Mercury in Coniferous and Deciduous Upland Forests in Northern New England, USA: Implications of Climate Change

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Abstract

Climatic changes in the northeastern U.S. are expected to cause coniferous stands to transition to deciduous stands over the next hundred years. Mercury (Hg) sequestration in forest soils may change as a result. In order to understand potential effects of such a transition, we studied aboveground vegetation and soils at paired coniferous and deciduous stands on eight mountains in Vermont and New Hampshire, USA. Organic horizons at coniferous stands accumulated more Total Hg (THg) (42 ± 6 g ha^{-1}) than deciduous stands (30 ± 4 g ha^{-1}). Total Hg pools in the mineral horizons were similar for coniferous (46 ± 8 g ha^{-1}) and deciduous stands (45 ± 7 g ha^{-1}). Soil properties (C, % clay, and pH) explained 56 % of the variation in mineral soil Hg concentration when multiple regressed. Foliar and bole wood Hg concentrations were generally greater for coniferous species than deciduous species. Using allometric equations, we estimated that aboveground accumulation of Hg in foliage and woody biomass was similar between vegetation types but coniferous stands have significantly smaller annual litterfall fluxes (0.03 g ha^{-1} yr^{-1}) than deciduous stands (0.24 g ha^{-1} yr^{-1}). We conclude that organic horizon Hg accumulation is influenced by vegetation type but mineral horizon Hg accumulation is primarily controlled by soil properties. Further investigations into the effect of vegetation type on volatilization, atmospheric deposition, and leaching rates are needed to constrain regional Hg cycling rates.

1. Introduction

Forest soils play a key role in the global Hg cycle because they sequester Hg from both natural and human sources (Nater and Grigal, 1992; Fitzgerald et al., 1998; Driscoll et al., 2007; Streets et al., 2011). The accumulation and retention of Hg in upland forest soils is an integral part of Hg biogeochemistry. Soils ultimately control Hg transport to downslope riparian areas, where it can be methylated to its most toxic form, methylmercury (Aastrup et al., 1991; Lorey and Driscoll 1999; Schwesig and Matzner, 2001; Grigal, 2003; Driscoll et al., 2007; Evers et al., 2007; Demers et al., 2013; Chalmers et al., 2014). Birds, fish, mammals, amphibians, and invertebrates across the northeastern US are reported to have elevated Hg concentrations in their bodies (Evers et al., 2007; Rimmer et al., 2010; Townsend and Driscoll, 2013; Richardson et al., 2015). Policy makers, resource managers, and scientists have recognized the need to limit Hg reaching terrestrial and aquatic organisms (USEPA, 2011). Greater knowledge of the processes that control Hg accumulation and retention in forest soils is needed to understand its fate and transport in forested ecosystems.

Climate change has the potential to alter the sequestration of Hg from forest soils via direct pressures (meteorological) or indirect pressures (changes to vegetation). Climate models have predicted regional increases in precipitation that could cause greater wet deposition of Hg (Tang and Beckage, 2010; Smith-Downey et al., 2010). Moreover, projected increases in mean annual temperatures may increase net primary productivity of vegetation in forests across the region, potentially increasing plant interception and litterfall inputs of Hg to soils (Tang and Beckage, 2010; Smith-Downey et al., 2010). Conversely, increased mean annual temperatures and soil moisture may release Hg from soils by enhancing the decomposition rate of soil organic matter (SOM) or volatilization (Smith-Downey et al., 2010; Blackwell et al., 2014). Climate change could have indirect consequences on forests that may also affect Hg cycling. In the northeastern US, forest stands of coniferous tree genera (gymnosperms such as *Abies balsamea*, *Picea rubens*., and *Pinus* spp.) are expected to be succeeded by deciduous tree genera (angiosperms such as *Acer* spp., *Fagus grandifolia*, and *Betula*, spp.) due to the increased mean annual temperature and precipitation (Tang and Beckage, 2010). For example, coniferous vegetation has been projected to lose an estimated 71–100 % of its current range to deciduous vegetation across the northeastern US by 2085 (Tang and Beckage, 2010; Tang et al., 2012). The potential shift from coniferous to deciduous type forests caused by climate change may potentially alter the accumulation and retention of Hg in the soil.

Vegetation type can affect many aspects of Hg cycling in forest soils. The varying foliar morphology and foliar biomass characteristics in different vegetation types can affect Hg in litterfall. For example, Juillerat et al. (2012) found coniferous species generally obtained higher Hg concentrations than deciduous species, which was attributed to their surface area:weight ratio and longer life span. Furthermore, physical attributes of the canopy structure of each species can directly affect the accumulation of Hg in foliage (Hall and St. Louis, 2004; Demers et al., 2007; Obrist et al., 2012; Blackwell and Driscoll, 2015). The greater total foliar biomass for deciduous species can cause significantly greater litterfall fluxes in deciduous-dominated forest stands (e.g. Demers et al., 2007; Juillerat et al., 2012; Obrist et al., 2012). Greater litterfall rates can increase the size of the Hg pool in the organic horizons (forest floor) and mineral horizons (Hall and St. Louis, 2004; Demers et al., 2007; Zhang et al., 2009; Obrist et al., 2012). Additionally, the lower N concentration and higher lignin fraction of coniferous litter is hypothesized to suppress decomposition and microbial reduction of Hg (Berg et al., 1993; Pokharel and Obrist, 2011; Obrist et al., 2012; Demers et al., 2013). Litter from coniferous vegetation can also affect soil properties that influence Hg sorption in soil (e.g., soil C and pH) (Grigal, 2003; Demers et al., 2007; Obrist et al., 2011; Stankwitz et al., 2012; Richardson et al., 2013). This could increase the mobility of Hg and decrease the Hg pool in the organic and mineral horizons (Demers et al., 2007).

Quantifying the effect of vegetation type on forest soil Hg concentrations and pools is needed in the northeastern US due to predicted changes in forest composition under a changing climate. Previous studies have found contrasting effects from vegetation type on Hg cycling in forest soils (Rea et al., 2002; St. Louis et al., 2004; Demers et al., 2007; Obrist et al., 2012). The objectives of this study were to: 1) quantify if Hg concentrations and pools in forests and their soils are significantly different at coniferous and deciduous stands, 2) determine if vegetation type affects the mobility of Hg in soils. Information from this study can enhance landscape to regional scale estimates of Hg sequestration in forest soils and better constrain Hg cycling in upland forest soils.

2. Materials and Methods

2.1 Mountain sites and forest stands

Eight pairs of coniferous and deciduous forest stands were studied (Table 1). Forest stands were located at eight mountain 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 separate north-south transect along the White Mountains of New Hampshire. Sampling sites were on west-facing slopes to avoid biases from aspect. Northern New England is 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 research group, 2013). The mean annual frost-free period ranges from 90 to 160 d (Soil Survey Staff, 2014).

At each mountain site, a coniferous stand and a deciduous stand within 50 m of each other were studied. Stands were 30-m-diameter circles. The frequency of each species and diameter at breast height (DBH) for all trees was determined for the 707-m^2 stand. Coniferous stands were inhabited with > 50 % coniferous genera, and deciduous stands were inhabited by > 60 % deciduous genera based upon basal area and stem frequency (Table 1). Basal area was estimated from DBH measurements (Whittaker et al., 1974). Coniferous species present were balsam fir (*Abies balsamea* Mill.), red spruce (*Picea rubens* Sarg.), and eastern hemlock (*Tsuga Canadensis* L.). Deciduous species present were American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), striped maple (*Acer pensylvanicum* Marsh.), paper birch (*Betula papyrifera* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.). Vegetation at all stands was secondary growth due to the historical clearing of the region in the 1800s and abandonment in the period from circa 1870 through 1920s (cf. 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 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). These ages may vary with site edaphic characteristics.

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 (cf. 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 (Bennett, 1996; 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., 1966; Ratcliffe, 2000).

2.2 Soil and vegetation sample collection

Late-season foliage and bole wood samples were collected from *Picea rubrus*, *Tsuga canadensis*, *Abies balsamea*, *Fagus grandifolia*, *Acer spp.*, and *Betula spp.* in triplicate from each forest stand in early October 2012, 2013, and 2014. 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 Hg concentrations because Hg deposition is greater in upper canopy leaves (Luyassert et al., 2002). Bole wood was sampled at DBH using an 4 mm increment corer. Foliage and bole wood samples were air-dried at 25 ºC 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 (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. Aboveground woody biomass and foliage biomass can vary with canopy geometry, tree morphology, and fitness of each tree (Ferrari and Sugita, 1996; Luyassaert et al., 2002). However, these estimates provide an approximation of values without permanent destruction.

Annual litterfall fluxes from deciduous vegetation were assumed to be the entire foliar biomass. Annual litterfall fluxes from balsam fir and eastern hemlock were assumed to be 1/3 the foliar biomass because Barnes and Wagner (1981) observed average needle longevity of 3 yr. Similarly, litterfall fluxes from*Picea rubens* was assumed to be 1/5 the foliar biomass because

Barnes and Wagner (1981) observed average time needle longevity of 5 yr. The annual litterfall for each stand was calculated as the summed litterfall contribution for each tree at each stand. Leaves from trees may fall beyond the boundaries of the 707-m^2 stand; thus, our litterfall values are likely overestimates (Ferrari and Sugita, 1996).

The soils at each forest stand were sampled between July and September 2012. To control for the effect of soil type on Hg accumulation, only Spodosols were studied. Soils were classified as Spodosols using U.S. 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 (white leached layer) and Bhs horizon (organic matter and iron oxide rich layer) were present. At each forest stand, three 15 × 15 cm square sections of organic horizons were separated from the underlying mineral soil and collected. Three morphological quantitative soil pits were by each master horizon (E, Bhs, B/C) until dense basal till was reached for each forest stand. 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 was excavated, 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 were separated, roots > 5 mm in diameter were removed, and samples 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 $\leq$ 2 mm.

A 2:5 soil−water slurry was used to determine soil pH. Slurries 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 % SOM. To determine the percent loss-on-ignition, a 4-g air-dried subsample was combusted at 475 °C for 8 h. Total C concentrations in leaves, bole wood, and soil were measured using a Carlo-Erba elemental analyzer. In brief, 6 ± 1 mg of sample ground to < 0.5 mm were analyzed. Every 20 samples included one blank, one Atropine SRM, and a duplicate. Total C and N concentrations in Atropine SRMs were with 3 % of its certified value and < 10 % relative percent difference. Because soil samples were strongly acidic soils derived from granite and metamorphic rocks such as phyllites and schists, the contribution of C from calcite concentrations was presumed to be negligible. Soil pH and total C for each horizon are given in Supplemental Table 1.

2.3 Total Hg quantification

Total Hg concentrations (THg) for the organic and mineral soil were quantified using a Direct Mercury Analyzer – 80 (Milestone Inc.) in which 100 ± 10 mg subsamples were weighed into steel boats and ashed at 650 °C. To ensure quality, every 15 samples included a duplicate, a preparation blank, and a standard reference material (SRM). Peach leaves SRM 1547 was used to quantify matrix effects for bole wood, leaf, and organic horizon samples, whereas Montana soil SRM 2711a was used for mineral soil samples (National Institute of Standards and Technology, Gaithersburg, MD). Preparation blanks were below detection limits, and duplicate variations were within 5 %. SRM Hg measurements were within 9 % of their certified values. Total Hg values for each horizon are given in Supplemental Table 1.

2.4 Exchangeable Hg quantification

Exchangeable Hg concentrations (EHg) for the organic and mineral soil were quantified using a modified $Mg(NO_3)_2$ extraction for ion-exchangeable Hg (Eganhouse et al., 1978; Crock, 1996; Amacher, 1996). The method used $Mg(NO_3)_2$ instead of $MgCl_2$ because Hg is able to form stable complexes with Cl^- ions in solution (Schuster, 1991). We chose to investigate exchangeable Hg to consider dissolved Hg transport, rather than transport of Hg by dissolved organic compounds. In brief, 1 g soil was shaken in 10 mL of 0.1 M $Mg(NO_3)_2$ for 24 hr. Samples were centrifuged at 3000 rpm for 20 min, and the supernatant was decanted. The slurry was rinsed with 10 mL 5 % ethanol, centrifuged, and decanted again. A subsample of 100 mg of combined extraction supernatant and rinse supernatant was analyzed for Hg concentration using a Direct Mercury Analyzer – 80 (Milestone Inc.) in quartz boats. Every 15 samples included a duplicate, a preparation blank, and a SRM of Hg in solution. Preparation blanks were below detection limits, and duplicate variations were within 10 %. SRM Hg measurements were within 10 % of their certified values.

2.6 Statistical analyses

Descriptive statistics were calculated in Matlab. The variations in THg and EHg concentration and pools in the organic and mineral horizons were compared between vegetation types (coniferous and deciduous) using a paired sample t-test. Stepwise linear regressions and multiple regressions were used to explore relationships between THg and EHg concentrations with other continuous variables (pH, % clay, soil C, latitude, and longitude).

3. Results and Discussion

3.1 Forest soil properties

3.1.1 Soil physical properties

Forest soil physical properties were generally similar at coniferous and deciduous stands. Soils were well-drained or excessively drained, sandy loam-textured Spodosols. The Oi and Oe horizon thicknesses were similar for both vegetation types, but Oa horizons were significantly thicker for coniferous stands (11.3 ± 1.5 cm) compared with deciduous stands (6.1 ± 0.5 cm) ($p < 0.05$). Although the thicknesses did vary significantly, the dry weight mass of the summed organic horizons was similar between vegetation types. Organic horizon thicknesses are similar to other studies conducted in this region (Juillerat et al., 2012; Richardson et al., 2013). Thicknesses of the mineral horizons (E, Bhs, and B/C) were similar for coniferous and deciduous stands. Mineral soil bulk density and texture were similar for all horizons for both vegetation types. Texture was dominated by sand, ranging from 49 to 88 % (Supplemental Table 1). In addition, the clay fraction was low, ranging from 1 to 11 %, which is similar to values reported in other studies in this region (Johnson and Petras, 1998; Juillerat et al., 2012). However, the % clay was significantly lower in the E horizons (5.2 ± 0.4 %) than in the Bhs (7.5 ± 0.5 %) and B/C horizons (6.5 ± 0.6 %) ($p < 0.05$). We attribute the difference in clay fraction to accumulation of Al and Fe oxy-hydroxides in the Bhs horizon (do Valle et al., 2005). This finding suggests that the soil samples in this study were comparable among all stands.

3.1.2 Soil chemical properties

The mean soil pH values were similar to those reported in Juillerat et al. (2012). Soil pH was significantly lower for the Oe, Oa, and B/C horizons at coniferous stands than at deciduous stands (Fig. 1). Soil C concentrations in the organic and mineral horizons were similar to Juillerat et al. (2012) and Obrist et al. (2011). Soil C concentration was significantly greater for Oa horizons at coniferous stands than at deciduous stands (Fig. 1). Soil C pools in the Oi and Oa horizons were significantly greater at coniferous stands than at deciduous stands (Fig. 1).

Our findings show that coniferous vegetation has a significant impact on soil pH and C concentration in the organic horizons. However, we did not observe these differences for mineral soil horizons. Our results show that coniferous-dominated stands have greater C storage in their organic horizons than do deciduous stands. The cause of the higher C in the Oa horizon at coniferous stands was unclear. It may have been caused by slower decomposition. It is generally accepted that litter from coniferous vegetation causes greater acidity in the organic horizon (cf. Pritchett and Fisher, 1987). In addition, coniferous litter is more recalcitrant because of its lower nutrient quality (lower % N and higher lignin content), which makes it less susceptible to microbial decomposition (McClaugherty et al., 1985; Berg et al., 1993; Moore et al., 1999; Talbot et al., 2012), allowing for greater accumulation of soil C (Figure 1). The greater C pool at coniferous stands implies that a future shift from coniferous to deciduous vegetation could reduce the accumulation of C in in the organic horizon of forest soils. Due to the strong link between C and Hg, smaller C pools could reduce the storage capacity of Hg in the organic horizons at deciduous stands. However, Demers et al. (2013) suggested that storage capacity of Hg is not limited by C but rather by S that coincides with C in SOM nonlinearly (i.e., S becomes limiting in soils with high C concentration). The effect of decreased C in soils needs further attention to determine if its relation to Hg is direct or indirect.

3.2 Hg concentrations and pools in forest soils

3.2.1 Total Hg in forest soils

We observed that organic horizons in coniferous stands have greater Hg concentrations and greater Hg pools than in deciduous stands, primarily in the Oi, Oe, and Oa horizons. The mean organic horizon THg concentration was 179 μg kg^{-1}, and mean mineral horizon THg concentration was 64 μg kg^{-1}. The THg concentrations were similar to those observed in forest soils in the northeastern US (e.g., Evans et al., 2005; Juillerat et al., 2012; Stankwitz et al., 2012; Richardson et al., 2013). Total Hg concentrations were significantly greater for the Oi, Oe, and Oa horizons at coniferous stands than at deciduous stands (Fig. 2). The summed organic horizon THg pools were greater for coniferous stands (53 ± 10 g ha^{-1}) than for deciduous stands (30 ± 6 g ha^{-1}). This pattern was largely driven by differences in the Oa horizons, in which Oa Hg pools at coniferous stands were 38 ± 6 g ha^{-1}, whereas deciduous stands were only 21 ± 4 g ha^{-1}. Mineral soil THg pools were similar for coniferous stands (46 ± 8 g ha^{-1}) and deciduous stands (45 ± 7 g ha^{-1}). Despite similar mineral soil pools, the total soil profile of Hg pools was greater at coniferous stands (90 ± 13 g ha^{-1}) than at deciduous stands (75 ± 5 g ha^{-1}).

Organic horizon Hg concentrations and pools may be greater at coniferous stands than at deciduous stands due to differences in physicochemical properties. The organic horizons at coniferous stands may receive less UV radiation, potentially decreasing photoreduction and volatilization of Hg (Carpi and Lindberg, 1997; Schlüter, 2000; Gabriel and Williamson, 2004). However, the soil properties related to Hg accumulation were significantly different at coniferous stands when compared with deciduous stands. Total C concentrations were greater for the Oa horizon at coniferous stands. Total Hg concentrations in the organic and mineral horizons were regressed with soil C, pH, % clay, latitude, and longitude using stepwise linear regressions and multiple regressions. Concentrations of THg in the organic horizons were weakly explained by soil C and pH, accounting for only 24 % of the variation (Table 2). These weak to poor correlations suggest other processes are responsible for THg. Based on the vertical THg distribution in the organic horizons shown in Figure 2, the THg concentrations are dependent on the vegetation type and degree of decomposition. Of the explanatory variables examined by stepwise linear regressions, only soil C, pH, and % clay were significant for mineral horizons (Table 2). For the mineral soil, soil C had the greatest explanatory power, and when multiple regressed with % clay and pH, the variables explained 56 % of the variation in THg (Table 2). This correlation suggests that accumulation of Hg is primarily driven by sorption, which is controlled by soil C, % clay, and pH, and matches observations by Obrist et al. (2011), Juillerat et al. (2012), Richardson et al. (2013), and Yu et al. (2014). However, nearly 40% of the variation in the mineral soil and 76 % of the variation in the organic horizons remains unexplained and could be due to other unconstrained variables; hydrology and sesquioxides are two prime examples. Sesquioxides, Al and Fe oxy-hydroxides, are important inorganic surfaces that may sorb Hg directly, or provide surfaces for organo-mineral complexation (Garbriel and Williamson, 2004; do Valle et al., 2005). These are particularly of interest for the Bhs horizons, which have accumulations of both sesquioxides and SOM.

It is possible that soils under coniferous vegetation at the most southern sites would accumulate more Hg than at the most northern sites due to a longer growing season. In addition, the soils of the White Mountains of New Hampshire may receive more atmospheric deposition of Hg than the Green Mountains in Vermont (Miller et al., 2005). However, we did not find a significant correlation for THg with longitude or latitude. This suggests that longitude and latitude did not affect accumulation consistently across the eight sites or that there was not a large enough sample size or difference to detect a significant trend with latitude or mountain range.

There are landscape-scale and regional-scale ramifications for greater Hg sequestration in forest soils underlying coniferous stands. First, it implies that a shift from coniferous to deciduous vegetation could reduce forest soil Hg pools in the study region by 24 %. Tang et al. (2012) have predicted that climatic changes could reduce coniferous stands (*Abies balsamea-Picea rubens*) by ~80% in New England using the LPJ-GUESS model. Moreover, Tang and Beckage (2010) calculated a 71–100 % loss of coniferous forests in northern New England by the year 2085 using the BIOME4 model. Tang and Beckage (2010) estimated that ~2.2 million ha of coniferous forests will transition to deciduous forests of northern hardwoods across northern New England by the year 2085. Our calculations project a 29 % reduction (12 g ha^{-1}) in Hg accumulation in upland forests. When extrapolated across the region, 27 Mg less Hg would be sequestered in forest soils as an indirect consequence of climate change. The reduced accumulation and retention may mean that less Hg is sequestered from the atmosphere or that Hg may leach faster into watersheds during the transition period (Aastrup et al., 1991; Schwesig and Matzner, 2001).

3.2.2 Exchangeable Hg in forest soils

Quantifying the exchangeability of Hg is important for considering its mobility in the soil profile. The objective of the extraction process used was to exchange Hg^{+2} from sorption sites with Mg^{+2}. The EHg concentrations were nearly uniform with depth, ranging between 1.1 and 9.8 µg kg^{-1}. Our results show EHg concentrations were similar for coniferous and deciduous stands in most soil horizons(Figure 3). By dividing EHg concentrations by the THg concentrations, we are able to examine the relative fraction of exchangeable Hg. In Figure 3, E horizons have a significantly greater exchangeability than all other organic and mineral horizons. However, % EHg was similar for coniferous and deciduous stands in all horizons (Fig. 3). On the basis of our results, Hg was strongly complexed in soil, regardless of vegetation type. Thus, a shift from a coniferous to a deciduous stand would not increase Hg mobility in soil. However, our method is limited in its ability to quantify the pool of Hg that may be mobilized via particulate or DOC leaching. For this reason, increased Hg mobility may have been better examined by quantifying Hg bound to mobile forms of organic matter rather than EHg that may become mobilized after dissolution.

Exchangeable Hg concentrations in the organic and mineral horizons were regressed with soil C, pH, % clay, latitude, and longitude using stepwise linear regressions and multiple regressions. Exchangeable Hg concentrations in the organic horizons were not significantly correlated with any of the explanatory variables. For the mineral horizons, only soil C and pH were significantly correlated with EHg. Mineral soil EHg concentrations were significantly correlated with soil C and pH, together explaining 33 % of the variation. Exchangeable Hg concentrations were poorly correlated with the six chosen explanatory variables, suggesting that other factors are responsible for the variation. These factors may include types of colloids (inorganic or organic) or character of sorption sites on SOM (Schuster, 1991; Gabriel and Williamson, 2004; Essington, 2003).

Our EHg and %EHg data also provide insight on the sorption and mode of illuviation of Hg. In the Spodosols studied, Hg was not ion exchangeable. Mercury species were likely immobilized by strong complexation or sorption to organic and inorganic colloids (Schuster, 1991), except for the E horizons. Sesquioxides, such as hematite, goethite, and gibbsite, and

SOM in the Bhs horizon can increase Hg complexation (Gabriel and Williamson, 2004). The high proportion of EHg suggests that Hg is weakly sorbed and is highly mobile due to the lack of SOM and sesquioxides. For the other soil horizons, complexation by organic colloids is most likely to be dominant over inorganic colloids due to the pH dependency of mineral surfaces in the Oa and Bhs horizons (Schuster, 1991; Gabriel and Williamson, 2004). The low ionic exchangeability of Hg agrees with previous studies that the downward transport of Hg in upland forest soils must be primarily via particulate transport, such as dissolved organic carbon (DOC) or inorganic nanoparticles (Demers et al., 2007; Schwesig and Matzner, 2001; Grigal, 2003; Gabriel and Williamson, 2004; Stankwitz et al., 2012). We observed less acidic soil pH values at deciduous stands, and thus the future shift in vegetation may raise the soil pH. This could further reduce Hg exchangeability and SOM mobility by decreasing their solubility, which is pH dependent (Schuster, 1991; Grigal, 2003; Gabriel and Williamson, 2004).

3.3 Hg concentrations and pools in aboveground biomass

3.3.1 Total Hg in foliage

Previous studies have shown that Hg concentration in foliage varies among tree genera (e.g., St. Louis et al., 2001; Grigal, 2002; Bushey et al., 2008; Juillerat et al., 2012). We expected THg concentrations to be greater in coniferous needles due to their longevity, which coincides with observations of higher Hg concentrations in conifer needles (Rasmussen et al., 1991; Hall and Louis, 2004; Obrist et al., 2012). We instead found that *Abies balsamea* and *Fagus grandifolia* had higher THg concentrations than *Picea rubens, Acer* spp., and *Betula* spp. (Fig. 4). Our results match the rankings of THg concentrations by Rea et al. (2002), Bushey et al. (2008), Juillerat et al. (2012), and Blackwell and Driscoll (2015). This suggests that differences in their physiology beyond vegetation type promote greater Hg sorption. For example, the Hg concentration for the foliage of *Picea rubens*, one of the three coniferous species, was not significantly different than the foliage of *Acer* spp., and *Betula* spp., common deciduous genera (Fig. 4). Hence, physiological properties unique to each species, such as leaf roughness, leaf area index, stomatal morphology, and cuticle material, may control Hg sorption on leaf surfaces and uptake (Browne and Fang, 1978; Weathers et al., 2006; Zhang et al., 2009; Obrist et al., 2012; Juillerat et al., 2012). Blackwell and Driscoll (2015) hypothesized that coniferous vegetation accumulate Hg at a slower rate than deciduous vegetation, but their longevity and multiple growing seasons is responsible for their higher contribution in litterfall. An additional physiological influence may be that Hg held on leaf surfaces for *Picea* spp., *Acer* spp., and *Betula* spp. may have greater revolatilization rates than for *Abies balsamea* and *Fagus grandifolia* (Hanson et al., 1995).

Mercury concentrations in foliage can also vary temporally, ranging from differences during the growing season (Rea et al., 2002; Juillerat et al., 2012) and among years sampled (Rea et al., 2002; Blackwell and Driscoll, 2015). Foliar Hg concentrations have been shown to increase an order of magnitude through the growing season (Rea et al., 2002). Thus, we sampled late-season foliage to estimate the maximum concentration of Hg obtained by foliage before senescence. In addition to seasonal variation, annual differences in Hg concentrations have been observed (Rea et al., 2002; Bushey et al., 2008) and were hypothesized to occur from annual variation in uptake and dry deposition onto leaves (Rasmussen, 1995; Grigal, 2002). However, we did not observe significant differences in THg concentrations in late-season foliage collected in 2012, 2013, and 2014 for any genus. This agrees with results from other studies (e.g., Bushey et al., 2008). In addition, the National Atmospheric Deposition Program (NADP) observed that annual Hg deposition rates from precipitation and dry deposition have been were relatively consistent during their monitoring of the region from 2003 to 2013 (NADP, 2007).

3.3.2 Total Hg in bole wood

Bole wood had significantly lower THg concentrations (8 ± 4 μg kg^{-1}) than foliar (35 ± 9 μg kg^{-1}). Wood THg concentrations ranged from 10 to 50 % of their respective foliar concentrations. Wood THg concentrations were greater for coniferous genera (11.7 ± 0.8 μg kg^{-1}) than for deciduous genera (5.3 ± 0.7 μg kg^{-1}) (Fig. 4). These values are similar to bole wood Hg concentrations in other studies (e.g., Obrist et al., 2012). The greater concentrations of Hg in coniferous tissue are likely due to ecophysiological properties, such as growth rate and root uptake (Rea et al., 2002). Although root uptake of Hg is generally considered a small contribution (Aastrup et al., 1991; Grigal, 2002; Rea et al., 2002; Schwesig and Krebs, 2003), it could differ among genera (Beauford et al., 1977) and could possibly be greater for coniferous vegetation. In addition, retention in the xylem could also vary for each genus (Bishop et al., 1998).

3.3.3 Aboveground biomass total Hg estimation

The foliar and woody biomass was calculated using 2012 basal area measurements for all trees within the 707-m^2 stands and allometric equations for each species (TerMikaelian and Korzukhin, 1997). It must be noted that these values are approximations, and biomass can vary with canopy geometry, tree morphology, and individual fitness of each tree (Ferrari and Sugita, 1996; Luyassaert et al., 2002; Bushey et al., 2008). From the allometric equations, we estimated that coniferous stands had significantly less foliar biomass (1650 ± 360 kg ha^{-1}) than deciduous stands (5680 ± 610 kg ha^{-1}). Similarly, coniferous stands had significantly less woody biomass (9070 ± 2220 kg ha^{-1}) than deciduous stands (24,500 ± 5480 kg ha^{-1}). The difference in foliar and woody biomass at coniferous and deciduous vegetation was a large but not surprising difference, considering the physiology and canopy structure of deciduous trees (Ferrari and Sugita, 1996).

Mercury pools in the aboveground biomass (foliage and wood) were calculated using averaged 2012, 2013, and 2014 THg concentration data with biomass estimates from allometric equations. Our results in Figure 5 show that coniferous and deciduous stands do not have significantly different foliar pools of THg despite significantly more foliar biomass at deciduous stands. However, woody biomass at coniferous stands has a significantly larger THg pool (0.30 ± 0.08 g ha^{-1}) than at deciduous stands (0.15 ± 0.04 g ha^{-1}). In spite of two thirds less woody biomass at coniferous stands than deciduous stands, wood biomass THg pools at coniferous stands were greater than deciduous stands. Foliar and wood biomass Hg concentrations can vary annually due to precipitation and temperatures (Risch et al., 2011; Obrist et al., 2012). Moreover, Hg concentrations can vary with the type of wood sampled (twigs, branches, bark, and bole wood), and vertical location in the canopy can also affect Hg estimates (Risch et al., 2011; Obrist et al., 2012). However, we believe our estimates of foliar Hg pools are representative values. For example, the calculated litterfall rates, based on foliar Hg biomass at the 16 stands, was 0.13 ± 0.04 g ha^{-1} yr^{-1}, which matched litterfall rates measured by Risch et al. (2011) (0.12 ± 0.01 g ha^{-1} yr^{-1}) and Rea et al. (2002) (0.16 ± 0.02 g ha^{-1} yr^{-1}). The litterfall fluxes at coniferous stands (~10 % of the total Hg deposited) and deciduous stands (~45% of the total Hg deposited) are similar to observations by Blackwell and Driscoll (2015) in the northern hardwood forest and *Picea* spp./*Abies* spp. forests. The litterfall rates were significantly lower for coniferous stands due to the smaller biomass and greater longevity of the coniferous foliage (Barnes and Wagner, 1981). Our calculated values may be lower than observed values due to the allometric equations used to estimate foliar biomass, as tree morphologies can vary from typical branch architecture.

We find that the Hg litterfall flux for coniferous stands (0.01 – 0.08 g Hg ha^{-1} yr^{-1}) is significantly smaller than the atmospheric deposition rate of Hg (0.24 – 0.26 g Hg ha^{-1} yr^{-1}) based upon estimates from Yu et al., (2014) for this region (Table S2). Moreover, estimated annual volatilization rates of Hg (0.02 – 0.08 g Hg ha^{-1} yr^{-1}) from Yu et al., (2014) are equal to or greater than coniferous litterfall rates. Mercury litterfall flux at deciduous stands (0.10 – 0.49 g Hg ha^{-1} yr^{-1}) was generally similar to atmospheric deposition rates of Hg and significantly greater than volatilization rates from Yu et al., (2014). Although these flux rates were not measured at the 8 mountain study sites, they provide an important comparison that the type of vegetation can significantly impact the flux of Hg to their underlying soils. However, vegetation has been shown to significantly influence throughfall and volatilization rate of Hg (Demers et al., 2007; Blackwell and Driscoll, 2015). Thus, site specific throughfall and volatilization rates are needed to fully quantify the effect of vegetation type on abiotic fluxes of Hg to their underlying soils.

4. Conclusions

We conclude that vegetation type significantly influenced Hg accumulation in the organic horizons of coniferous and deciduous forest stands, but not in the mineral horizons, which were controlled by soil properties. THg concentrations in the Oi, Oe, and Oa horizons were greater for coniferous stands than for deciduous stands. The summed organic horizon THg pools were greater for coniferous stands (53 ± 10 g ha^{-1}) than for deciduous stands (30 ± 6 g ha^{-1}). We calculated a 28 % lower (12 g ha^{-1}) Hg accumulation in soils at deciduous stands than at coniferous stands. Proposed mechanisms for this difference include litter quality, sorption capacity of SOM, and susceptibility for microbial decomposition. Mineral soil THg concentrations and pools did not significantly differ with vegetation type. Instead, soil C, % clay, and pH explained 56 % of the variation in total Hg concentrations in the mineral soil. The mobility of Hg did not vary significantly with vegetation type and was weakly explained by soil physicochemical properties. Our empirical data indicate that coniferous vegetation accumulate more Hg in their underlying soils, primarily in their organic horizons. We calculated a 28 % lower (12 g ha^{-1}) Hg accumulation in soils at deciduous stands than at coniferous stands. When extrapolated to the predicted ~2.2 million-ha loss of coniferous forests, the vegetation shift could represent ~27 Mg kg less Hg sequestered in the organic horizons across the region. Further investigations should evaluate the effect of vegetation type on Hg volatilization, atmospheric deposition, and leaching rates to constrain landscape and regional changes. This will better aid regional and global Hg models in implementing the effect of shifting vegetation type on future Hg pools in soils.

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Table 1. Forest stand descriptions

Site #	Elevation a.s.l.	Dominant vegetation type	Species present†	Stem density	Basal area	% Conifer by basal area	% Conifer by frequency	Soil Taxonomy (observed)
	m			stems ha^{-1}	m^2 ha^{-1}	%	%	
VT 1	601	Conifer	A,B,C,E,G,H	257	8	63	56	Frigid Oxyaquic Haplorthod
		Deciduous	A,B,C,E,G	329	14	4	22	Frigid Typic Haplorthod
VT 2	704	Conifer	A,B,C,F,G	302	11	68	52	Frigid Typic Haplorthod
		Deciduous	B,C,D,F,H	243	12	0	6	Frigid Typic Haplorthod
VT 3	608	Conifer	A,D,E,F	371	6	52	52	Frigid Typic Haplorthod
		Deciduous	C,D,E,F,G	314	18	0	0	Frigid Typic Haplorthod
VT 4	582	Conifer	A,C,F,G,H	357	20	99	64	Frigid Fragic Haplorthod
		Deciduous	C,D,E,F,G,H	214	6	40	32	Frigid Fragic Haplorthod
NH 1	680	Conifer	B,D,E,F,G,H	443	8	76	52	Frigid Oxyaquic Haplorthod
		Deciduous	B,C,D,G	271	16	0	0	Frigid Typic Haplorthod
NH 2	641	Conifer	A,B,C,E,F,G,H	429	9	54	64	Frigid Oxyaquic Haplorthod
		Deciduous	A,B,C,D,E,F,G	357	11	2	4	Frigid Typic Haplorthod
NH 3	610	Conifer	A,C,F,G,H	457	5	60	65	Frigid Oxyaquic Haplorthod
		Deciduous	C,D,E,F,G,H	414	14	13	28	Frigid Oxyaquic Haplorthod
NH 4	640	Conifer	C,G,H,I	314	9	89	73	Frigid Typic Haplorthod
		Deciduous	C,E,F,G,H	279	12	1	11	Frigid Oxyaquic Haplorthod

(†) A = *Abies balsamea*, B = *Acer pensylvanicum*, C = *Acer rubrum*, D = *Acer saccharum*, E =*Betula alleghaniensis*, F = *Betula papyrifera*, G = *Fagus grandifolia*, H = *Picea rubens*, I = *Tsuga canadensis*.

Table 2. Displayed are *R^2* values for stepwise and multiple linear regressions of site location and select soil properties with total Hg (THg) and exchangeable Hg (EHg) concentrations for organic and mineral horizons.

		Organic horizons		Mineral horizons	
Stepwise Linear regressions		THg	EHg	THg	EHg
		(μg kg^{-1})	(μg kg^{-1})	(μg kg^{-1})	(μg kg^{-1})
Soil C	(g kg^{-1})	0.19*	n.s.	0.37**	0.45**
% clay	(g g^{-1})	N/A	N/A	0.17*	n.s.
pH	log units	0.21*	n.s.	0.13*	0.36**
Latitude	d.d.†	n.s.	n.s.	n.s.	n.s.
Longitude	d.d.†	n.s.	n.s.	n.s.	n.s.
Multiple regressions variables:		Soil C, pH	-	Soil C, % clay, pH	Soil C, pH
		0.24*	-	0.56**	0.33**

†Decimal degrees

(*) = $p < 0.05$, (**) = $p < 0.001$

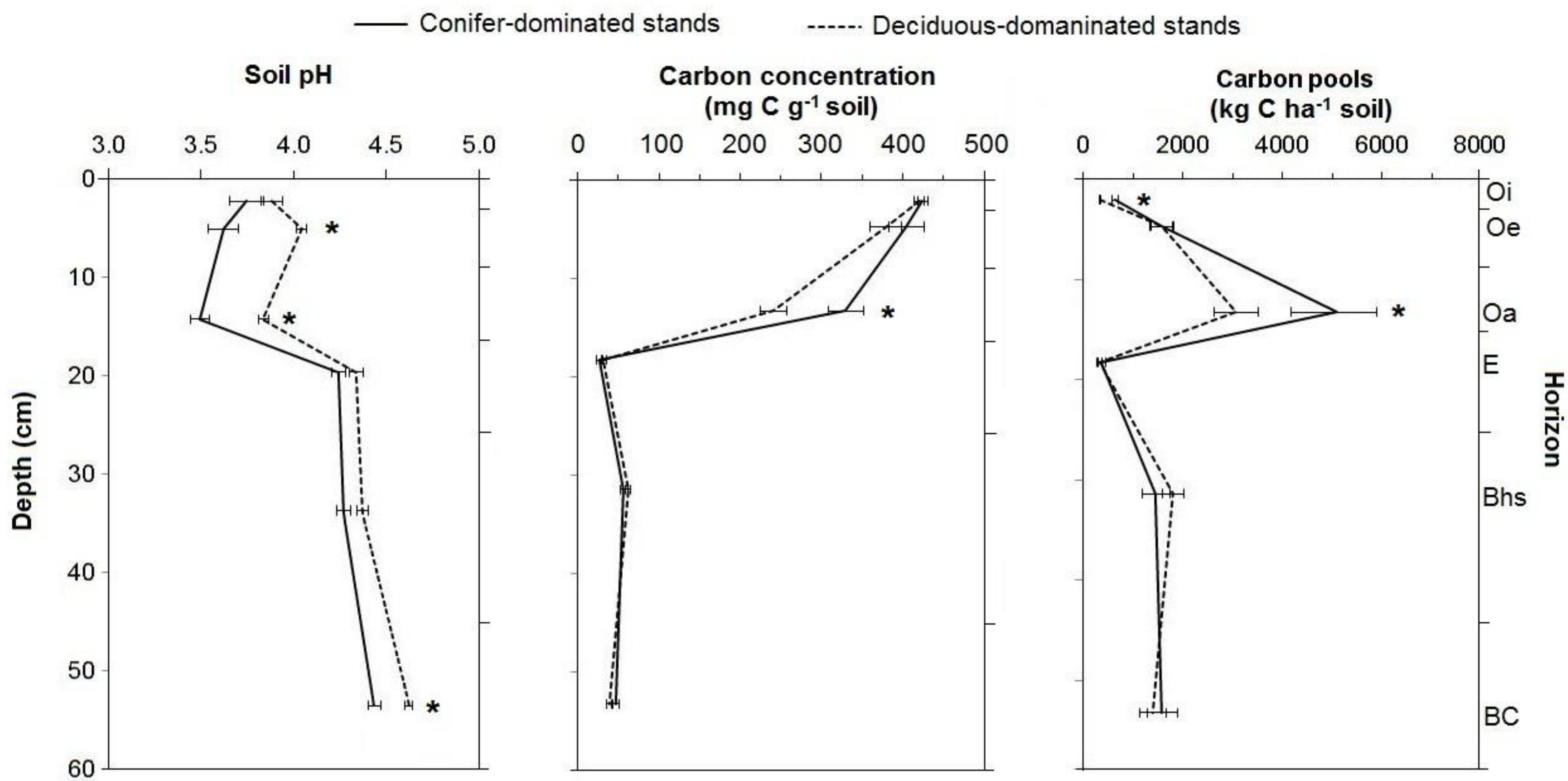

Figure 1 Soil pH, Carbon concentration, and Carbon pools for soil horizons at Conifer- and Deciduous-dominated stands. Mean values are given ± 1 standard error. (*) indicates a significant difference using two sample t-tests (P < 0.05).

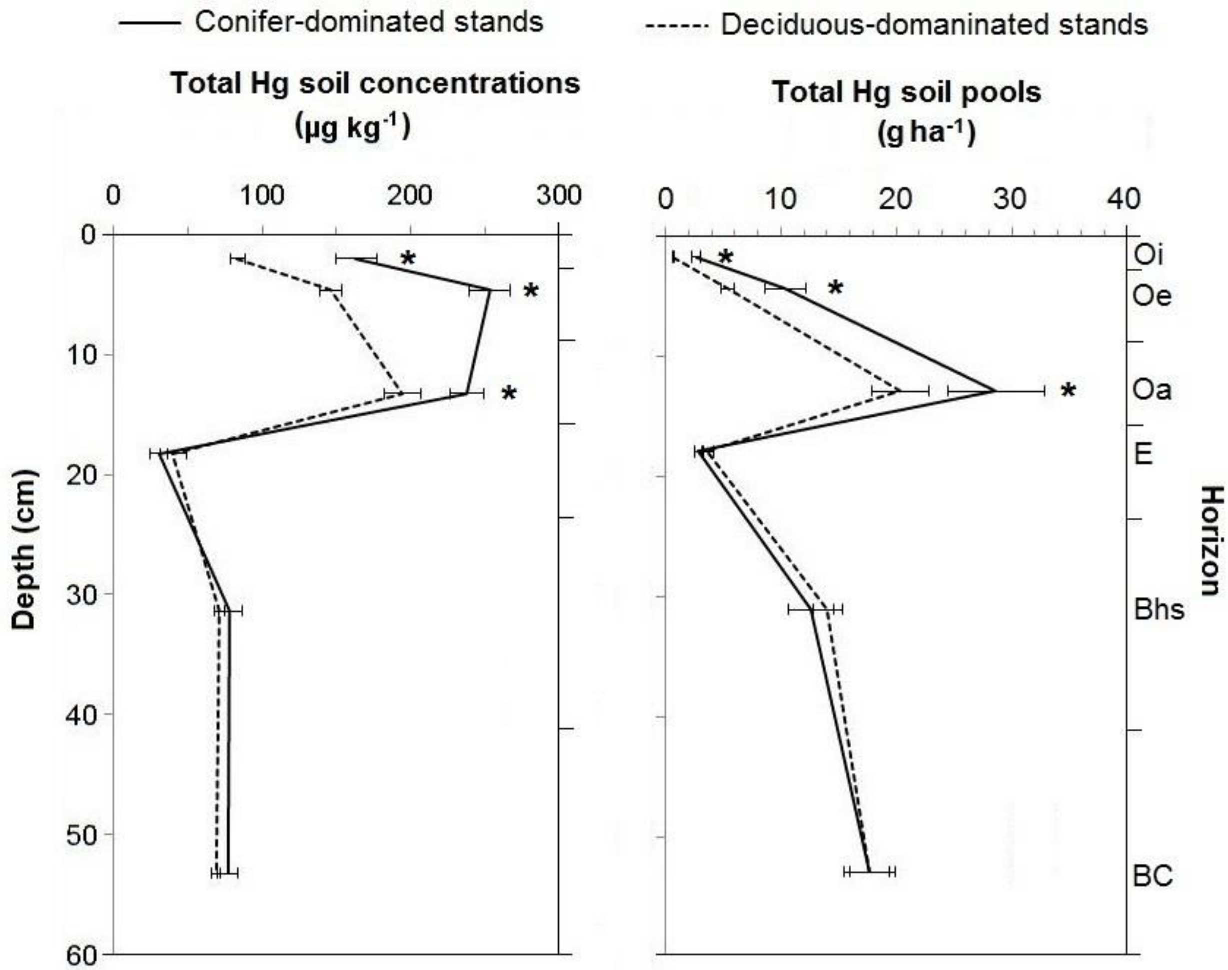

Figure 2 Total Hg (THg) concentrations in organic and mineral horizons at conifer and deciduous-dominated forest stands. Mean values are given ± 1 standard error. (*) indicates a significant difference using two sample t-tests (P < 0.05).

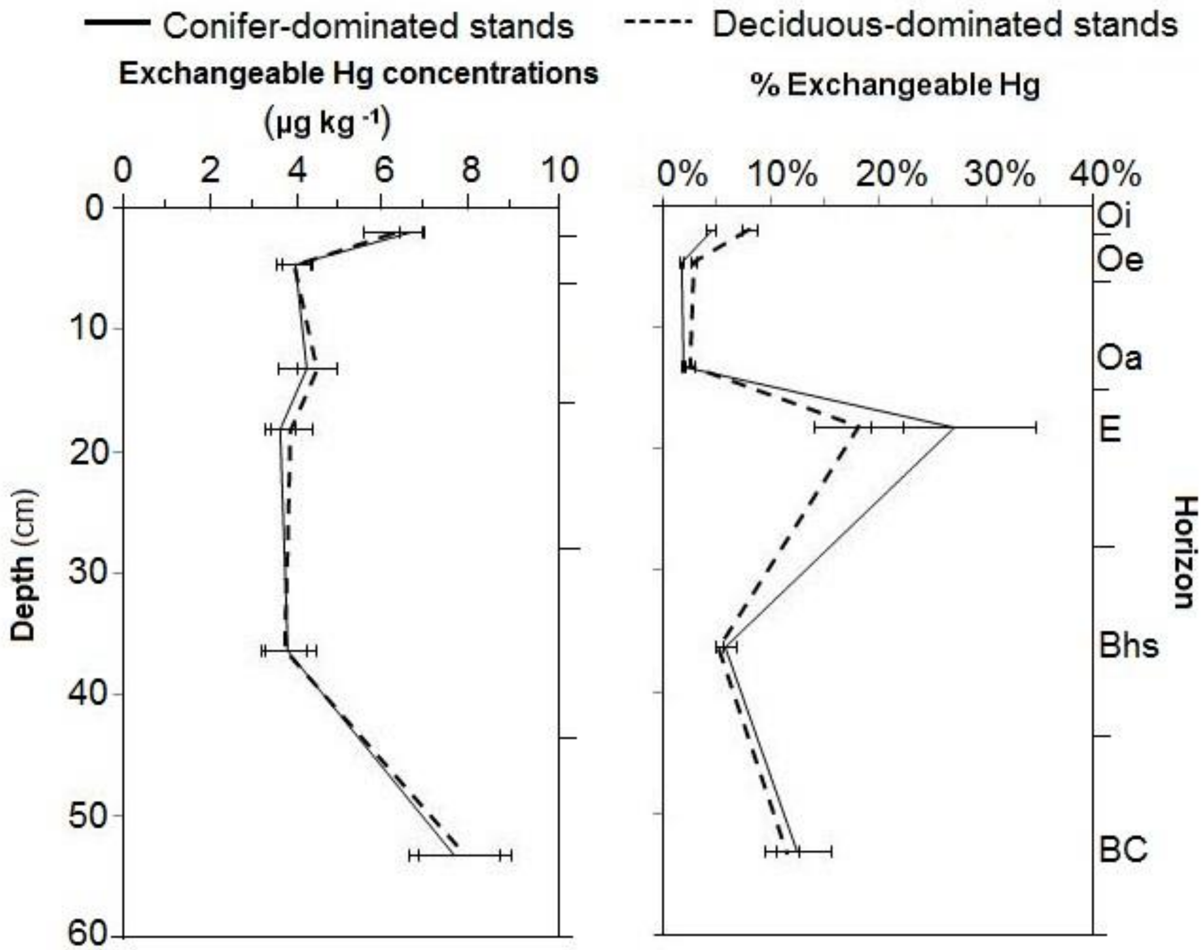

Figure 3 Exchangeable Hg (EHg) concentrations and % Exchangeable Hg in organic and mineral horizons at conifer and deciduous-dominated forest stands. Mean values are given ± 1 standard error. (*) indicates a significant difference using two sample t-tests (P < 0.05).

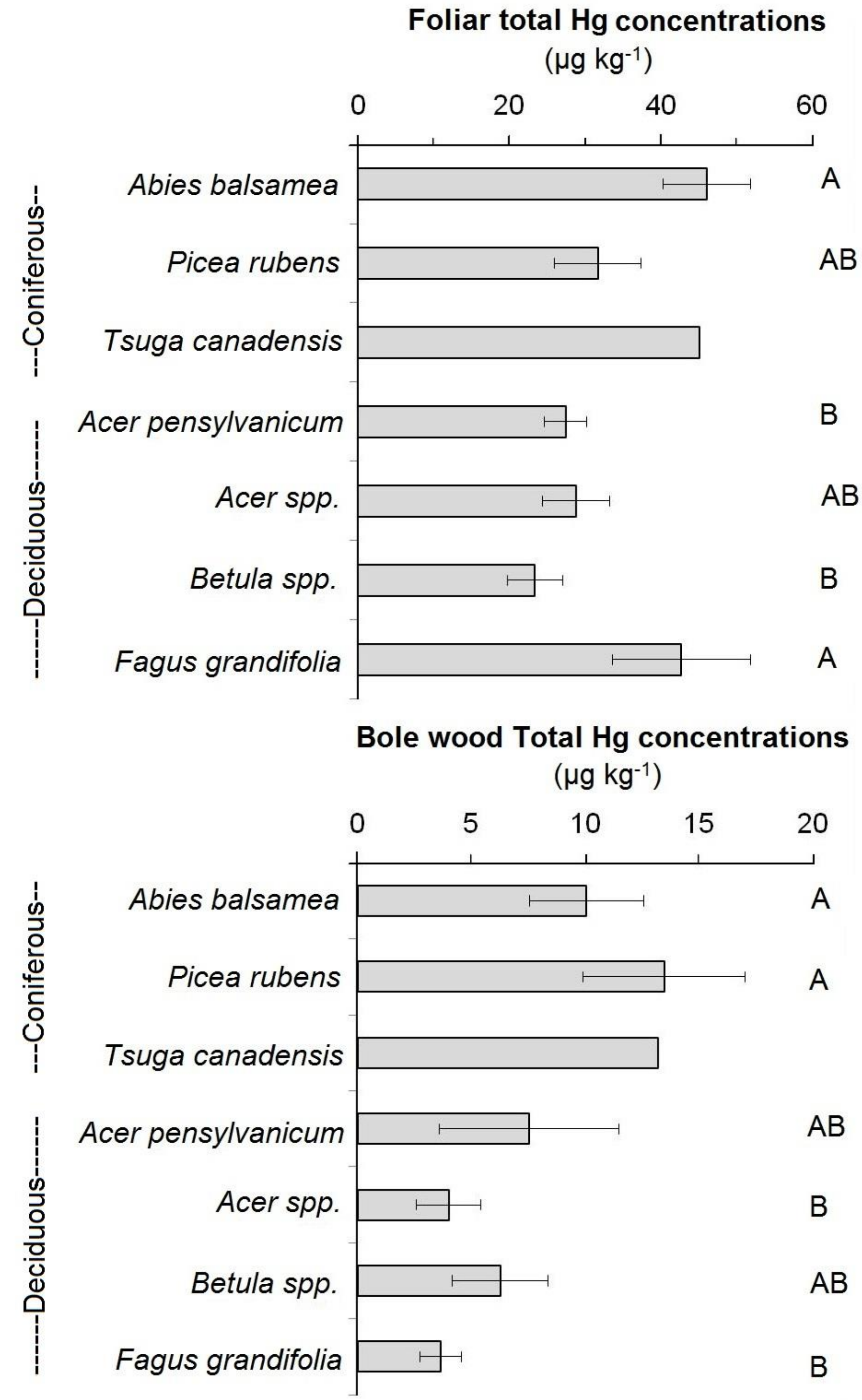

Figure 4 Total Hg concentrations in dry weight leaves and wood from 2012, 2013 and 2014 forest stand samplings. Mean values are given ± 1 standard error. Letters (A, B) indicates a significant difference using Kruskal-Wallis test with post-hoc ($P < 0.05$). Each species/genus ($n = 8$), except Tsuga canadensis ($n = 1$), which was not included in statistical analyses.

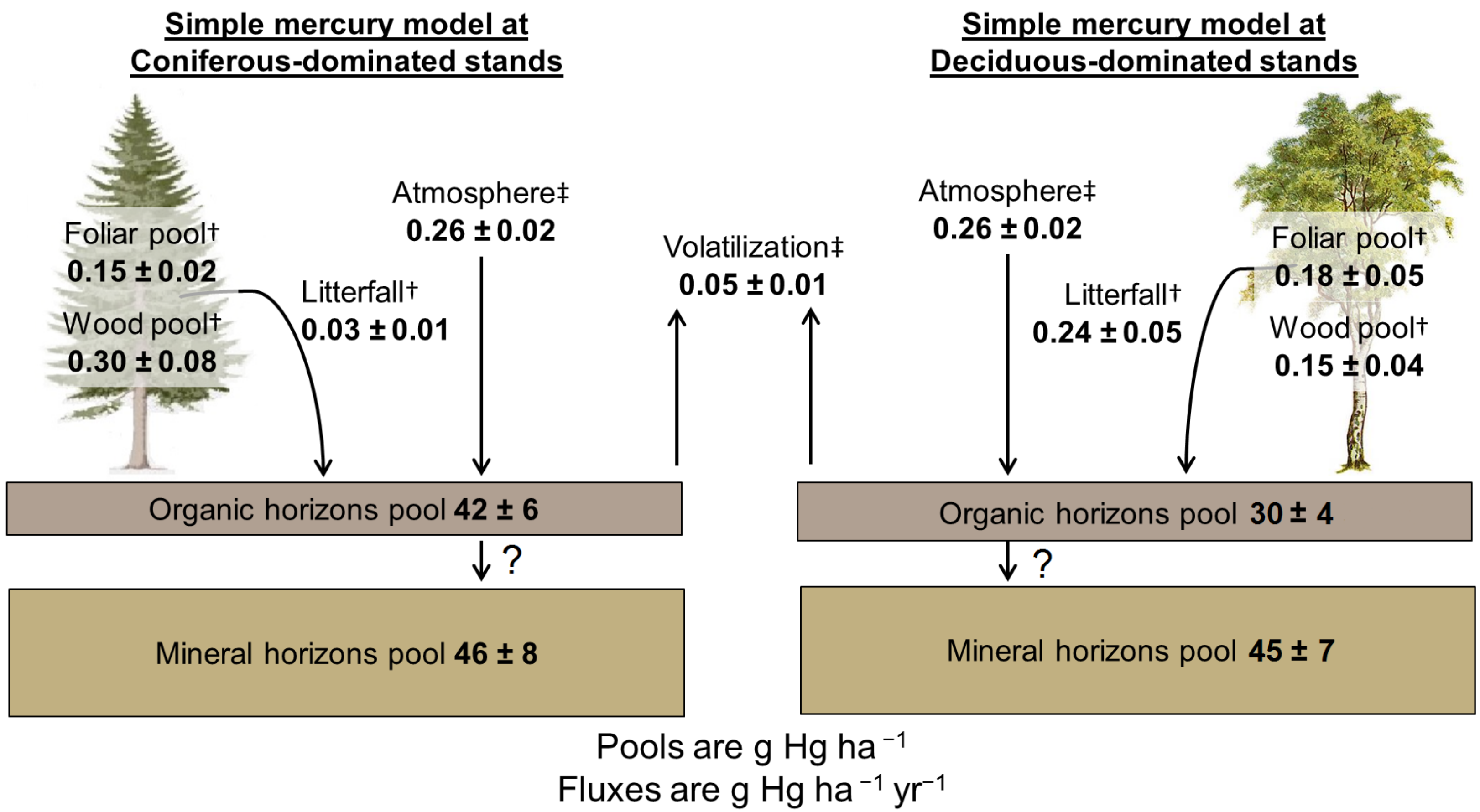

Figure 5 Total Hg pools in foliage, wood, organic, and mineral horizons at conifer and deciduous-dominated forest stands. See Method Section 2.5 for explanation of flux estimates. Mean values are given ± 1 standard error.
† Litterfall was estimated using foliar pools and senescence rates for each genus.
‡ Atmospheric deposition and volatilization rates were interpolated from Miller et al., (2005) and Yu et al., (2014).