

Forest Floor Lead Changes from 1980 to 2011 and Subsequent Accumulation in the Mineral Soil across the Northeastern United States

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Quantifying the transport rate of anthropogenic lead (Pb) in forest soils is essential for predicting air pollution impacts on northeastern United States soil quality. In 2011, we resampled the forest floor at 16 sites across the northeastern United States previously sampled in 1980, 1990, and 2002 and also sampled the upper two mineral soil horizons. The mean forest floor Pb concentration decreased from $151 \pm 29 \text{ mg kg}^{-1}$ in 1980 to $68 \pm 13 \text{ mg kg}^{-1}$ in 2011. However, the mean forest floor Pb amount per unit area remained similar ($10 \pm 2 \text{ kg ha}^{-1}$ in 1980 and $11 \pm 4 \text{ kg ha}^{-1}$ in 2011). Study sites were divided into three geographic regions: western, central, and northern. The modeled forest floor Pb response time ($1/k$) was longer at frigid soil temperature regime sites ($61 \pm 15 \text{ yr}$) compared with mesic sites ($29 \pm 4 \text{ yr}$). Mineral soil Pb concentration and amount were approximately four times greater at western and central sites compared with northern sites for both mineral horizons. Furthermore, mean isotope ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.201 ± 0.006) and $^{208}\text{Pb}/^{206}\text{Pb}$ (2.060 ± 0.021) indicated that Pb in the western and central forest floor and mineral soil was primarily gasoline derived. Our combined analytical approach using long-term forest floor monitoring and stable Pb isotopes suggest that the majority of anthropogenic Pb deposited on soils in the western and central sites has been transported to the mineral soil, whereas it continues to reside in the forest floor at northern sites.

LEAD (Pb) was atmospherically deposited across the northeastern United States from the 1920s through the early 1980s, primarily from the combustion of gasoline with a tetra-ethyl Pb additive (Johnson et al., 1982; Nriagu, 1990; Steinnes and Friedland, 2006). Lead emissions in the United States were drastically reduced over the decades after the implementation of the Clean Air Act of 1977 (Galloway et al., 1982; Nriagu, 1990; Miller and Friedland, 1994; Johnson et al., 1995). Atmospheric deposition of Pb in the northeastern United States decreased from a peak rate of approximately $350 \text{ g ha}^{-1} \text{ yr}^{-1}$ in the late 1970s (Siccama and Smith, 1978; Johnson et al., 1995) to approximately $6.5 \text{ g ha}^{-1} \text{ yr}^{-1}$ in the mid-1990s (Wang and Benoit, 1996; Kaste et al., 2006). Despite reductions of Pb emissions, the forest floor (i.e., organic horizons Oi + Oe + Oa) has retained much of the gasoline-derived Pb because of its strong affinity for sorption to soil organic matter (SOM) and mineral surfaces (Siccama and Smith, 1978; Friedland and Johnson, 1985; Wang et al., 1995; Kaste et al., 2003; Steinnes and Friedland, 2006; Kaste et al., 2006).

Various methods have been developed to understand Pb retention times in the forest floor. The most common methods include collecting leachate with lysimeters (e.g., Wang et al., 1995; Huang and Matzner, 2004), quantifying stable and radiogenic isotope fluxes (e.g., Kaste et al., 2003; Watmough et al., 2004), monitoring whole watershed catchments (e.g., Johnson et al., 1995; Wang and Benoit, 1996), and resampling long-term plots (e.g., Miller and Friedland, 1994; Yanai et al., 2004; Evans et al., 2005; Kaste et al., 2006; Johnson and Richter, 2010). The findings of these studies suggest the residence time of anthropogenic Pb in the forest floor to be between 17 and 250 yr, varying with site and soil properties (Friedland and Johnson, 1985; Friedland et al., 1992; Miller and Friedland, 1994; Wang et al., 1995; Kaste et al., 2003; Watmough et al., 2004; Yanai et al., 2004; Johnson and Richter, 2010). One common metric to describe residence time for a metal reservoir is response time, defined as $(1/k)$ by Miller and Friedland (1994). Understanding the variation in Pb response time from the forest floor is essential for predicting the long-term fate of this large repository of Pb in the terrestrial environment and may have implications for

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Abbreviations: RSD, relative standard deviation; SOM, soil organic matter; SRM, standard reference material.

predicting the fate and transport of other atmospherically deposited metals.

Field investigations suggest that the variation in Pb response time in the forest floor and accumulation in the mineral soil may be dependent on large-scale parameters such as annual precipitation and annual temperature (Miller and Friedland, 1994; Johnson et al., 1995; Kaste et al., 2006; Stankwitz et al., 2012) and soil properties such as pH, SOM, mineralogy, texture, slope position, and permeability (Johnson et al., 1995; Johnson and Petras, 1998; Strawn and Sparks, 2000; Klaminder et al., 2008). Soil properties may be even more important for Pb accumulation in the mineral soil; Spodic horizons have been demonstrated to be important net accumulators of anthropogenic Pb (Johnson et al., 1995; Wang and Benoit, 1996; Bindler et al., 1999; Kaste et al., 2003; Stankwitz et al., 2012). This may not be the case for other soil horizons that occur in the northeastern United States.

The purpose of this study was to quantify Pb response time in forest soils across the northeastern United States using current and prior samplings of 16 long-term (>30 yr) upland research sites. The objectives of this study were (i) to determine changes in forest floor Pb concentrations and amounts through time, (ii) to identify if regional factors (temperature regime, precipitation, elevation, latitude or longitude) or soil properties (pH, SOM, horizon thickness) explain forest floor Pb response time, and (iii) to quantify subsequent Pb accumulation in the mineral soil and its source using stable Pb isotopic composition.

Materials and Methods

Description of Study Areas

Twenty-five long-term upland forest research sites were established in 1980 as part of two larger studies on metals in the forest floor (Andresen et al., 1980; Johnson et al., 1982). Sixteen sites that had been resampled in 1990 and 2002 were again resampled in 2011 (Richardson et al., 2013) (Fig. 1). Sites were situated in a number of land types unlikely to be disturbed, primarily in National and State forests, on level ground to slopes less than 8%. Sites were grouped into three subregions: western, central, and northern (Fig. 1). Vegetation at each site ranged from predominantly northern hardwoods (*Quercus* spp., *Fagus* spp., *Acer* spp., *Betula* spp.) to predominantly conifers (*Pinus* spp., *Picea* spp., *Tsuga canadensis*) (Table 1). The soils were developed

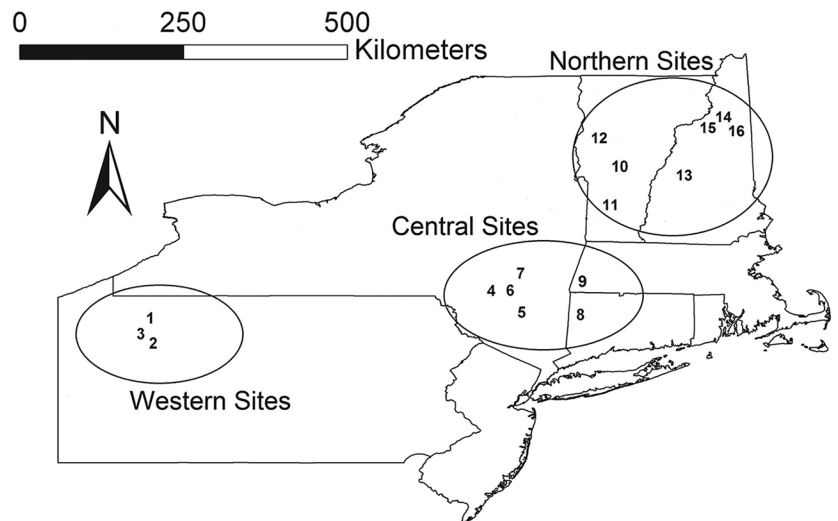


Fig. 1. Site locations and subregion grouping of sites.

Table 1. Site location, vegetation type, and soil taxonomy of the 16 sites sampled.

Region†	Site no.	Site name	Elevation	Latitude‡	Longitude‡	Vegetation	Drainage class§	Soil taxonomy (USDA system)
			m					
W	1	Heart's Content, PA	580	41.689	-79.252	pine/hemlock	ED	mesic Typic Dystrudepts
W	2	Cook's Forest, PA	430	41.347	-79.212	pine/hemlock	WD	mesic Typic Dystrudepts
W	3	Tionesta, PA	520	41.477	-79.379	oak	WD	mesic Typic Hapludults
C	4	Balsam Lake, NY	820	42.067	-74.574	northern hardwood	WD	frigid Lithic Dystrudepts
C	5	Mohonk, NY	366	41.770	-74.158	northern hardwood	WD	mesic Lithic Dystrudepts
C	6	Mt. Tremper, NY	305	42.071	-74.312	pine/hemlock	WD	mesic Typic Fragiudepts
C	7	Windham, NY	580	42.301	-74.170	northern hardwood	WD	frigid Typic Fragiudepts
C	8	Mohawk Mt, CT	503	41.820	-74.297	oak	WD	frigid Lithic Dystrudepts
C	9	Mt. Everett, MA	790	42.102	-73.431	oak/pitch pine	WD	frigid Lithic Dystrudepts
N	10	Sherburne Pass, VT	671	43.662	-72.833	northern hardwood	WD	frigid Typic Haplorthods
N	11	Bromley, VT	625	43.214	-72.967	northern hardwood	WD	frigid Lithic Haplorthods
N	12	Bristol Cliffs, VT	555	44.140	-73.064	pine/hemlock	ED	frigid Typic Haplorthods
N	13	Mt. Cardigan, NH	579	43.645	-71.933	spruce/hemlock	WD	frigid Typic Haplorthods
N	14	Valley Way, NH	433	44.369	-71.287	spruce/northern hardwood	WD	frigid Typic Haplorthods
N	15	Gale River, NH	440	44.232	-71.608	northern hardwood	WD	frigid Typic Dystrudepts
N	16	Wildcat Mt, NH	590	44.266	-71.238	spruce/northern hardwood	ED	frigid Lithic Dystrudepts

† C, central site; N, northern site; W, western site.

‡ Given in decimal degrees.

§ ED, excessively drained; WD, well drained. Data from Soil Survey Staff (2010).

from glacial till, outwash deposits, and outcrops (e.g., Siccama, 1974). Soils were classified on the basis of field observations as Spodosols or Inceptisols using soil taxonomy guidelines (Soil Survey Staff, 2010) except for site 3 (Tionesta, PA), which was an Ultisol (Table 1). Spodosols were found only at northern sites and comprised 78% of the soils at northern sites. Soils were also categorized by their mapped drainage class and soil temperature regime from the Web Soil Survey (Soil Survey Staff). Mean annual precipitation for each site was interpolated from a spatial model (1981–2010) from the PRISM Climate Group (2012).

Sample Collection and Preparation

Upland forest sites were sampled between July and September 2011 (Richardson et al., 2013) (Fig. 1). The forest floor at each site had been sampled three times previously in the same 30 m by 30 m plot in roughly the same months in 1980, 1990, and 2002 (Johnson et al., 1982; Friedland et al., 1992; Kaste et al., 2006). Previous investigators participated in the resampling of 6 of the 16 sites. Plots were relocated with high confidence using GPS and written instructions from previous surveys and confirmed with evidence of previous sample collection. Five forest floor (Oi + Oe + Oa horizons), three upper mineral horizon (A or E horizons), and three lower mineral horizon (Bw or Bs horizons) samples were collected from each site. Lower mineral soil (Bw or Bs horizons) was sampled at all sites except sites 4, 6, 7, 10, and 17 due to hardpan layer, extreme rock content, or lithic contact.

Forest floor was collected using the technique described by Johnson et al. (1982). Five 15 × 15 cm square sections of forest floor were separated from the underlying mineral soil and collected. In a nearby location, a trench was dug to allow access to the mineral soil. To avoid contamination from sampling adjacent horizons, the lower mineral horizon was sampled first, followed by the upper mineral horizon using hand trowels. The forest floor mass was calculated using oven-dried subsamples, and the volume was calculated using the area of the template and measured depths. Ensuring the 2011 sampling procedures was comparable with the prior sampling periods was important because the process can be subjective, and differences in collection methods may lead to artifacts (Federer, 1982; Friedland et al., 1992). The loss on ignition, forest floor depth, and forest floor mass samples were compared with the previous samplings to determine if conventions were similar (Fig. 2). Soil cores were collected using polypropylene tubes to estimate bulk density. Because the tubes used to estimate bulk density cannot collect rocks larger than 4 cm, the bulk density may underestimate the total rock fragments and potentially overestimate the amount of soil per unit area.

All samples were air-dried to a constant weight, and roots >5 mm in diameter were removed. Forest floor and mineral soil samples were milled and sieved, respectively, to ≤2 mm. Loss on ignition was used to estimate %SOM. To determine the percent loss on ignition, a 4-g air-dried subsample was combusted at 475°C for 8 h. Soil pH was determined using a 2:5 soil–water slurry. Slurries were shaken for 1 h using a wrist-action shaker and vacuum extracted through a Whatman 40 filter. The pH of the extract was measured with an ion selective electrode (8015 VWR). Soil particle size distribution was determined using a modified Bouyocous hydrometer method (Gee and Bauder, 1986). Thirty grams of soil were treated with 20 mL of 30% w/w

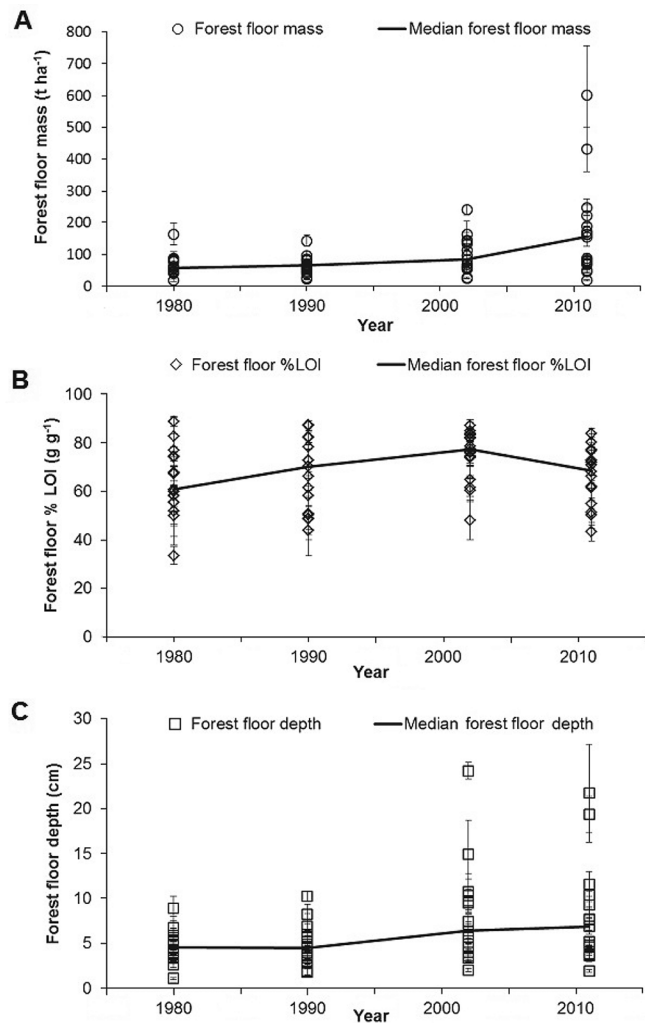


Fig. 2. Plots of the change in (A) forest floor mass, (B) forest floor percent loss on ignition (%LOI), and (C) forest floor depth of the 16 sites from 1980 to 2011. Forest floor mass in 2011 was significantly greater than the forest floor mass in 2002 ($P < 0.05$). Forest floor mass in 2002 and 2011 was significantly greater than the forest floor mass in 1990 and 1980 ($P < 0.05$). The %LOI was similar at all four collection dates. Forest floor depth was greater for the 2002 and 2011 sampling compared with the 1980 and 1990 sampling ($P < 0.05$).

hydrogen peroxide to oxidize SOM and dispersed overnight with 100 mL of 0.08 mol L⁻¹ sodium hexametaphosphate. The soil slurry was brought to 1 L using deionized water in a graduated cylinder. Hydrometer measurements were taken at 30 s, 60 s, 1.5 h, and 24 h after 30 s of mixing. Clay contents were determined from the 1.5- and 24-h measurements.

Lead Concentration and Stable Isotope Quantification

For total Pb measurements, 250 mg (±1 mg) subsamples were digested with 5 mL of a 1:9 ratio of trace metal grade HCl:HNO₃. The solution was allowed to effervesce for 24 h in lightly capped 50 mL polypropylene centrifuge tubes. The digestate solution was subsequently heated at 105°C for 1 h using a CEM MARS microwave digestion system. The digests were diluted with deionized water, filtered, and analyzed with an Agilent 7500cx series inductively coupled plasma–mass spectrometer (Agilent Technologies). With every 20 samples we included two replicates, a preparation blank, and a standard reference material (SRM). Peach leaves SRM 1547 and Montana

soil SRM 2711 from the National Institute of Standards and Technology were used as Pb SRMs for forest floor and mineral soils, respectively. An independently certified pine needles reference material (High-Purity Standards) was also used as a Pb SRM. All Pb concentrations for SRMs were within 7% of their certified values. Intrasample variation was <10%. Lead concentrations in the preparation blank samples were <1 ng g⁻¹. To ensure the Pb analysis was comparable with previous analyses, Pb concentration was determined for all forest floor samples from all sites using the previous method of hot plate digestion. A 2-g sample was dry ashed at 475°C and then boiled in 5% HNO₃ on a hot plate (Johnson et al., 1982; Friedland et al., 1992; Kaste et al., 2006). The solution was passed through a Whatman 41 filter and analyzed with a SpectroFlame inductively coupled plasma–optical emission spectrometer (SPECTRO Analytical Instruments). Measured Pb values from the inductively coupled plasma–mass spectrometry were plotted with inductively coupled plasma–optical emission spectrometer values and yielded a slope of 0.97 with an R² value of 0.96 (data not shown). All Pb concentrations and amounts from the sites measured in 1980, 1990, 2002, and 2011 are compiled in Table 2.

For stable Pb isotopic ratios, the extract solutions were diluted to approximately 10 µg kg⁻¹ of total Pb and analyzed by a sector field Element 2 inductively coupled plasma–mass spectrometer (Thermo-Finnigan). Data were collected for ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb with a mass window of 20% and with search and integration windows of 0 and 100%, respectively; sampling time was 10 ms, and 50 samples per peak were measured. Three replicates and 100 passes per replicate were performed. After every five samples, the NIST common Pb isotopic standard SRM 981 was run to check mass bias, verify Pb isotopic ratios, and monitor for instrument drift. All SRM 981 ²⁰⁶Pb/²⁰⁷Pb ratios were within 0.4% of their certified values. The relative standard deviation (%RSD) for the isotopic ratios of SRM 981 ranged from 0.02 to 0.7% RSD, with an average of 0.3% RSD for all measurements. The RSD of the extract solutions isotopic ratios ranged from 0.05 to 1%, with an average of 0.47%. The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratio was calculated as the ratio of the integrated counts for the three lead isotopes. A basic binary mixing model for ²⁰⁶Pb/²⁰⁷Pb from Komárek et al. (2008) was used to separate the % contribution from U.S. gasoline (Pb ore) and geogenic sources (Eq. [1]).

Table 2. Values for Pb concentration and amount in the forest floor at 16 sites in 1980, 1990, 2002, and 2011.

Site no.	Site name	Pb units	1980	1990	2002	2011
1	Heart's Content, PA	mg kg ⁻¹	294 ± 48†	115 ± 48	94 ± 38	115 ± 24‡
		kg ha ⁻¹	14 ± 1	6 ± 1	3 ± 1	2 ± 1‡
2	Cook's Forest, PA	mg kg ⁻¹	168 ± 13	112 ± 13	60 ± 8	41 ± 4‡
		kg ha ⁻¹	12 ± 2	5 ± 2	6 ± 1	1.8 ± 0.2‡
3	Tionesta, PA	mg kg ⁻¹	104 ± 15	76 ± 12	47 ± 8	36 ± 4‡
		kg ha ⁻¹	5 ± 1	2 ± 1	2 ± 1	0.6 ± 0.1‡
4	Balsam Lake, NY	mg kg ⁻¹	140 ± 14	122 ± 16	61 ± 11	81 ± 19‡
		kg ha ⁻¹	6 ± 1	6 ± 1	3 ± 1	7 ± 3
5	Mohonk, NY	mg kg ⁻¹	267 ± 15	198 ± 15	162 ± 11	114 ± 11‡
		kg ha ⁻¹	12 ± 4	18 ± 4	19 ± 3	19 ± 8
6	Mt. Tremper, NY	mg kg ⁻¹	163 ± 18	204 ± 20	73 ± 13	72 ± 13*
		kg ha ⁻¹	7 ± 1	12 ± 2	4.7 ± 1	12 ± 4
7	Windham, NY	mg kg ⁻¹	119 ± 24	62 ± 19	43 ± 19	62 ± 3*
		kg ha ⁻¹	16 ± 5	18 ± 4	10 ± 4	0.9 ± 0.2*
8	Mohawk Mt, CT	mg kg ⁻¹	132 ± 9	148 ± 9	128 ± 7	76 ± 8*
		kg ha ⁻¹	12 ± 1	10 ± 1	10 ± 1	14 ± 4
9	Mt. Everett, MA	mg kg ⁻¹	331 ± 37	201 ± 37	149 ± 26	120 ± 9*
		kg ha ⁻¹	21 ± 5	17 ± 5	19 ± 3	29 ± 12
10	Sherburne Pass, VT	mg kg ⁻¹	120 ± 11	94 ± 13	43 ± 11	30 ± 5*
		kg ha ⁻¹	6 ± 1	6 ± 1	3 ± 1	3 ± 1
11	Bromley, VT	mg kg ⁻¹	123 ± 12	70 ± 13	78 ± 9	50 ± 7*
		kg ha ⁻¹	7 ± 2	3 ± 2	12 ± 1	20 ± 11
12	Bristol Cliffs, VT	mg kg ⁻¹	145 ± 10	114 ± 10	84 ± 7	92 ± 8*
		kg ha ⁻¹	12 ± 2	9 ± 2	11 ± 1	15 ± 8
13	Mt. Cardigan, NH	mg kg ⁻¹	90 ± 15	63 ± 22	73 ± 9	29 ± 5**
		kg ha ⁻¹	4 ± 2	3 ± 2	7 ± 2	2 ± 1*
14	Valley Way, NH	mg kg ⁻¹	80 ± 6	78 ± 6	49 ± 4	52 ± 5‡
		kg ha ⁻¹	6 ± 1	5 ± 1	6 ± 1	12 ± 7
15	Gale River, NH	mg kg ⁻¹	67 ± 18	63 ± 16	58 ± 13	42 ± 11
		kg ha ⁻¹	4 ± 2	4 ± 2	8 ± 2	3 ± 1
16	Wildcat Mt, NH	mg kg ⁻¹	83 ± 16	91 ± 12	56 ± 9	78 ± 29
		kg ha ⁻¹	10 ± 2	12 ± 2	13 ± 3	28 ± 16

† Values are mean ± SE.

‡ Significant decrease between 1980 and 2011 values (*P* < 0.05).

$$\%USA \text{ Gasoline}_{\text{sample}} = \frac{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{sample}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{natural}}}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{gasoline}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{natural}}} \times 100\% \quad [1]$$

Based on previous work, we use the northeastern United States leaded gasoline endmember $^{206}\text{Pb}/^{207}\text{Pb}$ value of 1.195 (Sturges and Barrie, 1987; Graney et al., 1995; Teutsch et al., 2001; Carignan et al., 2002; Komárek et al., 2008). The 1.195 encompasses Pb ores sourced from Peru, Mexico, Australia, Canada, and the United States (Sturges and Barrie, 1987; Komárek et al., 2008). The other end member was the northeastern U.S. geogenic Pb, with a $^{206}\text{Pb}/^{207}\text{Pb}$ value approximated to be 1.215 (Graney et al., 1995; Taylor and McLennan, 1995; Teutsch et al., 2001; Kaste et al., 2003; Ndzangou et al., 2006; Komárek et al., 2008). The 1.215 geogenic Pb value is from heterogeneous rock sources spanning igneous, metamorphic and sedimentary sources (Graney et al., 1995). Lead sourced from sedimentary rocks also includes coal from West Virginia and Pennsylvania (Graney et al., 1995).

Lead Concentration in the Forest Floor through Time

The Pb concentrations were regressed using an exponential regression function (Eq. [2]) in Matlab (Mathworks). $[\text{Pb}_t]$ and $[\text{Pb}_0]$ from the exponential regressions were used to calculate a rate constant, k , for each site (Table 3). Response time, t_{resp} , was used to describe the retention time for Pb in the forest floor (Table 3). The t_{resp} parameter is the time required for a pulse to move through a reservoir not in steady state and was calculated using the k values with Eq. [3] (Miller and Friedland, 1994; Watmough et al., 2004).

$$[\text{Pb}_t] = [\text{Pb}_0]e^{-kt} \quad [2]$$

$$t_{\text{resp}} = 1/k \quad [3]$$

Table 3. The coefficient of determination, rate constant, and response time calculated for each exponential regression of Pb concentration through time.

Site no.	Site name	R^2	Rate constant yr^{-1}	Response time yr
1	Heart's Content, PA	0.58	0.029	35
2	Cook's Forest, PA	0.99	0.047	21
3	Tionesta, PA	0.99	0.035	29
4	Balsam Lake, NY	0.64	0.023	43
5	Mohonk, NY	0.99	0.026	39
6	Mt. Tremper, NY	0.71	0.034	29
7	Windham, NY	0.50	0.022	46
8	Mohawk, CT	0.61	0.017	59
9	Mt. Everett, MA	0.96	0.032	31
10	Sherburne Pass, VT	0.97	0.048	21
11	Bromley, VT	0.79	0.025	40
12	Bristol Cliffs, VT	0.79	0.016	63
13	Mt. Cardigan, NH	0.72	0.031	32
14	Valley Way, NH	0.79	0.017	59
15	Gale River, NH	0.84	0.014	71
16	Wildcat Mt., NH	0.38	0.007	143

Statistical Analyses

Descriptive statistics for Pb and soil properties were calculated using Matlab. In the text and figures, mean values are given ± 1 SE. To determine the mean Pb concentration, amount, and isotope values, the replicate samples (n) were averaged. The standard error was computed as the square root of the propagated error from the replicate samples squared and the individual measurement error squared all divided by N , the number of sites. The replicate sample size (n) and the number of sites (N) for each horizon are given in Table 4. Two-sample t tests were applied when data were found to be normally distributed using the Kolmogorov-Smirnov test. Differences in non-normally distributed data were determined with the Kruskal-Wallis test and evaluated with the Wilcoxon Signed-Rank test. Stepwise regressions were used to determine relationships between regional factors

Table 4. Selected chemical properties of the forest soils by subregion for the three depths sampled (± 1 SE).

Site	No. of sites	No. of total replicate samples	Thickness cm	soil pH†	%SOM‡	%Clay§
Western region	3				g g ⁻¹	
Forest floor		15	3.2 \pm 0.5	4.48 \pm 0.35	52 \pm 5	n.a.¶
Upper mineral soil		9	4.1 \pm 0.6	4.43 \pm 0.37	9 \pm 2	11 \pm 2
Lower mineral soil		9	5.9 \pm 0.5	4.38 \pm 0.32	5 \pm 1	12 \pm 3
Central region	6					
Forest floor		30	6.9 \pm 1.4	4.24 \pm 0.10	67 \pm 5	n.a.
Upper mineral soil		18	5.9 \pm 0.4	4.10 \pm 0.06	18 \pm 5	12 \pm 3
Lower mineral soil		9	9.7 \pm 1.2	4.12 \pm 0.19	7 \pm 4	6 \pm 2
Northern region	7					
Forest floor		35	8.7 \pm 1.8	3.97 \pm 0.04	73 \pm 3	n.a.
Upper mineral soil		21	6.4 \pm 0.9	3.69 \pm 0.03	9 \pm 2	14 \pm 2
Lower mineral soil		15	7.5 \pm 0.6	4.13 \pm 0.14	10 \pm 1	12 \pm 2

† Measured in a 2:5 soil water extract.

‡ Estimated from loss on ignition.

§ Determined by particle size distribution.

¶ Not available.

and soil properties with Pb concentration, amount, and t_{resp} . Linear regressions were visually analyzed for outliers and other goodness-of-fit characteristics, and passing correlations with R^2 values >0.25 and P values <0.05 were considered significant.

Results and Discussion

Decreasing Forest Floor Lead through Time

Lead concentration in the forest floor has continued to decrease since implementation of the Clean Air Act of 1977 (Nriagu, 1990; Johnson and Richter, 2010; Evans et al., 2005). The overall mean forest floor Pb concentration decreased from $151 \pm 29 \text{ mg kg}^{-1}$ in 1980 to $68 \pm 13 \text{ mg kg}^{-1}$ in 2011. Lead concentration at 14 of the 16 sites decreased significantly between 1980 and 2011 (Table 2). The mean percent decrease in Pb concentration between 1980 and 2011 was 67% for western sites, 52% for central sites, and 45% for northern sites. Central sites still have a higher forest floor Pb concentration than northern sites ($P < 0.05$), which likely reflects the original deposition pattern due to proximity to urban centers (Johnson et al., 1982; Evans et al., 2005; Johnson and Richter, 2010).

The observed decrease in Pb concentration likely resulted from at least two processes: (i) the dilution effect from the addition of new litter containing less Pb and (ii) leaching from the forest floor (Friedland et al., 1992; Kaste et al., 2006; Johnson and Richter, 2010). With the significant reduction in Pb emissions, new litterfall has a negligible Pb concentration compared with current forest floor Pb concentrations. For example, Watmough et al. (2004) found Pb concentrations to be $\sim 0.3 \text{ mg kg}^{-1}$ in foliage in south-central Ontario, Canada, whereas Smith and Siccama (1981) observed Pb concentrations of 4 to 14 mg kg^{-1} in foliage in 1975 at Hubbard Brook Experimental Forest, New Hampshire. The addition of the new litter with low Pb concentrations could decrease the measured forest floor Pb concentration without the physical loss of Pb. However, Johnson et al. (1995) and Kaste et al. (2003) demonstrated that Pb has been moving from the forest floor and entering the mineral soil using soil solution measurements and stable Pb isotope fluxes, respectively. Hence, we suspect that transport from the forest floor to the mineral soil is responsible for decreasing forest floor Pb concentrations.

The Pb amount per unit area decreased at only 6 of the 16 sites since the initial sampling in 1980 (Table 2), five of which had decreased since the 2002 sampling ($P < 0.05$). Overall, the mean Pb amount has not significantly decreased since the initial sampling in 1980. The overall mean forest floor Pb amount in 1980 ($10 \pm 2 \text{ kg ha}^{-1}$) was similar to the 2011 values ($11 \pm 4 \text{ kg ha}^{-1}$). It was expected that Pb concentration would be accompanied by decreases in Pb amount; however, changes in Pb amount may have been obscured by 200 to 600% increases in forest floor mass from 1980 to 2011. Significant increases in forest floor mass were observed in this study (Fig. 2), in previous samplings (Friedland et al., 1992; Kaste et al., 2006), in a study on companion sites from the original 1980 sampling (Johnson and Richter, 2010), and in a study across Bartlett and Hubbard Brook experimental forests (Yanai et al., 2004). Moreover, coefficients of variation for forest floor mass commonly range between 62 to 100% due to spatial heterogeneity (Yanai et al., 2004; Fahey et al., 2005). The mechanism driving the change in forest floor mass

remains unclear. Friedland et al. (1992) and Johnson and Richter (2010) have argued that if an apparent change in forest floor mass was an artifact derived from different sampling subjectivity, then an accompanying change in the physical properties of the forest floor sample (i.e., depth or %SOM) would be present. However, the %SOM did not decrease significantly between the 1980 and 2011 samplings for any site used in this study, suggesting that a greater inclusion of mineral soil did not occur. However, the forest floor depth was greater for the 2002 and 2011 samplings compared with the 1980 and 1990 samplings ($P < 0.05$) (Table 2). Deeper forest floor samples may have been collected due to different microtopography of the mineral soil surface. For sites without a significant change in forest floor depth but a greater forest floor mass, Johnson and Richter (2010) hypothesized that densification may occur from increasing stand age or a shift in SOM accumulation.

The decrease in forest floor Pb concentration at each site in the 1980, 1990, 2002, and 2011 samplings was adequately modeled by an exponential regression, with R^2 values >0.7 for 11 of the 16 sites. Only site 16 had an R^2 value less than 0.5 (Table 3). The rate constant from the exponential regressions k had a mean value of $0.027 \pm 0.003 \text{ yr}^{-1}$. The mean Pb response time (t_{resp}) for all sites was $46 \pm 7 \text{ yr}$. Western and central sites had t_{resp} values of $29 \pm 4 \text{ yr}$ and $42 \pm 5 \text{ yr}$, respectively. Northern sites had the longest t_{resp} value; it was estimated to be $61 \pm 15 \text{ yr}$, which is over three times longer than the 17-yr response time previously estimated by Miller and Friedland (1994) for the northern hardwood forest on Camels Hump, Vermont. It is similar to the Miller and Friedland (1994) estimate for the temperate coniferous forest of 77 yr and identical to the $61 \pm 12 \text{ yr}$ response time calculated from transport of radiogenic ^{210}Pb in a northern hardwood stand on Camels Hump, Vermont (Kaste et al., 2003; Stankwitz et al., 2012).

Due to the significant increase in forest floor mass, the t_{resp} was calculated using only the change in Pb concentration through time. Although Pb concentration is less affected by a change in forest floor mass or density (Yanai et al., 2004), it may be susceptible to the dilution effect described earlier. On the basis of a mass balance analysis, response times for Pb in the forest floor at central and northern sites may be longer than those calculated by changes in Pb concentration. This is reflected by our observation of no change in forest floor Pb amount at 10 of the 16 sites. The mean forest floor Pb amount at central and northern sites remained similar, with mean values of 12.2 ± 3.9 and $6.8 \pm 2.4 \text{ kg ha}^{-1}$ in 1980 compared with 13.6 ± 5.5 and 11.9 ± 5.6 in 2011, respectively. However, if we consider only central and northern sites with $<100\%$ increase in forest floor mass (sites 4, 8, 10, 13, and 15), there was a significant decrease in forest floor Pb amount from 7.1 ± 2.0 in 1980 to $3.2 \pm 0.9 \text{ kg ha}^{-1}$ in 2011. This suggests that approximately 54% of Pb had moved from the forest floor to the mineral soil at these central and northern sites. This may have been a general trend but was obscured by 200 to 600% increases in the forest floor mass from 1980 to 2011 (also observed by Yanai et al. [2004] and Johnson and Richter [2010]), resulting in a similar or in an increase in the perceived Pb amount. Although additional Pb to the forest floor could be introduced from local emissions or upward mixing from the mineral soil, it would not represent a significant input compared with peak Pb deposition in the early 1970s.

Forest Floor Lead Concentration, Amount, and Response Time Stepwise Regressions

Stepwise regressions were used to determine possible correlations between forest floor Pb concentration, Pb amount, and t_{resp} with regional factors (elevation, latitude, longitude, and mean annual precipitation) and soil properties (pH, % SOM, and thickness). Forest floor Pb concentration was not significantly correlated with any of the aforementioned variables ($P > 0.05$). Forest floor Pb amount was positively correlated with only t_{resp} ($R^2 = 0.44$; $P < 0.01$). The t_{resp} was positively correlated with forest floor thickness ($R^2 = 0.42$; $P < 0.01$) and site latitude ($R^2 = 0.31$; $P < 0.05$). Soil pH and SOM may not have correlated with t_{resp} due to the small range in values found in the forest floor. Climate has also been hypothesized to be one of the main parameters influencing Pb response time in the forest floor in our prior studies by controlling biological and chemical processes (Friedland et al., 1992; Miller and Friedland, 1994; Kaste et al., 2003; Kaste et al., 2006; Schroth et al., 2008). Mean annual precipitation from the PRISM Climate Group (2012) was not correlated with t_{resp} . When grouped by soil temperature regime, t_{resp} was significantly shorter for sites with mesic soils than for sites with frigid soils (Fig. 3B). The colder mean annual temperature likely decreased the decomposition rate, which increased forest floor turnover times and Pb retention (Berg and Tamm, 1991; Dörr and Münnich, 1991; Berg et al., 1993; Miller and Friedland, 1994; Kaste et al., 2006; Klaminder et al., 2006; Schroth et al., 2008; Johnson and Richter, 2010; Stankwitz et al., 2012). In addition, the forest stands at northern sites have more coniferous vegetation (Table 1), potentially decreasing the decomposition rate due to a higher lignin content (Berg et al., 1993) and increasing the Pb response time (Miller and Friedland, 1994; Stankwitz et al., 2012).

Lead in the Mineral Soil

The majority of studies on Pb in forest soils of the northeastern United States agree that substantial quantities of anthropogenic Pb from the combustion of gasoline have entered the mineral soil (e.g., Johnson et al., 1995; Wang and Benoit, 1996; Kaste et al., 2003; Yanai et al., 2004; Johnson and Richter, 2010). The mean Pb concentration in the mineral soil was $58 \pm 11 \text{ mg kg}^{-1}$ (median, 68 mg kg^{-1}). These values were greater than the 5 to 12 mg kg^{-1} and 26 to 32 mg kg^{-1} Pb reported by Smith and Siccama (1981) and Friedland and Johnson (1985), respectively. In our study, Pb concentration was greater in western and central sites when compared with northern sites for both mineral horizons ($P < 0.05$) (Fig. 4). The mean Pb amount in the mineral soil was $32 \pm 5.2 \text{ kg ha}^{-1}$ (median, 33 kg ha^{-1}), which was also higher than the 3 to 29 kg ha^{-1} and 14 to 24 kg ha^{-1} reported for forest soils in the northeastern United States by Smith and Siccama (1981) and Friedland and Johnson (1985), respectively. Western and central sites had greater Pb amounts in the lower mineral horizon compared with northern sites ($P < 0.05$) (Fig. 4).

We expected the majority of gasoline-derived Pb not to have leached into the mineral soil at northern sites on the basis of previous soil Pb studies (Wang et al., 1995; Kaste et al., 2006; Schroth et al., 2008). Kaste et al. (2003) observed that the majority of anthropogenic Pb was found in the Oa horizon of soils in the coniferous zone on Camels Hump, Vermont, which is geographically close and climatically similar to most of the

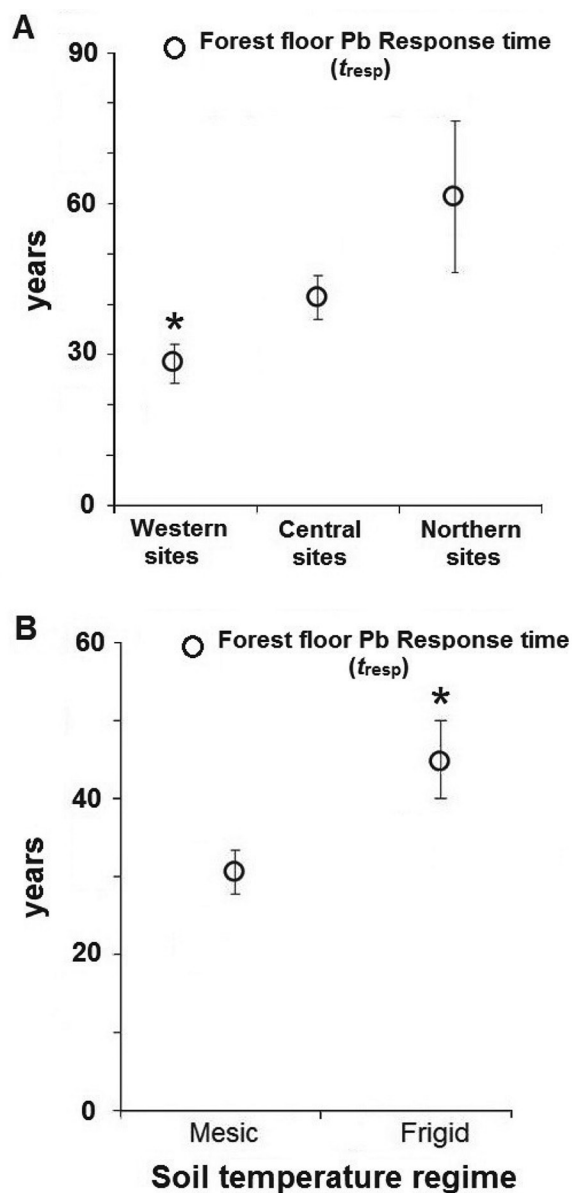


Fig. 3. (A) Response time displayed by site location. Western sites, $n = 3$; central sites, $n = 6$; and northern sites, $n = 7$. (B) Response time by soil temperature regime. Mesic sites, $n = 5$; frigid sites, $n = 11$. Values are mean ± 1 SE. *Significant at $P < 0.05$ (nonparametric Wilcoxon signed-ranks test).

northern sites. Our results support this finding because forest floor Pb concentration and amount were significantly greater than the lower mineral soil Pb concentration and the amount at northern sites, respectively (Fig. 4). Furthermore, forest floor Pb concentration and amount were equal to or lesser than lower mineral soil Pb concentration and amount at western sites, respectively (Fig. 4). Lead retention in the forest floor was longer at northern sites compared with western sites (Fig. 3), preventing its migration into the lower mineral soil horizons. Stepwise linear regressions were used to evaluate possible correlations between Pb concentration and amount in the upper and lower mineral horizons with regional factors (elevation, latitude, longitude, and mean annual precipitation) and soil properties (pH, %Clay, and %SOM). For the upper mineral horizon, Pb concentration was positively correlated with %SOM ($R^2 = 0.43$) and pH ($R^2 = 0.32$; $P < 0.05$). For the lower mineral horizon, Pb concentration and

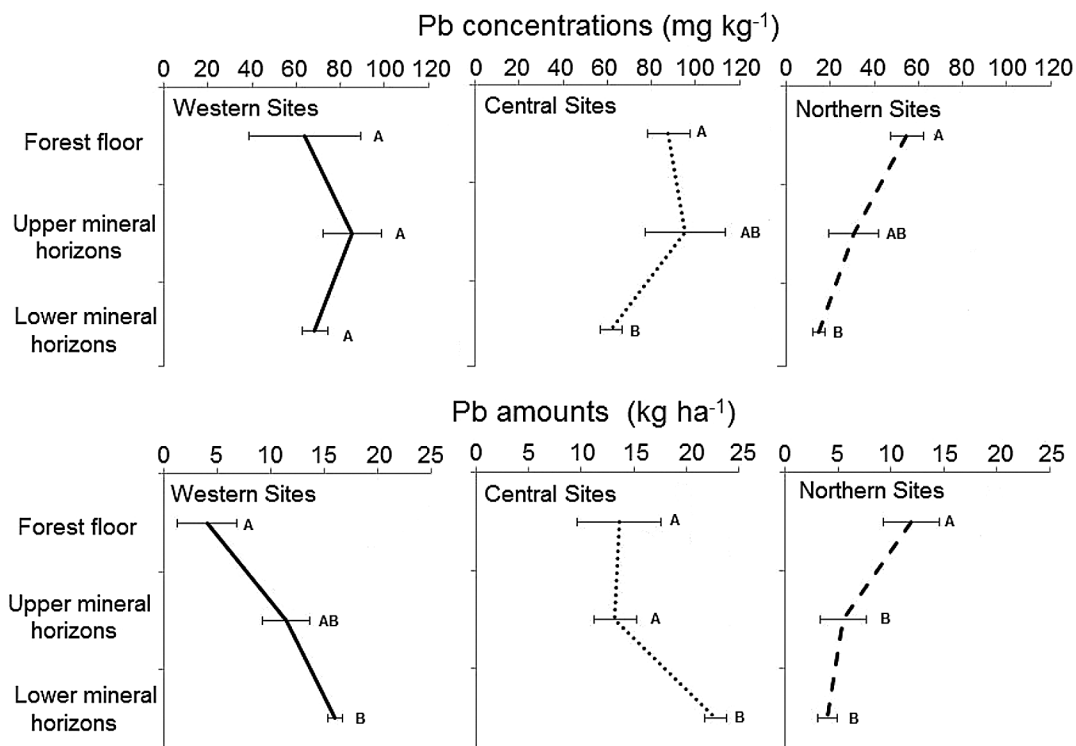


Fig. 4. The vertical distribution of Pb in the soil profile for the three subregions. Values are mean \pm 1 SE. *Significant at $P < 0.05$.

amount were significantly correlated with latitude ($R^2 > 0.75$; $P < 0.01$), longitude ($R^2 > 0.39$; $P < 0.05$), and %SOM ($R^2 > 0.26$; $P < 0.05$). These regressions suggest that Pb in the upper mineral horizon was more related with soil properties that influence sorption, whereas Pb in the lower mineral horizon varied more with regional factors. The %SOM and soil pH can influence Pb accumulation in mineral soil by controlling the sorption capacity (Strawn and Sparks, 2000). However, this may be an artifact of the regional effect because western sites had greater %SOM and a higher soil pH than northern sites for the upper mineral horizons (Table 4). The Pb in the lower mineral soil was strongly correlated with latitude and longitude because western sites had greater Pb concentration and amount compared with northern sites (Fig. 4). In addition, Pb in the lower mineral horizon may have correlated with latitude because warmer sites had significantly shorter retention time in the forest floor (Fig. 3) and have been reported to have faster transport velocities (Miller and Friedland, 1994). However, t_{resp} was not significantly correlated with Pb concentration and amount for either mineral horizon.

When the mineral horizons were analyzed by soil order, Inceptisols and Spodosols exhibited differences in soil properties and Pb accumulation (Table 5). Soil pH was higher for Inceptisols compared with Spodosols in both horizons ($P < 0.05$) (Table 5). The %SOM and thickness of the lower mineral horizons were greater for Spodosols compared with Inceptisols ($P < 0.05$) (Table 5). It was hypothesized that the Bs horizons would have greater Pb concentration and amount because of their accumulation of SOM and metal oxides. This was not the case for Pb concentration and amount because A and Bw horizons had significantly more Pb compared with the Bs horizons (Table 5). Inceptisols may have higher Pb concentration and amount in the mineral soil compared with Spodosols because Inceptisols likely had shorter t_{resp} values in their overlying forest floor. As gasoline-derived Pb continues to leach into the mineral soil at northern sites, the Bs horizons may be important in the future sorption of Pb with SOM and amorphous metal oxides (Johnson and Petras, 1998; Strawn and Sparks, 2000). Inceptisols, which do not possess a well-defined horizon of metal accumulation, may

Table 5. Mean values for Pb and chosen soil properties.

Soil type	Pb concentration	Pb amount	%SOM†	Soil pH	Depth
	mg kg ⁻¹	kg ha ⁻¹	w/w	log units	cm
Inceptisols					
Forest floor	84.4 \pm 9.5‡	13.5 \pm 3.4	65.5 \pm 3.8	4.16 \pm 0.07	7.7 \pm 1.7
A horizon	80.7 \pm 12.5	13.0 \pm 1.6	11.8 \pm 2.9	4.00 \pm 0.06	5.7 \pm 0.4
Bw horizon	57.3 \pm 4.8	19.2 \pm 2.1	7.1 \pm 2.3	4.01 \pm 0.08	7.6 \pm 0.9
Spodosols					
Forest floor	49.1 \pm 9.4	9.2 \pm 3.1	72.3 \pm 3.7	3.99 \pm 0.05	10.5 \pm 2.0
E horizon	26.6 \pm 11.7	1.7 \pm 0.3	7.3 \pm 1.3	3.75 \pm 0.04	5.3 \pm 0.7
Bs horizon	14.7 \pm 2.9	3.7 \pm 0.9	11.2 \pm 0.7	4.07 \pm 0.08	8.1 \pm 0.8

† Percent soil organic matter.

‡ Values are means \pm 1 SE.

not retain Pb as effectively. This may cause less accumulation of the approximately 13 kg ha⁻¹ of Pb in the A horizons of the Inceptisols of western and central sites.

Lead Stable Isotopes

The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios for the forest floor and for the upper mineral and lower mineral horizons were compared with published values of gasoline-derived and geogenic Pb across the northeastern United States (Sturges and Barrie, 1987; Graney et al., 1995; Taylor and McLennan, 1995; Teutsch et al., 2001; Carignan et al., 2002; Kaste et al., 2003; Komárek et al., 2008; Reimann et al., 2011) (Fig. 5). Despite concerns over the importance of biological processes in isotope mixing (e.g., Reimann et al., 2011), the contribution of gasoline-derived Pb and geogenic Pb can be identified with Pb stable isotope ratios (Steinnes et al., 2005; Komárek et al., 2008). The mean ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios for each subregion were primarily in the range of published values for gasoline-derived Pb in the United States (Fig. 5). Only the Pb in the lower mineral horizon of the northern sites could not be identified as dominantly gasoline-derived: two out of the five sites fell in the observed values of geogenic ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios (Fig. 5).

A basic binary mixing model for ²⁰⁶Pb/²⁰⁷Pb was used to quantify the % gasoline-derived and geogenic Pb contributions to the forest floor and mineral soil (Eq. [3]) (Komárek et al., 2008). The ²⁰⁶Pb/²⁰⁷Pb end-member for geogenic Pb for the northeastern United States derived from Graney et al. (1995), Taylor and McLennan (1995), Teutsch et al. (2001), and Kaste et al. (2003) was approximated to be 1.215 ²⁰⁶Pb/²⁰⁷Pb. The gasoline-derived ²⁰⁶Pb/²⁰⁷Pb end-member was based on Kaste et al. (2003), Sturges and Barrie (1987), Graney et al. (1995), and Komárek et al. (2008) values for the northeastern United States and was approximated as 1.19 ²⁰⁶Pb/²⁰⁷Pb. Using these values and the simple mixing model, the forest floor ²⁰⁶Pb/²⁰⁷Pb ratios at the three subregions were found to be dominated by gasoline-derived Pb, ranging between 87 and 96% (Fig. 6). This finding matches previous studies in the United States (e.g., Kaste et al., 2003) and other locations in the world (Steinnes et al., 2005). Upper mineral horizon ²⁰⁶Pb/²⁰⁷Pb ratios at the three subregions ranged between 65 and 79% gasoline-derived Pb (Fig. 6). The lower mineral horizons ranged from 52 to 72% gasoline-derived Pb, with the highest percentage at western sites and the lowest at northern sites (Fig. 6). The lower mineral horizon % gasoline-derived Pb was significantly lower than forest floor at the northern sites (*P* < 0.05) (Fig. 6). The ²⁰⁶Pb/²⁰⁷Pb ratios support our hypothesis that Pb in northern sites would have the lowest gasoline-derived Pb in the mineral soil. This is due either to greater response time in the forest floor or to more extractable geogenic Pb from pedogenesis.

Conclusions

On the basis of elevated Pb concentrations and stable Pb isotope ratios consistent with anthropogenic values in the

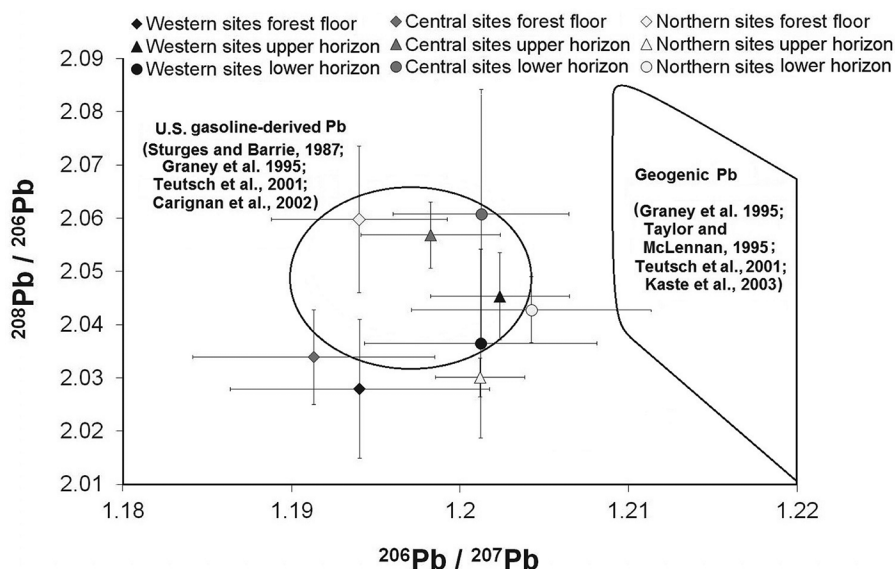


Fig. 5. The enclosed shapes for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios of United States gasoline-derived Pb and geogenic Pb are adapted from Teutsch et al. (2001) and Komárek et al. (2008). Shown are the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios for the three Pb isotopes and compared with other published values. Values are mean Pb ratios ± 1 SE.

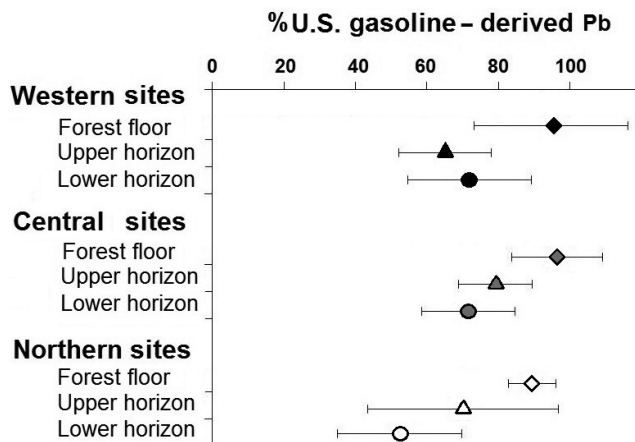


Fig. 6. The basic binary mixing model for ²⁰⁶Pb/²⁰⁷Pb was used to separate the % contribution from USA gasoline and natural sources using Eq. [1]. The results for each horizon at the three subregions are presented.

mineral soil, we concluded that gasoline-derived Pb has leached from the forest floor to the mineral soil across the northeastern United States. The mean ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios for each subregion were generally in the range of published values for United States gasoline-derived Pb, except for the lower mineral horizons at northern sites. Only the northern sites had ²⁰⁶Pb/²⁰⁷Pb ratios that differed significantly between the forest floor and mineral soil horizon. The future of Pb at western and central sites is unclear because they are dominated by Inceptisols, which generally lack horizons known for metal accumulation. Furthermore, the strong variation in *t_{resp}* and forest floor thickness with soil temperature regime suggests that temperature is a dominant variable controlling the movement of gasoline-derived Pb from the forest floor. Our findings identify a potential impact of a warmer climate on trace metal cycling, and further monitoring will be necessary to investigate the extent of Pb redistribution as it continues to leach through the mineral soil.

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