Spectroscopic Speciation and Quantification of Lead in Phosphate-Amended Soils

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ABSTRACT

The immobilization of Pb in contaminated soils as pyromorphite [$Pb_5(PO_4)_3Cl, OH, F$] through the addition of various phosphate amendments has gained much attention in the remediation community. However, it is difficult to fully determine the speciation and amount of soil Pb converted to pyromorphite by previously employed methods, such as selective sequential extraction procedures and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, which often lead to erroneous results in these non-equilibrated and heterogeneous systems. Statistical analysis by linear combination fitting (LCF) applied to X-ray absorption fine structure (XAFS) spectroscopic data of Pb-contaminated soil samples relative to known Pb reference material provides direct, in situ evidence of dominate Pb species in the amended soils without chemical or physical disruption to the Pb species as well as a weighted quantification output. The LCF–XAFS approach illustrated that pyromorphite concentration ranged from 0% (control soil) to 45% (1% phosphoric acid amendment, residence time of 32 mo) relative to the total Pb concentration. The Pb speciation in the nonamended control soil included Pb–sulfur species (galena + angelsite = 53%), adsorbed Pb (inner-sphere + outer-sphere + organic-bound = 45%), and Pb–carbonate phases (cerussite + hydrocerussite = 2%). The addition of P promoted pyromorphite formation and the rate of formation increased with increasing P concentration (up to 45%). The supplemental addition of an iron amendment as an iron-rich byproduct with triple superphosphate (TSP) enhanced pyromorphite formation relative to independent TSP amendment of like concentrations (41 versus 29%). However, the amendment of biosolids and biosolids plus TSP observed little pyromorphite formation (1–16% of total Pb), but a significant increase of sorbed Pb was determined by LCF–XAFS.

TAKING INTO consideration escalating pollution problems and public outcry in the United States and the ability of industry to financially handle such self-imposed issues, in 1992, the Remediation Technologies Development Forum (RTDF) was established. This partnership was created after industry counterparts approached the USEPA to identify and foster collaboration to develop and improve the environmental technologies needed to address their mutual cleanup problems in the safest, most cost-effective manner as research-focused RTDF action teams. One such action team, In-Place Inactivation Natural Ecological Restoration Technologies (IINERT) Soil-Metals, is the focus of this study. The mission of IINERT was to develop and demonstrate in-place inactivation and natural ecological restoration technologies that reduce and eliminate the risks to human health and the environment of metals in soil and to achieve regulatory and public acceptance of these technologies.

The IINERT technologies work to chemically and physically inactivate Pb found in contaminated soils by reducing the solubility and bioavailability without the need for removing the soil. In situ incorporation of chemicals such as phosphates, mineral fertilizers, iron oxyhydroxides, other minerals, biosolids, or limestone changes the molecular species of the soil Pb to less bioavailable forms. Alteration of the Pb species can significantly reduce its potential toxicity to humans and the environment although the total soil concentration of Pb does not necessarily change as a result of in situ immobilization. The chemicals used for inactivation also may increase the fertility of the soil and eliminate any toxicity to plants and soil organisms. Further, growing a plant cover physically stabilizes the soil and its contaminants in place, which, in turn, minimizes soil erosion and the transport of the metal-laden soil as dust. Of the treatment options available for remediating metal-contaminated soils, in situ inactivation appears to be the most cost-effective; however, understanding risk assessment and metal speciation are vital to substantiate immobilization as a remediation strategy.

Since soil Pb poses a health risk to humans, particularly children, and the environment, immobilization strategies may provide a suitable solution to limiting such risks. Immobilizing Pb as pyromorphite in soils has been extensively studied in the literature (Nriagu, 1974; Cotter-Howells and Thornton, 1991; Ma et al., 1993; Cotter-Howells et al., 1994; Ruby et al., 1994; Cotter-Howells, 1996; Laperche et al., 1997; Zhang et al., 1998; Traina and Laperche, 1999; Hettiarachchi et al., 2000; Pearson et al., 2000; Ryan et al., 2001; Eusden et al., 2002; Cao et al., 2003). Further, the technology for Pb immobilization by amendments of solid calcium phosphate materials has been patented (Ryan et al., 1996) as a remediation method. Once soil Pb is transformed to pyromorphite, the Pb is sequestered in a form that is biologically inert and environmentally stable (Jowett and Price, 1932; Baker, 1964; Nriagu, 1973; Scheckel and Ryan, 2002). However, the pinnacle of Pb immobilization research is to measure the amount of soil Pb converted to pyromorphite, which is problematic in such a heterogeneous and often non-equilibrated system. Still, to fully understand the rate and effectiveness of P amendments on the sequestration of Pb as pyromorphite, methodologies must be employed that examine the true speciation of Pb in situ so that the analysis method in itself does not alter Pb speciation. Selective sequential extraction (SSE) procedures have been employed showing that a substantial portion of the soil Pb is transformed to pyromorphite (Ryan et al., 2001; Cao et al., 2002, 2003; Melamed et al., 2003); however, these studies cannot rule out nor disprove the probability that pyromorphite formed as a result of the extraction

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Abbreviations: LCF, linear combination fitting; TSP, triple superphosphate; XAFS, X-ray absorption fine structure.

procedure (Scheckel et al., 2003) due to rapid kinetic formation of pyromorphite (Nriagu, 1973, 1974; Scheckel and Ryan, 2002). Other parallel studies have attempted to speciate Pb in P-amended soils based on energy dispersive X-ray (EDX) spectroscopy and scanning electron microscopy (SEM) (Davis et al., 1993; Yang et al., 2001; Cao et al., 2003); however, it is very difficult to distinguish the hexagonal crystals of pyromorphite from an array of hexagonal minerals found in soils and, additionally, EDX only provides a gross approximation of elements generally over a large beam spot size, which may indicate that the input amendment of P and contaminated soil Pb are both present within the beam window, but are not necessarily chemically associated as pyromorphite. Electron probe microanalysis (EPMA) studies have examined Pb in environmental samples (Davis et al., 1993; Link et al., 1994); however, this method is insensitive to chemical and physical aspects of submicron matrix heterogeneity and cannot distinguish effectively between metal adsorption and (co)precipitation in such a matrix.

Recent achievements for speciating metals in heterogeneous soil and sediment environments have been the tandem use of X-ray absorption fine structure (XAFS) spectroscopy and statistical analysis via linear combination fitting (LCF) or principle component analysis (PCA) (Beauchemin et al., 2002; Isaure et al., 2002; Roberts et al., 2002; Scheinost et al., 2002). This experimental approach combines the sensitive element species-specific, in situ capabilities of XAFS with the comprehensive detail of stringent statistical analysis by examining unknown spectra relative to well-characterized reference compounds to not only identify various species of a particular metal but also quantify the multiple components. This approach was employed to accomplish the objectives of this manuscript, which were to identify and quantify the chemical speciation of Pb in P-amended soils as a function of amendment type and aging time through the application of XAFS spectroscopy combined with LCF.

MATERIALS AND METHODS

Soil Samples

The field experiment was established in a residential setting adjacent to a Pb smelter, which operated from the 1880s to its closing in the late 1960s at Joplin, MO. The site was 42×47 m. Smelter emission was the primary source of Pb contamination to the site. The soil Pb concentration at the site is variable and ranges from 1100 to 5300 mg Pb kg^{-1} soil with the majority of the site being in the range of 2000 to 3000 mg Pb kg^{-1} soil. Preliminary microprobe analysis of the bulk samples indicated that the primary forms of soil Pb were carbonate, oxide, sulfate, and sulfide. The soil had a neutral pH (6.9–7.2), organic carbon content of 46 to 56 g kg^{-1}, a cation exchange capacity of 27.2 to 32.2 cmol kg^{-1}, and a Bray extractable P of 12 to 39 mg P kg^{-1} soil.

Treatments were installed during March 1997, using a completely randomized design with four replicates. A polyethylene membrane (HDPE) was placed around the perimeter of each of the 2×4-m plots to reduce the potential of inter-plot contamination. In addition to the phosphate treatment, an iron-rich waste product and composted biosolids were used (Fig. 1), which have been reported to reduce metal bioavailability (Brown et al., 1998; Basta and Sloan, 1999; Basta et al., 2001), were included as treatments as well as the influence of residence time.

Amendments were weighed and hand-applied on a per plot basis to the tilled soil. For the field study, triple superphosphate (TSP) and phosphoric acid (H_3PO_4) were purchased at a local fertilizer dealer in Joplin, MO. Rock phosphate (RP) was donated by Occidental Chemical Corporation (Dallas, TX). The iron-rich paint-processing by-product (IRR) was donated by DuPont (Wilmington, DE). The Compro composted biosolids (BS) was shipped from Montgomery County, MD. Applications were made on a dry weight basis with the assumption that the bulk density of 1 m^3 of soil = 1050 kg. Application rates of P treatments were calculated on the basis of total P addition. After amendments were applied in March 1997, plots were covered with a commercial landscape fabric to reduce erosion. In May 1997, the fabric was removed, $Ca(OH)_2$ (71% purity) was added and rototilled into each plot at a 10-cm depth to bring the pH to 7, and the plots were hand-seeded with 'Kentucky 31' tall fescue (*Festuca arundinacea* Schreb.). The amount of lime required ranged from 157 kg
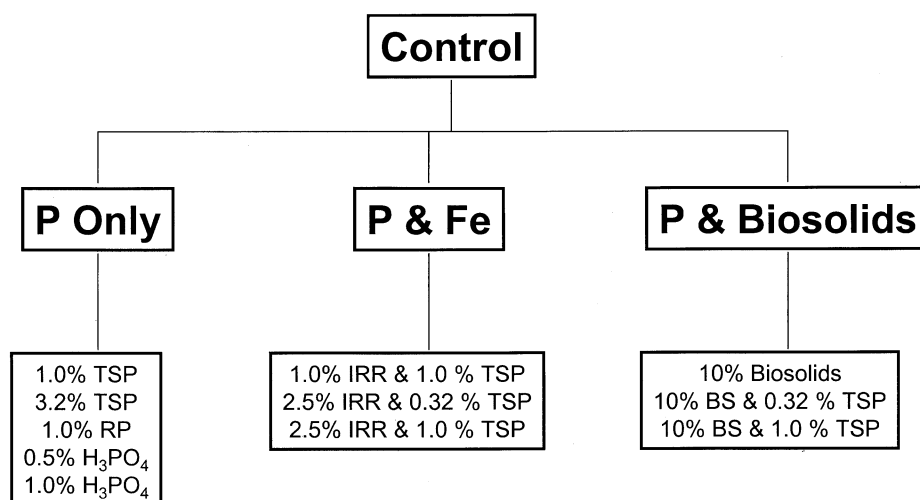

Fig. 1. Diagram of samples including control and three categories of amendments. Amendments included triple superphosphate (TSP), rock phosphate (RP), phosphoric acid (H_3PO_4), iron-rich waste (IRR), and composted biosolids (CB).

per plot (3.2% P TSP) to 39.4 kg per plot (10% compost + 0.32% P as TSP). This corresponds to approximately 200 Mg lime ha^{-1} for the 3.2% TSP and 50 Mg lime ha^{-1} for the 10% compost + 0.32% P treatments. In the case of the phosphoric acid treatments, the liquid-fertilizer-grade (85%) phosphoric acid and fertilizer-grade (45%) KCl were surface-applied and rototilled; 10 d later lime [Ca(OH)$_2$] was applied and hand-raked to incorporate to a depth of 10 cm. Thirty days later, the plots were seeded.

X-Ray Absorption Fine Structure Spectroscopy

The soil samples (<250-μm fraction, dry sieve) were analyzed by XAFS to determine the speciation of Pb. For XAFS analysis, the soils were loaded into Teflon sample cell holders and sealed with Kapton tape. Lead (13055 eV) L$_{III}$–XAFS data were collected at beamline X-11A using Si(111) monochromator crystals at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY. Five scans were collected at ambient temperature in fluorescence mode using a Kr-purged Lytle detector with an As filter to reduce scattered radiation and Al foil to diminish background fluorescence. Energy was calibrated to the first inflection of a Pb-metal foil standard and was collected simultaneously with

the spectrum of each sample. The electron beam energy was 2.5 GeV and the beam current varied from 300 to 100 mA. The collected scans for a particular sample were merged, the data were then normalized, and the background was removed by spline-fitting using WinXAS 1.3 (Ressler, 1998). In an initial attempt, the XAFS data were then converted to k space, windowed, and Fourier-transformed to convert to R space. Conventional shell-by-shell fitting of the radial structure functions (RSFs) was attempted by theoretical paths for Pb, O, and other backscatter atoms generated from crystallographic data of model compounds using FEFF 7.0 (Zabinsky et al., 1995). Variables obtained from the fits include the energy phase shift (ΔE_o), coordination numbers (N), bond distances (R), and Debye–Waller factors (σ^2) that were derived from nonlinear least squares fitting. Due to the multiple Pb species present, the spectra were an average of all signals and data analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy samples to determine these variables was not successful (data not shown) via traditional analysis methods. Alternatively, we examined the XAFS χ^3–function spectra by linear combination fitting (LCF) of reference spectra (from Fig. 2) to the collected soil sample spectra. Previous XAFS research has demonstrated the success of LCF and principle component analysis to identify and quantify the major metal
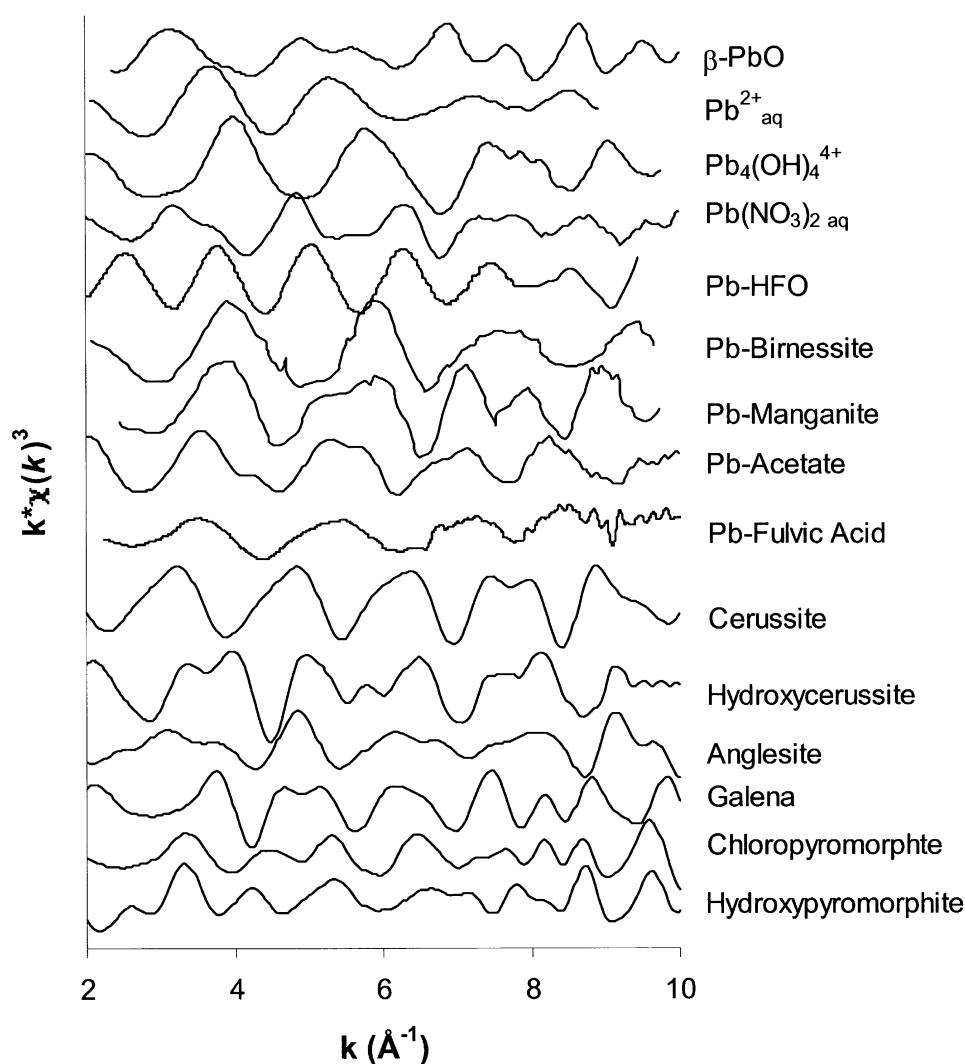

Fig. 2. Normalized Pb$_{LIII}$–X-ray absorption fine structure spectroscopy (XAFS) k^3–weighted chi spectra of reference samples employed as model components for linear combination fitting.

species present in samples (Manceau et al., 1996; Morin et al., 1999; Ostergren et al., 1999; Roberts et al., 2002; Scheinost et al., 2002).

Linear combination fitting refers to the process of selecting a multiple component fitting function (a Levenberg–Marquardt least-squares algorithm in this study) that minimizes the sum of the squares of residuals. During the fitting procedure, residual error (the normalized root square difference between the soil spectra and fitted data) was minimized by removal of non-essential reference components (i.e., component values of <1 were assigned a Table 1 value of zero) and continued until no net improvement of residual error was observed (Ostergren et al., 1999). The parameters of the theoretical function model are the desired physical descriptors of the measurements in which one attempts to fit the data to the model and report the parameter values (often as a weight or fractional percent of the total). The accuracy of the fitting procedure depends on data quality and measured limits in addition to how well the reference standards actually represent the soil samples (Roberts et al., 2002). The best fitting scenarios, determined by the smallest residual error and the sum of all fractions being close to 1, are shown in Table 1. A minimum of four components were necessary to fully describe any particular soil sample within 1% reproducible error indicating that four Pb species could be tested statistically stringent. The fundamental source of fitting error is typically due to the limited number of actuators that afford a limited number of degrees of freedom for which, in our case, we restricted error significantly.

To create a library of Pb XAFS reference spectra for LCF and principle component analysis fitting, Pb reference minerals and sorption samples were collected or synthesized (Fig. 2). The Pb mineral and chemical samples include: (i) Pb-acetate (ACS certified; Fisher Scientific, Fair Lawn, NJ); (ii) $PbSO_4$ (anglesite) (Aldrich Chemical Company, Milwaukee, WI); (iii) $PbCO_3$ (cerussite) (Aldrich); (iv) PbS (galena) (GFS Chemicals, Columbus, OH); (v) $Pb_5(PO_4)_3Cl$ (chloropyromorphite) and $Pb_5(PO_4)_3OH$ (hydroxypyromorphite) from a previous study (Scheckel and Ryan, 2002); (vi) hydroxycerussite (Paint Standard 2589; NIST, Gaithersburg, MD); (vii) β-PbO (Aldrich); and (viii) aqueous Pb by dissolving $Pb(NO_3)_2$, $Pb(ClO_4)_2$ (as Pb^{2+}) (ACS certified; Fisher Scientific), or $Pb_4(OH)_4^{4+}$ (synthesized according to Strawn and Sparks [1999]). These samples were diluted to a total concentration of 5000 mg kg^{-1}. Sorption samples were prepared under a N_2 environment at

pH 6 by reacting Pb with hydrous ferric oxide (HFO) (prepared according to Schwertmann and Taylor [1977]), birnessite, manganite ($\Gamma = 1$ μmol m^{-2}), and fulvic acid ($\Gamma = 2$ μmol m^{-2}) (Aldrich) for 3 d, at which point the solids were collected via centrifuging, placed into a sample holder under N_2, and refrigerated until analysis.

RESULTS AND DISCUSSION

Linear Combination Fitting–X-Ray Absorption Fine Structure Analysis

The results of LCF–XAFS analysis are shown in Fig. 3 for the control sample and selected amended samples. The solid curve represents the actual raw sample data and the dotted curve represents the results of the LCF–XAFS fits. As one can see, the LCF–XAFS fitted results describe the sample data quite well. By employing the reference spectra from Fig. 2 in the fitting procedure, step by step elimination of nonsignificant component reference spectra continued until the best statistical fit was achieved. For a more detailed explanation of the fitting procedure and method, see work by Ostergren et al. (1999), Beauchemin et al. (2002), Isaure et al. (2002), Roberts et al. (2002), and Scheinost et al. (2002). Below is discussion of LCF–XAFS results for all samples.

Speciation by Amendment Type

Control Samples

The primary Pb species in the control samples included organic-matter-sorbed Pb, anglesite, galena, and outer-sphere-adsorbed Pb (Table 1). The relative amounts of these Pb phases did not change significantly as field aging time increased from the start of treatment placement to 32 mo. These results appear reasonable since air deposition of crusted ore products and smelter emissions have been shown to contain galena from Pb ore, which over time can oxidize to anglesite (Reeson et al., 1990; Moenkeblankenburg et al., 1994; Hall et al., 1996; Laajalehto et al., 1997; Szargan et al., 1999). Additionally, the rather modest organic carbon content

Table 1. Linear combination fitting (LCF)–X-ray absorption fine structure spectroscopy (XAFS) analysis of amended soil samples yielding information on the solid-phase speciation of Pb.

Sample†	Weighted fraction percent determined by LCF						
	Inner-sphere	Outer-sphere	Organic-matter-sorbed	Cerussite	Anglesite	Pyromorphite	Galena
			%				
Control, 3 mo	1	7	37	2	32	0	21
Control, 18 mo	0	11	32	3	34	0	20
Control, 32 mo	0	9	32	0	43	0	16
1% P as TSP	10	7	29	14	11	29	0
3.2% P as TSP	7	5	19	11	16	41	1
1% Fe as IR + 1% P as TSP	6	17	11	0	35	31	0
2.5% Fe as IR + 0.32% P as TSP	7	0	46	11	9	27	0
2.5% Fe as IR + 1% P as TSP	10	11	15	4	20	41	0
1% P as RP	5	0	28	16	14	33	5
10% CB	0	3	60	24	12	1	0
10% CB + 0.32% P as TSP	2	6	73	9	5	2	3
10% CB + 1% P as TSP	6	10	53	12	17	16	2
0.5% P as H_3PO_4, 3 mo	12	6	29	12	4	35	0
0.5% P as H_3PO_4, 32 mo	11	6	26	13	6	37	0
1% P as H_3PO_4, 3 mo	13	6	18	3	17	43	0
1% P as H_3PO_4, 18 mo	15	8	16	2	17	45	0
1% P as H_3PO_4, 32 mo	14	8	15	4	16	45	0

† CB, composted biosolids; IR, iron-rich material; RP, rock phosphate; TSP, triple superphosphate.
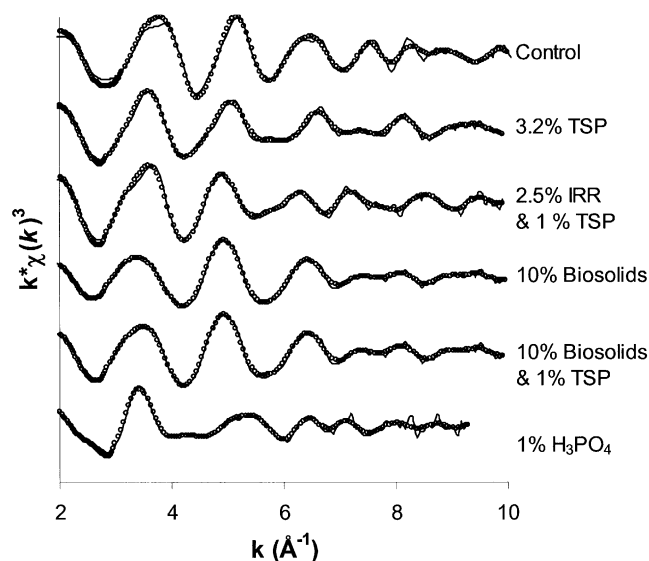
Fig. 3. Normalized Pb_{LIII}–X-ray absorption fine structure spectroscopy (XAFS) k^3–weighted chi spectra of field samples. The solid lines are the raw data and the dotted lines are the fit results from linear combination of k^3–weighted chi reference spectra from Fig. 2.

of 46 to 56 g kg^{-1} and the affinity of organic fractions for Pb (Sauve et al., 1997; Strawn and Sparks, 2000; Svete et al., 2001) provide a plausible explanation for the organic-matter-sorbed constituents determined by LCF–XAFS.

Phosphate Only

The effectiveness of phosphate-only amendments are shown in Table 1 for TSP (1.0 and 3.2% application rates), rock phosphate (1.0% application rate), and H_3PO_4 (0.5 and 1.0% application rates). The addition of P to the soils resulted in the transformation of up to 45% soil Pb to pyromorphite, with the most dramatic decrease of Pb species being galena relative to the control sample Pb species. As P application rate increased, the amount of pyromorphite identified by LCF–XAFS increased. Triple superphosphate at application rates of 1.0 and 3.2% observed pyromorphite concentrations of 29 and 41%, respectively. Phosphoric acid treatments of 0.5 and 1.0% resulted in 37 and 45% pyromorphite concentrations. The 1.0% rock phosphate treatment resulted in 33% of the soil Pb sequestered as pyromorphite. Overall, the effectiveness of phosphate-only amendments to precipitate pyromorphite increased in the order of triple super phosphate (29%) $\approx$ rock phosphate (33%) < phosphoric acid (45%).

Similar amendments have been applied in other field studies (Cao et al., 2002, 2003; Chen et al., 2003; Melamed et al., 2003), but the results of these investigations show significantly more pyromorphite formed (70–82%) through speciation via selective sequential extractions than in our LCF–XAFS study. However, it has been clearly documented that selective sequential extractions of P-amended samples may considerably overpredict the amount of pyromorphite due to pyromorphite formation during the extraction steps (Scheckel et al., 2003). This phenomenon of pyromorphite precipitation out of con-

text of the true form of the soil Pb may also occur during in vitro and in vivo studies, although it has not been examined (Zhang et al., 1998; Hamel et al., 1999; Arnich et al., 2003; Scheckel and Ryan, 2003).

Phosphate and Iron-Based Amendments

The addition of an iron-rich waste material in conjunction with TSP provided a boost for pyromorphite formation in that as iron-rich material concentration increased, the amount of Pb transformed to pyromorphite increased. Table 1 shows that the 1.0% TSP amendments with 1.0 and 2.5% iron-rich material measured 31 and 41% of the Pb as pyromorphite in which the 2.5% iron-rich treatment is statistically higher than the non-iron-rich, P only 1.0% TSP of 29% pyromorphite, indicating that sufficient iron amendments are necessary to see a beneficial gain of pyromorphite formation. The iron-rich material can serve as a potential sorbent phase for both Pb (Forbes et al., 1976; Ainsworth et al., 1994; Bargar et al., 1997, 1998; Ford et al., 1999; Elzinga et al., 2001) and P (Fontes and Weed, 1996; Persson et al., 1996; Slomp et al., 1996; Bastin et al., 1999; Mayer and Jarrell, 2000; Arai and Sparks, 2001). One noticeable difference in the P-only samples and the P and iron-rich samples was the increase in inner- and outer-sphere Pb sorption complexes and a significant decrease in organic-matter-sorbed Pb for the TSP + iron-rich amended samples (Table 1).

Phosphate and Composted Biosolids Amendments

Organic matter and organic materials in soils and sediments have a high affinity for Pb (Schnitzer, 1969; Bunzl et al., 1976; Schnitzer and Kerndorff, 1981; Gerritse and Driel, 1984; Pearson et al., 2000; Strawn and Sparks, 2000) and can promote the oxidation of environmentally important minerals such as galena (Alongi et al., 1996; Jahnke et al., 1997; Osei and Singh, 1999; Huling et al., 2001; Jorgensen et al., 2001). In the case of the composted biosolids amendment to the Joplin soils, the amount of Pb associated with the organic-matter-sorbed faction increased significantly relative to the control sample. Unfortunately, pyromorphite formation was not tremendously enhanced by composted biosolids amendments, which determined values of 1, 2, and 16% for composted biosolids treatments with 0, 0.32, and 1.0% TSP amendments, respectively. The insignificant formation of pyromorphite in the high organic material amendment may be explainable by recent work of Lang and Kaupenjohann (Lang and Kaupenjohann, 2003) that observed a reduction in pyromorphite formation with increasing concentrations of dissolved organic matter and attributed the reduction to (i) Pb–organic matter complexation decreasing the amount of pyromorphite formation, (ii) organic coatings on pyromorphite crystal seeds that inhibited further pyromorphite formation, and (iii) organic coatings on pyromorphite crystals that may enhance colloidal transport of pyromorphite thus removing it from the measured profile. We feel the first two points are most plausible since soil Pb concentration did not change significantly

over time. Regardless of the cause for little pyromorphite formation, recent studies on biosolids amendments to soils have shown that over time as the organic matter concentration degrades to background levels, the inorganic fraction of biosolids becomes an important factor in the retention of metals as either oxide sorbents or coprecipitates of amorphous iron, manganese, or aluminum oxides (Hettiarachchi et al., 2000, 2003). Long-term transformation of metals warrants the need for future monitoring of in situ remediation sites since environmental systems are seldom, if ever, in equilibrium (Sparks, 1999).

Speciation as a Function of Residence Time

The effect of aging time on Pb speciation was minor relative to the sample collection times of 0, 3, 18, and 32 mo (Table 1). The control samples observed a decrease in the amount of galena (21 to 16%) yielding an increase in anglesite concentration (32 to 43%) as a result of galena oxidation. Galena oxidation was probably enhanced as a result of perturbation of the soil profile during establishment of the field plots. A reduction in the amount of organic-matter-bound Pb was also observed within the control samples with aging time. The phosphoric acid treatments of 0.5 and 1.0% were examined as a function of time and demonstrated that the significant portion of Pb species alteration occurred within the first 3 mo relative to the untreated soil at time zero. As aging time increased from 3 to 32 mo, there was a slight increase in pyromorphite concentration at both H_3PO_4 treatments as well as minor differences in the other Pb species, suggesting that the overall reaction is mostly completed within 3 mo. The effect of residence time on the other P amendments was not measured.

CONCLUSIONS

Immobilization of metals within the natural environment either by changing environmental conditions (i.e., pH) or via sequestering amendments is proving to be a suitable and cost-effective way to treat an array of contaminated soils and sediments. Lead immobilization via P amendments appears to be a function of P concentration and P availability (solubility). As a low-cost alternative to site removal, pyromorphite formation in Pb-contaminated soils possesses great potential. However, evaluating the risk assessment related to fate, mobility, reactivity, transport, toxicity, and bioavailability requires methods that accurately determine the speciation of a metal in its natural state. We and others (Beauchemin et al., 2002; Isaure et al., 2002; Roberts et al., 2002; Scheinost et al., 2002) have demonstrated that LCF–XAFS can produce speciation and quantification results that are necessary to accurately predict risk. This methodology provides direct in situ measurements that neither chemically alters the species nor relies on visual evaluation to determine speciation.

The formation of pyromorphite through immobilization of Pb with P does possesses limitations. There are a number of constituents in soils that will compete with Pb for the P amendments, such as Al, Fe, Ca, Mg, and Mn phases. These elements can form respective metal phosphates or P can bind tightly to oxides of these elements. In fact, $MnHPO_4$, although minor in concentration, is an often-overlooked sink for phosphate in the environment. These phosphate reactions are a reasonable explanation why studies that have applied sufficient P amendment concentrations (up to 3.2%) relative to the soil Pb concentration only observe a portion of the Pb converted to pyromorphite. Thermodynamic calculations regarding the amount of P needed to satisfy all element requirements (i.e., formation of metal phosphates and sorption complexes with the above mentioned elements) for an "average" soil approach phosphate concentrations of >4% (Porter et al., 2004). However, this large input of phosphate into a soil would certainly raise concerns for nearby water environments as well as significantly alter the soil structure. But regardless, the ability to convert up to 45% of the soil Pb in our studies to pyromorphite resulted in a significant reduction in Pb bioavailability as examined by in vivo and in vitro experiments (Ryan et al., 2004).

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