td>Organic</td>
<td>LC</td>
<td>Fe-Ox</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-SWy2</td>
</tr>
<tr>
<td>Smectitic</td>
<td>K-SWy2</td>
<td>Fe-Ox</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LC</td>
</tr>
</tbody>
</table>

**Figure 3.2.** Experimental design (a) used to study the redistribution of Cu among ferrihydrite (Fe-Ox), organic matter (LC), and montmorillonite (K-SWy2). Copper was added to a system containing one single phase (b). After equilibration for 30 days (1st equilibration), the other two phases were added (c) and the system was equilibrated for 8 additional months (2nd equilibration).
Figure 3.3. Partitioning of Cu between the solution and the solid phase(s) as a function of time for the iron oxide, organic, and smectitic systems and their accumulations (rate of Cu removal). a) Removal of Cu from solution during the 1st equilibration. b) Cu accumulation during the 1st equilibration. c) Removal of Cu from solution during the 2nd equilibration. d) Cu accumulation during the 2nd equilibration.
Figure 3.4. Total Cu on ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) as a function of time. Panels at left of figure show the initial solid phases while panels at right of figure show the solid phases added in the 2nd equilibration (per system). Copper content in the Fe-Ox, LC, and K-SWy2 phases one day before the start of the 2nd equilibration are plotted (open symbols left panels) and used as a reference point for the last day of the 1st equilibration.
Figure 3.5. Total organic carbon (TOC) on ferrihydrite (Fe-Ox) and montmorillonite (K-SWy2) as a function of DOC during the second equilibration period.
Figure 3.6. Exchangeable Cu on ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) as a function of time. Solid phases on left panels are initial phases while solid phases on right panels are added phases.
Figure 3.7. DOC as a function of time for the iron oxide, organic, and smectitic systems.
Figure 3.8. Dissolved Cu species (total, labile, and free) as a function of DOC generated for the iron oxide, organic, and smectitic systems.
References


Chapter 4

Simultaneous sorption of cadmium, chromium, copper, and nickel by competing solid- and solution- soil constituents.

Abstract

Cadmium, Cr, Cu, and Ni sorption by ferrihydrite, leaf compost (LC), and montmorillonite (K-SWy2) was studied over 8 months in systems that emulate simultaneous effects of specific and non-specific sorption of metals in the presence of DOC and including rate-limiting physical processes using a compartmentalized reactor. Cadmium, Cr, Cu, and Ni concentrations in solution and exchangeable and total Cd, Cr, Cu, and Ni in individual solid phases were determined. Organic carbon in solution (DOC) and that retained by the mineral phases were also determined. Cadmium, Cr, Cu, and Ni sorption reached steady-state at different rates and accounted for 90 %, 82 %, 71 %, and 56 % of the total metal initially added (0.15 mg l\(^{-1}\) each) to the system, respectively. The remaining metal (10 % Cd, 18 % Ni, 29 % Cu, and 44 % Cr) stayed in solution and had different degrees of lability (Cd > Ni > Cu > Cr). An initial 25% of non-labile Cd dissolved species facilitated 35% of Cd sorption at 1 day of equilibration while 79% of non-labile Cu species caused 12% of Cu sorption. Increasing non-labile Cd (from 25 to 37%) and Cu (from 79 to 89%) species with time resulted in incomplete sorption. Initial formation of non-labile soluble complexes hinders metal sorption while the progressive formation of non-labile species over time results in incomplete metal sorption by the solid phases. LC effectively sorbed all four metals early in the experiment and continued sorbing Cd and Ni over time but not Cu and even desorbed Cr. K-SWy2 sorbed all four
metals initially but desorbed Cd and Ni over time. Fe-Ox sorbed small quantities of metals only indirectly through the sorption of DOC-metal complexes.

**Introduction**

Soils are multi-phase and multi-component systems. This complexity makes the identification of the individual contributions that the various soil constituents might have on metal retention or mobility difficult to discern. Soils contain mineral and organic solid phases that have a high affinity for trace metals as well as dissolved organic matter that can favor metal mobility or prevent metal retention (1-6). Therefore, the net accumulation (retention or mobility) of a given metal in a soil system will be the result of a complex web of simultaneous chemical interrelations mediated by a dynamic (temporal and spatially) soil solution. Efforts to understand these interrelations include numerous studies on sorption of metals by individual soil components in batch reactors and studies on specific and non-specific sorption of metals as determined by operationally defined chemical extractions. Yet, the competitive effects of dissolved organic matter and the rate-limiting physical processes have been largely ignored. In a recent study (1), the simultaneous and dynamic effects of specific and non-specific sorption of Cu by three soil solid phases in the presence of DOC and rate-limiting physical processes were investigated using a compartmentalized reactor and 8 months of equilibration. The authors concluded that solid- and solution- phase organic determined the concentration of Cu sorbed and its distribution among soil solids (1). The time scale over which sorption, desorption, and complexation processes take place in soils is key to better understand competition among soil phases.
The mechanisms involved in metal sorption have been extensively studied and are known to depend on soil (e.g. pH, organic matter content, texture, mineralogy) as well as on metal (e.g. charge, coordination chemistry, redox potential) properties. Ion exchange, chemisorption, and complexation reactions, for example, are likely mechanisms involved in the sorption of low levels of metals. The characteristic times for these reactions depend on the type of bond formed. In general, ion exchange reactions (outer-sphere complexes) are fast while reactions involving the formation of inner-sphere complexes tend to be slower (7). On the other hand, the mechanisms involved in metal mobility, such as metal complexation by dissolved organic matter, might largely depend on metal and dissolved organic matter properties as well as on their rates of reaction.

Ion exchange (cation exchange) occurs in permanently charged minerals and soil organic matter. The interaction between the cation and the surface is electrostatic in nature, reversible, and it takes place on a charge-by-charge basis. Cations with high charge and small hydrated radius are preferentially sorbed (8). According to these selectivity rules, ion exchange among Cd, Cr, Cu, and Ni will follow the trend Cr > Cu > Ni > Cd. Chemisorption occurs in variable charge mineral surfaces such as iron oxides, the edges of layer silicates, and organic matter. It involves the formation of inner-sphere complexes and can have covalent and/or ionic character. Chemisorption reactions are irreversible and highly specific. For a specific ligand, the more electronegative cations (Cu > Ni > Cd) are known to form the strongest covalent bonds with mineral surfaces (8). On the basis of electrostatics, however, highly charged cations with the greatest charge to radius ratio are preferentially chemisorbed (Cr > Ni > Cu > Cd) (8). The specific sorption of metals by organic matter is referred to as complexation. Similarly, in organic matter,
highly charged and more electronegative cations would be preferentially complexed over lower charge cations or less electronegative cations (8). Because dissolved organic matter is generally produced by hydrolysis and microbial decomposition of soil organic matter, similar functional groups and hence similar selectivity rules might apply for metal complexation in soil solution.

Although it is commonly reported that metal sorption by soil solids follows the order: organic matter > Al or Fe oxides > layer aluminosilicates clays, there is increasing evidence that suggests the contribution of iron oxides to metal sorption in soils might be overstated (1,9-12). The preference of specific metals for the various soil constituents is still subject to debate. One of the main deterrents in answering questions such as “where does the metal go?” is the inability to study the contribution of individual solid phases in metal retention because soil solids exist as soil aggregates. To generalize different behaviors among metals for the various solid phases is even more challenging and has not been reported. This work determines the overall sorption (partitioning) and distribution of low concentrations of Cd, Cr, Cu, and Ni among ferrihydrite, organic matter, and silicate clays interacting through a solution containing DOC during a 8 months equilibration period and using a compartmentalized batch reactor. The experimental design permits the assessment of competing chemical and physical processes that drive the overall sorption.

Materials and Methods

Solid Phases. The solid phases used as model soil components were ferrihydrite (Fe-Ox), leaf compost (LC), and potassium saturated montmorillonite (K-SWy2). Details about
their preparation and physical and chemical characteristics can be found in Martínez-Villegas and Martínez, 2008 (1).

**Sorption Studies.** Sorption studies were carried out in a multicomponent system. The multicomponent system consisted of a batch reactor with three solid phases contained within different compartments (dialysis bags) that shared the same external solution and thus permitted competition among the solid phases for Cd, Cu, Cr, and Ni sorption as well as competition among different metals for a solid phase (1,13). Details about the assemblage of the multicomponent system used in this study can be found in Martínez-Villegas and Martínez, 2008 (1). Briefly, a given amount (0.5 g) of an individual solid phase and 5 ml of 0.01 M KNO₃ were placed in a dialysis bag. Three dialysis bags, each containing Fe-Ox, LC, or K-SWy2, were placed together in a 1000 ml container with 975 ml of 0.01 M KNO₃. After equilibration for 24 h, a 1.5 ml aliquot of a solution containing 100 mg l⁻¹ of Cd(NO₃)₂, Ni(NO₃)₂, Cu(NO₃)₂, and Cr(NO₃)₃ was added to the reactor to yield a concentration of 100 mg of each metal per kg of solids. The pH in the reactor was kept between 6 and 6.5 by the addition of small amounts of 0.01 M HNO₃ or 0.01 M KOH using a pH-stat device. No Cr(III) precipitation was observed due to slow addition of the metals to the systems and to the presence of organics compounds dissolved in solution. Six reactors were prepared initially, and at specific time intervals (1 and 15 days, and 1, 2, 4, and 8 months) the experiments were stopped and the reactors disassembled for analyses of the solution and solid phases as described below. All the chemicals used were trace grade.

**Analyses of the Solution Phase.** Solutions were analyzed for total dissolved Cd, Cu, Cr, and Ni. Free Cu, labile Cu, and labile Cd were also determined. Free Cu
was determined using a Cu ion selective electrode (Cu–ISE; Thermo Electron Corporation Orion-94-29 vs Thermo Electron Corporation Ag/AgCl Orion 90-02). Labile concentrations of Cu and Cd were determined by differential pulse anodic stripping voltammetry (DPASV) using a Metrohm 797 VA Computrace with 813 Autosampler ($E_{d,Cd} = -0.55 \text{ vs. Ag/AgCl(satKCl)}$, $E_{d,Cu} = 0.02 \text{ vs. Ag/AgCl(satKCl)}$, $t_d = 120s, v = 15mV s^{-1}$). Labile concentrations are often assumed to represent the fraction of the total dissolved metal that is bio-available (14). Total dissolved Cd, Cu, Cr, and Ni were determined in acidified solutions by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) (Perkin-Elmer Ultima 5300 ICP). Non-labile concentrations of Cu and Cd were estimated as the difference of total dissolved minus labile metal. Dissolved organic carbon (DOC) was determined using a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

**Analyses of the Solid Phases.** The solid phases were analyzed for exchangeable and total metal concentrations. Exchangeable Cd, Cu, Cr, and Ni were determined on each solid phase by mixing 0.1 g of freeze-dried solid phase with 30 ml of 0.01 M Ca(NO$_3$)$_2$ for 2 h at 25 °C in an end to end shaker. The suspension was centrifuged (10 min at 5000 rpm), and the supernatant filtered through a 0.2 µm membrane, acidified to a pH < 2 with HNO$_3$, and stored at 4 °C until analysis by ICP-AES. The concentrations of Cd, Cu, Cr, and Ni in each solid phase were determined by digestion with Aqua Regia at near boiling temperature using 0.1 g of freeze-dried solid and 10 ml of Aqua Regia. Suspensions were allowed to evaporate to near dryness and the residues were re-dissolved in 5 ml of 2 N HNO$_3$, transferred quantitatively to 50 ml volumetric flasks, made to volume with deionized water, and mixed. Solutions were filtered (0.2 µm
membrane) and stored at 4 °C until analysis by ICP-AES for Fe-Ox and K-SWy2 samples. Based on the law of mass conservation, total metals in LC samples were estimated by subtraction as the difference between total metals in the solid phases (metal added minus metal remaining in solution) minus total metals in Fe-Ox plus K-SWy2. Specifically adsorbed (chemisorbed or complexed) metal concentrations were estimated as the difference between total and exchangeable metal for each solid phase. The concentration of total organic carbon (TOC) on the solid phases was determined by combustion using a soil solid module (SSM-5000) coupled with a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

Results

Multicomponent Systems: Behavior of Cd, Cu, Cr, Ni, and DOC. Ferrihydrite (Fe-Ox), leaf compost (LC), and montmorillonite (K-SWy2) were used as representatives of natural colloids from the fine fraction of soils. Particle size, effective cation exchange capacity, and surface area have been reported previously (1). The cumulative native concentrations of metals in the solid phases (0.5 mg Cd kg⁻¹, 26.3 mg Cu kg⁻¹, 59.33 mg Cr kg⁻¹, and 29 mg Ni kg⁻¹) were within or near the worldwide means of 0.06 to 1.1 mg Cd kg⁻¹, 6 to 80 mg Cu kg⁻¹, 7 to 221 mg Cr kg⁻¹, and 4 to 55 mg Ni kg⁻¹ (8). In addition to Cd, Cu, Cr, and Ni, carbon was detected in Fe-Ox and K-SWy2; the source of carbon might have been (at least partially) the reagents used to prepare or treat the samples. After spiking with Cd, Cu, Cr, and Ni, the total concentration of metals in the multicomponent system increased to 100.5 mg Cd kg⁻¹, 126.8 mg Cu kg⁻¹, 159.3 mg Cr kg⁻¹, and 129 mg Ni kg⁻¹.
Removal of metals from solution increased as a non-linear function of time (Figure 4.1). Cadmium removal was characterized by an initial sharp slope that decreased with time as 35.3 % of the initial Cd added to the system was removed after 1 day of equilibration, 80% during the first 15 days, and ~90% within the first month. Cadmium removal remained approximately constant after one month of equilibration. Nickel removal was characterized by a less sharp slope as 30% of the initial Ni added to the system was removed after 1 day of equilibration, 64.7% after 15 days, and 75 % after 2 months. Nickel removal remained at ~ 79 % after two months of equilibration. Nickel removal data at 1 month (38.7%) was considerably lower than expected and might be an outlier. Copper removal was 12% at 1 day and increased to 71% after 4 months of equilibration. Chromium removal increased smoothly over time from 20 % after 1 day of equilibration to 56% after 4 months. After equilibration for 8 months, the removal of metals from solution followed the trend: Cd > Ni > Cu > Cr (Figure 4.1). Figure 4.10 shows an alternative representation of the decreases in concentration over time in molar units.

Similar to metal removal from the solution, DOC increased sharply initially and reached quasi steady state after 4 months of equilibration (Figure 4.2a). At the time metals were added, DOC was already 6.6 mg l⁻¹ due to pre-equilibration of the multicomponent system for 24 h (open symbols in Figure 4.2a). DOC was generated from hydrolysis and decomposition of LC. During equilibration, the solution phase presented a gradual increase in coloration that prevailed after filtration. The solution changed from a transparent colorless solution initially to a transparent yellow solution after 4 months and remained approximately the same for up to 8 months. The
concentration of total dissolved metals showed an inverse relationship with DOC (Figure 4.9b). On the other hand, DOC underwent sorption onto the mineral phases (Figures 2b and c). Sorption of DOC by Fe-Ox, as determined by TOC measurements, increased with time reaching a steady-state value of 6050 mg kg$^{-1}$ after 4 months (Figure 4.2b). A similar trend was observed for K-SWy2, however, K-SWy2 sorbed less DOC reaching a value of 3940 mg kg$^{-1}$ (Figure 4.2b). Carbon sorption isotherms on Fe-Ox and K-SWy2 are presented in Figure 4.2c and show a sigmoidal-type sorption behavior.

**Cadmium speciation in solution and distribution among soil solids.** Total dissolved Cd decreased sharply during the first month of equilibration down to 10% of the Cd initially added to the system (Figures 4.3a and 9a). Labile Cd species decreased at a slightly faster rate than non-labile Cd species (Figure 4.3a). The concentration of non-labile Cd species increased with time. This can be seen as the difference between total dissolved and labile Cd species, which accounts for non-labile species, is slightly smaller after one day

\[
\text{LogCd}_{\text{non-labile,1day}} = \text{LogCd}_{\text{total,1day}} - \text{LogCd}_{\text{labile,1day}} = 6.06 - 6.19 = -0.13
\]

than after equilibration for 8 months

\[
\text{LogCd}_{\text{non-labile,8months}} = \text{LogCd}_{\text{total,8months}} - \text{LogCd}_{\text{labile,8months}} = 7.00 - 7.2 = -0.20
\]

Such increase is better appreciated in a figure of the relative percentages of labile and non-labile Cd species over time (Figure 4.3b), where an initial 25% of non-labile Cd species increased to 37% after 8 months of equilibration. In the solid phases, total Cd on LC increased sharply (from 69 to 240 mg kg$^{-1}$) within a month of equilibration and remained relatively constant (~236 mg kg$^{-1}$) for the duration of the experiment (Figure 4.3c). The total Cd concentration on K-SWy2 and Fe-Ox varied during the 8 months of
equilibration, decreasing exponentially on K-SWy2 and increasing on the Fe-Ox phase (Figure 4.3c). Exchangeable Cd paralleled increases in total Cd on LC (up to 48.3 mg kg$^{-1}$) and accounted for 20.5% of the total (Figure 4.3d). Exchangeable Cd decreased as a function of time on K-SWy2 (down to 3.3 mg kg$^{-1}$) but accounted for a large fraction (57%) of the total Cd (Figure 4.3d). Exchangeable Cd was lower than 2.1 mg kg$^{-1}$ on Fe-Ox (Figure 4.3d).

**Copper speciation in solution and distribution among soil solids.** Copper species in solution (total dissolved, labile, and free Cu) showed a logarithmic decay that stabilized after 4 months of equilibration (Figure 4.4a) with 29% of the Cu initially added to the system remaining in solution as total dissolved Cu (Figure 4.1). Because labile and free Cu species decreased at a faster rate than non-labile Cu species (Figure 4.4a), non-labile Cu species increased (from 79% to 89%) with time. This is shown by the relative percentages of free, labile, and non-labile Cu species in Figure 4.4b. Total Cu increased with time on LC, K-SWy2, and Fe-Ox (Figure 4.4c) being highest on LC. K-SWy2 presented increases in exchangeable Cu with equilibration time, accounting for up to 7% of the total Cu. Exchangeable Cu represented a low fraction (< 0.5 mg kg$^{-1}$) of the total Cu sorbed by Fe-Ox and LC (Figure 4.4d).

**Nickel distribution among soil solids.** The LC sorbed the most Ni initially and was the most effective solid in removing Ni from solution (total Ni increased from 116.5 to 304 mg kg$^{-1}$) (Figure 4.5a). Ni sorption decreased with time in K-SWy2 (from 30.5 to 15 mg kg$^{-1}$) but increased in Fe-Ox (from 0 to 8 mg kg$^{-1}$) (Figure 4.5a). Exchangeable Ni increased with increasing total Ni in the LC and accounted for 8% at the end of the experiment (Figure 4.5a and b). Variable concentrations of exchangeable Ni were present
in K-SWy2 (0.5 - 10.2 mg kg\(^{-1}\)) and Fe-Ox (0.6 - 2.7 mg kg\(^{-1}\)), but these represented a small fraction of the total Ni sorbed (Figure 4.5d).

**Chromium distribution among soil solids.** The native Cr content of the solid phases used in this experiment was 92.50 mg kg\(^{-1}\) in Fe-Ox, 38 mg kg\(^{-1}\) in LC, and 47.50 mg kg\(^{-1}\) in K-SWy2. During the 8 month equilibration, the Cr concentration in the LC also increased (Figure 4.6a). Total Cr increased in the Fe-Ox and K-SWy2 phases (Figure 4.6a). Exchangeable Cr was lower than 1.2 mg kg\(^{-1}\) on Fe-Ox, LC, and K-SWy2 (Figure 4.6b).

**Discussion.**

**Factors that influence metal sorption and the attainment of steady-state conditions:**

**Speciation of metals in solution.** Metal removal from solution increased with time, but it did so at different rates and to a different extent for each metal (Cd > Ni > Cu > Cr). This sequence of selectivity does not follow predictions for specific or non-specific metal sorption obtained from conventional batch studies (8). This is because in multicomponent systems the overall sorption results not only from the affinity of the solids for the metals but also from the effect DOC exerts on metal sorption. That is, in the multicomponent system, competition among different soil solid phases for metal sorption occurs simultaneously with metal complexation by DOC, similar to what occurs in natural soil environments. Multicomponent systems have been used previously to study the distribution and redistribution of Cu among organic matter, oxides, and silicate clays (1,13). Similar to the results of this study, Martínez-Villegas and Martínez (1) reported DOC interfered with Cu sorption by the same solid phases. Low molecular weight organic compounds that do not produce color (such as aliphatic compounds with a hard
character) must have been released to the solution phase initially, while higher molecular weight organics with conjugated double-bonds that produce characteristic yellow colors (i.e., fulvic and humic acids with a borderline or even softer character) must have been released after longer equilibration times. While DOC with a hard character can (immediately and continuously) complex hard acids (such as Cr$^{3+}$), DOC with a softer character (presumably released after longer equilibration times) can complex softer acids (such as Cd) more strongly since hard bases prefer to coordinate to hard acids and soft bases prefer to coordinate with soft acids (15). Rapid and continuous complexation of Cr$^{3+}$ by DOC could explain the linear relationship observed between total dissolved Cr and DOC (Figure 4.9a). On the other hand, a delayed complexation of Cd, along with an initially fast sorption of Cd (Figures 4.1 and 4.3a) by the solid phases (Figure 4.3c), could explain the non-linear relationship observed between Cd and DOC (Figure 4.9a). Hence, the total dissolved metal concentrations seem to respond, at least partially, to the different nature of DOC released over time and to the hard-soft character of the metals. As mentioned above, soluble organics were sorbed by the mineral phases present in the multicomponent system (Figure 4.2). It is therefore likely that decreases in total dissolved metals observed with increases in DOC (Figure 4.9b) were also due to sorption of metal-organic soluble complexes onto ferrihydrite and montmorillonite (Figures 4.2b and c).

The large percentage of labile Cd species (which includes the free hydrated metal ion and metal complexes that dissociate very rapidly to yield the free metal) early in the experiment (Figures 4.3a and b) might account for the initial sharp sorption of Cd (Figure 4.1). The formation of soluble non-labile Cd species might account for the incomplete sorption of Cd observed even after eight months of equilibration (Figures 4.1 and 4.3b).
In the case of Cu, however, the percentage of non-labile Cu species (Figure 4.4b) was significantly greater than non-labile Cd species (Figure 4.3b) and the initial sorption of Cu was lower than for Cd (Figure 4.1). It is therefore possible that the formation of non-labile Cu species in the multicomponent system hindered initial sorption of Cu. The continuous presence of non-labile Cu species with increasing time (Figure 4.4b) might prevent complete sorption of Cu by the solid phases (Figure 4.1). Similar findings have been reported elsewhere (1). Incomplete sorption of Cd, Cr, Cu, and Ni suggests that Fe-Ox, LC, and K-SWy2 were no longer capable of removing metals from solution thus inducing a steady state condition before saturation. This behavior indicates a high initial competition of the solids for metals that is outcompeted after longer equilibration times by the formation of strong metal-DOC complexes that remain in solution.

Speciation calculations using metal and DOC concentrations at specific times (data from Figures 4.2a and 4.9a) were performed using the speciation program Visual Minteq (16). These calculations predicted initial free metal species were highest for Cd (68 %) and Ni (44 %), low for Cu (2.5 %), and almost nonexistent for Cr (0.2 %) (Figure 4.7). These calculations also predicted free metal species decreased with time (from 68 to 21 % for Cd and from 44 to 9 % for Ni) while the formation of monodentate metal-fulvic acid species (from 30 to 70 % for Cd and from 55 to 91 % for Ni) increased. On the other hand, initial bidentate metal-fulvic acid species were highest for Cr (99.5 %), high for Cu (80 %), very low for Cd (0.4 %), and negligible for Ni. Opposite to free metal species, the percentage of bidentate complexes was predicted to remain constant (nearly 100 % for Cr) or to increase (from 80 to 97 % for Cu and from 0.4 to 9 % for Cd) with time. These speciation calculations are in reasonable agreement with our experimental Cd and Cu
data (Figures 4.3b and 4.4b) and provide important insights regarding the speciation of Ni and Cr in the multicomponent system. Furthermore, results from the speciation calculations support the framework on which we explain our observations: the initial formation of non-labile metal soluble complexes in the multicomponent system hinders metal sorption and that further increases in the percentage of non-labile species over time results in incomplete metal sorption by the solid phases.

**Speciation of metals in the solid phases.** Results from this study indicate solid phase sorption kinetics were metal specific (Figures 4.3c, 4.4c, 4.5a, and 4.6a). LC effectively sorbed all four metals initially and during the experiment period of the experiment. Sorption of Cd and Ni by LC proceeded faster than sorption of Cu and Cr. Similar to the initial sorption behavior of LC, K-SWy2 effectively sorbed metals early in the experiment; however, total Cd and Ni concentrations on K-SWy2 decreased with time. Fe-Ox did not sorb any metal at the onset of metal loading although a small quantity of metals sorbed onto the Fe-Ox phase after longer equilibration times. However, with the exception of Cd, Fe-Ox remained the least effective competitor in metal retention throughout the duration of the experiment. Furthermore, increasing metal sorption by Fe-Ox with increasing metal desorption by K-SWy2 (Figures 4.3c and 4.5a) suggests Fe-Ox served as a secondary sorbent in the redistribution of metals in the multicomponent system.

Similar to the results of metal speciation in solution, we find the trend of metal lability (defined as exchangeable metals) in the solid phase followed the order Cd > Ni > Cu > Cr. Furthermore, sorption kinetics (Figure 4.1) corresponds to characteristic times of fixation mechanisms (7). Cadmium underwent fast, and relatively large non-specific,
sorption by LC and K-SWy2 in the multicomponent system. In contrast, Cr underwent slower retention kinetics and stronger sorption by LC and K-SWy2. Hence, readily available metals (define as free and inorganic species and monodentate complexes in Figure 4.7) in solution undergo weak sorption promptly, while less available metals in solution undergo strong sorption slowly. Faster and weaker sorption of Cd as compared to Cu as well as desorption of readily sorbed Cd after longer equilibrations has been reported elsewhere (7).

Despite the well known capacity of iron oxides to sorb metals (17), we found Fe-Ox was the least effective competitor for Cu, Cr, and Ni sorption in the multicomponent system. We explain this low contribution as a result of both the blockage of Fe-Ox sites by sorbed DOC (Figures 4.2b and c) (1) and by a likely higher affinity between Cu, Cr and Ni and DOC than between these metals and iron oxides. Cadmium was an exception, as close to 12% of the added Cd was sorbed by Fe-Ox after 8 months. It has been suggested sorption of Cu by iron oxides is unlikely to occur in the presence of solid- and solution- phase organics (1). Similarly, our results suggest DOC outcompeted Fe-Ox in metal sorption as indicated by the initial negligible concentration of metals on Fe-Ox (Figures 4.3c, 4.4c, 4.5a, and 4.6a) despite high concentrations of metals (free, labile, and/or non-labile) in solution (Figures 4.3a, 4.4a, and 4.7). There is mounting evidence suggesting that the contribution of iron oxides to metal sorption in natural soil environments is low (1,9-12). Although Fe-Ox sorbed some Cd, Cr, Cu, and Ni with time, such sorption might have occurred indirectly through sorption of metal-DOC complexes. In fact, metal concentration on Fe-Ox increased linearly with increasing TOC (Figure 4.8a). It is therefore possible that sorption of metals by Fe-Ox occurred only
indirectly through the sorption of metal-DOC complexes rather than via direct metal-iron oxide interactions.

Different to Fe-Ox, the surface of K-SWy2 was active in metal sorption early in the experiment (Figures 4.3c, 4.4c, 4.5a, and 4.6a), especially when the concentration of TOC on K-SWy2 was low (Figures 4.2b and c). However, initial increases in TOC on K-SWy2 may be a result of sorption of Cr-DOC complexes (Figure 4.2c). We, in fact, observed a direct linear relationship between Cr and TOC in K-SWy2 during the entire period of the experiment (Figure 4.8b) that suggests the formation of ternary complexes (K-SWy2-Cr-DOC) on the surface of K-SWy2, thus protecting Cr against exchangeability. Similarly, Cu-DOC soluble complexes can undergo sorption forming K-SWy2-Cu-DOC ternary complexes that contribute to increasing DOC on K-SWy2.

Opposite to the behavior of Cr and Cu, the concentration of Ni and Cd in K-SWy2 decreased with increases in TOC. Decreasing Ni and Cd concentrations with increasing TOC suggest readily available metals (free metals and charged monodentate complexes) underwent sorption promptly (Figure 4.8b). These trends suggest the formation of Ni and Cd ternary complexes with K-SWy2 (K-SWy2-Ni-DOC and K-SWy2-Cd-DOC) is not significant.
Figure 4.1. Removal of Cd, Cr, Cu, and Ni from solution by the solid phases (Fe-Ox + LC + K-SWy2) as a function of time.
Figure 4.2. DOC as a function of time (a) and total organic carbon (TOC) on ferrihydrite (Fe-Ox) and montmorillonite (K-SWy2) as a function of time (b) and DOC (c).
Figure 4.3. Total dissolved and labile Cd (a) and relative proportions of labile and non-labile soluble Cd species (b). Total Cd (c) and exchangeable Cd (d) on individual solid phases as a function of time.
Figure 4.4. Total dissolved, labile, and free Cu (a) and relative proportions of free, labile, and non-labile soluble Cu species (b). Total Cu (c) and exchangeable Cu (d) on individual solid phases as a function of time.
Figure 4.5. Total (a) and exchangeable (b) Ni on individual solid phases as a function of time.
Figure 4.6. Total (a) and exchangeable (b) Cr on individual solid phases as a function of time.
Figure 4.7. Relative proportions of dissolved metal species predicted by Visual Minteq.
Figure 4.8. Metal concentration on ferrihydrite (Fe-Ox) (a) and montmorillonite (K-SWy2) (b) versus total organic carbon (TOC).
Figure 4.9. Total dissolved metal concentrations as a function of time (a) and DOC (b).
Figure 4.10. Cadmium, Cr, Cu, and Ni concentration in solution as a function of time.
References


Chapter 5
Conclusions and future work

Metal sorption by ferrihydrite, organic matter, and montmorillonite is disrupted by metal complexation processes and sorption of DOC on mineral phases. Metal complexation by DOC prevents complete metal sorption, and at the same time increases the potential for metal mobilization. The higher the affinity between DOC and the specific metal, the more likely the metal will remain in solution as a metal-DOC complex and the slower its rate of sorption. Conversely, the lower the affinity between DOC and the specific metal, the more likely the metal will undergo rapid sorption. Organic matter was the most effective solid phase in the sorption of metals followed by montmorillonite. Ferrihydrite was the least effective phase and seemed to sorb metals only indirectly via the sorption of metal-DOC complexes. DOC sorption onto ferrihydrite has the effect of blocking its reactive sites. DOC can also sorb on montmorillonite through a metal cation, forming montmorillonite–metal–DOC ternary complexes with specific metals. System perturbation, caused by the addition of solid phases, results in Cu desorption from all solid phases (ferrihydrite, organic matter, and montmorillonite) and in its redistribution between organic matter and montmorillonite, but not to ferrihydrite. These findings advance the knowledge of the most fundamental interactions among trace metals and soil phases. This knowledge is important in order to successfully decrease metal mobility and solubility when using amendments to remediate metal contaminated soils. Future work includes the study of similar metal–soil phase interactions using better approximations of natural soil environments such as well defined organo–mineral complexes that provide
intimate physical interactions among different phases. The use of organo–mineral complexes can allow to capture many possible combinations of static (e.g. clay mineralogy and organic matter content) and dynamic (e.g. microbial activity) soil properties occurring simultaneously among the many intimate associations of a soil particle. A first step to this future work is reported in Appendix B.
APPENDIX A

The soil as a reactor

No meaningful experiment can be conducted without a theoretical model. Using mass balance principles, the soil column in Figure 1a is regarded as a physical model for studying fundamental processes of metal retention in soils. Although a soil profile in nature is certainly a continuous system, we can take a snapshot of a convenient event at which water (or soil solution) does not move (i.e. saturation at any soil). This event denotes a flow condition of equilibrium and implies that the flux of water $q_w(z,t)$ through the soil profile is zero at any depth $z$ and at any time $t$ $q_w(z,t) = 0$. Hence, to simplify matters, equilibrium is assumed (note that the term equilibrium only denotes a flow condition). Second, we assumed that the soil has a given concentration of a trace metal (i.e. Cu). This concentration is the sum of pristine Cu plus anthropogenic Cu (e.g. addition of organic amendments, additives in animal feeds, and fertilizers; atmospheric deposition; accidental spills; etc.). Third, the inputs of Cu $I_{Cu,i}$ at the surface $z_0, i = 0$ are $I_{Cu,i=0}$. Similarly, the inputs of Cu $I_{Cu,d}$ above and $I_{Cu,i+\Delta z}$ below any layer of thickness $\Delta z$ are equal to zero for all times $\forall t \geq 0, I_{Cu,i} = 0$ and $\forall t \geq 0, I_{Cu,i+\Delta z} = 0$. A layer of thickness $\Delta z$ is a unit of longitude to describe the one-dimensional balance, and the sum of all the $z_i$ layers $\sum_{i=0}^{n} z_i$ accounts for the total depth $Z$. Fourth, the output (e.g. leaching) of Cu at the end $z_i = Z$ of the soil column is $I_{Cu,i=\infty}$. Fifth, temperature and Cu

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1 Fantastic title steal from Ritcher (1987)
concentration Cu are considered homogeneous through the whole soil profile. Finally, by closing-up to a layer $\Delta z$, we can see that a soil particle is an assemblage of three different phases (i.e. iron oxides, Fe-Ox; organic matter, LF; and silicate clay, KSWy2) that are interacting with the soil solution (Figure 1b). This assemblage is referred to as an organo-mineral complex.

Although these assumptions are seldom met exactly under natural conditions, they allow us to greatly simplify the complex reality of a soil system. In addition, there are cases of practical significance where these conditions are nearly met (e.g. heavy rains in dry climates with shallow soils overlying a fragipan and contaminated with heavy metals; saturated microenvironments in non-saturated soils; etc.).

Biochemical processes likely to occur between trace metals and soils are illustrated in Figure 1c. Note that soil solution acts as the medium that regulates the flow of a trace metal among the different gaseous, liquid, or solid phases. Since equilibrium was assumed, the flux of water is zero $q_s(z,t) = 0$. Additionally, Cu evaporation $q_g(z,t)$ and uptake $q_b(z,t)$ are zero by definition $q_g(z,t) \equiv 0$ and $q_b(z,t) \equiv 0$, respectively, due to the lack of Cu evaporation and to low biomass $W_b \approx 0$ respect to the total mass of the system.

Therefore, Cu can be only transferred to the three soil solid phases $q_{s,p}(z,t)$ or it can remain in solution as either free Cu ($Cu^{2+}$) or Cu complexed with organic or inorganic ligands $L^-$ (e.g. $CuL^-$). There is a number of processes taking place between Cu in solution and the solid phases (e.g. $q_{s,Fe-Ox}$, $q_{s,LC}$, $q_{s,KSWy2}$) for which Cu sorption is different than zero at any time greater or equal to zero $q_{s,p}(z,t) \neq 0, t \geq 0$ (Figure 1c). Note that in the previous description Cu does not transfer among the solid phases, but rather through
the solution phase. This physical model has been developed in the laboratory using a batch reactor ($\forall t \geq 0, I_{Cu,j} = 0$ and $\forall t \geq 0, I_{Cu,j+\Delta z} = 0$) with three compartments that share the same external solution and contain a fixed concentration of Cu (Figure 1d). Copper concentration in both soil solution and solid phases is a function of time $Cu = Cu(t)$ for all depths $z'$ contained in a layer $[z_i, z_{i+\Delta z}]$ for all times greater or equal to zero $Cu = Cu(t) \forall z' \in [z_i, z_{i+\Delta z}] \forall t \geq t_o$.

References


The soil as a reactor

Figure A.1. Schematic representation of a soil column as a reactor and the experimental approach used to study trace metal fate in soils using a multi-component model. Soil profile in (a) from USDA, 2006 and figure (c) modified from LINDSAY, 1979 and HESTERBERG, 1998.
Appendix B

Ternary Association of Soil Colloids

Copper distribution in ternary model associations of soil colloids containing alumina, hectorite, and humic acids.

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Abstract

Soils can prevent contamination of the environment by retaining trace metals on Fe/Al oxides, organic matter, and clays. Organo-mineral associations of these constituents might influence fixation or mobilization of trace metals in soils. For example, binary associations of humic acids-montmorillonite enhance trace metal sorption, while humic acids-ferrihydrite associations decrease it. Metal retention by organo-mineral complexes has not been well characterized. In order to further our understanding of metal-soil interactions, Cu was added to a laboratory-synthesized soil particle. The soil particle was prepared by coating a clay with aluminium oxides and organic matter, and Cu distribution among solids was followed over time using transmission electron microscopy (TEM) coupled with X-ray energy disperse spectroscopy (EDS). The objectives of this research were: (1) to synthesize a ternary model of soil colloids; (2) to image and analyze the ternary model of soil colloids; and (3) to determine the solid phase(s) responsible for Cu retention. Although TEM-EDX can certainly provide the clue and increase our capability of predicting the long-term fate of trace metals in soils, the project has proved to be very challenging and not conclusive data on which is the phase responsible for the Cu retention in the ternary model association is available yet.

Keywords: Copper, aluminum oxides, clays, hectorite, humic acids, sorption, organo-mineral associations, soil colloids, synthetic particles.
Introduction

Soils act as a barrier or filter that can prevent contamination of surface and ground waters, as well as the transfer of trace metals to biota. These beneficial effects of soils are a result of the retention capacity of its solid constituents (clays, oxides of Fe and Al, and organic matter) and their associations. These associations are usually emulated by organo-mineral complexes. An organo-mineral complex is a synthetic assemblage of two or more different phases (e.g. iron oxides, organic matter, and silicate clays) emulating a soil particle (Figure 1). Currently, studies on metal retention by organo-mineral complexes propose three different scenarios. The first, known as the **linear additive model**, proposes that an organo-mineral association act as a noninteractive sorbent mixture, and thus the sorption capacity of an organo-mineral association is the simple sum of the individual phases (I) (Figure 2). Zachara et al. (1994) (I) demonstrated that humic acids did not modify the intrinsic adsorptive behavior of gibbsite, Al-goethite, or kaolinite. Sorption of low aqueous concentrations of Co by humic acid-mineral associations simply augmented (10-60%), especially at pH 4.5-6.5 where humic acid adsorption onto the minerals was maximum and Co sorption onto the minerals was weaker. In contrast, the **supra-additive model** proposes that new high affinity metal complexation sites are created (2) and the overall adsorption of a specific metal might be underestimated if the linear additivity model is used to predict metal fixation in binary organo-mineral associations (3-8) (Figure 2). Tipping et al. (1983) suggested the creation of new, high affinity metal complexation sites in humic substances coating goethite. Finally, the **antagonistic model** proposes that phases interfere between each other and that the overall retention of a specific metal might be overestimated, if the **linear additive**
model is used (Figure 2). Cruz-Guzmán, et al. (2003) (9) found that humic acids onto ferrihydrite interfere with each other for metal sorption; most probably due to blockage of organic functional groups by ferrihydrite.

Using ternary model associations for sorption of inorganic and organic contaminants a group of researchers (9-11) has shown that the amount and nature of the surface that remains available after an inter-association of single soil constituents is the critical parameter in determining the sorptive behavior of the resultant aggregate. Hence, the intimate associations between individual components might cause some modification of their sorptive properties. Transmission electron microscopy (TEM) coupled with energy disperse spectroscopy (EDS) offers atomic scale imaging and qualitative elemental analysis which can be used for characterizing distribution and elemental associations of trace metals in organo-mineral complexes. TEM-ESD has proved to be useful for investigating trace metal distribution in the fine fractions of contaminated soils(12) and for characterizing structural alterations in the surface of clays due to metal sorption(13). TEM-EDS could help to elucidate the relative importance of mineral and organic phases in trace metal retention by soils. Learning how the contributions of trace metal binding by intermixed and complex surfaces in soil occur will provide critical information for a more adequate management of soils.

The objective of this paper was to identify the solid phase(s) responsible for the retention of Cu in a synthetic ternary model association of soil colloids (alumina / hectorite / humic acids) using TEM-EDS.
Materials and Methods

Solid Phases. The solid phases used as model soil colloids were aluminum oxide (Al-Ox), humic acids (HA), and hectorite (SHCa-1). Al-Ox was synthesized in the laboratory by dissolving 1.4 g of Al(NO$_3$)$_3$.9H$_2$O in 250 ml of deionized water and slowly (0.875 ml min$^{-1}$) adding 0.1 M KOH to bring the pH to 7 using a pH-stat device (Cole Parmer Eutech Instruments differential pH/ORP controller pH 200 and Master Flex C/L pumps). The precipitate was washed with deionized water and dialyzed (Spectra / Por 7 MWCO 10000) until free from electrolytes (final water conductivity < 3µS cm$^{-1}$). Al-Ox was also precipitated in the presence of hectorite as describe below. HA were used in this study as a prototype for soil organic matter. HA were purified from a humic acid, sodium salt from Aldrich by shaking a mass of 15 g with 100 ml of 0.5 mol l$^{-1}$ NaOH solution pH 13 for 18 h at 15 rpm in an end-over-end shaker. Both the NaOH solution and the humic acid suspension were degassed for 5 min with N$_2$ to minimized humic acid oxidation. The supernatant and the residue of the extraction were separated by centrifugation at 7500 rpm for 30 min. The supernatant was slowly acidified to pH <1 with 6 M HCl to precipitate humic acids. The precipitate was centrifuged at 7500 rpm for 30 min and washed several times until the absence of chloride ions in the washing water. The absence of chloride ions was verified by the absence of AgCl precipitate using a drop of AgNO$_3$. Purified HA were resuspended in 250 ml of deionized water to yield a concentration of 27.3 g l$^{-1}$. The CHN composition was 52.5 % C, 4.4 % H, and 0.63 % N. Hectorite (SHCa-1) was purchased from the Clay Minerals Society-Source Clay Repository and treated to remove carbonates and exchangeable divalent cations using 1 N sodium acetate buffered with acetic acid to pH 5 according to Jackson, 1956 (14).
Particles smaller than 2 µm were separated using sodium phosphate and ultrasound. The <2 µm fraction was collected and saturated with K⁺ using 1 M KCl (K-SHCa-1) and lyophilized (15). Hectorite was characterized for X-ray diffraction (XRD). Patterns of powdered samples were collected using a SCINTAG PAD V theta-2theta diffractometer with a liquid nitrogen cooled germanium solid state detector and CuKα radiation. All the chemicals used were trace grade.

**Ternary model associations of soil colloids.** A ternary association of Al-Ox / K-SHCa-1 / HA in a 1:10:1 ratio was prepared by precipitating Al-Ox on K-SHCa-1 and then adding HA. An aqueous solution 1.4 g Al(NO₃)₃.9H₂O in 250 ml deionized water was titrated against 1 M KOH to pH 7 with constant stirring and in the presence of 1 g K-SHCa-1. The precipitate (c.a. 1.1 g) was cleaned by dialysis until free of electrolytes (final water conductivity < 3 µS cm⁻¹). The precipitate and 917 µl of HA suspension were mixed in a 250 ml flask to form the ternary model association (Al-Ox / K-SHCa-1 / HA). The ionic strength (0.01 M), pH (6.0), and volume (250 ml) were adjusted with KNO₃, 1 M KOH, and deionized water, respectively. The suspension was transfer to a 500 ml high density polyethylene batch reactor. After equilibration for 24 h, an aliquot of 1.8 ml of 1000 mg l⁻¹ Cu(NO₃)₂ was added to the reactor to yield a concentration of 1500 mg Cu kg⁻¹ solids. The pH in the reactor was kept between 6 and 6.5 by addition of small amounts of 0.01 HNO₃ or 0.01 M KOH using a pH-stat device. The suspension in the reactor was kept under continuous stirring. Six more (control) reactors containing one single phase (Al-Ox, K-SHCa-1, or HA) with Cu and without Cu were also prepared. The reactors were sampled at specific time intervals (1, 3, 7, 15, and 28 days) for analyses of total dissolved
Cu and elemental analyses and imaging by transmission electron microscopy coupled with X-ray energy disperse spectroscopy (TEM-EDS) as described below.

**Analyses of dissolved Cu species.** Thirty ml samples, acidified and filtered (0.2 µm), were analyzed for total dissolved Cu. Total concentrations of Cu were determined by differential pulse anodic striping voltammetry (DPASV) using a Metrohm 797 VA Computrace ($E_d = 0.02V_{Ag/AgCl(satKCl)}, t_d = 120s, v = 15mVs^{-1}$).

**Electron Microscopy.** Specimens were prepared for TEM-EDS examination by transferring a few drops of suspension from each reactor onto a Mo 300 mesh grid. The grid was allowed to air-dry and stored until TEM-EDS analysis. Conventional TEM-EDS was performed using a Philips EM420T, tungsten-based 120 keV coupled with a Gresham Sirius 30Si(Li) X ray detector.

**Results and Discussion**

Aluminum oxide (Al-Ox), humic acids (HA), and hectorite (SHCa-1) were used as representatives of natural colloids from the fine fraction of soils. Their identification was consistent with data reported in the literature (16,17). Figure 3 shows the sorption of Cu by the ternary model association and the three single solid phases. Copper sorption by the ternary association reached 100 % at 1 day indicating a strong affinity of the ternary association for Cu. Similarly K-SHCa-1 reached 100 % of sorption of Cu at day. In contrast, Al-Ox and HA systems presented an initial sharp slope that decreased monotonously with time until it reached 70% and 65 % of sorption of Cu, respectively. Percentages of sorption lower than 100 % were perhaps artifacts likely due to dissolved Al-Ox and HA. In the case of Al-Ox, for example, it was clear some particles passed
though the 0.2 \( \mu \text{m} \) membrane. In the case of HA, the solution presented a brown transparent coloration that was not present in the reactor containing the Al-Ox / K-SHCa-1 / HA association. The reactors without Cu presented initial Cu concentrations lower that \( 10^{-5} \text{ mg l}^{-1} \).

Specimens of the Al-Ox / K-SHCa-1 / HA association as well as single Al-Ox and K-SHCa-1 with and without Cu are being imaged and analyzed by TEM-EDS. Although a large amount of images have been collected, there is not conclusive data showing which is the phase responsible for the Cu retention in the ternary model association yet.

**Acknowledgments**

This study is being funded by the NRI-USDA (2003-35107-13650) and the College of Agricultural Sciences at PSU. Nadia Martínez-Villegas is partially supported by CONACyT under fellowship No 154889. Special thanks to Ph. D. Trevor Clark for all his help and training on TEM. TEM work was done at MCL/MRI/PSU.
Figure B.1. Schematic representation of an anthropogenic trace metal entering the soil (a) and its microenvironment within (b) as well as its modeling in the laboratory as a ternary association of soil colloids contained in a batch reactor (c).
Figure B.2. Hypothetical kinds of interactions in binary organo-mineral associations.
Figure B.3. Sorption of Cu as a function of time.
References


(14) Jackson, M. L. *Soil chemical analysis -- advanced course*; Published by the author, Dep. of Soils, Univ. of Wis., Madison 6, Wis.: USA, 1956.


Dissolved Cu species in Facundo II and controls with Cu
Super Penguin to the... precipice
Nov 29, 2007

Free
- Al-Ox/K-SHCa-1/HA - Cu
- Al-Ox - Cu
- K-SHCa-1 - Cu
- HA - Cu

Labile
- Al-Ox/K-SHCa-1/HA - Cu
- Al-Ox - Cu
- K-SHCa-1 - Cu
- HA - Cu

Total
- Al-Ox/K-SHCa-1/HA - Cu
- Al-Ox - Cu
- K-SHCa-1 - Cu
- HA - Cu
Super Penguin to the... precipice
Nov 15, 2007
Hectorite saturated with K, but not CO$_3^{2-}$ removal.

Hectorite with CO$_3^{2-}$ removal and K-saturated
FACUNDO

Facundo I 100 mg kg\(^{-1}\) Cu - Brookhaven 2007

Two theta

0 d

100 d

60 d

30 d

15 d

7 d

1 d

0 d

135 d

109
Facundo II
Feb 04 2008

Ternary association (Al-Ox / K-SHCa-1 / HA)

- 0 days
- 1 day
- 3 days
- 28 days

Intensity

Field
Ternary association (Al-Ox / K-SHCa-1 / HA)

- 1 day
- 3 days
- 28 days
Dec 6, 2007
Dec 13, 2007
Jan 17, 2008
Jan 17, 2008
Jan 17, 2008
March 9, 2007
Minimum Mass Fraction Calculation

\[ 112.41 - 29.14 = 83.27 \]

\[ I_{Cu} = 112.41 \]

\[ I_{Cu}^b = 83.27 \]
APPENDIX C

Diffusion of Cu$^{2+}$ through a 0.01 µm polycarbonate membrane.

Diffusion of Cu$^{2+}$ through a 0.01 µm polycarbonate dialysis bag was tested. Seven dialysis bags (3.5x20 cm) (made from polycarbonate (PCTE) sheets (20x25 cm) from Sterlitech Corporation) were clamped (Spectra / Por closures 3.5 cm) and filled with 25 ml of 0.01 M KNO$_3$. These dialysis bags were placed in a 4 L beaker containing 3.5 L of 10 µM Cu$^{2+}$ in 0.01M KNO$_3$. The solution in the beaker was gently stirrer. External as well internal solutions were analyzed for Cu activity by Cu-ISE at specific time intervals. Copper activity inside the dialysis bag equaled the activity of the outside solution within 24 h.

Table C.1. Cupper activity inside and outside dialysis bag.

\[ pCu^{2+} = 10.6656 - 0.03645 \times E \text{ (mV)}; \ r=-0.9979 \]

<table>
<thead>
<tr>
<th>Time / hr</th>
<th>Inside</th>
<th>Outside</th>
<th>Cu$^{2+}$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>(Cu$^{2+}$) / M</td>
<td>E / mV</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3.587E-6</td>
<td>141.3</td>
</tr>
<tr>
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<td>5.47</td>
<td>1.093E-5</td>
<td>154.3</td>
</tr>
</tbody>
</table>
**Figure C.1.** Diffusion of Cu$^{2+}$ through the 0.1 um polycarbonate membrane.
Nadia Valentina Martínez Villegas

Education
•  •  •
2004 – 2008, Ph. D. in Soil Science, PSU, USA.

Refereed Papers
•  •  •

Teaching Experience
•  •  •
Thermodynamics II, UASLP, Instructor, Summer 2001; Fall 2002.
Chemistry A, UASLP, Instructor, 2 x Spring 2003.
Geometry and Trigonometry, UASLP, Instructor, 2 x Spring 2003.
Soil Environmental Chemistry, PSU, Teaching Assistant, Spring 2006.
Laboratory of Introduction to Soils, PSU, Instructor, Spring 2007.

Research Experience
•  •  •
Photocatalytic degradation of the herbicide Paraquat, UASLP, Summer Scholar, 1997.
Copper distribution in ternary model associations of soil colloids: TEM–EDS can provide the clue, Ph. D. Student, 2007 – 2008.
Remediation of As, Pb, and SO$_4^{2-}$ contaminated waters using a reactive permeable barrier, IPICyT, Postdoctoral Researcher, 2008 – 2009.

Distinctions
•  •  •
Fellowships
•  •  •

Grants
•  •  •
Copper (Cu) distribution in ternary model associations of soil colloids: TEM–EDS can provide the clue, CAS&DCSS/PSU, $2,000 USD, 2006.

Awards
•  •  •

Others
•  •  •