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Influence of coniferous and deciduous vegetation on major and trace metals in forests of northern New England, USA

J. B. Richardson · A. J. Friedland

Abstract

Aims Climate change and land-use are predicted to shift coniferous stands to deciduous stands in northern New England. This change in vegetation type may modify plant-soil cycling of major and trace metals, potentially affecting soil fertility and contaminant transport.
Methods We studied eight pairs of adjacent coniferous- and deciduous-dominated forest stands across northern New England, USA. We estimated the mean residence time (MRT) of each metal in organic horizons using calculated litterfall from allometric equations and interpolated atmospheric deposition rates.
Results Coniferous stands had 30–50 % smaller organic horizons pools of Ca, K, Mg, Mn, and Zn than deciduous stands. Mineral horizon metal pools were similar between vegetation types. Foliar metal concentrations and pools were smaller at coniferous stands than deciduous stands. The organic horizon MRT for Ca, Cd, Cu, K, Mg, and Mn was predicted to be 40–200 % longer for coniferous stands than deciduous stands.

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Conclusions Based upon our findings, we conclude that a shift from coniferous to deciduous vegetation could decrease the accumulation and retention of major metals in the organic horizons. Further investigations into the effect of vegetation type on mineral horizons are needed to constrain regional changes.

Introduction

Feedbacks between vegetation and soil influence local- to regional-scale biogeochemical processes, from the accumulation of carbon (C) in individual trees and their underlying soils (Cross and Perakis 2011), to watershed cycling of elements (Likens and Bormann 1995). Forest stands of coniferous tree genera (gymnosperms such as *Picea* spp., *Tsuga canadensis* L, *Pinus* spp., and *Abies* spp.) in northern New England are expected to be succeeded by deciduous tree genera (angiosperms such as *Acer* spp., *Fagus grandifolia* Ehrh., and *Betula* spp.) due to the increased mean annual temperature and mean annual precipitation across the region (Campbell et al. 2009; Tang and Beckage 2010). Under multiple scenarios, coniferous vegetation are projected to lose 71–100 % of their current range to deciduous vegetation across northern New England US by 2085 (Tang and Beckage 2010; Tang et al. 2012). In addition to climate change, timber harvesting may also reduce coniferous vegetation due to the preferential selection for certain

deciduous trees common in northern hardwood stands, such as *Acer* spp., *Betula* spp., and *Fagus grandifolia*, in forest regrowth following harvesting (Foster 1992). The potential shift from coniferous to deciduous forests may potentially modify the accumulation and retention of metals in the soil, but has received limited attention (Campbell et al. 2009).

Forest soils control the accumulation and cycling of macronutrient metals (Ca, K, Mg), micronutrient metals (Cu, Mn, Mo, Ni, Zn), and toxic metals (Cd, Pb) in terrestrial ecosystems (Likens and Bormann 1995; Berger et al. 2009; Huang et al. 2011). The cycling of plant-essential metals (Ca, K, Mg, Mn, and Zn) is important for plant growth and the loss of these metals can reduce the growth of economically significant tree species such as *Acer saccharum* (sugar maple) (St. Clair et al. 2008; Dauer et al. 2007). Additionally, forest soils also perform the ecosystem service of accumulating and retaining pollutant metals from anthropogenic emissions. Metals emitted from the combustion of coal (e.g., Mn) (Herndon et al. 2011), automobiles (e.g., Cu, Pb, and Zn) (Steinnes and Friedland 2006; Richardson et al. 2015), and industrial processes (Cd, Cu, Mn, Mo, Ni, Pb, Zn) (Steinnes and Friedland 2006; Van Hook et al. 1977;) have been widely deposited to forest soils in northern New England, USA. A change in the dominant type of vegetation comprising a forest can potentially cause a loss of the plant essential and pollutant metals from soil. Despite previous studies examining metals in forest soils, few studies have compared the role of vegetation type in major and trace metal accumulation and cycling.

A shift from coniferous and deciduous forest stands may affect metal cycling in forest soils in multiple ways. Variations in foliar ecophysiology and chemistry between the two vegetation types can affect metal fluxes in litterfall (Vogt et al. 1986; Binkley 1995; Berger et al. 2009; Huang et al. 2011; Kraepiel et al. 2015). A review by Augusto et al. (2015) concluded that deciduous species have 30–90 % higher Ca, Mg, and K concentrations than coniferous species, which was attributed to their lower lignin and cellulose components (Augusto et al. 2002; de Schrijver et al. 2012). Furthermore, physical attributes of the canopy structure, such as branching architecture, can directly affect the accumulation of metals in aboveground biomass (Van Hook et al. 1977; Prescott 2002; Augusto et al. 2015). The greater total foliar biomass for deciduous species generally causes substantially larger metal fluxes in litterfall at deciduous-dominated forest stands compared to coniferous-dominated stands (e.g., Carnol and Bazgir 2013). However, coniferous vegetation has been observed to have greater throughfall concentrations of metals (de Schrijver et al. 2008; Augusto et al. 2015), primarily due to greater atmospheric scavenging of wet and dry deposition particularly in months when deciduous trees are without leaves (Lovett 1994). Additionally, litter from coniferous vegetation is physically (e.g., surface area) and chemically different from deciduous stands (e.g., soil C and pH) and could affect the accumulation of metals in the organic and mineral horizons (Prescott 2002; Berger et al. 2009; Augusto et al. 2015).

Multi-element studies of major metals (plant-essential) and trace metals (potentially toxic) are necessary for ensuring soil fertility and estimating ecosystem services provided by the two prominent vegetation types in the forests of northern New England, USA. The objectives of this study were: 1) determine if metal concentrations or pools in forests and their soils are different at coniferous- and deciduous-dominated stands, 2) develop a simple box model to estimate metal residence in the organic horizons at coniferous and deciduous stands. We hypothesized that coniferous stands would have greater belowground major and trace metal pools, but deciduous vegetation would have greater aboveground major and trace metal pools. Based upon the behavior observed for other elements (e.g., Pb and Hg) in previous studies, we expected major and trace metals to have significantly longer residence times in soils at coniferous stands. Information from this study can help forest managers and biogeochemists assess the future impact of changing vegetation type on plant-essential and pollutant metal cycling in forests across the region.

Materials and methods

Mountain study sites and forest stands

Eight pairs of coniferous and deciduous forest stands in northern New England, USA were studied (Fig. 1). Forest stands were located at eight mountain study sites in the deciduous–coniferous transition zone between 650 and 750 m above sea level. Four mountains were located on a north–south transect along the Green Mountains of Vermont, and four sites were on a north–south transect along the White Mountains of New
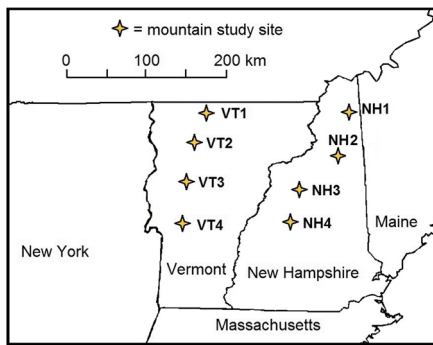
Fig. 1 Location of mountain study sites with adjacent coniferous- and deciduous-dominated stands

Hampshire. Mountain study sites were on west-facing slopes to avoid an aspect bias. Northern New England has a temperate climate, with mean annual temperatures at the stands ranging from 6 to 10 °C and mean annual precipitation ranging from 800 to 1300 mm (PRISM Climate Group 2012). The mean annual frost-free period ranges from 90 to 160 days (Soil Survey Staff 2014). Only sites on bench landform and well-drained soils were chosen. The soil parent material was glacial till for all stands, which was deposited during the retreat of the Laurentian ice sheet in the Wisconsian glaciation ~14,000 yr ago (see Siccama 1974; Soil Survey Staff 2010). Glacial till at sites NH 1–NH 4 was generally sourced from local bedrock: Bethlehem granodiorite with contributions of Concord granite, Kinsman granodiorite, and metasedimentary rocks from more northern formations (Lyons 1997). Glacial till at sites VT 1–VT 4 was locally sourced from the Waits River and Missisquoi formations, with additions of other metasedimentary formations (Doll et al. 1961).

One coniferous stand and one adjacent deciduous stand within 50 m of each other were studied at each mountain study site. Forest stands in this study were circular, with a 15 m radius. The frequency of each species and diameter at breast height (DBH) for all trees was determined. Basal area was estimated from DBH measurements (Whittaker et al. 1974). Coniferous species present were primarily *Abies balsamea* Mill. (balsam fir) and *Picea rubens* Sarg. (red spruce), with very minor constituents of *Tsuga Canadensis* L. (eastern hemlock) and *Pinus strobus* L. (white pine). Deciduous species present were *Fagus grandifolia* Ehrh. (American beech), *Acer saccharum* Marsh. (sugar maple), *Acer rubrum* L. (red maple), *Acer pensylvanicum* Marsh. (striped maple), *Betula papyrifera* Marsh. (paper birch), and *Betula*

alleghaniensis Britt. (yellow birch). Negligible deciduous constituents present were: *Prunus pensylvanica* L., (pin cherry) and *Fraxinus americana* L. (white ash). Coniferous stands were inhabited with 70 ± 6 % coniferous genera, and deciduous stands were inhabited with 93 ± 6 % deciduous genera based upon basal area (Table 1). Vegetation at all stands was secondary growth at all mountain study sites due to the historical clearing of the region in the 1800s and abandonment in the period from circa 1870 through 1920s (see Foster 1992). Coniferous stands were located away from trails and logging roads, in areas that were likely difficult for timber harvesting. Using DBH of *Acer saccharum*, *Picea rubens*, and *Abies balsamea* at each stand, we calculated growth rates from DBH measurements and allometric equations using parameters from Teck and Hilt (1991) and Kenefic and Nyland (1999). We calculated that stand ages ranged from 57 to 137 yr with a mean of 88 ± 9 yr (data not shown) (Lamson 1987). These ages may be under or overestimates due to variations in DBH growth from site hydrologic and edaphic characteristics (Lamson 1987).

Soil and vegetation sample collection

Late-season foliage and bolewood samples were collected from *Picea rubens*, *Tsuga canadensis*, *Abies balsamea*, *Fagus grandifolia*, *Acer spp.*, and *Betula spp.* in triplicate from each forest stand in early October 2012, 2013, and 2014. The concentration of metals within leaves prior to senescence generally agrees with concentrations measured in leaves that have senesced (e.g., Kraepiel et al. 2015). Foliage was collected from branches in the middle canopy, 3–6 m above the ground, using a stainless steel pole saw. By not collecting upper canopy foliage, we may have underestimated foliar metal concentrations because dry deposition of particulates to leaves is greater in upper canopy leaves (Luyssaert et al. 2002; Prescott 2002; Adriaenssens et al. 2012). Bolewood was sampled at DBH using a 4 mm increment corer. Although this provides a strong estimate of the metal concentration of the bolewood, greater inclusion of heartwood and sapwood may affect the estimates (Augusto and Bert 2005). Foliage and bolewood samples were air-dried at 25 °C for 3 wk and milled for homogeneity. Aboveground woody biomass and foliar biomass was estimated using allometric equations for each species from studies conducted in the northeastern US and southeastern Canada

Table 1 Forest stand descriptions

Site #	Mountain	Latitude	Longitude	Dominant vegetation type	Species present†	Stem density Stems ha⁻¹	% Conifer by basal area %	% Conifer by stem frequency %	Soil Taxonomy (USDA-NRCS)
VT 1	Jay	44.9333	−72.5609	Conif.	A, C, E, F, G, H, J	255	63	56	Oxyaquic Haplorthod
		44.9333	−72.5609	Decid.	A, C, E, F, G, J	326	4	22	Typic Haplorthod
VT 2	Mansfield	44.5308	−72.8319	Conif.	B, E, F, G, I, J	297	68	52	Typic Haplorthod
		44.5308	−72.8319	Decid.	B, D, E, F, H, J	241	0	6	Typic Haplorthod
VT 3	Ellen	44.1102	−72.9529	Conif.	A, B, D, G, I	368	52	52	Typic Haplorthod
		44.1102	−72.9529	Decid.	A, B, D, E, F	312	0	0	Typic Haplorthod
VT 4	Killington	44.6374	−72.8624	Conif.	B, E, F, G, H	354	99	64	Fragic Haplorthod
		44.6374	−72.8624	Decid.	A, B, D, E, F, H	212	40	32	Fragic Haplorthod
NH 1	Chase	44.9124	−71.1384	Conif.	A, B, D, F, I, H, J	439	76	52	Oxyaquic Haplorthod
		44.9124	−71.1384	Decid.	C, D, E, F, J	269	0	0	Typic Haplorthod
NH 2	Madison	44.3606	−71.2803	Conif.	A, B, E, F, G, H, I, J	425	54	64	Oxyaquic Haplorthod
		44.3606	−71.2803	Decid.	A, B, D, E, F, G, J	354	2	4	Typic Haplorthod
NH 3	Moosilauke	43.9798	−71.8271	Conif.	B, E, F, G, H, I	453	60	65	Oxyaquic Haplorthod
		43.9798	−71.8271	Decid.	A, B, D, E, F, H	411	13	28	Oxyaquic Haplorthod
NH 4	Cardigan	43.6447	−71.9328	Conif.	E, F, G, H	312	89	73	Typic Haplorthod
		43.6447	−71.9328	Decid.	A, B, E, F, H	269	1	11	Oxyaquic Haplorthod

(†) *A Betula alleghaniensis, B Betula papyrifera, C Betula cordifolia, D Acer saccharum, E Acer rubrum, F Fagus grandifolia, G Tsuga canadensis, H Picea rubens, I Picea glauca, J Acer pensylvanicum*

(Ferrari and Sugita 1996; Ter-Mikaelian and Korzukhin 1997; Jenkins et al. 2003). The foliar and woody biomass for each tree was summed for an estimate of total foliar and woody biomass at each stand. Estimates for foliage, aboveground woody biomass, and litterfall are based on allometric equations rather than empirical data. Allometric equations can better estimate the contribution of individual trees than randomly placed litterfall collectors (Yanai et al. 2012). However, aboveground woody biomass and foliage biomass can vary with canopy geometry, tree morphology, and fitness of each tree (Ferrari and Sugita 1996; Luyssaert et al. 2002), but these estimates provide an approximation of values without harvesting of the trees.

The soils at each forest stand were sampled between July and September 2012. Soils were classified as Spodosols using US Soil Taxonomy guidelines (Soil Survey Staff 2010). Soil taxonomy identification was based on soil pit descriptions and USDA-NRCS Web Soil Survey (Soil Survey Staff 2014). First, a trench was dug to ensure an E horizon and Bhs horizon were present. At each forest stand, three 15×15 cm square sections of organic horizons were separated from the underlying mineral soil and collected following the methods of Richardson et al. (2014). Three morphological quantitative soil pits were excavated for each forest stand using methods from Richardson and Friedland (2015). First, a 50×50 cm wooden frame was secured to the ground nearby by using 12 cm steel spikes. The organic horizons were removed using saws and clippers. Each master horizon (E, Bhs, Bs, BC) was excavated down to the dense-till, sieved to <2 cm, and weighed using an electronic portable scale. A 5-kg representative subsample was collected for each master horizon to determine field moisture content and rock fragments 0.2–2 cm in diameter. A separate subsample was collected from the face of each soil pit for chemical analyses. In total, 48 quantitative soil pits were excavated in this study. In the laboratory, the 15×15 cm blocks of organic horizon were separated into Oi (litter layer), Oe (fermentation layer), and Oa (humified layer) horizons. Roots >5 mm in diameter were removed and organic horizon layers were air-dried at 25 °C to a constant mass. Organic horizon masses were calculated using oven-dried subsamples. All mineral soil samples were air-dried to a constant weight, and roots >5 mm in diameter were removed. Organic horizons and mineral soil samples were milled and sieved, respectively, to ≤ 2 mm (Richardson et al. 2013).

Plant and soil analyses

A 2 : 5 soil−water suspension was used to determine soil pH. Suspensions were shaken for 1 hr using a wrist-action shaker and vacuum extracted through a Whatman 40 filter. The pH of the extract was measured with a pH meter (8015 VWR). The sand, silt, and clay fractions were measured using a modified Bouyocous hydrometer method (Gee and Bauder 1986). Loss-on-ignition was used to estimate % soil organic matter (SOM). To determine the percent loss-on-ignition, a 4-g air-dried subsample was combusted at 475 °C for 8 h. Mean soil pH, % LOI, % C, and % N for each horizon at coniferous and deciduous stands are given in Table 2.

Strong acid extraction was used to quantify the metal concentrations for the organic horizons, mineral horizons, leaves, and bolewood using the USEPA method 3051A (see Richardson et al. (2013). In brief, 500 mg (±5 mg) sub-samples were digested with 5 mL of a 1 : 9 ratio of trace metal grade hydrochloric acid : nitric acid (HNO_3, 70 %; HCl, 70 %). With every 20 digested samples we included: one randomly spiked sample, one replicate, one preparation blank; and one standard reference material (SRM). Peach leaves SRM 1547 and Montana soil SRM 2711 from the National Institute of Standards and Technology (National Institute of Standards and Technology Gaithersburg, MD) were used as reference materials. All measured metal concentrations for SRM materials were within 11 % of their certified values. Recovery rates for spiked samples were >88 %. Metal concentrations in the preparation blank samples were negligible (<0.1 %). Soil metal pools were calculated using the metal concentration and bulk mass per unit area of each horizon. Soil horizon metal concentrations are given in Fig. 2 and metal pools are given in Table 3. Metal concentrations in bolewood and foliage are listed in Supplemental Table 1 and 2.

Simple box model for organic horizon mean residence time

A simple box model was implemented for each of the forest stands to estimate the residence time of metals in the organic horizons. A box model for the mineral soil was not pursued due to limitations and site specific nature of weathering inputs, root uptake rates, and deep leaching rates of metals (see Drever, 1994; Friedland and Miller 1999). The pools of metals in the organic

Table 2 Mean values of soil properties of the organic and mineral horizons at coniferous- and deciduous-dominated stands

Dominant vegetation type	n	Horizon	Depth interval	pH	LOI %	Carbon %	Nitrogen %	Sand %	Silt %	Clay %
Coniferous	8	Oi	0–2	3.7 ± 0.1	89 ± 1	43 ± 1	1.8 ± 0.1	N/A	N/A	N/A
forest stand	8	Oe	2–5	3.6 ± 0.1	83 ± 4	41 ± 4	1.7 ± 0.2	N/A	N/A	N/A
	8	Oa	5–16	3.5 ± 0.1	79 ± 3	33 ± 4	1.5 ± 0.1	N/A	N/A	N/A
	8	E	16–21	4.1 ± 0.1	6 ± 1	3 ± 1	0.1 ± 0.1	70 ± 3	25 ± 3	5 ± 1
	8	Bhs	21–31	4.3 ± 0.1	16 ± 2	6 ± 1	0.3 ± 0.1	64 ± 4	27 ± 3	8 ± 1
	8	Bs	31–44	4.4 ± 0.1	10 ± 1	5 ± 1	0.2 ± 0.1	64 ± 3	28 ± 4	8 ± 1
	8	BC	44–53	4.5 ± 0.1	7 ± 1	5 ± 1	0.2 ± 0.1	65 ± 5	30 ± 4	6 ± 1
Deciduous	8	Oi	0–2	3.9 ± 0.1	88 ± 2	42 ± 3	1.8 ± 0.1	N/A	N/A	N/A
forest stand	8	Oe	2–5	4.0 ± 0.1	80 ± 3	38 ± 4	1.7 ± 0.2	N/A	N/A	N/A
	8	Oa	5–11	3.8 ± 0.1	54 ± 4	24 ± 3	1.2 ± 0.1	N/A	N/A	N/A
	8	E	11–15	4.3 ± 0.1	6 ± 1	3 ± 1	0.2 ± 0.1	68 ± 3	27 ± 3	6 ± 1
	8	Bhs	15–28	4.4 ± 0.1	16 ± 2	6 ± 1	0.3 ± 0.1	67 ± 2	25 ± 2	8 ± 1
	8	Bs	28–43	4.6 ± 0.1	12 ± 1	6 ± 1	0.2 ± 0.1	62 ± 1	32 ± 3	6 ± 1
	8	BC	43–55	4.7 ± 0.1	9 ± 1	4 ± 1	0.2 ± 0.1	65 ± 5	27 ± 4	6 ± 2

horizon are dependent on litterfall, atmospheric deposition, root uptake and leaching to the mineral horizons (Eq. 1). We estimated the mean residence time (MRT) for all metals at each of the sites by assuming the organic horizon pools and fluxes were in steady state. Although this is unlikely due to changing atmospheric deposition rates (see. Pratte et al. 2013; Sarkar et al. 2015) and forest maturation (Li et al. 2008; Richardson et al. 2014), it allows for a first order approximation of metal cycling in forest soils. Under the assumption of steady state, we can use either fluxes in or fluxes out to approximate MRT because they are assumed to be equal. We calculated organic horizon MRT in the organic horizon as the pool divided by the sum of the input fluxes: atmospheric deposition and litterfall (Eq. 2).

$$Pool_{Organic\ horizons} = F_{litterfall} + F_{atmdep} - F_{root\ uptake} \quad (1)$$
$$- F_{organic\_leaching}$$

$$MRT_{Organic\ horizons} = Pool_{Organic\ horizons} \Big/ \left(F_{litterfall} + F_{atmdep} \right) \quad (2)$$

We estimated annual atmospheric deposition of major and trace metals (wet + dry deposition) at the 16 stands from interpolations from studies conducted in the northeastern United States and southeastern Canada (Table 4). Annual litterfall fluxes of metals from

deciduous vegetation were assumed to be the entire late season foliar biomass. Annual litterfall fluxes of metals from *Abies balsamea* were assumed to be 1/3 the foliar biomass because Barnes and Wagner (1981) observed average needle longevity to be 3 yr. Similarly, litterfall fluxes from red spruce, were assumed to be 1/5 the foliar biomass because Barnes and Wagner (1981) observed average time needle longevity to be 5 yr. The annual litterfall for each stand were calculated as the summed litterfall contribution for each tree at stand. The metal flux from coarse woody debris was not included due to the wide variation in contribution at stands (Fahey et al. 2005).

We first conducted Eq, (1) under the assumption of equal atmospheric deposition for coniferous- and deciduous-dominated stands. This assumption may not be true because coniferous and deciduous stands have been found to have different atmospheric deposition and throughfall rates (Berger et al. 2009; Augusto et al. 2015) due to greater canopy density and leaf density for coniferous vegetation (Weathers et al. 2006; Adriaenssens et al. 2012). To determine the sensitivity of our simple box model approach, we ran our model under an additional scenario of unequal atmospheric deposition to test the importance of the variation between coniferous and deciduous stands. For unequal atmospheric deposition, we utilized the upper limit on atmospheric deposition variation between vegetation types by Augusto et al., (2015), in which atmospheric
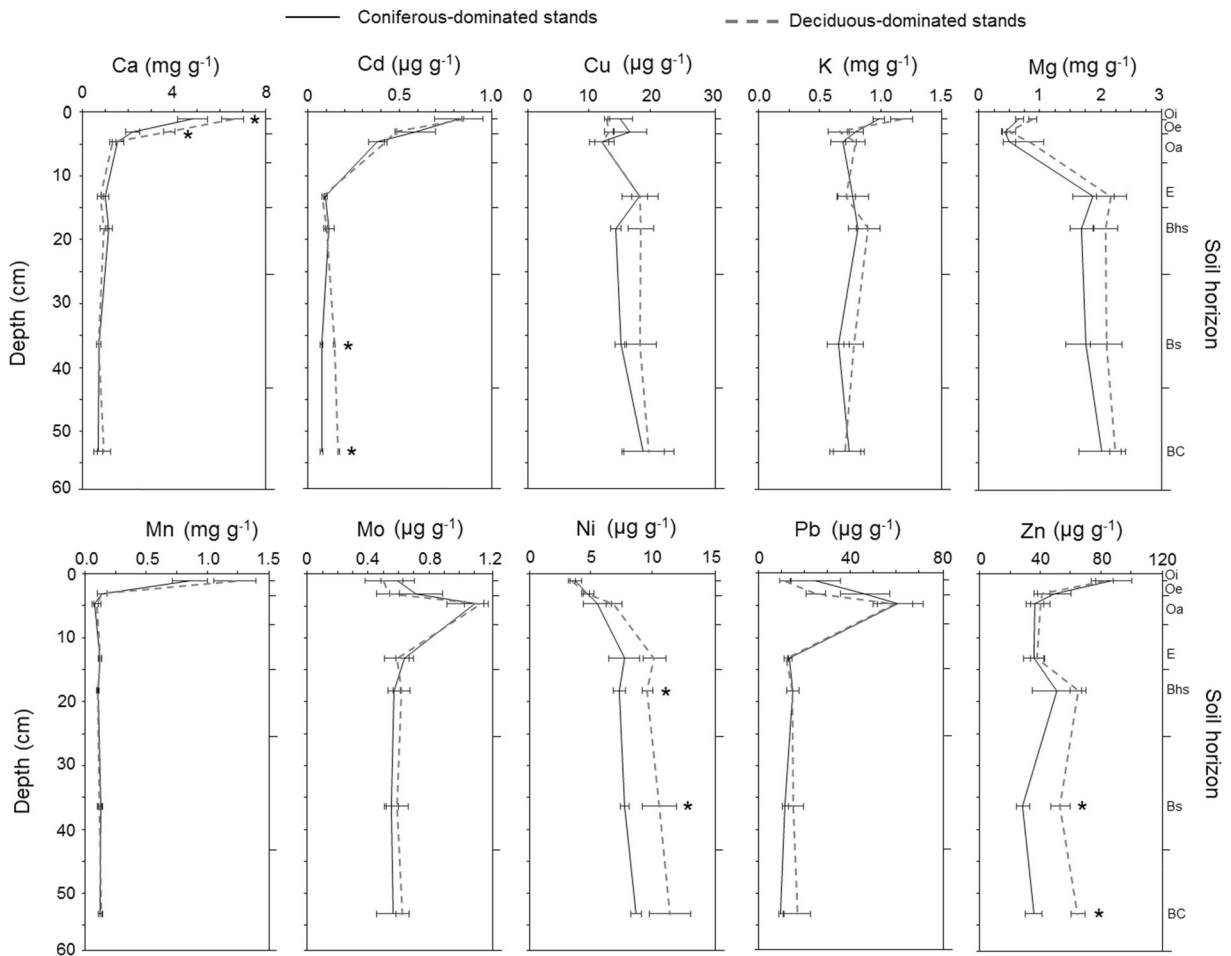
Fig. 2 Major and trace metal concentration (strong-acid extracted) profiles under coniferous- and deciduous-dominated stands. Mean concentrations are shown ± 1 s.e.

(*) indicates a significant difference between coniferous- and deciduous-dominated stands using non-parametric Wilcoxon rank sum test ($p < 0.05$)

deposition and throughfall of metals at deciduous stands was 50 % lower than at coniferous stands. The fluxes and model outputs for the sensitivity runs are given in Table 4.

Descriptive and statistical analyses

To calculate organic horizon pools, horizon mass per unit area were multiplied by metal concentrations for Oi, Oe, and Oa horizons and then summed. Similarly for the mineral horizon pools, horizon mass per unit area were multiplied by metal concentrations for the E, Bhs, Bs, and BC horizons and then summed. In the foliar and bolewood comparisons, data from 2012, 2013, and 2014 were combined. Descriptive statistics were calculated in Matlab. In-text mean values are given ± 1 standard error.

Data was tested for normal distribution using the Lilliefors test and logarithmically or exponentially transformed when necessary to establish normality. The variations in major and trace metal concentration and pools in the organic and mineral horizons were compared between vegetation types (coniferous and deciduous) using paired sample *t*-test. Multivariate analysis of variance (MANOVA) was used to determine if there was an overall significant difference in metal concentrations and pools between coniferous and deciduous stands. In most uses of the MANOVA, the different metals were the dependent variables. However, when comparing concentration profiles the horizons were the dependent variable and analyzing foliar concentrations among genera, the trees were the dependent variable.

Table 3 Major and trace metal pools in aboveground foliar and woody biomass and belowground in the organic and mineral horizons at the eight coniferous- and eight deciduous-dominated stands

Metal	Dominant vegetation type	n	Units	Organic horizons pool	Mineral horizons pool	Foliar pool	Woody biomass pool
Ca	Conifer	8	kg ha^{-1}	231 ± 32	859 ± 125	25 ± 3	94 ± 13
	Deciduous	8	kg ha^{-1}	346 ± 23*	799 ± 113	32 ± 3*	93 ± 9
Cd	Conifer	8	g ha^{-1}	86 ± 15	76 ± 12	2.1 ± 0.8	8.2 ± 2.6
	Deciduous	8	g ha^{-1}	85 ± 13	95 ± 13	3.5 ± 0.7	10.7 ± 1.7
Cu	Conifer	8	g ha^{-1}	2100 ± 320	12000 ± 1200	33 ± 7	199 ± 45
	Deciduous	8	g ha^{-1}	1900 ± 200	14000 ± 1300	24 ± 5	143 ± 37
K	Conifer	8	kg ha^{-1}	109 ± 10	700 ± 92	24 ± 3	49 ± 8
	Deciduous	8	kg ha^{-1}	146 ± 6*	703 ± 83	34 ± 6*	38 ± 6
Mg	Conifer	8	kg ha^{-1}	77 ± 9	1720 ± 149	4.8 ± 0.7	12 ± 1
	Deciduous	8	kg ha^{-1}	141 ± 20*	1920 ± 133	7.4 ± 0.9*	10 ± 1
Mn	Conifer	8	kg ha^{-1}	18 ± 2	102 ± 9	4.7 ± 1.1	10 ± 2
	Deciduous	8	kg ha^{-1}	34 ± 3*	103 ± 9	4.1 ± 1.4	8 ± 1
Mo	Conifer	8	g ha^{-1}	150 ± 20	460 ± 30	0.26 ± 0.05	1.07 ± 0.10
	Deciduous	8	g ha^{-1}	150 ± 20	470 ± 40	0.28 ± 0.06	0.80 ± 0.13
Ni	Conifer	8	g ha^{-1}	870 ± 150	7400 ± 770	20.6 ± 8.5	18.8 ± 3.0
	Deciduous	8	g ha^{-1}	1000 ± 160	9200 ± 720	18.5 ± 5.6	18.2 ± 4.1
Pb	Conifer	8	g ha^{-1}	9000 ± 1600	10500 ± 1400	2.3 ± 0.6	27 ± 8
	Deciduous	8	g ha^{-1}	8500 ± 1200	12300 ± 1500	1.4 ± 0.3*	15 ± 4
Zn	Conifer	8	g ha^{-1}	5900 ± 750	39500 ± 6300	381 ± 114	1380 ± 315
	Deciduous	8	g ha^{-1}	9600 ± 950*	52200 ± 6500	362 ± 131	1040 ± 280

(*) indicates a significant difference between coniferous- and deciduous-dominated stands using non-parametric Wilcoxon rank sum test ($p < 0.05$)

Results

Soil properties and metals

Generally, physical properties, such as bulk density, were similar at coniferous- and deciduous-dominated stands. Organic horizon pH was significantly lower for coniferous stands than deciduous stands ($p < 0.05$, Table 2). Moreover, the lower % SOM in the Oa horizon at deciduous stands was significantly lower compared to coniferous stands (Table 2). Most of the major and trace metal concentrations in the organic and mineral horizons were similar between coniferous- and deciduous-dominated stands. Calcium concentrations in the Oi and Oe horizons were significantly lower for coniferous stands than deciduous stands (Fig. 2, $p < 0.05$). Additionally, organic horizon pools of Ca, K, Mg, Mn, and Zn were lower for coniferous than deciduous stands (Table 3, $p < 0.05$). The MANOVA results show overall organic horizon metal pools were

significantly smaller for coniferous stands compared to deciduous stands ($p < 0.01$).

Mineral horizon concentrations of Cd, Ni, and Zn were lower for coniferous stands than deciduous stands (Fig. 2, $p < 0.05$). However, summed mineral horizon pools were similar for all metals between vegetation types (Table 3). Mineral horizon pH was significantly lower for E, Bhs, Bs, and BC horizons at coniferous stands than deciduous stands ($p < 0.05$, Table 2). We did not find an overall significant difference in mineral horizon metal concentrations and pools between coniferous and deciduous, using a MANOVA test ($p = 0.08$). Physical differences in the mineral horizons do not appear to have influenced the metal concentrations and pools. Thicknesses of the mineral horizons, E, Bhs, Bs and BC horizons, were similar for coniferous and deciduous stands. Soil texture was dominated by sand, ranging from 49 to 88 % but did not vary between vegetation types. Mineral soil bulk density was similar for all horizons for both vegetation types. We observed

Table 4 Simple box model fluxes to organic horizons for each metal. In the equal scenario, it was assumed atmospheric deposition is the same for both vegetation types

Metal	Dominant vegetation type	n	Units	Litterfall flux	†Atmospheric Hg deposition Equal	^Atmospheric Hg deposition Unequal	Units	Organic horizon MRT Equal	^Organic horizon MRT Unequal
Ca	Conifer	8	kg ha^{-1} yr^{-1}	8 ± 3	1.3 ± 0.1	1.3 ± 0.1*	yr	30 ± 6*	30 ± 6*
	Deciduous	8	kg ha^{-1} yr^{-1}	32 ± 3*	1.3 ± 0.1	0.7 ± 0.0	yr	12 ± 2	13 ± 3
Cd	Conifer	8	g ha^{-1} yr^{-1}	0.7 ± 0.3	0.8 ± 0.1	0.8 ± 0.1*	yr	60 ± 10*	60 ± 10
	Deciduous	8	g ha^{-1} yr^{-1}	3.5 ± 0.8*	0.8 ± 0.1	0.4 ± 0.0	yr	31 ± 9	41 ± 12
Cu	Conifer	8	g ha^{-1} yr^{-1}	11 ± 3	7.1 ± 0.2	7.1 ± 0.2*	yr	132 ± 23*	132 ± 23*
	Deciduous	8	g ha^{-1} yr^{-1}	38 ± 4*	7.1 ± 0.2	3.5 ± 0.1	yr	48 ± 10	54 ± 13
K	Conifer	8	kg ha^{-1} yr^{-1}	9 ± 3	0.50 ± 0.06	0.50 ± 0.06*	yr	17 ± 3*	17 ± 3*
	Deciduous	8	kg ha^{-1} yr^{-1}	36 ± 6*	0.50 ± 0.06	0.25 ± 0.02	yr	5 ± 1	5 ± 1
Mg	Conifer	8	kg ha^{-1} yr^{-1}	1.7 ± 0.7	0.29 ± 0.03	0.29 ± 0.03*	yr	48 ± 8*	48 ± 8*
	Deciduous	8	kg ha^{-1} yr^{-1}	7.4 ± 0.9*	0.29 ± 0.03	0.14 ± 0.01	yr	21 ± 4	22 ± 4
Mn	Conifer	8	kg ha^{-1} yr^{-1}	1.8 ± 0.3	0.02 ± 0.00	0.02 ± 0.00*	yr	30 ± 9*	30 ± 9*
	Deciduous	8	kg ha^{-1} yr^{-1}	4.1 ± 0.5*	0.02 ± 0.00	0.01 ± 0.00	yr	10 ± 2	10 ± 2
Mo	Conifer	8	g ha^{-1} yr^{-1}	0.09 ± 0.03	1.2 ± 0.2	1.2 ± 0.2*	yr	118 ± 24	118 ± 24
	Deciduous	8	g ha^{-1} yr^{-1}	0.28 ± 0.06*	1.2 ± 0.2	0.6 ± 0.1	yr	97 ± 2	170 ± 32
Ni	Conifer	8	g ha^{-1} yr^{-1}	9.0 ± 2.1	3.9 ± 0.2	3.9 ± 0.2*	yr	76 ± 13	76 ± 13
	Deciduous	8	g ha^{-1} yr^{-1}	7.3 ± 1.7	3.9 ± 0.2	2.0 ± 0.1	yr	108 ± 30	142 ± 52
Pb	Conifer	8	g ha^{-1} yr^{-1}	0.6 ± 0.2	6.9 ± 0.3	6.9 ± 0.3*	yr	1205 ± 278	1205 ± 278
	Deciduous	8	g ha^{-1} yr^{-1}	2.5 ± 0.3*	6.9 ± 0.3	3.5 ± 0.3	yr	943 ± 209	1540 ± 354
Zn	Conifer	8	g ha^{-1} yr^{-1}	131 ± 15	88 ± 5	88 ± 5*	yr	33 ± 7	33 ± 7
	Deciduous	8	g ha^{-1} yr^{-1}	515 ± 101*	88 ± 5	44 ± 3	yr	24 ± 6	28 ± 6

Under the unequal scenario, it was assumed that atmospheric deposition at deciduous stands is half the rate of atmospheric deposition at coniferous stands

† Annual atmospheric deposition (wet + dry deposition) for each metal at the 16 stands was interpolated from one or more of the following sources: Gélinas et al. 2000; Lawson et al. 2001; NADP 2007; Sarkar et al. 2015, and Likens 2015

^ For unequal fluxes, atmospheric deposition at deciduous stands were 50 % of the equal flux rate, based upon Augusto et al. (2015)

that metal concentrations and pools were significantly different among mountain study sites using the non-parametric Kruskal-Wallis test, combining data from coniferous and deciduous stands (Data not shown, mountain study sites = 8, number of soil pits = 6, $p < 0.01$).

Late-season foliage and bolewood metal concentrations

Major and trace metal concentrations in late-season foliage collected in 2012, 2013, and 2014 did not vary significantly from year to year (Data not shown). The coefficient of variation for metal concentrations between 2012 and 2014 ranged between 10 and 20 % for each metal and vegetation type. Foliar Ca and Mg concentrations in coniferous vegetation (*Abies balsmea, Picea*

rubens) were significantly lower compared to deciduous vegetation (*Acer spp., Betula spp., Fagus grandifolia*) (Fig. 3, $p < 0.05$). Examining all metals using MANOVA, foliar metal concentrations for coniferous vegetation were significantly lower than deciduous vegetation ($p < 0.01$). When considering individual tree genera, foliar Ca, Cd, K, Mg, Mn, Ni, Pb, and Zn concentrations were significantly greater for *Betula spp*. compared to other genera (Fig. 3, Supplemental Table 1). Cadmium and Zn concentrations in *Betula spp*. were an order of magnitude higher than other genera (Fig. 3).

Bolewood concentrations were found to be similar between coniferous and deciduous vegetation ($p > 0.05$, data not shown). Considering genera individually, *Betula spp*. had significantly higher bolewood concentrations of
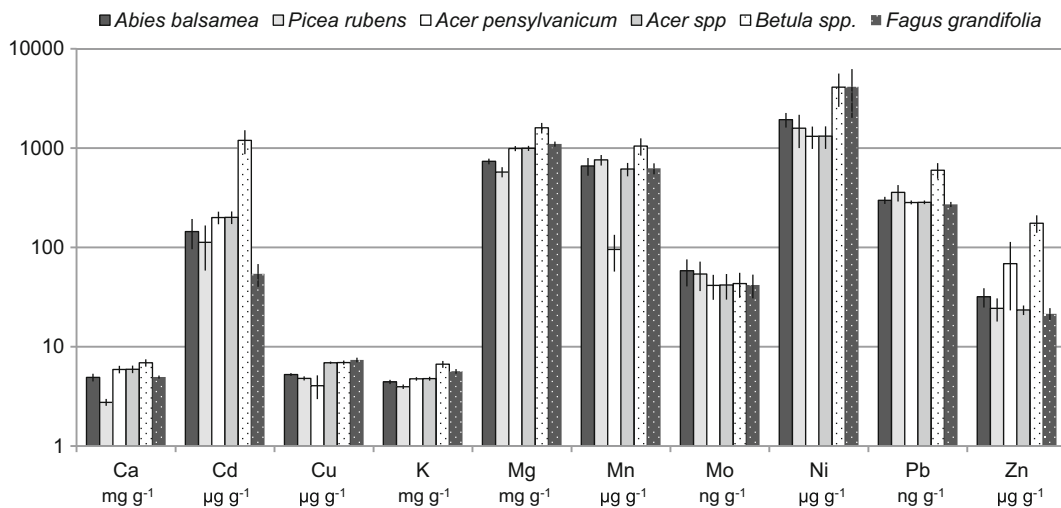
Fig. 3 Late-season foliar metal concentrations among the most abundant genera averaged across the eight mountain study sites from 2012 to 2014. Coniferous vegetation are *Abies balsamea* and *Picea rubens*, all other genera and species are deciduous

Cd and Zn than other genera (Fig. 4, Supplemental Table 2). In addition, *Picea rubens* bolewood had significantly greater concentrations of K, Mg, Mn, Mo, Ni, Pb, and Zn than deciduous genera such as *Fagus grandifolia* and *Acer spp.* (Fig. 4, $p < 0.05$).

Foliar and aboveground woody biomass metal pools

From the allometric equations, we estimated that coniferous stand foliar biomass (1650 ± 360 kg ha^{-1}) was significantly less than in deciduous stands (5680 ± 610 kg ha^{-1}). The foliar pools of Ca, Cu, K, Mg, and Pb were significantly smaller at

coniferous stands compared to deciduous stands ($p < 0.01$, Table 3). Although stem densities were similar among vegetation types, the woody biomass estimated at coniferous stands (9070 ± 2220 kg ha^{-1}) was significantly smaller than deciduous stands (24, 500 ± 5480 kg ha^{-1}). Despite the wide variation in aboveground biomass, metal pools in aboveground woody biomass were similar between the vegetation types for each metal ($p > 0.05$, Table 3). However, coniferous stands had significantly smaller metal pools in their aboveground woody biomass than deciduous stands on the basis of MANOVA test ($p < 0.05$). The average *Abies balsamea* tree had significantly less
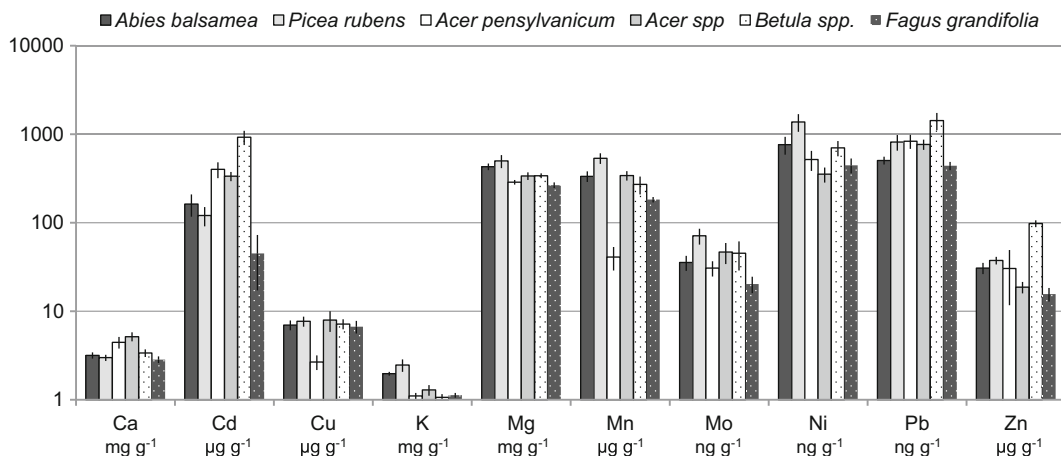

Fig. 4 Bolewood metal concentrations among the most abundant genera averaged across the eight mountain study sites from 2012 to 2014. Coniferous vegetation are *Abies balsamea* and *Picea rubens*, all other genera and species are deciduous

aboveground woody biomass (27 ± 5 kg) than the mean *Acer spp* (40 ± 6 kg), *Betula spp.* (245 ± 39 kg), and *Fagus grandifolia* (99 ± 38 kg).

Organic horizon simple box models

Under the assumption of steady state, the organic horizon MRT was calculated using atmospheric deposition and litterfall fluxes in Eqn 2 for each metal. The estimated litterfall fluxes for all metals except Ni were significantly smaller at coniferous stands than deciduous stands (Table 4). Comparing the atmospheric deposition flux to litterfall flux to the organic horizons, we estimate that atmospheric deposition is $\geq 50\%$ of the litterfall flux for Cd, Cu, Mo, Ni, Pb, and Zn (Table 4). We ran our model under the assumptions of both equal and unequal atmospheric deposition flux scenarios (Table 4).

Under the assumption of both steady state and equal atmospheric deposition rates, organic horizon MRT values ranged from 10 ± 2 yr for Mn at Deciduous stands to 1205 ± 278 yr for Pb at Coniferous stands (Table 4). Generally, MRT values for major plant essential metals (Ca, K, and Mg) were < 30 years while micronutrient and toxic trace metals had MRT values > 30 years (Cd, Cu, Mn, Mo, Ni, Pb and Zn) (Table 4). The calculated organic horizon MRTs were significantly greater for Ca, Cd, Cu, K, Mg, and Mn at coniferous stands when compared to deciduous stands (Table 4, $p < 0.05$). This is largely due to the smaller litterfall at coniferous stands compared to deciduous stands (Table 4, $p < 0.05$). Under the assumption of unequal atmospheric deposition in which fluxes to deciduous stands were 50 % smaller than at coniferous stands, but MRT values were similar to estimates under equal atmospheric deposition (Table 4). Organic horizon MRT times for Ca, Cd, Cu, K, Mg, and Mn MRT at coniferous stands were still significantly longer than deciduous stands (Table 4, $p < 0.05$). Using a MANOVA, we find that organic horizon MRT values are longer at coniferous stands than deciduous stands ($p < 0.01$).

Discussion

Major and trace metals in northern New England forest soils

Major and trace metal concentrations in the organic and mineral horizons were within the ranges observed by other studies in the northeastern United States (Gélinas et al. 2000; NADP 2007; Lawson et al. 2001; Likens 2015; Sarkar et al. 2015). On the basis of organic and mineral horizon concentrations, three distinctive patterns were observed: organic horizon-enriched (Ca, Cd, Mn, Mo, Pb), mineral horizon-enriched (Mg, Ni), and mixed profile (Cu, K, Zn). The organic horizon-enriched concentration pattern may be from translocation by vegetation (also referred to as uplift by Jobbágy and Jackson 2001) or anthropogenic deposition (Van Hook et al. 1977; Kraepiel et al. 2015). Calcium was greater in the organic horizons, likely due to translocation via litterfall from trees for continued growth and maintenance (Van Hook et al. 1977; Dauer et al. 2007). Moreover, Ca has been shown to be slowly leached in acidic forest soils using isotope labeling techniques (van der Heijden et al. 2014). Metals, such as Cd, Mn, and Pb, have been widely deposited to forests in the northeastern United States from anthropogenic sources and are enriched in the organic horizons above pre-industrial concentrations (Steinnes and Friedland 2006; Pratte et al. 2013; Richardson et al. 2015; Sarkar et al. 2015). The concentration profiles of these metals suggest that mineral horizon concentrations exceed the translocation to the organic horizons by vegetation, resulting from lower foliar and litterfall concentrations. Mixed concentration profiles for Cu, K, and Zn suggest they are minimally translocated to the organic horizons by trees due to either efficient resorption of the metals before leaf senescence (Duchesne et al. 2001) or cycling to the organic horizons are in a quasi-steady state.

Metals in organic horizons at coniferous and deciduous stands

Our results suggest that coniferous stands have smaller major and trace metals pools in their organic horizon than deciduous stands. It is important to note that coniferous stands were not 100 % coniferous (Table 1) and contained some deciduous trees. Similarly, deciduous stands contained coniferous vegetation as well. We hypothesized that coniferous stands would have greater belowground major and trace metal pools; however, the opposite was observed. The difference in organic horizon metal concentrations and pools between vegetation type arose from the ecophysiology of deciduous vegetation (Dauer et al. 2007), particularly the chemistry of their foliage and litterfall. Deciduous vegetation may have greater accumulation of major and trace metals in

the organic horizons due to root uptake or greater accumulation arising from soil physiochemical properties derived from their leaf litter. Root uptake and soil physicochemical properties are coupled and may affect uptake rates of metal from differences in availability due to pH (Friedland and Miller 1999; Augusto et al. 2015), fungal associations (Aubert et al. 2010; Carnol and Bazgir 2013), and mineral weathering rates (Drever, 1994; Binkley and Giardina 1998; Augusto et al. 2002).

Physical properties of the forest soil do not appear to have directly influenced the difference in organic horizon metal pools. The Oa horizons were significantly thicker for coniferous stands than deciduous stands (Table 2) and were expected to be linked to greater organic horizon metal pools. However, soil pH and % SOM may be responsible for greater metal concentrations and pools. Soil pH was significantly lower for coniferous stands than deciduous stands (Table 2), leading to potentially greater leaching of metals from coniferous organic horizons or greater retention in deciduous organic horizons (Dauer et al. 2007). Moreover, the lower % SOM in the Oa horizon at deciduous stands compared to coniferous stands suggests greater primary or secondary minerals may have increased major metal concentrations and pools. It must be noted that the strong acid digestion used to quantify the metal pools is incapable of digesting the majority of primary minerals; thus, major metals within primary minerals are unlikely to have contributed to the strong-acid extractable Ca, Mg, and K concentrations measured in the Oa horizon.

Our results suggest that most of the major and trace metal concentrations in the mineral horizons are similar between vegetation types. The difference in Cd, Ni, and Zn concentrations in the Bhs, Bs and BC horizons may have arisen from differences in soil chemical properties, vegetation type, or a combination of the two. Mineral horizon pH (Table 2) was significantly lower for E, Bhs, Bs, and BC horizons at coniferous stands than deciduous stands ($p < 0.05$), which may have increased the weathering or leaching rate of Cd, Ni, and Zn at coniferous stands. The mineral horizons may adsorb Cd, Ni and Zn at a higher rate than organic horizons due to secondary minerals such as Fe oxy-hydroxides or more recalcitrant SOM (Huang et al. 2011). In addition, vegetation type may have increased their mineral horizon concentrations due to greater translocation to the organic horizons by deciduous genera (Jobbágy and Jackson 2001). Despite the differences in Cd, Ni and Zn, the overall effect of vegetation type on metals in the mineral horizon may have been masked by differences among mountain study sites from site-dependent factors (Cross and Perakis 2011). We observed that metal concentrations and pools were significantly different among mountain study sites using the non-parametric Kruskal-Wallis test and combining data from coniferous and deciduous stands (Data not shown, $N=8$, $n=6$, $p<0.01$). These differences among mountain study sites may have arisen from factors not measured such as mineralogy, large rock fraction, and weathering rates (Friedland and Miller 1999; Cross and Perakis 2011).

Aboveground accumulations of metals

The observation of lower Ca, K, and Mg concentrations in coniferous foliage compared to deciduous foliage agrees with previous studies (e.g., St. Clair and Lynch 2005; Berger et al. 2009; Augusto et al. 2015). The lower concentrations of metals in coniferous foliage are likely due to ecophysiological properties such as higher cellulose and lignin concentrations in leaf tissue (Castro-Diez et al. 1997; Augusto et al. 2015). In addition, physiological properties unique to each species, such as leaf roughness, leaf area index, stomatal morphology, and cuticle material may control dry deposition accumulation on leaf surfaces and stomatal uptake (Browne and Fang 1978; Weathers et al. 2006). Major and trace metal concentrations of bolewood were generally lower than foliar concentrations due to the higher lignin and cellulose content (e.g., Van Hook et al. 1977; Berger et al. 2009). Bolewood concentrations were found to be similar between coniferous and deciduous vegetation but differed among genera. The higher bolewood metal concentrations in *Picea rubens* than deciduous genera may be due to the physiology of the tree and aboveground allocation of metals (Berger et al. 2009). This is inspite of observations that trees of the genus *Betula*, are known to accumulate metals in their woody tissues at higher concentrations than other northern hardwood genera (e.g., Wislocka et al. 2006).

We postulate that the smaller foliar pools of Ca, Cu, K, Mg, and Pb at coniferous stands were due to their lower foliar metal concentrations and smaller foliar biomass. This illustrates that coniferous stands have a smaller nutritional demand of major metals (Ca, K, Mg) and some trace metals than deciduous stands for annual foliage production. Assuming that the organic and

mineral horizons are the primary source of major and trace metals in the foliar pool, this implies that coniferous vegetation have a much smaller uptake of metals compared to deciduous vegetation and therefore have less of an impact on translocation of metals to the organic horizons via litterfall (Jobbágy and Jackson 2001).

Coniferous stands had significantly smaller metal pools in their aboveground woody biomass than deciduous stands on the basis of MANOVA test. This was expected due to the variation in the branch architecture and tree morphology between coniferous and deciduous vegetation. However, metal pools in aboveground woody biomass were similar between the vegetation types for each metal. Despite the greater woody biomass at deciduous stands, the higher metal concentrations in the bolewood of *Picea rubens* comprised a large enough metal pool for woody biomass metal pools to be similar between coniferous and deciduous stands. In addition, the maturity and size of the trees may lead to higher calculated concentrations in smaller, younger trees (Sette et al. 2013; Wernsdörfer et al. 2014). Thus, our estimates of metal concentrations and pools in the woody biomass of coniferous vegetation may have been overestimated because of their smaller average size and younger age.

We observed that aboveground major and trace metals pools in foliage and woody biomass were significantly smaller than belowground pools in the organic and mineral horizons (Table 3). For example, the organic and mineral horizon pools were > 4 orders of magnitude larger than foliar or woody biomass pools for Cu, Pb, and Zn (Table 3). The only pools that were similar in size were K and Mn. The combined foliar and woody biomass pools for K and Mn were roughly one-third of their respective organic horizon pools. The high uptake of Mn has been noted by Herndon et al. (2015) and been explained as potentially hazardous accumulations of Mn due to a negative correlation with photosynthesis rates (St. Clair and Lynch 2005). Thus, Mn pollution may be a wide-spread issue that few trace metal biogeochemical studies have taken note of across the northeastern U.S. (Herndon et al. 2011, 2015).

Organic horizon box model for coniferous and deciduous stands

We found that organic horizon MRT values for Ca, Cd, Cu, K, Mg, and Mn are longer at coniferous stands than deciduous stands. Our results support our initial hypothesis that MRT for major and trace metals in the organic horizons would be significantly longer at coniferous stands. The larger organic horizon metal pools and smaller litterfall fluxes are likely responsible for the greater MRT values at coniferous stands than deciduous stands. Comparisons of the sources of metals to the organic horizons illustrate the role of litterfall in the cycling of major and trace metals. Litterfall was > 95 % of the source for the major metals Ca, Mg, and K but atmospheric deposition was equally or more important for trace metals such as Cd, Mo, Ni, and Pb, accounting for ≥ 50 % of their flux to the organic horizons (Table 4). This illustrates that Cd, Mo, Ni, and Pb have been significantly influenced by atmospheric deposition in northern New England, US (Pratte et al. 2013; Sarkar et al. 2015). Moreover, this also illustrates that major metals are required in greater quantities by vegetation than trace metals because they occur in low concentrations in soils. On the basis of littefall and estimated MRT, we conclude that the cycling of major metals in the organic horizons is significantly affected by the overlying vegetation type but trace metal cycling is not affected by vegetation type.

The MRT values are useful as first-order approximations for the metals within soils at coniferous- and deciduous forests but are limited because of the assumptions used in our methods. The assumption of steady state for metal pools and fluxes are unlikely to be true due to changing deposition and organic horizon size over centuries. Thus, the MRT for recalcitrant pollutant metals, such as Pb, were poorly estimated. The organic horizon MRTs for Pb was estimated to be > 1000 years at both vegetation types, which significantly overestimates residence times calculated by Miller and Friedland (1994), Kaste et al. (2003), and Richardson et al. (2014) of < 100 years. The assumption that pools of Pb in the organic horizons are in steady state is unlikely to be true and is the source of the overestimation (Miller and Friedland 1994; Richardson et al. 2014). The aggradation of forest maturity and loss of primary succession species will likely decrease uptake and litterfall fluxes of metals (Carnol and Bazgir 2013; Augusto et al. 2015). Another potential error is the use of interpolated atmospheric deposition rates. The true atmospheric deposition at each site can vary from our interpolated values due to aspect, local topography, and many other geomorphic properties not taken into account. In addition, the atmospheric deposition that reaches the organic horizons after interacting with

foliage as throughfall or stemflow commonly has higher concentrations of Ca, Mg, and K due to canopy exchange processes (Berger et al. 2009; Adriaenssens et al. 2012; Carnol and Bazgir 2013). Thus, utilizing only atmospheric deposition rates is likely an underestimate of metals reaching the organic horizons.

Conclusions

We present evidence that vegetation type significantly influences organic horizon metal pools but not mineral horizons metal pools. Coniferous stands had 30–50 % smaller organic horizon pools of plant essential metals (Ca, K, Mg, Mn and Zn) than deciduous stands. We suggest the differences in organic horizon metal pools likely arose from differences in foliar chemistry, ecophysiology of the foliage, and resulting different soil properties. Mineral horizons concentrations and pools were generally similar for most metals at coniferous- and deciduous dominated stands. Deciduous vegetation had up to 60 % greater concentrations of plant-essential metals (Ca, K, Mg, Mn, Zn) in their foliage than coniferous vegetation. We estimated that coniferous stands have a much smaller litterfall flux of metals to the organic horizons compared to deciduous stands due to the differences in foliar chemistry.

Our box model estimated that Ca, Cd, Cu, K, Mg, and Mn organic horizon MRTs were greater for coniferous stands than deciduous stands. This was determined under the assumption of equal atmospheric deposition rates and using the assumption of 50 % greater atmospheric metal deposition at coniferous stands than deciduous stands. These results emphasize that coniferous stands cycle metals at a slower rate than deciduous stands. The shorter MRT in the organic horizons suggest plants control the accumulation of major metals in the organic horizons and are capable of cycling the organic horizon pool in less than half a century. Thus, a shift in vegetation type due to climate change or natural succession following clear-cutting can strongly change the vertical distribution of metals in soils over several decades. In addition, we observed litterfall was much smaller than interpolated atmospheric deposition values for trace metals (specifically Cu, Mo, Ni, and Pb), suggesting they are less driven by vegetation processes and more controlled by past anthropogenic emissions. Moreover, the longer MRT values predict these trace metals will be retained by the organic horizons for

decades or centuries longer than nutrient metals. Further investigations into the effect of vegetation type on belowground processes, particularly root uptake, mineral weathering, and sorption of leachates, are needed to constrain landscape and regional changes.

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