



# Manganese and Mn/Ca ratios in soil and vegetation in forests across the northeastern US: Insights on spatial Mn enrichment



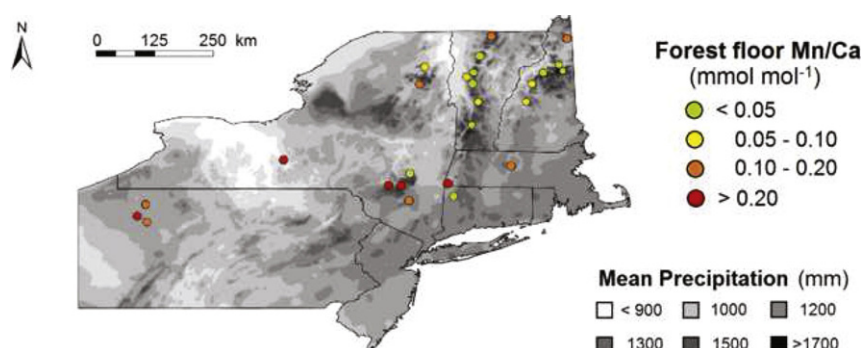
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## HIGHLIGHTS

- The first survey of Mn/Ca ratios in vegetation and soil across the northeastern U.S.
- Forest floor and mineral soil Mn/Ca decreased from Pennsylvania to New Hampshire.
- Foliage and bolewood Mn/Ca ratios decreased from Pennsylvania to New Hampshire.
- Enrichment factor for Mn/Ca ratios suggests soil horizons are enriched by 3.6 factor.
- It is hypothesized plant recycling of Mn will control retention of Mn in forests.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Manganese (Mn) cycling in the Critical Zone is important because of its role as an essential nutrient and potential toxicity to plants and organisms. Quantifying Mn enrichment in terrestrial environments has been limited since Mn is monoisotopic. However, elemental ratios of Mn/Ca ratios may be used to determine spatial Mn enrichment and in aboveground and belowground pools. The objectives of this study were to quantify the spatial variation in Mn concentrations and Mn/Ca ratios in foliage, bolewood, forest floor, and mineral soil horizons across the northeastern United States and compare Mn/Ca ratios to estimate enrichment. Forest floor and mineral soil samples were collected from 26 study sites across the northeastern United States and analyzed by strong acid digestion. Foliage and bolewood was collected from 12 of the 26 sites and analyzed for total Mn and Ca. Our results show forest floor and mineral soil horizon Mn concentrations and Mn/Ca ratios were higher at Pennsylvania and New York sites than New Hampshire and Vermont sites. Using a modified isotope equation, enrichment factors (EF) for Mn/Ca ratios were calculated to be ~3.6 in the forest floor, upper and lower mineral soil horizons at sites in New York and Pennsylvania compared to reference sites in New Hampshire and Vermont. Foliar and bolewood Mn concentrations also decreased from Pennsylvania towards New Hampshire. Moreover, foliar and bolewood Mn concentrations were strongly correlated to forest floor, upper, and lower mineral soil Mn concentrations. It was hypothesized that internal cycling (uptake, throughfall, and litterfall) of Mn controls retention of enriched Mn in forests. Geologic influences from a lithologic gradient and soil pH gradient could also influence Mn enrichment in addition to Mn pollution. Ratios of Mn/Ca and other elemental ratios hold promise as geochemical tracers but require further development.

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## 1. Introduction

Understanding manganese (Mn) cycling in the Critical Zone, the region between unweathered bedrock and the top of vegetation (Giardino

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and Houser, 2015), is important because of its role as an essential nutrient and potential toxicity to plants and organisms. Manganese is required by plants for structural components of chloroplasts and oxidation-reduction biochemical reactions (Burnell, 1988). In addition, manganese is needed by microbes for biogeochemical processes, such as white-rot fungi and need Mn for a lignin-degrading enzyme (Berg et al., 2015; Keiluweit et al., 2015). However, high Mn bioavailability in soil and water can lead to toxic effects in plants and has been linked to decline of sugar maples throughout the northeastern USA (Horsley et al., 2000; St. Clair and Lynch, 2005; Kogelmann and Sharpe, 2006). Because of its potential impacts on human health, Mn concentrations in drinking water are regulated by the United States Environmental Protection Agency (USEPA). For example, Woolf et al. (2002) and Bouchard et al. (2007) have observed impairment of cognitive development in children due to exposure to excessive Mn concentrations in drinking water due to groundwater sources.

Recent studies, such as Boudissa et al. (2006), Herndon and Brantley (2011), and Herndon et al. (2011) have noted that terrestrial ecosystems of North America have high concentrations in surface soils due to anthropogenic emissions. Although current Mn emission and atmospheric deposition rates are low, historical Mn emissions to the atmosphere and surface waters from human activities have estimated to be in the millions of kg range of Mn each year in the USA (USEPA, 2003; Herndon and Brantley, 2011). Metallurgical manufacturing, coal combustion, and domestic waste incineration have been substantial sources of Mn emissions (USEPA, 1984; Herndon and Brantley, 2011). However, surface soil concentrations can be elevated by a combination of sources in addition to atmospheric deposition (Millaleo et al., 2010; Herndon et al., 2011; Herndon and Brantley, 2011). Vegetation can increase Mn in surface soil horizons due to biological cycling by litterfall, throughfall, and uptake (Watmough et al., 2007; Kraepiel et al., 2015; Herndon et al., 2015).

Manganese does not have stable isotopes to track its movement or accumulation in the Critical Zone. However, elemental ratios may be developed to determine if terrestrial pools of Mn are enriched. Calcium may be cycled comparably to Mn by vegetation in terrestrial ecosystems (Gosz et al., 1983; Blum and Erel, 1997; Poszwa et al., 2000). Previous studies have observed that Ca and Mn accumulate comparably in soil and accrue similarly in plant tissues (c; Blum et al., 2008; Landre et al., 2010; Herndon et al., 2015). Deciduous vegetation has low resorption efficiency for Mn and Ca (Liu et al., 2014) and their accumulation in surface soils is dependent on vegetation cycling (Likens et al., 1998; Watmough et al., 2007). Assuming that ratios of Mn/Ca are cycled similarly in plants and soils, Mn/Ca ratio may be used to quantify enrichment of Mn through comparison with non-enriched terrestrial systems. A limiting factor for comparing Mn to Ca is their different geochemistry. Manganese is oxidation sensitive and may precipitate as a secondary oxide (Shanley, 1986; Horsley et al., 2000; Watmough et al., 2007; Herndon and Brantley, 2011) while Ca is not oxidation sensitive and its sorption is dominated by sorption to organic matter (Likens et al., 1998; Poszwa et al., 2000; Drouet and Herbauts, 2008). One assumption is that Mn pollution will source Mn at a much greater quantity than anthropogenic sources of Ca. NADP maps show that current deposition rates of Ca ranged from 0.3–1.2 kg ha<sup>-1</sup> in 2014 across the northeastern United States, with higher deposition in Pennsylvania and New York than New Hampshire and Vermont (NADP, 2015). However, if Mn enrichment is substantial, we assume the Mn/Ca ratio should reflect this despite higher Ca deposition in either part of the northeastern United States.

Studies such as Herndon et al. (2015) have estimated that surface mineral soil horizons across the northeastern United States are enriched with Mn. This ignores the forest floor (also known as the organic horizon and litter layer) and potential influence from vegetation. The forest floor has been used to identify spatial patterns of trace metal pollution such as Pb, Hg, Cu, Zn and other elements (Siccama and Smith, 1980; Johnson et al., 1982; Pouyat and McDonnell, 1991; Evans et al., 2005;

Kaste et al., 2006; Johnson and Richter, 2010; Richardson et al., 2013; Richardson et al., 2014; Richardson and Friedland, 2016). Thus, comparing the forest floor and mineral soil horizons with aboveground vegetation information across the northeastern United States may allow for identifying the spatial variation of Mn in forest soils and the role of vegetation. The objectives of this study were: 1) quantify the spatial variation in Mn and Mn/Ca ratios in the forest floor across the northeastern United States, 2) compare Mn/Ca ratios in late-season foliage and bolewood to forest floor and mineral soils horizons to infer influences from biological cycling. Information from this study can help assess terrestrial cycling of Mn and its dependence on biological cycling, geologic sources, and human inputs.

## 2. Materials and methods

### 2.1. Mountain sites and forest stands

Twenty six study sites across the northeastern United States were studied. Fifteen study sites were long-term research sites established to study Pb pollution (Johnson et al., 1982) and resampled in 2011 by Richardson et al. (2013). The other eleven study sites have been studied in other previous studies examining plant-soil interactions (two sites from Petrenko and Friedland, 2014; and eight sites from Richardson and Friedland, 2016; one sites from Richardson et al., unpublished). The mountain sites have mean annual temperatures ranging from 4 to 12 °C and mean annual precipitation ranging from 800 to 1300 mm (PRISM climate research group, 2012). Only forest stands on planar landforms and well-drained soils were chosen. Vegetation at all stands was secondary growth due to the historical clearing of the region in the 1800s (Foster, 1992). Bedrock ranged from sedimentary and low-grade metamorphic rocks (e.g. sandstones, shales, slates, mudstones) in Pennsylvania and New York to metamorphic and igneous rocks (e.g. phyllites, schists, granite) in Vermont and New Hampshire (Robinson and Kapo, 2003). The soil parent material for all sites (except Sites #1, 2, and 3) was predominately glacial-till deposited during the retreat of the Laurentian ice sheet ~14,000 years ago (Siccama, 1974; Pielou, 2008). Soil parent material at Sites #1, 2, and 3 are weathered sedimentary rocks with periglacial and eolian deposits (Pielou, 2008). All other soils were developed from glacial till, outwash deposits, or outcrops of weathered bedrock (c.f. Siccama, 1974; Kaste et al., 2006). The soils were well-drained and on level to shallow slopes (<12%). Soils were primarily classified as either Spodosols (Podzols in FAO/UNESCO) or Inceptisols (Cambisols in FAO/UNESCO) (Table 1), except Sites #1 and 3, which were classified as Ultisols (Acrisol in FAO/UNESCO). In general, more western sites were Ultisols and Inceptisols, central sites were Inceptisols and northern sites were Spodosols (Table 1). Vegetation at each site was mixed; sites ranged from primarily deciduous vegetation such as oaks (*Quercus* spp.), American beech (*Fagus grandifolia*), maples (*Acer* spp.), and birches (*Betula* spp.), to coniferous such as white pine (*Pinus strobus*), red spruce (*Picea rubens*), and eastern hemlock (*Tsuga canadensis*) (Table 1).

### 2.2. Soil and vegetation sample collection

Soil and vegetation sampling techniques are described in depth in Richardson et al. (2013), Petrenko and Friedland (2014) and Richardson and Friedland (2016). Late-season foliage and bolewood samples were collected from a subset of twelve sites (Sites 1–4, 19–26), from at least six trees of a genera at each forest stand in early October 2014 and late September 2016. Soils at each forest stand were sampled between July and September 2011, 2012 and 2016. Soils were classified as using US Soil Taxonomy guidelines (Soil Survey Staff, 2010). At each forest stand, three to five 225 cm<sup>2</sup> square sections of forest floor were collected. Soil profiles were sampled by each master horizon (A, E, B) until dense basal till or a hardpan was reached at each forest stand. A horizons (surface mineral horizons) and E horizons

**Table 1**  
Site location, vegetation type, and soil taxonomy.

Site #	Site name	Elev. (m)	Latitude (d.d.)	Longitude (d.d.)	Vegetation	Soil order	Soil temperature regime
1	Heart's Content, PA	580	41.689	-79.252	Pine/hemlock	Ultisol	Mesic
2	Cook's Forest, PA	430	41.347	-79.212	Pine/hemlock	Inceptisol	Mesic
3	Tionesta, PA	520	41.477	-79.379	Oak	Ultisol	Mesic
4	Yellow Barn, NY	440	42.334	-76.361	N. hardwood/oak	Inceptisol	Mesic
5	Balsam Lake, NY	820	42.067	-74.574	N. hardwood	Inceptisol	Frigid
6	Mohonk, NY	366	41.770	-74.158	N. hardwood	Inceptisol	Mesic
7	Mt. Tremper, NY	305	42.071	-74.312	Pine/hemlock	Inceptisol	Mesic
8	Windham, NY	580	42.301	-74.170	N. hardwood	Inceptisol	Frigid
9	Mohawk, CT	503	41.820	-73.297	Oak	Inceptisol	Frigid
10	Mt. Everett, MA	790	42.102	-73.431	Oak/pitch pine	Inceptisol	Frigid
11	Harvard Forest, NY	360	42.488	-72.188	N. hardwood	Inceptisol	Mesic
12	Whiteface, NY	1300	44.389	-73.897	Spruce/fir	Spodosol	Cryic
13	Newcomb, NY	550	43.969	-74.165	N. hardwood	Inceptisol	Frigid
14	Appalachian Gap, VT	778	44.211	-72.931	Spruce/fir	Spodosol	Frigid
15	Bromley, VT	625	43.214	-72.967	N. hardwood	Spodosol	Frigid
16	Bristol Cliffs, VT	555	44.140	-73.064	Pine/hemlock	Spodosol	Frigid
17	Gale River, NH	440	44.232	-71.608	N. hardwood	Inceptisol	Frigid
18	Wildcat Mt., NH	590	44.266	-71.238	Spruce/N. hardwood	Inceptisol	Frigid
19	Mt. Cardigan, NH	579	43.645	-71.933	Spruce/hemlock	Spodosol	Frigid
20	Chase Mt., NH	680	44.90	-71.14	N. hardwood	Spodosol	Frigid
21	Mt. Ellen, VT	608	44.11	-72.95	N. hardwood	Spodosol	Frigid
22	Jay Mt., VT	601	44.92	-72.54	N. hardwood	Spodosol	Frigid
23	Mt. Killington, VT	582	43.62	-72.86	N. hardwood	Spodosol	Frigid
24	Mt. Madison, NH	641	44.34	-71.27	N. hardwood	Spodosol	Frigid
25	Mt. Mansfield, VT	704	44.52	-72.83	N. hardwood	Spodosol	Frigid
26	Mt. Moosilauke, NH	610	43.99	-71.82	N. hardwood	Spodosol	Frigid

(eluviated horizons) were identified by color, pH, and %LOI. B horizons (horizons of accumulation) were identified and classified by color, pH, and %LOI. Upper mineral soil horizons were the first mineral soil horizon beneath the forest floor (A or E horizons). Lower mineral soil horizons were the mineral soil horizon beneath the first horizon. Five of the study sites had shallow soils in which a lower mineral soil horizon could not be collected. All vegetation and soil samples were dried at 25 °C to a constant weight and roots > 5 mm in diameter were removed and sieved to <2 mm.

### 2.3. Analytical methods

Whole forest floor samples (Oi + Oe + Oa horizons), <2 mm mineral soil subsamples, and ground foliage and bolewood samples were analyzed for Mn and Ca using a strong acid digestion. Soil and vegetation chemical analyses were oven-dried overnight at 105 °C, weighed, and then ashed for 5 h at 550 °C to oxidize organic matter. Soil samples were then pulverized in a boron carbide mortar and pestle < 100 µm. A strong acid digestion was used to quantify pseudo-total metals. This digestion focuses on metals that are potentially plant available immediately to decadal scales of time (exchangeable bound + organic matter bound + secondary oxide bound) without focusing on variations in primary minerals as with total soil digestions or variations in soil physicochemical properties as with extractable phases. See Kaste et al. (2006) or Richardson et al. (2014) for in-depth digestion details. In brief, soil subsamples were extracted with 3 mL of 1 M HNO<sub>3</sub> + 2 mL of distilled 1 M HCl (Trace metal grade, VWR Analytical, Radnor, PA, USA) for 2 h. The extracts were filtered to using Whatman 40 filtration paper to remove undigested mineral phases and diluted to 20 mL. Soil digests were diluted to 0.5 M HNO<sub>3</sub> and analyzed for metals by ICP-OES. With every 20 samples, at least one preparation blank, duplicate, and standard reference material (SRM) were included. Peach leaves SRM 1547 and Montana soil 2711 from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) were used as SRMs for organic samples and mineral soil samples, respectively. Recoveries for Mn and Ca were (89–99%) and (92–98%), respectively, of their certified values. Intra-sample duplicate variation was <10%. Manganese concentrations in the preparation blank samples were <0.1 ng g<sup>-1</sup>. Calcium concentrations in preparation blanks samples were <0.01 µg g<sup>-1</sup>.

### 2.4. Statistical methods and data analyses

Descriptive statistics were calculated in Matlab. Mean values given in the text, tables, and figures are shown ± 1 standard error. The variations in metal concentrations in the sites and tree genera were compared using the non-parametric Kruskal-Wallis test with post hoc Wilcoxon signed-rank test. Comparisons between two categorical variables (e.g. sedimentary vs. meta-igneous sites) were calculated using Mann-Whitney *U* test. Data was analyzed for outliers using Dixon's *Q*-test. Linear regressions were used to determine correlations Mn and Ca concentrations and Mn/Ca ratios with spatial data and soil physicochemical properties.

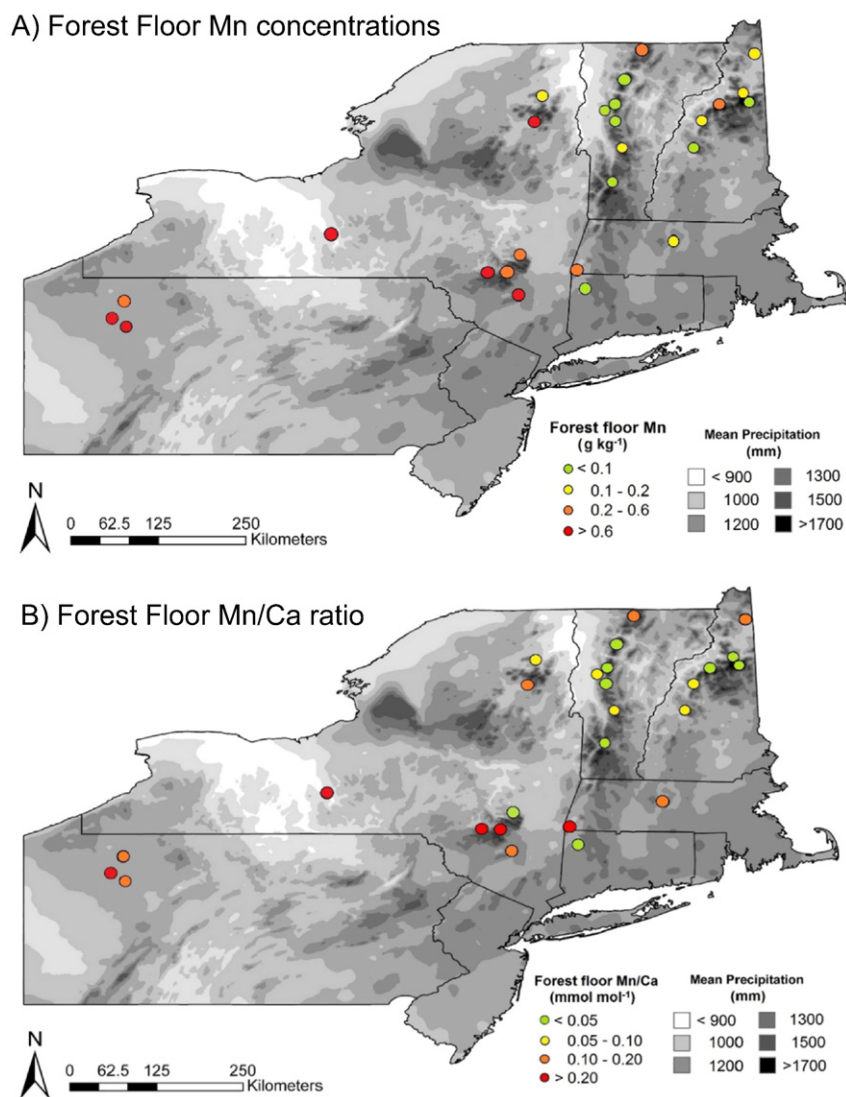
## 3. Results

### 3.1. Forest floor and mineral soil Mn and Ca concentrations

Forest floor and mineral soil concentrations of Mn and Ca were determined using a pseudo-total strong acid extraction. Forest floor data for each site is given in Supplemental Table 1. Forest floor concentrations of Mn ranged from 0.01 to 1.81 g kg<sup>-1</sup> with an average of 0.44 g kg<sup>-1</sup> and median of 0.17 g kg<sup>-1</sup>. Forest floor concentrations of Ca ranged from 0.6 to 6.3 g kg<sup>-1</sup> with an average of 2.2 g kg<sup>-1</sup> and median of 1.8 g kg<sup>-1</sup>.

Forest floor Mn/Ca ratios ranged from 0.01–0.51 mmol mol<sup>-1</sup> with an average of 0.13 mmol mol<sup>-1</sup> and median of 0.8 mmol mol<sup>-1</sup>. Since Mn and Ca concentrations were highest in Pennsylvania and New York sites and decreased with latitude and longitude, Mn/Ca ratio also followed this pattern (Fig. 1).

Upper mineral soil horizons (A and E horizons) were collected from 0 to 20 cm in depth from all 26 study sites. Lower mineral soil horizons (B, Bw, and Bhs horizons) ranged from 2 to 45 cm in depth and were collected at only 21 of the 26 study sites due to shallow bedrock and hardpans. Upper and lower mineral soil Mn concentrations ranged nearly two orders of magnitude, from 0.01 to 1.47 g kg<sup>-1</sup> (Supplemental Table 2). Upper mineral soil Mn concentrations (0.29 ± 0.07 g kg<sup>-1</sup>) were not significantly different from lower mineral soil Mn concentrations (0.31 ± 0.07 g kg<sup>-1</sup>). Mineral soil Ca concentrations ranged



**Fig. 1.** Forest floor Mn concentrations ( $\text{g kg}^{-1}$ ) and Mn/Ca ratio ( $\text{mmol mol}^{-1}$ ) at 26 sites (in circles) displayed with mean annual precipitation (1981–2011) map graphics from the PRISM Climate Group. Copyright © 2011, PRISM Climate Group, Oregon State University, <http://prism.oregonstate.edu>, Map created 10 21 2012. Color categories for Mn/Ca ratios are based upon quartiles of the data.

from  $0.06\text{--}1.51 \text{ g kg}^{-1}$ . Data for lower mineral soil horizons is given in Supplemental Table 3. The average Ca concentration was not significantly different between upper mineral soil ( $0.49 \pm 0.08 \text{ g kg}^{-1}$ ) and lower mineral soil ( $0.60 \pm 0.09 \text{ g kg}^{-1}$ ) horizons. Mineral soil Mn/Ca ratio ranged nearly two orders of magnitude, from  $0.08\text{--}6.43 \text{ mmol mol}^{-1}$ . Upper mineral soil Mn/Ca ratios ( $1.07 \pm 0.31$ ) were not significantly different from lower mineral soil Mn/Ca ratios ( $1.12 \pm 0.31 \text{ g kg}^{-1}$ ).

Linear regressions were performed to determine correlations of Mn and Ca concentrations and Mn/Ca ratios in forest floor and mineral soil horizons with study area location and physicochemical variables (Table 2). In brief, forest floor Mn and Ca concentrations and Mn/Ca ratios were negatively correlated with latitude and longitude (Table 2). Upper mineral soil Mn concentrations and Mn/Ca ratios were negatively correlated with latitude and longitude (Table 2). Upper mineral soil Ca concentrations did not correlate with spatial variables and only correlated negatively with pH (Table 2). However, lower mineral soil Ca concentrations were positively correlated with latitude (Table 2). Forest floor Mn and Ca concentrations were positively correlated with pH (Table 2). Upper mineral soil Mn/Ca ratios were also positively correlated with pH while lower mineral soil Mn/Ca ratios were negatively correlated with

%LOI (Table 2). Lower mineral soil Ca was positively correlated with %LOI (Table 2).

Forest floor Ca concentrations were not significantly correlated with upper mineral soil Ca concentrations, respectively ( $R < 0.50$ ). However, forest floor Mn concentrations and Mn/Ca ratios were significantly correlated with upper mineral soil Mn/Ca ratios ( $R = 0.52$ ). Forest floor Mn

**Table 2**

Forest floor, upper mineral soil and lower mineral soil horizons linear regression model outputs of Mn and Ca concentrations with soil and study site properties for all 26 study sites. n.s. denotes not significant ( $P > 0.05$ ).

R coefficients		Elevation	Latitude	Longitude	pH	%LOI
Forest floor	Ca	n.s.	−0.51	−0.53	0.72	n.s.
	Mn	n.s.	−0.57	−0.68	0.70	n.s.
	Mn/Ca	n.s.	−0.55	−0.65	0.51	n.s.
Upper Mineral soil	Ca	n.s.	n.s.	n.s.	−0.60	n.s.
	Mn	n.s.	−0.51	−0.68	n.s.	n.s.
	Mn/Ca	n.s.	−0.56	−0.67	0.78	n.s.
Lower mineral soil	Ca	n.s.	0.56	n.s.	n.s.	0.70
	Mn	n.s.	−0.51	−0.58	n.s.	n.s.
	Mn/Ca	n.s.	−0.63	−0.68	n.s.	−0.49



and Ca concentrations and Mn/Ca ratios were not significantly correlated with lower mineral soil Mn and Ca concentrations ( $R < 0.50$ ). Upper mineral soil Mn and Ca concentrations and Mn/Ca ratios were positively correlated with lower mineral soil Ca ( $R = 0.74$ ) and Mn ( $R = 0.92$ ) concentrations and Mn/Ca ratios ( $R = 0.85$ ), respectively.

An isotope equation for calculating relative enrichment or depletion ' $\delta$ ', was modified to quantify enrichment factors (EF) of Mn/Ca ratio in the forest floor and mineral soil horizons across the spatial gradient (Eq. (1)). An average of Mn/Ca ratios across sites in Vermont, New Hampshire, and Massachusetts was used as the reference Mn/Ca value.

$$EF = \frac{Mn/Ca_{\text{Sample}}}{Mn/Ca_{\text{Reference area average}}} - 1 \quad (1)$$

Forest floor Mn/Ca ratios across the reference area was 0.05. Upper mineral soil and lower mineral soil Mn/Ca ratios across the reference area were 0.41 and 0.44, respectively. Using Eq. (1), sites in Vermont, New Hampshire, and Massachusetts had calculated forest floor, upper mineral soil, and lower mineral soil EF values ranging between  $-0.8$  up to 3.5 but average 0.0 because they were the reference area (Fig. 2). Sites in New York, Pennsylvania, and Connecticut had much higher EF values for the forest floor ( $EF = 3.6 \pm 0.7$ ), upper mineral soil ( $EF = 3.7 \pm 1.5$ ), and lower mineral soil ( $EF = 3.5 \pm 1.3$ ) (Fig. 2).

### 3.2. Late-season foliage and bolewood Mn, and Ca concentrations

Late-season foliage and bolewood was collected from a subset of 12 sites (see Methods, Section 2.2). Manganese and Ca concentrations were averaged among genera to determine Mn and Ca concentrations for each site (Table 3). Foliar Mn concentrations among sites ranged from 0.32 to 3.08  $\text{g kg}^{-1}$  with a median of 0.81  $\text{g kg}^{-1}$  and an average of  $1.10 \pm 0.25 \text{ g kg}^{-1}$ . Foliar Ca concentrations ranged from 4.1 to 6.3  $\text{mg g}^{-1}$  with a median of 5.0  $\text{g kg}^{-1}$  and an average of  $4.9 \pm 0.2 \text{ g kg}^{-1}$  (Table 3). Foliar concentrations of Mn and Ca varied significantly among genera (Table 6). Foliar Mn concentrations were lowest for striped maple and highest for white pine and oaks. Bolewood Mn concentrations ranged from 0.19–0.80 across sites and had a median of 0.31  $\text{g kg}^{-1}$  with an average of  $0.36 \pm 0.05 \text{ g kg}^{-1}$  (Table 3). Bolewood Ca concentrations were varied among sites, ranging from 2.2 to 4.8  $\text{g kg}^{-1}$  with an average of  $3.3 \pm 0.3 \text{ g kg}^{-1}$  and median of 2.9 (Table 3). Bolewood Mn concentrations were lowest for striped maple and highest for oak and spruce. Foliar Mn and Ca concentrations were significantly higher than bolewood Mn and Ca concentrations across sites.

Linear regressions were performed to determine if foliar and bolewood Mn and Ca concentrations correlated with forest floor and mineral soil concentrations and also with study area location and physicochemical variables. Foliar and bolewood Mn concentrations and Mn/Ca ratios were negatively correlated with elevation, latitude, and longitude (Table 4). Foliar Ca concentrations were not correlated with any spatial variables while bolewood Ca concentrations were positively correlated with elevation, latitude, and longitude (Table 4). Moreover, foliar Mn concentrations were positively correlated with forest floor, upper mineral soil, or lower mineral soil Mn concentrations (Table 5). Conversely, foliar Ca concentrations were not correlated with forest floor, upper mineral soil, or lower mineral soil Ca concentrations (Table 5). Similarly, foliar Mn/Ca ratios were positively correlated with forest floor, upper mineral soil, or lower mineral soil Mn/Ca ratios (Table 5). Foliar and bolewood Mn concentrations were significantly correlated with forest floor pH and Mn concentrations (Table 5).

Manganese and Ca concentrations and Mn/Ca ratios in foliage and bolewood were compared for vegetation that were found across the spatial gradient, in Pennsylvania and New York sites as well in New Hampshire and Vermont sites (Fig. 3). In Panel A, foliar Mn concentrations were significantly higher at Pennsylvania and New York sites compared to New Hampshire and Vermont sites for Eastern hemlock and

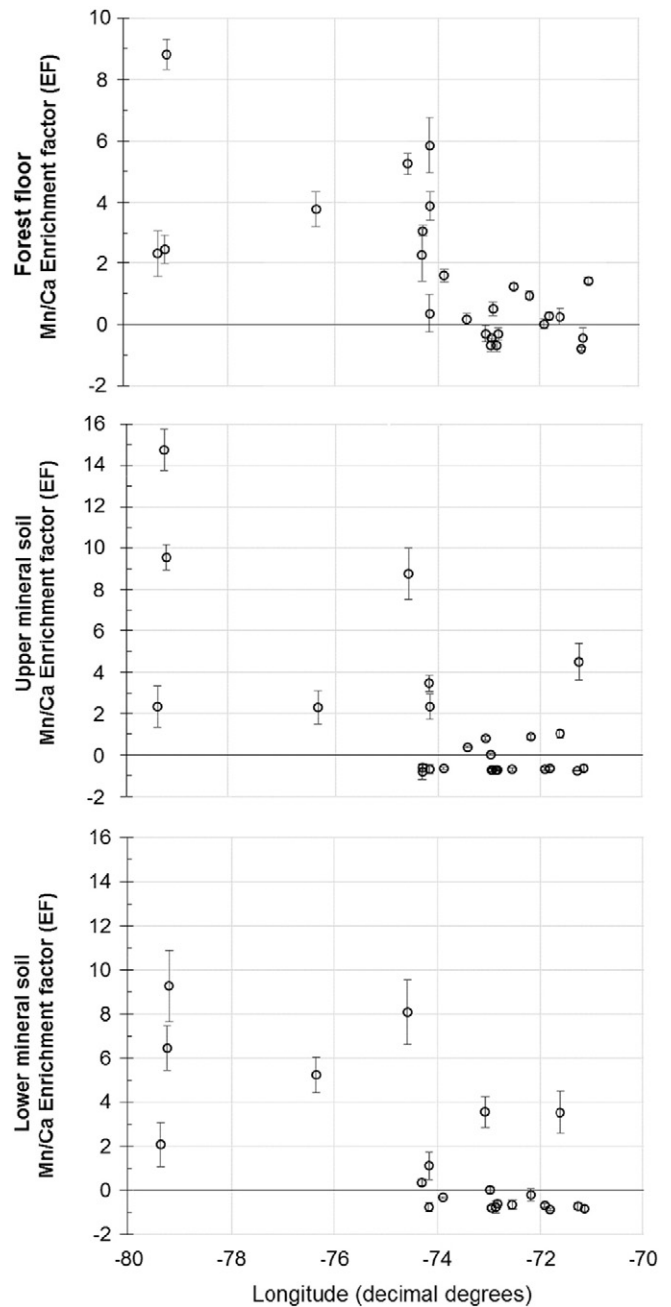


Fig. 2. Forest floor, upper mineral soil, and lower mineral soil Mn/Ca ratio enrichment factors calculated using Eq. (1) at sites across the northeastern United States. Forest floor and upper mineral soil plots included all 26 sites while lower mineral soil plot only had 21 sites due to shallow bedrock.

maples. However, maple foliar and bolewood Ca concentrations were lower for Pennsylvania and New York sites than New Hampshire and Vermont sites. Eastern hemlock and maples foliar and bolewood Mn/Ca ratios were greater for Pennsylvania and New York sites to New Hampshire and Vermont sites (Fig. 3, Panels E and F).

## 4. Discussion

### 4.1. Spatial variation of Mn and Mn/Ca in the forest floor and mineral soil

The first objective of this study was to determine the spatial variation in Mn concentrations and Mn/Ca in the forest floor and mineral soil horizons across sites to understand the spatial extent of enrichment of Mn concentrations. Our Mn concentrations were comparable to other

**Table 3**

Total Ca and Mn concentrations in late-season foliage and bolewood by across the 12 study area subset. All genera at each site were averaged together.

Site	Foliar Ca g kg <sup>-1</sup>	Foliar Mn g kg <sup>-1</sup>	Foliar Mn/Ca mmol mol <sup>-1</sup>	Bolewood Ca g kg <sup>-1</sup>	Bolewood Mn g kg <sup>-1</sup>	Bolewood Mn/Ca mmol mol <sup>-1</sup>
Hearts Content, PA	4.2 ± 0.3	1.56 ± 0.15	0.29 ± 0.03	2.2 ± 0.2	0.35 ± 0.04	0.13 ± 0.02
Cook Forest, PA	4.2 ± 0.3	2.44 ± 0.27	0.45 ± 0.06	2.4 ± 0.3	0.60 ± 0.07	0.20 ± 0.03
Tionesta, PA	5.3 ± 0.5	3.08 ± 0.48	0.46 ± 0.09	2.7 ± 0.3	0.80 ± 0.18	0.22 ± 0.05
Yellow Barn SF NY	4.1 ± 0.3	1.09 ± 0.09	0.22 ± 0.02	2.3 ± 0.2	0.29 ± 0.03	0.10 ± 0.01
Mt. Cardigan, NH	4.2 ± 0.3	0.93 ± 0.24	0.17 ± 0.0	2.8 ± 0.3	0.43 ± 0.11	0.11 ± 0.02
Chase Mt., NH	4.3 ± 0.3	0.52 ± 0.14	0.10 ± 0.03	3.8 ± 0.3	0.36 ± 0.12	0.07 ± 0.03
Mt. Ellen, VT	5.0 ± 0.8	0.55 ± 0.10	0.10 ± 0.03	3.2 ± 0.6	0.31 ± 0.08	0.08 ± 0.02
Jay Mt., VT	5.4 ± 0.5	0.99 ± 0.25	0.13 ± 0.03	2.8 ± 0.3	0.31 ± 0.07	0.08 ± 0.02
Mt. Killington, VT	5.9 ± 0.8	0.49 ± 0.10	0.08 ± 0.03	4.0 ± 0.5	0.22 ± 0.06	0.05 ± 0.02
Mt. Madison, NH	5.0 ± 0.7	0.70 ± 0.23	0.11 ± 0.03	4.4 ± 0.6	0.28 ± 0.07	0.06 ± 0.02
Mt. Mansfield, VT	6.3 ± 1.1	0.32 ± 0.06	0.05 ± 0.02	4.8 ± 1.1	0.18 ± 0.05	0.04 ± 0.01
Mt. Moosilauke, NH	5.8 ± 0.8	0.57 ± 0.09	0.08 ± 0.02	3.5 ± 0.4	0.19 ± 0.03	0.04 ± 0.01

previous studies in Vermont and New Hampshire (Evans et al., 2005; Schide and Munroe, 2015). Our results also show that there is a strong spatial gradient of Mn concentrations; New Hampshire and Vermont sites had lower Mn concentrations sites than Pennsylvania and New York sites, which was illustrated in Fig. 1. The spatial variation in forest floor Mn concentrations was found to be significant by correlations with latitude and longitude (Table 2). The Mn/Ca ratio was calculated to determine if the higher Mn concentrations in the forest floor at western sites were simply due to a relative enrichment of elements. If an overall enrichment of elements had occurred, then normalizing Mn to Ca ratios should show comparable Mn/Ca ratios across the study region. Some sites with relatively high forest floor Mn concentrations had relatively low to moderate Mn/Ca ratios (e.g. Sites #8 and #13). However, the overall pattern of decreasing Mn/Ca concentrations with latitude and longitude remained (Fig. 1; Table 3). Thus, it may be surmised that Mn concentrations were higher at sites in Pennsylvania and New York than expected if due to an overall enrichment of elements.

Moreover, this pattern continued into the mineral soil horizons. Upper and lower mineral soil concentrations were higher in Pennsylvania and New York sites than Vermont and New Hampshire and negatively correlated with latitude and longitude. Similar to the forest floor, Mn/Ca ratios in the upper and lower mineral soil horizons were still higher at Pennsylvania and New York sites and negatively correlated with latitude and longitude. By calculating the enrichment factor (EF) for the forest floor, upper mineral soil, and lower mineral soil horizons (Fig. 2), Mn/Ca ratios were shown to on average ~ 3.6 higher at sites in New York and Pennsylvania than more eastern reference sites in New Hampshire and Vermont quite consistently. Thus, forest floor, upper mineral soil, and lower mineral horizons at more western sites have on average 360% more Mn than would be expected based upon forest soils of New England. One important assumption is that forest soils of New Hampshire and Vermont are representative of non-enrichment but could also be interpreted as depleted in Mn/Ca with respect to Pennsylvania and New York. However, studies such as Herndon et al. (2015) note that mineral soil horizons in New Hampshire and Vermont are non-enriched in Mn with respect to soil parent material.

Observations in this study are in agreement with previous studies that identified soils in Pennsylvania as enriched in Mn (Herndon et al.,

2011; Herndon et al., 2015). One difference from previous studies was the use of a strong acid digestion compared to a total soil digestion. The technique used in this study focused on metals in non-primary mineral phases and avoided differences in exchangeable fractions which relate more to soil sorption capacity than total elements present. While total soil digestions are able to quantify total Mn with respect to weathered minerals and mass transfer coefficients, it does not measure the fraction most available to plants and organisms.

Using any digestion or extraction method, however, has been limited in determining if surface soils and aboveground tissues are enriched in Mn due to atmospheric deposition of Mn pollution or natural Mn enrichment from biological cycling by foliar inputs (Jobbágy and Jackson, 2001; Kraepiel et al., 2015). There are a multitude of industrial Mn pollution sources located in and near Pennsylvania and Ohio (Herndon et al., 2011; Carter et al., 2015; Herndon et al., 2015). Because of their location, these point sources are most likely to substantially impact forest soils of Pennsylvania and New York and unlikely to affect New Hampshire and Vermont due to their distance. For example, work by Carter et al. (2015) has shown that one of the largest emitters of Mn in the United States, a ferromanganese refinery, had been enriched the top 1 m of soil around the facility by 800 g Mn m<sup>-2</sup>. Moreover, Boudissa

**Table 5**

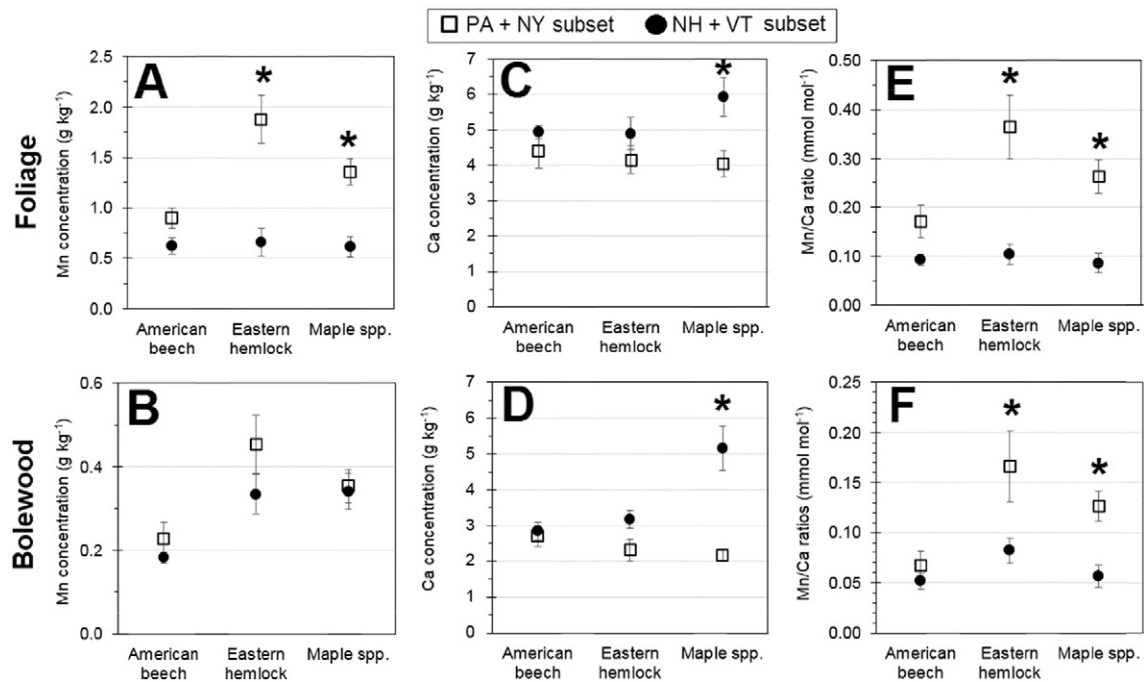
Foliage and bolewood linear regression model outputs of Mn and Ca with soil physico-chemical properties. (n.s.) denotes not significant (P &gt; 0.05).

R coefficients		Forest floor pH	Forest floor %LOI	Forest floor Ca	Forest floor Mn	Forest floor Mn/Ca
Foliar	Ca	n.s.	n.s.	n.s.	n.s.	n.s.
	Mn	0.83	-0.61	0.89	0.84	0.57
	Mn/Ca	0.76	-0.57	0.84	0.91	0.52
Bolewood	Ca	n.s.	-0.61	n.s.	-0.59	n.s.
	Mn	0.58	0.44	-0.20	0.75	0.53
	Mn/Ca	n.s.	n.s.	n.s.	0.79	n.s.
		Upper mineral soil pH	Upper mineral soil %LOI	Upper mineral soil Ca	Upper mineral soil Mn	Upper mineral soil Mn/Ca
Foliar	Ca	n.s.	n.s.	n.s.	n.s.	n.s.
	Mn	n.s.	n.s.	n.s.	0.85	n.s.
	Mn/Ca	n.s.	n.s.	n.s.	0.82	n.s.
Bolewood	Ca	n.s.	-0.60	n.s.	-0.59	n.s.
	Mn	0.59	n.s.	n.s.	0.75	0.53
	Mn/Ca	n.s.	n.s.	n.s.	0.79	n.s.
		Lower mineral soil pH	Lower mineral soil %LOI	Lower mineral soil Ca	Lower mineral soil Mn	Lower mineral soil Mn/Ca
Foliar	Ca	n.s.	n.s.	n.s.	n.s.	n.s.
	Mn	n.s.	-0.62	-0.53	0.86	n.s.
	Mn/Ca	n.s.	-0.67	-0.64	0.82	n.s.
Bolewood	Ca	n.s.	n.s.	n.s.	-0.54	n.s.
	Mn	n.s.	n.s.	n.s.	0.77	n.s.
	Mn/Ca	n.s.	-0.59	-0.54	0.79	n.s.

**Table 4**

Foliage and bolewood linear regression model outputs of Mn and Ca with location data at subset of 12 sites. n.s. denotes not significant (P &gt; 0.05).

R coefficients		Elevation	Latitude	Longitude
Foliar	Ca	n.s.	n.s.	n.s.
	Mn	-0.68	-0.84	-0.86
	Mn/Ca	-0.74	-0.89	-0.90
Bolewood	Ca	0.73	0.69	0.68
	Mn	-0.50	-0.67	-0.67
	Mn/Ca	-0.68	-0.83	-0.84



**Fig. 3.** A comparison of Mn and Ca concentrations in foliage (Panels A, C, E) and bolewood (Panels B, D, F) between Pennsylvania (PA) and New York (NY) sites to New Hampshire (NH) and Vermont (VT) sites. For PA + NY sites, data are from American beech (8 trees, 1 site), Eastern hemlock (12 trees, 2 sites), and Maple spp. (8 trees, 1 site). For NH + VT sites, data are from American beech (24 trees, 8 sites), Eastern hemlock (15 trees, 8 sites), and Maple spp. (24 trees, 8 sites). (\*) indicates a significant difference ( $P < 0.05$ ).

et al. (2006) found a manganese alloy production plant in Beauharnois, Quebec, CA, had enriched nearby soils up to  $283 \text{ g kg}^{-1}$ , or 20,000 times higher than forest soils of Vermont and New Hampshire. Although direct point source pollution from these two large Mn emission sources is distant from the forest soils of Vermont and New Hampshire, it is difficult to assess if they have had any impact on the forests of New England.

Manganese is sourced from biological cycling, chemical weathering, and human pollution and this study was not designed to test if Mn enrichment was due to anthropogenic pollution or natural enrichment. The spatial gradient coincides with a lithologic gradient, sedimentary rocks in the western sites of Pennsylvania and New York and high-grade metamorphic and igneous rocks in New Hampshire and Vermont. Although various studies have demonstrated and quantified anthropogenic inputs as the source of Mn to forests of Pennsylvania and surrounding areas, lithologic sources are an important Mn source with the potential to influence the Mn/Ca ratio.

One limitation for applying Mn/Ca ratios to soil are the different geochemical behaviors of Mn and Ca. Manganese has a more complex geochemical behavior than Ca in soil; Mn may precipitate or sorb onto secondary oxide minerals and change oxidation state (Watmough et al., 2007), while Ca soil biogeochemistry is dominated by sorption to organic matter and biological uptake (Likens et al., 1998; Drouet and Herbauts, 2008). Land and Öhlander (2000) estimated that weathering and mobilization of Mn from soils in northern Sweden was 4–7 times slower than for Ca. Moreover, lower acidity may influence greater retention of Mn in soils at Pennsylvania and New York sites. This study observed a positive correlation of forest floor pH and Mn concentrations and Mn/Ca ratio. Lower Mn solubility and mobility in soils with higher pH may also be an important factor in the spatial gradient of Mn concentrations and Mn/Ca ratio in the forest floor. However, Watmough et al. (2007) observed lower Mn uptake by vegetation in soils with higher soil pH. Moreover, Ca was also positively correlated with soil pH and had a corresponding increase in Ca with soil pH. Thus, effects from a higher soil pH should be taken into account by normalization using the Mn/Ca ratio. Subsequent work may further our understanding of the change in the Mn/Ca ratio during weathering and biological cycling.

#### 4.2. Mn and Mn/Ca in foliage and bolewood

Foliage and bolewood from dominant tree genera were collected from a subset of twelve sites to determine if there are spatial variations in Mn and Ca concentrations in aboveground vegetation. Foliage and bolewood concentrations were similar to previous studies conducted in southern Canada and in the northeastern United States (e.g. Dasch et al., 2006; Landre et al., 2010; Kraepiel et al., 2015). Foliar and bolewood Mn concentrations exhibited an identical spatial pattern as Mn in the forest floor and mineral soil, with decreasing Mn concentrations from Pennsylvania towards New Hampshire (Table 4). Moreover, foliar and bolewood Mn concentrations were strongly correlated to forest floor, upper, and lower mineral soil Mn concentrations (Table 5). This strongly suggests that accumulation of Mn in vegetation was directly controlled by presence in soil, which was greater at sites in Pennsylvania and New York. This relationship was not observed for Ca concentrations. Foliar Ca concentrations were not significantly different spatially (Table 4). Bolewood Ca concentrations had the opposite pattern as Mn concentrations and significantly increased from Pennsylvania to New Hampshire. Lastly, foliar and bolewood Ca concentrations were not correlated with forest floor, upper mineral soil, or lower mineral soil Ca concentrations. These weak correlations suggest that accumulation of Ca in aboveground tissues was driven less by availability in soil and may instead depend on internal cycling efficiencies of uptake, throughfall and litterfall (Likens et al., 1998; Blum et al., 2008) and atmospheric sources. Previous studies have shown that atmospheric sources of Ca to vegetation in the northeastern US is small but non-negligible (Bailey et al., 1996; Likens et al., 1998).

Foliar and bolewood Ca and Mn concentrations varied significantly with genera (Table 6). Birches had the highest foliar Ca concentrations while red spruce had the lowest foliar Ca concentrations (Table 6). White pine had the highest Mn concentrations while striped maple had the lowest Mn concentrations (Table 6). However, tree genera composition of the forest stands were not homogeneous across the spatial gradient (more white pine and oaks in Pennsylvania and New York; more birches and red spruce in Vermont and New Hampshire). Thus,

**Table 6**

Total Ca and Mn concentrations in late-season foliage and bolewood by genera across the 12 study area subset.

Site	Foliar Ca g kg <sup>-1</sup>	Foliar Mn g kg <sup>-1</sup>	Foliar Mn/Ca mmol mol <sup>-1</sup>	Bolewood Ca g kg <sup>-1</sup>	Bolewood Mn g kg <sup>-1</sup>	Bolewood Mn/Ca mmol mol <sup>-1</sup>
American beech	4.7 ± 0.3	0.7 ± 0.1	0.13 ± 0.03	2.8 ± 0.3	0.20 ± 0.03	0.06 ± 0.01
Birch spp.	6.9 ± 0.6	1.0 ± 0.2	0.12 ± 0.03	3.4 ± 0.3	0.27 ± 0.06	0.06 ± 0.02
Eastern Hemlock	4.5 ± 0.4	1.4 ± 0.3	0.26 ± 0.07	2.7 ± 0.3	0.41 ± 0.06	0.13 ± 0.03
Maple spp.	5.1 ± 0.5	0.9 ± 0.1	0.16 ± 0.02	3.9 ± 0.6	0.35 ± 0.04	0.09 ± 0.01
Oak spp.	4.5 ± 0.5	2.0 ± 0.5	0.34 ± 0.07	2.4 ± 0.3	0.55 ± 0.15	0.16 ± 0.03
Red spruce	2.8 ± 0.2	0.8 ± 0.1	0.21 ± 0.03	3.0 ± 0.2	0.54 ± 0.08	0.13 ± 0.02
Striped maple	5.9 ± 0.5	0.1 ± 0.0	0.01 ± 0.01	4.5 ± 0.7	0.04 ± 0.01	0.02 ± 0.01
White pine	4.3 ± 0.3	2.1 ± 0.3	0.37 ± 0.05	2.4 ± 0.2	0.50 ± 0.08	0.16 ± 0.03

comparisons of foliar and bolewood concentrations for each genera along the spatial gradient are limited. However, American beech, Eastern hemlock, and maples were present in across the spatial gradient. Foliar Mn concentrations of Eastern hemlock and maples were significantly higher at Pennsylvania and New York sites compared to New Hampshire and Vermont sites (Fig. 3, Panel A). In addition, foliar and bolewood Mn/Ca ratios for Eastern hemlock and maples were greater at Pennsylvania and New York sites to New Hampshire and Vermont sites (Fig. 3, Panels E and F).

These results suggest that the accumulation of Mn in foliage and bolewood by Eastern hemlock and maples was affected by the spatial gradient. Because of the previously mentioned correlation between foliage and bolewood Mn concentrations with forest floor and mineral soil Mn concentrations, we surmise that spatial variation in foliage was directly linked to soil sources of Mn. The spatial variation in Mn in foliage and bolewood may be greater than observed. Significant differences in foliage across landscapes and regions can be difficult due to local heterogeneity and microtopography. For example, Berg et al. (2015) observed trees within a single stand can have considerable variations in Mn concentrations due to heterogeneous soil biogeochemical properties. However, these results demonstrate that Mn and Mn/Ca ratios in aboveground tissues are different across the spatial gradient.

In addition to understanding spatial patterns, foliage and bolewood samples can provide insight on the role of biological cycling for Mn and Ca. Our results suggest that the plant-soil system in forests of Pennsylvania and New York is enriched in Mn relative to forests of Vermont and New Hampshire. The enrichment of Mn in foliage, bolewood, forest floor and mineral soil can be interpreted by two general hypotheses. In the first hypothesis, foliar and bolewood Mn strongly correlate with forest floor and mineral soil because current deposition of Mn are increasing aboveground and belowground sources. In the second hypothesis, foliar and bolewood Mn strongly correlate with forest floor and mineral soil Mn because vegetation are cycling existing Mn sources in the forest soil. Although atmospheric deposition of Mn is a non-negligible source to forests across the northeast United States, we argue the second hypothesis is the dominant cause for higher Mn concentrations in foliage and bolewood. Herndon et al. (2011) has suggested that Mn deposition rates in the northeastern US have substantially decreased due to less industrial manufacturing and coal combustion in the region (e.g. Carter et al., 2015). Thus, current atmospheric deposition of Mn in Pennsylvania (e.g. 1.0–4.3  $\mu\text{g cm}^{-2} \text{year}^{-1}$ ; Herndon et al., 2011) and New York is unlikely to have caused the observed foliar Mn concentrations, which roughly contain ~50–6000 mg of Mn per leaf. Lastly, because bolewood is separated from the ambient atmosphere by outer layers of bark and cambium tissue, the direct influence of atmospheric deposition of Mn in bolewood can be assumed to be minimal. Baes and McLaughlin (1984) in Tennessee and Frelich et al. (1989) in Wisconsin did not observe significant trends for Mn concentration with tree age-related trends in xylem, phloem and cambium wood. This suggests Mn incorporation into wood has been constant and not directly influenced by changes in atmospheric deposition of pollutant Mn.

In either case, biological cycling of Mn in forests via foliage via litterfall is a significant source to forest soils (Carnol and Bazgir, 2013; Augusto et al., 2015; Richardson and Friedland, 2016). Richardson and Friedland (2016) estimated that litterfall fluxes could recycle the entire forest floor Mn pools within 10–30 years in forests across New Hampshire and Vermont. For this reason, it is important to note that vegetation may be the most important driver for Mn, particularly its biological uplift and retention in the forest floor and surface soil (Jobbágy and Jackson, 2001; Carnol and Bazgir, 2013; Augusto et al., 2015), which has been one of the foundational observations for Ca by Likens et al. (1998). Thus, the impact of human Mn pollution on cycling of Mn by vegetation in forests of the northeastern United States remains to be quantified, but vegetation will control its retention in surface soils, particularly the forest floor.

## 5. Conclusions

Comparisons of Mn/Ca in foliage, bolewood, forest floor, and mineral soil horizons show that there was a significant spatial gradient in Mn accumulation in vegetation and soils across the northeastern United States. Manganese concentrations in aboveground tissues were correlated with Mn in the forest floor and mineral soil horizons. It was surmised that forest floor and mineral soil horizons Mn concentrations were controlling Mn in foliage and bolewood across the spatial gradient. Because of the strong linkage between plants and soil, it appears the plant-soil system has been enriched with Mn at Pennsylvania and New York sites. In addition, the strong correlation between foliage and the forest floor demonstrates that internal cycling via uptake, throughfall and litterfall of Mn by vegetation will strongly influence the retention of Mn in these soils.

By calculating the enrichment factor (EF) of Mn using Mn/Ca ratio, it was determined that the forest floor, upper mineral soil, and lower mineral soil horizons in Pennsylvania and New York were enriched by a factor of 3.6 on average, when compared to forest soils of New Hampshire and Vermont. However, the application of Mn/Ca ratios is limited and requires additional studies to determine when and the extent of Mn/Ca fraction processes. In particular, Herndon et al. (2015) suggested that plants have greater uptake rates of Mn relative to Ca. Thus, current application of Mn/Ca ratios is limited but ratios of Mn/Ca and other elemental ratios such as Mn/Sr hold promise as important geochemical tracers and laboratory-based experiments such as mesocosm studies are needed for their further development.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.12.170>.

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