

Fate and Speciation of Gasoline-Derived Lead in Organic Horizons of the Northeastern USA

James M. Kaste,* Benjamin C. Bostick, Andrew J. Friedland, Andrew W. Schroth, and Thomas G. Siccama

ABSTRACT

Although legislation in the late 1970s significantly reduced atmospheric lead (Pb) inputs to ecosystems in North America, organic (O) horizons in forests of the northeastern USA still contain up to 30 kg of gasoline-derived Pb ha⁻¹. The residence time, geochemical behavior, and fate of this contaminant Pb in soils is poorly understood. Here we use forest floor time series data and synchrotron-based X-ray techniques to examine the mobility and speciation of Pb in O horizons collected from remote sites across the northeastern USA. At high elevation (>800 m) sites in Vermont and New York, samples collected from similar locations in 1980, 1990, and early 2000 had indistinguishable Pb contents, ranging ($\pm 1\sigma$) from 11 to 29 kg Pb ha⁻¹. However, at lower elevation and lower latitude sites with mixed vegetation, significant decreases in Pb amount were observed during the two-decade study period. Lower elevation sites ranged from 10 to 20 kg Pb ha⁻¹ in 1980, and from 2 to 10 kg Pb ha⁻¹ 20 yr later. Lead-enriched soil grains were determined to be amorphous with microfocused X-ray diffraction, and Pb concentrations correlated well with Fe on maps generated via microfocused X-ray fluorescence. Bulk Pb L_{III}-edge X-ray absorption spectroscopy of coniferous O horizon samples indicate that Pb is binding to iron-rich soil particles by inner-sphere complexes, most likely to amorphous Fe oxides. Based on our paired regional and microscopic observations, we conclude that Pb is strongly retained in well-drained O horizons, and mobility is governed by decomposition and colloidal transport.

LEAD is perhaps the most widely dispersed trace metal in the environment (Galloway et al., 1982; Nriagu, 1996). Smelting, fossil fuel combustion, waste incineration, and, most notably, the combustion of leaded-gasoline emitted particulate Pb into the atmosphere in a legacy whose origins can be traced back thousands of years (Hong et al., 1994). Since the residence time of aerosols in the troposphere is on the order of weeks (Koch et al., 1996), this lead was deposited to land via wet and dry deposition both locally and regionally with respect to the pollution source (Erel et al., 2002). Within the northeastern USA, total Pb deposition is estimated at 10 to 50 kg Pb ha⁻¹ (Johnson et al., 1982; Miller and Friedland, 1994; Marsh and Siccama, 1997), and most of it was deposited in the early to middle 20th century during the peak time period of leaded-gasoline use (Miller and Friedland, 1994; Johnson et al., 1995). Transporta-

tion corridors and high-elevation forests received the highest inputs of anthropogenic Pb (Johnson et al., 1982). Although Pb can be disruptive to essential ecosystem processes and toxic to soil microorganisms, aquatic species, and humans (Liang and Tabatabai, 1977; Tyler, 1989, 1990; Ekenler and Tabatabai, 2002), the behavior and ultimate fate of this contaminant Pb in soils has remained unclear.

Researchers assessing the fate of atmospheric Pb in soils have relied on repeated sampling, isotopic studies, and models capturing the Pb source term and the current distribution in the soil profile. Since the canopy and the forest floor is the initial receptor of atmospherically delivered Pb in watersheds, there has been a considerable amount of research focusing on the O horizon. In particular, O horizon time series data have been used to show that the distribution of Pb in the upper soil horizons has changed over the past few decades (Friedland et al., 1992; Johnson et al., 1995; Yanai et al., 2004; Evans et al., 2005). Yanai et al. (2004) documented a decline in Pb from the O_{ie} horizon between the late 1970s to the early 1990s in remote forest soils in New Hampshire. Johnson et al. (1995) and Friedland et al. (1992) concluded that some fraction of gasoline-derived Pb had moved from the O horizon to the mineral soil during the 1980s at the Hubbard Brook Experimental Forest (HBEF) and at selected remote sites in the northeastern USA, respectively. Other researchers have used O horizon time series data to model the response time (*e*-folding time) of forest floor Pb and to project steady-state Pb forest floor levels (Miller and Friedland, 1994; Wang and Benoit, 1997). While the transport mechanism of this pollutant Pb in soil has not been directly determined, many have suggested that particulate or dissolved organic matter would strongly bind to Pb and therefore would govern its mobility (Dorr and Munnich, 1989; Dorr and Munnich, 1991; Miller and Friedland, 1994; Wang and Benoit, 1997; Semlali et al., 2001; Tipping et al., 2003).

More recently, Pb isotopes have been used to directly detail the distribution and behavior of atmospherically delivered Pb in soils. Measurements of ²⁰⁶Pb/²⁰⁷Pb have been used to show that anthropogenic Pb is distributed throughout organic and mineral soils at forested sites in Sweden and Norway (Bindler et al., 1999; Steinnes et al., 2005). Kaste et al. (2003) used ²¹⁰Pb to model the response time of atmospherically delivered Pb in the O horizon at Camels Hump Mountain in Vermont. They concluded that the forest floor response time was between 60 and 150 yr, depending on vegetation zone and elevation. Using ²⁰⁶Pb/²⁰⁷Pb, they also demonstrated that some gasoline-derived Pb had migrated out of the O horizon and into the mineral soil, but that all of the atmospheric Pb was retained in the upper 20 cm of the

J.M. Kaste, B.C. Bostick, and A.W. Schroth, Dep. of Earth Sciences, Dartmouth College, HB 6105 Fairchild Hall, Hanover, NH 03755; J.M. Kaste, A.J. Friedland, and A.W. Schroth, Environmental Studies Program, Dartmouth College, HB 6182 Steele Hall, Hanover, NH 03755; T.G. Siccama, Yale School of Forestry and Environmental Studies, 370 Prospect St., New Haven, CT 06511. Received 27 Sept. 2005. *Corresponding author (jim.kaste@dartmouth.edu).

Published in Soil Sci. Soc. Am. J. 70:1688–1698 (2006).
Soil Chemistry and Forest, Range & Wildland Soils
doi:10.2136/sssaj2005.0321

© Soil Science Society of America
677 S. Segoe Rd., Madison, WI 53711 USA

soil profile. Generally, soils in Europe show a deeper penetration of anthropogenic Pb in the soil profile than is typically observed in the USA, but the anthropogenic Pb found deep in the mineral soil of sites in Europe is probably “old” Pb, deposited before the introduction of leaded-gasoline (Bacon and Hewitt, 2005; Steinnes and Friedland, 2005). The direct uptake of atmospherically delivered Pb by vegetation in boreal forests and by grasses appears to be low (Bacon et al., 2005; Klaminder et al., 2005).

The geochemical behavior of anthropogenic Pb in soils is complex, and may be impacted by climate, organic matter type, and soil parent material. Several works have demonstrated the importance of Pb phosphate minerals for controlling Pb solubility and migration in soils (Ruby et al., 1994). Nriagu (1974) used thermodynamic data to argue that Pb orthophosphates (e.g., pyromorphite) were the most stable Pb phase in many soils and sediments, and would likely sequester fallout Pb. He further suggested that because of the extremely low solubility of Pb phosphate minerals, Pb deposition could potentially reduce phosphorous availability, which could have ecological repercussions. Most recently, biologically mediated pyromorphite precipitation has been directly observed (Jackson et al., 2005). Because soil organisms can have a very high turnover rate, these authors suggested that biogenic precipitation could play an important role in Pb geochemistry in contaminated soils. Selective chemical extractions have been applied to speciate Pb in soils, but have yielded variable results possibly in part because of complications associated with the technique (Nirel and Morel, 1990). Furthermore, different soil types appear to sequester Pb via different mechanisms. While Teutsch et al. (2001) found that most of the anthropogenic Pb in roadside soils from their study in Israel was associated with carbonates and iron oxides, Emmanuel and Erel (2002) reported that organic matter was largely responsible for Pb retention in O horizons from the Czech forest. Within O horizons, extractions targeting organic matter and reducible oxides can liberate a significant quantity of Pb (Ho and Evans, 2000; Johnson and Petras, 1998; Kaste et al., 2005).

The speciation of contaminant Pb in soils has direct implications for forest and human health. While Nriagu (1974) suggested that significant Pb inputs to soils could decrease phosphate availability, others have clearly demonstrated that heavy metals in soils can inhibit decomposition and essential ecosystem recycling processes (Ekenler and Tabatabai, 2002; Tyler, 1976). The development of synchrotron-based X-ray experiments to determine the coordination environment of Pb in environmental samples gives considerable promise for understanding the speciation and behavior of contaminant metals in heterogeneous environments. X-ray absorption spectroscopy (XAS) and X-ray microprobe techniques can be used to directly determine the coordination environment and elemental and phase associations of trace metals in soil (Manceau et al., 1996; Jackson et al., 2005). The purposes of this study are to (i) quantify Pb mobilization from O horizons in the northeastern USA

using forest floor time series data, and (ii) use modern synchrotron-based XAS and microprobe X-ray fluorescence and X-ray diffraction techniques to gain insight into the partitioning behavior of Pb in organic-rich soil horizons.

MATERIALS AND METHODS

Field Sites and Sampling

Samples collected for this study are part of a regional forest floor sampling survey described in Friedland et al. (1992). This decadal sampling survey examines the composition and mass of surficial organic matter from a variety of undisturbed soils from a range of Northeastern deciduous, coniferous, and mixed forests (Fig. 1, Table 1). The O horizons sampled in this survey are from non-carbonate soils with little to no biological mixing, and are largely mor-type (i.e., thick humus layer) horizons. With the exception of the sites in Pennsylvania, soils are generally developed on glacial till or outwash deposits. Soils are commonly Spodosols, particularly in New Hampshire, Vermont, and northern New York, while sites in Connecticut, southern New York, and Pennsylvania are more commonly Inceptisols. Sites typically have a gentle to zero slope.

At each of our sites of approximately 30 m by 30 m, we quantitatively sampled the O horizon at five random locations during the summers of 2001 and 2002. At Camels Hump Mountain, we have four sites in the Northern Hardwood Zone, where vegetation is dominated by beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and white birch (*Betula papyrifera* var. *cordifolia*). We also maintain four sites in the Spruce-Fir Zone, where vegetation is dominated by hemlock (*Tsuga canadensis*), yellow birch (*B. alleghaniensis*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*), and maintain three sites in the mixed Hardwood/Spruce/Fir zone. The O horizon is collected by cutting around a wooden template (15 cm × 15 cm) using stainless steel saws and knives. The cut area is peeled away from the template and excavated until mineral soil (A or E) is observed, and we carefully separate a “plug” of O horizon from the mineral soil with a stainless steel paint-scraper. Once extracted, any mineral soil on the base of the sample is manually removed, and each O horizon plug is stored in a plastic bag. At Camels Hump Mountain (VT) and on Whiteface Mountain (NY), the O horizon was subsampled (Oi, Oe, Oa) for XAS and microprobe analysis. Here we report on the Pb content of the O horizon sampled in similar locations at identical sites during three different time periods: 1980, 1990, and in 2001–2002. Site descriptions and additional data from 1980 and 1990 are described in more detail elsewhere (Craig, 1991; Friedland and Johnson, 1985; Friedland and Miller, 1999; Friedland et al., 1986, 1992; Siccama, 1974).

Metal and Organic Matter Determination

Organic soil horizon samples were dried at 105°C for 48 h. The samples were weighed to determine total O horizon mass, and then ground and homogenized in a stainless-steel Wiley Mill. Total metal content was determined by ashing 2 g of ground soil at 475°C for 6 h (Friedland et al., 1992). The ash was then dissolved in boiling 1:1 HNO₃ (1 part H₂O, 1 part concentrated nitric acid) for 20 min in a silica crucible. Nitric acid extracts were then filtered (Whatman #41) and diluted with deionized water. Diluted extracts were analyzed on an ICP-OES for major (Al, Ca, Fe, K, Mg, Mn, Na) and trace elements (Cd, Cu, Pb, Zn). Recoveries of Pb for NIST SRM 1575 Pine needles are within 8% of the certified values with this method, and Pb was not detected in blanks via ICP-OES

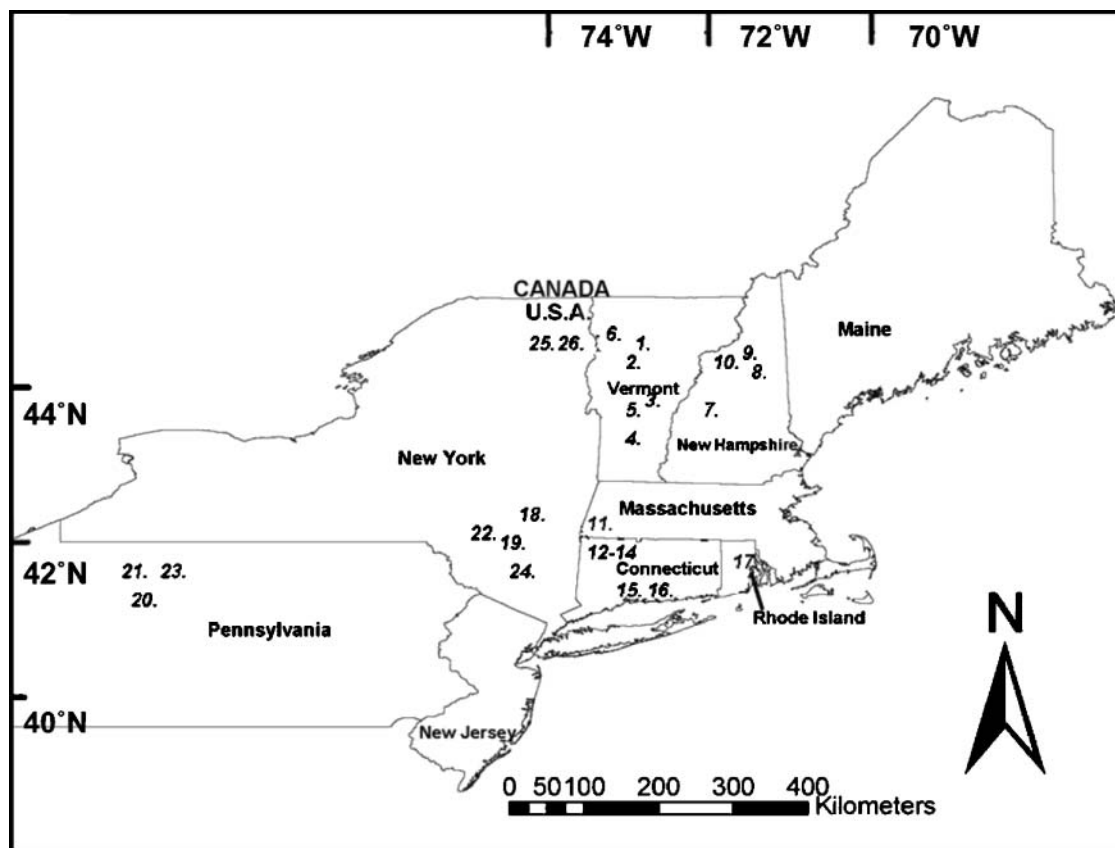


Fig. 1. Locations sampled in 1980, 1990, and early 2000 in the northeastern regional forest floor survey.

(detection limit 60 ng g^{-1}). Analysis via graphite furnace atomic absorption spectrometry verified that digestion blanks were at least 2.5 orders of magnitude lower in Pb than the sample digests. Organic matter content was quantified by the mass lost on ignition during the ashing procedure. Here we report Pb concentrations (mg kg^{-1}) and total Pb amounts (kg ha^{-1}) in O horizons sampled from across the northeastern USA. Lead amounts were calculated by multiplying the concentration of Pb measured in each O horizon by the O horizon mass that was collected at each site.

Microfocused X-Ray Experiments and X-Ray Absorption Spectroscopy

The goal of using synchrotron-based microfocused X-ray fluorescence (μSXRF) and X-ray diffraction ($\mu\text{SXR D}$) is to determine the grain-scale elemental distribution and mineralogy of Pb and other metals in O horizon samples. X-ray absorption studies (XAS) allow us to determine the coordination environment of Pb in our samples and characterize the neighboring atoms that might govern Pb retention and mobility. These techniques can be advantageous over traditional chemical extractions because samples are analyzed directly in an unaltered and relatively natural state. Field-moist samples were ground using a mortar and pestle, mounted on Teflon templates, and covered with Kapton tape for analysis in the X-ray beam. Bulk Pb XAS was done using beamline X9B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, and beamline 2–3 at the Stanford Synchrotron Light Source (SSL S). Samples were mounted between the first and second ionization chambers (I_0 and I_1), and an elemental Pb foil was mounted between the second and third chambers (I_1 and I_2) for calibration at 13055 eV . XAS data were collected at

the Pb L_{III} edge over the energy range of 12.8 to 13.9 keV . Extended X-ray absorption fine-structure (EXAFS) spectral analysis and shell fitting was done with WinXAS 2.3, using theoretical phase and amplitude functions derived by FEFF 7.02. The coordination number (CN), bond distance (R), and Debye-Waller factor (σ^2) for each shell was determined on unfiltered spectra in which the energy shift (ΔE_0) was fixed using the value from the filtered fit of the first shell (Pb-O). The amplitude reduction factor was fixed at 0.9 . Given the limited k-range of the data (up to 9 \AA^{-1}) that is inherent with Pb EXAFS, we used the standard convention of fixing σ^2 at 0.01 for all shells to minimize the number of fit parameters (Ostergren et al., 2000; Sauve et al., 2000; Templeton et al., 2003).

Microfocused SXR F and SXR D analysis of selected samples were done using beamline X26A at NSLS, which is equipped with a Si (111) monochromator with 1 eV nominal resolution (Miller et al., 2005). Ground organic horizons were mounted on Kapton tape. Microfocused XRF spectra and maps were collected using 13.1 keV incident X-rays, and the X-ray spot size was approximately $6 \mu\text{m} \times 8 \mu\text{m}$. Maps were made using a step size of $10 \mu\text{m}$ on an area of $0.5 \times 0.5 \text{ cm}$. Elemental fluorescence intensities for Pb, Fe, Ca, and other metals were collected using a Canberra 9-element Ge Array detector with integrated count times of 2 s/pixel . X-ray fluorescence peak intensities are approximately proportional to elemental abundance; however, the data are presented in raw counts because of the considerable errors in determining accurate concentrations from low integration times. At regions of interest within the XRF maps, $\mu\text{SXR D}$ was employed to quantify any crystalline phases that might be present in the samples.

Microfocused SXR D patterns at specific regions of interest were collected to identify the mineralogy of crystalline phases using a Bruker SMART 1500 charge-coupled device (CCD) sys-

Table 1. Sampling sites in the regional forest floor survey. Numbers correspond with the map (Fig. 1). Mean \pm 1 SE given for Pb concentration (mg kg^{-1}) and amount (kg ha^{-1}). Confidence Level (C.L.) determined by Analysis of Variance (ANOVA, Tukey-Kramer Honestly Significant Difference). "No Change" indicates no significant change detected at a C.L. \geq 90%. NA indicates data not available.

Site	Elevation m	Vegetation	1980 Pb	1980 Pb	1990 Pb	1990 Pb	2001-2002	2001-2002 Pb	Change @ C.L.
			mg kg^{-1}	kg ha^{-1}	mg kg^{-1}	kg ha^{-1}	Pb mg kg^{-1}	kg ha^{-1}	
1. Camels Hump Mtn., VT	550-750	N. Hardwood	111 \pm 6	7.0 \pm 0.8	89 \pm 5	4.7 \pm 0.7	62 \pm 4	4.7 \pm 0.5	Decrease @ 90%
	750-950	N. Hardwood/ Spruce/Fir	197 \pm 17	17.2 \pm 2.2	146 \pm 16	13.8 \pm 2.1	99 \pm 12	12.5 \pm 1.5	No Change
2. Appalachian Gap, VT	950-1200	Spruce/Fir	180 \pm 15	18.7 \pm 1.8	213 \pm 14	19.5 \pm 1.7	155 \pm 10	20.4 \pm 1.2	No Change
	778	Spruce/Fir	191 \pm 19	17.5 \pm 2.8	143 \pm 19	15.5 \pm 2.8	68 \pm 13	14.1 \pm 2.0	No Change
3. Bristol Cliffs, VT	555	Red Pine	145 \pm 10	11.8 \pm 1.5	114 \pm 10	9.2 \pm 1.5	84 \pm 7	11.3 \pm 1.1	No Change
4. Bromley Mtn., VT	625	N. Hardwood	123 \pm 12	6.9 \pm 1.9	70 \pm 13	3.0 \pm 2.1	78 \pm 9	12.0 \pm 1.4	No Change
5. Sherburne Pass, VT	671	N. Hardwood	120 \pm 11	5.5 \pm 1.2	94 \pm 13	6.2 \pm 1.3	43 \pm 11	3.1 \pm 1.2	No Change
6. East Woods, VT	100	Oak-Pine	NA	NA	131 \pm 30	10 \pm 1.8	98 \pm 2	7.3 \pm 2.1	No Change
7. Mt. Cardigan, NH	579	N. Hardwood/ Spruce/Fir	90 \pm 15	4.3 \pm 2.4	63 \pm 22	2.5 \pm 3.5	73 \pm 9	6.9 \pm 1.5	No Change
8. Wildcat Mtn., NH	590	N. Hardwood/ Spruce/Fir	83 \pm 16	9.7 \pm 2.2	91 \pm 12	12.1 \pm 1.7	56 \pm 9	12.5 \pm 1.2	No Change
9. Gale River, NH	440	N. Hardwood	67 \pm 18	3.8 \pm 2.3	63 \pm 16	4.0 \pm 2.1	58 \pm 13	7.8 \pm 1.7	No Change
10. Valley Way, NH	433	N. Hardwood/ Spruce/Fir	80 \pm 6	5.7 \pm 0.9	78 \pm 6	4.8 \pm 0.9	49 \pm 4	5.9 \pm 0.6	No Change
11. Mt. Evereff, MA	790	Pitch Pine/Oak	331 \pm 37	20.8 \pm 4.5	201 \pm 37	17.2 \pm 4.5	149 \pm 26	19.3 \pm 3.2	No Change
12. Mohawk Mtn., CT	503	Mixed Oak	132 \pm 9	11.7 \pm 1.3	148 \pm 9	10.1 \pm 1.3	128 \pm 7	9.8 \pm 1.0	No Change
13. Catlin Woods, CT	290	White Pine	106 \pm 24	14.6 \pm 1.7	130 \pm 4	12.7 \pm 1.3	61 \pm 17	6.1 \pm 1.3	Decrease @ 95%
14. Cathedral Pines, CT	260	White Pine/ Hemlock	162 \pm 7	15 \pm 3	102 \pm 13	8 \pm 1	94 \pm 18	9 \pm 2	Decrease @ 99%
15. North Haven, CT	20	Pitch Pine/Oak	134 \pm 2	29.6 \pm 3.3	187 \pm 22	17.5 \pm 1.9	106 \pm 6	12.5 \pm 2.3	Decrease @ 99%
16. North Madison, CT	100	Oak/Hickory	NA	NA	123 \pm 11	9.0 \pm 0.4	65 \pm 2	4.2 \pm 0.3	Decrease @ 99%
17. Eppley Preserve, RI	80	White Pine	NA	NA	97 \pm 4	5.8 \pm 0.7	63 \pm 7	4.5 \pm 0.7	No Change
18. Windham, NY	580	N. Hardwood	119 \pm 24	15.7 \pm 4.5	62 \pm 19	18 \pm 3.5	43 \pm 19	9.6 \pm 3.5	No Change
19. Tremper Mtn., NY	305	Pine/Hemlock/ N. Hardwood	163 \pm 18	7.1 \pm 1.3	204 \pm 20	11.7 \pm 1.5	73 \pm 13	4.7 \pm 1.0	Decrease @ 95%
20. Cook Forest, PA	430	Pine/Hemlock/ N. Hardwood	168 \pm 13	13.7 \pm 1.2	112 \pm 13	6.1 \pm 1.2	60 \pm 8	3.2 \pm 0.7	Decrease @ 99%
21. Hearts, PA	580	Pine/Hemlock/ N. Hardwood	294 \pm 48	12.2 \pm 1.6	115 \pm 48	5.4 \pm 1.6	94 \pm 38	6.2 \pm 1.3	Decrease @ 95%
22. Balsam Lake, NY	820	N. Hardwood	140 \pm 14	6.3 \pm 1.2	122 \pm 16	6.3 \pm 1.3	61 \pm 11	3.0 \pm 0.9	Decrease @ 90%
23. Tionesta, PA	520	Oak	104 \pm 15	5.3 \pm 0.7	76 \pm 12	1.7 \pm 0.6	47 \pm 8	1.7 \pm 0.4	Decrease @ 99%
24. Mohonk, NY	366	Pine/Hemlock/ N. Hardwood	267 \pm 15	11.6 \pm 3.8	198 \pm 15	17.7 \pm 3.8	162 \pm 11	18.6 \pm 2.8	No Change
25. Whiteface Mtn., NY	1300	Spruce/Fir	N.A.	N.A.	126 \pm 30	17.8 \pm 4.4	139 \pm 23	15.0 \pm 2.6	No Change
26. Ellis Mtn, NY	520	Oak	107 \pm 5	7.1 \pm 1.0	80 \pm 5	8.8 \pm 1.0	43 \pm 4	3.5 \pm 0.9	Decrease @ 99%

tem and a calibrated incident photon wavelength of 0.9464 Å. Given the beam size of this system, we can identify and characterize very small crystals and aggregates. Data were processed with Fit2D software packages for integrating the 2D Debye-Scherrer rings and diffraction peaks to 1D 2 θ scans. Backgrounds resulting from anomalous diffraction of the Kapton mount were subtracted before analysis. Microfocused X-ray absorption near-edge structure (XANES) was used in addition to μ SXRD at selected regions of interest to help speculate Pb directly.

RESULTS AND DISCUSSION

Regional Forest Floor Survey

Organic horizon Pb concentrations and amounts measured in 1980, 1990, and in early 2000 are given in Table 1. A Tukey-Kramer Honestly Significant Difference analysis of variance (ANOVA) test was used to determine if the amount of Pb in the forest floor changed over the study period. ANOVA test results and the maximum confidence level (CL) are given in the last column (Table 1). We acknowledge that forest floor sampling can be subjective, and comparisons between studies should be done with caution (Federer, 1982). However, the organic matter percentage measured in the samples can be used as a relative check of the consistency of the

collections. The data set means for organic matter content of O horizons collected in 1980, 1990, and early 2000 were 65, 70, and 66%, respectively, and significant changes in organic matter content were not detectable using ANOVA. These data suggest that during each time period we sampled a similar soil horizon, and thus the collections from different time periods are comparable. We eliminated any samples that were collected but that had an organic matter content <40% from the dataset, because such samples are technically A horizons.

The concentration of Pb in rainfall in the northeastern USA dropped quickly after the passage and implementation of the Clean Air Act in the late 1970s (Johnson et al., 1995), and is currently on the order of 0.5 ng g^{-1} (Wang et al., 1995). Assuming a 1.1 m yr^{-1} precipitation rate, then loadings to the surface via wet deposition are currently on the order of 0.6 $\text{mg m}^{-2} \text{yr}^{-1}$. Since dry deposition may account for anywhere between 10 and 40% of total Pb deposition (Galloway et al., 1982), current gross Pb loadings to the surface are probably on the order of 1 $\text{mg m}^{-2} \text{yr}^{-1}$. Although inputs have been relatively low over the course of our study period (annually <0.1% of the forest floor Pb standing crop), 15 out of 26 sites showed no significant decrease in Pb amount from 1980 to 2002. For the most part, the forest floor Pb inventory at sites north of 42° N did not change sig-

nificantly over the 21-yr study period, and no high elevation O horizons in the spruce-fir forest zone had a significant decrease in Pb amount during the study period.

While the majority of sites did not show a significant change in forest floor Pb during the two-decade study period, forest floor Pb appears to be lower than estimated Pb inputs to the northeast during the 20th century. Total Pb deposition to soils in the northeastern USA has been estimated to range from 9 to 50 kg Pb ha⁻¹ (Johnson et al., 1995; Marsh and Siccama, 1997; Miller and Friedland, 1994), with higher amounts delivered to high elevation sites and near urban areas. Organic horizons sampled in early 2000 had Pb burdens ranging from 2 to 30 kg Pb ha⁻² (Table 1), which is substantially lower than inventories predicted if the O horizon completely retained all of the atmospheric Pb. While it is difficult to generalize at regional scales, detailed studies have detected that anthropogenic Pb has leached into underlying mineral soil in parts of the northeastern USA and Canada (Johnson et al., 1995, 2004; Marsh and Siccama, 1997; Kaste et al., 2003; Watmough and Hutchinson, 2004). This process appears to be occurring most dramatically at sites in the lower latitude portion of our study area where decomposition is faster and thinner O horizons persist.

The amount of Pb in the O horizon decreased significantly (at least 90% confidence) at 11 out of the 26 sites during the two-decade study period. Of the 11 sites that decreased, 9 of these are among our southernmost field sites (south of 42° N latitude, Fig. 1). Some of the forest floor Pb decreases between 1980 and 2002 were substantial. In Connecticut, Pb amounts in O horizons from Catlin Woods (13) and North Haven (15) decreased by 58%, and Cathedral Pines (14) O horizon Pb decreased by 40% during the study period. In southwestern Pennsylvania, Tionesta (23), Hearts Mountain (21), and Cook Forest (20) had O horizon Pb amount declines of 68, 49, and 77%, respectively. The lower elevation stands at Camels Hump (1) also had a significant decrease in O horizon Pb, probably because of the faster organic matter turnover here relative to the higher elevation sites on the mountain. However, Pb averages at these sites also have considerably lower standard errors because of the larger number of sampling locations we maintain there. We thus were more easily able to detect a significant difference at the Camels Hump Mountain sites. At the Hubbard Brook Experimental Forest (HBEF), approximately 30% of the atmospheric Pb has migrated out of the forest floor and into the mineral soil (Johnson et al., 1995). Yanai et al. (2004) demonstrated that Pb amounts in the organic-rich surficial soil horizons (defined in study as O+A) did not change significantly between 1979 and 1994 in selected stands from the White Mountain National Forest in central New Hampshire. However, they reported a significant redistribution of Pb from the Oi+Oe horizons to the Oa and A horizons. A paired *t* test comparison of 1980 and 1990 Pb amounts from the regional survey described here (Fig. 1) also identified a significant decrease in O horizon Pb in mixed-vegetation forests at low elevation and low latitude (Friedland et al., 1992).

Any changes in forest floor Pb most likely represents a migration of Pb from the O horizon to the mineral soil (Johnson et al., 1995; Kaste et al., 2003; Miller and Friedland, 1994). Lateral migration of the Pb by throughflow or by overland flow erosion seems unlikely. Dissolved losses of Pb in streamwater are very low; measurements of streams and seeps in central New Hampshire are reported to be 10 pg Pb g⁻¹ (Wang et al., 1995). Particulate-losses of Pb from watersheds have also been observed to be a small flux relative to the standing crop of Pb in the forest floor (Smith and Siccama, 1981; Turner et al., 1985). The fibrous nature and high permeability of the forest floor generally keeps erosion, which could remove Pb from surface soils at our sites, to a minimum (Johnson et al., 1968). Measurements of Pb isotopes in mineral soils has confirmed that some Pb has migrated out of the O horizon here and elsewhere in North America, especially at sites with thin (<8 cm) O horizons (Kaste et al., 2003; Watmough and Hutchinson, 2004).

The relative retention of Pb by the O horizon in our regional study and elsewhere appears to be related to organic matter turnover. Lower latitude and lower elevation sites in Pine, Oak, or Northern Hardwood forests have a higher tendency for Pb losses from the forest floor, and these are typically sites with more rapid decomposition and thinner O horizons. Specifically, our sites in southwestern Pennsylvania had the most substantial declines in O horizon Pb. Average O horizon thickness here is 3 ± 1 cm, reflecting the relatively rapid turnover of organic matter. In contrast, O horizons sampled from central New Hampshire have thicknesses of 13 ± 6 cm; O horizon Pb amounts did not change at these sites during the study period. Along the elevation gradient at Camels Hump Mountain we can observe this effect on a single mountain. The O horizon in the deciduous zone at Camels Hump ranges from 4 to 7 cm in thickness, and some Pb losses were detected. Higher elevation soils in the coniferous zone sites at Camels Hump have forest floor thicknesses ranging from 10 to 20 cm, where no change in Pb inventory was observed over our study period. However, elevation, vegetation, and latitude are not the only factors that control organic matter turnover. Watmough and Hutchinson (2004) measured Pb in soils collected from stands of white pine and sugar maple in Ontario. Here, very thin O horizons (<2 cm) persist presumably because the high pH of the underlying carbonates facilitates organic matter decomposition. They used measurements of ²⁰⁶Pb/²⁰⁷Pb to show that the forest floor was a relatively insignificant reservoir of Pb: it contained <3% of the total anthropogenic soil Pb inventory. Figure 2 shows the correlation (*p* < 0.01) between O horizon thickness and calculated annual Pb loss for our study sites.

Speciation and Phase Associations of Lead in O Horizons

From the O horizon survey data we conclude that organic matter turnover controls the residence time of Pb in the O horizon, and that O horizons in high elevation

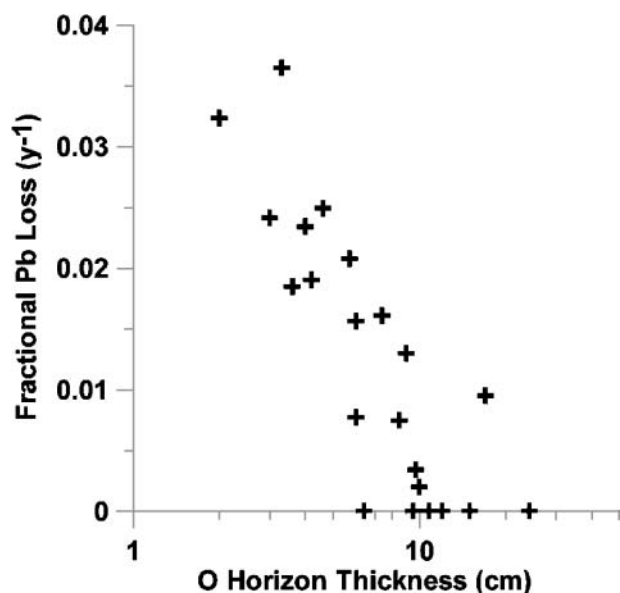


Fig. 2. The fractional amount of Pb loss calculated over the study period is significantly correlated with the thickness (cm) of the forest floor at each site. A logarithmic fit to these data give $r^2 = 0.65$.

coniferous forest can quantitatively retain atmospheric Pb on time scales of at least decades. The precise mechanism of this relatively strong Pb retention by O horizons is unknown. To elucidate the mechanisms of Pb retention in O horizons, we use a combination of synchrotron-based studies as described above. Microfocused SXRF mapping provides grainscale information about elemental abundances and correlations to determine the composition of Pb-rich (and Pb-poor) grains, and μ SXRD can be used to determine the mineralogy of any Pb-bearing crystalline phases. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies are used to characterize the coordination environment and nearest neighbor atoms of Pb within the O horizon.

A representative μ SXRF map of Pb on a moderately decomposed litter layer (Oe/Oa) collected from the coniferous zone of Whiteface Mountain is given in Fig. 3. This sample is mostly organic matter, having an 80.3% loss on ignition. Similar maps were generated for Ca, Cr, Fe, Mn, Ti, and Zn on the sample, and correlation coefficients between Pb and the other elements (XRF per pixel) were calculated on the log-normalized data (Table 2). Calcium, Fe, and Pb XRF data on two transect plots (X

to X' and Y to Y', Fig. 3) are given in Fig. 4. Lead had the strongest correlation with Fe (linear r^2) on the μ SXRF map (Fig. 3, Table 2).

While the μ SXRF data demonstrate that Pb may be associated with an Fe-rich phase, correlation alone is insufficient to conclude that interactions with Fe control Pb retention. Lead concentrations are also significantly correlated to all other elements analyzed on the map ($p < 0.01$; Table 2) due to the large number of data points (~ 3000) and the relatively heterogeneous sample distribution on the Kapton tape. The distribution of Pb is not homogenous and highly concentrated regions exist in certain parts of the sample (Fig. 3 and 4). While a heterogeneous distribution of Pb on the μ SXRF images could result from an uneven distribution of the soil grains and thus low or high counts could result from the absence or presence of soil in the beam path, relative fluorescence intensities of Ca, Fe, and Pb suggest otherwise. Elevated amounts of Ca occur in spots where Pb, Fe, and other elements are absent, and Pb and Fe coincide more closely than any of the other elements that we scanned for (Fig. 4 and Table 2). In fact, in all of our transects that we examined on the map given in Fig. 3 and on maps generated on similar samples, Pb peaks typically coincided with Fe peaks, although not all Fe peaks contained excessive Pb. Since Ca is a structural cation in organic molecules, Ca should be useful as a proxy for organic matter in the XRF maps. Using this proxy, we conclude that Pb interactions with organic molecules may not be the dominant Pb scavenging mechanism in our samples.

We used microfocused XRD to identify the mineralogy of areas containing elevated Pb that we identified in the XRF maps. Very few diffraction peaks were evident in the XRD patterns of Pb-rich regions in O horizons from Whiteface and Camels Hump (Fig. 5). While the diffraction patterns contain few discernable peaks, some have a broad background characteristic of poorly crystalline or amorphous phases. Pyromorphite and other Pb-containing minerals are usually sufficiently structured to contain diffraction peaks or rings (Jackson et al., 2005), but we found no evidence for crystalline phases at Pb-rich regions of interest. Because the use of XRD to identify trace metal mineralogy in heterogeneous samples such as ours has limitations and will certainly be dependent on the concentration of such phases, we cannot completely rule out the presence of crystalline Pb minerals on our samples. However, our XRD data which suggests that crystalline phases are insignificant corroborates additional data from XANES and EXAFS detailed below.

Given the relatively high correlation of Pb and Fe in these samples we hypothesize that non-crystalline iron (hydr)oxides, which adsorb Pb strongly (Jackson et al., 2005; Sauve et al., 2000; Trivedi et al., 2003) are responsible for the strong Pb retention in these samples. The bulk XANES and microfocused XANES (on Pb-enriched regions) data we collected and analyzed were most consistent with a Pb(II) phase that is complexed via inner-sphere adsorption (Bargar et al., 1997a, 1997b, 1998). Bulk EXAFS on select samples from coniferous

Table 2. Correlation coefficients between Pb and other metals analyzed by XRF microprobe ($n = 3400$) on an Oe/Oa (3 to 4 cm depth) sample from the coniferous zone on Whiteface Mtn (Map given in Fig. 3). Data were log transformed to obtain a more normal distribution; all metals had a significant correlation ($p < 0.01$) with Pb.

Metal	Pb correlation coefficient (r^2)
Ca	0.14
Cr	0.23
Fe	0.50
Mn	0.23
Ti	0.48
Zn	0.30

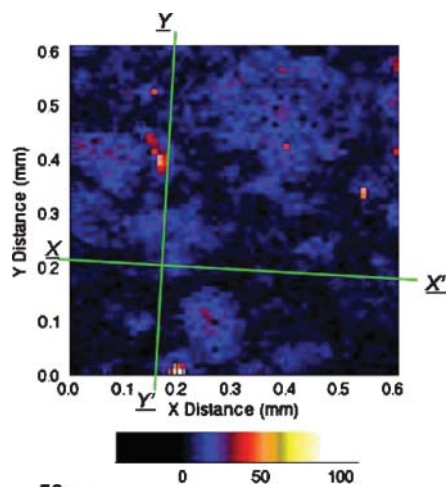


Fig. 3. Micro-focused SXRF map of an Oe/Oa horizon collected from Whiteface Mtn. Units are in total counts of Pb collected over a 2 s interval.

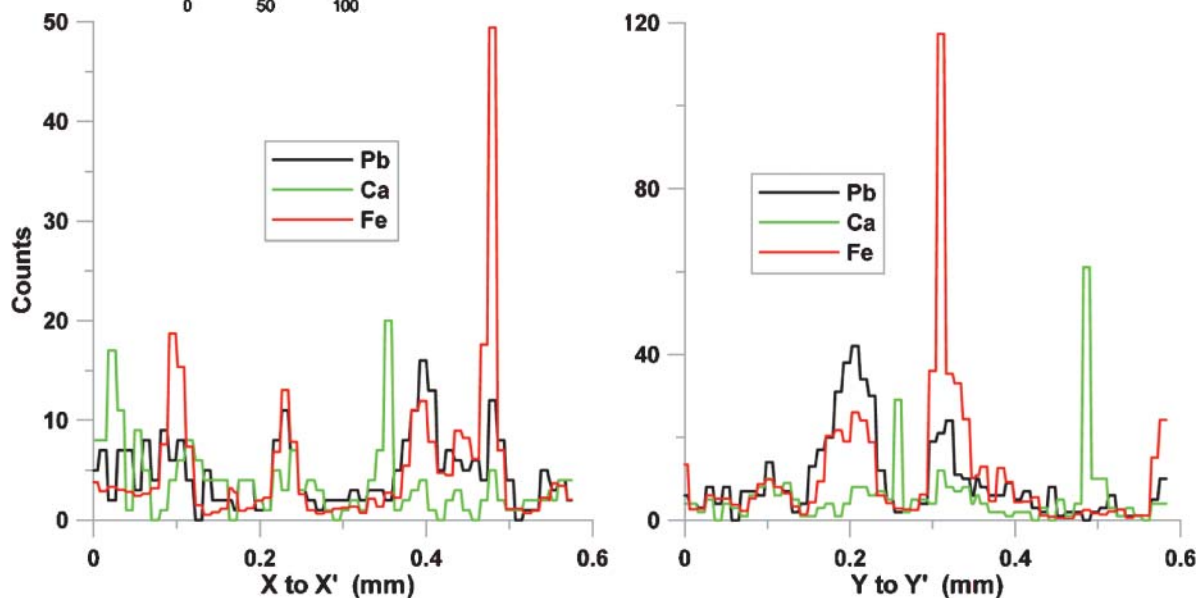


Fig. 4. Micro-focused XRF data collected for Ca, Pb, and Fe on transects from X to X' and Y to Y' on Fig. 3. Fe data are shown 5% scaled.

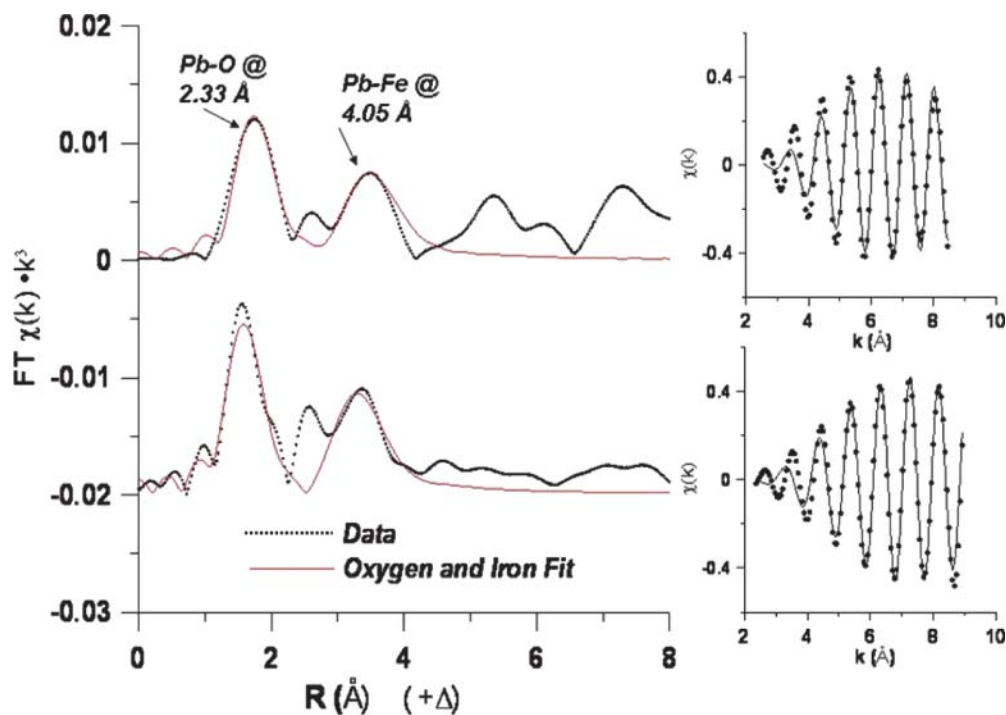


Fig. 6. Pb L_{III} radial distribution functions (left) derived from XAS experiments given for two Oa samples collected from the coniferous zone at Camels Hump Mountain. Theoretical shell fitting was done using an oxygen and an iron shell in FEFF 7.02. On the right, Fourier-filtered data from the backtransformed spectrum over $R + \Delta = 2.9$ to 4.1 \AA are given; these data are used to derive the Pb-Fe coordination numbers and interatomic distances that we report in the text.

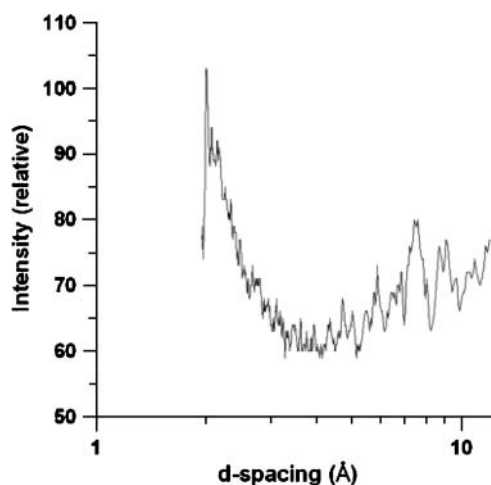


Fig. 5. An example X-ray diffraction tracing obtained using micro-focused XRD on Pb-enriched soil grains identified in Fig. 3. Since substantial diffraction peaks are not evident, crystalline Pb minerals not likely to be significant in the O horizon.

forests gives more direct information on the type of interactions that Pb is having with the soil matrix. Radial distribution functions (RDFs) for the Pb L_{III} electron in two samples are given in Fig. 6. The Pb RDFs generated from the EXAFS spectra contain two principal features near 1.8 and 3.5 Å (not corrected for phase-shifts). The first shell is best fit with 3 to 4 oxygen atoms at a distance of 2.27 to 2.33 Å. This partially dehydrated coordination environment is typical of Pb^{2+} bound as inner-sphere complexes (Bargar et al., 1997b; Xia et al., 1997) and is considerably shorter than aqueous Pb^{2+} , which has a first coordination shell of 8 to 9 oxygen atoms at 2.5 Å (Bargar et al., 1997a). However, it is not possible to differentiate between Pb^{2+} bound to organic matter, iron (hydr)oxides, and clay minerals based on the first shell alone. The second feature in the RDFs, however, helps to constrain the types of surfaces (or complexes) on which Pb is retained. The second shell is best fit with 1 to 2 Fe atoms at 4.00 to 4.05 Å (Fig. 6). This feature could not be effectively fit with carbon or any other atom, and the lower coordination number is indicative of an adsorbed complex rather than a crystalline material. We thus conclude that Pb is adsorbed to Fe-phases based on the bulk XAS experiments. Pb-Fe distances of 3.3 to 4 Å previously have been described for Pb adsorbed to hematite and goethite in experimental systems (Bargar et al., 1997b; Ostergren et al., 2000; Templeton et al., 2003; Trivedi et al., 2003). The exact Pb-Fe distances are governed by the geometry of Pb^{2+} adsorption complexes on the mineral surfaces. While Pb-Fe separations of 3.3 to 3.4 Å usually result when Pb binds to edges of Fe octahedra in bidentate mononuclear complexes, corner-sharing bridging bidentate bonding of Pb to surface Fe octahedral can yield Pb-Fe separations \geq 3.9 Å (Bargar et al., 1997b). Trivedi et al. (2003) demonstrated that the specific type of Pb binding to ferrihydrite was pH dependent, and noted a switch to corner-sharing complexes as pH dropped below neutral. Given the acidic nature of O horizons (pH typically 4–5), the corner sharing complexes of Pb on Fe phases we report

here are consistent with other works. While we have good evidence that Pb is coordinating with Fe in our samples, it appears that other phases may be present as well. Our spectra aren't entirely explained by iron and oxygen, and one additional peak is present in the radial distribution functions at approximately 2.5 Å (not corrected for phase-shift) in Fig. 6. Theoretical shell fitting of this feature is possible with either sulfur or a phosphorous atom at a distance of 3.3 Å. Interactions between Pb, P, and S could result if organic matter functional groups were binding to Pb.

The Behavior of Lead in Organic Horizons

Although Pb deposition to forests has been relatively low since 1980, O horizons sampled recently still have significant Pb burdens. At 11 of our sites, the amount of Pb in the O horizon dropped significantly during the two-decade study period. These sites were largely concentrated in the southern portion of our study area, where forest floor thickness and mass were lower, presumably from a more rapid turnover of organic matter (Fig. 1). At the remainder of our sites, which were generally north of the 42nd parallel, forest floor Pb inventories remained remarkably constant from 1980 through early 2000. While variability can often mask a change in forest floor chemistry, more intensive sampling at the high elevation stands at Camels Hump Mountain revealed that most of the Pb deposited there in the 20th century has remained in the O horizon. The retention of Pb we observe in our field-based O horizon survey work are consistent with experimental results. Lomander and Johansson (2001) found that the Pb concentration in Spruce needles in litterbags incubated in Norway Spruce stands increased in concentration by a factor of more than 10 during 6 yr of decomposition. Over the same time interval, other metals were not enriched from decomposition; the concentration of Cd, Mn, and Zn decreased due to export from the experimental litterbag. Thus it appears that O horizons strongly fix Pb, preventing leaching and migration through the soil profile, and can immobilize Pb for at least several decades.

While crystalline Pb phosphates (which conceivably also could contain Fe) are predicted to control Pb geochemistry in soils, neither the XRD nor the XAS data support the presence of pyromorphite or other crystalline Pb minerals in the O horizon (Fig. 5, 6). A pyromorphite structure has several oxygen atoms surrounding Pb at distances of 2.7 to 2.9 Å, which was not apparent in our bulk XAS (Fig. 6). We suggest, however, that organic and iron mineral surfaces limit Pb^{2+} activity in soil solutions, which prevents crystalline Pb phases such as pyromorphite from forming. For example, Lang and Kaupenjohann (2003) found that dissolved organic matter could significantly inhibit pyromorphite precipitation by lowering dissolved Pb activities. Alternatively, organic matter turnover may immobilize phosphate and thereby maintain a geochemical environment that is undersaturated with respect to pyromorphite.

Our combination of μ SXRF, μ SXRD, and XAS data support the conclusion that a significant fraction of Pb

is associated with amorphous Fe (Hydr)oxides in these organic-rich horizons. Pb levels are correlated with Fe concentrations in μ SXRF scans, and bulk XAS demonstrates that Pb is bound to the soil by inner-sphere adsorption. We find that theoretically fitting O and Fe atoms at distances of 2.3 and 4.0 Å, respectively, provide the closest match to our observed spectra. These results are consistent with Kaste et al. (2005), who found that much (>30%) of Pb retained in the O horizons of both coniferous and deciduous forests could be effectively removed by extractions that target reducible Fe phases. The remaining Pb in these samples appeared to be associated with organic matter surfaces.

Since we collected our soils from well-drained sites, the iron in the O horizon that we suggest is interacting with the Pb probably comes from the organic matter itself. Fresh litter samples analyzed from selected sites within our regional study had iron concentrations ranging from 250 to 550 mg kg⁻¹. Iron is highly insoluble under oxic conditions, and probably mineralizes as the organic matter decomposes. Bulk O horizon Fe contents are on the order of a few thousand milligrams per kilogram of Fe, which can be explained by a relative enrichment of Fe as carbon is lost from the horizon. Because secondary Fe phases can have a strong affinity for trace metals (Morin et al., 1999), it seems plausible that mineralized iron could sequester Pb. While many researchers have shown that organic matter can strongly bind to metals and limit mobility (Tipping, 1994; Sauve et al., 2003; Tipping et al., 2003) we suggest that the organic matter itself may not be directly responsible for this strong retention in soils studied here.

Our data indicate that Pb in O horizons of the northeastern USA differs considerably from the species that was originally deposited from fossil fuel combustion. Lead species emitted from automobile exhaust was dominated by particulate lead halides and double salts with ammonium halides (e.g., PbBrCl, PbBrCl · 2NH₄Cl). The halides from automobile exhaust break down rapidly in the atmosphere, possibly from reactions with atmospheric acids (Biggins and Harrison, 1979). Lead phases in the atmosphere, and presumably the compounds delivered to the surface of the earth (i.e., vegetation and soils) are suspected to be in the form of PbSO₄ (Olson and Skogerboe, 1975). Interestingly, Ostergren et al. (2000) noted that sulfate significantly enhanced the inner-sphere adsorption of Pb to goethite, and observed a shift of the adsorption mechanism of Pb from face-sharing to corner sharing with increasing sulfate. The Pb-Fe distances they reported for corner sharing Pb complexes on goethite (3.9 Å) also are similar to those found in this study. While we did not observe goethite in our samples, amorphous Fe phases appear to be ubiquitous in O horizons and could potentially form coatings on organic matter. Thus, the presence of sulfate in these systems may facilitate Pb adsorption to colloidal Fe phases within these organic-rich horizons. Given both the inherent stability of Pb²⁺ on iron oxides (Sauve et al., 2000) and the extremely low solubility of Fe oxides under oxic conditions, we suggest that Pb binding to Fe phases is the mechanism for the relatively long residence time

of gasoline-derived Pb reported for the forest floor (Johnson et al., 1995; Kaste et al., 2003; Yanai et al., 2004).

ACKNOWLEDGMENTS

We thank Rebecca Aledort, Phil Mone, and Heather Franco for help with soil collection, and Paul Zietz and Andrew Quicksall for laboratory assistance. This research was funded by the Northeastern States Research Cooperative, administered through the USDA Forest Service, and is a contribution of the Northeastern Ecosystems Research Cooperative. We also thank the Vermont Department of Forest, Parks, and Recreation for permission to do this work. Portions of this research were carried out at the National Synchrotron Light Source (operated by Brookhaven National Laboratory) and Stanford Synchrotron Radiation Laboratory (operated by Stanford University), national user facilities supported by the U.S. Department of Energy, Office of Basic Energy Sciences with additional funding from the National Institutes of Health. We thank Antonio Lanzirotti for help with the microprobe work on X26a at NSLS. The authors are also grateful to three anonymous reviewers who helped improved the manuscript.

REFERENCES

- Bacon, J.R., and I.J. Hewitt. 2005. Heavy metals deposited from the atmosphere on upland Scottish soils: Chemical and lead isotope studies of the association of metals with soil components. *Geochim. Cosmochim. Acta* 69:19–33.
- Bacon, J.R., I.J. Hewitt, and P. Cooper. 2005. Lead in grass in the Scottish uplands: Deposition or uptake? *J. Environ. Mon.* 7:785–791.
- Bargar, J.R., G.E. Brown, and G.A. Parks. 1997a. Surface complexation of Pb(II) at oxide-water interfaces.1. XAFS and bond-valence determination of mononuclear and polynuclear Pb(ii) sorption products on aluminum oxides. *Geochim. Cosmochim. Acta* 61:2617–2637.
- Bargar, J.R., G.E. Brown, and G.A. Parks. 1997b. Surface complexation of Pb(II) at oxide-water interfaces.2. XAFS and bond-valence determination of mononuclear Pb(II) sorption products and surface functional groups on iron oxides. *Geochim. Cosmochim. Acta* 61:2639–2652.
- Bargar, J.R., G.E. Brown, and G.A. Parks. 1998. Surface complexation of Pb(II) at oxide-water interfaces: III. XAFS determination of Pb(II) and Pb(II)-chloro adsorption complexes on goethite and alumina. *Geochim. Cosmochim. Acta* 62:193–207.
- Biggins, P.D.E., and R.M. Harrison. 1979. Atmospheric chemistry of automotive lead. *Environ. Sci. Technol.* 13:558–565.
- Bindler, R., M.L. Brannvall, I. Renberg, O. Emteryd, and H. Grip. 1999. Natural lead concentrations in pristine boreal forest soils and past pollution trends: A reference for critical load models. *Environ. Sci. Technol.* 33:3362–3367.
- Craig, B.W. 1991. Temporal and spatial changes of trace metals in the forest floor from the northeastern U.S. M.S., Dartmouth College, Hanover, NH.
- Dorr, H., and K.O. Munnich. 1989. Downward movement of soil organic-matter and its influence on trace-element transport (Pb-210, Cs-137) in the soil. *Radiocarbon* 31:655–663.
- Dorr, H., and K.O. Munnich. 1991. Lead and cesium transport in European forest soils. *Water Air Soil Pollut.* 57–8:809–818.
- Ekenler, M., and M.A. Tabatabai. 2002. Effects of trace elements on beta-glucosaminidase activity in soils. *Soil Biol. Biochem.* 34:1829–1832.
- Emmanuel, S., and Y. Erel. 2002. Implications from concentrations and isotopic data for pb partitioning processes in soils. *Geochim. Cosmochim. Acta* 66:2517–2527.
- Erel, Y., T. Axelrod, A. Veron, Y. Mahrer, P. Katsafados, and U. Dayan. 2002. Transboundary atmospheric lead pollution. *Environ. Sci. Technol.* 36:3230–3233.
- Evans, G.C., S.A. Norton, I.J. Fernandez, J.S. Kahl, and D. Hanson. 2005. Changes in concentrations of major elements and trace metals

- in northeastern US-Canadian sub-alpine forest floors. *Water Air Soil Pollut.* 163:245–267.
- Federer, C.A. 1982. Subjectivity in the separation of organic horizons of the forest floor. *Soil Sci. Soc. Am. J.* 46:1090–1093.
- Friedland, A.J., B.W. Craig, E.K. Miller, G.T. Herrick, T.G. Siccama, and A.H. Johnson. 1992. Decreasing lead levels in the forest floor of the northeastern USA. *Ambio* 21:400–403.
- Friedland, A.J., and A.H. Johnson. 1985. Lead distribution and fluxes in a high-elevation forest in northern Vermont. *J. Environ. Qual.* 14: 332–336.
- Friedland, A.J., A.H. Johnson, and T.G. Siccama. 1986. Zinc, Cu, Ni and Cd in the forest floor in the northeastern United States. *Water Air Soil Pollut.* 29:233–243.
- Friedland, A.J., and E.K. Miller. 1999. Major-element cycling in a high-elevation Adirondack forest: Patterns and changes, 1986–1996. *Ecol. Appl.* 9:958–967.
- Galloway, J.N., J.D. Thornton, S.A. Norton, H.L. Volchok, and R.A.N. McLean. 1982. Trace-metals in atmospheric deposition— a review and assessment. *Atmos. Environ.* 16:1677–1700.
- Ho, M.D., and G.J. Evans. 2000. Sequential extraction of metal contaminated soils with radiochemical assessment of readsorption effects. *Environ. Sci. Technol.* 34:1030–1035.
- Hong, S.M., J.P. Candelone, C.C. Patterson, and C.F. Boutron. 1994. Greenland ice evidence of hemispheric lead pollution 2-millennia ago by Greek and Roman civilizations. *Science* 265:1841–1843.
- Jackson, B.P., P.L. Williams, A. Lanzirrotti, and P.M. Bertsch. 2005. Evidence for biogenic pyromorphite formation by the nematode *Caenorhabditis elegans*. *Environ. Sci. Technol.* 39:5620–5625.
- Johnson, N.M., G.E. Likens, F.H. Bormann, and R.S. Pierce. 1968. Rate of chemical weathering of silicate minerals in New Hampshire. *Geochim. Cosmochim. Acta* 32:531–545.
- Johnson, C.E., and R.J. Petras. 1998. Distribution of zinc and lead fractions within a forest spodosol. *Soil Sci. Soc. Am. J.* 62:782–789.
- Johnson, C.E., R.J. Petras, R.H. April, and T.G. Siccama. 2004. Post-glacial lead dynamics in a forest soil. *Water Air Soil Pollut. Focus* 4:579–590.
- Johnson, C.E., T.G. Siccama, C.T. Driscoll, G.E. Likens, and R.E. Moeller. 1995. Changes in lead biogeochemistry in response to decreasing atmospheric inputs. *Ecol. Appl.* 5:813–822.
- Johnson, A.H., T.G. Siccama, and A.J. Friedland. 1982. Spatial and temporal patterns of lead accumulation in the forest floor in the northeastern United States. *J. Environ. Qual.* 11:577–580.
- Kaste, J.M., A.J. Friedland, and E.K. Miller. 2005. Potentially mobile lead fractions in montane organic-rich soil horizons. *Water Air Soil Pollut.* 167:139–154.
- Kaste, J.M., A.J. Friedland, and S. Sturup. 2003. Using stable and radioactive isotopes to trace atmospherically deposited Pb in montane forest soils. *Environ. Sci. Technol.* 37:3560–3567.
- Klaminder, J., R. Bindler, O. Emteryd, and I. Renberg. 2005. Uptake and recycling of lead by boreal forest plants: Quantitative estimates from a site in northern Sweden. *Geochim. Cosmochim. Acta* 69: 2485–2496.
- Koch, D.M., D.J. Jacob, and W.C. Graustein. 1996. Vertical transport of tropospheric aerosols as indicated by Be-7 and Pb-210 in a chemical tracer model. *J. Geophys. Res. Atmos.* 101:18651–18666.
- Lang, F., and M. Kaupenjohann. 2003. Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. *Eur. J. Soil Sci.* 54:139–147.
- Liang, C.N., and M.A. Tabatabai. 1977. Effects of trace-elements on nitrogen mineralization in soils. *Environ. Pollut.* 12:141–147.
- Lomander, A., and M.B. Johansson. 2001. Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (*Picea abies*) needle litter during decomposition. *Water Air Soil Pollut.* 132:165–184.
- Manceau, A., M.C. Boisset, G. Sarret, R.L. Hazemann, M. Mench, P. Cambier, and R. Prost. 1996. Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. *Environ. Sci. Technol.* 30:1540–1552.
- Marsh, A.S., and T.G. Siccama. 1997. Use of formerly plowed land in New England to monitor the vertical distribution of lead, zinc and copper in mineral soil. *Water Air Soil Pollut.* 95:75–85.
- Miller, E.K., and A.J. Friedland. 1994. Lead migration in forest soils— response to changing atmospheric inputs. *Environ. Sci. Technol.* 28: 662–669.
- Miller, L.M., R.J. Smith, M.E. Ruppel, C.H. Ott, and A. Lanzirrotti. 2005. Development and applications of an epifluorescence module for synchrotron x-ray fluorescence microprobe imaging. *Rev. Sci. Instrum.* 76 (6): Art. No. 066107 JUN 2005.
- Morin, G., J.D. Ostergren, F. Juillot, P. Ildefonso, G. Calas, and G.E. Brown. 1999. XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes. *Am. Mineral.* 84:420–434.
- Nirel, P.M.V., and F.M.M. Morel. 1990. Pitfalls of sequential extractions. *Water Res.* 24:1055–1056.
- Nriagu, J.O. 1974. Lead orthophosphates. 4. Formation and stability in environment. *Geochim. Cosmochim. Acta* 38:887–898.
- Nriagu, J.O. 1996. A history of global metal pollution. *Science* 272: 223–224.
- Olson, K.W., and R.K. Skogerboe. 1975. Identification of soil lead compounds from automotive sources. *Environ. Sci. Technol.* 9: 227–230.
- Ostergren, J.D., G.E. Brown, G.A. Parks, and P. Persson. 2000. Inorganic ligand effects on Pb(II) sorption to goethite (alpha-FeOOH)— II. Sulfate. *J. Colloid Interface Sci.* 225:483–493.
- Ruby, M.V., A. Davis, and A. Nicholson. 1994. In-situ formation of lead phosphates in soils as a method to immobilize lead. *Environ. Sci. Technol.* 28:646–654.
- Sauve, S., S. Manna, M.C. Turmel, A.G. Roy, and F. Courchesne. 2003. Solid-solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil. *Environ. Sci. Technol.* 37:5191–5196.
- Sauve, S., C.E. Martinez, M. McBride, and W. Hendershot. 2000. Adsorption of free lead (Pb²⁺) by pedogenic oxides, ferrihydrite, and leaf compost. *Soil Sci. Soc. Am. J.* 64:595–599.
- Semlali, R.M., F. van Oort, L. Denaix, and M. Loubet. 2001. Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. *Environ. Sci. Technol.* 35:4180–4188.
- Siccama, T.G. 1974. Vegetation, soil, and climate on green mountains of Vermont. *Ecol. Monogr.* 44:325–349.
- Smith, W.H., and T.G. Siccama. 1981. The Hubbard Brook ecosystem study— Biogeochemistry of lead in the northern hardwood forest. *J. Environ. Qual.* 10:323–332.
- Steinnes, E., and A.J. Friedland. 2005. Lead migration in podzolic soils from Scandinavia and the United States of America. *Can. J. Soil Sci.* 85:291–294.
- Steinnes, E., T.E. Sjøbakk, C. Donisa, and M.L. Brännvall. 2005. Quantification of pollutant lead in forest soils. *Soil Sci. Soc. Am. J.* 69:1399–1404.
- Templeton, A.S., T.P. Trainor, A.M. Spormann, M. Newville, S.R. Sutton, A. Dohnalkova, Y. Gorby, and G.E. Brown. 2003. Sorption versus biomineralization of Pb(II) within Burkholderia cepacia biofilms. *Environ. Sci. Technol.* 37:300–307.
- Teutsch, N., Y. Erel, L. Halicz, and A. Banin. 2001. Distribution of natural and anthropogenic lead in Mediterranean soils. *Geochim. Cosmochim. Acta* 65:2853–2864.
- Tipping, E. 1994. Wham— a chemical-equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site electrostatic model of ion-binding by humic substances. *Comput. Geosci.* 20:973–1023.
- Tipping, E., J. Rieuwerts, G. Pan, M.R. Ashmore, S. Lofts, M.T.R. Hill, M.E. Farago, and I. Thornton. 2003. The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environ. Pollut.* 125:213–225.
- Trivedi, P., J.A. Dyer, and D.L. Sparks. 2003. Lead sorption onto ferrihydrite. 1. A macroscopic and spectroscopic assessment. *Environ. Sci. Technol.* 37:908–914.
- Turner, R.S., A.H. Johnson, and D. Wang. 1985. Biogeochemistry of lead in McDonalds branch watershed, New-Jersey pine barrens. *J. Environ. Qual.* 14:305–314.
- Tyler, G. 1976. Heavy-metal pollution, phosphatase-activity, and mineralization of organic phosphorus in forest soils. *Soil Biol. Biochem.* 8:327–332.
- Tyler, G. 1989. Uptake, retention and toxicity of heavy-metals in lichens— A brief review. *Water Air Soil Pollut.* 47:321–333.
- Tyler, G. 1990. Bryophytes and heavy-metals— A literature-review. *Bot. J. Linn. Soc.* 104:231–253.
- Wang, E.X., and G. Benoit. 1997. Fate and transport of contaminant lead in spodosols: A simple box model analysis. *Water Air Soil Pollut.* 95:381–397.
- Wang, E.X., F.H. Bormann, and G. Benoit. 1995. Evidence of com-

- plete retention of atmospheric lead in the soils of northern hardwood forested ecosystems. *Environ. Sci. Technol.* 29:735–739.
- Watmough, S.A., and T.C. Hutchinson. 2004. The quantification and distribution of pollution Pb at a woodland in rural south central Ontario, Canada. *Environ. Pollut.* 128:419–428.
- Xia, K., W. Bleam, and P.A. Helmke. 1997. Studies of the nature of Cu^{2+} and Pb^{2+} binding sites in soil humic substances using x-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 61: 2211–2221.
- Yanai, R.D., D.G. Ray, and T.G. Siccama. 2004. Lead reduction and redistribution in the forest floor in new hampshire northern hardwoods. *J. Environ. Qual.* 33:141–148.