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Lead Sequestration and Species Redistribution During Soil Organic Matter Decomposition

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The turnover of soil organic matter (SOM) maintains a dynamic chemical environment in the forest floor that can impact metal speciation on relatively short timescales. Here we measure the speciation of Pb in controlled and natural organic (O) soil horizons to quantify changes in metal partitioning during SOM decomposition in different forest litters. We provide a link between the sequestration of pollutant Pb in O-horizons, estimated by forest floor Pb inventories, and speciation using synchrotron-based X-ray fluorescence and X-ray absorption spectroscopy. When Pb was introduced to fresh forest O_i samples, it adsorbed primarily to SOM surfaces, but as decomposition progressed over two years in controlled experiments, up to 60% of the Pb was redistributed to pedogenic birnessite and ferrihydrite surfaces. In addition, a significant fraction of pollutant Pb in natural soil profiles was associated with similar mineral phases (∼20–35%) and SOM (∼65–80%). Conifer forests have at least 2-fold higher Pb burdens in the forest floor relative to deciduous forests due to more efficient atmospheric scavenging and slower organic matter turnover. We demonstrate that pedogenic minerals play an important role in surface soil Pb sequestration, particularly in deciduous forests, and should be considered in any assessment of pollutant Pb mobility.

Introduction

The combustion of leaded gasoline during the 1900s resulted in the deposition of 1–4 g/m^2 of Pb across the landscape of the northeastern U.S (*1, 2*). Surveys of the Pb content of the forest floor across the region concluded that the majority of the Pb deposited on the landscape was initially sequestered by these reactive and chemically complex soil horizons (*3, 4*). Due to the toxicity of Pb to humans and ecosystems and the potential threat of concentrated gasoline-derived Pb in surface soils to these receptors, researchers have sought to determine the residence time of Pb in the forest floor and the geochemical parameters governing the mobility of Pb in such environments (*5*). In general, this work has found that the residence time of Pb in the forest floor is relatively long, and that most of the gasoline-derived Pb initially sequestered by this reservoir remains there for 50–250 years (*1, 6–8*).

Organic matter has highly reactive surfaces with an affinity for metals, and Pb sequestration in the forest floor has been attributed to inner and outersphere adsorption processes (*9, 10*). At pH ranges typical of forest floors in soils of the northeastern U.S. (pH ∼ 3–5), soil organic matter (SOM) and pedogenic Fe/Al/Mn oxides/oxyhyroxides will readily adsorb dissolved free Pb (*10*). Due to the strong affinity of Pb^{2+} for organic ligands, it was thought that in the forest floor, which by definition consists of at least 40% SOM, the sequestered gasoline-derived Pb was adsorbed to the abundant reactive sites on SOM surfaces (*3, 11*). It followed that as decomposition of this SOM progressed, Pb migration to underlying mineral soils should occur. Presumably the Pb would either precipitate with dissolved organic carbon (DOC) and be adsorbed to pedogenic mineral phases in $E/B_s/B_h$ horizons or would be exported from the soil with DOC or particulate matter (*1, 6, 12*). Interestingly, as more advanced analytical techniques have been implemented to examine Pb fate in soils, a more complex picture of gasoline-derived Pb solid phase association in the forest floor is emerging with important ramifications for Pb flux and sequestration in these soils. Kaste et al. (2006) used synchrotron-based X-ray absorption spectroscopy (XAS) to show that a component of pollutant Pb in the forest floor of the northeastern U.S. is associated with Fe (*8*). In addition, hydroxylamine hydrochloride extractions, which target reducible fractions of the soil (i.e., Fe/Mn minerals but not SOM), removed 30–40% of total gasoline-derived Pb in forest floor samples (*13*). This body of work indicates that pedogenic mineral phases, which differ significantly in geochemical stability and physical mobility relative to SOM, could be sequestering a significant component of gasoline-derived Pb in the forest floor. Therefore, the stability/mobility of such mineral phases would need to be considered when assessing the fate of this pollutant in soils. The relative contribution of various solid phases to Pb sequestration in the forest floor has yet to be examined, but it is likely to be dynamic depending on SOM quality, maturity, composition, and pedochemical environment.

Regional forest floor surveys indicate that Pb inventories and sequestration differ by forest type, with high elevation spruce-fir forests sequestering more Pb over time relative to adjacent lower elevation northern hardwood forests (Figure S1, Supporting Information) (*6*). However, the transition between deciduous and conifer forests is often tied to changes in elevation and latitude. Thus, strong Pb enrichment and retention by high elevation soils may also result from numerous coupled soil forming processes. For example, atmospherically derived Pb deposition is greater at high elevation forests due to high exposure to Pb-enriched cloudwater and increased deposition of pollutant-laden precipitation associated with orographic precipitation enhancement (*14*). Both of these mechanisms increased gasoline-derived Pb loading to high elevation conifer forests and contribute to Pb inventory trends shown in Figure S1, but are independent of forest type (*14*).

If much of the Pb was initially adsorbed to SOM upon deposition, organic matter decomposition should influence Pb migration rates and the associated efflux of Pb complexed with DOC. The association between gasoline-derived Pb and DOC export in watersheds and soils has been established, supporting the influence of decomposition on this process (*15*). Lead residence times in forest floors of lowland or young

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successional deciduous forests are shorter (50−70 yrs) than high elevation spruce fir or mature boreal forests (150−250 yrs), perhaps because higher decomposition rates might accelerate Pb export to underlying mineral soils in lowland deciduous forest floors (*6, 7*). Organic matter decomposition is slower at high elevation conifer forest soils due to cooler temperatures and low quality litter relative to lowland northern hardwood forests (*16*). All of these processes can contribute to higher amounts and increased residence time of gasoline-derived Pb in montane spruce/fir forest floors relative to lowland northern hardwood forest floors. In addition, if mineral phases are sequestering much of the Pb in the forest floor, both litter and soil solution chemistry could influence the composition and abundance of mineral phases available to sequester Pb in this reservoir.

Here, we determine the effect of litter quality/chemistry and related components of decomposition on Pb content, speciation, and distribution in the forest floor. We examine forest floor compositions where soil forming factors other than forest type are similar to determine the influence of these forest types on inventories of forest floor Pb. In addition, we explore Pb solid phase association in O-horizons of multiple forest types and degrees of decomposition to determine the role of litter quality and maturity in Pb sequestration within the forest floor. This work improves our understanding of Pb behavior across ecosystems and within soil profiles over time with relevance to the parameters governing Pb sequestration in surface soils.

Materials and Methods

Forest Floor Surveys. Quantitative forest floor samples (15 × 15 cm, $n = 4$ under each forest type) were randomly collected and analyzed following the protocol of Kaste et al. (2006) (*8*). Sites selected for forest floor sampling were at Marsh-Billings-Rockefeller National Historical Park (MBRNHP) located near Woodstock, VT and Bristol Cliffs VT (*8, 17*). These sites contain northern hardwood forests and monoculture plantation style stands of conifer forests of comparable stand age. We sampled forest floors in areas where conifer and deciduous forests of similar age were adjacent to one another on similar slope, aspect, parent material and soil type. Forest floor sampling protocol and site locations have been previously described in detail (*8, 17*). The boundary between the forest floor and the mineral soil is operationally defined as the point where bulk sample mass loss on ignition (LOI) decreases to 40%. Visual estimates of mineral content and humification of SOM are used to identify this boundary while sampling in the field, and LOI measurements can be used to confirm our field-based differentiation of forest floor and mineral soil. All forest floor samples used in this study have an LOI of 40% or greater. Forest floor samples were oven-dried at 105 °C to remove water for mass measurements. Subsamples were then ashed at 450 °C to measure mass loss on ignition (LOI) to determine organic matter content. The ashed samples were then exposed to a 1 M hot HNO_3 extraction (intended to target "pollutant" Pb) that was analyzed by ICP-OES for major and trace elements (*8, 13, 18*). Accurate recoveries (within 5%) of Pb were confirmed by analyzing NIST SRM 1575 by the same method.

Decomposition Experiment. We conducted a decomposition experiment over 2 years to simulate labile carbon decomposition in the forest floor after Pb deposition, which allows us to examine changes in solid phase association of Pb that resulted from SOM decomposition on this time scale. This was necessary because the gasoline-derived pulse of Pb is now associated with more mature (at least 25 year old) sections of the forest floor, so it is difficult to examine Pb speciation by XAS in field samples of young SOM because of their low Pb concentration (*19*). Samples were collected from the surface (upper 1 cm) of the forest floor (O_i-horizon) of red pine (*Pinus strobes*), Norway spruce (*Picea abies*), and northern hardwood (a mixed forest of sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*)) forests of MBRNHP. Homogenized subsamples of the O_i-horizon were spiked to 200 mg/kg total Pb with a 0.01 Pb-NO3 solution at pH 5 (adjusted with NaOH). Samples were exposed to ambient laboratory conditions in acid washed polypropylene containers and wetted on a weekly basis to approximately 50% saturation with distilled water. The containers for the decomposition experiment were open at the top, to allow for gas exchange, but closed at the bottom so that no leaching occurred. Partially decomposed litter samples were collected bimonthly and stored at 4 °C upon collection. The extent of decomposition was monitored by mass measurements taken prior to each sampling event and by determining sample C:N over the duration of the experiment with a Carlo Erba C−H−N analyzer. Previously mentioned forest floor samples were collected from intact soil profiles to study Pb speciation in natural, relatively mature SOM of each forest type with the inclusion of the effect of the leaching process that occurs in soils. Major element and Pb concentrations in decomposition experiment samples were measured using the same method of forest floor compositional analyses described above.

Synchrotron-Based Analyses. Extended X-ray absorption fine structure (EXAFS) spectroscopic analyses were performed on bulk soil samples and on subsamples from the decomposition experiment to determine Pb speciation. EXAFS provides an in situ, element-specific probe of speciation for solid phase Pb in a variety of mineral and organic soil matrices (*20, 21*). All bulk EXAFS data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 11−2 using Si(220) monochromator crystals. Four to 10 scans were collected for each sample, with higher concentration standards and decomposition experiment samples generally requiring fewer sweeps than some of the natural forest floor samples. The monochromator energy of each spectrum was calibrated using Pb metal foil between the second and third ionization chambers; its absorption edge was calibrated to an edge of 13055 eV.

Initially, EXAFS spectra were Fourier transformed and fit by theoretical "shell fitting" of the radial distribution function (RDF) to calculate nearest neighbor and second nearest neighbor bond distances and coordination numbers (fitting parameters and methods are discussed in detail in ref 8. Due to the complex and variable coordination environment of Pb in heterogeneous soil matrices, information regarding the relative contribution of Pb species to RDF of spectra by conventional "shell fitting" is limited (*20, 21*). As such, EXAFS spectra were also fit by least-squares fitting with combinations of spectra of known references using the SIXPACK interface (*22*). Fitting was conducted with k^3-weighted data generally to a k (Å^{-1}) range of 1.5−9 for samples. This limited k-range reflects the low concentration (frequently <100 mg/kg) and disordered coordination environment of Pb in these samples. The suite of standards included in fitting was based on fits of spectra RDF, the elemental composition of O_i samples used (Supporting Information Table S2), and likely mineral, organic, and amorphous phases present in these soils. Fits were optimized where the only adjustable fitting parameters were the fractions of standard spectra used to fit the data given the constraint of these fractions summing to unity. Best fits were determined by the combination of spectra that produced the lowest residual (the normalized root square of the difference between the fit and the data). Fit error was also calculated using SIXPAK's least squares fitting interface (*22*).

To characterize Pb speciation using this approach, a suite of Pb standards must be employed that is representative of the complexity and diversity of potential Pb sequestering phases within the forest floor. The diversity of organic matter compounds within organic horizons is well-documented and makes it difficult to use individual laboratory synthesized organic reference compounds (i.e., Pb-oxalate, Pb-citrate, etc.) that represent potential Pb associated organic compounds in these surface soils (*23*). To best represent the more diverse suite of organic compounds likely to complex with Pb in the forest floor, we used Pb adsorbed to fresh hardwood and conifer litter samples ($t = 0$) collected while live on tree limbs to minimize the potential influence of inorganic mineral phases in these standards. These fresh litter samples were spiked to ~200 ppm Pb under the same methodology as the decomposition experiment and were refrigerated and analyzed at SSRL within 1 week of preparation. While we acknowledge that these organic matrices could be somewhat different from those encountered in more mature sections of the forest floor, synthesizing Pb-SOM standards from forest floor samples would include significant mineral fractions that would likely sequester Pb in addition to organics, thereby precluding their use as a Pb-SOM reference material. We believe that these standards are the most suitable and complete option for Pb associated with diverse chemistry of SOM, but acknowledge that they are a source of uncertainty in the technique.

It is important to mention that our reference spectra for adsorbed Pb complexes on minerals and organic matter were synthesized at Pb concentrations similar to those found in forest soils across the northeast rather than those of extremely high Pb concentration that have been used for many previous EXAFS-based studies of highly contaminated sites or theoretical experiments. Standards synthesized under lower Pb concentrations produce a relatively "noisy" signal that increases the residual of our fits, and shortens the range of our chi function for these standards (Figure S1). We attribute the relatively high uncertainty (compared to other studies of more concentrated samples) of our fits to the lower quality of spectral data associated with low concentration samples and standards (*24*). However, we believe these standards replicate geochemical conditions within the forest floor more thoroughly than highly concentrated standards and more likely replicate the coordination environment of Pb bound to these amorphous and organic solid phases at surface coverages representative of these soil horizons. We feel this is a vital component to processing data in soils that have Pb concentrations that range from 50 to 150 ppm typical of northeastern forest floor. In addition to Pb-SOM standards, we began fits with laboratory synthesized Pb adsorbed to ferrihydrite ($Pb-Fe(OH)_3$), goethite(Pb-FeOOH), birnessite (nominally $Pb-MnO_2$), gibbsite($Pb-Al(OH)_3$), and crystalline galena (PbS) and pyromorphite ($Pb_5(PO_4)_3Cl$); a likely suite of solid phases with the potential to sequester Pb that could form in the forest floor. Typically, stable fits required contributions from Pb sorbed to SOM, ferrihydrite, and birnessite (Figure S1).

Microfocused X-ray fluorescence (μXRF) analyses of select decomposition and forest floor samples were performed on beamline X26A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The beamline is equipped with a Si(111) monochromator with 1 eV nominal resolution. Decomposition samples were mounted on Kapton tape. XRF spectra, and maps were collected using 13.1 keV incident X-rays with an X-ray spot diameter of approximately 6 μm. XRF maps were made using a step size of 10 μm on an area of 0.5 × 0.5 cm. Elemental intensities of Pb, Fe, Ca, and other elements were made using a Canberra 9-element Ge detector with integrated count times of 2 s^*pixel^{-1}. Elemental peak intensities are approximately proportional to concentration, but data are presented in raw counts because of the considerable error in determining accurate concentrations from low integration times employed for this study.

TABLE 1. Forest Floor and Pb Inventories[a]

sample site	northern hardwood ($Pb\ kg \cdot ha^{-1}$)	red pine ($Pb\ kg \cdot ha^{-1}$)	Norway spruce ($Pb\ kg \cdot ha^{-1}$)
MBRNHP	0.74 (0.18)	2.0 (0.37)	1.7 (0.26)
Bristol Cliffs	7.0 (1.1)	11.8 (1.5)	NA

[a] Numbers in parentheses refer to the standard error of $n = 4$ samples of forest floor collected from each forest type at each sample site.

Results and Discussion

Forest Floor Surveys. Lead inventories in the forest floor are generally higher in high elevation spruce/fir forests relative to lowland northern hardwood forests. Trends in forest floor Pb inventories observed on Camels Hump, VT, in 2002 (Figure S1) are typical of montane forest floor elevational profiles of the region (*4*). The study sites at MBRNHP and Bristol Cliffs can be used to isolate the effect of forest type on Pb inventories because conifer and deciduous stands are found at the same elevation with similar climate, topography, parent material, and age (*8, 17*). Lead inventories in northern hardwood forest floors of MBRNHP and Bristol Cliffs are consistent within the range predicted by Miller and Friedland (1994) for these elevations in Vermont, confirming that Pb in our samples is primarily gasoline-derived (*1*). Forest floors under conifer species, as predicted, contained more Pb than northern hardwood forest floors (Table 1). In general, there appears to be at least a 2-fold increase in forest floor Pb inventories with a shift from northern hardwood to conifer forest, even at a constant elevation (Table 1). This indicates that the higher aerosol interception capability, perhaps coupled with the slower decomposition of conifer SOM, have resulted in twice the amount of Pb in conifer forest floors. These data demonstrate that forest type influences atmospherically derived Pb inventories in the forest floor when other soil forming factors are similar. The higher amount of Pb in Bristol Cliffs (560 m elevation) forest floors relative to those collected at MBRNHP (350 m elevation) forest floors is likely primarily due to elevational and geographic differences between the two sites. Importantly, irrespective of differences between site-specific environmental conditions, the higher Pb inventories in conifer forest floors relative to comparable northern hardwood forest floors is similar and consistent in magnitude across these spatially distinct areas.

Decomposition Experiment

O-Horizon Properties. O-horizon samples lost between 15 and 26% of their mass over the 2 year duration of the decomposition experiment, confirming the turnover of organic matter in our controlled environment. Changes in carbon to nitrogen ratios (C:N) were also used to monitor the extent of decomposition of litter samples over the 2 year duration of the experiment. Monitored C:N consistently declined during the decomposition experiment (Table S1), also indicating that significant carbon mineralization occurred in the samples. The bulk composition of the O-horizons was rich in a variety of major elements that could produce secondary minerals capable of sequestering Pb (i.e., Fe, Mn, S) during decomposition process (Supporting Information Table S2), typical of forest floors underlying temperate forests (*19*).

Pb Speciation and Distribution in Experimental Samples. Synchrotron-based μXRF maps provide spatial data of elemental concentrations that can be used to infer phase

TABLE 2. Correlation Coefficients for Pb and Select Element Fluorescence Based on Compositional Maps

Element	NH $t = 0$ (r)	NH $t = 1$ year month (r)	NS $t = 0$ (r)	NS $t = 1$ year (r)
Ca	0.10	0.55	0.17	0.46
Fe	0.06	0.65	0.32	0.61
Mn	0.09	0.64	0.03	0.74

association of specific elements with Pb in our litter samples (*8*). In this case, we use Ca as a proxy for organic matter (blue), and Fe (red), and Mn (correlation data only given in Table 2) as indicators of pedogenic mineral phases such as ferrihydrite/goethite (Fe) and birnessite (Mn). To explore these relationships more quantitatively, we can calculate correlation coefficients between counts of the Pb in each pixel and counts of other elements of interest (Ca, Fe, Mn). Compositional maps of O-horizon samples prior to decomposition ($t = 0$) suggest that Pb is not uniformly distributed across the sample, but there is also not a strong correlation between Pb and Ca, Fe, or Mn (Figure 1, Table 2). Following 1 year of decomposition, several changes in Pb, Fe, and Mn distribution are evident (Figure 1, Table 2). It can be seen in Figure 2 that Pb and Fe became more concentrated in "hotspots" following decomposition. Quantitatively, increased Pb concentration on specific areas of the sample after decomposition is observed in a 2 fold increase in the standard deviation/Pb counts per pixel (relative to the average pixel value for the whole map) between $t = 0$ and $t = 1$ yr samples. Additionally, over time and decomposition, correlations in both conifer and deciduous samples become stronger between Pb and all elements, with a Pb association with both Mn and Fe greater than that with Ca (Table 2). These data suggest that as decomposition progressed in our experiment, Pb became increasingly distributed on surfaces associated with Fe and Mn, and to some extent Ca. These 1 year compositional maps give similar elemental correlations to those of pollutant Pb in forest floor samples of the northern forest, which indicates that our experimental samples to some extent simulated the behavior of aged pollutant Pb in the forest floor (*8*). The increasing association of Pb with Fe and Mn is likely due to the mobilization of Pb initially bound to labile SOM and subsequent adsorption of this Pb to reactive surface sites on pedogenic mineral phases (Tables 2 and S2). Iron and Mn concentrations in O-horizons used in the experiment are quite high (Table S2) and likely form insoluble oxyhydroxides following mineralization. These data suggest that this mineralization affects Pb speciation on very short timescales (<1 year) in forest soils during decomposition of labile SOM. This partitioning of Pb during decomposition was confirmed through analysis of bulk EXAFS spectra by conventional shell fitting of the RDF of experimental samples. It is visually evident that the spectra change during decomposition and are quite similar to observed spectra of Pb contaminated soil samples where Pb has been demonstrated to be bound to Mn and Fe phases in addition to SOM (*8, 21*) (Figure S2). While there is consistently a nearest neighbor peak of Pb−O around 2.3 Å (typical of Pb sequestered by inner sphere adsorption processes, but insufficient to differentiate phases to which Pb is bound), a second nearest neighbor shell develops as decomposition progresses that is typical of pedogenic Mn and Fe phases (3.2−4.06 Å) (Supporting Information Table S3). The increasing coordination number of this peak during decomposition suggests that these Fe/Mn phases sequester more Pb in the experimental samples as decomposition progresses supporting data collected by μXRF (Table S3). However, due to the previously mentioned complexities associated with shell fitting Pb spectra with multiple components, trends in coordination number produced by shell fitting of second nearest neighbor peaks are semiquantitative at best (*21*). We can quantify changes in the relative fractions of organic and mineral-associated Pb using linear combination fitting of EXAFS spectra.

EXAFS spectra change measurably over the decomposition continuum, indicating that Pb solid phase association in this sample matrix over time is quite dynamic. Linear combination fitting of bulk EXAFS spectra fitting consistently identified three Pb phases in experimental samples: Pb adsorbed to SOM, Pb adsorbed to ferrihydrite, and Pb adsorbed to birnessite (Figure 2). Initially, in every case, much of the Pb in samples exhibiting little decomposition (t = 2 months)

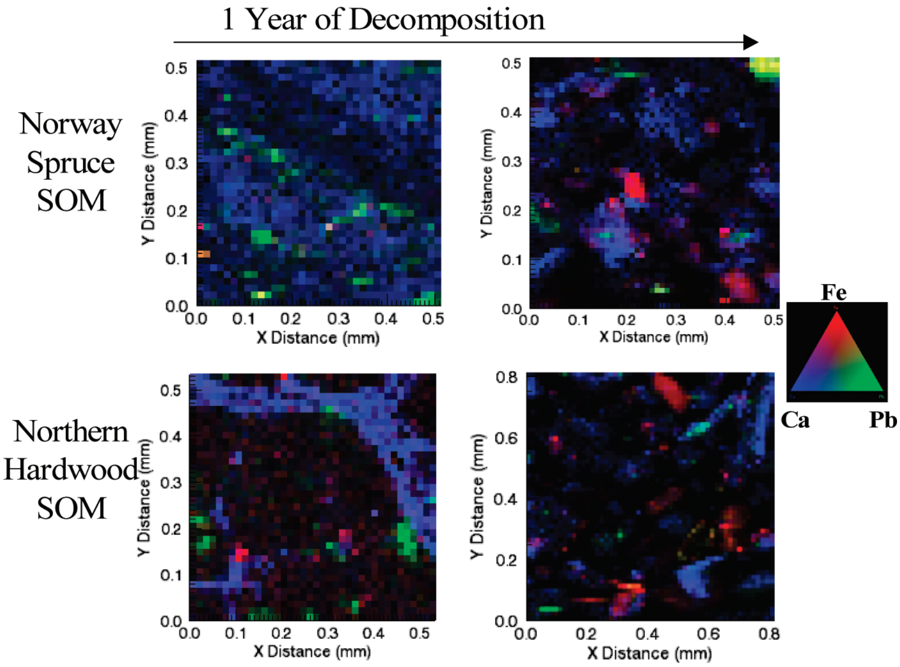

FIGURE 1. Synchrotron-based μXRF compositional maps of t = 0 and t = 1 year of decomposition of Pb spiked conifer and deciduous litters. Pb, Fe, and Ca are indicated by green, red, and blue, respectively. All data were collected on beamline X26A at NSLS.

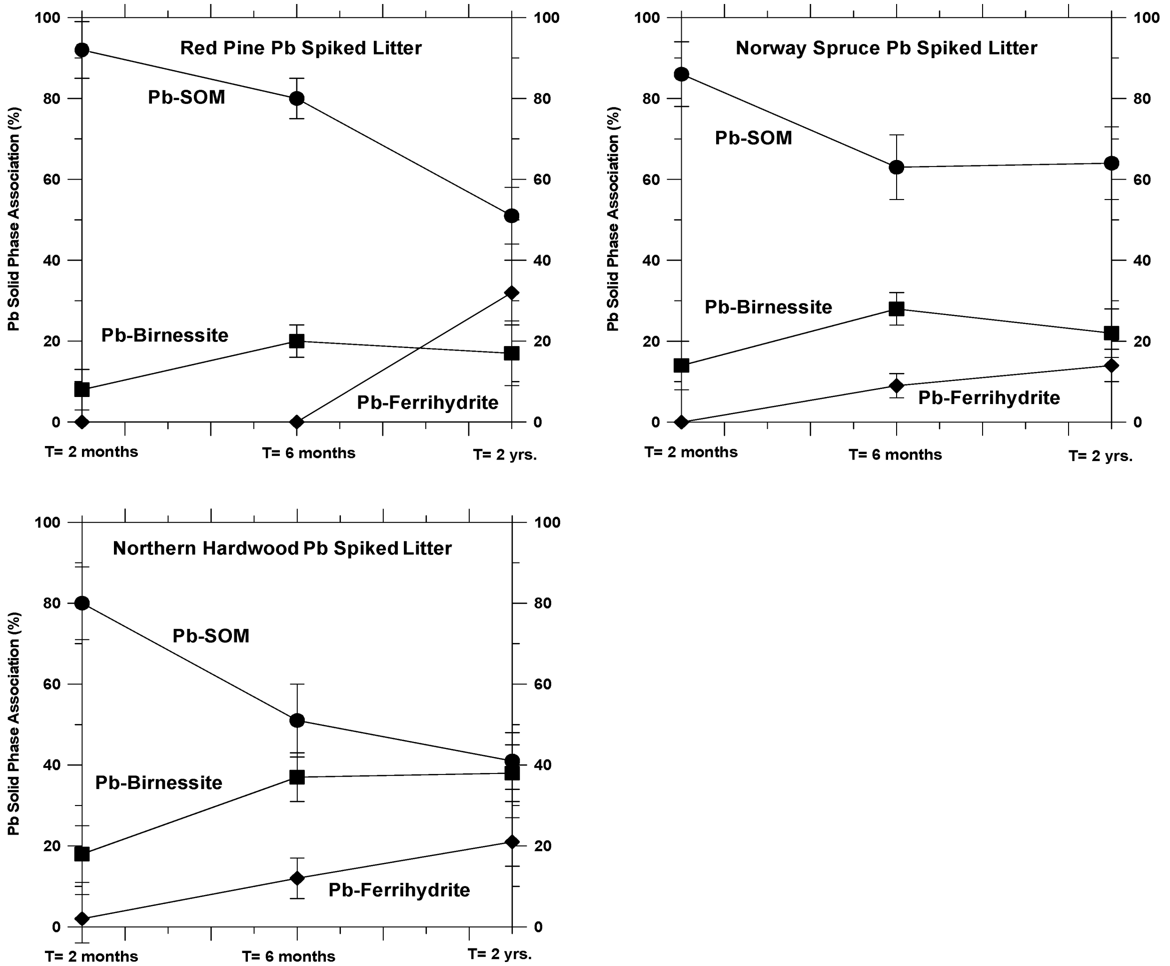

FIGURE 2. Fractions of Pb solid phase association in Pb spiked litters and gasoline-derived Pb bearing forest floors as determined by linear combination fitting of EXAFS data with the chi function of standards presented in Figure 3. All data were collected on beamline 11−2 at SSRL. Error bars are calculated using the SIXPAK least-squares fitting interface (*22*).

was bound to SOM, with minor contributions of Pb adsorbed to secondary mineral phases (Figure 2). However, as decomposition of the experimental samples progressed, an increasing amount of the spiked Pb became associated with the pedogenic minerals birnessite and ferrihydrite (Figure 2). Both of these mineral phases have a well-documented high affinity for surface complexation with free Pb (Mn oxides > Fe oxides) and if present would certainly scavenge labile Pb from solution (*25, 26*). The EXAFS data support those generated by synchrotron-based μXRF compositional maps and conclusively demonstrate that the sequestration of Pb in the forest floor is dynamic over time. An increasing fraction of Pb becomes bound to inorganic mineral phases on relatively rapid decomposition timescales on the order of a few months to years with up to 60% of the spiked Pb adsorbed to pedogenic minerals after 2 years of decomposition (Figure 2).

It is interesting to note that a greater amount of Pb is bound to these mineral phases in the northern hardwood decomposition experimental samples relative to either of the conifer litters (Figure 2). Perhaps this is due to more rapid decomposition of SOM in high quality deciduous litters, which could, particularly in the closed system of the experiment, mobilize more Pb initially bound to labile SOM and produce more pedogenic minerals that readily sequester the previously SOM-associated Pb. This could indicate that the stability of Pb bound to pedogenic mineral phases is more important in governing Pb sequestration in northern hardwood O-horizons relative to those of the conifer forests. Additional observations of these species specific trends in Pb speciation during decomposition are warranted to confirm this inference.

Speciation of Pollutant Pb in the Soil Profile. Lead speciation data from MBRNHP forest floor samples represent the solid phase association of pollutant Pb that has been in the soil profile over roughly 25−50 years of decomposition and leaching (*27*). These samples were optimally fit with significant fractions of Pb adsorbed to SOM (65−80%) and ferrihydrite (15−30%), demonstrating that indeed pedogenic mineral phases are an important mechanism for the sequestration of Pb that remains in the regional forest floor (Figure 3). Fractions of pollutant Pb bound to peodgenic minerals identified by XAS in these samples are consistent with those identified by selective extractions of Kaste et al. 2005. In addition, the fraction of Pb associated with pedogenic minerals was higher in northern hardwood forest floors relative to either conifer species, supporting the results from the decomposition study. This suggests that indeed these mineral phases sequester more Pb in deciduous O-horizons relative to conifer O-horizons. Interestingly, however, all natural forest floor samples were optimally fit with significantly less Pb bound to mineral phases than 2 year experimental samples and show little contribution of birnessite to Pb sequestration in natural forest floor samples (Figure 2 and 3). It would be expected that if Pb association with pedogenic minerals increases during decomposition as observed in the experimental data, and our experiment is accurately simulating pedochemical conditions of the forest floor, the forest floor samples should have a higher fraction of Pb associated with pedogenic mineral phases relative to

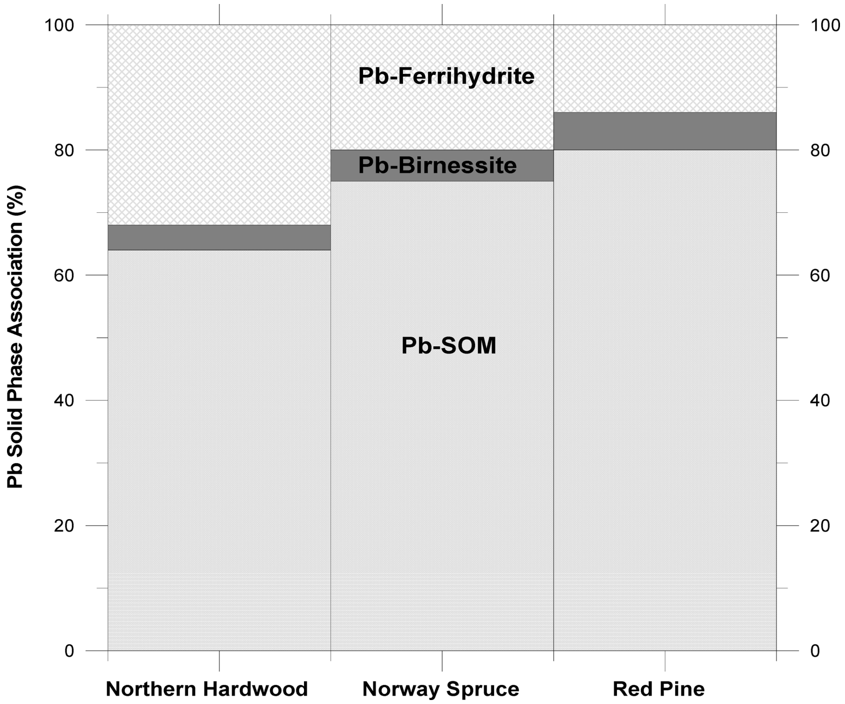

FIGURE 3. Speciation of gasoline-derived Pb in forest floor samples from MBRNHP. All data were collected on beamline 11−2 at SSRL. SIXPAK calculated error for species used for fits range from 4 to 9%.

samples that have only undergone 2 years of decomposition. The most likely explanation for this discrepancy is related to differences in Mn leaching during decomposition in our closed laboratory experiments relative to those processes that occur in the soil profile. We speculate that under actual field conditions, Mn leaches from organic soil horizons in low concentrations over time, some of which precipitates as birnessite-like phases at depth as soil pH rises. In addition, Mn is also tightly cycled by forests, inhibiting the precipitation of abundant Mn mineral phases in this section of the soil. Manganese leaching and cycling by forests is well-documented in similar acidic soils under temperate forests (*28*). In our experiments, mineralized Mn cannot be leached or taken up by vegetation from within the experimental vessel and thus accumulates to form birnessite. Since this pooling and evaporative concentration of Mn would be less likely in natural open soil systems, it is not surprising that these phases are less prevalent in field-based samples. Ferric iron, produced by the mineralization of iron in SOM (and/or perhaps atmospheric deposition) in the oxidizing environment of these soil horizons, however, is highly insoluble, even under the pH conditions encountered in the forest floor and could rapidly precipitate as ferrihydrite prone to sequester Pb. The enrichment of Fe and depletion of Mn with depth in O-horizons has been observed by numerous researchers and supports this explanation (*29*). We therefore conclude that ferrihydrite represents a more important sink of pollutant Pb in the forest floor relative to Mn phases in most natural environments. Alternatively, Pb bound to Mn colloidal phases could be preferentially physically transported from the soil during and after precipitation events, as a correlation between increased Pb flux and colloidal loads has been observed in forested watersheds (*30*). The strong retention of pollutant Pb in the forest floor certainly complicates this interpretation, nor is a mechanism for preferential mobility of Mn colloidal phases in the forest floor is not immediately evident (*8*).

Environmental Implications. Pb solid-phase association varies dramatically and systematically on very short decomposition timescales, becoming increasingly associated with pedogenic Mn/Fe mineral phases as decomposition of SOM progresses. The mineral phases appear to be relatively more important to dictating Pb sequestration in the forest floor of deciduous vegetation relative to conifer vegetation of the northern forest. When assessing the potential threat of the pollutant Pb pool that remains in regional O-horizons, parameters governing Fe/Mn phase stability (i.e., soil horizon redox status) should be considered in conjunction with those governing decomposition rates in the soil to accurately predict the mobility of this pollutant in the soil environment. In temperate forests where active atmospheric deposition of concentrated Pb persists (i.e., smelters), more Pb will be deposited on and retained by conifer forest floors relative to deciduous forest floors. Migration of Pb from such soil horizons will be tied to both Fe/Mn mineral phase stability and SOM susceptibility to microbially induced decomposition, with mineral phases representing a higher percentage of solid sequestered Pb in deciduous forest floors.

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Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.

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