

Relation of enhanced Pb solubility to Fe partitioning in soils

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“Capsule”: *Quantitative data are provided to help determine the relationship between Pb solubility and Fe partitioning in soils.*

Abstract

It is well documented that Pb solubility may be related to Fe chemistry in soils and enhanced Pb solubility may occur under certain reducing conditions; however, quantification of such relationships is unavailable. Based on metal classification, Pb (II) and Fe (II) are similar in some chemical characteristics. Thus, competition between Pb and Fe for ligands in soils may be important in determining Pb solubility. In this paper, Pb solubility was examined in a sandy soil after spiking with Pb and incubating for 40 days under water-flooded or non-water-flooded conditions. Solution chemistry in soil columns was adjusted using different concentrations of NaCl, CaCl₂ and deionized water of varying pH before incubation. The results showed that Pb solubility in the soil was not correlated well with pH, dissolved organic C or aqueous Fe concentrations. However, an index of Fe partition behavior using the ratio of aqueous Fe to sorbed Fe was related to Pb solubility. Enhanced Pb solubility occurred only when the index was $< \sim 2$ kg l⁻¹. The index can be a simple measure of Fe's ability to compete with Pb for ligands in solution. The ability of Fe to compete with Pb decreases as the index decreases and as the ratio approached its minimum, substantial increases in Pb solubility will be expected. In general, the index was not sensitive to changes in solution chemistry. A similar trend was observed using one data set published in the literature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Pb contamination in soils is of environmental significance due to its toxicity to both humans and animals (Ma et al., 1995). In general, Pb mobility is low because of its low solubility. The low solubility may be further reduced as a result of its interactions with the soil's solid phase via sorption and ion exchange. However, enhanced Pb solubility has been found under both laboratory and field conditions (Amrhein et al., 1994; Glazovskaya, 1994). As a result, Pb may migrate through a soil profile to contaminate groundwater.

Although much effort has been spent to model heavy metal solubility (Sposito, 1984; Cederberg et al., 1985), such prediction under field conditions involves large uncertainty. It is in part due to the difficulty in assessing the effects of dynamic soil solution chemistry on heavy

metal speciation. However, changes in solution chemistry, such as pH, redox potential and ionic strength, may shift the Pb-retention processes significantly. These impacts may be further complicated by aqueous Pb competition with other metals for ligands, which may enhance Pb mobility under certain conditions (Amrhein et al., 1994).

It has been well documented that in natural aquatic environments, Pb (II) and Fe (II) have similar affinity to complex with ligands, and thus they show similar patterns of species distribution (Turner et al., 1981). Furthermore, Nieboer and Richardson, (1980) explained the similar behavior based on metal classification: both Pb (II) and Fe (II) are similar in electronegativity and covalent index and they both are in 'transient class'. This evidence implies that it is important to examine Fe chemistry when studying Pb solubility. In fact, good correlation ($r^2 = 0.71-0.91$, $P < 0.05$) between concentrations of aqueous Pb and Fe in sediments has been reported (Routh and Ikramuddin, 1996; Lee et al., 1997). In the soil environment, data published by

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Karczewska (1996) showed that concentrations of soluble Fe and Pb was related ($r^2=0.54$, $P<0.05$) in several polluted soils near a Cu smelter. These published experimental data along with the theoretical evidence suggest that Pb and Fe solubility are related in a soil.

In addition, there are two other possible factors that may contribute to the correlation between Pb and Fe in solution. First, Fe (oxy)hydroxides are good sorbents for aqueous Pb (Benjamin and Leckie, 1981; Laxen, 1985; Ainsworth et al., 1994), and their dissolution or precipitation may release or sorb Pb. In soils, dissolution of Fe (oxy)hydroxides is generally promoted by reducing Fe (III) to Fe (II), which is sensitive to soil redox status (Gotoh and Patrick, 1974; Lindsay, 1979). Under oxidizing conditions, Fe (oxy)hydroxides tend to immobilize Pb (Gambrell et al., 1980); whereas under reducing conditions they dissolve to release Pb (Gambrell, 1994). Second, soil organic carbon, especially dissolved organic carbon (DOC), is an important factor controlling Pb and Fe solubility in soil (Davis, 1984; Laxen, 1985; Dorr and Munnich, 1991). DOC functions as a ligand to complex with Pb and Fe to increase their solubility (Davis and Leckie, 1978). On the other hand, DOC may also be sorbed by Fe (oxy)hydroxides under certain conditions, via ligand exchange, or hydrophobic interaction (Murphy and Zachara, 1995), thus decreasing Pb and Fe solubility.

Despite all the circumstantial evidence that Fe solubility impacts Pb solubility in soil, there has been little effort to quantify the relationship between the two. This may be due to the complication we discussed above. However, understanding the relationship between heavy metal solubility and Fe chemistry in a dynamic soil system may provide important information for assessing potential mobility of heavy metals in soil environments, which cannot be modeled successfully at the present time. In this paper, we took a phenomenological approach to understand how Fe chemistry affects the occurrence of enhanced Pb solubility.

Soil redox status varies temporally. The intensity of redox status can be described by redox potential in general. In surface soil it is influenced by rainfall, bioactivity, and changes in land use, whereas in vadose zone by fluctuation in water table (Boul et al., 1997).

The redox potentials of sediments that remain saturated can be measured readily, whereas characterization of the redox status in a soil is still a challenge. As mentioned previously, however, soil redox status affects metal solubility greatly under certain conditions. To evaluate the effect of varying redox status, saturated/unsaturated (aerobic/anaerobic) incubation techniques have recently been developed (Amrhein et al., 1994; Karczewska, 1996). Water-flooded incubation was used to effectively lower soil redox potential to study the speciation and fate of heavy metals in contaminated soils (Karczewska, 1996). Even though saturation rarely happens in surface soils, some valuable information may be obtained from such a study. In this paper, two redox statuses in soils will be obtained under non-water-flooded (aerobic) and water-flooded (anaerobic) incubations.

The major objective of this paper was to examine the relationship between enhanced Pb solubility and Fe partitioning in soils with different solution chemistry. Throughout this paper, Fe partition was expressed as a ratio of aqueous to sorbed Fe (II) unless otherwise specified. The results showed that enhanced Pb solubility was related to this ratio in the soil.

2. Materials and methods

2.1. Location and characteristics of soil sample

The soil samples used for this study were collected in March 1996 from a research site in Hawthorne, FL, USA. The soil is an acidic fine sand (typic quartzipsamment) with a spodic horizon below 2 m. The samples were collected from 2 to 20 cm below the surface after removing organic residue. The samples were air-dried, sieved through a 2-mm screen, and stored at 4°C prior to use. Some characteristics of the soil are listed in Table 1.

2.2. Column experiment

A series of 60-ml columns (diameter = 2.6 cm), which were pre-packed with a layer (~3 mm) of acid-washed

Table 1
Selected characteristics of the soil used in this study

| pH (1:1) | Organic C ^a (mg g ⁻¹) | Extractable Fe ^b (mg kg ⁻¹) | Total concentrations ^a (mg kg ⁻¹) | | | | | Texture ^c (%) | | |
|----------|---|---|--|-----|----|----|-----|--------------------------|------|------|
| | | | Al | Fe | Ca | Na | Pb | Sand | Silt | Clay |
| 5.4 | 6.0 | 810 | 2067 | 976 | 87 | 27 | 1.3 | 94.6 | 4.5 | 0.9 |

^a Ma et al. (1997).

^b Heron et al. (1994).

^c Day (1965).

Ottawa sand (20–30 mesh) at the bottom, were packed with 40 g of soil sample. The columns were then packed with another layer of the acid-washed sand on the top to minimize disturbance on the soil from influents. All the columns were set on a Centurion Vacuum Extractor (Centurion International, Lincoln, NE, USA) for incubation and leaching. The experiment procedure was as follows:

1. Prewetting soil columns: 30 ml of deionized distilled water (DDW) was slowly poured into each column and the soil columns were saturated for 48 h before the water was extracted out of the bottom of the columns.
2. Addition of aqueous Pb: 30 ml of 0.48 mM $\text{Pb}(\text{NO}_3)_2$ was added to 12 soil columns and 30 ml of 3.68 mM $\text{Pb}(\text{NO}_3)_2$ to 16 soil columns. The solutions were extracted after 24 h at 2.5 ml h^{-1} . This resulted in Pb-loading rates of 0.36 (low Pb loading) and 2.90 mmol kg^{-1} (high Pb loading) in two groups of soil columns.
3. Addition of electrolyte solutions: 30 ml of different electrolyte solutions was added to different columns to vary solution chemistry. DDW of pH 5.5, and 2.17 and 4.35 mM NaCl were added to the first 12 soil columns; 0.52, 1.08, and 2.17 mM NaCl, 0.25, 0.55, and 1.10 mM CaCl_2 , and DDW of pH 4.5 and 5.5 to the 16 soil columns. The solution was extracted out after 24 h at 2.5 ml h^{-1} . For the first 12 soil columns with low Pb loading, each treatment was replicated four times (three treatments) and for the 16 soil columns with high Pb loading, each treatment was duplicated (eight treatments). Consequently, soil columns in each treatment (a total of 11 treatments) varied not only in Pb loadings but also in pH and composition of electrolyte solutions.
4. Incubation of soil columns: the columns with the same treatment (with the same Pb loading rate and electrolyte solution) were evenly divided into two parts, and thus the 28 soil columns were further divided into two subgroups (14 soil columns each) for incubation. One subgroup was filled with 30 ml of DDW (2 cm above the soil surface) for water-flooded incubation. The other subgroup was incubated as it is for non-water-flooded incubation. All soil columns were incubated for 40 days at room temperature.
5. Leaching: DDW was added to each soil column to make 30 ml of standing water above the soil for all columns before leaching. The leaching was conducted at 60 ml h^{-1} and approximately 25 ml leachates were collected. The soil samples with moisture content of about 25% in the columns were sealed and stored in refrigerator for further analysis.

2.3. Sample separation and analysis

Separation and analysis were conducted for both leachates and leached soil samples to examine Pb solubility in the soil. The pH was measured immediately after the leachates were collected. The leachates were filtered through 0.22- μm membrane filters. The filtrates were analyzed for DOC, total Pb and Fe concentrations. The frozen soil columns were immersed in warm water to push the soil out of the columns with minimum disturbance. The intact soils from the columns were then divided into three equal sections (top, middle and bottom) for further analysis. The Fe (II) extracted from the soil presented in this paper, however, was averaged over the three sections since there were no significant differences through the three sections.

2.4. Fe (II) content in the leached soil

Approximately 0.6 g of the leached soil was transferred to 5 ml of 0.5 M of HCl in a glass scintillation vial of known weight and the mixtures were swirled for about 30 s. After 0.5 h of settling, 0.1 ml of the supernatant was transferred to 10 ml of ferrozine (1 g l^{-1}) in a 50 mM HEPES (*N*-2-hydroxyethylpiperazine-*N*-2-ethanesulfonic acid) buffer at pH = 7 (Lovely and Phillips, 1987; Heron et al., 1994). After mixing for 15 s, the mixture was filtered through 0.22- μm membrane filters. Concentrations of Fe (II) were determined by measuring the absorbency of the filtrates at 562 nm (Stookey, 1970). In this paper, we assumed that aqueous Fe primarily consists of Fe (II) since the solubility of Fe (III) is extremely low and Fe (III) concentration is negligible in most soils (i.e. total Fe concentrations \approx total Fe (II) concentrations).

2.5. Analytical methods

All experiments were conducted in acid-washed (5% HNO_3) labware. All chemicals used in this study were of analytical grade or better. DDW from a Barnstead NANOpure water system was used. DOC was analyzed using Shimadzu 5000A Carbon Analyzer. Total metal concentrations in the filtrates were analyzed by an atomic absorption spectrophotometer (Perkin-Elmer 2380) equipped with a graphite furnace atomizer. Flame atomic absorption was used to analyze metal concentrations $> 1 \text{ mg l}^{-1}$ and graphite furnace atomizer was used to measure metal concentrations $< 1 \text{ mg l}^{-1}$. 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 precision of the method. The spike recovery and precision were found to be within $100 \pm 10\%$.

3. Result and discussion

3.1. Pb solubility

Aqueous Pb concentrations in leachates showed strong pH-dependence with $r^2=0.92$ for soils with Pb loading of $2.90 \text{ mmol kg}^{-1}$ (high Pb loading, Fig. 1A). Aqueous Pb concentrations decreased as pH increased from 4 to 6. It has long been recognized that pH is an important factor affecting metal solubility, with aqueous metal concentration increasing as pH decreases (Chuan et al., 1996). Leachate Pb concentrations in soils with Pb loading of $0.36 \text{ mmol kg}^{-1}$ (low Pb loading, Fig. 1A) were also correlated with pH with a correlation coefficient of $r^2=0.51$ ($P<0.05$). However, they increased as pH increased from 6.1 to 6.8. Obviously,

mechanisms that determined aqueous Pb concentrations in soils with low Pb loading were different from that with high Pb loading. It seemed that DOC was a primary factor in determining Pb concentrations in soils with low Pb loading as reflected by their correlation coefficient of $r^2=0.47$, $P<0.05$ (i.e. Pb concentrations increased as DOC concentrations increased) (Fig. 1B). However, such correlation did not exist for soils with high Pb loading ($r^2=0.24$) possibly due to the fact that Pb solubility was strongly correlated to pH, meaning free Pb cation was the dominant species.

Beside pH, redox status is another factor affecting metal solubility in soil (Chuan et al., 1996). Stumm (1984) suggested that it is reasonable to measure important redox species instead of redox potential to indicate redox status in natural systems. We used aqueous Fe as

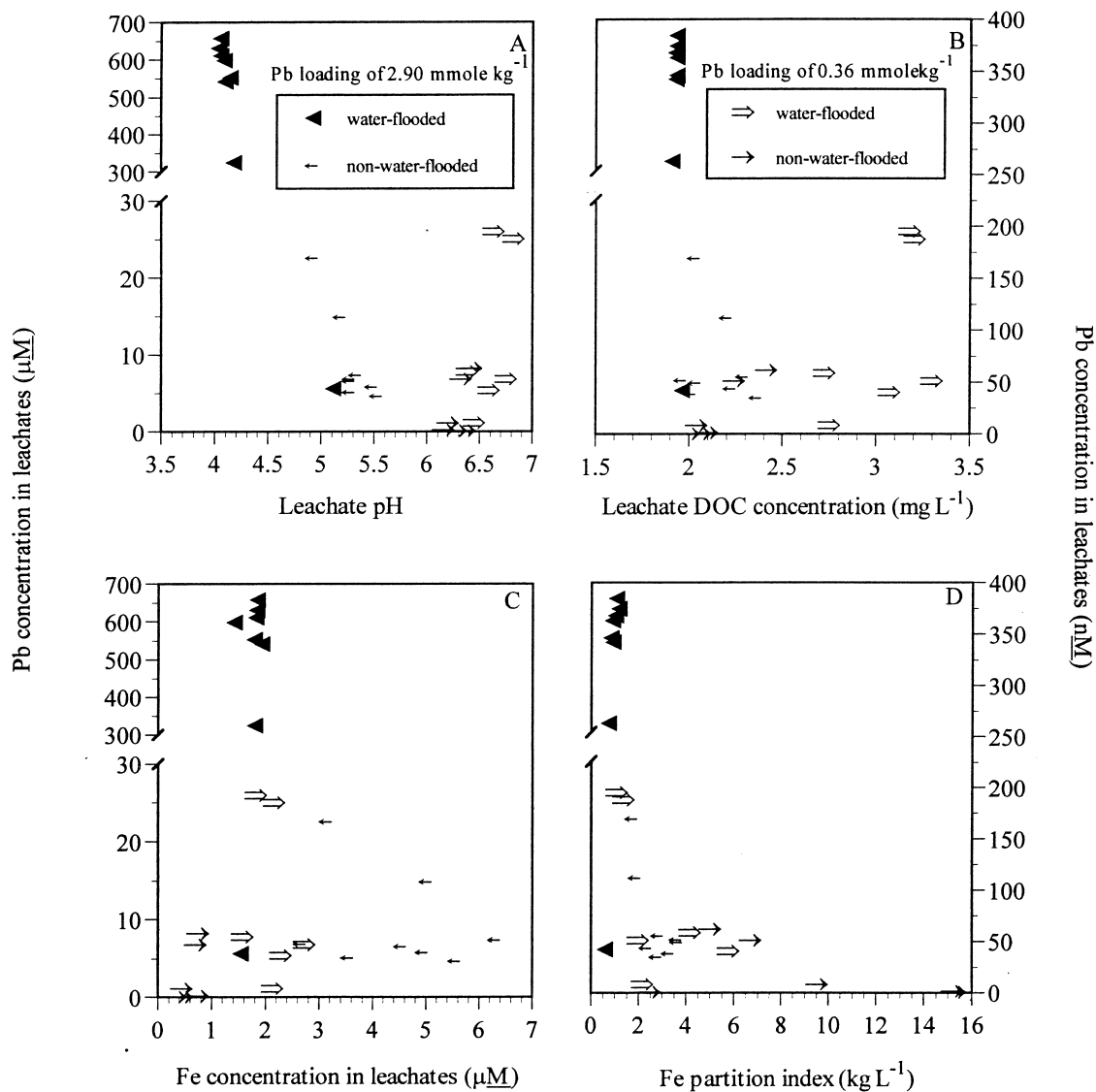


Fig. 1. Relation between Pb solubility and leachate pH, dissolved organic carbon (DOC), leachate Fe concentration, and the ratio of aqueous Fe to sorbed Fe (II) concentrations in a sandy soil. Data from $2.90 \text{ mmol kg}^{-1}$ Pb loading rate read from the left y-axis and data from $0.36 \text{ mmol kg}^{-1}$ Pb loading rate read from the right y-axis.

a measure of redox status for soils. As expected, aqueous Fe concentrations were much higher in soils under water-flooded incubation than non-water-flooded incubation (Fig. 1C). In soils with low Pb loading, aqueous Fe concentrations were over three times greater under water-flooded incubation (averaged 2.12 nM) than under non-water-flooded incubation (averaged 0.57 nM). Similarly, the average aqueous Fe concentrations in soils with high and low Pb loading were 4.46 and 1.74 μM , respectively. Greater aqueous Fe concentrations in soils with high Pb loading than with low Pb loading was mainly due to pH difference in the soils (Fig. 1A, C). However, there was no relationship shown between aqueous concentrations of Fe and Pb for soils of either Pb loading rates (Fig. 1C). It was reported that aqueous Pb and Fe concentrations are linearly related due to the fact that heavy metals are released from Fe (oxy)hydroxide surface when it dissolves (Chuan et al., 1996). In our study, however, this was not the case (Fig. 1C), suggesting that aqueous Pb may not be controlled by the Fe (oxy)hydroxide surface alone. Coincidentally, similar controversial results have also been reported by other researchers (Gambrell et al., 1991). This evidence implied that, contrary to our intuition, aqueous Fe concentration is not necessarily related to Pb solubility and there must be some additional factors involved in the relationship, which will be discussed in the following section. Nevertheless, as expected, aqueous Pb concentrations were much (52 times) greater under water-flooded incubation (averaged 490 μM) than under non-water-flooded incubation (averaged 9.4 μM) in soils with high Pb loading (Fig. 1). Similarly, aqueous Pb concentrations were 91 and 22 nM, respectively, for soils with low Pb loading.

3.2. Pb solubility and Fe partitioning

As discussed previously, pH was related to Pb solubility in the soil. However, even for the same soil, the relation between aqueous Pb and pH differed with Pb loading rates (Fig. 1A). In other words, there was no simple relation between pH and Pb solubility when the solution chemistry varies greatly for the soil. The same is true for the relationships between Pb and DOC concentrations and Pb and Fe concentrations (Fig. 1B, C).

As an alternative approach, we defined the ratio of aqueous Fe to sorbed Fe (II) concentrations as a Fe partitioning index. In this study, sorbed Fe (II) was operationally defined as Fe (II) that was extracted by 0.5 M HCl (Lovely and Philips, 1987; Heron et al., 1994). By definition, the Fe partitioning index represents the relative affinity of aqueous Fe to solid phases in a soil: a larger value indicates a lower affinity of aqueous Fe to solid phases. Fig. 1D is a plot between aqueous Pb concentrations in leachates and Fe partitioning index. For soils with low Pb loading and incubated under water-flooded

condition, the relation between aqueous Pb and Fe partitioning index was approximately parabolic ($r^2=0.91$, $P>0.05$). In general, aqueous Pb concentrations increased as the index decreased. However, as the index decreased to below 2 kg l^{-1} , the increases in Pb concentrations were substantial (Fig. 1D). A similar trend was also observed for soils with high Pb loading and incubated under non-water-flooded condition, i.e. substantial increases in Pb concentrations in leachates were observed when the index was, coincidentally, $<2 \text{ kg l}^{-1}$.

However, no enhanced Pb solubility was found in soils with low Pb loading and incubated under non-water-flooded condition, which may be because the Fe indexes for all the soil columns were $>2 \text{ kg l}^{-1}$. However, for soils with high Pb loading rate and incubated under water-flooded condition, extremely high Pb concentrations were observed, which may be because the Fe indexes for all the soil columns were $<2 \text{ kg l}^{-1}$. These results suggest that, in this study, the Fe index $<2 \text{ kg l}^{-1}$ was a necessary condition for the occurrence of enhanced Pb solubility. Obviously, compared to pH, DOC and aqueous Fe concentrations, a more consistent relation between aqueous Pb concentrations in leachates and the Fe partitioning indexes in soils was observed. In fact the overall relation of aqueous Pb to the Fe partitioning index for all the soil columns was parabolic ($r^2=0.74$, $P<0.05$).

For a pH-dependent process, the Kurbatov equation (Kurbatov et al., 1951) has been successfully used to describe the macroscopic behaviors of metal partitioning in natural aquatic systems (Balistrieri and Murry, 1983; Tessier et al., 1985; Fuller et al., 1996). In our system, the aqueous Fe concentrations in soils with both high ($r^2=0.61$, $P<0.05$) and low ($r^2=0.55$, $P<0.05$) Pb loading rates were correlated to pH. Thus, the Kurbatov equation could be applied to our system as follows: $\log(\text{Fe index}) \approx -\chi\text{pH} - \log K_p + \log N_s$, where χ is a macroscopic proton coefficient, K_p a Kurbatov partition coefficient, and N_s the total number of exchangeable sites (Balistrieri and Murry, 1983; Fuller et al., 1996). Assuming that the above equation was correct, then the Fe index was related to pH in addition to χ , K_p , and N_s . In a dynamic soil system, χ , K_p , and N_s are barely constant (Balistrieri and Murry, 1983). It suggested that the Fe index that we defined contains more necessary information in defining Pb solubility in a soil than pH itself.

As shown in the Kurbatov equation, the Fe index is a lumped parameter that is contributed by the properties of both soil solution (pH and χ) and solid (K_p and N_s) and that determine Fe partitioning. To evaluate the relationship between the Fe index and other metal solubility, it is expected that the more Fe-like a metal is, the more related may be its solubility to the Fe index. As mentioned previously, Pb (II) shows some similarity

to Fe (II) in both metal classification and speciation distribution in aquatic systems (Nieboer and Richardson, 1980; Turner et al., 1981). Therefore, it is expected that aqueous Pb concentrations in soil were related to the Fe index, which was confirmed by Fig. 1D.

Turner et al. (1981) reported that in natural water systems Pb (II) and Fe (II) exhibit similarity, meaning that Fe (II) may be a major competitive cation to Pb (II) for a ligand in solution. Therefore, it is important to evaluate the competition between Fe (II) and Pb (II) for ligands. It should be pointed out that, in this paper, we did not emphasize the competition between Fe (II) and Pb (II) for adsorption sites on solid phases. The reason is that some research has shown that the competition may be insignificant (Rose and Bianchi-Mosquera, 1993; Coughlin and Stone, 1995). In our study, soil solution chemistry varied with soil columns. These variations may shift the ligand competition. At the present time, it is difficult to fully evaluate their effect on metal solubility in the soil, especially when DOC is involved. The Fe index defined in this paper, however, may serve as a simple measure of competing ability of Fe with Pb for ligands. At this stage it is more important to look at the conceptual nature of the index than the detailed mechanistic interpretation, which will be explored further in a later paper.

Assuming that Fe and Pb compete for ligands in a soil solution, we inferred the following. As the Fe partition index increases, there is more aqueous Fe and/or less sorbed Fe, which means there is more competition for ligands from aqueous Fe in the soil and thus results in less aqueous Pb in the soil. On the other hand, as Fe partition index decreases, there is less aqueous Fe and/or more sorbed Fe, which means there is less competition for ligands from aqueous Fe and thus this results in more aqueous Pb in the soil as shown in Fig. 1D.

In principle, there exists a minimum Fe index for a soil, at which the aqueous Pb concentration is minimized and the resulted sorbed Pb is maximized. If the aqueous Fe concentration approaches zero (i.e. all aqueous Fe was transferred onto sorbed form), the Fe index is zero. With this condition, Pb dominates the ligand competition in the solution, so that a substantial increase in Pb solubility would be expected. The overall trend shown in Fig. 1D confirmed this rationale in principle. In reality, however, aqueous Fe concentrations cannot truly be zero. Therefore, the Fe index must be larger than zero. Theoretically, in a soil the minimum aqueous Fe concentration is mainly determined by the solubility of Fe minerals and the corresponding maximum sorbed Fe concentrations is solid dependent. Therefore, the Fe index is generally insensitive to solution chemistry for a given soil. Since it is impossible to accurately measure the maximum sorbed Fe concentrations for a soil solid phase, no attempt was made to evaluate the real value of the minimum Fe index from

the definition for the soil we used. However, the minimum Fe index when enhanced Pb solubility occurred was approximately 2 kg l^{-1} in the soil studied, which was estimated from the relationship between Pb solubility and Fe index (Fig. 1D). As expected, the minimum did not vary much with incubation conditions and Pb loading rates (Fig. 1D). It has been noticed that the Fe index went lower than the minimum value and Pb concentrations in some soil columns still stayed low even when the Fe index was less than $\sim 2 \text{ kg l}^{-1}$ (Fig. 1D). The causes are unclear at the present time. It might be due to the formation of new Fe or Pb minerals or the over-extraction of 0.5 M HCl for Fe (II) from the solid phases. Nevertheless, the significance in the relation between Pb solubility and Fe index was that enhanced Pb solubility does not occur unless the Fe index was below $\sim 2 \text{ kg l}^{-1}$ (Fig. 1D). It should be noted that the above interpretation is purely thermodynamic, i.e. no model has been needed.

3.3. Pb solubility and Fe partitioning using published data

In the discussion above, sorbed Fe was defined as the Fe (II) fraction extracted by 0.5 M HCl, which is supposed to extract exchangeable, adsorbed and freshly precipitated Fe (II) (Heron et al., 1994). In the literature, however, such data are unavailable. In order to conceptually test the relation between Pb solubility and Fe partitioning index that we presented above using available data in the literature, other extractants equivalent to 0.5 M HCl have to be used.

Karczewska (1996) examined heavy metals via a sequential extraction in soils polluted by a Cu smelter. In the study, heavy metals were fractionated into seven fractions, i.e. soluble (1 M NH_4NO_3), exchangeable (1 M NH_4OAc), bound in MnO_x (1 M $\text{NH}_2\text{OH-HCl}/1 \text{ M NH}_4\text{OAc}$) and others. We assumed that Pb and Fe extracted by 1 M NH_4NO_3 is equivalent to the aqueous Pb and Fe concentrations and sum of exchangeable Fe and bound to MnO_x was equivalent to Fe (II) extracted by 0.5 M HCl as we presented previously. The Fe index was calculated using the total sorbed Fe instead of Fe (II) since the quantity of the latter is unavailable. However, the Fe index calculated from either total Fe or total Fe (II) should be consistent in concept since Fe (III) is even more competitive compared with Fe (II). A plot of aqueous Pb concentrations to Fe indexes (Fe concentration extracted by 1 M NH_4NO_3 /the sum of Fe concentrations extracted by 1 M NH_4OAc and 1 M $\text{NH}_2\text{OH-HCl}/1 \text{ M NH}_4\text{OAc}$) was shown in Fig. 2. A similar trend shown in Fig. 1D was observed: enhanced Pb solubility occurred only when the Fe index was low. In other words, substantial increases in Pb solubility was observed at the lowest Fe partition index and in this particular case the Fe index was zero. As the author

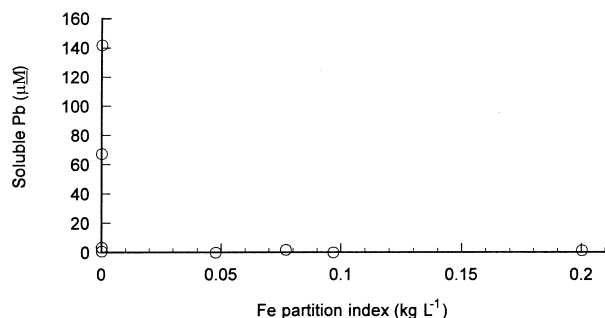


Fig. 2. Relationship between soluble Pb concentrations and the ratio of soluble to sorbed Fe in contaminated soils. Data are taken from Karczewska (1996).

pointed out (Karczewska, 1996), the soil samples were collected from various locations near a smelter site in Poland and there were large variations in soil properties among the samples (e.g. cation exchange capacity: 10–84 meq kg⁻¹; organic C: 0.05–1.42%; clay content: 1–6%; Karczewska, 1996). This suggested that the relationship between Pb and Fe partition index may be applicable to field data even with large spatial variability in soil properties.

It has been noticed that there is a significant difference in the x-axis scale between Figs. 1D and 2. It may be attributed to: (1) the soils the figures represent are different; (2) the aqueous Fe concentrations (for calculating the index) in Fig. 1D are those in pore water while in Fig. 2 they are those extracted by 1 M NH₄NO₃; and (3) the denominators for the indexes are the Fe (II) concentration extracted by 0.5 M HCl and the sum of the total Fe concentration extracted by 1 M NH₄OAc and NH₂OH-HCl/1 M NH₄OAc for Figs. 1D and 2, respectively.

3.4. Implication of this research

Partition coefficients (K_d) are important parameters in assessing the potential impacts from metal-contaminated soils. However, K_d is not a constant in a dynamic soil environment. It is not only determined by the characteristics of solid phases but also varies greatly with solution chemistry. In a given soil system, the variation is mainly determined by metal solubility. There are several speciation models available to describe the interactions of metals and soil components to predict their solubility. Unfortunately, such predictions generally lack certainty primarily because of the soil's dynamic nature.

At the present time, accurately assessing changes in solution chemistry in field conditions is difficult, if not impossible. This information, however, is critical to estimate the solubility of heavy metals in speciation models. In contrast, the approach presented in this paper provides a simple relation between the probability in enhanced Pb solubility (or K_d) and Fe partition index, which is generally not sensitive to changes in

solution chemistry for a given soil. In this approach, we simply can determine the minimum Fe index by mimicking a field condition to predict the possibility of enhanced Pb mobility (the lower K_d). Of course, more work is needed to further test this concept in different soils and determine the ranges of Fe index in which enhanced Pb mobility may occur.

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