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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.

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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 ± 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.

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

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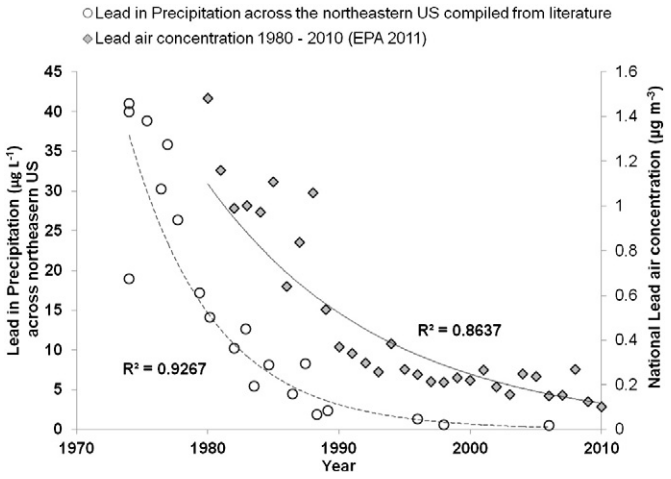

Fig. 1. The concentration of Pb in precipitation from across the northeastern US and the National Lead air concentration modeled with exponential regression. Data are from Chan et al. (1976), Smith et al. (1986), Pike and Moran (2001), Lawson et al. (2003) and Song and Gao (2009). National Lead Air concentration 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.

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	Year sampled
			g ha^{-1} yr^{-1}	
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

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