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Lead Phosphate Solubility in Water and Soil Suspensions

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The widespread occurrence of soil Pb contamination requires a good understanding of the factors controlling Pb solubility. Pb solubility will often be controlled by phosphates, which are used to reduce environmental risks of Pb-contaminated soils. The solubility equilibria of two different synthetic lead phosphate minerals were determined electrochemically across a wide range of pH and Pb and phosphate concentrations. The resulting chemical equilibrium data could not be explained by standard solubility equations, although a simple empirical regression explained the data very well. The same lead phosphate mineral was then added to two different soils which were equilibrated across a pH range 4−8. Differential pulse anodic stripping voltammetry was used to determine the ASV-labile Pb in the extracted soil solutions, and the free Pb^{2+} ion activity was calculated. The free Pb^{2+} activity in the soil solutions followed the expected pH relationship, highest solubility at low pH and gradual decrease with increasing pH. In contrast, total dissolved Pb was high at low pH, decreased until pH of ∼6, and then increased again at higher pH. This behavior is attributed to the strong Pb-complexing capacity of the soil organic matter which is solubilized at neutral pH and above.

Introduction

Lead contamination is widespread in industrialized countries, most urban soils having total Pb levels above the geochemical "background levels" of 10−20 mg of Pb kg^{-1} (*1*). Even in contaminated soils, most of the Pb is insoluble, precipitated or bound to the soil solids. Since only the metal dissolved in the soil solution is potentially available to plants and soil organisms in the short term, the low solubility of Pb-bearing minerals such as carbonates, phosphates, and sulfides may control Pb bioavailability depending upon soil conditions and the initial form of the Pb contamination. The least soluble Pb minerals in aerobic soils are the lead phosphates. Consequently, in many situations, the soil solution concentration of phosphate may control the solubility and availability of Pb (*2*).

Phosphate amendments have been used to reduce the solubility and bioavailability of Pb in contaminated soils (*3*, *4*). In this respect, land application of sewage sludge and manure establish a high soil phosphate availability, which can be expected to reduce Pb solubility.

The potential effect of increased soil phosphate levels upon the solubility of Pb in contaminated soils can be predicted using theoretical solubility equilibrium data. Unfortunately, experimental data for the solubility of lead phosphates are scarce, and these few studies were made under specific and narrow experimental conditions. Specifically, the existing solubility products for orthophosphates, pyromorphites, and other phosphate phases were derived under conditions of very low pH and very high phosphate and Pb activity (*5*, *6*). Thus, the estimated solubility products may not apply satisfactorily over the wider range of pH, phosphate activity, and Pb^{2+} activity relevant to soils.

Various solubility diagrams have been presented to explain the solubility of Pb and the interactions with various other mineral phases (*5*, *7*). It should be noted that such diagrams, while a reasonable representation of pure synthetic systems, may be less applicable to soils. In soils, the presence of additional cations and anions, a heterogeneous adsorptive mineral phase, and an ill-defined organic matter component limit theoretical solubility diagrams to no more than a representation of potential trends. Reactive surfaces often control metal solubility in soils with low to moderate contamination, only with severe loadings does mineral precipitation control solubility (*8*, *9*). In addition, dissolved organic matter can enhance metal solubility; organic matter in the solid phase contributes to metal adsorption and modifies reactive mineral surfaces.

The objectives of this study were to (1) determine the solubility of two synthetic lead phosphate precipitates over a wide range of pH and Pb and phosphate levels and (2) investigate the solubility equilibrium of the same lead phosphate mineral phase mixed with soil, thus exploring the pH-dependent solubility of Pb in the presence of excess phosphate in soils.

Materials and Methods

Analytical Determinations. Previous solubility studies of lead phosphates were restricted by the detection limit of flame atomic absorption spectrometry (*5*, *6*). In this study, the activity of free Pb^{2+} ions is determined electrochemically, using a Pb ion-selective electrode for the synthetic systems and differential pulse anodic stripping voltammetry (DPASV) for the soil solution speciation of Pb.

Lead ion-selective electrodes have been shown to give a Nernstian response to the activity of free Pb^{2+} ions down to $\sim10^{-10}$ M (*10*) and $\sim10^{-11.8}$ M in Pb activity-buffered solutions (*11*). This sensitivity is sufficient to measure the solubility of lead phosphate minerals over a wide range of conditions. The Pb ion-selective electrode is subject to interference from other metals (Cu, Fe, and Hg) (*11*). This prevents its use with soil solution extracts, particularly because many contain significant quantities of dissolved Fe in solution.

Soil solution extracts were therefore analyzed for Pb using ASV, yielding the concentration of labile Pb (*12*, *13*). Using the analysis for total dissolved Pb by graphite furnace atomic absorption spectrometry (GFAAS) and subtracting the ASV-labile Pb, we obtain the concentration of nonlabile Pb in the soil solution:

$$\text{(nonlabile Pb)} = \text{(dissolved Pb by GFAAS)} - \text{(ASV-labile Pb)} \quad (1)$$

The ASV-labile Pb pool includes inorganic complexes and excludes organic complexes which are not sufficiently labile to be detected by the ASV Hg electrode (*13*). If we assume that most organically complexed Pb is in electrochemically

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TABLE 1. The Stability Constants for Calculations of Free Pb^{2+} Ion Activity in Soil Solution (*22*, *25*)

equation	log *K*
$Pb^{2+} + H_2O \Leftrightarrow PbOH^+ + H^+$	−7.71
$Pb^{2+} + 2H_2O \Leftrightarrow Pb(OH)_2^0 + 2H^+$	−17.12
$Pb^{2+} + 3H_2O \Leftrightarrow Pb(OH)_3^- + 3H^+$	−28.06
$Pb^{2+} + HCO_3^- \Leftrightarrow PbHCO_3^+$	3.45
$Pb^{2+} + CO_3^{2-} \Leftrightarrow PbCO_3^0$	6.27
$Pb^{2+} + 2CO_3^{2-} \Leftrightarrow Pb(CO_3)_2^{2-}$	9.49
$Pb^{2+} + NO_3^- \Leftrightarrow PbNO_3^+$	1.17
$Pb^{2+} + Cl^- \Leftrightarrow PbCl^+$	1.58
$Pb^{2+} + SO_4^{2-} \Leftrightarrow PbSO_4^0$	2.62

TABLE 2. The Stability Constants Were Taken from ref 25, and References Therein (*26*−*29*)[a]

equation	log *K*
$H^+ + IDA \Leftrightarrow HIDA^-$	9.34
$2H^+ + IDA \Leftrightarrow H_2IDA$	11.94
$H^+ + H_2IDA \Leftrightarrow H_3IDA^+$	13.74
$Na^+ + IDA \Leftrightarrow NaIDA^-$	0.36
$Pb^{2+} + IDA \Leftrightarrow PbIDA$	7.50
$Pb^{2+} + 2IDA \Leftrightarrow PbIDA_2$	16.9
$Pb^{2+} + H^+ + IDA \Leftrightarrow PbHIDA^+$	10.2
$Pb^{2+} + NO_3^- \Leftrightarrow PbNO_3^+$	1.17

[a] The IDA constants were compiled and interpolated to 0.02 M ionic strength, and for the other constants the values at 0.1 M ionic strength were used.

TABLE 3. Basic Soil Properties before Addition of Lead Phosphate

soil	land use	pH_{CaCl_2}	soil O.M. (% C)	total Pb (mg/kg)	dissolved Pb (μg L^{-1})	labile Pb (nM)
Macdonald	forest	5.11	5.46	19.5	1.0	4.3
Cornell	orchard	6.19	4.77	151	7.1	15.1

nonlabile form, the activity of Pb^{2+} ions can then be calculated using known formation constants to partition the measured ASV-labile inorganic Pb into the various potential inorganic ion pairs or complexes and free ionic Pb^{2+} (eq 2 and Table 1).

$$\text{free } Pb^{2+} = (\text{labile Pb by ASV}) - [PbOH^+ + Pb(OH)_2^{\,0} + Pb(OH)_3^{\,+} + PbHCO_3^{\,-} + PbCO_3^{\,0} + Pb(CO_3)_2^{\,2-} + PbNO_3^{\,+} + PbCl^+ + PbSO_4^{\,0}] \quad (2)$$

This calculated free Pb^{2+} activity could overestimate activity because it would not account for weak organic ligands that might form ASV-labile complexes with Pb. A similar speciation calculation was performed to calculate the activity of $H_2PO_4^-$ from the concentration of dissolved inorganic phosphate determined by the molybdate blue reaction, the dissociation reaction data given in ref 7 and the appropriate solution chemical properties.

Synthetic Lead Phosphate Preparation. Two different solids were prepared according to methods obtained from the literature (*5*). We have chosen solids which were simple to prepare and which contained only Pb and PO_4 without other ions, so as to simplify the comparison between the aqueous and the soil systems. Secondary Pb orthophosphate ($PbHPO_4$) was made by slowly adding 500 mL of 0.1 M Na_2HPO_4 to 500 mL of 0.1 M $Pb(NO_3)_2$ at 80 °C and maintaining at low heat on a hot plate for 3 h. The slurry was stirred for 24 h and stored in the original solution. This precipitate consisted of crystalline platelets identified as $PbHPO_4$ by matching the X-ray diffraction pattern to that of known minerals at the X-ray diffraction facility in the Geology Department of Cornell University. The procedure to prepare tertiary Pb orthophosphate [$Pb_3(PO_4)_2$] was similar, using lead acetate instead of $Pb(NO_3)_2$. The resulting precipitate was rinsed with distilled-deionized water (dH_2O) three times after cooling and stored in dH_2O. This less crystalline solid was identified as $\beta Pb_9(PO_4)_6$ using X-ray diffraction.

Equilibration and Analysis. Both materials were equilibrated in the laboratory at 23 ± 1 °C for 20 and 100 days after adding 20 mL of suspension (~0.3 g of solids) to 30 mL centrifuge tubes and adding aliquots of NaOH (0−0.3 mL of 5 M solution), HNO_3 (0−0.05 mL of 10% solution), $Pb(NO_3)_2$ (0−0.2 mL of 0.01 M solution), and Na_2HPO_4 (0−0.5 mL of 0.001 M solution) in various combinations to obtain a range of phosphate, Pb, and pH. To approach equilibrium from over and under saturation, half of the treatment combinations had the original solution replaced with dH_2O before adding the reagent aliquots. Finally, the ionic strength of the solutions was adjusted with $NaNO_3$ to 0.1 M (which is necessary to use the ion-selective electrode). The free Pb^{2+} activity was measured in the equilibrated supernatants after centrifugation (10 min at 15000*g*) using a Pb ion-selective electrode (Orion 948200), a double-junction reference electrode (Orion 900200), and an Orion 701A pH meter. The pH was measured using a Fisher 805MP meter and a combination glass electrode (Orion 91-55). The phosphate in solution was determined using the molybdate blue colorimetric method. Electrolytic conductivity was measured using a YSI model 31 meter to estimate the ionic strength (IS).

Ion-Selective Electrode Calibration. The ion-selective electrode determination of free Pb^{2+} activity was made using a modification of a method used for copper in soil solutions (*14*). The procedure consists of calibrating the ion-selective electrode using metal buffer solutions of known activity which then allows direct measurement of the electrode potential and, therefore, the metal activity in the samples. The inner reference electrode was filled with standard calomel electrode solution (Orion solution 900002) and the outer compartment filled with 10% KNO_3 (Orion 90-00-03). To reduce the drift due to redox reactions on the surface of the electrode, it was calibrated every five samples and polished with 3 μm aluminum oxide polishing strips (Orion 301044). The standard curve relating electrode potential measurements to activity was made using Pb activity buffers containing 10^{-3} M iminodiacetic acid and 10^{-4} M $Pb(NO_3)_2$ in 0.1 M KNO_3. The Pb^{2+} activity in the buffers was pH dependent and calculated using MINEQL$^+$ (*15*), and the constants were given in Table 2. The Pb^{2+} activity in the buffers varied from $pPb^{2+} = 4.06$ at pH 4 to $pPb^{2+} = 11.85$ at pH 10. By comparison to the Cu electrode, the Pb electrode gave a similarly linear response, which however, tended to drift between each polishing and calibration while maintaining a similar response slope. Frequent renewal of the electrode surface by polishing and recalibration improved the accuracy of the method (for analytical details on Pb ion-selective electrodes, see refs 10 and 11).

Soil and Precipitates. For this experiment, we used two soils, an uncontaminated calcareous forest soil and an orchard soil contaminated with Pb from sewage sludge and Pb arsenate pesticides. We have chosen soils with similar organic matter levels because we wanted to study the impact of a moderate level of soil Pb contamination upon the solubility of the added Pb while keeping the effect of organic matter level constant. The forest soil is an Inceptisol from the Morgan Arboretum on the Macdonald Campus of McGill University (Ste-Anne-de-Bellevue, QC); the orchard soil is an Alfisol from the Cornell University Orchard (Ithaca, NY). Basic soil properties can be found in Table 3.

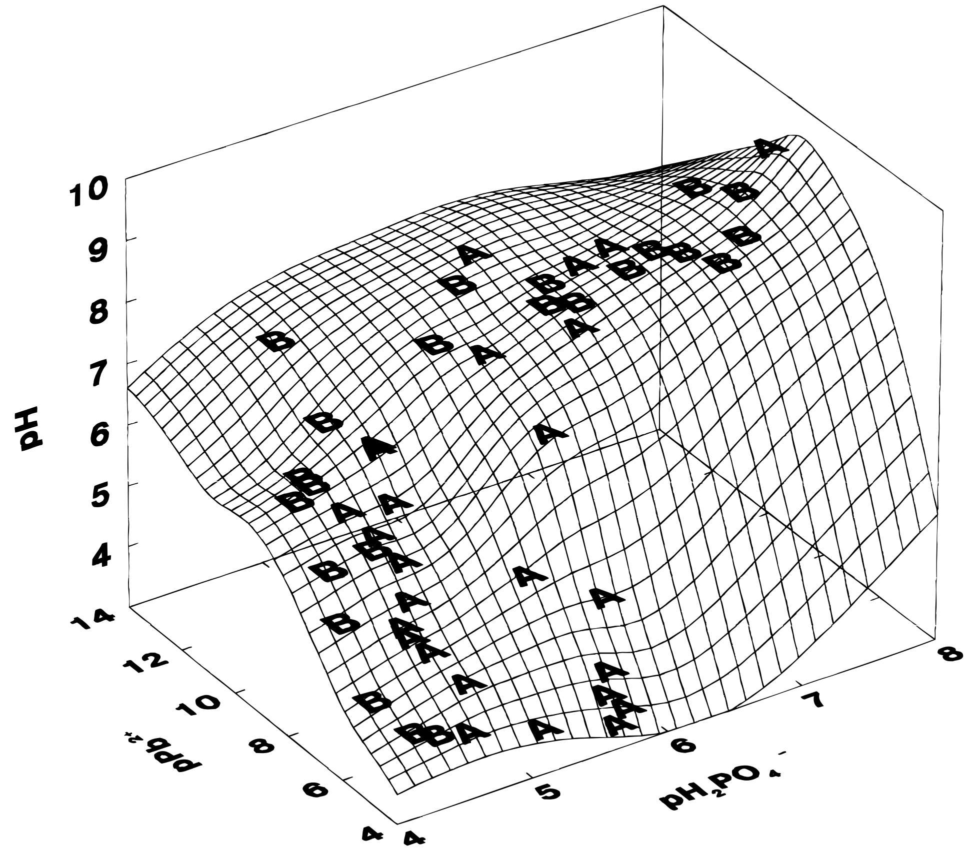

FIGURE 1. The solubility of the two synthetic lead phosphates for 20 and 100 day equilibrations, A represents $PbHPO_4$ and B represents $\beta Pb_9(PO_4)_6$. The plotted surface is a distance-weighted least-square smoothing (*15*).

Ten grams of soil and 20 mL of 0.01 M KNO_3 were added to 30 mL centrifuge tubes. The soil was extracted using KNO_3 because neutral salt extractions are often used to evaluate soil metal bioavailability (*9, 14*), and although some $PbNO_3^+$ is formed, this is accounted for by eq 2 and in most cases, it is negligible. Fifteen tubes were used for each soil, with up to 3 mL of 0.1 M KOH or HNO_3 added to generate a pH range 4−8. The tubes were shaken and equilibrated for 2 days before a 0.5 mL spike of the $PbHPO_4$ slurry was added to each tube. This spike is equivalent to an increase of ~530 mg of Pb kg^{-1} of dry soil, enough to consider the soil markedly contaminated (pristine soils generally contain between 10 and 20 mg of Pb kg^{-1}).

The spiked soils were then shaken every other day for a month (10 m at 200 rpm on a reciprocal shaker). The bottles were kept loosely covered (to prevent dust deposition) but not closed, so as to allow for gas exchange and keep the solutions aerobic and in equilibrium with atmospheric CO_2. Then, the tubes were centrifuged at 15000*g* to separate the supernatants. The pH and electrolytic conductivity were determined in the supernatants before filtration. The solutions were then passed through 0.22 μm cellulosic membranes, and analyzed for labile Pb by ASV and for phosphate by colorimetry. The extracts were made 1 mM in Na_4EDTA (ultrapure grade) to preserve the samples before total dissolved Pb was determined by GFAAS with a Varian Zeeman SpectrAA instrument.

Results

Synthetic Lead Phosphate. The solubility data for both lead phosphate mineral phases were not statistically different. The solubility after equilibration for 20 and 100 days were not different either, suggesting that there is no significant solubility change occurring between 20 and 100 days. The results are combined and illustrated in Figure 1. The data are only presented graphically but the complete dataset can be obtained from the authors. The solubility relationship involving pPb^{2+}, pH, and $pH_2PO_4^-$ was highly significant. However, it did not seem to match that of any of the known $Pb\text{-}PO_4$ mineral phases, including pyromorphite, which is considered the least soluble lead phosphate mineral under these conditions. The $PbHPO_4$ system could not be readily distinguished from $\beta Pb_9(PO_4)_6$ on the basis of solubility. The free Pb^{2+} activity in the solution was lower in this pure system than would be expected from mineral equilibria in a soil where solubility is controlled by $PbHPO_4$ (*7*).

Calculations of the ion activity product (IAP) for the $PbHPO_4$ mineral phase theoretically controlling Pb solubility ($^{c*}K_{s0}$ based on the reaction $PbHPO_4 + H^+ \leftrightarrow Pb^{2+} + H_2PO_4^-$; using the Davies equation for activity coefficients) shows a significant pH-dependent effect (Figure 2a). The scatter in the estimates of solubility could be attributed to the presence of more than one mineral phase or perhaps a single phase of variable crystallinity. The resulting IAP using the whole data set was -7.53 ± 1.89. While quite variable, this IAP is clearly lower than the log $^{c*}K_{s0}$ value of −4.25 found by Nriagu (*5*). Much of this discrepancy can probably be attributed to the pH trend of the IAP and the possible presence of multiple phases of different mineralogy and crystallinity (*16, 17*). The data show that the solution concentrations were all below the levels required for saturation with respect to of PbO, $Pb(OH)_2$, or $PbCO_3$. Nriagu (*5*) determined log $^{c*}K_{s0}$ at very acidic pH values (2−4) which Figure 2a indicates are likely to produce less negative estimates of IAP which may not reliably be extrapolated to more typical soil conditions. Nriagu (*5*) also discussed the possible transformation of $PbHPO_4$ into $Pb_3(PO_4)_2$ or other lead phosphates as the solution conditions vary.

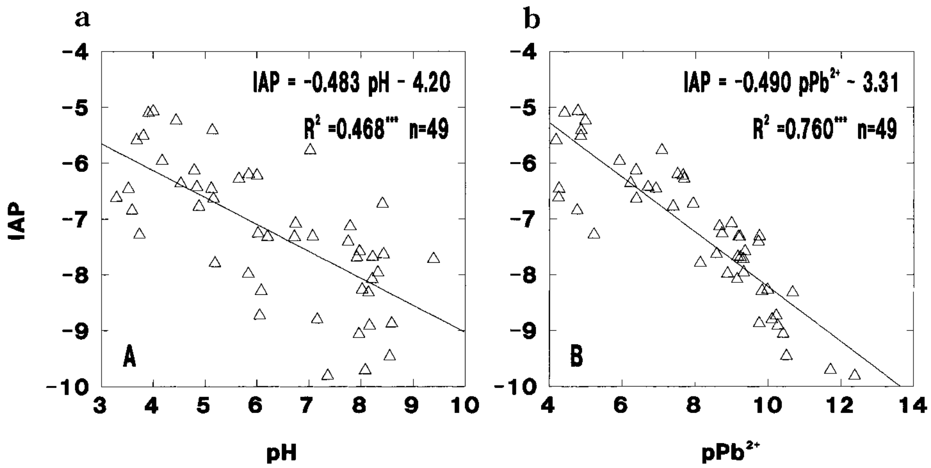

FIGURE 2. The IAP for the synthetic Pb-PO$_4$ as a function of pH (A) and as a function of pPb^{2+} (B).

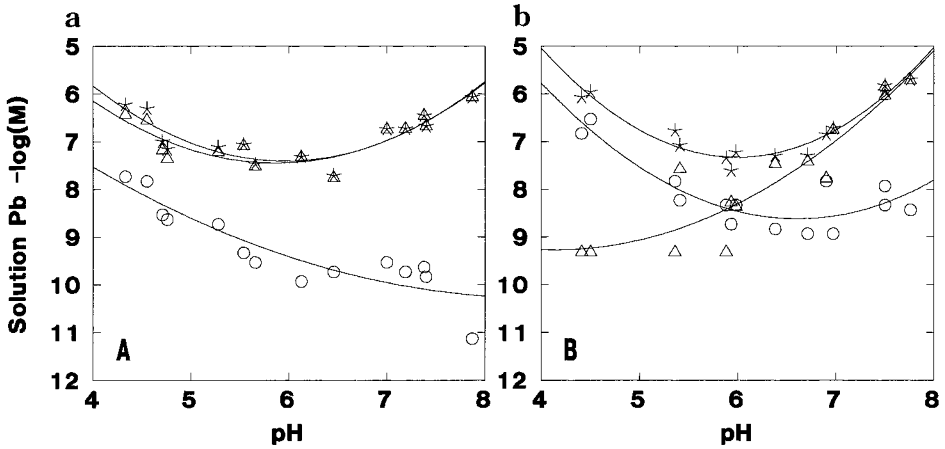

FIGURE 3. The free Pb^{2+} activity (○) (by ASV), the OM-bound Pb in solution (△), and the total dissolved Pb (*) (by GFAAS) in the soil solutions equilibrated with a 530 mg of Pb kg^{-1} spike of PbHPO$_4$. The data are presented as a function of pH and the units are $-$log(M). The data for the forest soil are in panel A, and the data for the orchard soil are in panel B. The lines are quadratic smoothing.

The effect of pH could also be partly explained by incongruent surface processes such as competitive adsorption of Pb^{2+} and other cations on the surface exchange sites of the precipitated minerals, since some phosphate minerals have substantial adsorption capacity for metals (*18*). If the free Pb^{2+} concentration is partly controlled by adsorption of Pb^{2+} ions onto the surfaces of the minerals, then we might expect a relationship between the observed IAP and pPb^{2+}. Indeed, as Figure 2b illustrates, more of the scatter in the IAP of PbHPO$_4$ is explained by the solution pPb^{2+} instead of pH.

The chemical equilibrium data described by Figure 1 are most accurately modeled using an empirical linear regression:

$$\mathrm{pPb}^{2+} = 1.47\mathrm{pH} - 0.98\mathrm{p}(\mathrm{H_2PO_4}^-) + 4.13 \qquad R^2 = 0.836,\ n = 49 \quad (3)$$

where each variable and the whole regression are significant ($p < 0.001$). The addition of a class factor in the regression to distinguish the two mineral phases shows no significant differences ($P > 0.8$) between the solubility relationships of PbHPO$_4$ and βPb$_9$(PO$_4$)$_6$.

The best-fit relationship described by eq 3 has a coefficient of about 1.5 for pH and 1 for pH$_2$PO$_4^-$. Although this regression is highly significant and describes the Pb, pH, and pH$_2$PO$_4^-$ relationships of Figure 1 by a very simple model, this is an empirical oversimplification of limited use, derived from a simple synthetic solid/solution system in the absence of any organic ligands or soil. Nevertheless, the solubility results suggest that under realistic pH and Pb and phosphate solubility conditions of soils, solubility functions more complex than eq 3 are unlikely to be justified statistically or conceptually. If a simple batch equilibration cannot be explained with straightforward solubility equilibrium relationships, it would be quite surprising if those equilibrium equations were successful in explaining the behavior of Pb in contaminated soils.

Soil and Precipitates. The Pb dissolved in the soil solution (measured by GFAAS) includes uncomplexed metal, inorganic ion pairs, and organic complexes. The labile Pb pool measured by ASV reflects only the metal in solution that is available for reduction at the electrode surface (mainly free metal and labile complexes). By partitioning the labile Pb pool into those ion pairs calculated to be most prevalent in the solution (namely PbOH$^+$, Pb(OH)$_2^0$, Pb(OH)$_3^+$, PbHCO$_3^-$, PbCO$_3^0$, Pb(CO$_3$)$_2^{2-}$, PbNO$_3^+$, PbCl$^-$, and PbSO$_4^0$), an estimate of free Pb^{2+} was obtained by difference (eq 2 and Figure 3). At neutral pHs and higher, organic matter solubility increases and may cause the “ASV-labile” Pb to include some labile organic complexes. Any ASV-labile organically bound Pb would have been included in the inorganic fraction by default, causing an overestimate of the free Pb^{2+} activity. If the short-term bioavailability of Pb is controlled solely by the free metal ions in solution (calculated from the ASV-labile Pb pool), then this study shows that at pH above 6, the presence in soil of more than 500 mg of Pb kg^{-1} as lead phosphate generates a free Pb^{2+} ion activity in the soil solution below 10^{-9} in the pristine calcareous soil and below 10^{-8} in the contaminated orchard soil. The Pb^{2+} activities measured in the orchard soil are higher and more variable than those for the pristine forest soil. This may be the result of differences in the soil properties as well as the higher initial Pb content of the orchard soil, which was contaminated by lead arsenate and sewage sludge.

In contrast to the estimated free Pb, the dissolved Pb includes nonlabile dissolved organic complexes and is up to 5 orders of magnitude higher than free Pb in these soils (Figure 3). Both soils had a similar relation of dissolved Pb to pH. The dissolved Pb diminished from 124−228 μg of Pb L^{-1} at pH 4.3−4.5 in both soils down to 3−12 μg of Pb L^{-1} between pH 5.5 and 6.5. Further pH increase raised the total dissolved Pb, up to 420 μg of Pb L^{-1} in the orchard soil at pH 7.8 and 310 in the forest soil at pH 7.5 (Figure 3). These are very high solubilities relative to various groundwater quality standards [e.g., 10−15 μg of Pb L^{-1} (*19*)], and imply that lead phosphates are not sufficiently insoluble to prevent groundwater contamination in moderately contaminated soils at low and high pH (5 > pH > 7). Figure 3a shows that in the forest soil, most of the Pb dissolved in the soil solution is bound to dissolved organic matter. In the orchard soil, nonlabile Pb constitutes most of the dissolved Pb at pH 6 and above; only under more acidic conditions does the labile Pb become predominant over the nonlabile forms of Pb. At higher pH, the dissolved Pb in nonlabile complexes increases significantly in both soils (Figure 3), and it appears that dissolved organics solubilize Pb from the phosphate minerals, effectively mobilizing the metal. Other researchers have noted greater solubility of Pb and other metals in contaminated soils as the pH is raised above 6 (*20*−*22*).

The bioavailability of Pb complexed with dissolved organic matter is not well-known. It may be tightly bound and unavailable for release to the soil solution. Furthermore, the increased solubility of Pb at pH above 6.5 raises concerns for metal mobility, irrespective of the actual bioavailability of the Pb in the solution. We used KOH (as opposed to lime) to increase the pH in this experiment, which may have generated higher dissolved organic matter concentrations than an equivalent addition of $CaCO_3$. Nevertheless, liming contaminated soils to pH 7 or higher increases the dissolved organic matter (*20*, *21*) and correspondingly generate a significant increase in the dissolved Pb in the soil solution. Even if this Pb pool is potentially unavailable for biological uptake, it is still in a mobile form and prone to leaching (*23*). We hypothesize that at the higher soil pH, the strong complexation of Pb by dissolved organic matter dissolves a fraction of the lead phosphate, despite the low solubility of this mineral. Thus, soil remediation by phosphate addition to reduce the solubility of Pb is not likely to be completely successful in immobilizing this metal, although it may limit its toxicity.

In a different experiment, Ma et al. (*24*) added rock phosphate to various Pb-contaminated soils and found that, after up to 8 weeks of incubation, the phosphate did not significantly reduce the extractability of Pb by EDTA-NH_4OAc (*24*). The EDTA extraction is considered an estimate of the soil metal pool associated with organic matter, therefore, also suggesting that phosphate amendments have little impact on the retention of Pb by the organic components of contaminated soils.

Synthetic Mineral vs Soil Solubility. The solubility of both synthetic lead phosphate phases was described very well using eq 3. In the soil equilibration experiment, the soil pH and solution $pH_2PO_4^-$ were used to attempt to predict Pb^{2+} activity using eq 3, assuming that these lead phosphate phases controlled the solubility. The predicted activities are compared to the actual measurements in Figure 4. Although the regression for the whole dataset (full line) shows a close fit to the 1:1 line (dotted line), the actual data points show wide variations between predicted and measured values. Even though both soils had similar properties (except total Pb content), free Pb^{2+} activity is overestimated in most cases for the forest soil (circles in Figure 3) and drastically underestimated in four cases in the orchard soil (triangles in Figure 4). The most likely explanation is that the difference in total metal content between the two soils is large enough to modify the free metal activity. This suggests that solubility in soils is not controlled by chemical equilibrium with a pure solid phase (which would be independent of the total content) but by surface retention processes which vary with the level of saturation of adsorption sites (*8*, *9*).

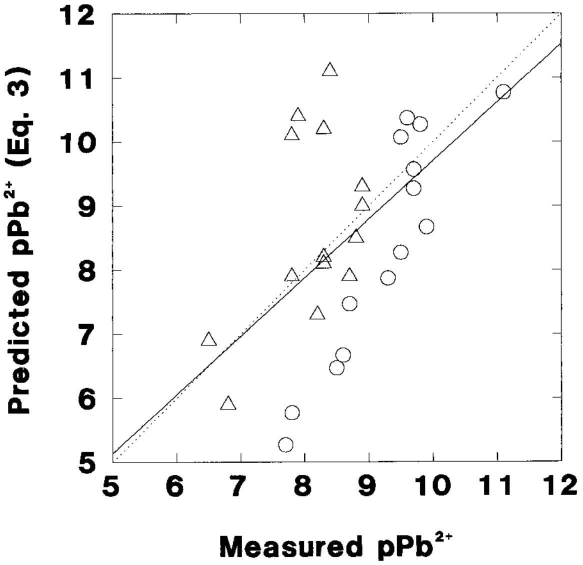

FIGURE 4. The free Pb^{2+} activity predicted using eq 3 as a function of the measured values. The ○ represent the forest soil, the △ represent the orchard soil, the full line represents the linear regression for the dataset, and the dotted line is the 1:1 perfect fit. The units are −log(M).

Conclusions

The solubility of two synthetic Pb-PO_4 phases was measured using a Pb ion-selective electrode in a batch equilibration under a wide range of conditions. The resulting chemical equilibria are impossible to explain using a simple mineral solubility equation. Furthermore, the highly significant empirical solubility relationship derived from the data for pure lead phosphate systems is not applicable to soil systems, probably because surface reactions and soil organic matter play an important role in determining the solubility of Pb. At low pH, adsorption by soil reduces the solution concentration of Pb below what is observed in pure systems. At higher pH, dissolved organic matter increases the dissolved Pb in the soil solution. Although this may be partly an artefact due to the use of KOH to increase the pH, we can expect a qualitatively similar trend using lime in the field.

Although phosphate amendments and lime are beneficial in reducing the solubility, mobility, and bioavailability of Pb, the optimum pH to reduce solubility is between 5.5 and 6.5. Higher pH increases organic matter solubility, which may induce dissolution of lead phosphate by organic complexation reactions.

Acknowledgments

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Literature Cited

(1) Holmgren, G. G. S.; Meyer, M. W.; Chaney, R. L.; Daniels, R. B. *J. Environ. Qual.* **1993,** *22*, 335−348.
(2) Ma, Q. Y.; Traina, S. J.; Logan, T. J. *Environ. Sci. Technol.* **1993**, *27*, 1803−1810.
(3) Rabinowitz, M. B. *Bull. Environ. Contam. Toxicol.* **1993**, *51*, 438−444.
(4) Davenport, J. R.; Peryea, F. J. *Water, Air, Soil Pollut.* **1991**, *57/58*, 101−110.
(5) Nriagu, J. O. *Inorg. Chem.* **1972**, *11*, 2499−2503.
(6) Nriagu, J. O. *Geochim. Cosmo. Acta* **1974**, *38*, 887−898.
(7) Lindsay, W. L. *Chemical Equilibria in Soils;* John Wiley: New York, 1979.
(8) Sauvé, S.; McBride, M. B.; Norvell, W. A.; Hendershot, W. H. *Water, Air, Soil Pollut.* **1997**, *100*, 133−149.
(9) McBride, M. B.; Sauvé, S.; Hendershot, W. H. *Eur. J. Soil Sci.* **1997**, *48*, 337−346.
(10) Hansen, E. H.; Rùzicka, J. *Anal. Chim. Acta* **1974**, *72*, 365−373.
(11) Kivalo, P.; Virtanen, R.; Wickström, K.; Wilson, M.; Pungor, E.; Horvai G.; Tóth, K. *Anal Chimi. Acta* **1976**, *87*, 401−409.
(12) Figura, P.; McDuffie, B. *Anal. Chem.* **1980**, *52*, 1433−1439.
(13) Florence, T. M. *Analyst* **1986**, *111*, 489−505.
(14) Sauvé, S.; McBride, M. B.; Hendershot, W. H. *Arch. Environ. Contam. Toxicol.* **1995**, *29*, 373−379.
(15) Wilkinson, L. *SYSTAT for windows: Statistics - Version 5*; SYSTAT Inc.: Evanston, IL, 1992.
(16) Lindsay, W. L.; Stephenson, H. F. *Soil Sci. Soc. Amer. Proc.* **1959**, *23*, 12−18.
(17) Cotter-Howells, J. *Environ. Pollut.* **1996**, *93*, 9−16.
(18) Ma, Q. Y.; Traina, S. J.; Logan, T. J.; Ryan, J. A. *Environ. Sci. Technol.* **1994**, *28*, 1219.
(19) CCME, CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites. *Interim Canadian Environmental Quality Criteria for Contaminated Sites*; CCME EPC-CS34, Canadian Council of Ministers of the Environment, Winnipeg, Manitoba, Canada, 1991.
(20) Waller, P. A.; Pickering, W. F. *Chem. Speciat. Bioavail.* **1993**, *5*, 11−22.
(21) Bruemmer, G. W.; Gerth, J.; Herms, U. *Z. Pflanzenernaehr. Bodenk.* **1986**, *149*, 382−398.
(22) Lumsdon, D. G.; Evans, L. J.; Bolton, K. A. *J. Soil Contam.* **1995**, *4* (2), 137−150.
(23) McBride, M. B; Richards, B.; Steenhuis, T.; Russo, J. J.; Sauvé, S. *Soil Sci.* **1997**, *162*, 487−500.
(24) Ma, L. Q.; Choate, A. C.; Rao, G. N.; *J. Environ. Qual.* **1997**, 26, 801−807.
(25) Smith, R. M.; Martell, A. E. *Critical Stability Constants, Volume 6, Second Supplement*; 1989; p 643.
(26) Calì, R.; Pizzarelli, E.; Sammatanos, S. *Thermochim. Acta* **1980**, *35*, 169−179.
(27) Maeda, M.; Ohnishi, M.; Nakagawa, G. *J. Inorg. Nucl. Chem.* **1981**, *43*, 107−110.
(28) Vasil'ev, V. P.; Romanova, L. M. *Russ. J. Inorg. Chem.* **1982**, *27*, 1734−1739.
(29) Felcman, J.; Fraústo da Silva, J. J. R. *Talanta* **1983**, *30*, 565−570.

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