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Using Stable and Radioactive Isotopes To Trace Atmospherically Deposited Pb in Montane Forest Soils

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Atmospheric deposition of lead (Pb) throughout the 1900s resulted in elevated amounts of this toxic metal even in remote forest soils of the northeastern United States. Soils can act as a net sink for metals and thus minimize groundwater and surface water contamination. Recent studies utilizing forest floor temporal data and models of total Pb in precipitation, surface soils, and streams have estimated the time scale of Pb release from soils. However, due to the limited availability and spatial variability of forest floor survey data, other methods for quantifying anthropogenic Pb movement are needed. This study uses the isotopic composition (^{206}Pb/^{207}Pb) of soil Pb and measurements of ^{210}Pb and ^{226}Ra to directly trace the transit of atmospherically deposited Pb in the soil profile. We also report on the recovery of an enriched ^{207}Pb dose applied in 1984 to the surface of a soil plot in the coniferous forest at Camels Hump in Vermont. The isotopic composition of soil Pb in low elevation deciduous forests suggests that approximately 65% of the original atmospheric Pb load has migrated from the forest floor to the upper 10 cm of the mineral soil. Higher elevation sites with coniferous vegetation have thicker forest floors, which have prevented significant amounts of Pb from entering the mineral soil. After 17 years, the soil organic horizon in the coniferous zone prevented any penetration of the applied Pb into the mineral soil. Using ^{210}Pb budgets in different soil compartments, we determine forest floor response times for atmospherically delivered Pb to be approximately 60 years in the low elevation deciduous forest zone and 150 years for the high elevation spruce-fir forest zone at Camels Hump. According to its distribution in the soil profile, we conclude that a dispersed release of anthropogenic Pb to groundwater and surface water is possible this century. Our results also offer independent confirmation of Pb deposition models previously generated for the region.

Introduction

A significant amount of anthropogenic lead (Pb) was deposited on soils and surface waters in the northeastern United States throughout most of the 20th century. The dominant source of this Pb was the combustion of gasoline containing lead additive in automobile engines (*1*). Lead was emitted to the atmosphere associated with aerosols and introduced to terrestrial ecosystems via rainfall and dry deposition. Total deposition of Pb to remote forests in the northeastern United States during the 20th century is estimated at 10−40 kg ha^{-1}, depending on elevation and forest canopy type (*2*, *3*). Concentrations of Pb in the forest floor (i.e., the organic or mor horizon overlying the mineral soil where loss on ignition >40%) sampled across the northeastern United States in the early 1980s ranged from 50 to 330 mg kg^{-1}, which is typically 1−2 orders of magnitude higher Pb concentration than what resides in the parent material at these locations (*4*, *5*).

Atmospheric deposition of Pb to watersheds in the United States declined rapidly after 1977 amendments to the Clean Air Act. Between 1975 and 1989, the annual volume-weighted mean concentration of Pb in bulk precipitation decreased from 23 μg L^{-1} to 0.85 μg L^{-1} at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (*3*). Although atmospheric loading of Pb on watersheds in the United States has reduced considerably, a large pool of potentially labile Pb remains in these soils. Due to the potential toxicity of Pb and the possibility of surface and/or groundwater contamination, an accurate understanding of the behavior and residence time of Pb in soils is desirable.

Earlier investigations documented the forest floor as a net sink of atmospherically deposited Pb and suggested that Pb leaching from the forest floor to the mineral soil and thus to groundwaters and streams would be negligible over the next few decades (*4*, *6*, *7*). These studies estimated Pb residence times in the forest floor to be on the order of hundreds of years due to the high affinity of Pb to organic complexes. However, more recent investigations have documented a decrease in Pb concentrations and amounts in the forest floor (*8*, *3*) and suggested a net loss of Pb from the forest floor, presumably to the mineral soil below or to streams. In 1997, Marsh and Siccama (*9*) reported that at five previously plowed forested sites in New England, approximately 35% of the anthropogenically derived Pb was in the forest floor, with the remaining in the upper mineral soil.

Miller and Friedland (*2*) developed a Pb deposition time series for the 1900s and calculated response times (the time it takes for a reservoir to decrease to the 1/e (ca. 37%) of its original amount) for Pb storage in the forest floor as 17 y in the northern hardwood forest zone and 77 y in the subalpine spruce-fir zone. They suggested that transport from the forest floor to the mineral soil was dominated by Pb bound to organic colloids and that the movement of Pb in soils could be tightly linked with carbon cycling. A box model analysis of data from soils at the HBEF (*10*) also suggested that Pb loss from the forest floor, presumably to the mineral soil, was significant and that particulate transport was the mechanism. This model suggested that the forest floor Pb content would reach equilibrium in ca. 100 years in the northern hardwood forest. The dynamics of Pb in the mineral soil and its residence time there is not well described and subject to some debate (*2*, *10*, *11*).

Stable Pb isotopes offer a powerful tool for separating anthropogenic Pb from natural Pb derived from mineral weathering (*12*). This is particularly useful for studying the

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mineral soil, where geogenic Pb often dominates. The three radiogenic stable Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) have a heterogeneous distribution in the earth's crust primarily because of the differences in the half-lives of their respective parents (^{238}U, $T_{1/2} = 4.7 \times 10^9$ yr; ^{235}U, $T_{1/2} = 0.7 \times 10^9$ yr; ^{232}Th, $T_{1/2} = 14 \times 10^9$ yr). The result is that the ore bodies from which anthropogenic Pb are typically derived are usually enriched in ^{207}Pb relative to ^{206}Pb and ^{208}Pb when compared with Pb found in granitic rocks. Graney et al. (*13*) analyzed a dated core from Lake Erie and found that the ^{206}Pb/^{207}Pb value in sediment deposited in the late 1700s was 1.224, but in 20th century sediment the ratio ranged from 1.223 to 1.197. This shift in Pb isotopic ratio represents the introduction of a significant amount of anthropogenic Pb into the environment. Bindler et al. (*14*) and Emmanuel and Erel (*15*) analyzed the isotopic composition of Pb in soil profiles in Sweden and the Czech Republic, respectively, and determined that mineral soils immediately below the organic horizon had a mixture of both anthropogenic and native (geogenic) Pb.

Radon-daughter ^{210}Pb also provides a tool for tracing atmospherically delivered Pb in soils (*16*). After ^{222}Rn ($T_{1/2} =$ 3.8 days) is produced from the decay of ^{226}Ra ($T_{1/2} = 1600$ years), some fraction of the ^{222}Rn escapes from rocks and soils to the atmosphere. It then decays relatively rapidly to ^{210}Pb ($T_{1/2} = 22.3$ years) which has a tropospheric residence time of a few weeks (*17*). Fallout ^{210}Pb is deposited onto forests via wet and dry deposition, similar to anthropogenic Pb deposition in forests, thus we use it as a tracer for non-native Pb in soils. ^{210}Pb is convenient to use for calculating the residence time of Pb in the forest floor because its atmospheric and soil fluxes can be assumed to be in steady-state at undisturbed sites. Atmospheric ^{210}Pb (^{210}Pb$_{ex}$ hereafter, ^{210}Pb in "excess" of that supported by ^{222}Rn in the soil) must be calculated by subtracting the amount of ^{210}Pb formed in soils by the in-situ decay of ^{222}Rn from the total ^{210}Pb.

In this study, stable Pb isotopes and radioactive ^{210}Pb are used to trace the transit and partitioning of atmospherically delivered pollutant Pb in forest soils. At one plot at Camels Hump in Vermont, U.S.A. we recover an enriched ^{207}Pb tracer that was applied on the forest floor in 1984. We also study the distribution of stable and radioactive Pb isotopes at unmanipulated soil profiles at Camels Hump to obtain direct evidence for atmospherically delivered Pb transit into and within the mineral soil. Our purpose was to characterize the distribution of atmospheric Pb in forest soils and assess the possibility of surface and groundwater contamination by the large pool of Pb which was deposited in the northeastern United States in the 1900s.

Methods

Camels Hump Study Site. Camels Hump is part of the Green Mountain Anticlinorium in Vermont, U.S.A. (44°18′ N, 72°53′ W; summit elevation = 1245 m). Camels Hump has a mixture of sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula alleghaniensis* Britt.) at lower elevations and grades to a red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* (L.) Mill) dominated forest above 800 m. Soils are typically Spodosols developed on Wisconsin-age till. The region receives approximately 1 m yr^{-1} precipitation. The entire mountain is part of the Vermont State Parks System, so the vast majority of the land is free of recent disturbance (*18*, *19*). We chose Camels Hump as our study site because it has been studied intensively for several decades, and it provides two distinct vegetation zones for comparison study (*2*, *18*−*22*).

Application of Enriched ^{207}Pb. A Pb dose was applied to the soil surface in a simulated acid rainfall. The solution had a pH of 3.8 and contained representative concentrations of the major cations and anions found in rainfall in the Northeast in the 1980s. The solution also contained 6.25 mg L^{-1} of Pb as PbCO$_3$ made with 91.6% ^{207}Pb (Oak Ridge National Laboratory #4647-0252). While this Pb concentration is 3 orders of magnitude greater than that found in ambient rainfall, it was necessary to put this much Pb in solution to ensure that we would detect the Pb isotopic enrichment signal in samples taken subsequently. The solution was placed into a portable backpack sprayer and 4 L of solution were sprayed onto the surface of each of two 1 × 1 m plots in July, 1984 at an elevation of 975 m in the coniferous forest zone of Camels Hump.

Field Collection. In Summer 2001, one of the manipulated plots ("manipulated plot" hereafter) was relocated on Camels Hump. First, the forest floor was quantitatively collected with a 15 × 15 cm template. Plastic gloves were used during the collection process. We used a stainless steel saw to section the forest floor into an Oi, Oe, and upper and lower Oa horizons. A trench was then dug around the plot, and a plastic trowel used to clean the profile face. We quantitatively sampled mineral soil at 4 cm depth resolution in triplicate by pressing acid-washed polypropylene centrifuge tubes into clean faces of the pit. Several control pits were excavated in a similar manner 5−10 m upslope of the manipulated plots, and samples were collected as described above. In addition, a pit at a lower elevation (620 m, Pit LE620 hereafter) in the deciduous forest zone was excavated and samples were collected as above. Additional forest floor samples for total Pb analysis and radionuclide analysis were collected in a manner similar to that described in Friedland et al. (*8*). Mineral soil was collected below some of these forest floor samples, also for radionuclide analysis, by using a 5 cm diameter plastic core tube.

Extractions. Samples were removed from the centrifuge tubes for extractions with acid-washed plastic spoons. The samples were not sieved to avoid contamination. We used two different extractions on the soil samples to quantify partitioning of Pb: (1) "labile Pb" was extracted by combusting 2 g soil in a silica crucible for 8 h at 500 degrees C. The ash was then dissolved in 20 g of 1 N nitric acid at 110° for 2 h. This extraction was designed to recover all of the anthropogenic Pb in the soil samples (*23*), but we acknowledge that it will certainly solubilize some geogenic Pb as well. As discussed later, stable Pb isotopes are used to assign anthropogenic Pb in the labile Pb extractions; (2) "Exchangeable" Pb was removed by shaking 2 g of field moist soil with 50 g of 0.25 N NH$_4$Cl buffered to pH 3.5 with 0.15 N HAc for 2 h. The slurry was then centrifuged, and the solution was passed through an acid-washed 0.45 μm syringe filter. All reagents used were Trace Metal Grade.

Lead amounts in organic soil extracts were determined via a SpectroFlame ICP-OES. Pb amounts in mineral soil extracts were determined via a Perkin-Elmer Graphite Furnace AAS due to a severe Al interference in the ICP emission spectrum at the Pb 220.353 line. Recovery of Pb from 2 standard reference materials (NIST SRM 1575 Pine Needles, NIST SRM 2710 Montana Soil) was 95−102% for the labile Pb digestion procedure determined on both instruments. Since all organic and mineral horizons were collected quantitatively, we present both concentrations of Pb (μg g^{-1}) and total amounts (kg ha^{-1}).

Measurement of ^{206}Pb/^{207}Pb Isotope Ratios by ICPMS. The extraction solutions were diluted to a total lead concentration of 1−5 μg/L, after which they were analyzed using a sector field ICPMS instrument (Element 1, Finnigan MAT, Bremen, Germany). For each sample the instrument scanned 1200 times across the ^{206}Pb and ^{207}Pb peaks in order to minimize noise. The analysis of one sample took 90 s. The ^{206}Pb/^{207}Pb ratio was calculated as the ratio of the integrated counts for the two lead isotopes after correction for mass discrimination (<0.1%) and detector dead time (approximately 5−10 ns). The mass discrimination correction was

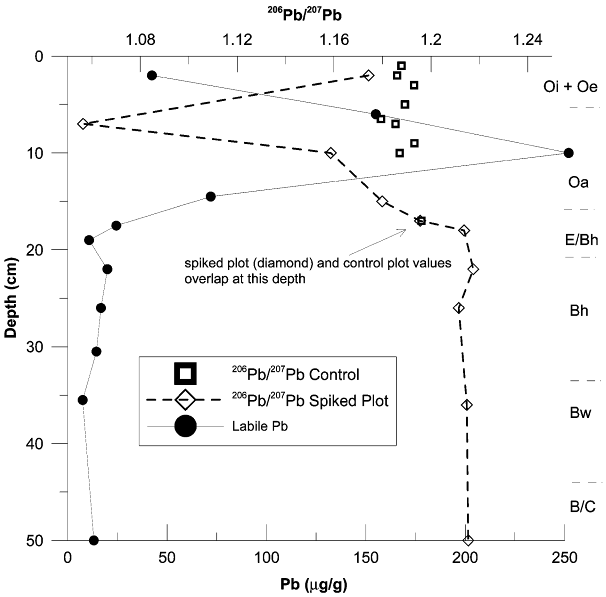

FIGURE 1. Concentrations and isotopic composition (mean of two vertical profiles) of labile soil Pb in the manipulated plot at Camels Hump. 1 SE is smaller than the symbol size for all plotted data. Field-distinguishable soil horizons are given on the right-hand side. Note that the isotopic composition of the upper mineral soil (E/Bh horizon) at the manipulated plot was identical to that of the control plot sample collected upslope.

performed using a certified reference material (NIST SRM 981 Natural Lead; isotopic). Correction factors were calculated with each batch of samples, and all data were background subtracted. The relative standard deviation (%RSD) on the final isotopic ratios were in the 0.05–0.20% RSD range for all samples.

Radionuclide Analysis. ^{210}Pb and other isotopes in the ^{238}U series were determined on a Canberra Broad Energy Intrinsic Ge Detector. Organic horizon samples were ground-up in a stainless steel Wiley Mill, and approximately 100 oven-dried grams were packed into a 235 mL Rubbermaid Container for gamma-counting. For mineral soil, 15 g of sieved (<2 mm) soil was ground and packed into a small Petri dish for counting. Extreme care was taken to correct for the self-adsorption of the low energy ^{210}Pb photon in samples. Efficiency calibration was thus done by spiking representative soil samples (some organic, some mineral) with 1 g of a certified U ore (CRM BL-5) which was guaranteed to have the ^{238}U chain in secular equilibrium. Efficiency of the detector could then be directly determined at each energy of interest for our sample composition, density, and geometry (*24*). Samples were counted at least 50 ks to obtain sufficient counting statistics.

^{210}Pb was determined by its photopeak at 46.6 kev, and its grandparent ^{226}Ra was determined at 186 kev. The contribution of ^{235}U at 186 kev was removed by measuring ^{234}Th, assuming secular equilibrium between ^{238}U and ^{234}Th, and using the $^{235}U/^{238}U$ activity ratio of 0.04605 (*25*). Peak area determinations were calculated by Genie 2K software. Since all organic and mineral horizons were collected quantitatively, we present both concentrations of radionuclides (Bq kg^{-1}) and total amounts (Bq m^{-2}).

Results and Discussion

Lead Isotope Ratios and Labile Pb in Soils. Figure 1 and Table 1 give the Pb isotopic and concentration data for the manipulated plot. Approximately 7 cm of forest litter accumulated since the application in 1984, which was determined from measurements above plastic flagging that had been placed on the forest floor in 1984. The buried flagging does not necessarily indicate an increase in forest floor thickness over the past 17 years, because it did not remain perfectly level with the surface, as it was pushed into the profile. The forest floor was 17 cm thick, and depth to parent material (till) was 51 cm from the surface. Labile Pb extracted from mineral soil collected directly below the forest floor at the manipulated plot has the identical $^{206}Pb/^{207}Pb$ composition as that of similar samples from control plots (Figure 1). To determine the amount of enriched ^{207}Pb application recovered from each sample, we used the following mixing equation (*26*)

TABLE 1. Soil Physical Properties, Pb Amounts, Pb Composition, Recovered Pb Application at the Manipulated Plot[a]

sample depth (cm)	DI pH	b.d. (g cm^{-3})	$^{206}Pb/^{207}Pb$	acid-extractable Pb (μg g^{-1})	recovered ^{207}Pb application (mg m^{-2})
0–4	4.1	0.07	1.174 ± 0.006	42.4 ± 7.2	0.31
4–8	3.5	0.13	1.057 ± 0.01	155 ± 10	22.9
8–12	3.4	0.15	1.159 ± 0.003	252 ± 1.0	8.57
12–17	4.4	0.21	1.180 ± 0.001	72.0 ± 19.0	1.04
17–18	4.1	0.53	1.197 ± 0.006	24.5 ± 4.3	0
18–20	4.4	0.64	1.215 ± 0.003	10.8 ± 3.0	0
20–24		0.67	1.218 ± 0.0005	20.0 ± 8.5	0
24–28		0.69	1.215 ± 0.001	16.8 ± 1.7	0
28–33	5.5	0.72	1.215 ± 0.001	14.5 ± 0.41	0
33–38		0.70	1.215 ± 0.0003	7.6 ± 0.1	0
sum					32.8 ± 4.5

[a] Mean of two profiles and 1 sigma given. Soil horizons with plotted data are given in Figure 1. The recovery of the ^{207}Pb application was calculated using eq 1, with 1.187 as the background Pb composition.

$$\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_{\mathrm{sample}} = \frac{\mathrm{Pb_{app}Ab_{app}}^{206}W_{\mathrm{bck}} + \mathrm{Pb_{bck}Ab_{bck}}^{206}W_{\mathrm{app}}}{\mathrm{Pb_{app}Ab_{app}}^{207}W_{\mathrm{bck}} + \mathrm{Pb_{bck}Ab_{bck}}^{207}W_{\mathrm{app}}} \quad (1)$$

where Pb_{app} and Pb_{bck} are the Pb application and background concentrations of Pb in the sample, respectively. W_{app} and W_{bck} are the atomic weights of Pb in the application and background, respectively. Ab_{app}^{206} and Ab_{bck}^{206} are the isotopic abundance of ^{206}Pb in the application and background, respectively, and similar terms exist for the abundances of ^{207}Pb in the application and background. The background isotopic signature of the forest floor does not change systematically with depth and is in a fairly tight range for all control plots ($^{206}Pb/^{207}Pb$ mean ± 1 SE = 1.187 ± 0.002; n = 12) (Figure 1). This was not expected, because the isotopic composition of atmospheric Pb has varied over the past century (*13*). However, it is likely that physical and chemical mixing in the soil has homogenized the Pb composition over the past several decades. Since "labile Pb" was determined by the ashing/nitric leach procedure, we can solve eq 1 for the concentration of applied Pb (Pb_{app}) in each sample.

The 17 cm thick forest floor contained 33 mg m^{-2} of the Pb application. Greater than 94% of the recovered ^{207}Pb enrichment was in the upper Oa horizon (4–12 cm). It is apparent from the distribution of Pb isotopes at the manipulated plot (Figure 1, Table 1) that no significant Pb penetrated to the mineral soil in the 17 years since it was applied. Although only 25 mg of Pb application was applied to 1 m^2, we only sampled a portion of that plot, and spatial heterogeneity of the application can probably explain the excess application that we "recovered".

Since the concentration of Pb in the forest floor ranges from 40 to 250 μg Pb g^{-1}, and vegetation typically has 1–2 μg Pb g^{-1}, we can assume that forest floor Pb is anthropogenic in origin. This is further supported by the very small variation of the isotopic composition of forest floor Pb. With that

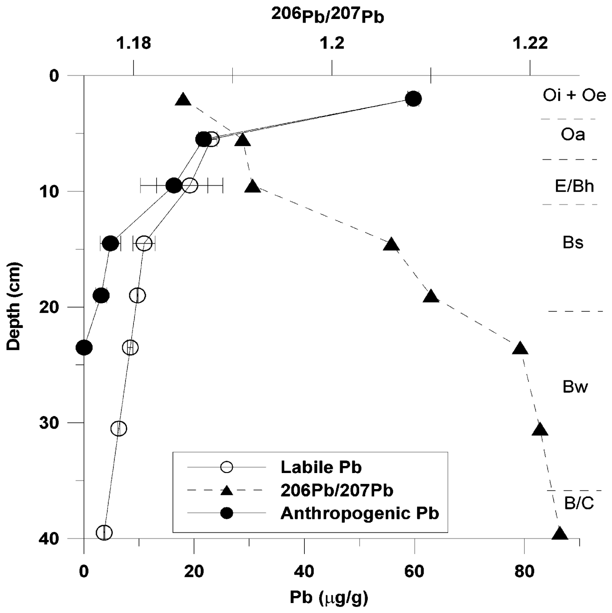

FIGURE 2. Concentrations and isotopic composition (mean of two vertical profiles) of labile soil Pb in Pit LE620. 1 SE is approximately the symbol size for the isotopic data, but 1 SE bars are given for the concentration data. Field-distinguishable soil horizons are given on the right-hand side. The isotopic composition of native Pb is taken to be that of the deepest three samples.

assumption, the forest floor at the manipulated plot had 32 kg Pb ha^{-2} anthropogenic Pb in the forest floor. Beneath the upper 5 cm of the mineral soil, the $^{206}Pb/^{207}Pb$ remains relatively constant at 1.215 ± 0.001 (mean ± 1 SE), which we take to be the isotopic composition of geogenic Pb at this site. Using the isotopic composition and amounts of labile Pb, a modification of eq 1, and soil masses collected from the quantitative horizon collection, we determined that the upper mineral soil contains only 2.0 kg anthropogenic Pb ha^{-1}, which makes 34 kg total anthropogenic Pb ha^{-1} at this high elevation site. This model assumes however, as our data suggest, that the isotopic composition of anthropogenic Pb has been homogenized in the forest floor, and the composition of atmospheric Pb entering the mineral soil has a $^{206}Pb/^{207}Pb = 1.187$.

"Exchangeable" Pb extracted from the organic horizons was 3−7% of the labile Pb extracted. The amount of exchangeable ^{207}Pb application, determined from the isotopic composition and amounts of Pb recovered by the NH_4Cl solutions, was 4.2% of the total application recovered. Therefore, the enriched ^{207}Pb application had the same fraction of exchangeable Pb as the total Pb had. In the mineral soil, 0−2% of the labile Pb was exchangeable.

Figure 2 and Table 2 give the Pb isotopic and concentration data for Pit LE620 in the deciduous forest zone. The forest floor at this site was 7 cm thick, and depth to parent material was 40 cm from the surface. The $^{206}Pb/^{207}Pb$ of labile Pb in mineral soil systematically decreases with depth, and the deepest samples had $^{206}Pb/^{207}Pb = 1.221 \pm 0.002$, which we take to be the isotopic composition of Pb weathered from minerals at this site. Using a modified eq 1, and an assumed anthropogenic Pb composition $^{206}Pb/^{207}Pb = 1.187$, the forest floor at pit LE620 contains 4.7 kg of anthropogenic Pb ha^{-2}, while the mineral soil had 8.7 kg anthropogenic Pb ha^{-1}. It should be noted, that soils in New England can have a large fraction of stones (grain diameter > 2 mm), in which case our Pb inventories would be overestimates. Quantitative pit data (Friedland, unpublished) suggests that this overestimate would be on the order of 15%.

Ecosystem Inventories of Atmospheric Pb. Atmospheric Pb is delivered to ecosystems via wet and dry deposition, so the canopy will intercept a fraction of the incoming Pb, and the forest floor will intercept the remainder. Over time, litterfall will deliver Pb originally retained by the canopy to the forest floor. Leaves and branches have ^{210}Pb activities near that of surface soils. ^{210}Pb in deciduous leaves and branches were measured at 99 Bq kg^{-1}, while coniferous leaves and branches were 248 Bq kg^{-1}. However, due to decreases in Pb emissions, total Pb in foliage sampled recently is generally <1 mg kg^{-1} (*27*). Coniferous leaves and branches have higher ^{210}Pb activities by over a factor of 2, which can be attributed to (1) higher leaf area index, thus better scavenging capacities for aerosols, (2) cloud impaction at higher elevations generally occupied by coniferous species, and (3) increased precipitation at higher elevations (*28*).

Our total inventories of anthropogenic Pb in soils are generally consistent with that predicted by Pb deposition models developed for the region. Miller and Friedland (*2*) predicted a total anthropogenic Pb deposition of 22 kg ha^{-1} in the northern hardwood forest zone and 35 kg ha^{-1} in the spruce-fir zone at Camels Hump. Johnson et al. (*3*) calculated Pb deposition at approximately 9 kg ha^{-1} from 1926 to 1989 at the HBEF. We recovered 13 kg ha^{-1} and 34 kg ha^{-1} anthropogenic Pb at our northern hardwood forest zone and spruce-fir forest zone pits, respectively. Considering the spatial variability of Pb deposition in forests (*22*), our pit inventories are in broad agreement with predicted Pb loading.

The distribution of fallout ^{210}Pb and its grandparent ^{226}Ra in profiles at the manipulated plot and at LE620 are given in Figures 3 and 4, respectively. In Table 3, inventories of $^{210}Pb_{ex}$ (^{210}Pb in excess of that supported by the in-situ decay of ^{222}Rn) are given for several forest floor samples and mineral soil cores collected from the deciduous and coniferous forest zones. We adopt the method of Wallbrink and Murray (*29*) to estimate the fraction of ^{210}Pb which is supported by soil ^{222}Rn to determine excess or atmospheric ^{210}Pb. This method uses the deficiency of ^{210}Pb to ^{226}Ra measured at depth to estimate the fraction of ^{222}Rn which escapes the soil.

Forest Floor Response Times. The response time of the forest floor Pb, t_{resp}, is of great interest because the forest floor was the initial receptor for the bulk of the atmospheric Pb deposited on ecosystems. Miller and Friedland (*2*) developed a depositional model of Pb to ecosystems and coupled this with forest floor Pb data from Camels Hump obtained in 1966 and again in 1980. A disadvantage of this technique is that it depended on just three data points to fit in the model equations to solve for the appropriate k (k = fraction of Pb lost from the forest floor per year, where $t_{resp} = 1/k$). Table 4 summarizes forest floor survey data collected at Camels Hump and the HBEF over the past 2 decades, and it is clear that the measured k can vary dramatically for samplings at the same watershed. Johnson et al. (*3*) calculated k for Watershed 6 at the HBEF using soil solution Pb fluxes for the 1985−1987 time period. They obtained a k of 0.0075 y^{-1}, and noted that this single k value did not accurately reflect the changing Pb content of the forest floor observed between 1977 and 1987. They suggested that differences in the rate of Pb loss for different time periods may be due to a fundamental change in the biogeochemistry of Pb.

There are a few possible explanations for the wide range in apparent k values within a watershed. If, as many researchers suggest, Pb mobility is tightly linked to carbon, then changes in decomposition could result in changes in observed Pb mobility. Also, the "changes" in k could possibly

TABLE 2. Data Summary for Pit LE620[b]

sample depth (cm)	DI pH	b.d. (g cm^{-3})	^{206}Pb/^{207}Pb	acid-extractable Pb (μg g^{-1})	acid-extractable Pb (g m^{-2})	*f*	anthropogenic Pb (kg ha^{-2})
0–4[a]	4.2	0.12	1.185	59.8	0.29	1.0	2.9
4–7[a]	3.4	0.27	1.191	23.1	0.19	0.94	1.8
7–12	4.3	0.72	1.192 ± 0.007	19.2 ± 6.1	0.69	0.85	5.9
12–17	4.0	0.76	1.206 ± 0.004	10.9 ± 2.2	0.41	0.44	1.8
17–21		0.79	1.210 ± 0.002	9.71 ± 0.04	0.31	0.32	1.0
21–26	4.3	0.93	1.219 ± 0.0006	8.35 ± 0.54	0.39	0	0
26–35	4.8	0.88	1.221 ± 0.001	6.31 ±0.18	0.50	0	0
36–43		0.94	1.223 ± 0.0003	3.66 ± 0.01	0.24	0	0
sum					3.11		13.4 ± 2.5

[a] Large sample homogenized, no replications. [b] Mean of two profiles ± 1 sigma. Soil horizons with plotted data are given in Figure 2. *f* is the fraction of anthropogenic Pb calculated (eq 1) with 1.187 as the anthropogenic ^{206}Pb/^{207}Pb end member, and the mean ^{206}Pb/^{207}Pb of the three deepest samples (not distinguishable at 2 sigma) as the geogenic end member.

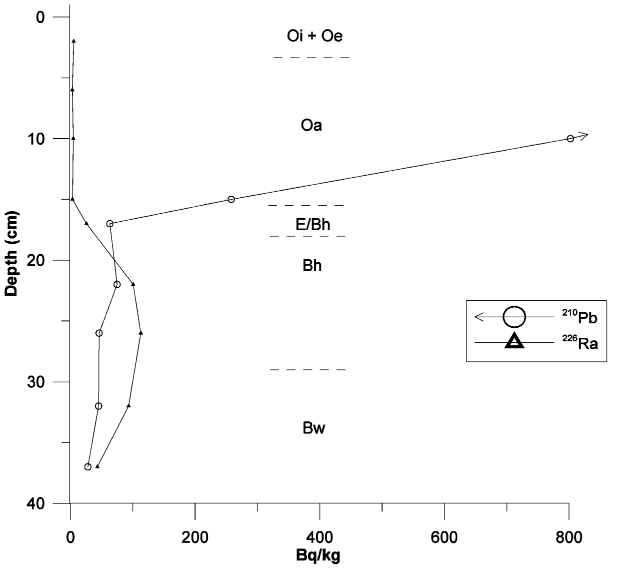

FIGURE 3. Radionuclide activities in the manipulated plot at Camels Hump. ^{210}Pb activities above 10 cm plot around 1000 Bq kg^{-1}, with ^{226}Ra negligible. Below the Bh/E horizon, ^{210}Pb is well below the ^{226} Ra value, so atmospheric ^{210}Pb is likely negligible. Counting errors are on the order of 5% and generally smaller than the plot symbol. Field-distinguishable soil horizons are given.

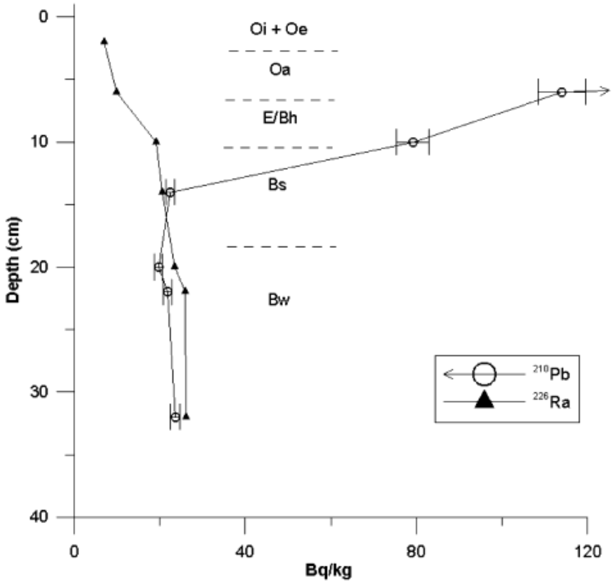

FIGURE 4. Radionuclide activities at Pit LE620. ^{210}Pb activities above 10 cm plot around 1000 Bq kg^{-1}, with ^{226}Ra negligible. Below the Bs horizon, ^{210}Pb is well below the ^{226}Ra value, so atmospheric ^{210}Pb is likely negligible. Counting errors are on the order of 5% (given for ^{210}Pb) and generally 2× the size of the plot symbol. Field-distinguishable soil horizons are given.

be explained by the data on which the rate constant calculations rely on. Quantitative forest floor data must be used with great care because (1) separation of the forest floor from the underlying mineral soil can be subjective (*30*), and (2) spatial heterogeneity of Pb deposition within even small areas can be large. For example, Craig (*22*) repeatedly sampled forest floor during 1 growing season and found that the range of Pb amount in the forest floor varied by a factor of at least 5 ($n = 35$) in a 1 ha area. At Watershed 6 in the HBEF, a sampling of the forest floor in 1992 revealed 10.2 kg Pb ha^{-1} compared to 7.5 kg Pb ha^{-1} found in 1987 (Table 2). It is unlikely that enough Pb deposition occurred during that time interval to increase the Pb amount in the forest floor by 25%. Watershed 5 in the HBEF was sampled twice in the summer of 1982. Pb amounts in the forest floor were 7.33 ± 0.44 kg ha^{-1} in a July collection and 8.54 ± 0.58 kg ha^{-1} in a separate survey sampled in August. These observations and others have led to conclusions by many that forest floor data can be highly variable. Therefore, the use of such data in models can be problematic.

Atmospheric ^{210}Pb inventories in the forest floor and the underlying mineral soil can be used to calculate forest floor response times, and they are not dependent on time series forest floor data. ^{210}Pb is constantly being deposited on ecosystems from the decay of atmospheric ^{222}Rn, and this delivery can be assumed relatively constant on a decadal time scale. Due to the half-life of ^{210}Pb, soil compartment inventories reflect an average of processes over the past century. Historic records suggest that some sites above 600 m at Camels Hump have been selectively cut for sugaring operations over the last century, but never cleared for pasture (*18*, *19*). Since our study plots have not been significantly disturbed over the past century, and our measured ^{210}Pb$_{ex}$ inventories are within or above the range suggested by deposition measurements and models for the region (*31*), we feel that a steady-state assumption is justified. When atmospheric ^{210}Pb is in steady-state in soils, a simple mass balance for ^{210}Pb$_{ex}$ in the forest floor is

$$\frac{\mathrm{d}A}{\mathrm{d}t} = F_{\mathrm{in}} - \lambda A - F_{\mathrm{out}} \tag{2}$$

where A is the activity of ^{210}Pb$_{ex}$ in the forest floor (Bq m^{-2}), λ is the decay constant of ^{210}Pb (0.031 y^{-1}), F_{in} is the annual input flux in of ^{210}Pb, and F_{out} is the annual ^{210}Pb flux out of the forest floor, due to leaching into the underlying mineral soil. F_{in} can be solved for by using the total ^{210}Pb$_{ex}$ inventory (I_t) observed at one site (forest floor + mineral soil) and

TABLE 3. $^{210}Pb_{ex}$ Inventories, the Calculated Annual Flux To Support the Total Inventories, and Calculated Forest Floor Response Times for Atmospherically Deposited Pb Assuming a Steady-State Soil-Atmosphere-$^{210}Pb_{ex}$ System[a]

	n	atmospheric ^{210}Pb inventory (Bq m^{-2})	F_{in} calculated atmospheric flux (Bq m^{-2} y^{-1})	F_{out} flux to mineral soil (Bq m^{-2} y^{-1})	response time (y)
deciduous zone					
forest floor	5	4510 ± 550			61 ± 12
mineral soil	3	2000 ± 300			
total		6510	214	74	
coniferous zone					
forest floor	5	14600 ± 2700			152 ± 24
mineral soils	3	2130 ± 280			
total		16730	550	96	

[a] Means ± 1 SE given.

TABLE 4. Pb Amounts (kg ha^{-1}) in the Forest Floor Sampled during Different Years, with 1 SE Given

year	HBEF[a] watersheds 5[c] and 6	HBEF[a] watershed 1	camels hump[b] <750 m	camels hump[b] >900 m
1980			8.44 ± 0.86	19.98 ± 1.17
1982	7.33 ± 0.40,[c] 8.54 ± 0.58,[c] 8.65 ± 0.60			
1987	7.50 ± 0.69			
1990			5.89 ± 1.07	19.38 ± 1.16
1992	10.20 ± 0.72			
1996		9.17 ± 0.59		
1997	6.83 ± 0.60			
1998		8.16 ± 0.70		
2000		8.07 ± 0.51		
2001			6.31 ± 0.54	17.5 ± 2.1
range in *k*	−0.13 to 0.44	−0.03 to −0.006	−0.033 to 0.006	−0.003 to −0.009

[a] Data obtained from the Hubbard Brook Ecosystem Study. [b] Data for 1980 and 1990 obtained from Friedland et al. 1992, and 2001 data from this work. [c] Watershed 5 was sampled twice during 1982. *k* ranges are given for each watershed (watershed 6 only in the first column), calculated by pairing different years and assuming no significant intervening Pb input.

calculating the annual flux needed to support that inventory, similar to Hess (*32*)

$$I_t = F_{in}(t_0)e^{-\lambda(t_0)} + F_{in}(t_1)e^{-\lambda(t_0-t_1)} + F_{in}(t_2)e^{-\lambda(t_0-t_2)} + ... \quad (3)$$

where t_0 is the present time and t_1, t_2, etc. are years of each input. We calculate an average F_{in} for a steady-state system achieved after 130 years (Table 3).

Since ^{210}Pb is at steady-state, and concentrations in the forest floor should remain relatively constant, $dA/dt = 0$, hence we can solve for F_{out}:

$$F_{out} = F_{in} - \lambda A \quad (4)$$

F_{out} can be used in the simple steady-state model to determine the residence time of ^{210}Pb in the forest floor. Residence times can then be used to estimate the response time of the forest floor to atmospherically delivered Pb, which is not in steady-state, assuming that leaching of Pb directly downward into the underlying mineral soil is the dominant loss mechanism (Table 3). Our Pb response times are in the range reported by Bindler et al. (*14*) for boreal forest mor layers in southern Sweden. They calculated response times of 36−111 years using Pb deposition chronology reconstructed from bog cores and anthropogenic Pb inventories in soils.

The enriched ^{207}Pb dose applied in 1984 can also be used to estimate the forest floor response time for the coniferous zone. If the response time of atmospherically delivered Pb in the coniferous forest was less than 150 years, then at least 10% of the application would have migrated to the underlying mineral soil. Since none of the dose could be found in the mineral soil, and we recovered all of the applied Pb in the forest floor, the response time of the coniferous zone soil must be >150 years.

Transit of Atmospherically-Delivered Pb in the Vadose Zone. Dissolved losses of Pb^{2+} from soils horizons are probably very low (*10*, *11*). Pb binding to organic matter and iron is strong, and natural soils generally have aqueous phase Pb concentrations <1% of the Pb in the solid phase (*33*). In the mineral soils at Camels Hump, <2% of the labile Pb was exchangeable. This is similar to the 0−1% exchangeable Pb reported by Johnson and Petras (*34*) for the mineral soils at HBEF. The fraction of exchangeable ^{207}Pb application (amount of Pb application recovered by the exchange extraction divided by the amount of Pb application recovered by the "labile Pb" extraction) was equal to the exchangeable fraction of the total Pb in the forest floor. The ^{207}Pb application was therefore bound as strongly to the forest floor as the pre-1980s anthropogenic Pb. Our results and others (*23*) suggest that strong complexation of Pb by soil must be accomplished on relatively short time scales.

Numerous researchers have proposed that migration via dissolved organic matter and/or colloids may be the dominant mechanism of Pb transport in soils (*2*, *10*, *35*, *36*). Dörr and Münnich (*35*) used ^{14}C and $^{210}Pb_{ex}$ soil measurements and found that atmospheric carbon and atmospheric ^{210}Pb had identical downward transfer velocities in the soil profile. Wang and Benoit (*10*) suggested that a linear rate of particulates from the forest floor would be a good approximation of Pb transport. Our data set is also consistent with this hypothesis that Pb mobility is linked to organic matter decomposition. According to our $^{210}Pb_{ex}$ data, forest floor response times are higher by a factor of at least 2 in the coniferous zone. Slower decomposition rates are likely here because C decomposition is temperature dependent, and coniferous litter decomposes generally at a slower rate than deciduous litter (*37*). However, the difference in Pb response times can also be a result of the different thicknesses of the forest floor. The average thickness of the forest floor at Camels Hump is 6 and 10 cm in the deciduous and coniferous zones, respectively (Friedland, unpublished data). Pb in either dissolved or particulate form will have to migrate further in the coniferous forest zone before exiting the forest floor and penetrating mineral soil.

Although the response times of atmospherically delivered Pb in the forest floor are different for the two forest zones, the overall penetration of atmospheric Pb into the soil profile is similar, at least at our two pits. Both ^{206}Pb/^{207}Pb and ^{210}Pb$_{ex}$ data suggest that penetration of atmospherically delivered Pb is limited to the upper 20 cm of the soil, regardless of which soil horizons the Pb resides in (Figures 1−4). Our data are limited to our 4−5 cm sampling resolution, but there is not a clear difference in the vertical Pb mobility between the two vegetation types with our data set.

Other direct data on the distribution of atmospheric Pb in soil profiles is relatively scarce. The ^{206}Pb/^{207}Pb data at LE620 are similar to what Bindler et al. (*14*) reported for a spodosol in Sweden. They found that approximately 15−30% of the anthropogenic Pb resided in the approximately 6 cm mor layer at their forested sites, and the remainder in the mineral soil. The majority of the anthropogenic Pb was in the Bs soil horizon, but they found detectable quantities of anthropogenic Pb between 20 and 60 cm from the soil surface. Emmanuel and Erel (*15*) used stable isotope techniques and a sequential extraction scheme and demonstrated that anthropogenic Pb was found in the mineral soil primarily in adsorbed and organic soil fractions in the Czech Republic. Schleich et al. (*38*) sampled soil profiles from a 40 year old spruce stand in Germany. They reported Pb$_{ex}$ to a depth of approximately 13 cm below the surface, and a large fraction of the atmospheric ^{210}Pb was beneath the O horizon.

Since atmospheric Pb has penetrated into the mineral soil in at both sites, localized zones of thin soils near the water table may allow slow leakage of the anthropogenic Pb load into streams. Shallow-flow in the organic horizon which short-circuits the mineral soil during high flow events will also contribute Pb to streamwaters (*39*, *40*). Since the average soil depth at Camels Hump is approximately 60 cm (*18*), and our profiles had anthropogenic Pb as deep as 20 cm depth, direct contact between the anthropogenic Pb front and the water table is not occurring yet for most soils in the watershed. Detailed anthropogenic Pb depth-profiles and high-resolution soil depth data are needed to accurately quantify the extent and timing of the leakage of mineral anthropogenic Pb into the hydrocycle. Contact between the saturated zone and the anthropogenic Pb front in well-drained soils is probably likely this century. According to the distribution of anthropogenic Pb in soils, its release to the groundwater will be dispersed over time, so concentrations of total Pb in waters should never increase dramatically, which is consistent with the conclusions of Wang and Benoit (*10*).

Stable and radioactive Pb isotopes offer a powerful tool for obtaining direct evidence of the distribution of atmospherically delivered Pb in soil profiles. Forest-floor response times and atmospheric Pb transit can be determined independent of long-term survey data. This can be useful in areas which are not the subject of long-term biogeochemical modeling, but it is also useful to couple the isotope data with long-term budget data when possible.

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