

Lead Reduction and Redistribution in the Forest Floor in New Hampshire Northern Hardwoods

Ruth D. Yanai,* David G. Ray, and Thomas G. Siccama

ABSTRACT

Because of the affinity of organic matter for lead, atmospheric loadings of this pollutant have been strongly retained in the forest floor. With the regulation of Pb emissions, loadings have decreased. We measured changes in Pb in forest floor horizons at a variety of northern hardwood sites in New Hampshire from the late 1970s to the 1990s. In all seven of the sites in which horizons were distinguished within the forest floor, Pb was found to be declining in the upper (Oie) horizon, but not in the underlying Oa and A horizons. At the Hubbard Brook Experimental Forest (HBEF), this loss from the Oie resulted in a 36% loss of Pb from the forest floor as a whole between 1976 and 1997 ($p < 0.001$). In contrast, in six stands in the Bartlett Experimental Forest (BEF), losses of Pb averaging $>50\%$ from the Oi and Oe horizons ($p = 0.01$) between 1979 and 1994 were compensated by gains in the Oa and A horizons. Similarly, at seven additional stands in the White Mountain National Forest, changes in the forest floor as a whole from 1980 to 1995 were not statistically significant (redistribution within the forest floor was not evaluated at these sites). Lead concentrations were highest in the Oe or Oie in the 1970s, but were highest in the Oa horizon in the 1990s. There was no significant pattern of Pb loss or retention as a function of stand age across all the sites.

LEAD IS AN ELEMENT that can be toxic to a variety of organisms, and one that has been elevated by orders of magnitude by human activities. More than 95% of the lead now cycling in the biosphere is anthropogenic in origin (Smith and Flegal, 1995). Combustion of leaded gasolines has been the most important source of Pb to biological cycles. At one time, rainwater exceeded the USEPA standards for Pb in drinking water (Smith and Siccama, 1981).

The affinity of soil organic matter for Pb (Schnitzer and Skinner, 1967; Strawn and Sparks, 2000) has protected aquatic systems and public water supplies from much of the Pb deposited in precipitation. In forested ecosystems, Pb is strongly retained by the forest floor. High concentrations of Pb in the forest floor were reported at the height of Pb deposition, even in remote areas (Parker et al., 1978; Heinrichs and Mayer, 1980; Smith and Siccama, 1981). Samples collected in 1980 from nine northeastern states ranged from 0.7 to 1.8 g Pb m⁻², depending on the forest type (Johnson et al., 1982). Sites at higher elevations tended to have more Pb in the forest floor, presumably because precipitation increases with elevation (Miller and Friedland, 1994),

and older forest floors had more Pb, reflecting the duration of the exposure to deposition (Johnson et al., 1982).

Forest floors were observed to accumulate Pb over time from the 1960s to the 1970s. White pine (*Pinus strobus* L.) stands in central Massachusetts had nearly doubled the Pb content of the forest floor between 1962 and 1978 (Siccama and Smith, 1980). In northern hardwood and boreal forest at Camels Hump, VT, Pb concentrations about doubled between 1966 and 1977 (Friedland et al., 1984). In both studies, the majority of the Pb deposited from the atmosphere over the measured interval was retained in the forest floor (Siccama and Smith, 1980; Friedland et al., 1984).

The regulation of Pb in gasoline, beginning in 1975, reduced the atmospheric deposition of this element. For example, at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, precipitation in 1989 contained only 3% as much Pb as it did in 1977 (Johnson et al., 1995). The forest floor was expected to continue to accumulate Pb at a low rate, because Pb residence times were estimated to be hundreds of years (Friedland and Johnson, 1985; Turner et al., 1985). Surprisingly, the forest floor at this site had 29% less Pb in 1987 as in 1977 (Johnson et al., 1995). Similarly, in a study of 30 sites in the northeastern USA, 12% of Pb in the forest floor was lost between 1980 and 1990 (Friedland et al., 1992). The fact that Pb is disappearing from the forest floor could be cause for concern, although soil water and stream export of Pb has been observed to be low in a variety of systems (Van Hook et al., 1977; Heinrichs and Mayer, 1980; Turner et al., 1985; Wang et al., 1995).

We hypothesized that Pb would be found deeper in the forest floor over time, because the majority of the litter input, now nearly free of Pb, enters from above. Previous studies of changes in Pb have not distinguished horizons within the forest floor. The effect of stand age and elevation on the retention of Pb in the forest floor is also unknown, although the amount of organic matter and Pb stored in the forest floor is known to be greater in older stands and in those at higher elevation (Johnson et al., 1982).

We studied changes in Pb in the forest floor in two independent sets of samples initially collected for other purposes. At the HBEF, we collected forest floor samples at seven different dates from 1976 to 1997 in a single watershed. This data set provides the best remeasurement sequence of forest floors in the region. Two other watersheds at HBEF provide ancillary data. In the second study, we measured changes in the forest

R.D. Yanai, SUNY College of Environmental Science and Forestry, Syracuse, NY 13210; D.G. Ray, Woods Hole Research Center, Woods Hole, MA 02543; and T.G. Siccama, Yale Univ., New Haven, CT 06511. Received 9 July 2002. *Corresponding author (rdyanai@mailbox.syr.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: BEF, Bartlett Experimental Forest; HBEF, Hubbard Brook Experimental Forest; WMNF, White Mountain National Forest.

floor at two points in time in 13 additional stands of different ages, all in the White Mountains of New Hampshire. We distinguished horizons within the forest floor at the HBEF and at six of the additional stands, which allowed us to test whether Pb was moving down through the forest floor. We also tested the importance of elevation and stand age in the loss or retention of Pb by the forest floor. This information should be useful to predicting the fate and transport of Pb in forested ecosystems.

METHODS

The Forest Floor

We define the forest floor to include the A horizon, if present (Yanai et al., 2000). The O horizon by definition contains a minimum of 20% organic C (Soil Survey Staff, 1975) or roughly 40% organic matter (Federer, 1982). The A horizon was separated from the Oa horizon at Bartlett Experimental Forest (BEF), but is included with the Oa horizon at HBEF. Here we refer to these samples as Oa-A, for consistency with the BEF samples, but they were called Oa (or H) in previous publications (Smith and Siccama, 1981; Yanai et al., 1999). The Oi and Oe horizons were also divided at BEF, but collected together at the HBEF, where we refer to them as the Oie horizon. The Oi, Oe, and Oa horizons are distinguished by their rubbed fiber content (Soil Survey Staff, 1975). All the horizon separations are subjective in the field (Federer, 1982). For both studies, the same investigators were involved in distinguishing horizons at all sampling dates. The consistency of horizon separations is evidenced by the consistency of organic matter fractions over time and between sites (Yanai et al., 1999, 2000).

Site Descriptions

Hubbard Brook Experimental Forest

The HBEF is located in the central White Mountains of New Hampshire, USA (43°56' N, 71°45' W). Samples for this study were collected from Watershed 6, a 13.2-ha natural area which serves as the reference watershed for the HBEF and has not been experimentally manipulated. Species composition varies along an elevational gradient, dominated by American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britton), and sugar maple (*Acer saccharum* Marsh.) at the lower elevations (550–630 m); sugar maple and beech at mid-elevations (630–700 m); and balsam fir [*Abies balsamea* (L.) Mill.], red spruce (*Picea rubens* Sarg.), and white birch [*Betula papyrifera* var. *cordifolia* (Marsh.) Regal] at higher elevations (>700 m). Soils are acidic, well-drained Spodosols (mostly Typic Haplorthods and Fragiorthods) derived from glacial till and of varying depth. Further descriptions of the HBEF are available in various publications (e.g., Whittaker et al., 1974; Bormann and Likens, 1979; Johnson et al., 1991; Likens and Bormann, 1995; Likens et al., 1998).

Three watersheds at the HBEF—W6, W5, and W1—have been sampled for forest floor properties at different times and somewhat different intensities (Table 1). The reference watershed, W6, was sampled on seven occasions between 1976 and 1997. At three of the dates (1976, 1977, and 1982) the forest floor was collected as a whole, while at the others (1978, 1987, 1992, and 1997) Oie and Oa-A horizons were distinguished. Individual plots consisted of 15 by 15 cm square blocks of excavated forest floor material and each sample date

included between 58 and 87 plots (Table 1), randomly located within elevational strata (16–27 at low elevation, 21–26 at mid-elevation, and 21–34 at high elevation). An adjacent watershed, W5, was sampled using the same methods in 1982 before it was whole-tree harvested. We did not include in our analysis another data set from W5 (Huntington et al., 1988) from the same date, because it used different sampling methods. Finally, W1 was sampled in 1996, 1998, and 2000, in association with an experimental addition of calcium silicate, which we assumed would not affect the behavior of Pb in the forest floor.

Bartlett Experimental Forest

The BEF is also located in the central White Mountains of New Hampshire, USA (43°50' to 44°13' N, 71°14' to 71°44' W). Elevations of our sites at BEF range from 305 to 365 m. The northern hardwood stands are dominated by beech, yellow birch, and sugar maple, along with red maple (*Acer rubrum* L.), and paper birch (*Betula papyrifera* Marsh) (Yanai et al., 2000). Some of the younger, even-aged stands contain significant amounts of pin cherry (*Prunus pennsylvanica* L.f.). Soils at these sites are coarse-loamy, mixed, frigid Typic Haplorthods.

The BEF study involves six even-aged stands spanning a range of ages representing a number of developmental stages. The stands were sampled in 1979 (Federer, 1984) and again 15 yr later in 1994 (Yanai et al., 1999, 2000). All sampled stands originated following clearcutting between about 1875 and 1985. This remeasured chronosequence provides observations from stands of different ages (two stands were the same age), from 11 to 119 yr following treatment. Forest floor samples at the BEF were separated into Oi, Oe, Oa, and A horizons. Plots ($n = 10$) were established at regular intervals along six systematically located transect lines in 1979 and along five of the previously established lines in 1994. Each plot consisted of a 10 by 10 cm square block of excavated forest floor material. Plots within a line were composited by horizon, providing six and five samples per stand in 1979 and 1994, respectively. We also report on combined Oie and Oa-A layers for the BEF because these were collected at the HBEF.

White Mountain National Forest

Seven additional stands were sampled in the White Mountain National Forest (WMNF), ranging in latitude from 43°56' to 44°13' N, in longitude from 71°14' to 71°44' W, and in elevation from 455 to 550 m. Soils were coarse-loamy, mixed, frigid Typic Haplorthods. Sampling methods were similar to those used at the BEF: five transects of 10 plots each were sampled in 1980 (Federer, 1984) and 1995 (Yanai et al., 1999, 2000). The forest floor blocks were not subdivided into horizons in 1980, so only the forest floor as a whole (O-A) can be assessed for change over time at these sites.

Laboratory Analyses

Both sets of samples from BEF were analyzed at the same time, as were both sets of samples from the WMNF, to control for variation in laboratory procedures. Samples from the HBEF were analyzed over a longer period of time. Forest floor samples from all sites were analyzed using similar procedures. Samples were dried to a constant weight, screened to remove coarse fragments in the case of BEF and WMNF samples (Yanai et al., 1999), then ground with a Wiley mill. Loss on ignition was used to estimate organic mass. Ashed subsamples from each horizon were dissolved in 6 mol L⁻¹ nitric acid and analyzed by inductively coupled plasma spectroscopy (ICP).

Table 1. Forest floor mass, organic fraction, Pb content, and Pb concentration of the forest floor at Hubbard Brook Experimental Forest (HBEF), Bartlett Experimental Forest (BEF), and other locations in the White Mountain National Forest (WMNF).†

Forest	Stand	Stand age	Sample year	Elevation	Horizon	Sample	Mass		Organic mass		Pb content		Pb concentration	
							m	n	kg m ⁻²		g m ⁻²		mg kg ⁻¹	
BEF	H1	40	1979	335	FF	6	13.72	1.96	5.23	0.58	0.41	0.06	30.13	1.42
BEF	H1	55	1994	335	FF	5	12.63	1.00	6.12	0.57	0.47	0.04	37.10	2.24
BEF	H2	104	1979	335	FF	6	17.80	5.16	8.25	1.47	0.69	0.13	42.49	3.70
BEF	H2	119	1994	335	FF	5	12.72	2.19	7.01	1.52	0.50	0.07	41.09	2.98
BEF	H3	104	1979	457	FF	6	12.84	0.63	8.71	0.53	0.60	0.10	46.60	6.83
BEF	H3	119	1994	457	FF	5	11.13	0.74	7.87	0.72	0.39	0.02	35.41	1.27
BEF	H4	45	1979	366	FF	6	10.31	0.73	4.70	0.71	0.58	0.09	55.80	8.01
BEF	H4	60	1994	366	FF	5	7.32	1.58	3.54	0.54	0.47	0.20	59.38	11.34
BEF	H5	12	1979	366	FF	6	9.98	0.86	4.51	0.26	0.41	0.03	41.41	2.74
BEF	H5	27	1994	366	FF	5	9.64	1.40	4.94	0.60	0.44	0.09	46.00	5.06
BEF	H6	0	1979	366	FF	6	11.84	1.05	6.03	0.37	0.50	0.03	42.61	2.19
BEF	H6	11	1994	366	FF	5	10.13	1.92	5.53	0.83	0.48	0.06	49.81	4.80
WMNF	C3	10	1980	488	FF	5	8.90	1.51	4.14	0.69	0.47	0.06	55.51	5.30
WMNF	C3	25	1995	488	FF	5	12.16	1.61	3.88	0.68	0.60	0.11	46.26	4.46
WMNF	M3	70	1980	457	FF	5	11.77	1.26	8.67	0.96	0.70	0.10	59.31	4.16
WMNF	M3	85	1995	457	FF	5	18.49	1.67	7.21	1.05	0.86	0.05	35.56	6.02
WMNF	M4	30	1980	457	FF	5	12.08	1.35	7.06	0.83	0.60	0.09	49.26	3.94
WMNF	M4	45	1995	457	FF	5	13.31	2.67	4.28	0.80	0.61	0.12	33.33	5.14
WMNF	M5	4	1980	457	FF	5	8.16	0.41	5.15	0.46	0.49	0.08	60.77	9.54
WMNF	M5	19	1995	457	FF	5	9.63	1.31	3.72	0.58	0.51	0.05	54.23	9.97
WMNF	M6	1	1980	518	FF	5	9.81	1.60	6.72	1.20	0.45	0.05	47.30	3.05
WMNF	M6	16	1995	518	FF	5	13.28	3.41	4.07	0.50	0.58	0.11	42.94	9.75
WMNF	T20	22	1980	518	FF	5	9.00	0.25	5.49	0.28	0.53	0.03	58.96	4.05
WMNF	T20	37	1995	518	FF	5	8.01	0.73	2.25	0.16	0.39	0.04	41.52	2.62
WMNF	T30	32	1980	549	FF	5	14.49	2.03	4.89	0.47	0.53	0.09	36.01	2.43
WMNF	T30	47	1995	549	FF	5	8.98	1.24	2.87	0.42	0.41	0.08	48.56	6.26
HBEF	W1	86	1996	490-740	FF	84	16.21	1.12	7.75	0.48	0.91	0.06	62.04	3.03
HBEF	W1	88	1998	490-740	FF	97	14.80	1.56	8.69	0.82	0.82	0.07	60.59	2.48
HBEF	W1	90	2000	490-740	FF	100	15.46	0.99	8.29	0.53	0.81	0.05	55.00	2.04
HBEF	W5	72	1982	500-750	FF	245	12.18	0.56	6.70	0.30	0.79	0.04	73.40	2.00
HBEF	W6	66	1976	550-790	FF	59	18.86	2.33	6.72	0.59	1.07	0.09	77.77	4.84
HBEF	W6	67	1977	550-790	FF	58	13.49	1.91	6.06	0.54	1.00	0.07	98.42	6.06
HBEF	W6	68	1978	550-790	FF	58	12.70	1.01	6.61	0.53	0.96	0.06	86.41	4.26
HBEF	W6	72	1982	550-790	FF	68	10.90	0.66	6.32	0.49	0.87	0.06	82.10	3.53
HBEF	W6	77	1987	550-790	FF	70	12.86	1.97	6.21	0.75	0.75	0.07	69.84	3.11
HBEF	W6	82	1992	550-790	FF	80	16.75	1.30	7.67	0.64	1.02	0.07	68.09	3.15
HBEF	W6	87	1997	550-790	FF	87	11.50	0.89	6.28	0.46	0.68	0.06	59.89	2.73
BEF	H1	40	1979	335	Oi	6	0.35	0.02	0.31	0.02	0.01	0.00	20.02	0.52
BEF	H1	55	1994	335	Oi	5	0.42	0.07	0.38	0.07	0.00	0.00	6.67	0.60
BEF	H2	104	1979	335	Oi	6	0.35	0.06	0.31	0.05	0.01	0.00	20.83	1.15
BEF	H2	119	1994	335	Oi	5	0.37	0.05	0.33	0.05	0.00	0.00	11.48	2.10
BEF	H3	104	1979	457	Oi	6	0.35	0.02	0.33	0.02	0.01	0.00	22.75	2.21
BEF	H3	119	1994	457	Oi	5	0.41	0.05	0.38	0.05	0.00	0.00	7.84	1.86
BEF	H4	45	1979	366	Oi	6	0.49	0.02	0.44	0.02	0.01	0.00	27.98	5.74
BEF	H4	60	1994	366	Oi	5	0.41	0.05	0.35	0.05	0.01	0.00	13.02	3.26
BEF	H5	12	1979	366	Oi	6	0.31	0.04	0.31	0.04	0.01	0.00	25.92	1.57
BEF	H5	27	1994	366	Oi	5	0.36	0.06	0.31	0.05	0.00	0.00	8.46	1.57
BEF	H6	0	1979	366	Oi	6	0.31	0.01	0.28	0.01	0.01	0.00	29.64	6.19
BEF	H6	11	1994	366	Oi	5	0.35	0.08	0.30	0.07	0.00	0.00	14.16	3.58
BEF	H1	40	1979	335	Oe	6	1.61	0.14	0.95	0.11	0.09	0.01	53.29	3.93
BEF	H1	55	1994	335	Oe	5	1.91	0.07	1.44	0.09	0.07	0.01	35.94	8.63
BEF	H2	104	1979	335	Oe	6	1.70	0.13	1.35	0.11	0.14	0.01	80.26	3.70
BEF	H2	119	1994	335	Oe	5	1.63	0.38	1.29	0.33	0.07	0.02	36.80	4.40
BEF	H3	104	1979	457	Oe	6	2.71	0.18	2.30	0.21	0.18	0.01	67.24	1.95
BEF	H3	119	1994	457	Oe	5	3.01	0.27	2.61	0.29	0.09	0.01	30.43	2.21
BEF	H4	45	1979	366	Oe	6	2.41	0.31	1.65	0.11	0.21	0.03	95.17	19.88
BEF	H4	60	1994	366	Oe	5	1.46	0.21	1.07	0.13	0.06	0.01	41.87	5.11
BEF	H5	12	1979	366	Oe	6	2.21	0.42	1.39	0.17	0.15	0.02	68.87	4.54
BEF	H5	27	1994	366	Oe	5	2.48	0.53	1.69	0.28	0.12	0.03	49.51	4.87
BEF	H6	0	1979	366	Oe	6	2.70	0.46	1.65	0.17	0.17	0.02	69.24	8.18
BEF	H6	11	1994	366	Oe	5	1.86	0.12	1.54	0.13	0.09	0.01	50.27	4.79
HBEF	W1	86	1996	490-740	Oie	84	3.55	0.20	2.93	0.18	0.19	0.02	53.21	3.36
HBEF	W1	88	1998	490-740	Oie	97	3.85	0.26	3.20	0.24	0.18	0.02	43.80	2.58
HBEF	W1	90	2000	490-740	Oie	100	4.61	0.22	3.39	0.18	0.18	0.01	38.42	1.86
HBEF	W6	68	1978	550-790	Oie	58	3.05	0.26	2.52	0.22	0.36	0.05	115.01	4.01
HBEF	W6	77	1987	550-790	Oie	70	3.83	0.27	2.73	0.21	0.30	0.03	75.66	3.47
HBEF	W6	82	1992	550-790	Oie	80	3.30	0.19	2.59	0.14	0.22	0.02	63.79	3.15
HBEF	W6	87	1997	550-790	Oie	87	3.38	0.16	2.80	0.14	0.15	0.01	40.57	2.51
BEF	H1	40	1979	335	Oa	6	4.53	0.47	2.69	0.32	0.17	0.02	38.61	3.93
BEF	H1	55	1994	335	Oa	5	6.64	0.91	3.54	0.48	0.31	0.05	46.71	4.01
BEF	H2	104	1979	335	Oa	6	7.90	1.16	4.68	0.74	0.32	0.05	42.56	4.52
BEF	H2	119	1994	335	Oa	5	7.08	2.41	4.34	1.62	0.30	0.10	47.36	6.05
BEF	H3	104	1979	457	Oa	6	8.10	0.57	5.57	0.48	0.36	0.11	43.15	9.70
BEF	H3	119	1994	457	Oa	5	7.05	0.65	4.74	0.53	0.28	0.02	39.90	2.06
BEF	H4	45	1979	366	Oa	6	2.73	1.05	1.54	0.66	0.15	0.08	49.72	8.96
BEF	H4	60	1994	366	Oa	5	2.99	0.81	1.52	0.40	0.19	0.05	68.20	11.16

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Table 1. Continued.

Forest	Stand	Stand age	Sample year	Elevation	Horizon	Sample	Mass	Organic mass		Pb content		Pb concentration		
								kg m ⁻²		g m ⁻²		mg kg ⁻¹		
				m		n								
BEF	H5	12	1979	366	Oa	6	2.91	<i>0.69</i>	<i>1.74</i>	<i>0.43</i>	0.13	<i>0.03</i>	44.58	3.70
BEF	H5	27	1994	366	Oa	5	2.44	<i>1.52</i>	<i>1.42</i>	<i>0.86</i>	0.16	<i>0.10</i>	51.39	14.08
BEF	H6	0	1979	366	Oa	6	4.66	<i>0.43</i>	<i>2.87</i>	<i>0.31</i>	0.20	<i>0.02</i>	43.07	4.64
BEF	H6	11	1994	366	Oa	5	4.94	<i>2.29</i>	<i>2.69</i>	<i>1.03</i>	0.24	<i>0.09</i>	55.58	3.87
HBEF	W1	86	1996	490–740	OaA	84	12.66	<i>1.08</i>	<i>4.82</i>	<i>0.40</i>	0.72	<i>0.05</i>	67.44	3.43
HBEF	W1	88	1998	490–740	OaA	97	10.95	<i>1.49</i>	<i>5.50</i>	<i>0.74</i>	0.64	<i>0.07</i>	73.98	3.43
HBEF	W1	90	2000	490–740	OaA	100	10.85	<i>0.92</i>	<i>4.90</i>	<i>0.44</i>	0.62	<i>0.05</i>	66.70	2.82
HBEF	W6	68	1978	550–790	OaA	58	10.18	<i>1.02</i>	<i>4.31</i>	<i>0.48</i>	0.64	<i>0.05</i>	76.16	4.10
HBEF	W6	77	1987	550–790	OaA	70	9.72	<i>2.01</i>	<i>3.75</i>	<i>0.70</i>	0.49	<i>0.06</i>	66.73	3.41
HBEF	W6	82	1992	550–790	OaA	80	13.80	<i>1.27</i>	<i>5.21</i>	<i>0.60</i>	0.82	<i>0.07</i>	68.12	3.54
HBEF	W6	87	1997	550–790	OaA	87	9.42	<i>0.85</i>	<i>4.03</i>	<i>0.39</i>	0.62	<i>0.06</i>	74.24	3.84
BEF	H1	40	1979	335	A	6	7.23	<i>1.80</i>	<i>1.29</i>	<i>0.23</i>	0.15	<i>0.04</i>	21.77	2.35
BEF	H1	55	1994	335	A	5	3.66	<i>0.58</i>	<i>0.75</i>	<i>0.10</i>	0.09	<i>0.01</i>	25.82	3.78
BEF	H2	104	1979	335	A	6	7.85	<i>5.12</i>	<i>1.91</i>	<i>1.27</i>	0.22	<i>0.15</i>	26.51	4.05
BEF	H2	119	1994	335	A	5	3.64	<i>1.54</i>	<i>1.04</i>	<i>0.41</i>	0.13	<i>0.05</i>	35.73	5.98
BEF	H3	104	1979	457	A	6	1.67	<i>0.29</i>	<i>0.51</i>	<i>0.10</i>	0.05	<i>0.01</i>	28.46	3.85
BEF	H3	119	1994	457	A	5	0.66	<i>0.12</i>	<i>0.15</i>	<i>0.02</i>	0.02	<i>0.00</i>	31.85	2.58
BEF	H4	45	1979	366	A	6	4.69	<i>0.56</i>	<i>1.08</i>	<i>0.08</i>	0.20	<i>0.03</i>	44.23	9.31
BEF	H4	60	1994	366	A	5	2.46	<i>0.81</i>	<i>0.60</i>	<i>0.16</i>	0.22	<i>0.15</i>	64.53	25.99
BEF	H5	12	1979	366	A	6	4.55	<i>0.77</i>	<i>1.34</i>	<i>0.47</i>	0.12	<i>0.02</i>	26.80	2.73
BEF	H5	27	1994	366	A	5	4.36	<i>0.94</i>	<i>1.52</i>	<i>0.37</i>	0.16	<i>0.04</i>	36.78	8.70
BEF	H6	0	1979	366	A	6	4.17	<i>0.86</i>	<i>1.23</i>	<i>0.21</i>	0.12	<i>0.02</i>	30.10	2.22
BEF	H6	11	1994	366	A	5	2.98	<i>0.88</i>	<i>0.99</i>	<i>0.30</i>	0.14	<i>0.04</i>	48.64	10.44

† Means and standard errors (in italics). Sample *n* refers to individual plots at HBEF and composited lines at BEF and WMNF (see text for details).

We report Pb concentrations on a dry weight basis. Because chemical analyses were performed on individual horizons, mass-weighted concentrations were calculated for all combined layers.

Statistical Analyses

The HBEF data set was analyzed separately from the BEF and WMNF data sets, because the amounts of Pb and the changes over time differed between the two studies. Mean values at the stand level were used to test hypotheses about changes in forest floor properties over time. Dependent variables did not require transformation to meet tests for normality of the residuals.

Relationships between forest floor properties and stand age, elevation, or time of measurement were tested using linear regression. Paired *t* tests were used to test for change over time in stands at the BEF and WMNF, which were sampled only twice. Differences were determined by comparing stand level means at the two sampling dates. Minimum detectable differences were determined based on inverse *t* tests with $\alpha = 0.05$.

RESULTS

Forest Floor Totals

The forest floor as a whole (O + A horizons) was measured at 16 sites for intervals ranging from 4 to 21 yr (Table 1). At the most intensively measured site, W-6 at the HBEF, the forest floor lost 0.25 g Pb m⁻² from 1976 to 1997, to total 36% of the initial Pb content ($p = 0.002$, linear regression; Fig. 1a). Another site at HBEF, W-1, was sampled three times in 4 yr, with results very similar to W-6, except for slightly higher mass (Fig. 1c) and Pb content (Fig. 1a).

Changes in Pb content in 13 additional sites (six at the BEF and seven elsewhere in the WMNF) during a 15-yr interval (Fig. 1a) were not statistically significant ($p = 0.63$, paired *t* test). The behavior of these forest floors is significantly different from those at HBEF: a

mean change in Pb content of 0.08 g m⁻² across the 13 stands would have been detectable at $p = 0.05$.

Like Pb contents, concentrations of Pb at HBEF declined by 29 mg kg⁻¹ (ppm), or 32%, in the forest floor as a whole between 1976 and 2000 ($p < 0.001$, linear regression) (Fig. 1b). The change in Pb concentrations at BEF and WMNF was not statistically distinguishable from zero ($p = 0.10$, paired *t* test) and was less than the rate of loss at HBEF (a mean change of 7 mg kg⁻¹ would have been statistically detectable).

The amount and concentration of Pb in the forest floor was higher at the HBEF than at the other sites by about 40% for content and 22% for concentration (Fig. 1). The mass of the forest floor was similar at the HBEF, BEF, and WMNF sites (Fig. 1c). Older stands tended to have more massive forest floors than younger stands ($r^2 = 0.28$; $p < 0.001$ for linear regression on all observations; $r^2 = 0.30$; $p = 0.02$, using average values for each stand). There was no significant effect of stand age on Pb contents or concentrations or changes in these variables (Fig. 1a and b).

Changes within Horizons

For eight of the sites, the forest floor was divided into Oie and Oa-A horizons. The underlying Oa-A is more massive (Fig. 2c) and has greater Pb contents (Fig. 2a) than the Oie. Declines in Pb were more evident in the upper portions of the forest floor (Oie) than in the Oa-A (Fig. 2a and b).

Declines in Pb contents in Oie horizons were similar in magnitude at the HBEF and BEF (Fig. 2a). At HBEF W-6, the Pb content of the Oie horizon declined by 59% from 1977 to 1997 ($p = 0.0004$), accounting for the overall change taking place in the forest floor. At the BEF, the Pb content of the Oie declined by 47% between 1979 and 1994 ($p = 0.01$). In contrast, the Pb content of the underlying Oa-A horizon did not change

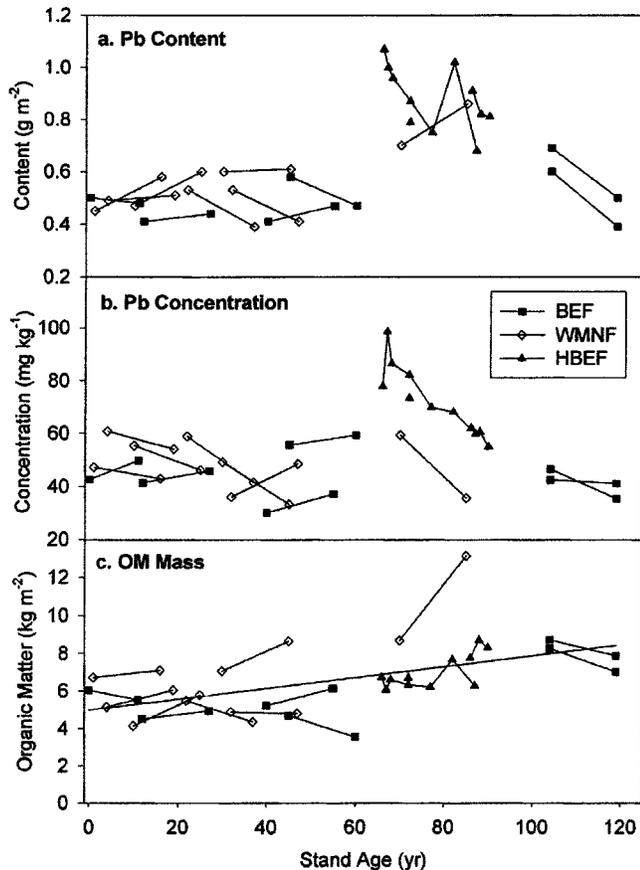


Fig. 1. (a) Lead content, (b) concentration of Pb per unit organic matter, and (c) organic matter content of the forest floor as a function of stand age in three stands at the HBEF, six stands at the BEF, and seven stands elsewhere in the WMNF. At HBEF, W6 was sampled seven times, W1 was sampled three times, and W5 was sampled once. Lead content of W6 = 1.78 g m^{-2} to $0.0118 \text{ g m}^{-2} \text{ yr}^{-1} \times \text{age (yr)}$.

significantly over time at HBEF ($p = 0.77$) or at BEF ($p = 0.88$).

Like Pb contents, concentrations of Pb in the Oie horizon declined dramatically (Fig. 2b), by almost 65% at the HBEF ($p < 0.0001$) and by 45% at the BEF ($p = 0.002$). In contrast, in the Oa-A horizon, Pb concentrations were stable within detection limits at HBEF and increased by 29% at BEF ($p = 0.03$). Concentrations of Pb were greater in the Oie than Oa horizon at the beginning of the measurement period, but were lower in the Oie than the Oa at both locations at the most recent observations.

The forest floor was divided into four horizons (Oi, Oe, Oa, A) at the BEF. Changes within these horizons provide finer resolution of Pb dynamics, and confirm that Pb was found deeper in the profile over the period of observation (Fig. 3). The uppermost Oi horizon declined in Pb concentration (Fig. 3b) by 58%, on average, during the 15-yr period ($p < 0.0001$); the Oe horizon experienced an average 44% loss ($p = 0.004$). In contrast, Pb concentrations increased by 18% in Oa and 37% in A horizons ($p = 0.05$ and 0.01 , respectively). Changes in Pb content (Fig. 3a) were not as consistent, with the loss being statistically significant only in the Oe

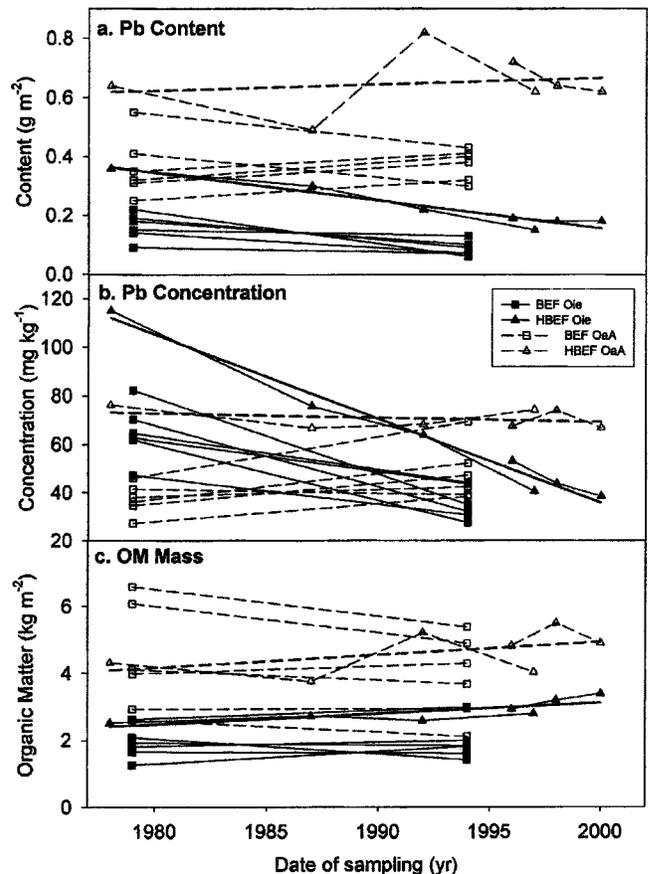


Fig. 2. Change over time in (a) Pb content (HBEF, Oie $r^2 = 0.91$, $p < 0.001$, OaA $r^2 = 0.17$, $p = 0.74$; BEF, Oie $r^2 = 0.55$, $p = 0.004$, OaA $r^2 = 0.10$, $p = 0.90$); (b) Pb concentration (HBEF, Oie $r^2 = 0.99$, $p < 0.001$, OaA $r^2 = 0.07$, $p = 0.47$; BEF, Oie $r^2 = 0.72$, $p < 0.001$, OaA $r^2 = 0.21$, $p = 0.08$); and (c) organic mass (HBEF, Oie $r^2 = 0.54$, $p = 0.04$, OaA $r^2 = 0.07$, $p = 0.29$; BEF, Oie $r^2 = 0.10$, $p = 0.86$, OaA $r^2 = 0.06$, $p = 0.56$) of Oie and Oa-A horizons at Hubbard Brook and Bartlett Experimental Forests.

horizon ($p = 0.01$). Changes in organic matter content within horizons (Fig. 3c) were also mostly insignificant (the A was significantly less massive in 1994 than 1979; $p = 0.04$).

Elevational Effects

At the HBEF, 58 to 87 samples were collected at each sampling date from elevations ranging from about 550 to 800 m. Concentrations of Pb invariably increased with elevation (Fig. 4b). Since forest floor mass (Fig. 4c) declines dramatically with elevation, however, the Pb contents of forest floors at high elevation were not always greater than those at low elevation (Fig. 4a). Lead contents were more often greater at high elevation at the earlier measurement dates, but this decrease over time in the slope of Pb content with elevation was at best modestly significant ($p = 0.08$).

In the 13 stands of the BEF and WMNF, elevations ranged from about 300 to 550 m. There were no significant relationships between elevation and Pb content or concentration, and the slopes of these regressions did not change significantly between 1979–1980 and 1994–1995 (data not shown).

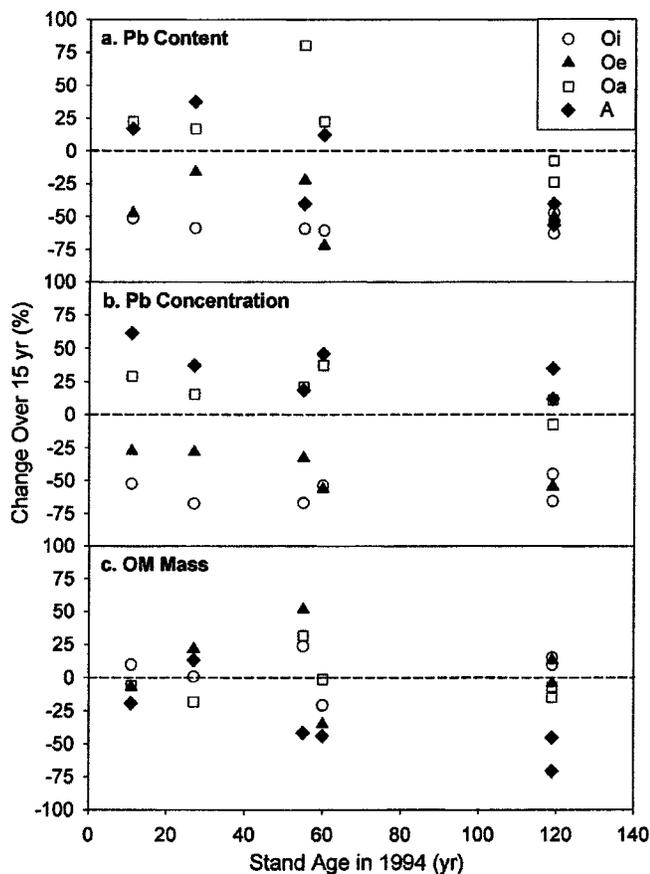


Fig. 3. Changes within stand in (a) Pb content, (b) Pb concentration, and (c) organic mass by horizon at Bartlett Experimental Forest measured in 1980 and 1995, plotted as a function of stand age.

DISCUSSION

The high affinity of organic matter for Pb was the basis for previous predictions that Pb would be retained in the forest floor for many decades. Steady state calculations of mean residence times treated the forest floor as a single pool (e.g., Friedland and Johnson, 1985; Turner et al., 1985), as did the more sophisticated calculation of mean response time based on time-varying inputs of Pb (Miller and Friedland, 1994). Consideration of dynamics within the forest floor provides a slightly different perspective on the potential for Pb to move through the soil profile. Early in the time period we studied, the highest concentrations of Pb were measured in the uppermost portions of the forest floor (Fig. 2), consistent with atmospheric sources of Pb and with other measurements taken from 1962 to 1981. But after Pb emissions were curtailed in 1977, the upper part of the forest floor was the locus of inputs of organic matter low in Pb, relative to the accumulations in the forest floor. The differentiation of horizons within the forest floor in our studies revealed that Pb is now concentrated deeper in the forest floor than it was two decades ago. By the end of our study period, the upper portions of the forest floor (Oie) had lower concentrations than the Oa-A, a reversal of the previous pattern (Fig. 2).

Much of the downward movement of Pb that we observed can be attributed to litter additions at the top of

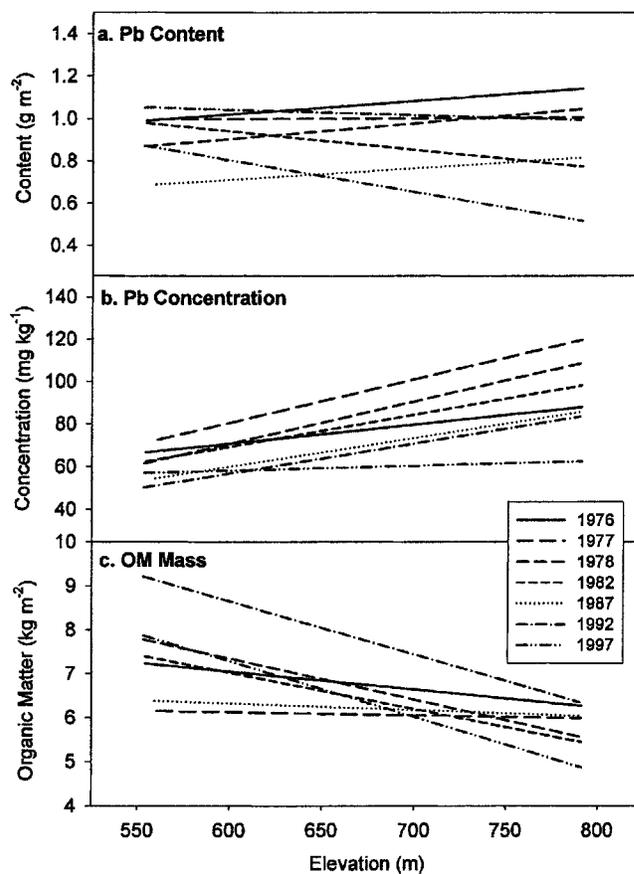


Fig. 4. Elevational patterns in (a) Pb content, (b) Pb concentration, and (c) organic mass of the forest floor in HBEF W-6 for seven sampling dates: 1976, 1977, 1978, 1982, 1987, 1992, and 1997.

the forest floor. Some may be due to migration of Pb in the soil solution or in particulate matter (Wang and Benoit, 1996). At Camel's Hump in Vermont, Pb has migrated from the forest floor into the upper 10 cm of the mineral soil (Kaste et al., 2003). At the HBEF, the Pb lost from the upper forest floor was not retained within the forest floor: the lower Oa-A remained about constant, and the Pb contents of the forest floor as a whole declined significantly from 1976 to 1997. In contrast, at the BEF sites, declines in concentrations of Pb in the Oi and Oe were compensated by significant increases in the Oa and A. Although the observed increases in Pb contents were not statistically significant in the Oa-A, they were sufficient to prevent detectable losses of Pb from the forest floor as a whole. Similarly small changes in Pb contents took place in forest floors of the additional WMNF sites. One difference between the HBEF and the other studies is that forest floor sampling commenced earlier, in 1976, instead of in 1979 or 1980. The most rapid losses of Pb at the HBEF occurred in the earliest portion of the record (Fig. 1). We can imagine that losses from the forest floor might have been greater at the BEF and WMNF sites if they had been sampled somewhat earlier.

Another difference between the HBEF and the BEF-WMNF sites, besides the timing of sampling, is their elevation. The greater Pb content of the forest floor at

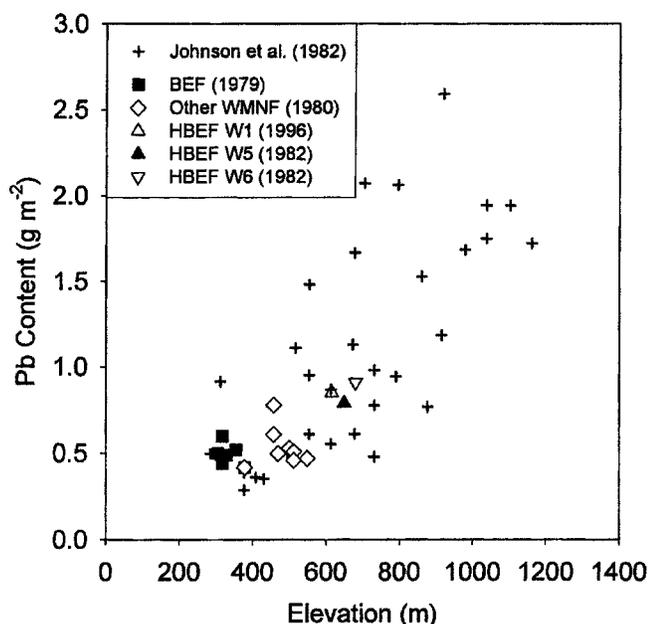


Fig. 5. Forest floor Pb content as a function of elevation for 32 stands reported by Johnson et al. (1982) and the 16 stands reported in this study.

Hubbard Brook is consistent with previous observations of forest floor Pb as a function of elevation in the Taconic, Green, and White Mountains (Johnson et al., 1982) (Fig. 5). The pattern of greater Pb in the forest floor at higher elevations is explained by greater wet and dry deposition velocities (Miller and Friedland, 1994). Within the HBEF sites, Pb concentrations increased significantly with elevation. The most surprising result is perhaps the absence of a consistent pattern in Pb content with elevation at HBEF, in spite of consistent increases in concentration. Similarly, in testing for patterns with time, concentrations of Pb changed more systematically than Pb contents. This raises questions about the consistency of forest floor sampling over time.

Variation in the organic mass of the forest floor could be due in part to environmental factors such as changes in organic matter inputs, occasioned by defoliation events, windstorms, or processes affecting root dynamics. Some of the variation, however, is probably due to measurement error, and specifically to the difficulty of distinguishing horizon boundaries in the field (Federer, 1982). The high organic mass of the forest floor collected at HBEF in 1992 (Fig. 1c; Table 1) is probably due to sampling under wet conditions, as it is more difficult to see mineral grains in moist samples (Yanai et al., 1999).

When monitoring change over time in the forest floor, the choice of concentration or contents as the indicator variable depends on the depth distribution of the element in question. When concentrations vary dramatically with depth, it is possible to introduce spurious but statistically significant changes over time in elemental concentrations merely by sampling to different depths (Yanai et al., 1999). In the case of Pb, since concentrations are similar in the upper and lower portions of the forest floor (Fig. 2b), variation in the depth of samples collected has a greater effect on Pb contents, and Pb

concentration values are less sensitive to variation in sampling methods. Indeed, Pb concentrations were more consistent than Pb contents in our data sets (Fig. 1–4, comparing a and b). For elements that decline with depth in the forest floor, such as C, N, P and exchangeable bases, contents will be less sensitive to sampling error than concentrations. Since it is far easier to collect “grab” samples for chemical analysis than “quantitative” samples for calculation of contents, concentration may be the better parameter for future monitoring of the fate of Pb in the forest floor.

In the future, we can anticipate that the upper portions of the forest floor will continue to decline in Pb content and concentration, as litter low in Pb is added to the surface. In the sites we studied, peak concentrations of Pb are now in the Oa horizon, in contrast to two decades ago, when Pb concentrations were highest at the surface. The fate of Pb in the Oa horizon is linked to humus decomposition and complexation; the rate of loss of Pb from the forest floor could provide insight into the dynamics of C cycling as well as that of heavy metals.

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