Effects of incubation on solubility and mobility of trace metals in two contaminated soils

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"Capsule": Iron is important in controlling metal solubility and mobility in flooded soils.

Abstract

Much research has focused on changes in solubility and mobility of trace metals in soils under incubation. In this experiment, changes in solubility and mobility of trace metals (Pb, Cu and As) and Fe in two contaminated soils from Tampa, Florida and Montreal, Canada were examined. Soils of 30 g were packed in columns and were incubated for 3–80 days under water-flooding incubation. Following incubation, metal concentrations in pore water (water soluble) and in 0.01 M CaCl₂ leachates (exchangeable + water soluble) were determined. While both soils were contaminated with Pb (1600–2500 mg kg⁻¹), Tampa soil was also contaminated with As (230 mg kg⁻¹). Contrast to the low pH (3.8) of Tampa soil, Montreal soil had an alkaline pH of 7.7 and high Ca of 1.6%. Concentrations of Fe(II) increased with incubation time in the Tampa soil mainly due to reductive Fe dissolution, but decreased in the Montreal soil possibly due to formation of FeCO₃. The inverse relationship between concentrations of Pb and Fe(II) in pore water coupled with the fact that Fe(II) concentrations were much greater than those of Pb in pore water may suggest the importance of Fe(II) in controlling Pb solubility in soils. However, changes in concentrations of Fe(II), Pb, Cu and As in pore water with incubation time were similar to those in leachate, i.e. water soluble metals were positively related to exchangeable metals in the two contaminated soils. This research suggests the importance of Fe in controlling metal solubility and mobility in soils under water-flooded incubation.

1. Introduction

Trace metal mobility and solubility in soils are of environmental significance due to their potential toxicity to both humans and animals (Chirenje et al., 2003; Ma et al., 1995). Trace metal mobility is closely related to metal solubility, which is further regulated by adsorption, precipitation and ion exchange reactions in soils. Although much effort has been spent on modeling trace metal solubility (Cederberg et al., 1985; Martin et al., 2003; Sposito, 1984), such predictions under field conditions suffer from much uncertainty. This is partially due to the difficulty in assessing the effects of dynamic soil solution chemistry on trace metal speciation (Jensen et al., 1999). However, changes in soil solution chemistry, such as pH, redox potential and ionic strength, may also significantly shift the retention processes of trace metals by soils (Gerringa et al., 2001). These effects may be further complicated by ligand competition from other cations (Amrhein et al., 1994; Norrstrom and Jacks, 1998).

Soil redox status varies temporally and spatially. In a surface soil, it is influenced by rainfall, bioactivity, and changes in land use, whereas in vadose zones it varies mostly with the fluctuation of water table (Boul et al., 1997). Reduction in redox potential may cause changes in metal oxidation state, formation of new low-soluble minerals, and reduction of Fe, resulting in release of associated metals (Amrhein et al., 1994; Baumann et al., 2002; Chuan et al., 1996; Masscheleyn et al., 1991). Various techniques have been developed to experimentally evaluate the effects of redox status on metal mobility. These include redox-controlled batch experiments...
using suspensions (Chuan et al., 1996; Masscheleyn et al., 1991), saturated/unsaturated (aerobic/anaerobic) incubation (Amrhein et al., 1994; Karczewska, 1996; Ma et al., 1995) and water-flooding incubation with soils (Karczewska, 1996; Dong et al., 1999). However, contradictory data may result when different techniques are employed. Based on redox-controlled suspension experiments, Chuan et al. (1996) reported that aqueous concentrations of Pb, Cd and Zn increased whereas those of Fe(II) increased as redox potential decreased, suggesting metal sorption onto surfaces of Fe (hydr)oxides is a dominant process in controlling aqueous metal concentrations. On the other hand, in the experiments using saturated soil pastes, Amrhein et al. (1994) found that concentrations of Cu and Cd decreased whereas those of Fe(II) increased in pore water as the redox potential decreased. However, they could not confirm precipitation of known Cu or Cd minerals under the experimental conditions. Similar contradictory results are found in other studies (Masscheleyn et al., 1991; Dong et al., 1999; Ma et al., 1995). It should be pointed out that in these studies, the samples used for analyzing metal concentrations were actually different. They can be generally classified into two groups: (1) pore water and leachate from soil leached with pure water, and (2) filtrates separated from the suspension and leachate from soil leached with electrolyte solution. Generally speaking, metals in the first group of samples are water soluble, whereas those of the second group include both exchangeable and water soluble form. A natural question is: how do metal concentrations in soil solution change with those on exchange sites during incubation? Unfortunately, this question has not been emphasized in the literature. However, such knowledge may help to explain the contradictory results of metal solubility and mobility in incubated soils.

In a previous experiment, Pb solubility is examined in a sandy soil spiked with Pb and incubated for 40 days under water-flooding and non-water-flooding conditions (Dong et al., 1999). Solution chemistry in soil columns is adjusted prior to incubation by varying pH and/or by adding different concentrations of NaCl and CaCl2. Lead solubility in the incubated soil is related to the ratio of aqueous Fe to 0.5 M HCl extractable Fe (II) from soil in addition to soluble Fe. In this experiment, we extended our study from a synthetically-contaminated soil to two trace metal contaminated soils. In addition to Pb, concentrations of Cu and As were presented for comparison. Our primary objective of this paper was to examine the importance of Fe in controlling solubility and mobility of trace metals in contaminated soils during incubation, by comparing metal concentrations in pore water and in 0.01 M CaCl2 leachate.

2. Materials and methods

2.1. Location and characteristics of soil samples

The two Pb-contaminated soils used in this study were collected from Montreal, Canada and Tampa, Florida. The soils were contaminated through past Pb-battery recycling activities and smelting operations. Selected characteristics of the soils are listed in Table 1.

2.2. Column experiment

2.2.1. Packing soil columns

Thirty grams of air-dried soil (moisture content: 9.0 and 2.3% for the Montreal and Tampa soils, respectively) was placed in syringes (d=2.6 cm, 60 ml) that were prepacked with 5.0 g acid-washed sand (20–30 mesh) at the bottom. During packing, the columns were set vertically and gently shaken for ~30 min to minimize the packing effects. This resulted in 2.6×5.2 and 2.6×7.0 cm soil columns for the Montreal and Tampa soils, respectively.

2.2.2. Incubation

Soil columns were set vertically and pre-wetted by pumping distilled deionized water (DDW) from the bottom at a flow rate of 0.95 ml/min until the water level was 1.5 cm above the soil surface. The columns were incubated under water-flooding condition for 3–80 days. During incubation, the redox status in the columns was monitored with combination redox electrodes, which were located at the interface between soil and water in the columns to minimize significant disturbance to the soil cores. The electrodes thus monitored the redox potential of the interfaces between soil and water. Among replicates, their redox potentials were maintained as close as possible. Four soil columns for each soil were incubated to a specific redox status. Two of the columns were used for leaching (metal mobility), and the

Table 1
Selected characteristics of the soils used in this study

<table>
<thead>
<tr>
<th>Soil location</th>
<th>PH (1:1)</th>
<th>CEC (cmol/kg)</th>
<th>Organic carbon (%)</th>
<th>Particle size distribution (%)</th>
<th>Total element analysis (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Clay</td>
<td>Silt</td>
</tr>
<tr>
<td>Montreal, Canada</td>
<td>7.67</td>
<td>29.0</td>
<td>0.24</td>
<td>49</td>
<td>40</td>
</tr>
<tr>
<td>Tampa, Florida</td>
<td>3.80</td>
<td>2.71</td>
<td>0.83</td>
<td>4.0</td>
<td>28</td>
</tr>
</tbody>
</table>

* bd: below detection limit.
other two for analyzing metal concentrations in pore water (metal solubility).

2.2.3. Leaching

Once the redox potential monitored had reached to a certain level, the water on top of the soil column was carefully removed with a pipette, and a rubber stopper was placed to seal the syringes. The columns were then placed upside down. The lower end of the column was connected via a needle, to a reservoir of 0.01 M CaCl₂ placed upside down. The effluent from the top of the column was collected with a fraction collector under N₂ atmosphere.

2.2.4. Analyses of leachates

Each fraction of the effluents was filtered through a 0.22-μm membrane filter under N₂ atmosphere, acidified to pH <2 and stored for analyses of metals.

2.3. Extraction of pore water from soils

Metal concentrations in pore water were determined in an incubated, but unleached soil column for each incubation time. Pore water was separated from the soil by a centrifugation method described by Nkeda-kizza et al (1982) and Dao and Lavy (1978) after the standing water on the top of soils was removed. The pore water was then filtered with a 0.22-μm membrane filter prior to metal analyses.

2.4. Analytical methods

All experiments were conducted in duplicate in acid-washed (5% HNO₃) labware. All chemicals used in this study were of analytical grade or better. Distilled deionized water from a Barnstead Nanopure water system was used. Total concentrations of Pb, Cu and As were determined using an atomic absorption spectrophotometer (Perkin-Elmer SIMMA 6000). Multi-level standards (Fisher Scientific) for all metals were prepared in the same matrix as the extracting reagents to minimize matrix effects. Blanks were used for background correction and other sources of error. At least one duplicate and one spike sample were run for every 20 samples to verify the precision and accuracy of the analytical method, which were both within 100% ± 10%.

Fe(II) concentrations in pore water and leachates were determined using 0.1-ml aliquots of the filtrates, which were immediately transferred to 10 ml of ferrozine (1 g l⁻¹) in 50 mM HEPES (N-2-hydroxyethylpiperazine-N-2-ethanesulfonic acid) buffer at pH = 7 (Lovely and Philips, 1987; Heron et al, 1994). Concentrations of Fe (II) were determined by measuring the absorbency of the filtrates at 562 nm (Stookey, 1970).

3. Results and discussion

While both soils were contaminated with Pb (1600–2500 mg kg⁻¹), compared to Montreal soil, As and Cu concentrations in Tampa soil were much greater (Table 1). Therefore, As and Cu concentrations in pore water and 0.01–CaCl₂ leachate were determined only for Tampa soil. Contrast to the low pH (3.8) of Tampa soil, Montreal soil had an alkaline pH of 7.7 and high Ca concentration of 1.6%. The significant differences in pH and Ca contents between the two soils may have been responsible for the different behaviors of Fe and Pb solubility observed in these soils.

3.1. Changes in trace metal solubility with incubation

Concentrations of trace metals and Fe (II) in pore water of the two contaminated soils varied with incubation time (Fig. 1). With incubation Fe(II) concentrations decreased in the Montreal soil (Fig. 1A) whereas they increased in the Tampa soil (Fig. 1B). However, the opposite trend was observed for Pb concentrations in the two soils. In other words, concentrations of Fe (II) and Pb in both soils were inversely related during incubation (Fig. 1). Concentrations of As and Cu in the Tampa soil, on the other hand, increased initially, then decreased. They were below detection limits (5 ppb) in the Montreal soil.

The inverse relationship between Fe(II) and Pb concentrations in pore water in both soils may suggest that competition between Pb and Fe for aqueous ligands (e.g. dissolved organic carbon for the Tampa soil and CO₃²⁻ for the Montreal soil) may be important in determining Pb concentrations in pore water. It has been well documented that Fe(II) and Pb(II) have similar affinity to various ligands (Turner et al., 1981; Nieboer and Richardson, 1980). As aqueous Fe(II) increased with incubation due to reductive Fe dissolution (Martin et al., 2003), it displaced Pb previously bound with the ligands and causing more aqueous Pb (II) onto exchange sites. We have previously demonstrated that Pb solubility in a synthetically-contaminated soil is inversely related to aqueous Fe concentrations during incubation (Dong et al., 1999).

In a similar experiment, Amrhein et al. (1994) used soils incubated under water-flooded conditions, and found increased Fe (II) concentrations in pore water with incubation time possibly as a result of reductive Fe dissolution (Amrhein et al., 1994). This is consistent with the result for the Tampa soil (Fig. 1B), but contrary to those for the Montreal soil (Fig. 1A). As indicated by high soil pH (7.7) and high Ca content (1.6%) (Table 1), it was very likely that there were significant amounts of calcite in the Montreal soil. The unexpected reduction in Fe(II) concentrations in the Montreal soil may be caused by formation of FeCO₃ as concentrations of
Fe(II) were substantially greater than those of Pb (Fig. 1A). Total Fe concentration in the Montreal soil was 26 times greater than that in the Tampa soil (Table 1), yet the highest Fe (II) concentration in pore water of the Montreal soil was approximately 1200 times lower than that of the Tampa soil (Fig. 1). The significant reduction of aqueous Fe concentrations during incubation was probably a result of FeCO₃ precipitation. This was confirmed using MINTEQA2 speciation model (Allison et al., 1991) assuming that calcite in the soil was in equilibrium with pore water. The details were discussed elsewhere (Dong, 1999). Thus, behaviors of Pb and Fe(II) in the Montreal soil may be described as follows: as a result of reductive Fe dissolution, more Pb was released from solid phases; the released Pb stayed in pore water due to lack of competition from Fe(II), which was precipitated as FeCO₃.

Chuan et al. (1996) examined the release of trace metals from a contaminated soil suspended in water (soil:water = 1:7), and found that aqueous concentrations of Pb, Cd and Zn were positively correlated to Fe concentrations. The authors concluded that trace metals are released from Fe (oxy)hydroxide surfaces as the solids dissolve. This is contrary to what we observed for Pb in both the Tampa and Montreal soils. Amrhein et al. (1994) reported that, under water-saturated
incubation condition, i.e. with moisture content at field capacity (soil:water = 1:0.2), Cd and Cu concentrations in pore water decreased, but that Fe(II) increased with time. This is consistent with our results in terms of the inverse relationship between aqueous Pb and Fe(II) in pore water. Those conflicting relationships between Fe(II) and trace metal concentrations in solution, which is often simply attributed to variation of soil characteristics, may result from different soil/water ratios used in these studies.

In Montreal soil, with incubation, As and Cu concentrations in pore water increased initially, then decreased (Fig. 1B). However, As concentrations increased where Cu concentrations decreased in the leachate (Fig. 2B). Masscheleyn et al. (1991) examined arsenic release from a contaminated soil in an incubated suspension (soil:water = 1:6) and found that soluble arsenic increased as redox potential decreased (from +500 to −200 mv). This has been attributed to both As(V) reduction to As(III) and release of adsorbed As due to reductive Fe dissolution. However, analyses of pore water in soils after water-flooding incubation showed a different trend (Onken and Hossner, 1996). They found that soluble arsenic concentrations increased initially and then decreased with incubation, with maximum concentration occurring at 20–30 days after flooding incubation. Analysis of the solid phase showed that reduction in soluble arsenic could be attributed to surface binding of arsenic when the soil was incubated for >20–30 days. The results of Onken and Hossner (1996)
are consistent with our data, i.e. with Fe reductive dissolution, As concentrations increased initially and then decreased (Fig. 1B).

3.2. Changes in trace metal mobility with incubation

Metal mobility in this experiment was evaluated based on the amounts of cumulative metals leached with 32 pore volumes (one pore volume = ~11.5 ml) of 0.01 M CaCl₂ solution. After one pore volume trace metal concentrations were either undetectable (Montreal soil) or with no significant changes (Tampa soil). Metals leached with CaCl₂ solution include both soluble and exchangeable (Dong et al., 1999). For Montreal soil, the cumulative leached-Pb increased with incubation (Fig. 2A), consistent with the overall trend shown in Pb concentrations in pore water (Fig. 1A). However, the cumulative leached-Fe showed a different trend from Fe (II) in pore water, suggesting that Fe(II) on exchange sites was not proportional to that in aqueous phase assuming Fe(II) soluble Fe (Dong et al., 1999). The significant reduction in Fe(II) concentrations after 80 days incubation in the Montreal soil is consistent with the predicted Fe precipitation as FeCO₃. For the Tampa soil, changes in metal mobility with incubation time can be divided into two groups: Pb and Cu decreased with incubation whereas As and Fe increased (Fig. 2B), which were mostly consistent with data for pore water (Fig. 1B).

In the Tampa soil, as incubation time increased from 3 to 60 days, Fe (II) concentrations in pore water increased by ~5 times (Fig. 1B), whereas its cumulative leached-Fe increased by ~12 times (Fig. 2B). It is implied that Fe(II) concentrations on exchange sites increased significantly with incubation. With reductive Fe dissolution, previously blocked exchangeable sites are exposed, Fe (II) concentrations on exchange sites may increase as a result. For the Montreal soil, a sharp increase in cumulative leached-Fe, compared with Fe(II) concentrations in pore water, was observed after 20-days incubation (Figs. 1A and 2A), suggesting that exchangeable Fe (II) became dominant in the cumulative leached-Fe. In fact, there was 5.6 μmol Fe leached during 7–16 pore volumes (mostly exchangeable) out of a total of 7.1 μmol of cumulative leached-Fe after 20 days of incubation.

For the Tampa soil, changes in Pb concentrations in pore water and the cumulative leached-Pb with incubation were similar, i.e. both decreased (Figs. 1B and 2B). As aqueous Fe (II) increases with incubation due to reductive Fe dissolution, more aqueous Pb (II) may be forced onto exchange sites. If this were simply the case, however, the amounts of cumulative leached-Pb should increase with incubation, which was not true (Fig. 2B). It is difficult to imagine that large amounts of Pb were present on exchange sites without some being adsorbed chemically on to the surfaces, which may not be displaced by 0.01 M CaCl₂ solution. There were significant differences in Pb concentrations in pore water and those cumulatively leached. Whereas the Pb concentration in pore water decreased exponentially, the cumulative leached-Pb decreased only linearly (incubation time <30 days). This smaller decrease in cumulative leached-Pb than that in Pb concentrations in pore water may be caused by the presence of larger amounts of exchangeable Pb.

Interestingly, arsenic concentrations in pore water in the Tampa soil first increased (<30 days) and then decreased with incubation, whereas the amount of cumulative leached-As increased with incubation (Fig. 2B). It is possible that, as Fe “coatings” were reduced with reductive Fe dissolution, soil cation exchange capacity (CEC) increased. This, along with increases in aqueous Fe (II) concentrations, may cause more Pb (II) to occupy exchange sites. As a result, the exchange sites carried more positive charges and thus held more anionic arsenic.

As discussed above, CEC increases with reductive Fe dissolution at pH lower than PZC of Fe minerals. The consequent redistribution of metals between solution and exchange sites is probably determined not only by the magnitude of CEC, but also by the characteristics of the metal ions and the competing ions and ligands. Therefore, changes in aqueous metal concentrations in a soil with incubation can be complicated. It seems that, however, the following interactions have to be taken into consideration: (1) reductive Fe dissolution results in release of Fe (II) and adsorbed trace metals while simultaneously frees exchange sites; (2) Fe (II) and trace metals compete for ligands to stay in solution and compete for exchange sites to stay on solid phases; and (3) as a result of multivalent trace metal cations occupying on exchange sites, an increase in positive charge on solid phases may in turn hold more negatively-charged species of trace metals. In a given soil system, different processes may be important in controlling metal concentrations in soil solution.

Numerous researchers have reported on changes in solubility and mobility of trace metals with incubation. However, reported data have often been contradictory. This is in part due to the differences in soil/water ratios used in various experiments including metal concentrations determined in pore water, in filtrates separated from soil suspensions, and in leachate from a soil leached with pure water or an electrolyte. Additionally, changes in aqueous trace metal concentrations with incubation reported in literature can be confusing. For example, metal concentrations in pore water or metal mobility leached by pure water may decrease with incubation when no precipitation is observed. Therefore, the roles of Fe in controlling metal concentrations in these systems need to be considered. We suggested that CEC of a soil may change with incubation under
water-flooding condition, and thus might greatly affect metal solubility and mobility.

References


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