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Forest floor lead, copper and zinc concentrations across the northeastern United States: Synthesizing spatial and temporal responses

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HIGHLIGHTS

• We present forest floor Pb, Cu, and Zn concentrations from 16 sites over 30 yrs.
• We modeled forest floor Pb, Cu, and Zn at 16 sites and from 17 additional studies.
• Lead concentrations decreased at 1.1% per year after removal from gasoline.
• Copper and Zn decreases are less clear due to continued deposition or biocycling.

ARTICLE INFO

ABSTRACT

Understanding how metal concentrations in soil have responded to reductions of anthropogenic emissions is essential for predicting potential ecosystem impacts and evaluating the effectiveness of pollution control legislation. The objectives of this study were to present new data and synthesize existing literature to document decreases in Pb, Cu, and Zn concentrations in forest soils across the northeastern US. From measurements at 16 sites, we observed that forest floor Pb, Cu, and Zn concentrations have decreased between 1980 and 2011 at an overall mean rate of $1.3 \pm 0.5\%$ yr^{-1}. E-folding times, a concentration exponential decay rate $(1/k)$, for Pb, Cu and Zn at the 16 sites were estimated to be 46 ± 7, 76 ± 20 and 81 ± 19 yr, respectively. Mineral soil concentrations were correlated with forest floor concentrations for Pb, but not for Cu and Zn, suggesting an accumulation in one pool does not strongly influence accumulation in the other. Forest floor Pb, Cu and Zn concentrations from our sites and 17 other studies conducted from 1970–2014 in remote forests across the northeastern US were compiled into pooled data sets. Significant decreasing trends existed for pooled forest floor Pb, Cu, and Zn concentrations. The pooled forest floor Pb e-folding time was determined to be 33 ± 9 yrs, but the explanatory power of pooled Cu and Zn regressions were inadequate for calculating e-folding times ($r^2 < 0.25$). Pooled Pb, Cu, and Zn concentrations in forest floor were multiple-regressed with latitude, longitude, elevation, and year of sampling, cumulatively explaining 55, 38, and 28% of the variation across compiled studies. Our study suggests anthropogenic Pb in the forest floor will continue to decrease, but decreases in forest floor Cu and Zn concentrations may be masked by spatial heterogeneity or are at a new steady state.

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1. Introduction

Human activities have drastically altered the natural cycling of many trace metals in terrestrial environments (Steinnes and Friedland, 2006; Schlesinger and Bernhardt, 2013). In particular, lead (Pb), copper (Cu), and zinc (Zn) have been widely emitted as air pollutants from automobile, municipal, and industrial sources, enriching their concentrations in rural and remote terrestrial ecosystems across the US (Galloway et al., 1980; Shacklette and Boerngen, 1984; Nriagu 1990; Smith et al., 2014) and globally (Galloway et al., 1982; Nriagu and Pacyna, 1988; Rauch and Pacyna, 2009). Monitoring trace metal concentrations in the forest floor (Oi + Oe + Oa horizons) in the northeastern US has been done, because of the possible deleterious effects on organisms and as a tracer of natural processes. Forest floor Pb, Cu and Zn concentrations of 100–300 mg kg^{-1} have been considered too low to negatively impact vegetation and microorganisms (Buchauer, 1973; Johnson et al., 1982; Friedland et al., 1984; Sharma and Dubey, 2005; Johnson and Richter, 2010). However, terrestrial bioaccumulation of potentially hazardous amounts of Pb can be attained by biotas that consume soil organic
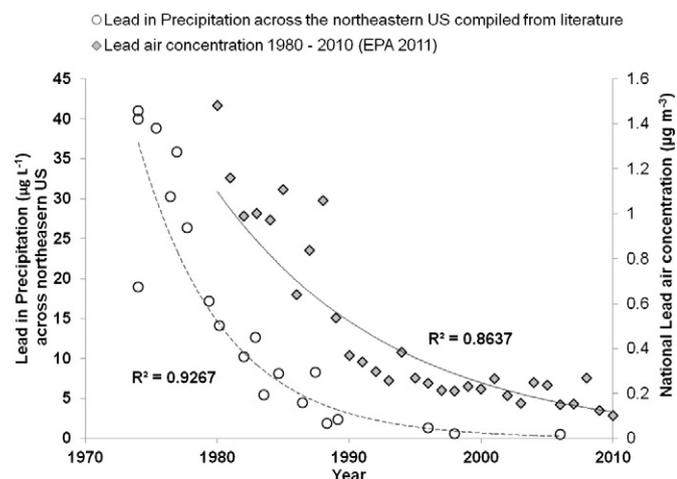
Fig. 1. The concentration of Pb in precipitation from across the northeastern US and the National Lead air concentration modeled with exponential regression. Data are from Chan et al. (1976), Smith et al. (1986), Pike and Moran (2001), Lawson et al. (2003) and Song and Gao (2009). National Lead Air concentration data are from USEPA National Air Quality data available at www.epa.gov/airquality/lead,accessed 27/3/2014 (c.f. US EPA, 2011).

matter (SOM), such as earthworms (Ernst et al., 2008). Thus, continued monitoring is still required to determine the effect on wildlife health.

Understanding how forests have responded to reductions of anthropogenic emissions is essential for determining ecosystem impacts and evaluating the effectiveness of pollution control legislation. Lead emissions have been specifically targeted by the Clean Air Act Amendments of 1970 (84 Stat. 1676, P.L. 91–604) and the 1990 Clean Air Act Amendments (104 Stat. 2468, P.L. 101–549). The removal of tetra-ethyl Pb from gasoline decreased Pb concentrations in the atmosphere across the United States (Galloway et al., 1982; Nriagu and Pacyna, 1988;

Rauch and Pacyna, 2009) (Fig. 1). Lead concentration in precipitation has decreased substantially (Fig. 1). This decline in precipitation concentration was accompanied by a similar decline in Pb atmospheric deposition rates (Table 1). For example, Pb deposition rates at HBEF fell from 352 g m^{-2} yr^{-1} in 1976 to 57 g m^{-2} yr^{-1} in 1983 (Table 1). These reductions highlight the success of the Clean Air Act Amendments. Although Cu and Zn emissions have not been explicitly targeted for reduction by the US EPA (c.f. US EPA, 2011), their deposition rates have also decreased across the northeastern US. From Lazrus et al. (1970) and Smith et al. (1986), Cu and Zn deposition rates in the northeastern US have decreased an order of magnitude, from 160–1200 g ha^{-1} yr^{-1} in 1966 to 17–76 g ha^{-1} yr^{-1} in 1983 (Table 1). The decreases in deposition rates could have arisen from decreased industrial processing in the region, increased regulation on particulate matter emission, combustion of coal with fewer trace metals, or the use of improved technologies in the aforementioned activities (Nriagu and Pacyna, 1988; Rauch and Pacyna, 2009). Thus, it was hypothesized that Cu and Zn in forest ecosystems of this region would decrease as well.

Repeated measurements of forest floor Pb, Cu, and Zn concentrations have been one of the most common methods to document the effect of atmospheric deposition to forests soils (e.g. Siccama and Smith, 1980; Kaste et al., 2006; Yanai et al., 2004; Evans et al., 2005; Johnson and Richter, 2010; Richardson et al., 2014). The documentation of Pb, Cu, and Zn concentrations in the forest floor in the northeastern US by multiple investigators at different times and locations offers a possibility to detect large scale changes (e.g. Friedland et al., 1992; Richardson et al., 2014). The use of a single location or set of sites may not fully elucidate these larger, regional trends. Recent studies have suggested metals, particularly Pb, are not decreasing in soils across the United States in urban and suburban/rural areas, presumably because of the stability of Pb binding with soil and organic matter particles (Semlali et al., 2004; Mielke et al., 2011; Datko-Williams et al., 2014). The purposes of this study are: 1) to present new forest floor Pb, Cu, and Zn data and analyses; and (2) synthesize existing literature on forest floor concentrations across the northeastern US to quantify the response of remote forest ecosystems to decreasing emissions and atmospheric deposition.

2. Methods

2.1. Description of study areas

The forest floor was studied at forest sites that had been established in 1980 as part of two larger studies on metals in the forest floor (Johnson et al., 1982). Sixteen of the original forest sites were re-sampled in 1990, 2002, and 2011 (Richardson et al., 2014) (Fig. 2). Vegetation at each site ranged from predominantly northern hardwoods (*Quercus* spp., *Fagus grandifolia*, *Acer* spp., *Betula* spp.) to predominantly conifers (*Pinus* spp., *Picea* spp., *Tsuga canadensis*) (Table 2). The soils sampled were developed from glacial till, outwash deposits, and outcrops (Siccama, 1974; Andresen et al., 1980). Soils ranged in development, (Inceptisols, Spodosols and Ultisols) and in mean annual soil temperature (mesic and frigid) (Table 2). Soils were well-drained to excessively-drained and on slopes less than 11%. Additional soil information of the study sites is available in Richardson et al. (2013, 2014).

2.2. Sample collection

The re-sampling of the sixteen upland forest sites occurred between July and early-October in 1990, 2002 and 2011 (Friedland et al., 1992; Kaste et al., 2006; Richardson et al., 2014) (Fig. 2). The forest floor at each site was sampled in the same 30 × 30 m^2 plot and roughly the same months (Johnson et al., 1982; Friedland et al., 1986, this study). Five forest floor samples were collected from each site. Information regarding the sampling methods can be found in Andresen et al. (1980) and Johnson et al. (1982). In brief, five 15 × 15 cm^2 square sections of

Table 1
Atmospheric deposition rates of Pb, Cu and Zn in precipitation from Lazrus et al. (1970) and Smith et al. (1986).

Study	Metal	Location	Deposition rate g ha^{-1} yr^{-1}	Year sampled
Lazrus et al. (1970)	Pb	Nantucket, MA	850	1966
	Pb	Albany, NY	430	1966
	Pb	Caribou, ME	440	1966
Smith et al. (1986)	Pb	Hubbard Brook, NH	352	1975
	Pb	Hubbard Brook, NH	359	1976
	Pb	Hubbard Brook, NH	195	1977
	Pb	Hubbard Brook, NH	141	1978
	Pb	Hubbard Brook, NH	155	1979
	Pb	Hubbard Brook, NH	70	1982
	Pb	Hubbard Brook, NH	57	1983
Lazrus et al. (1970)	Cu	Nantucket, MA	564	1966
	Cu	Albany, NY	168	1966
	Cu	Caribou, ME	276	1966
Smith et al. (1986)	Cu	Hubbard Brook, NH	18	1975
	Cu	Hubbard Brook, NH	12	1976
	Cu	Hubbard Brook, NH	10	1977
	Cu	Hubbard Brook, NH	26	1978
	Cu	Hubbard Brook, NH	16	1979
	Cu	Hubbard Brook, NH	14	1982
	Cu	Hubbard Brook, NH	17	1983
Lazrus et al. (1970)	Zn	Nantucket, MA	756	1966
	Zn	Albany, NY	1200	1966
	Zn	Caribou, ME	636	1966
Smith et al. (1986)	Zn	Hubbard Brook, NH	175	1975
	Zn	Hubbard Brook, NH	182	1976
	Zn	Hubbard Brook, NH	116	1977
	Zn	Hubbard Brook, NH	98	1978
	Zn	Hubbard Brook, NH	278	1979
	Zn	Hubbard Brook, NH	54	1982
	Zn	Hubbard Brook, NH	76	1983

Fig. 2. Location of 16 sites that were sampled in 1980, 1990, 2002 and 2011 in this study. Gray shaded areas are forested areas and non-shaded areas are urban areas, agricultural fields or water bodies. This map is derived from Blackard et al. (2008) map of contiguous U.S. Forest/Non-forest map available at by the United States Department of Agriculture Forest Service Survey at http://data.fs.usda.gov/geodata/rastergateway/biomass/.

forest floor were collected. Care was exercised in separating the forest floor from the underlying mineral soil and avoiding previously sampled points. A description of similar sampling methods and data of mineral soil inclusion in the forest floor depth is discussed in great detail in Richardson et al. (2014). In 2011, mineral soil samples were also collected from the upper-most mineral soil horizon when present, ca. 0–15 cm in depth. Forest floor and mineral soil samples from the regional sampling 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. A 4 g air-dried sub-sample was combusted at 475 °C for 8 h to estimate %SOM (g organic matter per g soil). For soil pH, 2:5 soil–water slurries were shaken for 1 h using a wrist-action shaker, vacuum extracted through a Whatman 40 filter and measured with an ion-selective electrode (8015 VWR).

2.3. Pb, Cu and Zn quantification

For the 1980, 1990, and 2002 forest floor samples, a 2 g sample was dry ashed at 475 °C for 6 h and then boiled in 1:1 HNO_3:H_2O solution on a hot plate (Johnson et al., 1982; Friedland et al., 1992; Kaste et al., 2006). The solution was filtered (Whatman 41), diluted with deionized water and analyzed with a SpectroFlame ICP-OES (SPECTRO Analytical Instruments, Kleve, Germany). We included a duplicate, a preparation blank, a sample spike, and a standard reference material (SRM) for every set of 20 samples. Recoveries for Pine Needles SRM 1575 from National Institute of Standards and Technology (NIST) and were within 10% of their certified values (NIST, Gaithersburg, MD, USA). Preparation blanks were <0.1% of the sample Pb, Cu, and Zn concentration.

For the 2011 forest floor and mineral soil samples, Pb, Cu, and Zn concentrations were measured using a strong-acid extraction following EPA method 3051A. In brief, 250 ± 1 mg sub-samples were digested with 5 mL of a 1:9 ratio of trace metal grade HCl:HNO_3 in 50 mL polypropylene centrifuge tubes (Fisher Scientific, Waltham, MA, USA). The resulting extract was microwave digested at 105 °C for 1 h using a CEM MARS microwave digestion system (CEM, Matthews, NC, USA). The digests were diluted with deionized water, filtered with a 2 μm syringe filter and analyzed with an Agilent 7500cx series inductively coupled plasma–mass spectrometer (Agilent Technologies, Santa

Table 2
Site location, vegetation type, soil taxonomy, and select forest floor properties.

Site	Site name	Elevation (m)	Latitude	Longitude	Vegetation	Soil Great Group[a]	Forest floor depth (cm)	% SOM (g g^{-1})	pH
1	Heart's Content,PA	580	41.689	−79.252	Pine/Hemlock	Dystrudepts	4 ± 1	51 ± 5	4.04 ± 0.03
2	Cook's Forest, PA	430	41.347	−79.212	Pine/Hemlock	Dystrudepts	4 ± 1	62 ± 5	4.22 ± 0.09
3	Tionesta, PA	520	41.477	−79.379	Oak	Hapludults	2 ± 1	43 ± 4	5.17 ± 0.10
4	Balsam Lake, NY	820	42.067	−74.574	N. Hardwood	Dystrudepts	4 ± 1	61 ± 8	4.52 ± 0.09
5	Mohonk, NY	366	41.770	−74.158	N. Hardwood	Dystrudepts	7 ± 2	71 ± 4	4.14 ± 0.08
6	Mt. Tremper, NY	305	42.071	−74.312	Pine/Hemlock	Fragiudepts	8 ± 1	66 ± 5	4.61 ± 0.13
7	Windham, NY	580	42.301	−74.170	N. Hardwood	Fragiudepts	10 ± 1	71 ± 4	3.99 ± 0.09
8	Mohawk, CT	503	41.820	−74.297	Oak	Dystrudepts	8 ± 1	50 ± 6	4.08 ± 0.07
9	Mt. Everett, MA	790	42.102	−73.431	Oak/Pitch Pine	Dystrudepts	10 ± 1	84 ± 2	4.13 ± 0.08
10	Sherburne Pass, VT	671	43.662	−72.833	N. Hardwood	Haplorthods	5 ± 1	55 ± 6	3.99 ± 0.07
11	Bromley, VT	625	43.214	−72.967	N. Hardwood	Haplorthods	19 ± 4	72 ± 7	3.92 ± 0.05
12	Bristol Cliffs, VT	555	44.140	−73.064	Pine/Hemlock	Haplorthods	9 ± 2	77 ± 4	3.81 ± 0.12
13	Mt. Cardigan, NH	579	43.645	−71.933	Spruce/Hemlock	Haplorthods	5 ± 1	80 ± 3	4.21 ± 0.04
14	Valley Way, NH	433	44.369	−71.287	Spruce/N. Hardwood	Haplorthods	12 ± 3	77 ± 5	4.00 ± 0.07
15	Gale River, NH	440	44.232	−71.608	N. Hardwood	Haplorthods	5 ± 1	73 ± 6	4.02 ± 0.04
16	Wildcat Mt, NH	590	44.266	−71.238	Spruce/N. Hardwood	Dystrudepts	22 ± 8	73 ± 6	3.87 ± 0.04

[a] Based on USDA Soil Taxonomy.

Table 3

Mean Cu and Zn forest floor concentration data at each site with standard error in within parentheses. The r^2, k and t_{efold} values are calculated from exponential regression of Cu and Zn concentration through time for each site.

	1980	1990	2002	2011	r^2	k	t_{efold}
	Cu (mg kg^{-1})					yrs^{-1}	yrs
Heart's Content, PA	13.8 (1.5)	15.4 (0.9)	9.3 (1.5)	8.8 (1.7)	0.76	0.018	56
Cook Forest, PA	11.6 (1.7)	11.0 (1.6)	2.8 (0.8)	9.8 (1.4)	0.26	0.020	50
Tionesta, PA	7.8 (1.2)	10.1 (0.8)	5.2 (0.8)	10.0 (1.1)	0.00	0.000	–
Balsam Lake, NY	13.8 (0.6)	11.3 (0.8)	6.0 (0.6)	11.0 (0.6)	0.26	0.013	77
Mohonk, NY	15.2 (1.2)	12.4 (0.5)	11.6 (1.8)	10.9 (1.0)	0.91	0.010	100
Mt Tremper, NY	10.4 (0.9)	14.4 (3.8)	14.9 (9.6)	8.5 (3.2)	0.26	0.005	200
Windham, NY	35.4 (4.4)	18.1 (2.0)	17.4 (2.0)	10.6 (0.9)	0.93	0.037	27
Mohawk, CT	21.6 (3.9)	16.0 (2.5)	15.9 (1.2)	13.4 (7.5)	0.86	0.014	71
Mt. Everett, MA	26.2 (2.2)	24.0 (2.6)	13.2 (3.5)	10.0 (7.0)	0.95	0.033	30
Sherburne Pass, VT	12.8 (1.0)	12.3 (1.3)	5.2 (1.3)	2.3 (0.6)	0.91	0.059	17
Bromley, VT	13.2 (1.1)	22.0 (8.1)	8.6 (1.9)	2.2 (0.5)	0.67	0.059	17
Bristol Cliffs, VT	11.6 (0.5)	9.9 (0.9)	6.7 (0.9)	5.8 (0.8)	0.98	0.024	42
Mt Cardigan, NH	9.6 (1.9)	12.1 (2.0)	9.2 (5.3)	6.4 (0.6)	0.53	0.014	71
Valley Way, NH	10.6 (1.0)	9.0 (0.9)	11.5 (2.9)	8.6 (3.2)	0.25	0.003	333
Gale River, NH	8.0 (1.6)	9.9 (0.7)	6.5 (1.0)	4.2 (0.9)	0.69	0.022	45
Wildcat Mt, NH	12.6 (1.6)	7.4 (0.8)	11.0 (1.0)	3.2 (0.7)	0.55	0.034	29
	Zn (mg kg^{-1})					yrs^{-1}	yrs
Heart's Content, PA	95 (8)	89 (11)	60 (5)	49 (8)	0.95	0.022	45
Cook Forest, PA	96 (7)	47 (5)	49 (5)	48 (7)	0.57	0.019	53
Tionesta, PA	52 (7)	94 (16)	82 (2)	85 (15)	0.25	0.013	79
Balsam Lake, NY	109 (12)	74 (19)	38 (6)	45 (6)	0.85	0.032	31
Mohonk, NY	127 (24)	51 (2)	40 (4)	46 (2)	0.68	0.032	31
Mt Tremper, NY	113 (9)	129 (8)	132 (8)	112 (13)	0.00	0.000	–
Windham, NY	99 (5)	82 (8)	68 (8)	56 (6)	1.00	0.018	56
Mohawk, CT	67 (6)	65 (5)	63 (3)	59 (5)	0.92	0.004	250
Mt. Everett, MA	119 (7)	65 (12)	47 (7)	60 (4)	0.63	0.023	43
Sherburne Pass, VT	108 (17)	64 (10)	47 (10)	31 (2)	0.99	0.039	26
Bromley, VT	82 (14)	129 (57)	50 (10)	31 (6)	0.67	0.037	27
Bristol Cliffs, VT	92 (10)	68 (14)	42 (5)	64 (8)	0.45	0.016	63
Mt Cardigan, NH	88 (19)	90 (25)	67 (10)	79 (4)	0.40	0.006	167
Valley Way, NH	59 (9)	75 (4)	41 (2)	44 (9)	0.54	0.015	67
Gale River, NH	49 (12)	65 (4)	35 (9)	77 (15)	0.05	0.001	–
Wildcat Mt, NH	54 (7)	68 (6)	48 (5)	53 (9)	0.26	0.004	250

Clara, CA, USA). We included a duplicate, a preparation blank, a sample spike, and a standard reference material for every 20 samples. We used NIST 1547 Peach Leaves for forest floor, and NIST 2711 Montana Soil for mineral soil standard reference materials, respectively. All Pb, Cu, and Zn concentrations for SRMs were within 10% of their certified values. Intra-sample variation was < 10%. Preparation blanks had Pb, Zn, and Cu concentrations <1 μg kg^{-1}. To ensure the Pb, Cu, and Zn ICP-MS results were comparable with previous ICP-OES methods, concentrations were also determined for the 2011 forest floor samples using the previous method of hot plate digestion and ICP-OES analysis. Measured Pb, Cu, and Zn values from the ICP-MS were plotted with ICP-OES values for each sample and yielded slopes of 0.92–0.96 with r^2 values > 0.92 and p-values < 0.01 (data not shown). Lead concentrations for the sites can be found in Richardson et al. (2014) and Cu and Zn concentrations are given in Table 3. Mineral soil Cu and Zn concentrations are given in Table 4. From these data, we are confident that our new digestion method and previous digestion method have produced similar quantitative measurements.

Table 4

Copper and Zinc concentrations and select soil properties at our 16 sites.

Site	Site name	Mineral soil Cu	Mineral soil Zn	Mineral soil depth interval	% SOM	pH
		mg kg^{-1}	mg kg^{-1}	cm	(g g^{-1})	
1	Heart's Content,PA	4(1)	30(10)	0–5	19 ± 2	3.72 ± 0.10
2	Cook's Forest, PA	2(1)	14(4)	0–4	8 ± 1	3.93 ± 0.04
3	Tionesta, PA	13(1)	106(9)	0–4	8 ± 1	3.51 ± 0.02
4	Balsam Lake, NY	3(1)	14(2)	0–6	14 ± 3	3.69 ± 0.04
5	Mohonk, NY	35(30)	21(5)	0–5	10 ± 1	3.71 ± 0.06
6	Mt. Tremper, NY	2(1)	10(3)	0–6	6 ± 2	4.03 ± 0.14
7	Windham, NY	6(1)	45(1)	0–7	32 ± 1	4.14 ± 0.14
8	Mohawk, CT	36(7)	25(4)	0–6	7 ± 4	3.69 ± 0.23
9	Mt. Everett, MA	104(47)	52(9)	0–6	10 ± 7	4.10 ± 0.16
10	Sherburne Pass, VT	6(1)	20(2)	0–6	17 ± 3	3.96 ± 0.10
11	Bromley, VT	14(1)	34(18)	0–6	13 ± 1	4.06 ± 0.02
12	Bristol Cliffs, VT	3(1)	6(2)	0–7	8 ± 3	3.71 ± 0.18
13	Mt. Cardigan, NH	4(1)	4(1)	0–5	4 ± 2	5.17 ± 0.02
14	Valley Way, NH	6(4)	5(2)	0–5	7 ± 1	4.28 ± 0.07
15	Gale River, NH	5(2)	10(2)	0–8	5 ± 1	3.78 ± 0.02
16	Wildcat Mt, NH	5(2)	8(4)	0–8	3 ± 1	3.71 ± 0.07

2.4. Literature compilation

Forest floor Pb, Cu, and Zn data from this study was compiled with forest floor concentration, latitude, longitude, elevation, and year of sampling data from other published sources (Supplemental Tables 1, 2 and 3) to form pooled data sets. In total, the pooled data sets for Pb, Cu, and Zn consisted of 174, 115, and 131 site collections, respectively. Many sites were sampled on multiple occasions through time. Field collection and analytical measurement techniques of Pb, Cu, and Zn were comparable to our methods used: multiple forest floor samples collected as a whole unit down to the mineral soil, oven-dried, homogenized, strong acid-digested and analyzed by flame atomic absorption spectrophotometry, graphite furnace atomic absorption spectrophotometry, or ICP-OES.

2.5. Statistical analyses

Descriptive statistics for Pb and soil properties were calculated using Matlab (Mathworks Inc, Natick, MA, USA). In the text and figures, mean values are given ± 1 standard error. Forest floor Pb, Cu, and Zn concentrations from the 16 sites and the pooled forest floor Pb, Cu, and Zn concentration data sets were plotted and individually regressed with sampling year by an exponential model (cf. Supplemental Figs. 1 and 2). The e-folding time, (t_{efold}) is defined in Eq. (1) as an interval of time required for a metal concentration to decrease to steady state after an initial pulse, analogous to a concentration exponential decay rate. Assuming the decrease in concentration in the forest floor can be described with Eq. (2) based on analyses following Miller and Friedland (1994) and Richardson et al. (2014), we can determine the e-folding time by substituting in Eq. (1) into Eq. (2) to create Eq. (3). The solution to Eq. (3) is Eq. (4), which states that the slope of the exponential regression, k, can be used to estimate the e-folding time (t_{efold}). Using these assumptions, t_{efold} then approximates the time required for the forest floor metal concentration to return to steady state following a single-event pulse.

$$\frac{1}{e} = \frac{\left[Metal_{t_{efold}} \right]}{\left[Metal_{pulse} \right]} \tag{1}$$

$$\left[Metal_{t_{efold}} \right] = \left[Metal_{pulse} \right] e^{-kt_{efold}} \tag{2}$$

$$\frac{1}{e} = e^{-kt_{efold}} \tag{3}$$

$$\frac{1}{k} = t_{efold} \tag{4}$$

We did not calculate t_{efold} values for exponential regressions with $r^2 < 0.25$ (Table 3) because of their low explanatory power. Digital elevation maps (1 − arc sec) was gathered from the USGS National Map Viewer (Gesch et al., 2009; http://nationalmap.gov/index.html) and forest cover maps were obtained from the USDA Forest Service (Blackard et al., 2008, http://data.fs.usda.gov/geodata/rastergateway/biomass/). For all regressions, Pb, Cu, and Zn concentrations were logarithmically-transformed to achieve a normal distribution and reduce the influence of outliers. Pooled forest floor Pb, Cu, and Zn concentrations were spatially interpolated using latitude (1 − arc sec, decimal degrees), longitude (1 − arc sec, decimal degrees), elevation (1 − arc sec, meters) and forest cover (1 − arc sec, forest/nonforest) rasters.

3. Results

3.1. Forest floor Lead, Copper, and Zinc through time at the 16 sites

The change in forest floor Pb at the 16 sites is described in detail in Richardson et al. (2014). In brief, the forest floor Pb concentration decreased significantly between 1980 and 2011 at 14 of the 16 sites, with an average concentration reduction of 52% ± 5% (Richardson et al., 2014). The annual % change in Pb concentration was calculated to be −2.0% ± 0.3% yr^{-1} across the 16 sites. The mean forest floor Cu concentration, 7.9 ± 0.9 mg kg^{-1} in 2011, was significantly less than 14.6 ± 1.8 mg kg^{-1} in 1980 ($p < 0.05$). Forest floor Cu concentrations decreased significantly over three decades at 9 of the 16 sites with an average decrease of 41% ± 7% at an overall rate of −1.1 ± 0.7% yr^{-1}. Forest floor Zn concentrations decreased at 10 of the 16 sites from a mean of 88 ± 6 mg kg^{-1} in 1980 to 57 ± 5 mg kg^{-1} in 2011 ($p < 0.05$). The average forest floor Zn concentration decrease was 27% ± 10% at an overall rate of −0.8 ± 0.6% yr^{-1}. The average mineral soil concentrations were 63 ± 12 mg Pb kg^{-1}, 15 ± 6 mg Cu kg^{-1} and 24 ± 6 mg Zn kg^{-1}; concentrations at each site are given in Table 4. Forest floor concentrations of Cu and Zn were significantly decreased at our 16 sites. However, were inadequate to assign a t_{efold} values for since the correlations were weak ($r < 0.50$) and the trends had less than 50% explanatory power ($r^2 < 0.25$).

The change in forest floor Pb, Cu and Zn concentrations at the 16 sites with exponential regressions are plotted in Supplemental Fig. 1. E-folding times ($1/k$) for Pb, Cu and Zn at the 16 sites were estimated to be 46 ± 7 yr, 76 ± 20 yr and 81 ± 19 yr, respectively. Forest floor Cu and Zn concentrations in 2011 were compared with elevation, longitude, soil pH or % SOM using linear regression, but were not significant. Forest floor Cu concentrations in 2011 were negatively correlated with latitude ($r^2 = 0.55$, $p < 0.01$). Lead t_{efold} was correlated with forest floor thickness ($r^2 = 0.42$, $p < 0.01$) and site latitude ($r^2 = 0.31$, $p < 0.05$) (Richardson et al., 2014). Zinc t_{efold} values were not correlated with site location or soil properties. Copper t_{efold} values were negatively correlated with % soil organic matter ($r^2 = 0.28$, $p < 0.05$) but positively correlated with forest floor pH ($r^2 = 0.64$, $P < 0.01$). Forest floor Cu concentrations in 2011, Zn concentrations in 2011, Zinc t_{efold} and Copper t_{efold} values generally were poorly explained by site characteristics and soil properties (Supplemental Table 4), suggesting additional properties not quantified are important for their accumulation and retention (discussed later in Section 4.2).

3.2. Forest floor Lead, Copper and Zinc through time across compiled studies

Pooled forest floor Pb, Cu and Zn concentrations between 1972 and 2010 were compared with year-sampled using an exponential model (Supplemental Fig. 2). Exponential regressions for Pb, Cu and Zn were significant, although year-sampled explained only > 25% of the variation for Pb (Supplemental Fig. 2). Using this regression, a t_{efold} for the pooled forest floor Pb concentrations across the northeastern US from the compiled literature was 33 ± 9 yrs (Supplemental Fig. 2). Pooled forest floor Pb, Cu and Zn concentrations were logarithmically-transformed and regressed with latitude, longitude, elevation and year-sampled to create a basic spatial estimate through time. The r values and p values for each regression and the multiple-regressions are given in Supplemental Table 5. Using the pooled data set, model coefficients for the multiple-regressions with Pb, Cu and Zn are given in Eqs. (5), (6) and (7), respectively. Spatial interpolations were created using Eqs. (5)–(7) with rasters of latitude (decimal degrees), longitude (decimal degrees), elevation (meters) and forest cover for 1980 and 2010 using the Map Algebra function in ArcGIS.

$$Log_{10}\left(Pb \ mg \ kg^{-1} \right) = 0.0004 Elevation - 0.0667 Latitude - 0.0086 Year + 21.6$$
$$r^2 = 0.55, p < 0.001$$
$$\tag{5}$$

$$Log_{10}\left(Cu\ mg\ kg^{-1}\right) = -0.0001 Elevation - 0.1022 Latitude$$
$$-0.00634 Longitude - 0.0342 Year + 20.7 \quad (6)$$

$r^2 = 0.39, p<0.001$

$$Log_{10}\left(Zn\ mg\ kg^{-1}\right) = 0.0002 Elevation - 0.0087 Year + 19.2 \quad (7)$$
$r^2 = 0.28, p<0.01$

From the spatial and temporal multiple regressions, the highest forest floor Pb and Cu concentrations occur in Pennsylvania, New Jersey, Connecticut, Rhode Island, and Massachusetts. In addition, Pb concentrations were moderately high in areas of high elevation in northern New York, Vermont and New Hampshire. Forest floor Zn concentrations were highest at lower elevations, coinciding with metropolitan areas and northern hardwood forests.

4. Discussion

4.1. Changes in forest floor Lead, Copper and Zinc concentrations

The removal of tetra-ethyl lead from gasoline caused a gradual decrease in forest floor Pb concentrations across the entire northeastern US, and was reflected in data from our study sites, and with the pooled data set. Forest floor Pb concentrations at our 16 sites had a t_{efold} of 46 ± 7 yr, which is significantly longer than 33 ± 9 yrs t_{efold} calculated for the compiled literature. The pooled forest floor Pb concentrations data set has a much shorter t_{efold}, possibly as an artifact of the sampling location and time. The Pb pooled data set includes studies from the 1970s, which generally had greater Pb concentrations because the studies coincided with higher deposition rates and were conducted at higher elevations compared to data from our 16 sites. Decreases in forest floor Cu and Zn concentrations through time were markedly slower and less clear, but significant at our 16 sites and in the pooled data sets. Although not explicitly limited by US EPA regulations, Cu and Zn deposition has been decreasing from reduced regional industrial processing, stricter regulations on combustion of coal and improved technologies controlling particulate matter emissions have likely driven this trend (Nriagu and Pacyna, 1988; Rauch and Pacyna, 2009). However, particulate emissions of Pb, Cu, and Zn from automobiles are unlikely to have decreased (Harrison et al., 1981; Sternbeck et al., 2002; Datko-Williams et al., 2014).

The accumulation of anthropogenic Pb in the mineral soil has been well-document by previous studies (e.g. Smith and Siccama, 1981; Miller and Friedland, 1994; Johnson et al., 1995; Kaste et al., 2003; Richardson et al., 2014). Anthropogenic Pb, commonly bound to organic and mineral colloids, moves from the forest floor to the mineral soil (Friedland and Johnson, 1985; Johnson and Petras, 1998; Kaste et al., 2003; Klaminder et al., 2006; Schroth et al., 2008). Similar mechanisms likely control the transport of plant-essential metals such as Cu and Zn (Johnson and Petras, 1998; Kaste et al., 2011). Mineral soil concentrations were significantly correlated with forest floor concentrations for Pb ($p < 0.05$, $r^2 = 0.32$), but not for Cu ($p = 0.35$, $r^2 = 0.09$) or Zn ($p = 0.64$, $r^2 = 0.03$). Lead in the mineral soil is coupled to forest floor Pb because the forest floor is a dominant source of this element. However, Cu and Zn concentrations in the forest floor and mineral soil were poorly correlated, suggesting accumulation in the forest floor and mineral soil are independent. The poor correlations could have arisen from a new steady state of Cu and Zn in the ecosystem or varying sorption and retention in the mineral soil. Although leaching from the forest floor is considered the dominant process responsible for decreasing Pb concentrations, it may not be as important for Cu and Zn due to biological cycling (uptake from the forest floor, incorporation in tissue, and return to the forest floor as litter) or other site characteristics and soil properties. Copper and Zn share many geochemical properties;

both are generally found in the 2^+ valence state and are chalcophilic elements commonly found sorbed or precipitated with sulfides (Adriano, 2001). Thus, Cu and Zn can be sourced from sulfide minerals in metamorphic and sedimentary rocks of the region and be retained in the soil bound to thiol groups in organic matter (Adriano, 2001). However, the acidity (commonly soil pH < 4.0) and low clay amounts in the soils of this region would depress sorption in the forest floor and mineral soil. Moreover, the poor correlation between forest floor and mineral soil concentrations for Cu and Zn suggest weathering of geologic material in the soil is unlikely controlling forest floor concentrations.

Uptake of Pb by vegetation has been estimated to be small compared to soil pools and leaching rates (Klaminder et al., 2006), suggesting that its redistribution back to the surface is negligible. In contrast, Cu and Zn are essential for plant nutrition and are rapidly cycled through soil and vegetation (Heinrichs and Mayer, 1980; Li et al., 2008; Johnson and Richter, 2010). It is possible that uptake by vegetation is responsible for the incorporation of pollutant Cu and Zn into the existing forest biogeochemical cycle. This may explain the slow decreases in concentration through time at our 16 study sites (Supplemental Fig. 1) and the overall weak trends for pooled forest floor Cu and Zn concentrations through time (Supplemental Fig. 2). The role of biological cycling may be enhanced at certain sites because common trees genera, such as *Betula* spp. and *Populus* spp., are known metal bioaccumulators and retain more Cu and Zn in their ecosystem (Siccama and Smith, 1980; Migeo et al., 2009). Moreover, other edaphic soil properties, such as mineral soil concentrations and soil parent material, could mask decreases in Cu and Zn concentrations in the forest floor. For example, mineral soil Cu and Zn concentrations at our sites ranged from 1.2–198 mg kg^{-1} and 4.8–126 mg kg^{-1}, respectively. This could shift the uptake of Cu and Zn from the forest floor and mineral soil, depending on their relative concentrations.

An underlying assumption linking changes in forest floor Pb, Cu, and Zn concentrations to trends in regional atmospheric deposition is that the forests are near steady state, in which uptake rates are equal to litterfall rates. However, this may not be true for many sites. Litterfall from vegetation could increase or decrease forest floor metal concentrations through input and dilution, respectively. Litterfall concentrations of Cu and Zn in northeastern US are of a similar magnitude to concentrations found in the forest floor: Cu = 5–10 and 20–300 mg Zn kg^{-1} (Rea et al., 2002). Although forest floor Cu, and especially, Zn concentrations can be heavily influenced by litterfall concentrations, we did not observe increasing forest floor concentrations. Moreover, changes in litterfall contributions or belowground biological processes such as root uptake could affect the forest floor Cu and Zn concentration.

Conversely, dilution occurs through addition of biomass with low concentrations of Pb, Cu, and Zn to the existing pool while maintaining the inventory of previously contained metals. Forest floor dry weight mass was significantly greater in 2011 than 1980 ($p < 0.01$) at 10 of the 16 sites in this study, but was not correlated with significant decreases in Pb, Cu, and Zn concentrations ($r^2 < 0.25$, $p > 0.05$). This suggests dilution may have contributed, but did not drive decreases in forest floor concentrations of Pb, Cu, and Zn. Moreover, the dilution effect may be most important for Pb, because new litterfall has a negligible concentration of Pb, but less important for Cu and Zn because litterfall still contains appreciable amounts of these metals. Lead concentrations in the Oi horizon reported in Friedland et al. (1984) ranged from 65–225 mg kg^{-1} while Oi horizons ranged from 5–19 mg kg^{-1}. For Cu and Zn, however, reported Oi concentrations are similar for Friedland et al. (1984), with values ranging from 8.1–19 mg Cu kg^{-1} and 42–115 mg Zn kg^{-1}. Litterfall input and dilution may influence forest floor Pb but not Cu and Zn because of their greater uptake and litterfall rate from vegetation. The opposite process of increased uptake may also be due to aggrading forest age and species composition. Hence, changes in forest floor Pb, Cu, and Zn concentrations may also be decreasing from decreased litterfall, increased dilution or increased uptake.
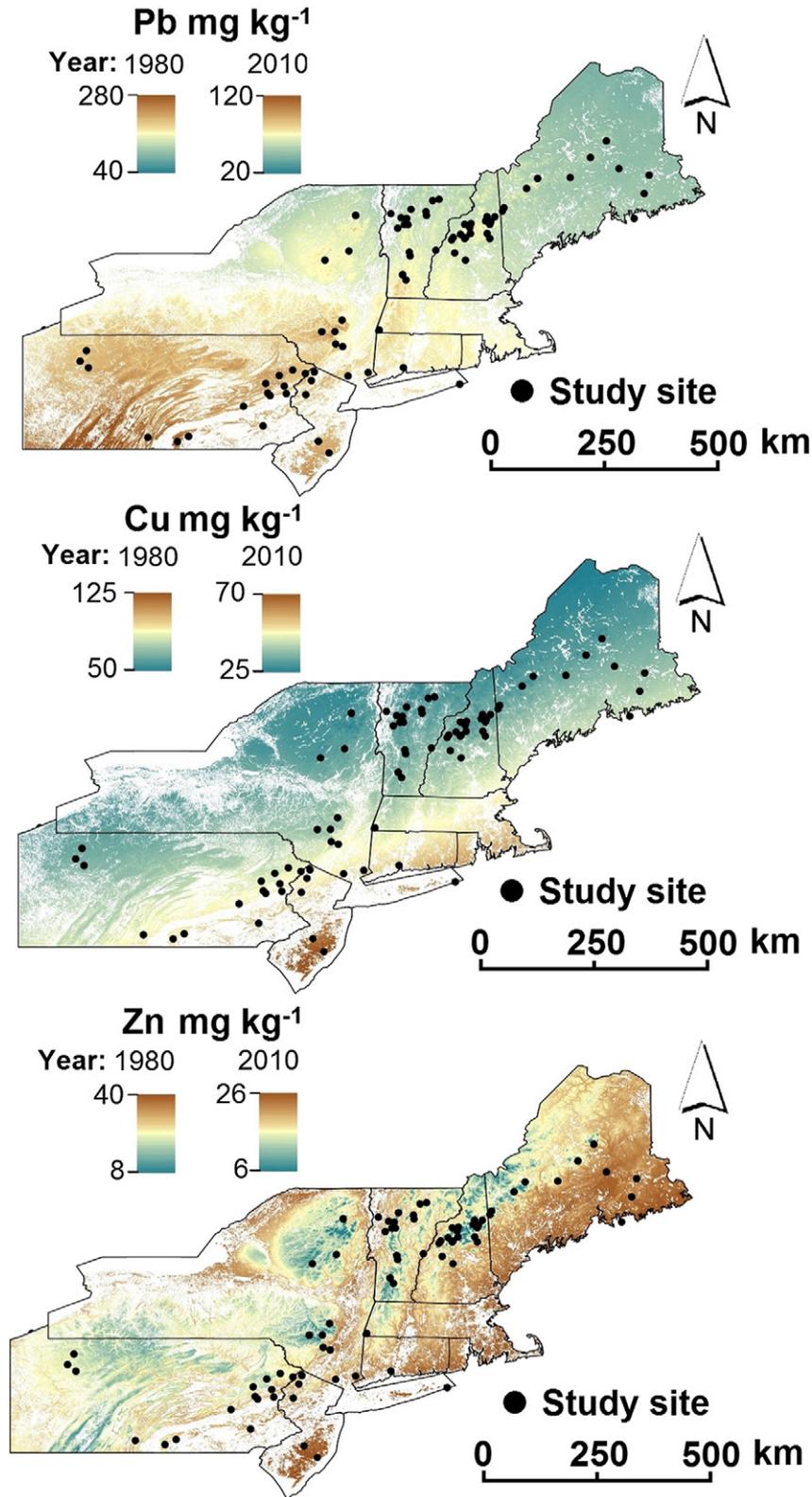
Fig. 3. Spatial statistical model of Pb, Cu and Zn concentration in forest floor at sites in remote locations across the northeastern US. The model estimates are from multiple-regression of Pb, Cu and Zn concentrations with year-sampled, elevation, latitude, and longitude (Eqs (1), (2), (3), Table 6). Multiple-regressions were significant ($P < 0.01$) and Pb, Cu and Zn R^2 values were 0.55, 0.38 and 0.28, respectively. Data are from Reiners et al. (1975), Siccama et al. (1976), Andresen et al. (1980), Johnson et al. (1982), Hanson et al. (1982), Moyse and Fernandez (1987), Herrick and Friedland (1990), McNulty et al. (1991), Friedland et al. (1992), Siccama et al. (1997), Yanai et al. (2004), Evans et al. (2005), Kaste et al. (2006), McGee et al. (2007), Johnson and Richter (2010), Richardson et al. (2014, in revision). For the model, the number of sites varying in location or time analyzed were N = 212 for Pb, N = 153 for Cu and N = 163 for Zn. It should be noted the majority of the sites were sampled multiple times, at least 9 years apart. The spatial model does not incorporate effects from metropolitan areas and other point sources. Digital elevation and other spatial maps were gathered from the USGS National Map (Gesch et al., 2009; http://nationalmap.gov/index.html, accessed 15/1/2014).

It is necessary to consider the ultimate fate of Pb, because of the significant decreases across the region. From previous studies, it appears that the fate of anthropogenic forest floor Pb is to accumulate in the mineral soil horizons, such as the Bs and Bw horizons (Johnson et al., 1995; Kaste et al., 2003; Richardson et al., 2014). Lead is strongly retained by SOM and mineral soils generally contain 5–18% SOM. Thus, mineral soils will retain much of the anthropogenic Pb and groundwater contamination is unlikely (Miller and Friedland, 1994; Johnson et al., 1995). The ultimate fate of pollutant Cu and Zn is unclear. The data from our 16 sites suggest that forest floor concentrations of both metals are slowly decreasing, at half the rate of Pb. As mentioned earlier, biogeochemical cycling may have adjusted to include atmospherically deposited Cu and Zn at a new steady state. Whether or not this constitutes a favorable change in edaphic quality of the soil has received little attention (Heinrichs and Mayer, 1980).

4.2. Modeling of forest floor Lead, Copper and Zinc concentrations

In addition to temporal changes, forest floor Pb, Cu, and Zn concentrations and their e-folding times were found to be correlated with multiple spatial variables. Forest floor Pb was dependent on latitude, which was attributed to decomposition and forest floor turnover rates (Richardson et al., 2014). Moreover, the pooled forest floor Cu concentrations were better negatively correlated with elevation ($r^2 = 0.16$, $p < 0.05$) and latitude ($r^2 = 0.23$ $p < 0.05$) than time ($r^2 = 0.10$ $p < 0.05$) (Supplemental Table 5). Thus, assessing the change in Cu and Zn concentrations through time required taking spatial variables into account. Our multiple-regression spatial models of forest floor Pb, Cu and Zn concentrations were able to estimate the remote forested areas that have been most impacted by Pb, Cu and Zn pollution (Fig. 3). The correlation between forest floor Pb and Cu concentrations with elevation is likely due to the orographic effects of deposition, climate, and vegetation. Higher elevations receive greater deposition of trace metals due to greater precipitation and cloud interception (e.g. Reiners et al., 1975; Miller and Friedland, 1994; Stankwitz et al., 2012). Similarly, coniferous vegetation can better intercept cloudwater than deciduous litter, producing a similar effect on deposition rate (Berg et al., 1993; Miller and Friedland, 1994; Stankwitz et al., 2012). In addition, cooler climates and coniferous litter promote slower decomposition rates compared with warmer climates and deciduous litter, resulting in longer forest floor turnover times and metal retention (Berg et al., 1993; Miller and Friedland, 1994; Stankwitz et al., 2012; Richardson et al., 2014).

Although not explicitly considered in this model, industrial and metropolitan areas likely caused the significant relationship between forest floor Pb, Cu, and Zn concentrations with lower latitudes and elevations. Higher concentrations of Pb, Cu. and Zn in Pennsylvania, New Jersey and New York may have arisen from smelting (e.g. Smelter in Palmerton, PA, c.f. Johnson and Richter, 2010), metal-refining (Cu-refiners in Perth Amboy, New Jersey, c.f. Andresen et al., 1980), vehicle-derived suspended particulates (Harrison et al., 1981; Sternbeck et al., 2002), coal combustion in the Ohio Valley and metropolitan emissions (New York City, c.f. Pouyat and McDonnell, 1991). Soils in proximity to urban areas may have soil Pb, Cu, and Zn concentrations an order of magnitude higher than remote forests (Harrison et al., 1981; Datko-Williams et al., 2014). A significant influence is likely from particulates derived from vehicles (e.g. brakepad particulates), which can be a major source of particulate Pb, Cu, and Zn to forest soils (Smith, 1976; Sternbeck et al., 2002; Datko-Williams et al., 2014). This effect may be especially pronounced near urban areas and major transportation corridors such as Western Pennsylvania, New Jersey, Connecticut, and eastern Massachusetts (Fig. 3) (Smith, 1976; Johnson et al., 1982; Datko-Williams et al., 2014). Remote forests in Vermont, New Hampshire, and Maine had relatively lower concentrations of all metals mostly as a result of the greater distances from anthropogenic sources. The

Pb, Cu and Zn spatial statistical models could be improved with more studies and expansive sampling in the future but will inevitably be temporally limited.

The majority of the variation in Cu and Zn data remains unexplained by spatial and temporal variables, and may only be remediated with additional biological and point source information. Our investigations of regional trends in pooled forest floor Cu and Zn data sets with site characteristics and soil properties were limited by previous investigations. The most important factors not considered are the effects of tree species composition, stand age, SOM, soil pH, and parent material. Although % SOM and soil pH were measured at our stands, the impact of these variables were not investigated as other previous studied did not quantify them, failed to physically report them or measured and provided in an inconsistent manner. The lack of consistent reporting of basic site characteristics and soil properties is of concern for the utility of regional studies and their ability to be used in long-term syntheses. Thus, future regional studies must detail additional site characteristics to better constrain soil parameters that influence trace metal retention.

5. Conclusions

We observed that forest floor Pb, Cu and Zn concentrations decreased from 1980 to 2011. E-folding times for Pb, Cu and Zn at the 16 sites we studied were estimated to be 46 ± 7, 76 ± 20 and 81 ± 19 yrs, respectively. Using the pooled data set compiled from the literature, we found that exponential regressions showed t_{efold} for Pb was 33 ± 9 yr, faster than the estimate from our 16 sites. The coefficients of determination from the Cu and Zn regressions were inadequate for quantifying pooled t_{efold} values. Mineral soil concentrations were correlated with forest floor concentrations only for Pb, suggesting their accumulation is linked (i.e. forest floor Pb is the source of mineral soil Pb). Mineral soil and forest floor concentrations were poorly correlated for Cu and Zn, suggesting they are accumulating independently. Biological or soil processes may be the cause of the disconnected accumulations. Forest floor Pb, Cu, and Zn concentrations were multiple-regressed with latitude, longitude, elevation and year of sampling, cumulatively explaining 55, 39, and 28% of the variation in the pooled data sets, respectively. Although elevation, latitude and longitude were the only variables explicitly used in the regression models, the spatial distributions of forest floor Pb and Cu concentrations highlight the importance of proximity to emission sources and orographic effects. Zinc weakly correlated with elevation but its spatial pattern is complex because of its biological importance and site dependent factors. The spatial and temporal patterns of Cu and Zn from the compiled literature may have been masked heterogeneity among studies or cycling by vegetation may have adjusted to incorporate pollutant Cu and Zn at a new steady state. Lead has received much attention but monitoring other pollutant trace metals is necessary to understand multi-decadal responses to anthropogenic pressures.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.10.023.

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