

Dissolved and Labile Concentrations of Cd, Cu, Pb, and Zn in Aged Ferrihydrite–Organic Matter Systems

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The relative efficiencies of an organic and a mineral component of soils in controlling Zn, Cd, Cu, and Pb solubility and dissolution initially and during aging at pH 5.5 for up to 200 days is investigated. Metal retention by a natural organic matter (leaf compost) and a mineral model system (ferrihydrite) were tested for the organic and hydrous ferric oxide components separately (ORG and HFO) and in a mixed system (HFO–ORG). Total dissolved (by ICP) and labile (by dpass) concentrations of metals in solution were measured. Initial Cd and Zn solubility in the systems followed the order: HFO > HFO–ORG > ORG. After aging for about 200 days, however, Cd and Zn solubility was HFO = HFO–ORG > ORG. Thus, the organic adsorbate proved to be more efficient in Zn and Cd removal from solution under the conditions used in this study. The HFO system resulted in the highest Cu solubility at intermediate aging times. However, during longer aging, total dissolved Cu increased in the ORG system whereas that in the HFO decreased, so that Cu solubility was lower in HFO after about 200 days. Lead solubility generally remained very low (<0.05 μM) except in the ORG system in which the total dissolved Pb reached 0.25 μM . The ORG system shows that about 75% of total dissolved Cu and 80% of total dissolved Pb exist as nonlabile organo-metal complexes, while soluble nonlabile complexes account for about 40% of dissolved Zn. Cadmium complexation (nonlabile) in the ORG system was minimal, thus Cd exists mostly in the free ionic form or as weak (labile) organic complexes.

Introduction

Iron oxides and organic matter coexist in soils and serve as reactive adsorbents of heavy metals. Both have a high surface area and a high reactivity that is associated with surface functional groups (1). Iron oxides and organic matter are intimately associated in soils, probably as oxide–organic complexes; thus, their individual function is difficult to discern. The tendency of a metal to react with the mineral or the organic component of soils could potentially limit its solubility, which will ultimately determine its bioavailability and toxicity. Due to competition among multiple and mixed solid phases for metal retention, it is difficult to assess what soil component (mineral or organic) is responsible for the long-term solubility control of metals in soils. This results in uncertainty about the importance of reactions with organic

and iron oxide colloids as mechanisms by which metal ions are retained in soils.

Controls on metal solubility by oxides have been attributed to ion exchange reactions, specific adsorption to surface hydroxyl groups, coprecipitation, and at higher loadings and pH, multinuclear complex or mixed-cation hydroxide complex formation at the surface or precipitation as the discrete oxide or hydroxide. Metal retention by hydrous ferric oxide follows the general order: $\text{Pb} \geq \text{Cu} \gg \text{Zn} > \text{Cd}$. Studies on metal adsorption and coprecipitation with iron oxides show a retention time (aging) effect that usually results in decreased metal solubility (2–5). Although iron (hydr)oxides may be an important sink for metal retention in the long term and have been used in attempts to remediate metal-contaminated soils, Martínez and McBride (ref 2 and references therein) showed that, even when metals are coprecipitated with iron (hydr)oxides and aged for long periods of time, residual solubilities of free Cd, Cu, and Zn can be high enough to reach reported phytotoxicity values or allow excessive uptake by crops.

Soil organic matter has been recognized as a critical component in the retention of heavy metals in soils (6, 7). Organic matter contains S, O, and N functional groups that bind heavy metals strongly. X-ray absorption spectroscopy (XAS) and electron spin resonance (ESR) studies indicate that Pb, Cu, and Zn form inner-sphere complexes with soil humic substances (8–10). Lead, Cu, and Zn coordinate with oxygen ligands while Zn also coordinates with sulfur (thiol) containing functional groups. Although metal dissolution during long-term decomposition of organic matter has not been investigated in detail, several studies indicate that metals become more available after incubation of soils amended with metal-contaminated organic materials such as sewage sludge (11–13). Increases in metal availability were related to organic matter decomposition. Furthermore, organic matter decomposition produces soluble organic ligands (dissolved organic carbon, DOC) that may change metal speciation in solution, thus influencing metal adsorptivity, mobility, toxicity, and bioavailability. Nevertheless, field studies have shown that chemical extractability (14) and bioavailability (15) remain constant with time after the sludge application is terminated.

Few studies have compared the relative importance of an organic and a mineral soil component in their ability to remove metals from solution (16–20). In a study in which individual materials (organic and iron oxide) were equilibrated to simulate a multicomponent system (20), Cu was shown to concentrate in the organic component. Using single systems, organic matter was found a more efficient adsorbent in removing Cu from solution at pH 5–5.5 than goethite (16). In the acid pH range (pH < 6.5), mineral-bound organic matter enhances the adsorption of some metals (e.g., Cu and Co), thus reducing their solubility (18, 19). At neutral pH, the mineral component controlled metal solubility while dissolved organic matter increased metal dissolution by forming soluble metal–organic complexes.

This study investigates the initial solubility and long-term (up to 200 days) dissolution of important trace elements (Cd, Cu, Pb, and Zn) from separate and mixed iron oxide–organic matter systems. Metal–organic matter (ORG) and ferrihydrite (HFO) and ferrihydrite–organic matter (HFO–ORG) metal coprecipitates are formed, and their efficacy in maintaining low metal concentrations in solution is compared. The mixed system is used in an attempt to represent a “model soil”. Solution concentration of metals are determined where total dissolved concentrations are measured by inductively coupled

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plasma emission spectrometry (ICP), and labile concentrations are measured by differential pulse anodic stripping voltammetry (dpasv). Discrimination between total dissolved and labile concentrations of metals provides information on the formation and stability of soluble metal–organic complexes.

DPASV-Labile Metals. Labile metal represents the fraction of total dissolved metal determined by stripping analysis. This fraction includes the free hydrated metal ions and the labile metal complexes, which are complexes that dissociate very rapidly to yield the free metal (21). It is often assumed that the labile metal represents the metal fraction that is bioavailable and, therefore, similar to the toxic fraction of the dissolved metal (22). Differential pulse anodic stripping voltammetry (dpasv) involves two steps. In the first, the deposition (preconcentration) step, metal ions in the sample solution are reduced at negative (cathodic) potential and concentrated into a mercury electrode. The amalgamated metals are measured in the second (stripping) step by applying a positive (anodic) potential scan and measuring the peak currents produced as the system reaches the oxidation potential of the metals.

Several factors affect what would be measured as dpasv-labile metals. In the theory of labile/inert discrimination, a lability criterion has been developed using the ratio of the kinetic current to the diffusion current (i_k/i_d) as an index of the lability of complexes. The kinetic current (i_k) is the current observed for a metal ion complex and depends on the rate constant for dissociation of the complex. The diffusion current (i_d) is the current for the same concentration of the metal ion but in the absence of ligand. It depends on the time necessary to cross the diffusion layer, which in turn depends on the layer thickness and the diffusion coefficient of the metal ion. Using this criterion, together with stability (thermodynamic equilibrium parameters (e.g., dissociation and formation constants), metal complexes are calculated to be labile or nonlabile by anodic stripping methods [for details on this theory the reader is referred to a review by Florence (23) and the references therein]. The deposition potential, if sufficiently negative, may lead to the direct reduction of some metal complexes. Also, the complex is dpasv-labile if the rate of dissociation is similar (rapid) as compared to the time scale of the stripping measurement. Thus, based on these parameters and on empirical measurements, the free metal ion and weak inorganic and organic complexes are dpasv-labile. Among the characteristics determining the lability of metal-organic complexes are the degree of aromaticity of the organic material and the functional group involved in complexation. Fulvic acids were suggested to form both labile and nonlabile complexes with Cu (24). The fulvic acids varied in degree of aromaticity, with the nonlabile Cu–fulvic acid complexes resulting from the fulvic acid with high aromatic proton signal (by nuclear magnetic resonance, NMR). Also, it has been suggested that Cu binding involves S and N functional groups to form nonlabile organic complexes (23).

Experimental Section

Batch-type reaction experiments were used to monitor the total dissolved (determined by inductively coupled plasma emission spectrometry, ICP) and labile (determined by differential pulse anodic stripping voltammetry, dpasv) solution concentrations of Cd, Cu, Pb, and Zn after all four metals in combination were sorbed or coprecipitated and aged in single and mixed solid phases. The pH of the suspensions was initially raised to pH 6, because this is a pH typical for soils and it prevents the precipitation of metals. The suspension pH was stabilized at pH 5.5 during aging and was kept at that value. All aging experiments used mixed batch reactors that were maintained at room temperature (23 °C) in the presence of ambient CO₂. The metal concen-

trations chosen (in all experiments) were based on approximate levels that may occur in the fine fraction of soils (that fraction that is considered most reactive) subjected to heavy sewage sludge application under the current U.S. EPA regulations and that have been observed in a number of contaminated soils. They are as follows [mg of metal (kg of solid)⁻¹]: 100, 1500, 1500, and 3000 mg kg⁻¹ for Cd, Cu, Pb, and Zn, respectively, and they represent the concentrations in the solid phase if complete sorption or coprecipitation occurred. The solid phases studied were hydrous ferric oxide (HFO), organic matter (ORG), and a mixed solid containing hydrous ferric oxide and organic matter (HFO–ORG). The ICP detection limits (3σ criterion) were estimated to be 0.03, 0.003, 0.03, and 0.05 μM for Zn, Cd, Pb, and Cu, respectively, by the method used in this study. We used an axial ICP–OES instrument manufactured by Trulogic Systems, Inc. DPASV detection limits are about one-fifth of those determined by ICP. Analytical methods are within a 5% RSD.

Metals–Iron Oxide Coprecipitate (HFO). A coprecipitate was formed by the titration of solutions containing 4.95×10^{-3} M Fe [as Fe(NO₃)₃], 3.91×10^{-7} M Cd (as cadmium acetate), 1.04×10^{-5} M Cu (as copper acetate), 3.3×10^{-6} M Pb (as lead acetate), and 2.02×10^{-5} M Zn (as zinc acetate) to pH 6 with 0.1 M KOH in 1 mM KNO₃ background electrolyte and aged for up to 200 days. The Fe concentration used was calculated to yield 0.33 g of iron oxide (as α-FeOOH). The concentrations used represent loadings of 0.004 mol of Zn²⁺/mol of Fe³⁺, 7.9×10^{-5} mol of Cd²⁺/mol of Fe³⁺, 0.0006 mol of Pb²⁺/mol of Fe³⁺, and 0.002 mol of Cu²⁺/mol of Fe³⁺; all four metals in combination were coprecipitated with Fe³⁺ for a total of 0.0069 mol of M²⁺/mol of Fe³⁺. At the end of the titration (pH 6), the added OH/Fe ratio was 3.40 in a total volume of 750 mL. This suspension was sampled periodically for metal analysis and pH measurement. At each time interval, a subsample was removed and centrifuged for 10 min at 15 000 rpm (27 000 rcf). The supernatant was then filtered through a 0.2-μm polycarbonate membrane filter; acidified by the addition of 1 M HCl; and analyzed immediately for labile Cd, Cu, Pb, and Zn by dpasv. Acidification of the supernatants, used to stabilize the solutions during storage, had no effect on dpasv-labile metals in the HFO system because of the absence of soluble metal complexes in this system (2). The filtered supernatants were also analyzed for total dissolved Cd, Cu, Pb, and Zn by ICP. Although the pH of the suspension was initially raised to 6, the HFO coprecipitate was stabilized at a pH of about 5.5 after about 100 days.

Metals–Organic System (ORG). A leaf compost (predominantly sugar maple) was used as a natural model system for organic matter in our experiments. It was collected from a rural location near Ithaca, NY, air-dried, ground in a Waring blender, and sieved to <1 mm. The leaf compost had a pH of 7.12 in water and an organic carbon content of 37.9% (by a combustion method). Elemental analysis of the leaf compost, performed by ICP of a HNO₃ digest, was 2.5, 2.6, 56, 4.8, 4.9, 98, 2.5, 19, 18, and 188 mg kg⁻¹ of P, S, Ca, Fe, Al, Si, Cd, Cu, Pb, and Zn, respectively. These values represent the average of duplicate analysis. The pH of the leaf compost was adjusted to about 5.5 by addition of small quantities of 1 M HNO₃, dialyzed to remove excess salts, and freeze-dried prior to use.

The pH of a suspension containing Cd (3.91×10^{-7} M as cadmium acetate), Cu (1.04×10^{-5} M as copper acetate), Pb (3.3×10^{-6} M as lead acetate), Zn (2.02×10^{-5} M as zinc acetate), and leaf compost (0.33 g) was raised to pH 6 by using 0.1 M KOH in 1 mM KNO₃ background electrolyte (total volume of 750 mL) and aged for up to 200 days. Small aliquots of base were needed since the suspension's initial pH was 4.30. In this system, the pH stabilized at about 5.8 so that addition of acid (1 mM HNO₃) was necessary to keep the pH

constant at 5.5 using a pH-stat device. The suspension was sampled periodically for metal analysis as described previously. Nonacidified, filtered supernatants were analyzed by dpass immediately after their collection. Filtered and acidified (for sample preservation) supernatants were analyzed by ICP. The supernatants obtained from this system (ORG) had a yellow color even after filtration. The yellow color was not present in the HFO or HFO-ORG systems, both of which had colorless supernatants.

Metals-Iron Oxide-Organic Coprecipitate (HFO-ORG). A coprecipitate was formed by increasing the pH of a suspension containing Cd (7.82×10^{-7} M as cadmium acetate), Cu (2.08×10^{-5} M as copper acetate), Pb (6.6×10^{-6} M as lead acetate), Zn (4.04×10^{-5} M as zinc acetate), Fe (4.95×10^{-3} M as $\text{Fe}(\text{NO}_3)_3$), and leaf compost (0.33 g) to pH 6 by using 0.1 M KOH in 1 mM KNO_3 background electrolyte (total volume of 750 mL) and aged for up to 200 days. Thus, a 1:1 iron oxide:leaf compost ratio (by weight) was used in the HFO-ORG system. The suspension had an initial pH of 2.6. At the end of the titration, the OH/Fe ratio was 3.23, and the pH was 6, but decreases in suspension pH with aging of the HFO-ORG coprecipitate were observed. The pH was maintained at 5.5 throughout the experiment using a pH-stat device. The suspension was sampled periodically in the same manner as described above, and metal analysis was performed as for the ORG system.

Base and/or acid additions were insignificant to the total volume of the systems maintained at constant pH over the aging period. Control experiments without trace metals were conducted in the same manner as described above and yielded metal solution concentrations below the detection limits of the methods used in this study. The concentration of dissolved organic carbon (DOC) in the supernatants was estimated by colorimetry. The absorbance of the supernatants was calibrated with the absorbance of soil extracts (at $\lambda = 254$ nm) of known DOC (25). Sulfur (organic plus sulfate) in the supernatants was determined by ICP. The solid phases were characterized by infrared (FTIR) and X-ray diffraction (XRD) as described previously (26).

Results and Discussion

The solid phases were characterized to test for the presence of iron oxide in the HFO-ORG system since organics may interfere in their formation (1). X-ray diffraction provided evidence for the formation of noncrystalline iron oxide after coprecipitation in the presence of the organic material as a 2-line ferrihydrite was present in both the HFO and HFO-ORG systems. Thus, initial Fe^{3+} complexation with organic matter did not prevent oxide formation, although some complexation may have occurred. Furthermore, inspection of the HFO-ORG system by FTIR confirmed the presence of a solid phase with characteristic absorption bands of both the HFO and ORG systems.

Metal Dissolution from Single and Mixed Systems. Variable concentrations of Cd, Cu, Pb, and Zn remained in solution after their simultaneous retention by organic matter (ORG) and coprecipitation with iron oxide (HFO) and an iron oxide-organic matter mixed (HFO-ORG) system (Figures 1 and 2, Table 1). Cadmium equilibration with ferrihydrite (HFO) resulted in about $0.3 \mu\text{M}$ Cd in solution even after 200 days (Figure 1). Initial soluble Cd in the organic (ORG) and mixed (HFO-ORG) systems was lower than in the HFO system; however, solubility in these organic-containing systems increased with time (Figure 1 and Table 1). Yet, after aging for about 200 days, Cd solubility showed a lower value in the ORG system and reached a similar (higher) concentration in the HFO and HFO-ORG systems. The solubility behavior of Zn was similar to that of Cd in the HFO-ORG and ORG systems, with Zn solubility increasing with time. This behavior of Cd and Zn suggests increases in

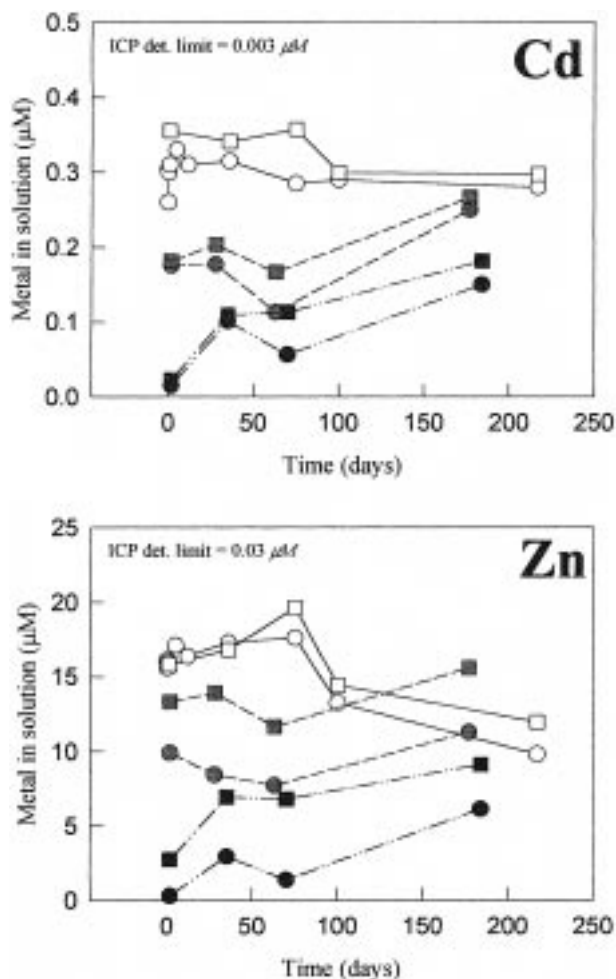


FIGURE 1. Total dissolved (ICP) and labile (ASV) concentrations of Cd and Zn in ferrihydrite (HFO), organic matter (ORG), and ferrihydrite-organic matter (HFO-ORG) systems as a function of time. Symbols as in Figure 2.

dissolved organic matter resulting in the release of metals into solution. Some reduction in dissolved Zn was observed from the HFO system after 200 days of equilibration (Figure 1). After 200 days of aging, labile Zn concentrations were similar in the HFO and HFO-ORG systems and lower in the ORG system. In general, and during reaction for up to 200 days, dissolved (both total and labile) Zn and Cd concentrations decreased in the order: HFO \geq HFO-ORG $>$ ORG, indicating that the 100% organic system was more effective in Zn and Cd removal from solution (Figure 1). Cadmium and Zn solubilities in the HFO-ORG system, although ferrihydrite was formed, suggest that some of the Fe reacted with organic matter functional groups, forming iron-organic matter complexes. This is suggested in a schematic diagram showing the effect organic matter content has on the formation of various iron oxides (1). As in our experiments (HFO-ORG system), high organic matter content and high Fe supply (1:1 organic matter:iron oxide ratio by weight) can result in the formation of ferrihydrite and iron-organic complexes. Iron complexation with organic matter will block and therefore reduce the quantity of adsorption sites otherwise available for Zn and Cd complexation. Thus, Zn and Cd solubilities encountered in the HFO-ORG system can be explained by the blockage of reaction sites with Fe. This effect is not seen for Pb and Cu (Figure 2), presumably because of their stronger affinity for organic matter, allowing them to compete effectively with Fe and outcompete Zn and Cd for reaction sites (27, 28). Kerndorff and Schnitzer (28) showed that, as the pH increases from 2.4 to 5.8, Pb and Cu

TABLE 1. ICP-Total Dissolved Metal at Initial and Final Equilibration Times Expressed as % of Total Metal Added^a

system	equilibration	metal in solution (% of total added)			
		Zn	Cd	Pb	Cu
HFO	initial	34 (35)	40 (29)	0 (0)	4.8 (1.3)
	final	26 (21)	33 (32)	0 (0)	2.0 (2.4)
HFO-ORG	initial	29 (21)	20 (20)	0 (0)	1.1 (1.9)
	final	34 (25)	30 (28)	0 (0)	0.8 (0.4)
ORG	initial	6.0 (0.7)	2.6 (1.7)	0.8 (0.1)	2.3 (0.9)
	final	20 (13)	20 (17)	3.7 (0.4)	8.7 (2.1)

^a Numbers in parentheses are dpassv-labile metals (as % of total metal added).

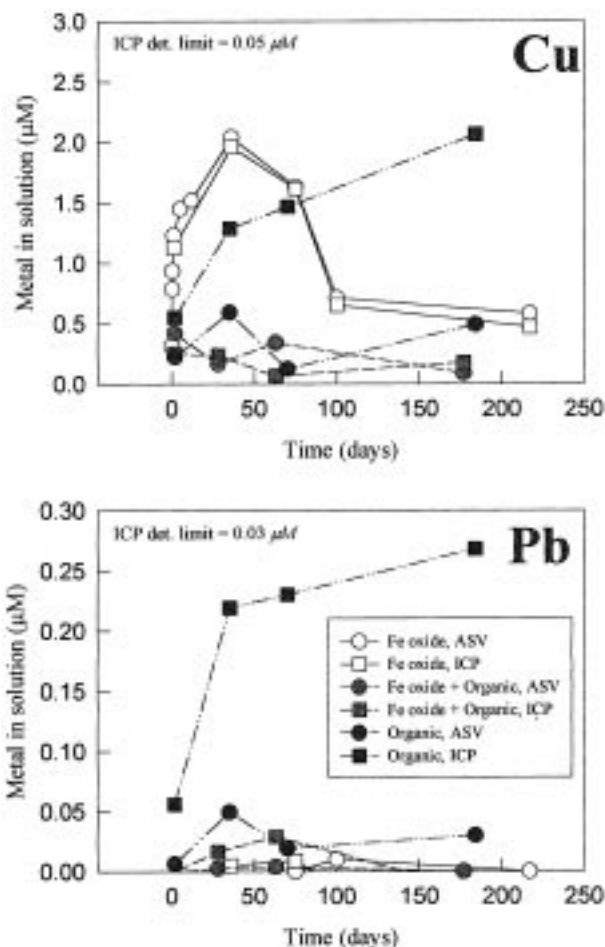


FIGURE 2. Total dissolved (ICP) and labile (ASV) concentrations of Cu and Pb in ferrihydrite (HFO), organic matter (ORG), and ferrihydrite-organic matter (HFO-ORG) systems as a function of time.

become more efficient competitors with Fe for reaction sites on humic acid.

As shown in Figure 2, the HFO coprecipitate resulted in the highest concentration of dissolved Cu at intermediate aging times (discussion on possible mechanisms can be found in ref 2). However, after about 200 days, the HFO-ORG system controlled Cu solubility at the lowest level (Figure 2). Copper dissolution from the ORG system was very pronounced, with solubility increasing over the period of the experiment. Reasons for this will be discussed in a later section. Lead was efficiently removed from solution by the HFO and HFO-ORG coprecipitates (Table 1 and Figure 2). Its solubility ranged from below 5 nM to 0.05 µM, suggesting a high efficiency of iron oxide and mixed iron oxide-organic matter in reducing Pb concentrations in solution (Figure 2). As for Cu, total dissolved Pb in the ORG system increased with

aging, and possible mechanisms for this will be discussed in a later section.

The results obtained for Pb and Cu suggest that these elements compete more effectively than Zn or Cd with Fe for complexation sites in the HFO-ORG system. Comparison of metal dissolution (for up to 200 days) from single and mixed systems indicate that ferrihydrite alone is not as efficient an adsorbent for Zn, Cd, and Cu as organic matter or a mixed ferrihydrite-organic matter system, although it is very effective in removing Pb from solution (Table 1).

Concentration in Solution: Total Dissolved (ICP) and Labile (dpassv) Metals. Total dissolved (by ICP) and labile (by dpassv) concentrations of Cd, Cu, Pb, and Zn were similar in the HFO system, indicating that all dissolved metals in this pure mineral system were in the free cation or labile (inorganic) complex form. In contrast, there were differences between total dissolved and labile concentrations of Zn in the HFO-ORG and ORG systems and of Cu and Pb in the ORG system (Figures 1 and 2). During sampling, it was noticed that the supernatants obtained from the HFO and HFO-ORG systems were colorless whereas the supernatants obtained from the ORG system were yellow even after filtration. Thus, we estimated dissolved organic carbon (DOC) in the systems (by colorimetry) and found increased concentrations of DOC in the ORG system as aging time increased (Figure 3). No DOC was detected in the HFO-ORG system by the method used in this study. However, this does not necessarily rule out the presence of soluble low molecular weight organic compounds as aliphatic compounds do not produce color. Increases in DOC with aging of the systems can be accounted for by (i) microbial oxidation of organic matter and (ii) physical disruption and dissolution induced by prolonged stirring. The lack of measurable DOC (by colorimetry) in the HFO-ORG system suggests that either soluble organics are adsorbed by the iron oxide or that the iron oxide acts as a flocculant, preventing oxidation and/or physical disruption of the organic material. In addition, although DOC was not detected colorimetrically in the HFO-ORG system, the concentration of soluble S increased after ~175 days (0.04-0.14 mg of S L⁻¹ in solution). An increase in soluble S was also observed in the ORG system (0.09-0.52 mg of S L⁻¹ in solution). This result may indicate an increase in soluble organics (organic S) or of dissolved sulfate due to organic matter decomposition.

Differences in total dissolved (ICP) and labile (dpassv) concentrations of Zn indicate some degree of Zn complexation in the HFO-ORG and ORG systems (Figure 1 and Table 1). Although iron oxide serves as a sink for soluble organics, some may remain in solution and form soluble complexes with Zn. These zinc-organic complexes are evidently not all dpassv-labile (Figure 1). Thus, total dissolved Zn consists of the free metal cation and dpassv-labile and nonlabile complexes. As the dissolved concentration of Zn increases with DOC in the ORG system (Figure 3), labile Zn increases proportionately. That is, at low DOC content (1.7 days) most of the dissolved Zn is complexed (nonlabile), but as DOC (and time) increases, the nonlabile (complexed) Zn is constant

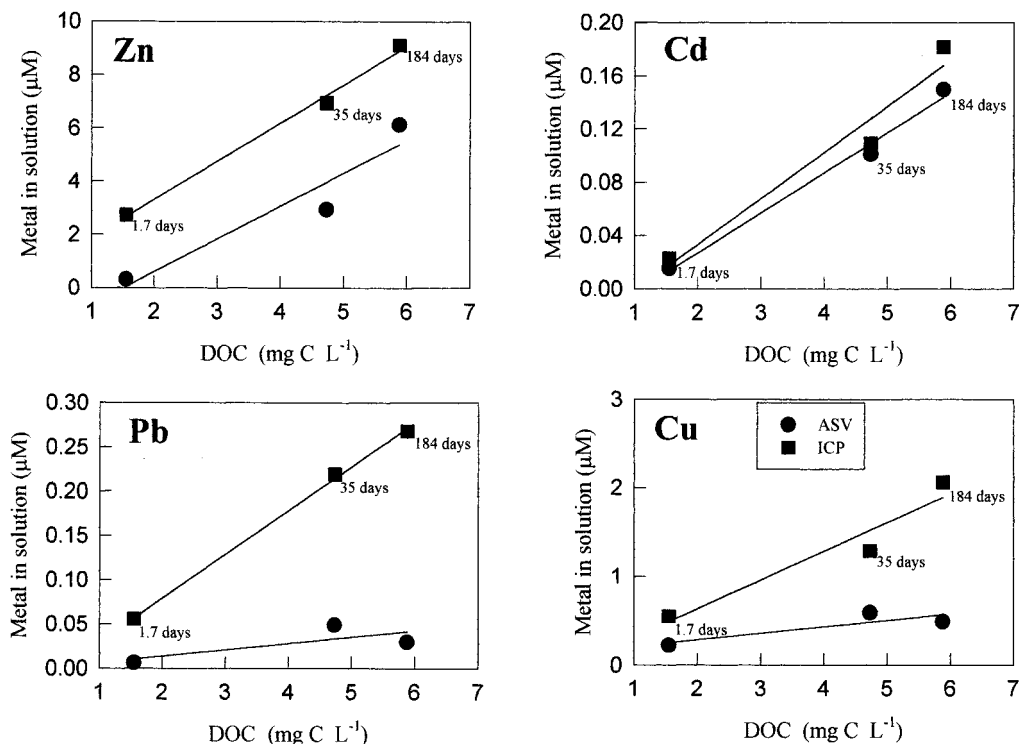


FIGURE 3. Relationship between dissolved metals (ICP-total dissolved and ASV-labile) and dissolved organic carbon (DOC) in the organic (ORG) system.

at about 40% of the total dissolved concentration; thus, labile Zn increases with time.

Concentrations of total dissolved and dpasv-labile Cd are similar in the HFO-ORG and ORG systems (Figure 1). But since dissolved Cd (both total and labile) increases in proportion to DOC in the ORG system (Figure 3), it is reasonable to suggest that low molecular weight organics react with Cd to form dpasv-labile complexes that have the effect of increasing Cd solubility over time (21). Then Cd exists in solution as both the free ionic cation and as weak (dpasv-labile) organic complexes. It has been shown that >80% of DOC has a molecular weight of >10 000 (29). However, Cd is mostly associated with the DOC fraction with molecular weight between 1000 and 10 000 (29).

Total dissolved and dpasv-labile concentrations of Pb and Cu in the HFO and HFO-ORG coprecipitates are similar (Figure 2). Thus, in the systems containing HFO, dpasv-labile equates to total dissolved metal, and Pb and Cu exist as free ions and labile complexes in solution. Lead and Cu dissolution from the HFO-ORG system is limited to very low concentrations (Figure 2). Although Pb and Cu react strongly with dissolved organic matter that promotes metal dissolution from adsorption sites (1, 30), the HFO-ORG system is evidently very efficient in Cu and Pb removal from solution (Table 1). This is probably the result of the high affinity that iron oxides and organic matter have for Pb and Cu and to the tendency of Pb and Cu to form complexes with high molecular weight soluble organics, which are then preferentially adsorbed by iron oxide surfaces. This leaves little Pb or Cu in solution, mostly in the uncomplexed form.

The relationships between Pb and Cu dissolution and dissolved organic carbon (DOC) in the ORG system are presented in Figure 3. DPASV-labile concentrations of Pb (0.006–0.050 μM) and Cu (0.2–0.5 μM) remain low with aging despite increases in DOC. However, total dissolved concentrations of Pb and Cu increase linearly with DOC, suggesting Pb and Cu complexation with nonlabile soluble organics (Figure 3). After equilibration of the ORG system for 184 days, 80% of the total dissolved Pb and 75% of the total dissolved

Cu were complexed. Humic and fulvic acids are known to reduce the dpasv-labile concentrations of Pb and Cu (31). Similar correspondence between DOC concentrations and dissolved Cu and other metals has been observed in soils (32, 33), suggesting that DOC controls solubility of some metals.

Differences between total dissolved and labile metal concentrations follow the trend: Pb (ORG) \geq Cu (ORG) > Zn (ORG and HFO-ORG) \gg Cd (ORG and HFO-ORG). These results could be explained by competition among metals for dissolved organic carbon since Cu and Pb complex more strongly with organic matter than Zn and Cd (34). This competition effect was investigated by Piotrowicz et al. (24) in a study in which fulvic acid was added to a solution containing Pb, Cu, Zn, and Cd. After fulvic acid addition, all the Cd remained labile and only part of the Zn became nonlabile.

Environmental Implications. The concentration of dissolved trace metals depends strongly on the particular metal and adsorbent. After equilibration for about 200 days, labile concentrations of Cu and Pb were particularly low in the HFO-ORG and HFO systems, respectively. The organic material limited labile Cd and Zn solubility more effectively than iron oxide. Increases in DOC with aging, however, were accompanied by increases in dissolved concentrations of Zn and Cd (ORG system). In the case of Cd, and to a lesser extent Zn, increases in the labile concentrations of these metals (which is believed to represent the metal fraction that is bioavailable and potentially toxic) also occurred over time. This time-dependent increase in metal lability suggests that decomposition or hydrolysis of organic matter in metal-contaminated soils could increase metal solubility or toxicity. It is recognized, however, that laboratory studies may need corrections for ionic strength, solid concentration effects (solid:solution ratio), and ion competition (e.g., Ca) to make a more representative comparison. Our experiments were run for about 200 days, and although our natural organic system (leaf compost) was relatively stable to decomposition, this equilibration time was sufficient for DOC to appear in

the system. Increases in DOC from the ORG system promoted the formation of soluble (nonlabile) organic complexes with Cu and Pb, which could in field situations enhance metal mobility through the soil. However, mixed solid phases (iron oxides and organic matter in soil systems for example) may provide favorable conditions for readsorption of copper- and lead-organic complexes, as suggested by the low concentrations of dissolved Cu and Pb found in the HFO-ORG system.

Acknowledgments

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