

1 **List of correction made to manuscript**

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3 **Reviewer #1 Specific comment #1**

4 L452: ...flux rates ...: I assume you meant fluxes (delete rate)

5

6 **Author response SC #1:** We have changed “flux rates” to “fluxes”.

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

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17

18 **Abstract**

19 Climatic changes in the northeastern U.S. are expected to cause coniferous stands to
20 transition to deciduous stands over the next hundred years. Mercury (Hg) sequestration in forest
21 soils may change as a result. In order to understand potential effects of such a transition, we
22 studied aboveground vegetation and soils at paired coniferous and deciduous stands on eight
23 mountains in Vermont and New Hampshire, USA. Organic horizons at coniferous stands
24 accumulated more Total Hg (THg) ($42 \pm 6 \text{ g ha}^{-1}$) than deciduous stands ($30 \pm 4 \text{ g ha}^{-1}$). Total
25 Hg pools in the mineral horizons were similar for coniferous ($46 \pm 8 \text{ g ha}^{-1}$) and deciduous
26 stands ($45 \pm 7 \text{ g ha}^{-1}$). Soil properties (C, % clay, and pH) explained 56 % of the variation in
27 mineral soil Hg concentration when multiple regressed. Foliar and bole wood Hg concentrations
28 were generally greater for coniferous species than deciduous species. Using allometric equations,
29 we estimated that aboveground accumulation of Hg in foliage and woody biomass was similar
30 between vegetation types but coniferous stands have significantly smaller annual litterfall fluxes
31 ($0.03 \text{ g ha}^{-1} \text{ yr}^{-1}$) than deciduous stands ($0.24 \text{ g ha}^{-1} \text{ yr}^{-1}$). We conclude that organic horizon Hg
32 accumulation is influenced by vegetation type but mineral horizon Hg accumulation is primarily
33 controlled by soil properties. Further investigations into the effect of vegetation type on
34 volatilization, atmospheric deposition, and leaching rates are needed to constrain regional Hg
35 cycling rates.

36 1. Introduction

37 Forest soils play a key role in the global Hg cycle because they sequester Hg from both
38 natural and human sources (Nater and Grigal, 1992; Fitzgerald et al., 1998; Driscoll et al., 2007;
39 Streets et al., 2011). The accumulation and retention of Hg in upland forest soils is an integral
40 part of Hg biogeochemistry. Soils ultimately control Hg transport to downslope riparian areas,
41 where it can be methylated to its most toxic form, methylmercury (Aastrup et al., 1991; Lorey
42 and Driscoll 1999; Schwesig and Matzner, 2001; Grigal, 2003; Driscoll et al., 2007; Evers et al.,
43 2007; Demers et al., 2013; Chalmers et al., 2014). Birds, fish, mammals, amphibians, and
44 invertebrates across the northeastern US are reported to have elevated Hg concentrations in their
45 bodies (Evers et al., 2007; Rimmer et al., 2010; Townsend and Driscoll, 2013; Richardson et al.,
46 2015). Policy makers, resource managers, and scientists have recognized the need to limit Hg
47 reaching terrestrial and aquatic organisms (USEPA, 2011). Greater knowledge of the processes
48 that control Hg accumulation and retention in forest soils is needed to understand its fate and
49 transport in forested ecosystems.

50 Climate change has the potential to alter the sequestration of Hg from forest soils via
51 direct pressures (meteorological) or indirect pressures (changes to vegetation). Climate models
52 have predicted regional increases in precipitation that could cause greater wet deposition of Hg
53 (Tang and Beckage, 2010; Smith-Downey et al., 2010). Moreover, projected increases in mean
54 annual temperatures may increase net primary productivity of vegetation in forests across the
55 region, potentially increasing plant interception and litterfall inputs of Hg to soils (Tang and
56 Beckage, 2010; Smith-Downey et al., 2010). Conversely, increased mean annual temperatures
57 and soil moisture may release Hg from soils by enhancing the decomposition rate of soil organic
58 matter (SOM) or volatilization (Smith-Downey et al., 2010; Blackwell et al., 2014). Climate
59 change could have indirect consequences on forests that may also affect Hg cycling. In the

60 northeastern US, forest stands of coniferous tree genera (gymnosperms such as *Abies balsamea*,
61 *Picea rubens*., and *Pinus* spp.) are expected to be succeeded by deciduous tree genera
62 (angiosperms such as *Acer* spp., *Fagus grandifolia*, and *Betula*, spp.) due to the increased mean
63 annual temperature and precipitation (Tang and Beckage, 2010). For example, coniferous
64 vegetation has been projected to lose an estimated 71–100 % of its current range to deciduous
65 vegetation across the northeastern US by 2085 (Tang and Beckage, 2010; Tang et al., 2012). The
66 potential shift from coniferous to deciduous type forests caused by climate change may
67 potentially alter the accumulation and retention of Hg in the soil.

68 Vegetation type can affect many aspects of Hg cycling in forest soils. The varying foliar
69 morphology and foliar biomass characteristics in different vegetation types can affect Hg in
70 litterfall. For example, Juillerat et al. (2012) found coniferous species generally obtained higher
71 Hg concentrations than deciduous species, which was attributed to their surface area:weight ratio
72 and longer life span. Furthermore, physical attributes of the canopy structure of each species can
73 directly affect the accumulation of Hg in foliage (Hall and St. Louis, 2004; Demers et al., 2007;
74 Obrist et al., 2012; Blackwell and Driscoll, 2015). The greater total foliar biomass for deciduous
75 species can cause significantly greater litterfall fluxes in deciduous-dominated forest stands (e.g.
76 Demers et al., 2007; Juillerat et al., 2012; Obrist et al., 2012). Greater litterfall rates can increase
77 the size of the Hg pool in the organic horizons (forest floor) and mineral horizons (Hall and St.
78 Louis, 2004; Demers et al., 2007; Zhang et al., 2009; Obrist et al., 2012). Additionally, the lower
79 N concentration and higher lignin fraction of coniferous litter is hypothesized to suppress
80 decomposition and microbial reduction of Hg (Berg et al., 1993; Pokharel and Obrist, 2011;
81 Obrist et al., 2012; Demers et al., 2013). Litter from coniferous vegetation can also affect soil
82 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).

106 At each mountain site, a coniferous stand and a deciduous stand within 50 m of each
107 other were studied. Stands were 30-m-diameter circles. The frequency of each species and
108 diameter at breast height (DBH) for all trees was determined for the 707-m² stand. Coniferous
109 stands were inhabited with > 50 % coniferous genera, and deciduous stands were inhabited by >
110 60 % deciduous genera based upon basal area and stem frequency (Table 1). Basal area was
111 estimated from DBH measurements (Whittaker et al., 1974). Coniferous species present were
112 balsam fir (*Abies balsamea* Mill.), red spruce (*Picea rubens* Sarg.), and eastern hemlock (*Tsuga*
113 *Canadensis* L.). Deciduous species present were American beech (*Fagus grandifolia* Ehrh.),
114 sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), striped maple (*Acer*
115 *pensylvanicum* Marsh.), paper birch (*Betula papyrifera* Marsh.), and yellow birch (*Betula*
116 *alleghaniensis* Britt.). Vegetation at all stands was secondary growth due to the historical
117 clearing of the region in the 1800s and abandonment in the period from circa 1870 through 1920s
118 (cf. Foster, 1992). Coniferous stands were located away from trails and logging roads, in areas
119 that were likely difficult for timber harvesting. Using DBH of *Acer saccharum*, *Picea rubens*,
120 and *Abies balsamea* at each stand, we calculated growth rates using parameters from Teck and
121 Hilt (1991) and Kenefic and Nyland (1999). We calculated that stand ages ranged from 57 to 137
122 yr with a mean of 88 ± 9 yr (data not shown). These ages may vary with site edaphic
123 characteristics.

124 Only sites on bench landform and well-drained soils were chosen. The soil parent
125 material was glacial till for all stands, which was deposited during the retreat of the Laurentian
126 ice sheet in the Wisconsinian glaciation ~14,000 yr ago (cf. Siccama, 1974; Soil Survey Staff,
127 2010). Glacial till at sites NH 1–NH 4 was generally sourced from local bedrock: Bethlehem
128 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 °C for 3 wk and milled for homogeneity. Aboveground woody biomass and foliar biomass was estimated using allometric equations for each species from studies conducted in the northeastern US and southeastern Canada (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

152 Barnes and Wagner (1981) observed average time needle longevity of 5 yr. The annual litterfall
153 for each stand was calculated as the summed litterfall contribution for each tree at each stand.
154 Leaves from trees may fall beyond the boundaries of the 707-m² stand; thus, our litterfall values
155 are likely overestimates (Ferrari and Sugita, 1996).

156 The soils at each forest stand were sampled between July and September 2012. To
157 control for the effect of soil type on Hg accumulation, only Spodosols were studied. Soils were
158 classified as Spodosols using U.S. Soil Taxonomy guidelines (Soil Survey Staff, 2010). Soil
159 taxonomy identification was based on soil pit descriptions and USDA-NRCS Web Soil Survey
160 (Soil Survey Staff, 2014). First, a trench was dug to ensure an E horizon (white leached layer)
161 and Bh_s horizon (organic matter and iron oxide rich layer) were present. At each forest stand,
162 three 15 × 15 cm square sections of organic horizons were separated from the underlying mineral
163 soil and collected. Three morphological quantitative soil pits were by each master horizon (E,
164 Bh_s, B/C) until dense basal till was reached for each forest stand. First, a 50 × 50 cm wooden
165 frame was secured to the ground nearby by using 12-cm steel spikes. The organic horizons were
166 removed using saws and clippers. Each master horizon was excavated, sieved to < 2 cm, and
167 weighed using an electronic portable scale. A 5-kg representative subsample was collected for
168 each master horizon to determine field moisture content and rock fragments 0.2–2 cm in
169 diameter. A separate subsample was collected from the face of each soil pit for chemical
170 analyses. In total, 48 quantitative soil pits were excavated in this study. In the laboratory, the 15×
171 15 cm blocks of organic horizon were separated into Oi (litter layer), Oe (fermentation layer),
172 and Oa (humified layer) horizons were separated, roots > 5 mm in diameter were removed, and
173 samples were air-dried at 25 °C to a constant mass. Organic horizon masses were calculated
174 using oven-dried subsamples. All mineral soil samples were air-dried to a constant weight, and

175 roots > 5 mm in diameter were removed. Organic horizons and mineral soil samples were milled
176 and sieved, respectively, to ≤ 2 mm.

177 A 2:5 soil–water slurry was used to determine soil pH. Slurries were shaken for 1 hr
178 using a wrist-action shaker and vacuum extracted through a Whatman 40 filter. The pH of the
179 extract was measured with a pH meter (8015 VWR). The sand, silt, and clay fractions were
180 measured using a modified Bouyocous hydrometer method (Gee and Bauder, 1986). Loss-on-
181 ignition was used to estimate % SOM. To determine the percent loss-on-ignition, a 4-g air-dried
182 subsample was combusted at 475 °C for 8 h. Total C concentrations in leaves, bole wood, and
183 soil were measured using a Carlo-Erba elemental analyzer. In brief, 6 ± 1 mg of sample ground
184 to < 0.5 mm were analyzed. Every 20 samples included one blank, one Atropine SRM, and a
185 duplicate. Total C and N concentrations in Atropine SRMs were with 3 % of its certified value
186 and < 10 % relative percent difference. Because soil samples were strongly acidic soils derived
187 from granite and metamorphic rocks such as phyllites and schists, the contribution of C from
188 calcite concentrations was presumed to be negligible. Soil pH and total C for each horizon are
189 given in Supplemental Table 1.

190 2.3 Total Hg quantification

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

198 were within 5 %. SRM Hg measurements were within 9 % of their certified values. Total Hg
199 values for each horizon are given in Supplemental Table 1.

200 *2.4 Exchangeable Hg quantification*

201 Exchangeable Hg concentrations (EHg) for the organic and mineral soil were quantified
202 using a modified $\text{Mg}(\text{NO}_3)_2$ extraction for ion-exchangeable Hg (Eganhouse et al., 1978; Crock,
203 1996; Amacher, 1996). The method used $\text{Mg}(\text{NO}_3)_2$ instead of MgCl_2 because Hg is able to form
204 stable complexes with Cl^- ions in solution (Schuster, 1991). We chose to investigate
205 exchangeable Hg to consider dissolved Hg transport, rather than transport of Hg by dissolved
206 organic compounds. In brief, 1 g soil was shaken in 10 mL of 0.1 M $\text{Mg}(\text{NO}_3)_2$ for 24 hr.
207 Samples were centrifuged at 3000 rpm for 20 min, and the supernatant was decanted. The slurry
208 was rinsed with 10 mL 5 % ethanol, centrifuged, and decanted again. A subsample of 100 mg of
209 combined extraction supernatant and rinse supernatant was analyzed for Hg concentration using
210 a Direct Mercury Analyzer – 80 (Milestone Inc.) in quartz boats. Every 15 samples included a
211 duplicate, a preparation blank, and a SRM of Hg in solution. Preparation blanks were below
212 detection limits, and duplicate variations were within 10 %. SRM Hg measurements were within
213 10 % of their certified values.

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218 *2.6 Statistical analyses*

219 Descriptive statistics were calculated in Matlab. The variations in THg and EHg
220 concentration and pools in the organic and mineral horizons were compared between vegetation

221 types (coniferous and deciduous) using a paired sample t-test. Stepwise linear regressions and
222 multiple regressions were used to explore relationships between THg and EHg concentrations
223 with other continuous variables (pH, % clay, soil C, latitude, and longitude).

224 **3. Results and Discussion**

225 *3.1 Forest soil properties*

226 *3.1.1 Soil physical properties*

227 Forest soil physical properties were generally similar at coniferous and deciduous stands.
228 Soils were well-drained or excessively drained, sandy loam-textured Spodosols. The Oi and Oe
229 horizon thicknesses were similar for both vegetation types, but Oa horizons were significantly
230 thicker for coniferous stands (11.3 ± 1.5 cm) compared with deciduous stands (6.1 ± 0.5 cm) (p
231 < 0.05). Although the thicknesses did vary significantly, the dry weight mass of the summed
232 organic horizons was similar between vegetation types. Organic horizon thicknesses are similar
233 to other studies conducted in this region (Juillerat et al., 2012; Richardson et al., 2013).
234 Thicknesses of the mineral horizons (E, Bhs, and B/C) were similar for coniferous and deciduous
235 stands. Mineral soil bulk density and texture were similar for all horizons for both vegetation
236 types. Texture was dominated by sand, ranging from 49 to 88 % (Supplemental Table 1). In
237 addition, the clay fraction was low, ranging from 1 to 11 %, which is similar to values reported
238 in other studies in this region (Johnson and Petras, 1998; Juillerat et al., 2012). However, the %
239 clay was significantly lower in the E horizons (5.2 ± 0.4 %) than in the Bhs (7.5 ± 0.5 %) and
240 B/C horizons (6.5 ± 0.6 %) ($p < 0.05$). We attribute the difference in clay fraction to
241 accumulation of Al and Fe oxy-hydroxides in the Bhs horizon (do Valle et al., 2005). This
242 finding suggests that the soil samples in this study were comparable among all stands.

243 *3.1.2 Soil chemical properties*

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

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

267

268 3.2 Hg concentrations and pools in forest soils

269 3.2.1 Total Hg in forest soils

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

283 Organic horizon Hg concentrations and pools may be greater at coniferous stands than at
284 deciduous stands due to differences in physicochemical properties. The organic horizons at
285 coniferous stands may receive less UV radiation, potentially decreasing photoreduction and
286 volatilization of Hg (Carpi and Lindberg, 1997; Schlüter, 2000; Gabriel and Williamson, 2004).
287 However, the soil properties related to Hg accumulation were significantly different at
288 coniferous stands when compared with deciduous stands. Total C concentrations were greater for
289 the Oa horizon at coniferous stands. Total Hg concentrations in the organic and mineral horizons

290 were regressed with soil C, pH, % clay, latitude, and longitude using stepwise linear regressions
291 and multiple regressions. Concentrations of THg in the organic horizons were weakly explained
292 by soil C and pH, accounting for only 24 % of the variation (Table 2). These weak to poor
293 correlations suggest other processes are responsible for THg. Based on the vertical THg
294 distribution in the organic horizons shown in Figure 2, the THg concentrations are dependent on
295 the vegetation type and degree of decomposition. Of the explanatory variables examined by
296 stepwise linear regressions, only soil C, pH, and % clay were significant for mineral horizons
297 (Table 2). For the mineral soil, soil C had the greatest explanatory power, and when multiple
298 regressed with % clay and pH, the variables explained 56 % of the variation in THg (Table 2).
299 This correlation suggests that accumulation of Hg is primarily driven by sorption, which is
300 controlled by soil C, % clay, and pH, and matches observations by Obrist et al. (2011), Juillerat
301 et al. (2012), Richardson et al. (2013), and Yu et al. (2014). However, nearly 40% of the
302 variation in the mineral soil and 76 % of the variation in the organic horizons remains
303 unexplained and could be due to other unconstrained variables; hydrology and sesquioxides are
304 two prime examples. Sesquioxides, Al and Fe oxy-hydroxides, are important inorganic surfaces
305 that may sorb Hg directly, or provide surfaces for organo-mineral complexation (Garbriel and
306 Williamson, 2004; do Valle et al., 2005). These are particularly of interest for the Bhs horizons,
307 which have accumulations of both sesquioxides and SOM.

308 It is possible that soils under coniferous vegetation at the most southern sites would
309 accumulate more Hg than at the most northern sites due to a longer growing season. In addition,
310 the soils of the White Mountains of New Hampshire may receive more atmospheric deposition of
311 Hg than the Green Mountains in Vermont (Miller et al., 2005). However, we did not find a
312 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 $9.8 \mu\text{g kg}^{-1}$. 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

336 concentrations, we are able to examine the relative fraction of exchangeable Hg. In Figure 3, E
337 horizons have a significantly greater exchangeability than all other organic and mineral horizons.
338 However, % EHg was similar for coniferous and deciduous stands in all horizons (Fig. 3). On the
339 basis of our results, Hg was strongly complexed in soil, regardless of vegetation type. Thus, a
340 shift from a coniferous to a deciduous stand would not increase Hg mobility in soil. However,
341 our method is limited in its ability to quantify the pool of Hg that may be mobilized via
342 particulate or DOC leaching. For this reason, increased Hg mobility may have been better
343 examined by quantifying Hg bound to mobile forms of organic matter rather than EHg that may
344 become mobilized after dissolution.

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

355 Our EHg and %EHg data also provide insight on the sorption and mode of illuviation of
356 Hg. In the Spodosols studied, Hg was not ion exchangeable. Mercury species were likely
357 immobilized by strong complexation or sorption to organic and inorganic colloids (Schuster,
358 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).

371

372 3.3 Hg concentrations and pools in aboveground biomass

373 3.3.1 Total Hg in foliage

374 Previous studies have shown that Hg concentration in foliage varies among tree genera
375 (e.g., St. Louis et al., 2001; Grigal, 2002; Bushey et al., 2008; Juillerat et al., 2012). We expected
376 THg concentrations to be greater in coniferous needles due to their longevity, which coincides
377 with observations of higher Hg concentrations in conifer needles (Rasmussen et al., 1991; Hall
378 and Louis, 2004; Obrist et al., 2012). We instead found that *Abies balsamea* and *Fagus*
379 *grandifolia* had higher THg concentrations than *Picea rubens*, *Acer* spp., and *Betula* spp. (Fig.
380 4). Our results match the rankings of THg concentrations by Rea et al. (2002), Bushey et al.
381 (2008), Juillerat et al. (2012), and Blackwell and Driscoll (2015). This suggests that differences

382 in their physiology beyond vegetation type promote greater Hg sorption. For example, the Hg
383 concentration for the foliage of *Picea rubens*, one of the three coniferous species, was not
384 significantly different than the foliage of *Acer* spp., and *Betula* spp., common deciduous genera
385 (Fig. 4). Hence, physiological properties unique to each species, such as leaf roughness, leaf area
386 index, stomatal morphology, and cuticle material, may control Hg sorption on leaf surfaces and
387 uptake (Browne and Fang, 1978; Weathers et al., 2006; Zhang et al., 2009; Obrist et al., 2012;
388 Juillerat et al., 2012). Blackwell and Driscoll (2015) hypothesized that coniferous vegetation
389 accumulate Hg at a slower rate than deciduous vegetation, but their longevity and multiple
390 growing seasons is responsible for their higher contribution in litterfall. An additional
391 physiological influence may be that Hg held on leaf surfaces for *Picea* spp., *Acer* spp., and
392 *Betula* spp. may have greater revolatilization rates than for *Abies balsamea* and *Fagus*
393 *grandifolia* (Hanson et al., 1995).

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

405 annual Hg deposition rates from precipitation and dry deposition have been were relatively
406 consistent during their monitoring of the region from 2003 to 2013 (NADP, 2007).

407 3.3.2 Total Hg in bole wood

408 Bole wood had significantly lower THg concentrations ($8 \pm 4 \mu\text{g kg}^{-1}$) than foliar (35 ± 9
409 $\mu\text{g kg}^{-1}$). Wood THg concentrations ranged from 10 to 50 % of their respective foliar
410 concentrations. Wood THg concentrations were greater for coniferous genera ($11.7 \pm 0.8 \mu\text{g}$
411 kg^{-1}) than for deciduous genera ($5.3 \pm 0.7 \mu\text{g kg}^{-1}$) (Fig. 4). These values are similar to bole
412 wood Hg concentrations in other studies (e.g., Obrist et al., 2012). The greater concentrations of
413 Hg in coniferous tissue are likely due to ecophysiological properties, such as growth rate and
414 root uptake (Rea et al., 2002). Although root uptake of Hg is generally considered a small
415 contribution (Aastrup et al., 1991; Grigal, 2002; Rea et al., 2002; Schwesig and Krebs, 2003), it
416 could differ among genera (Beauford et al., 1977) and could possibly be greater for coniferous
417 vegetation. In addition, retention in the xylem could also vary for each genus (Bishop et al.,
418 1998).

419 3.3.3 Aboveground biomass total Hg estimation

420 The foliar and woody biomass was calculated using 2012 basal area measurements for all
421 trees within the 707-m² stands and allometric equations for each species (TerMikaelian and
422 Korzukhin, 1997). It must be noted that these values are approximations, and biomass can vary
423 with canopy geometry, tree morphology, and individual fitness of each tree (Ferrari and Sugita,
424 1996; Luyssaert et al., 2002; Bushey et al., 2008). From the allometric equations, we estimated
425 that coniferous stands had significantly less foliar biomass ($1650 \pm 360 \text{ kg ha}^{-1}$) than deciduous
426 stands ($5680 \pm 610 \text{ kg ha}^{-1}$). Similarly, coniferous stands had significantly less woody biomass
427 ($9070 \pm 2220 \text{ kg ha}^{-1}$) than deciduous stands ($24,500 \pm 5480 \text{ kg ha}^{-1}$). The difference in foliar

428 and woody biomass at coniferous and deciduous vegetation was a large but not surprising
429 difference, considering the physiology and canopy structure of deciduous trees (Ferrari and
430 Sugita, 1996).

431 Mercury pools in the aboveground biomass (foliage and wood) were calculated using
432 averaged 2012, 2013, and 2014 THg concentration data with biomass estimates from allometric
433 equations. Our results in Figure 5 show that coniferous and deciduous stands do not have
434 significantly different foliar pools of THg despite significantly more foliar biomass at deciduous
435 stands. However, woody biomass at coniferous stands has a significantly larger THg pool ($0.30 \pm$
436 0.08 g ha^{-1}) than at deciduous stands ($0.15 \pm 0.04 \text{ g ha}^{-1}$). In spite of two thirds less woody
437 biomass at coniferous stands than deciduous stands, wood biomass THg pools at coniferous
438 stands were greater than deciduous stands. Foliar and wood biomass Hg concentrations can vary
439 annually due to precipitation and temperatures (Risch et al., 2011; Obrist et al., 2012). Moreover,
440 Hg concentrations can vary with the type of wood sampled (twigs, branches, bark, and bole
441 wood), and vertical location in the canopy can also affect Hg estimates (Risch et al., 2011; Obrist
442 et al., 2012). However, we believe our estimates of foliar Hg pools are representative values. For
443 example, the calculated litterfall rates, based on foliar Hg biomass at the 16 stands, was $0.13 \pm$
444 $0.04 \text{ g ha}^{-1} \text{ yr}^{-1}$, which matched litterfall rates measured by Risch et al. (2011) ($0.12 \pm 0.01 \text{ g}$
445 $\text{ha}^{-1} \text{ yr}^{-1}$) and Rea et al. (2002) ($0.16 \pm 0.02 \text{ g ha}^{-1} \text{ yr}^{-1}$). The litterfall fluxes at coniferous stands
446 (~10 % of the total Hg deposited) and deciduous stands (~45% of the total Hg deposited) are
447 similar to observations by Blackwell and Driscoll (2015) in the northern hardwood forest and
448 *Picea* spp./*Abies* spp. forests. The litterfall rates were significantly lower for coniferous stands
449 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 ($0.01 - 0.08 \text{ g Hg ha}^{-1} \text{ yr}^{-1}$) is significantly smaller than the atmospheric deposition rate of Hg ($0.24 - 0.26 \text{ g Hg ha}^{-1} \text{ yr}^{-1}$) based upon estimates from Yu et al., (2014) for this region (Table S2). Moreover, estimated annual volatilization rates of Hg ($0.02 - 0.08 \text{ g Hg ha}^{-1} \text{ yr}^{-1}$) from Yu et al., (2014) are equal to or greater than coniferous litterfall rates. Mercury litterfall flux at deciduous stands ($0.10 - 0.49 \text{ g Hg ha}^{-1} \text{ yr}^{-1}$) was generally similar to atmospheric deposition rates of Hg and significantly greater than volatilization rates from Yu et al., (2014). Although these ~~fluxes~~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 ($53 \pm 10 \text{ g ha}^{-1}$) than for deciduous stands ($30 \pm 6 \text{ g ha}^{-1}$). We calculated a 28 % lower (12 g ha^{-1}) Hg accumulation in soils at deciduous stands than at

Comment [JR1]: The only correction made throughout the manuscript.

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

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719 **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)	720
	m			stems ha ⁻¹	m ² ha ⁻¹	%	%		721
VT 1	601	Conifer	A,B,C,E,G,H	257	8	63	56	Frigid Oxyaquic Haplorthod	722
		Deciduous	A,B,C,E,G	329	14	4	22	Frigid Typic Haplorthod	723
VT 2	704	Conifer	A,B,C,F,G	302	11	68	52	Frigid Typic Haplorthod	724
		Deciduous	B,C,D,F,H	243	12	0	6	Frigid Typic Haplorthod	725
VT 3	608	Conifer	A,D,E,F	371	6	52	52	Frigid Typic Haplorthod	726
		Deciduous	C,D,E,F,G	314	18	0	0	Frigid Typic Haplorthod	727
VT 4	582	Conifer	A,C,F,G,H	357	20	99	64	Frigid Fragic Haplorthod	728
		Deciduous	C,D,E,F,G,H	214	6	40	32	Frigid Fragic Haplorthod	729
NH 1	680	Conifer	B,D,E,F,G,H	443	8	76	52	Frigid Oxyaquic Haplorthod	730
		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	

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

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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.

Stepwise Linear regressions			Organic horizons		Mineral horizons	
			THg	EHg	THg	EHg
			($\mu\text{g kg}^{-1}$)	($\mu\text{g kg}^{-1}$)	($\mu\text{g kg}^{-1}$)	($\mu\text{g kg}^{-1}$)
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**

737

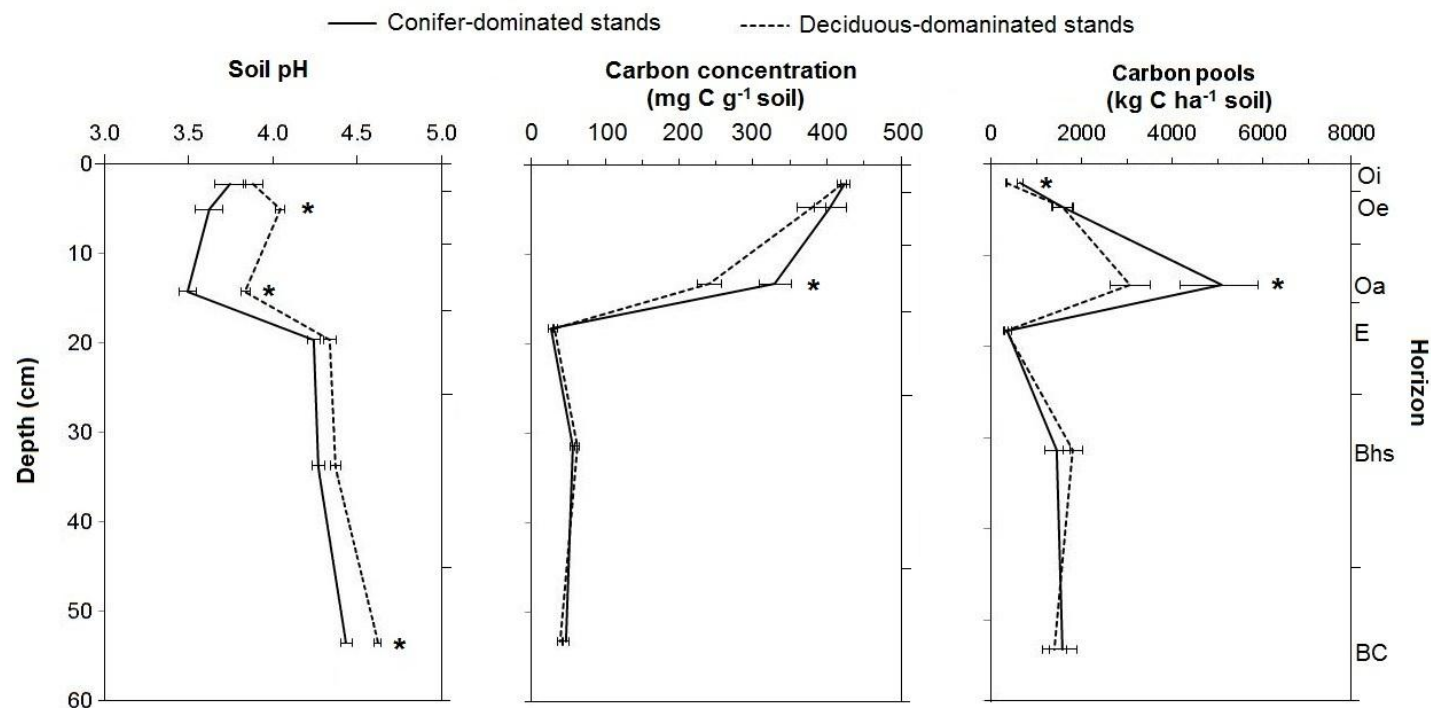
[†]Decimal degrees

738

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

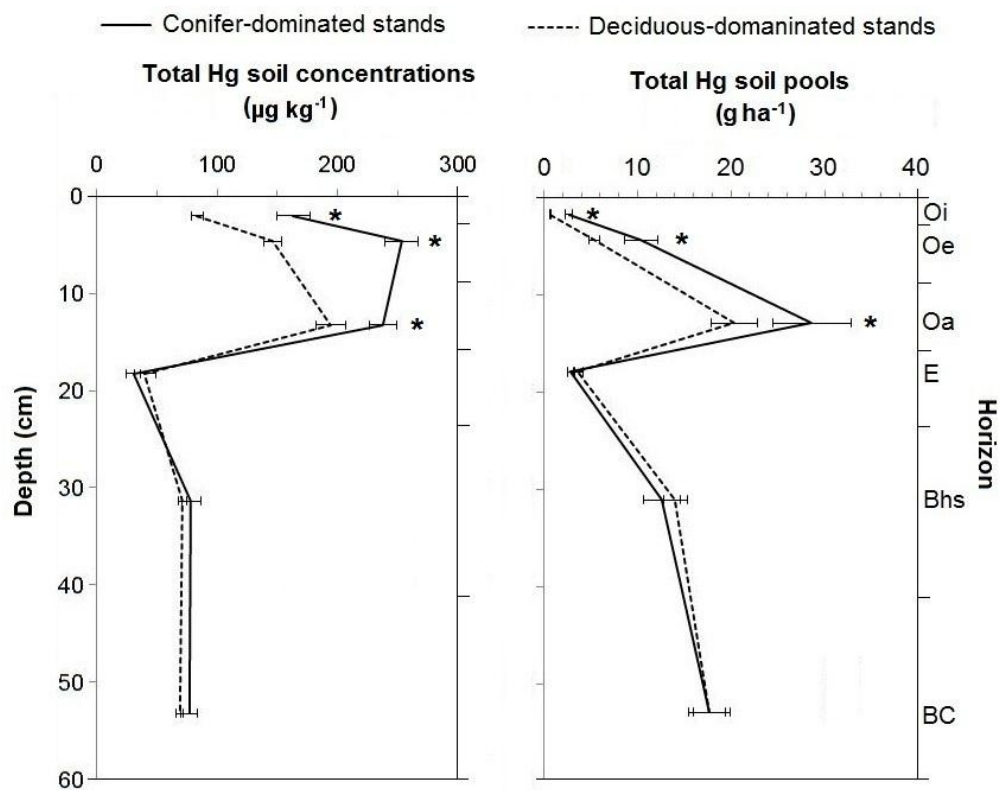
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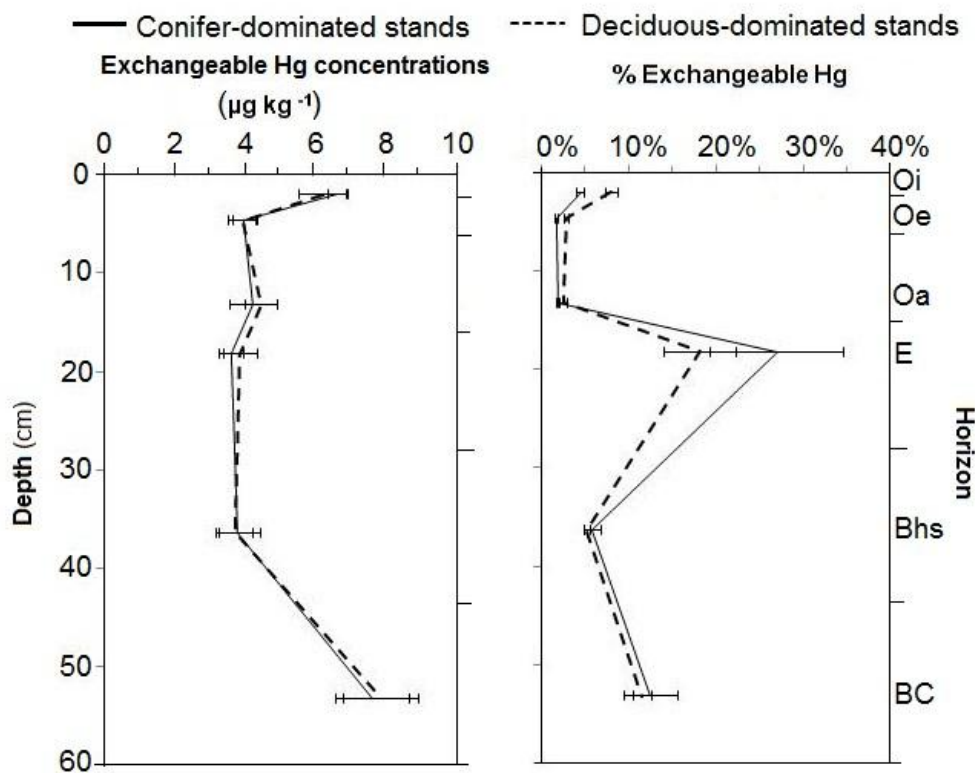


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742 **Figure 1 Soil pH, Carbon concentration, and Carbon pools for soil horizons at Conifer- and Deciduous-dominated**
 743 **stands. Mean values are given ± 1 standard error. (*) indicates a significant difference using two sample t-tests (P**
 744 **< 0.05).**



745
 746 **Figure 2 Total Hg (THg) concentrations in organic and mineral horizons at conifer**
 747 **and deciduous-dominated forest stands. Mean values are given ± 1 standard**
 748 **error. (*) indicates a significant difference using two sample t-tests ($P < 0.05$).**



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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 ($P < 0.05$).

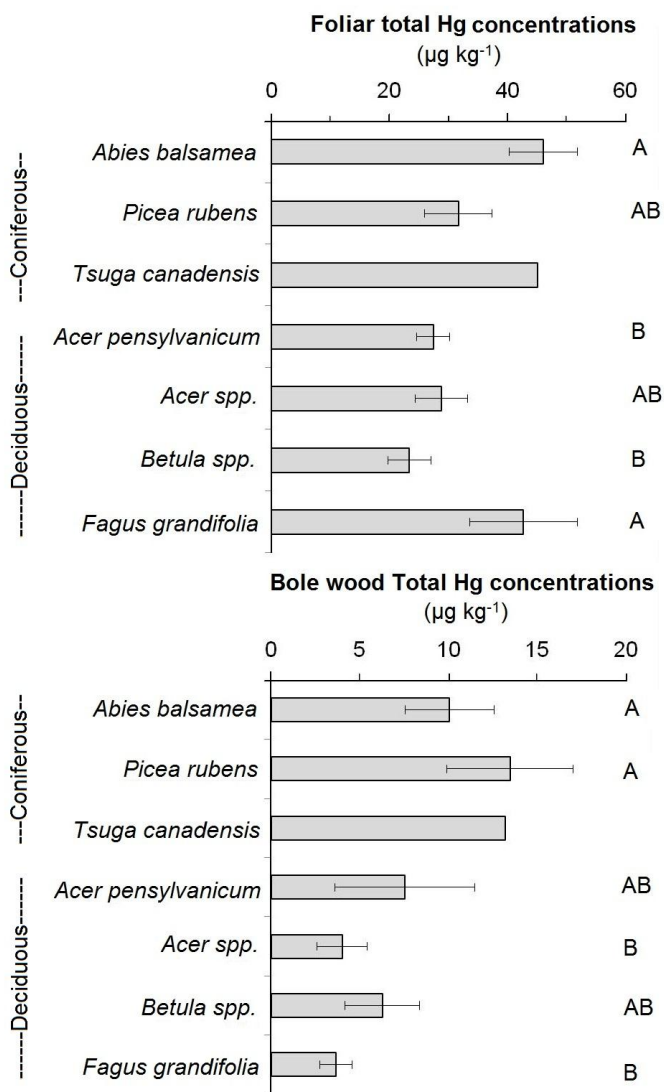
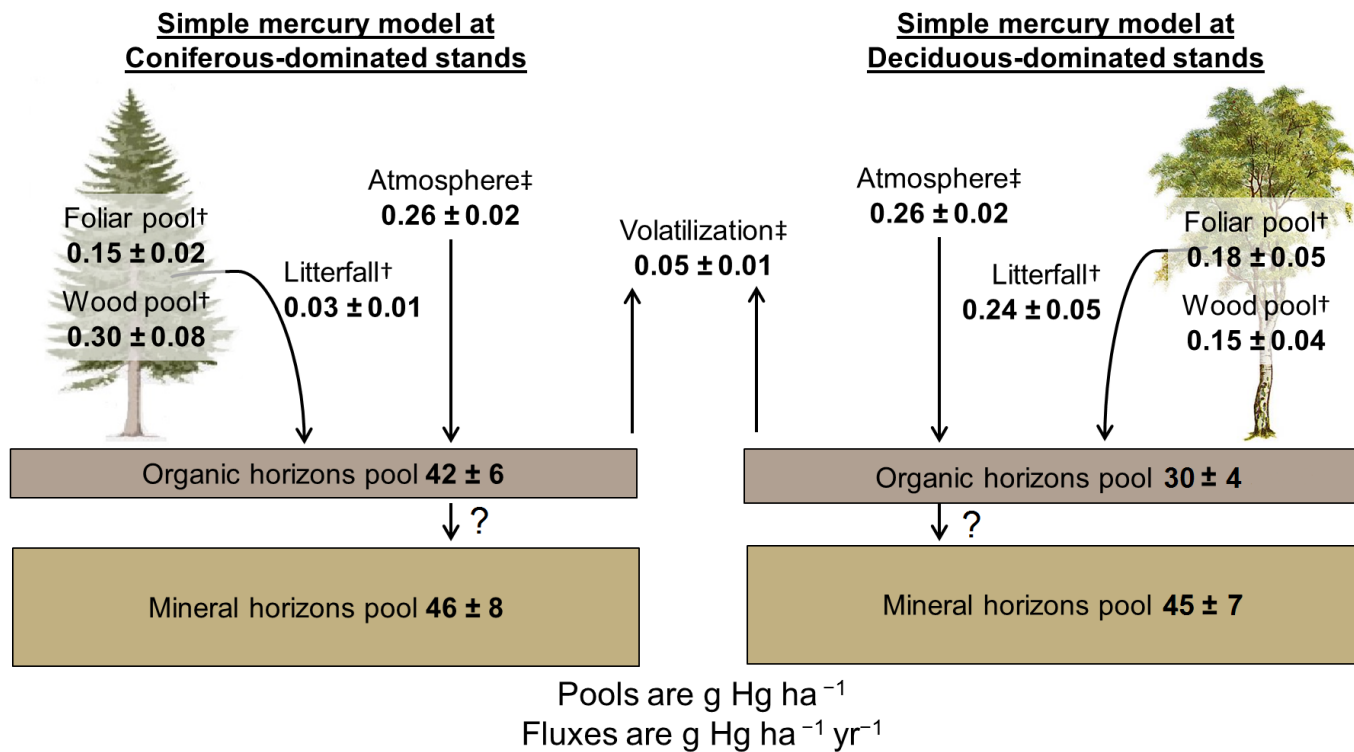


Figure 4 Total Hg concentrations in dry weight leaves and wood from 2012, 2013 and 2014 forest stand samplings. Mean values are given ± 1 standard error. Letters (A, B) indicates a significant difference using Kruskal-Wallis test with post-hoc ($P < 0.05$). Each species/genus ($n = 8$), except *Tsuga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



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761 **Figure 5 Total Hg pools in foliage, wood, organic, and mineral horizons at conifer and deciduous-dominated**
 762 **forest stands. See Method Section 2.5 for explanation of flux estimates. Mean values are given ± 1 standard error.**
 763 **† Litterfall was estimated using foliar pools and senescence rates for each genus.**
 764 **‡ Atmospheric deposition and volatilization rates were interpolated from Miller et al., (2005) and Yu et al., (2014).**
 765