# POTENTIALLY MOBILE LEAD FRACTIONS IN MONTANE ORGANIC-RICH SOIL HORIZONS

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**Abstract.** Anthropogenic emissions during the 20th century resulted in global lead (Pb) contamination of soils. Recent studies have demonstrated that the organic horizons of temperate montane Spodosols in the northeastern United States retain Pb on timescales of 50 to 150 years. The precise mechanism(s) of this strong Pb partitioning to organic-rich soil material remain elusive, but a detailed understanding of Pb retention by organic layers and mineral topsoils is critical for predicting the fate of pollutants deposited on ecosystems. Here we use selective extractions to quantify potentially mobile pools of Pb in the surface horizons of relatively remote montane Spodosols from New Hampshire and Vermont. Using 10 consecutive rinses of water, we extracted a total of 1 to 5% of the carbon, and 4 to 12% of the Pb. Dialysis equilibration experiments demonstrate that this Pb is >5,000 molecular weight, and not truly dissolved as $Pb^{2+}$. When soil was extracted with a single rinse of 0.02 M HCl (pH 1.7), 5 to 11% of the Pb was mobilized. However, hydroxylamine hydrochloride in 0.02 M HCl (a reducing agent) extracted 30 to 40% of the Pb. Repeated rinses with sodium hydroxide and sodium pyrophosphate, which target organic matter but may extract other soil phases removed 16 to 75% and 60 to 100% of the Pb, respectively. We show that significant Fe, Pb, and Al can be released from soils under reducing conditions, and that this fraction can be underestimated if sodium pyrophosphate is used in a previous step for leaching the organic-metal phase, as is typically done in sequential extraction schemes. Our results indicate that inorganic phases play an important role in determining Pb mobility and bioavailability, even in surface soil horizons dominated by organic matter.

**Keywords:** decomposition, extractions, forest floor, lead, mobility, organic, soil

## 1. Introduction

Anthropogenic emissions have made Pb one of the most widely dispersed trace metals in the environment. Soils in the northeastern United States received total atmospheric burdens of 1 to 4 g Pb $m^{-2}$ in remote environments (Johnson *et al.*, 1995a; Miller and Friedland, 1994), and near urban areas anthropogenic Pb loads have been more than twice that (e.g., Pouyat and McDonnell, 1991). The forest canopy acts as the initial receptor for much of the atmospherically-delivered Pb, and dissolved Pb in rain/throughfall is also efficiently retained by the forest litter (Oi). Subsequent litterfall and decomposition leads to a Pb-enriched forest floor (i.e., the

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organic layer overlying the mineral soil). Numerous studies have documented forest floor Pb concentrations of 75 to 300 $\mu$g g$^{-1}$, which is typically one to two orders of magnitude higher than the parent material at these locations (Siccama *et al.*, 1980; Pouyat and McDonnell, 1991; Friedland *et al.*, 1992; Marsh and Siccama, 1997; Mellor and Bevan, 1999). Recent studies have shown that at least some fraction of the Pb has been moving down into the mineral soil beneath (Miller and Friedland, 1994; Johnson *et al.*, 1995a; Bindler *et al.*, 1999; Kaste *et al.*, 2003), and several have suggested that Pb is moving in association with soil organic matter (Tyler, 1981; Miller and Friedland, 1994; Dörr, 1995; Wang and Benoit, 1997). Lead can be toxic: laboratory evidence suggests that concentrations as low as 200 mg kg$^{-1}$ can disrupt organic matter decomposition and associated N and P mineralization processes necessary for the effective recycling of essential nutrients in ecosystems (Rühling and Tyler, 1973; Ekenler and Tabatabai, 2002). Hence, a detailed evaluation of Pb retention, mobility, and bioavailability in soils is desirable.

Selective chemical extractions are widely used to identify the mechanisms of metal partitioning to soils (Gibbs, 1973; Tessier *et al.*, 1979; Sposito *et al.*, 1982; Ryan *et al.*, 2002). Lead is generally not readily exchangeable, i.e., the amount of Pb removed from soils by weak acid or salt solutions is usually less that 5% (Johnson and Petras, 1998; Sposito *et al.*, 1982). This is probably due to the hydrolysis constant for Pb and its relatively high electronegativity, which allows it to form strong coordination complexes with oxygen on mineral surfaces and organic matter functional groups (Abd-Elfattah and Wada, 1981). The fraction of Pb assigned as “organically bound” is typically high in organic horizons. Emmanuel and Erel (2002) reported that approximately 25 to 50% of the anthropogenic Pb in surface soils from the Czech Republic was associated with organic matter, and the rest was attributed to “surface bound” Pb. Johnson and Petras (1998) reported that over 60% of the Pb was bound to organics in the forest floor at the Hubbard Brook Experimental Forest (HBEF). Ho and Evans (2000) determined that about 40% of the soil lead was released by oxidizing extractions, presumably bound to organics in contaminated soils near Toronto, Canada. Most of the remaining Pb in the latter two studies was partitioned in a “residual” phase, i.e., Pb released only by strong acid digestions.

Although organic-Pb complexes are often an important phase of Pb in soils, the techniques by which “organically-bound” Pb is assigned varies considerably for different studies, and may not be comparable. Two common but contrasting techniques for releasing metals involve either organic matter destruction with an oxidizing agent (acidified $H_2O_2$, pH 9 NaOCl) or the use of reagents to mobilize soil organic matter. The acidified $H_2O_2$ procedure has been criticized for destroying other soil phases such as clays and sulfides in addition to organic matter (Papp *et al.*, 1991; Ryan *et al.*, 2002). Reagents used to mobilize soil organic matter, either through complexation with a pyrophosphate solution or by de-protonation of functional groups with an alkaline solution are common techniques of isolating organically-bound metals from soils and sediments. It is unclear which organic fractions are mobilized with sodium hydroxide and sodium pyrophosphate solutions, and whether or not the results are comparable for Pb. Hall and Pelchat (1997) reported that 0.1 M NaOH treatment of an international reference lake sediment extracted significantly more C and Hg but less Zn than a similar strength $Na_4P_2O_7$ solution.

While traditional extractions for organically-bound metals typically rely on destruction or mobilization of the soil organic matter, the portion of “organically bound” Pb that can be mobilized by water is rarely quantified, and could be significant. Qualls *et al.* (1991) found that up to 40% of freshly fallen leaf litter was extractable in water. Since the forest canopy scavenges significant amounts of aerosols from the troposphere (Russell *et al.*, 1981) and the Oi layer scavenges metals from throughfall solutions, litter could be a source of mobile organic-Pb complexes. Tam *et al.* (1991) found that approximately 10% of the total Pb in a litter layer was removed by a single water extraction (passing through a 2.5-$\mu$ m filter). In another study, Qualls (2000) repeatedly rinsed a forest floor sample with de-ionized water and found that 2.4% of the total carbon pool was extracted by water. We take a similar approach in this study, with an interest in the Pb that is associated with water-extractable C.

The purpose of this study was to characterize and quantify the pool of water-mobilized carbon and associated Pb present in forest floor samples and A horizons from selected sites in Vermont and New Hampshire, USA. We also compare the results of two common techniques used to extract organically-bound metals from soils, and use other established extraction techniques to better understand how surface organic horizons retain Pb.

## 2. Methods

Organic surface horizons of soil were collected using a 15 × 15 cm wooden template (Friedland *et al.*, 1992) from Camels Hump in Vermont, U.S.A. (44°18′ N; 72°53′ W), and Mount Cardigan (43°39′ N; 71°56′ W) in New Hampshire, U.S.A. Soils are well-drained Spodosols developed on till dominated by granite, quartzite, and mostly non-calcareous metamorphic rocks. Vegetation at Mount Cardigan is dominated by beech (*Fagus grandifolia)*, sugar maple (*Acer saccharum)*, and white birch (*Betula papyrifera* var. *cordifolia)* at lower elevations, and hemlock (*Tsuga canadensis*) at higher elevations. At Camels Hump, vegetation in the deciduous zone at lower elevations is similar to the Cardigan deciduous zone, but at higher elevations the forest is dominated by yellow birch (*B. alleghaniensis*), red spruce (*Picea rubens)* and balsam fir (*Abies balsamea).* Forest floor thickness ranged from 6 to 15 cm, and organic matter percent (OM%, as loss on ignition) is given in Table I. Mineral soils beneath the forest floor at our sites contained 5 to 14% OM. After collection, samples were placed in zip-lock bags, and each sample was homogenized using a stainless steel knife on a plastic cutting board. Samples were

TABLE I

Sample descriptions and results for total Pb, C, and N analyses, and extracted (<0.45 $\mu$m) Pb and C from soil samples

| Location | Forest zone | Soil horizon | OM (%) | N (mg g$^{-1}$) | C (mg g$^{-1}$) | WEOC (mg g$^{-1}$) | WE-Pb ($\mu$g g$^{-1}$) | NaOH-Pb ($\mu$g g$^{-1}$) | $Na_4P_2O_7$-Pb ($\mu$g g$^{-1}$) | $NH_2OH{\cdot}HCl$-Pb[a] ($\mu$g g$^{-1}$) | "Total" Pb ($\mu$g g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cardigan | Deciduous | Oi + Oe + Oa | 35 | 12 | 234 | 11 | 3.15 ± 0.05 | 10.6 ± 1.5 | 17.6 ± 0.2 | 0.5 ± 0.1 | 29.0 ± 0.4 |
| Cardigan | Deciduous | A | 11 | 3 | 59 | 2.9 | 3.20 ± 0.07 | 14.4 ± 0.7 | 14.4 ± 0.7 | 3.4 ± 0.6 | 25.8 ± 0.4 |
| Cardigan | Coniferous | Oi + Oe + Oa | 87 | 19 | 527 | 9.9 | 3.48 ± 0.14 | 29.0 ± 0.6 | 56.8 ± 2.8 | n.d. | 76.4 ± 6.1 |
| Camels Hump | Deciduous | Oe | 87 | 29 | 487 | 17 | 6.04 ± 0.08 | 45.4 ± 2.3 | 106 ± 6 | n.d. | 125 ± 4.4 |
| Camels Hump | Deciduous | Oa | 58 | 19 | 325 | 4.2 | 2.91 ± 0.20 | 39.0 ± 1.1 | 51.9 ± 2.6 | 2.2 ± 0.3 | 76.6 ± 2.1 |
| Camels Hump | Coniferous | Oi + Oe + Oa | 87 | 27 | 488 | 22 | 9.58 ± 0.29 | 19.1 ± 0.1 | 83.6 ± 4.2 | n.d. | 115 ± 10 |
| Camels Hump | Coniferous | Oa/A | 42 | 14 | 236 | 10 | 10.7 ± 0.2 | 79.1 ± 0.1 | 105 ± 3 | 4.4 ± 0.5 | 106 ± 3.6 |

All values are per g dry soil/mass, means ± 1 S.E. given for 3 replications.

[a] Samples were extracted with $NH_2OH{\cdot}HCl$ only after the $Na_4P_2O_7$ extraction. NaOH-Pb and $Na_4P_2O_7$-Pb refer to Pb released by NaOH and $Na_4P_2O_7$ extraction (sum of 2 washes for each), respectively on fresh samples as described in the methods sections. WEOC and WE-Pb are the total water-extracted C pools and the presumably associated Pb (WE-Pb) released by 10 leaches. Since these soils are acidic, and developed on non-calcareous till, all carbon is assumed as organic.

refrigerated at 4 °C after collection and extracted within 2 weeks. All extractions were done on field moist samples.

### 2.1. QUANTIFYING THE POOL OF WATER-EXTRACTABLE ORGANIC CARBON AND Pb

Seven grams (ca. 3.5 oven-dried g) of field-moist soil were placed in 50 ml polypropylene centrifuge tubes with 45 g of deionized water. Extractions were done in triplicate. The tubes were shaken on a Burrell wrist-action shaker. One extract was sampled daily for five days to establish the time it takes for soil and dissolved organic carbon to reach equilibrium. For this experiment, 1.5 g of solution was sampled daily, and replaced with an equivalent mass of fresh water each time to keep the soil:solution constant and not significantly disturb the equilibration process. This experiment suggested that >94% of the water-extractable organic carbon and Pb are released in the first four days (Figure 1). This is somewhat longer than in a similar study by Qualls (2000), who found that 24 h was sufficient to bring the water-soil slurry into equilibrium for a forest floor sample collected from the eastern slope of the Sierra Nevada Mountains. All subsequent samples were equilibrated on the wrist-action shaker for four days before the extract solution was removed, as described below.

After shaking, samples were centrifuged for 15 min at 1400× gravity. Approximately 40 g of water was then removed carefully with a 10 ml pipette, to minimize removal of particulates from the sample. The extracted solution was then filtered through a 0.45-$\mu$m polypropylene syringe filter, which was first purged with de-ionized water to minimize sample contamination. Fresh de-ionized water was added to the soil sample in the centrifuge tube and this was repeated 10 times. Total Pb

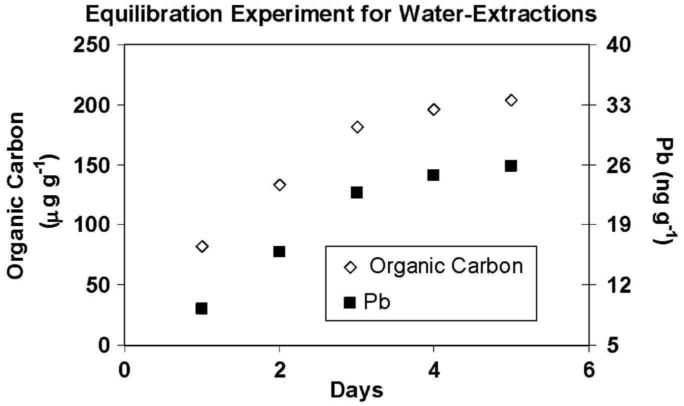

*Figure 1.* Concentrations of <0.45 $\mu$m organic carbon and Pb per g solution in water extracts of a deciduous forest floor (Oi+Oe+Oa) from Mount Cardigan sampled daily over a five day period.

and C extracted by this technique were calculated by using the asymptote of plots typical of Figure 2, which shows the cumulative Pb and C removed with progressive water extractions.

All filtered water extracts were analyzed for Pb on a Perkin-Elmer Graphite Furnace Atomic Absorption Spectrometer (GFAAS). Extract blanks were performed with each batch (blanks and samples received identical treatment), and were always below the detection limit (0.5 ng Pb per g solution). Filtered water extracts were analyzed for total organic carbon on an Apollo 9000 carbon analyzer. Since our sites are generally acidic (soil pH < 5.5), carbonate minerals are not typically present. Therefore we assumed total carbon was primarily organic.

## 2.2. DIALYSIS OF WATER-EXTRACTABLE MATTER

We used equilibration dialysis to determine the relative size range of Pb released by water-extracts. Filtered forest floor extracts from both deciduous and coniferous forest zones were placed in sealed 5000 MWCO Spectra/Por Cellulose Ester Dialysis Membranes sacks. The sealed membranes were immersed in de-ionized water inside acid-washed polypropylene bottles. Bottles were then sealed, and shaken for 48 h. Water from both inside and outside the membrane sacs was analyzed for Pb with GFAAS. A control solution of dissolved $Pb^{2+}$ was completely equilibrated (equal amounts inside and outside membrane) after 48 h.

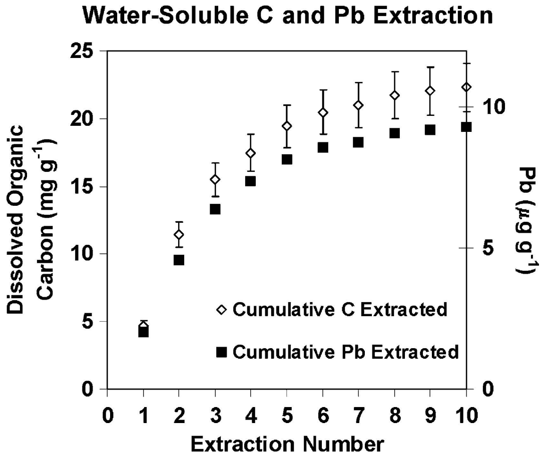

*Figure 2.* Cumulative organic carbon and Pb (<0.45 $\mu$m) extracted from a coniferous forest floor sample (Oi+Oe+Oa) from Camels Hump by water. Each extraction was allowed to equilibrate approximately four days. 1 SE is given for the C, 1 SE error bars for the Pb are approximately half that. Concentrations given per dry soil mass.

### 2.3. Sodium pyrophosphate and sodium hydroxide extractions

Three grams of field-moist soil (ca. 1.5 oven-dried grams) were equilibrated with 50 g 0.1 M NaOH for 16 h on a wrist-action shaker. After shaking, the samples were centrifuged (15 min at 1400× gravity) and filtered as described above for the water extracts. This was repeated with fresh solution once. Similar extractions were preformed with 0.1 M $Na_4P_2O_7$ (pH 10), but this was equilibrated for 2 h (Hall *et al.*, 1996a). All NaOH and $Na_4P_2O_7$ extractions were done in duplicate, and Pb analyzed via a Spectroflame ICP-OES.

### 2.4. Easily reducible metal-phase extractions

Pb bound to easily reducible minerals was extracted with 0.25 M $NH_2OH{\cdot}HCl$ (hydroxylamine hydrochloride) in 0.02 M HCl. Samples extracted with $NH_2OH{\cdot}HCl$ were initially extracted after repeat 0.1 M $Na_4P_2O_7$ extractions, to preclude significant metal contributions from organics (Hall *et al.*, 1996b). Another batch was done without the previous $Na_4P_2O_7$ treatment. Pre-treated soil residues were rinsed with deionized water once immediately before the $NH_2OH{\cdot}HCl$ extraction to remove entrained pyrophosphate solution. The $NH_2OH{\cdot}HCl$ was equilibrated with the soil sample for 3 h at 50 °C on a mechanical shaker. The slurry was centrifuged, and filtered through a 0.45 $\mu$m filter. The filtered solution was analyzed for Pb via GFAAS.

Since the hydroxylamine hydrochloride solution is acidic (pH 1.7), and thus could result in Pb exchange from surfaces other than the reducible minerals targeted by the reducing agent, a few samples were extracted with 0.02 M HCl at 50 °C for 3 h on a mechanical shaker. This was done to see if the addition of the reducing agent made a significant difference in the amount of metal extracted.

### 2.5. Metal, C, and N determination in extracts and soils

"Total Pb" was determined by ashing 2 g of soil material at 475 °C for 6 h. Ash was dissolved in boiling 1:1 $HNO_3$ for 20 min in a silica crucible. Diluted nitric acid solutions were then analyzed on the GFAAS for Pb. Recoveries of Pb for NIST SRM 1575 Pine Needles are within 5% of the certified values with this method (Friedland *et al.*, 1992). We acknowledge that this procedure does not release all the Pb from silicates present in the sample, but it should recover all anthropogenic Pb (Karamanos *et al.*, 1976) and any geogenic Pb present in organic matter or associated with secondary minerals. Carbon and nitrogen were determined on pulverized oven-dry samples via a Carlo Erba C-H-N Analyzer. Although we use two different instruments to quantify Pb in extracts, a subset of samples were analyzed on both ICP-OES and GFAAS, and results were comparable within 7%. ICP-OES was also used to determine Fe, Al, and Mn in selected extracts.

## 3. Results from Selective Extractions

Table I contains sample descriptions and the extracted and total N, C, and Pb data. All concentrations are given per oven-dry (105 °C) mass. Total Pb ranged from 26 to 125 $\mu$g g$^{-1}$. Water-extractable Pb was 3 to 11 $\mu$g g$^{-1}$, or 4 to 12% of the total Pb. The water-extractable pool of C was on the order of 1 to 5% of the total C. Pb was undetectable outside the dialysis membrane sacs, except for the control $Pb^{2+}$ solution, which demonstrated complete equilibrium. Only a few percent (2 to 7%) of the organic carbon passed through the 5000 MWCO membrane. Samples were analyzed before and after dialysis experiments to obtain a mass balance of Pb and verify that significant amounts of Pb were not binding to the dialysis membrane. Since the detection limit of the GFAAS was approximately 0.5 ng Pb per g solution, we calculate that a maximum of 5% of the Pb in the water extracts could have passed through the 5,000 MWCO membrane.

Pb released by repeat extractions of $Na_4P_2O_7$ solutions represented 60 to 100% of the total Pb. Repeat NaOH extractions recovered 17 to 70% of the total Pb. The second $Na_4P_2O_7$ and NaOH extractions contributed an additional 10 to 22% and 7 to 21% of the Pb, respectively, demonstrating that one extraction is not sufficient to quantify these pools. Pb, Fe, Mn, and Al released by the reducing agent $NH_2OH{\cdot}HCl$ was very low or not detected in forest floor samples if preceded by a sodium pyrophosphate extraction (Table I).

Table II gives results for 3 additional samples from Mt. Cardigan that were extracted by various treatments, and the extracts were analyzed for Al, Fe, Mn, and Pb. All extractions here were done in duplicate. The data for Pb are graphed in Figure 4. It is apparent that the sodium pyrophosphate extraction removed significant Al, Fe, Mn, and Pb, and if this extraction precedes the hydroxylamine hydrochloride treatment, it can result in an underestimate of the "reducible" metal fraction. This explains the relatively low values for Pb in the $NH_2OH{\cdot}HCl$ extractions given in Table I, which were done after repeat sodium pyrophosphate extractions. It appears that the $Na_4P_2O_7$ extractions are not completely specific to organic matter. While Bascomb and Thanigasalam (1978) demonstrated that 0.1 M $Na_4P_2O_7$ does not dissolve poorly-crystalline Fe, Jeanroy and Guillet (1981) found that $Na_4P_2O_7$ extracts of a $B_{Fe}$ horizon of a podsol contained large amounts of solid Fe phases. Shuman (1982) also noted that $Na_4P_2O_7$ extracted Fe oxides from soils, although it is unclear if this represented suspended fine Fe particles or dissolved species.

The hydroxylamine hydrochloride extractions, if done without pre-extractions did not dissolve significant organic matter (<1% of the total organic matter), but yielded significant amounts of all of the metals analyzed. Comparatively, the 0.02 MHCl extraction (Table II; Figure 4) extracted very little Pb (<15%), which gives strong evidence that the reducing conditions, not just the acidic conditions can result in significant (30% or greater) Pb mobilization from the horizons studied here. It is interesting to note that the Mn extracted by the HCl and the $NH_2OH{\cdot}HCl$

TABLE II

Al, Fe, Mn, and Pb ($\mu$g element per g dry soil, $<0.45\,\mu$m) extracted by single treatments of chemical extractions on (a) Maple–Beech forest floor sample (Oi+Oe+Oa) from Mt. Cardigan, (b) a Spruce–Fir forest floor sample (Oi+Oe+Oa) from Mt. Cardigan, and (c) an A horizon from the Spruce–Fir forest at Mt. Cardigan

| Extract | Al | Fe | Mn | Pb |
|---|---|---|---|---|
| | (a) | | | |
| NaOH | 524 ± 39 | 778 ± 69 | 79.9 ± 1.9 | 13.7 ± 1.3 |
| $Na_4P_2O_7$ | 497 ± 15 | 449 ± 36 | 256 ± 2 | 32.5 ± 2.4 |
| 0.02 M HCl | 109 ± 4 | 4.2 ± 0.8 | 230 ± 10 | 2.5 ± 1.1 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[a] | 29.6 ± 3.3 | 41.8 ± 5.1 | 5. 9 ± 2.0 | 0.37 ± 0.1 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[b] | 240 ± 25 | 168 ± 25 | 290 ± 49 | 14.2 ± 0.5 |
| "Total" | 1140 ± 10 | 1940 ± 60 | 377 ± 23 | 44.1 ± 1.8 |
| | (b) | | | |
| NaOH | 646 ± 33 | 1450 ± 70 | 25. 2 ± 2.9 | 17.5 ± 1.7 |
| $Na_4P_2O_7$ | 647 ± 32 | 1290 ± 90 | 85.0 ± 7.7 | 42.2 ± 2.0 |
| 0.02 M HCl | 193 ± 4 | 11.9 ± 4.1 | 81.9 ± 5.4 | 4.81 ± 0.4 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[a] | 101 ± 12 | 155 ± 23 | 2.7 ± 0.7 | 0.84 ± 0.3 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[b] | 376 ± 21 | 430 ± 66 | 103 ± 5 | 19.8 ± 4.0 |
| "Total" | 2200 ± 300 | 4680 ± 450 | 130 ± 7 | 67.5 ± 2.6 |
| | (c) | | | |
| NaOH | 745 ± 12 | 992 ± 28 | 2.70 ± 0.20 | 18.3 ± 1.1 |
| $Na_4P_2O_7$ | 775 ± 32 | 1531 ± 19 | 2.25 ± 0.75 | 30.1 ± 0.9 |
| 0.02 M HCl | 303 ± 2 | 6.0 ± 0.8 | 6.22 ± 0.63 | 6.22 ± 0.94 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[a] | 78 ± 11 | 51 ± 8 | 1.5 ± 0.3 | 1.8 ± 0.4 |
| 0.25 M $NH_2OH{\cdot}HCl$ in 0.02 M HCl[b] | 442 ± 22 | 389 ± 11 | 5. 21 ± 0.23 | 21.7 ± 1.6 |
| "Total" | 1770 ± 300 | 4520 ± 1260 | 26.9 ± 6.6 | 55.4 ± 1.7 |

[a] Hydroxylamine hydrochloride extraction done after a sodium pyrophosphate extraction.

[b] Hydroxylamine hydrochloride extraction done on fresh soil sample, with no pre-extraction. Means ± 1 SE are given for the extraction data. Percent organic matter (OM) is given for each sample in Figure 4.

were similar. This contrasts to the behavior of Fe, Al, and Pb, which showed significant increases from the addition of the reducing agent, and we therefore conclude that Mn phases don't play a dominant role in Pb geochemisty in organic-rich soils sampled here. While the amount of extracted Al was higher with the addition of the reducing agent to the HCl, Al compounds could not have undergone reduction; Al is probably adsorbed to the Fe phases. Using these extraction data, we hypothesize that Al and Pb adsorption to reducible Fe oxides is a significant process fixing these metals to the soils, despite relatively high organic matter contents.

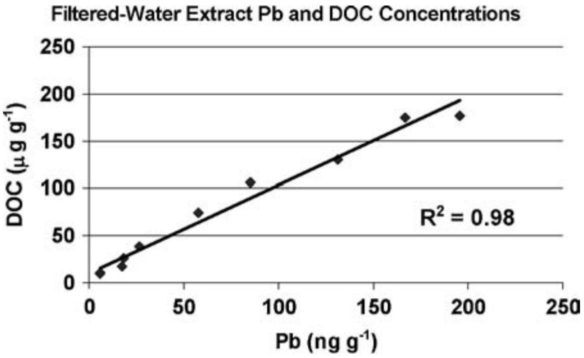

*Figure 3*. Correlation of extracted ($<0.45\ \mu$m) Pb and organic carbon in successive water extractions of a coniferous forest floor sample (Oi+Oe+Oa) from Camels Hump. Concentrations given per g solution.

## 4. Lead Mobility in Soils

Fresh litter, in the absence of significant pollution has Pb concentrations on the order of 1 $\mu$g g$^{-1}$ (Rea *et al.*, 2002), as Pb uptake by vegetation is low (Siccama and Smith, 1978). The forest floor samples collected were still high in Pb (up to 125 $\mu$g g$^{-1}$), even though most Pb deposition occurred at the study sites before 1980 (Johnson *et al.*, 1995a). The relative enrichment of Pb in the forest floor results from decomposition processes as $CO_2$ is evolved and as other compounds are removed from the soil (e.g., leaching). Lead is relatively insoluble in soils, and under most conditions it will be bound to a solid phase (Sauvé *et al.*, 1998, 2000). Laboratory experiments have suggested that binding to amorphous Fe hydroxides is the most efficient mechanism of maintaining low levels of $Pb^{2+}$ in soil solutions (Sauvé *et al.*, 2000). Extraction experiments in this study suggest that forest floor Pb is bound to organic matter and reducible oxides.

Mobilization of organic matter, either in dissolved or particulate form probably plays an important role controlling Pb mobility in the soil. Several researchers have suggested a strong link between the movement of organic matter and vertical migration of Pb (Dörr and Munnich, 1989; Miller and Friedland, 1994; Dörr, 1995; Wang and Benoit, 1997). The downward migration of organic acids from the forest floor is an important process in soil development, particularly for spodosols. McDowell and Wood (1984) demonstrated that organic carbon ($<0.45\mu$m) concentrations in forest floor soil solutions were an order-of-magnitude higher than in solutions in the underlying mineral soil. They concluded that coprecipitation of Fe and organics in the mineral soil maintained low DOC concentrations in drainage waters of the Hubbard Brook Experimental Forest (HBEF). We show that the pool of water-extractable organic carbon (WEOC) in the forest floor ranges from 60 to 530 mg g$^{-1}$, representing approximately 1 to 5% of the total organic carbon.

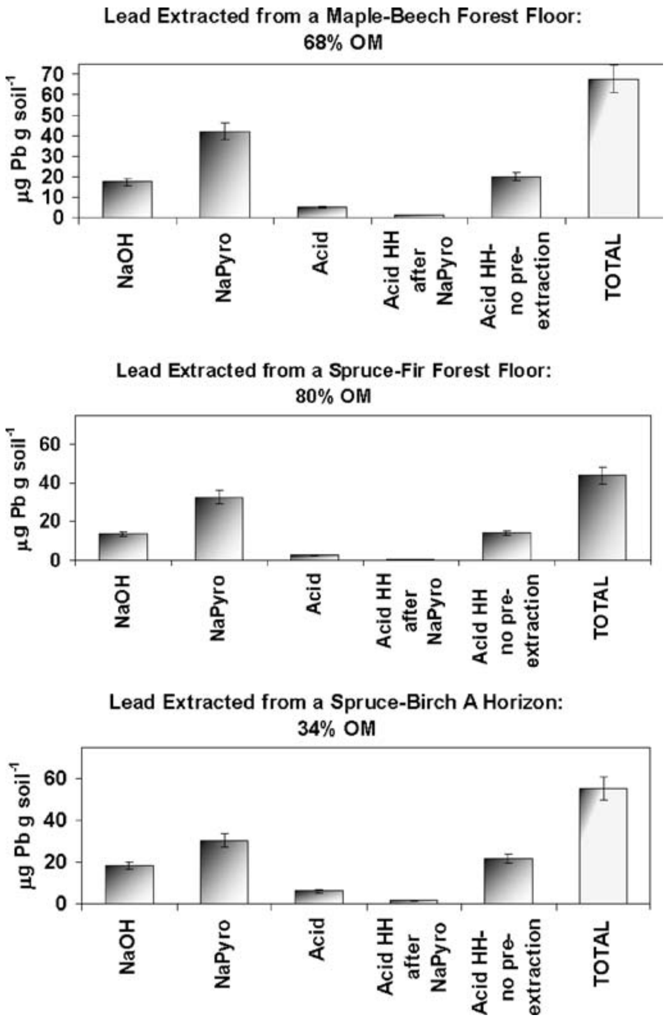

*Figure 4.* Bar graphs of the Pb data given in Table II. Percent organic matter (OM) given for each sample. 1 standard error is plotted. Concentrations given per dry soil mass.

Qualls (2000) used a similar extraction technique and reported that WEOC represented 2.4% of the organic C in a forest floor sample from the Sierra Nevada Mountains. Because water-extractable Pb and WEOC showed similar behavior in the equilibration experiment (Figure 1) and dialysis experiments, and were tightly correlated in the successive water extractions ($r^2 = 0.98$, Figure 3), it appears that the pool of water-extractable organic matter comprises a pool of potentially mobile Pb complexes. Sauvé *et al.* (1998) demonstrated that above pH 4, more than half of Pb present in soil solutions in equilibrium with leaf compost was complexed with OM. Organically complexed Pb extractable by water ranges from 3 to 11 $\mu$g Pb g$^{-1}$, comprising 5 to 15% of the total Pb. The water-extractable organic complexes are $>$5000 MWCO, which demonstrates the importance of Pb transport by colloids. Wang and Benoit (1996) analyzed soil solutions beneath the forest floor horizon at the Hubbard Brook Experimental Forest (HBEF), and determined that 50% of the Pb was within colloidal matter ($>$3000 MWCO). A subsequent box model analysis of Pb amounts in the forest floor at HBEF suggested that all of the Pb export from the forest floor to the mineral soil is associated with particles (Wang and Benoit, 1997).

The fact that the pool of water-extractable Pb represents a minor portion of the total Pb in the organic samples tested ($<$15%) is consistent with relatively long residence time of Pb in the forest floor (Yanai *et al.*, 2004; Kaste *et al.*, 2003). However, other pools may contribute to the transport of Pb. Two different extractants of organics and associated metals, NaOH and $Na_4P_2O_7$, suggest that a large fraction of the Pb in the forest floor is associated with organic matter that is not readily removed by water. However, as the extractions indicate, that fraction can be released either by changing the pH (NaOH) or by complexation ($Na_4P_2O_7$). The difference in Pb amounts released by NaOH and $Na_4P_2O_7$ may be caused by (1) redistribution or precipitation of Pb in the high pH ($>$13) NaOH extracts, (2) suspended Fe or Mn particles containing Pb peptized by the $Na_4P_2O_7$ reagent (Jeanroy and Guillet, 1981), or (3) difference in the type of organic matter released by the two reagents. Although the pH of the NaOH extract is higher than that of the $Na_4P_2O_7$ solution (pH 10), the amount of organic matter released by both solutions should prevent precipitation and readsorption of Pb onto other phases. If trace metals are adsorbed to colloidal phases as described above, $Na_4P_2O_7$ extractions could lead to an overestimate of “organically-bound” metals. This is a likely scenario for samples in this study, because $NH_2OH{\cdot}HCl$ extractions done without prior treatments of $Na_4P_2O_7$ demonstrate that Pb associated with reducible minerals is significant. Additionally, the difference in Pb amounts removed by the NaOH and $Na_4P_2O_7$ could be because these two reagents release different types of organic matter. Schnitzer and Schuppli (1989) demonstrated that $Na_4P_2O_7$ solutions are more effective than NaOH solutions at extracting organic matter that is complexed to soil particles. Because of its ability to complex with cations which link soil organic matter, substances which are typically insoluble under ambient soil conditions and even in alkaline solutions could be extracted by the $Na_4P_2O_7$.

The preferential retention of Pb by relatively insoluble and decomposed organics in the forest floor is consistent with recent soil surveys and isotopic studies (Yanai *et al.*, 2004; Kaste *et al.*, 2003) which demonstrate that the response time of forest floor Pb (non steady-state residence time; the time it takes for the forest floor Pb pool to decrease to $1/e$, or 37% of its initial amount) is on the order of 5 to 15 decades in spodosols of the northeastern United States. This is significantly longer than the turnover time of forest floor C (10 to 20 y) in similar forests (Johnson *et al.*, 1995b; Simmons *et al.*, 1996; Schlesinger, 1997). A Pb deposition and transport model (Miller and Friedland, 1994) showed significant redistribution (73%) of atmospheric Pb from the forest floor to the mineral soil at a low elevation deciduous site at Camels Hump Mountain, but none at a higher elevation coniferous zone

($>$900 m). They suggested that the increased Pb transit at the low elevation sites was a direct result of higher decomposition rates. More recently, Kaste *et al.* (2003) used budgets of atmospherically-deposited $^{210}$ Pb in the soils at Camels Hump Mountain to calculate forest floor Pb response times to be 60 years in the low elevation deciduous forest, and 150 years in the high elevation spruce fir forest. The results of forest floor repeated inventory studies for Pb transport have given mixed results. Yanai *et al.* (2004) demonstrated that Pb amounts in the forest floor (defined in study as O + A) did not change significantly between 1980 and 1995 in selected stands from the White Mountain National Forest in central New Hampshire. At the Hubbard Brook Experimental Forest, also in central New Hampshire, a 36% loss of forest floor Pb was detected from 1976 to 1997 (Yanai *et al.*, 2004; Johnson *et al.*, 1995a). However, forest floor samples collected in 1997–2000 from Watersheds 1 and 6 at the HBEF had between 0.68 to 0.82 g Pb m$^{-2}$, still a large fraction of the total calculated Pb deposition to the Hubbard Brook Forest of approximately 0.9 g Pb m$^{-2}$ (1926–1989; Johnson *et al.*, 1995a). Therefore, current Pb amounts in the forest floor are still a significant fraction of the total deposition ($>$60%), despite several cycles of C turnover. It seems likely that Pb is preferentially incorporated into recalcitrant, slowly decomposing organic matter in the forest floor, or it is possible that organic matter associated with substantial Pb might decompose at a slower rate (Rühling and Tyler, 1973; Ekenler and Tabatabai, 2002). We show evidence here that a significant portion of the Pb may also partition into reducible mineral phases in organic-rich soil horizons, a process that could potentially be linked to the mineralization of organic matter.

## 5. Conclusions

Lead is released from organic rich horizons of Vermont and New Hampshire Spodosols by extractions targeting organic matter and by the reducing agent $NH_2OH{\cdot}HCl$. Water-extractable C and Pb represented only small portions of total C (1 to 5%) and total Pb (4 to 12%), and these Pb phases are $>$5000 molecular weight. NaOH and $Na_4P_2O_7$ extractions removed most of the Pb, indicating that much of the Pb is bound to organics that are not in the immediately releasable pool. $Na_4P_2O_7$ extracted significantly more Pb than NaOH from all but one of the samples in this study, probably because it dissolves or disperses other soil phases. From our chemical extraction data, it appears that easily reducible oxides (possibly Fe minerals) comprise a significant portion of the potentially labile Pb pool, even in horizons dominated by organic matter.

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