

Reviewer #1 comments

We thank the reviewer for carefully reading and providing excellent comments to improve our study. Below, we outline in a point-by-point response how we addressed concerns through additional analyses and expanded our discussion where suggested.

General comment #1:

I think it would be important to provide more justifications for how the equations of the box model were set up. For example I cannot understand why the organic horizon does not have a volatilization flux but the mineral horizon has a volatilization loss. Also I cannot understand the reason why the input flux in the mineral soil depends on the litterfall flux and precipitation flux, which go into the organic horizon, or there is no dependency of the input flux in the mineral horizon on the size of the overlying organic horizon.

Author response #1: We have removed the box model. However, we still include the estimated litterfall fluxes and atmospheric deposition rates to illustrate that the variation in litterfall fluxes between vegetation types is important to consider.

General comment #2:

One important simplification was that the authors set the precipitation input equal for the two forest types. However other studies (e.g. Demers et al. 2007 and Blackwell and Driscoll 2015) found significant differences in throughfall Hg deposition between coniferous and deciduous forests. Demers et al 2007 for example found a 3 to 4.5 times higher throughfall deposition in coniferous forests than in deciduous forests. In my opinion the negligence of this difference in throughfall deposition in the model needs to be shown to have an insignificant effect on the calculated mean residence times.

Author response #2: We have removed the box model but still discuss the importance of considering vegetation type on Hg deposition via throughfall (atmospheric deposition) and litterfall.

General comment #3:

Another simplification is that the Hg deposition flux set to be constant to today's fluxes. It is clear that with changed in anthropogenic emissions the deposition flux has been highly variable in the last decades (e.g. Yin et al. 2014). I think that a better justification for the model as it is set up as well as a sensitivity analysis on the appropriateness of the simplifications made would greatly enhance the robustness of the results.

Author response #3: We have removed the simple two box model.

Specific comment #1

111465-L12-14 : Is an increase of precipitation expected for the whole globe or in Particular for the studied region? Please provide a reference to climate model in addition to the Hg deposition model reference (Smith-Downey et al. 2010)

Author response SC #1: We have added the reference Tang and Beckage (2010). Their study estimated regional increases in both precipitation and temperature. We now state this in our introduction section.

Specific comment #2

11467: What do the authors think is the reason for some sites being populated by coniferous forests and other sites by deciduous forests. Are there some ecological factors or some differences in the soil properties that favor one or the other type of forest stands?

Author response SC #2: It is not completely clear why each stand was populated by coniferous and deciduous vegetation at each mountain site. The coniferous and deciduous stands were sampled in the vegetation transition zone, where mean annual temperature and mean annual precipitation is within tolerable ranges for vegetation types. Soil type and hydrology were similar for the coniferous and deciduous stands. Ecological pressures that were not quantified may have led to preference of coniferous or deciduous vegetation. Potentially pressures from logging may have led to dominance of one vegetation type. For example, coniferous stands were located in areas that would have been difficult to access for logging while historically logged areas (Mt. Madison for example) have clearly been logged allowing for deciduous trees to dominate. We have added this point to our Material and Methods section.

Specific comment #3

114474-L20-L26: Given the high abundance of reduced sulfur in organic soils (in the order of 1mg/g) I find it hard to imagine that the sorption capacity for Hg (order of few hundred ng/g) is reached under natural uncontaminated conditions. Concerning Hg complexation by S in soils Skyllberg et al., 2006, ES&T might provide important insights

Author response SC #3: As stated in the later part of the sentence, S may limit Hg sorption in soil and S corresponds roughly linearly with C. We suggest the C pool will be decreased in the future at coniferous stands, and since S roughly corresponds with C linearly, it too will be decreased in the future. However, we do not state that the sorption capacity will be a limiting factor for Hg storage or accumulation in the future.

Specific comment #4

11475-L18-20 : Based on your measurements you estimate a approx. 5 to 10 times lower litterfall flux for coniferous stands compared to deciduous stands (Table S2), how does this go along with the statement that : "Organic horizon Hg concentrations and pools may be greater at coniferous stands than at deciduous stands due to litterfall inputs..."?

The contribution of litterfall to the total atmospheric deposition used in the model was approx. 50% for deciduous forests and only 10% for coniferous forests (Table S2). In particular the percentage of litterfall in coniferous forests is relatively low compared to studies measuring input fluxes with mass balance approaches (e.g. Gridal et al. 2000 Biogeochem, Demers et al. 2007 Ecol Appl., St Louis et al. 2001 ES&T). More recent studies based on stable Hg isotopes suggested even higher contributions of litterfall for deciduous (Demers et al. 2013, Glob. Biogeochem. Cycl.) as well as coniferous (Jiskra et al. 2015, ES&T) forests. It would be

appreciated if the authors could discuss this discrepancy of litterfall contribution in particular in the coniferous forests compared to literature.

Author response SC #4: We now have corrected the statement to read: “Organic horizon Hg concentrations and pools may be greater at coniferous stands than at deciduous stands due to differences in physicochemical properties.”. It is true that the coniferous litterfall fluxes were significantly smaller at coniferous stands compared to deciduous stands, but we attribute the greater Hg pool to its physical and chemical properties, which makes it decompose slower and retain more Hg. Our Hg litterfall estimates agree with previous studies estimates of Hg (Demers et al., 2007 *Ecol App* and in particular, Blackwell and Driscoll 2015 *ES&T*, where our values fall within their hardwood forest and transition to spruce/fir forests.

The relative fraction of Hg input from litterfall and atmospheric deposition is likely not comparable across studies such as Grigal et al., (2000) and other studies conducted at lower elevations and in other regions. Because of the elevation effect, see Stankwitz et al., 2012, *ES&T* and Blackwell and Driscoll 2015 *ES&T*, we would expect litterfall to contribute significantly less than atmospheric deposition. In addition, atmospheric deposition in the mountains are likely different than in the Midwestern states. We have added the following sentences to the discussion: “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/Balsamea* forests. ... 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.”

Specific comment #5

11475-L2-4: The vertical profile of organic horizons also represent different age of the organic carbon (the lower the horizon generally the older is the organic carbon). Given that the atmospheric Hg deposition was very variable in the last decades to centuries (e.g. yin et al, 2014) the vertical Hg profile should also be discussed with respect to soil/OC age resp. Time of deposition

Author response SC #5: This is a very interesting notion of documenting deposition history in the organic horizons, a method that has been demonstrated with some success by Klaminder et al., (2008) *Geochimica et Cosmochimica Acta*. However, this approach is limited to atmospheric deposition as pulses in regional deposition history but not slowly increasing deposition through time. Atmospheric deposition of Hg in the northeastern U.S. and southern Canada show a variable deposition history with some records showing 4x greater Hg deposition while others show no increase in Hg deposition (Pratt et al., 2013, *Atmospheric Environment*). With such a varied history, we cannot show a pulse or increasing trend in Hg deposition vertically in the soil profile without ignoring soil processes.

Moreover, our study lacks a vertical sampling regime capable of showing historical changes in Hg deposition. Currently, our profile shows E horizons having the lowest Hg concentration and pool, which could erroneously lead to the conclusion that deposition was historically lower at this period of time. However, the Hg concentration profile primarily shows the occurrence of podzolization and eluviation of organic matter and Hg from the E horizon.

Specific comment #6:

1177-L1-L5 : If I understand this statement right, you suggest that with the change from coniferous forests to deciduous forests, the underlying soils would convert to soils similar to deciduous forests and therefore the Hg pools would adapt also to deciduous forest pools. The organic pools of coniferous forests have been formed from coniferous organic matter are therefore less decomposable (eg. higher C/N ratios and more lignin fraction as you explain in the introduction) than deciduous soils. I find it hard to understand how these soil conditions and as a consequence of that the Hg pool should change in short to mid-term when the vegetation on the soils changes. I would suggest to provide more explanation/justification for the suggested loss of 30 % of Hg in the soil pool based on vegetation change.

Author response SC #6: Overall, we expect coniferous organic horizons to convert to deciduous organic horizons as the species composition changes. Essentially, there will be fewer coniferous needles and more deciduous leaves in the litterfall, so the organic horizon material will convert from coniferous properties (low pH, higher % C) to deciduous properties (higher pH, less % C). We have added the following sentence to the discussion: “As the species composition transitions from coniferous to deciduous, the soil properties (pH, C concentration) and associated Hg storage are expected to change as well.”

The source or fate of the 30% less Hg is unclear but we have proposed a few possible mechanisms. In our conclusions section we suggest “The effect of lower Hg storage in the organic horizons is unclear: Hg may be volatilized to the atmosphere, illuviated to lower horizons, or lost from the soil profile by leaching at a greater rate by transitioning from a coniferous to deciduous forest stand.”

Specific comment #7:

11483-L11-12 : On page 11481-L12 you concluded that the mean residence time of Hg in mineral soils of coniferous forests was significantly longer than of deciduous stands, how does this go along with the statement : “We conclude that vegetation type significantly influenced Hg accumulation and retention in the organic horizons but not in the mineral horizons, which were controlled by soil properties.”?

Author response SC #7: We have removed our box model and derived mean residence times of Hg in the organic and mineral horizons.

Specific comment #8:

11483-L17: Did you mean microbial reduction and volatilization? (Hg can not be decomposed, please change the terminology)

Author response SC #8: We were originally referring to decomposition of the SOM complexing the Hg, allowing for volatilization, but we have adopted the suggestion due to its clarity.

Reviewer #2 comments

We are grateful for the reviewers for insightful comments to improve our study and corrections found. Below, we outline in a point-by-point response how we addressed concerns through additional analyses and expanded our discussion where suggested.

Review Comment #1

Page 6, lines 16-18: In figure 4, the species is *Picea rubens* instead *Picea rubrus* as it in line 16. Please, check it.

Author response #1: The species has been corrected from *Picea rubrus* to *Picea rubens*.

Review Comment #2

Page 7 line 22-23: This is only a doubt. The mass of O subhorizons estimated from the samples separated in the laboratory was that for samples collected using the 3 15*15 cm sections or was that derived from the material removed when you used the 50*50 cm wooden frame?

Author response #2: The organic horizons were collected as three 15x15 cm blocks and separated in the laboratory. This has been clarified to “In the laboratory, the 15× 15 cm blocks of organic horizon were separated into Oi (litter layer), Oe (fermentation layer), and Oa (humified layer) horizons. Roots > 5 mm in diameter were removed and organic horizon layers were air-dried at 25 °C to a constant mass.”.

Review Comment #3

Page 8, lines 5-8: Only as consideration. Attending to soil pH values (which are strongly acid in most of the soils analyzed), the calculation of SOM by loss of ignition would not be necessary as SOM could be estimated directly using total C and the Van Bemmelen factor.

Author response #3: The Van Bemmelen factor utilizes an equally uncertain assumption but generally agrees to our SOM values in the mineral soil with 2 % of our LOI estimations.

Review Comment #4

Page 8, line 9: There is no information about the procedure for determination of particle size distribution in mineral soil horizons. Please, could you include a brief description or a reference of the method used?

Author response #4: We utilized the particle size analysis from Methods of Soil Analysis and have added the citation and reference for Gee and Bauder, 1986.

Review Comment #5

Page 11, lines 21-22: Did the authors consider any explanation for this difference in clay content among mineral soil horizons? Could be this related to podzolization?

Author response #5: We have added a brief explanation to the discussion about the difference in clay fraction within the soil profile, and we attribute the variation in clay to Al and Fe oxyhydroxides from podsolization and cite the reference do Valle et al., 2005, Chemosphere 58, 779-792.

Review Comment #6

Page 12, lines 3-4: No asterisks were shown in figure 1 for E and Bs horizons. So, were the differences in soil pH also significant for these horizons between both types of forest?

Author response #6: The soil pH was not significantly different for the E and Bhs horizons and this has been corrected throughout the manuscript.

Review Comment #7

Page 14, lines 12-13: Regarding sesquioxides, there are several studies that revealed the role of these soil compounds in Hg retention and storage, especially in podzolic soils such as those assessed in the present study. Perhaps the authors could add some comments regarding this issue.

Author response #7: We have added the following sentences to address this point: “Sesquioxides, Al and Fe oxyhydroxides, 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.”

Review Comment #8

Page 14, lines 24-25: This is only a personal opinion to put under author's consideration. Perhaps the reduction (24%) in Hg soil pool due to potential changes in vegetation could be overestimated. It should be take into account that part of the Hg storage in the soil, especially for mineral soil horizons, is consequence of long-term soil processes which extent in time more than a few decades, which could be probably the time spam for the change in vegetation from coniferous to deciduous forest. The idea behind this comment is that, Hg pool in mineral horizons is expected to be less dynamic than that from organic horizons as in them, Hg is probably bound (strongly bound) to well humified organic matter or Fe and Al oxyhydroxides. Thus, the response of the Hg pool in mineral horizons could be not significantly modified due to a vegetation change.

Author response #8: We completely agree that changes to the mineral soil horizons Hg pool is controlled by many other processes than vegetation and on a different time scale as well.

However, the main conclusion from Page 14 is that there is a 24% reduction in the total soil pool, primarily due to differences in the organic horizons. The organic horizons are expected to be dynamic and directly influenced by the vegetation.

Review Comment #9

Page 15, lines 13-14: It seems, from figure 3, that the greater differences in EHg occur in the Oa subhorizons and in the E horizons. Please, check the sentence you wrote in lines 13-14 of this page.

Author response #9: All EHg concentrations were similar between vegetation type and with depth. This has been corrected throughout the manuscript.

Review Comment #10:

Page 15, lines 18-19: In regard to this comment, the change in vegetation suggested by the authors could lead to a minor acidification in organic horizons which, at the same time, could result in a minor production of dissolved organic matter which is considered one of the main Hg transporters in podzols. Did you consider the Hg mobility in these terms and their potential consequences in a scenario of vegetation change?

Author response #10: We observed a more alkaline pH at deciduous stands, and thus a shift in vegetation would be expected to raise the pH. We now briefly mention this potential effect at the end of subsection 3.2.2.

Review Comment #11

Page 16, lines 3-14: Regarding this paragraph, it is missed some information about the distribution of Fe and Al oxyhydroxides in the mineral horizons. Results from these soil compounds could help to a better interpretation of the greater exchangeability of Hg in mineral horizons. A comment related to this will be welcomed.

Author response #11: We have added the following sentence to the paragraph: “Sesquioxides, such as hematite, goethite, and gibbsite, and SOM in the Bh horizon can increase Hg complexation (Gabriel and Williamson, 2004).”.

Review Comment #12

Page 16, lines 22-23: I consider that could be better to maintain the use of the scientific names of the trees throughout the text, instead of the local/common names.

Author response #12: This has been adopted, now only scientific names are used consistently through the text.

Review Comment #13

Page 17, line 6: Is there any reason to use capital letters for common tree names when in the previous page you used lower case letters?

Author response #13: We now only use the scientific names, where the genus is capitalized and the species is lower case.

Review Comment #14

Page 17, lines 22-23: This comment is, in general, related to this subsection (3.3.1). It is worried that, although the authors compared and discussed widely with other studies, there was no references to your own data of foliar Hg concentrations. Please, could you do somewhat about this?

Author response #14: We previously made two references to our own foliar Hg concentration data in subsection 3.3.1. However, we have added to the discussion and have added the following sentence: “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).”.

Review Comment #15

Page 18, lines 20-21: In figure 5, data of Hg pools in organic and mineral horizons from deciduous-dominated stands are not in bold as the other values of Hg pools and fluxes. Please, check it.

Author response #15: The deciduous-dominated stands pools values have been emboldened.

Review Comment #16

Page 18, lines 25-27: Part of this sentence is repeated, as it was already considered in a previous phrase. Please check it.

Author response #16: This has been corrected and now reads: “In spite of two-thirds less woody biomass at coniferous stands than deciduous stands, the aboveground THg pools at coniferous stands were greater than deciduous stands.”.

Review Comment #17

Page 20, lines 3-12: This comment is regarding uncertainties in Hg MRT estimation treated in these lines. Could be the potential mobilization of Hg from organic horizons to mineral horizons, and its consequent accumulation in illuvial horizons of podzols, another source of uncertainty in MRT calculation in the studied soils?

Author response #17: This is certainly true but we have removed the box model and MRT estimates from the manuscript.

Review Comment #18:

Page 21, lines 20-21: I am somewhat disagree with the latter part of this conclusion. The authors consider that physico-chemical soil properties are scarcely involved in Hg mobility. I think that this perspective is due to the approach used by the authors to assess the fraction of Hg mobility. Possibly, as in podzols is widely recognized that Hg could be mobilized by DOC, other soil extractions more closely related with organic matter dynamics (such as Na-pyrophosphate) could be a better approach to determine a true mobile Hg fraction in soil. So, I suggest that the authors should consider that the approach used to estimate Hg mobility was not the more suitable one.

Author response #18: We agree that the soil properties are important for Hg mobility but since we did not measure or discuss DOC or other organic matter focused extractions, we limited in our discussion on these topics. We have added the following sentence to the methods “We chose to investigate exchangeable Hg to consider dissolved Hg transport, rather than transport of Hg by dissolved organic compounds.”. Also we added the following sentence to our results and discussion section: “However, our method is limited in quantifying 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.”.

Review Comment #19:

Page 21, lines 25-26: Could be this estimation wrong?

$12 \text{ g ha}^{-1} * 7000 \text{ ha} = 84000 \text{ g Hg}$, i.e. 84 kg Hg (instead of 840 kg). Could you check this?

Author response #19: This calculation was incorrect. I contacted the authors from which the 7000 ha estimate was obtained and they provided the correct area of the current coniferous area in New England, which is 2.2 million hectares. 12 g Hg ha^{-1} across 2.2 million hectares is 27 Mg of Hg.

Review Comment #20:

Page 22, lines 1-2: I would also include the possibility of the accumulation of Hg, leached from uppermost mineral soil horizons, in illuvial Bs/Bhs horizons of podzols soils. It should be consider the role of these subsurface soil horizons in Hg storage in upland soils, as well as its environmental function as an additional barrier against Hg mobilization to groundwaters and surface waters.

Author response #20: We have added illuviation as a potential process of Hg loss from the organic horizons.

1 **Mercury in Coniferous and Deciduous Upland Forests in Northern New England, USA:**
2 **Implications [of](#) Climate Change**

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4
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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) ($42 \pm 6 \text{ g ha}^{-1}$) than deciduous stands ($30 \pm 4 \text{ g ha}^{-1}$). Total Hg pools in the mineral horizons were similar for coniferous ($46 \pm 8 \text{ g ha}^{-1}$) and deciduous stands ($45 \pm 7 \text{ g ha}^{-1}$). 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 \(\$0.03 \text{ g ha}^{-1} \text{ yr}^{-1}\$ \) than deciduous stands \(\$0.24 \text{ g ha}^{-1} \text{ yr}^{-1}\$ \).](#) We conclude that organic horizon Hg 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.

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Deleted: We estimated Hg mean residence time (MRT) in the organic and mineral horizons at coniferous and deciduous stands using a simple two-box model. Organic horizon MRT were longer at coniferous stands ($183 \pm 44 \text{ yr}$) than deciduous stands ($65 \pm 15 \text{ yr}$). Mineral soil horizon MRT values were also longer for coniferous stands ($386 \pm 57 \text{ yr}$) than for deciduous stands ($188 \pm 27 \text{ yr}$).

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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

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

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

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96 2007; Obrist et al., 2011; Stankwitz et al., 2012; Richardson et al., 2013). This could increase the
97 mobility of Hg and decrease the Hg pool in the organic and mineral horizons (Demers et al.,
98 2007).

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

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108 2. Materials and Methods

109 2.1 Mountain sites and forest stands

110 Eight pairs of coniferous and deciduous forest stands were studied (Table 1). Forest
111 stands were located at eight mountain sites in the deciduous–coniferous transition zone between
112 650 and 750 m above sea level. Four mountains were located on a north-south transect along the
113 Green Mountains of Vermont, and four sites were on a separate north-south transect along the
114 White Mountains of New Hampshire. Sampling sites were on west-facing slopes to avoid biases
115 from aspect. Northern New England is a temperate climate, with mean annual temperatures at the
116 stands ranging from 6 to 10 °C and mean annual precipitation ranging from 800 to 1300 mm
117 (PRISM climate research group, 2013). The mean annual frost-free period ranges from 90 to 160
118 d (Soil Survey Staff, 2014).

125 At each mountain site, a coniferous stand and a deciduous stand within 50 m of each
126 other were studied. Stands were 30-m-diameter circles. The frequency of each species and
127 diameter at breast height (DBH) for all trees was determined for the 707-m² stand. Coniferous
128 stands were inhabited with > 50 % coniferous genera, and deciduous stands were inhabited by >
129 60 % deciduous genera based upon basal area and stem frequency (Table 1). Basal area was
130 estimated from DBH measurements (Whittaker et al., 1974). Coniferous species present were
131 balsam fir (*Abies balsamea* Mill.), red spruce (*Picea rubens* Sarg.), and eastern hemlock (*Tsuga*
132 *Canadensis* L.). Deciduous species present were American beech (*Fagus grandifolia* Ehrh.),
133 sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), striped maple (*Acer*
134 *pensylvanicum* Marsh.), paper birch (*Betula papyrifera* Marsh.), and yellow birch (*Betula*
135 *alleghaniensis* Britt.). Vegetation at all stands was secondary growth due to the historical
136 clearing of the region in the 1800s and abandonment in the period from circa 1870 through 1920s
137 (cf. Foster, 1992). Coniferous stands were located away from trails and logging roads, in areas
138 that were likely difficult for timber harvesting. Using DBH of *Acer saccharum*, *Picea rubens*,
139 and *Abies balsamea*, at each stand, we calculated growth rates using parameters from Teck and
140 Hilt (1991) and Kenefic and Nyland (1999). We calculated that stand ages ranged from 57 to 137
141 yr with a mean of 88 ± 9 yr (data not shown). These ages may vary with site edaphic
142 characteristics.

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Deleted: sugar maple, red spruce, and balsam fir

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143 Only sites on bench landform and well-drained soils were chosen. The soil parent
144 material was glacial till for all stands, which was deposited during the retreat of the Laurentian
145 ice sheet in the Wisconsinian glaciation ~14,000 yr ago (cf. Siccama, 1974; Soil Survey Staff,
146 2010). Glacial till at sites NH 1–NH 4 was generally sourced from local bedrock: Bethlehem
147 granodiorite with contributions of Concord granite, Kinsman granodiorite, and metasedimentary

151 rocks from more northern formations (Bennett, 1996; Lyons, 1997). Glacial till at sites VT 1–VT
152 4 was locally sourced from the Waits River and Missisquoi formations, with additions of other
153 metasedimentary formations (Doll et al., 1966; Ratcliffe, 2000).

154 2.2 Soil and vegetation sample collection

155 Late-season foliage and bole wood samples were collected from *Picea rubrus*, *Tsuga*
156 *canadensis*, *Abies balsamea*, *Fagus grandifolia*, *Acer spp.*, and *Betula spp.* in triplicate from
157 each forest stand in early October 2012, 2013, and 2014. Foliage was collected from branches in
158 the middle canopy, 3–6 m above the ground, using a stainless steel pole saw. By not collecting
159 upper canopy foliage, we may have underestimated foliar Hg concentrations because Hg
160 deposition is greater in upper canopy leaves (Luyassert et al., 2002). Bole wood was sampled at
161 DBH using an 4 mm increment corer. Foliage and bole wood samples were air-dried at 25 °C for
162 3 wk and milled for homogeneity. Aboveground woody biomass and foliar biomass was
163 estimated using allometric equations for each species from studies conducted in the northeastern
164 US and southeastern Canada (Ferrari and Sugita, 1996; Ter-Mikaelian and Korzukhin, 1997;
165 Jenkins et al., 2003). The foliar and woody biomass for each tree was summed for an estimate of
166 total foliar and woody biomass at each stand. Aboveground woody biomass and foliage biomass
167 can vary with canopy geometry, tree morphology, and fitness of each tree (Ferrari and Sugita,
168 1996; Luyassaert et al., 2002). However, these estimates provide an approximation of values
169 without permanent destruction.

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

Moved (insertion) [1]

Deleted: of Hg

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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-m² 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 Bh_s 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, Bh_s, 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 ≤ 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.

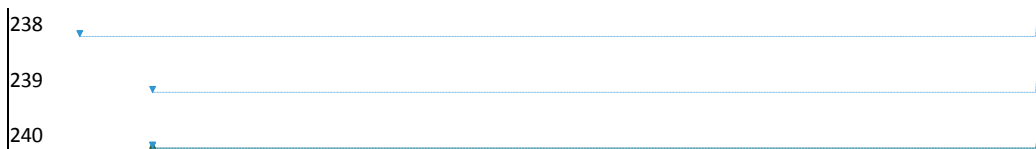
2.3 Total Hg quantification

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 $\text{Mg}(\text{NO}_3)_2$ extraction for ion-exchangeable Hg (Eganhouse et al., 1978; Crock, 1996; Amacher, 1996). The method used $\text{Mg}(\text{NO}_3)_2$ 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 $\text{Mg}(\text{NO}_3)_2$ 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

Deleted: 2.5 Hg simple two-box model

Deleted: A simple two-box model was implemented for each of the stands to estimate the residence time of Hg in the organic and mineral horizons. We estimated the mean residence time (MRT) for each of the sites by assuming the organic and mineral horizon Hg pools and fluxes were in steady state. Although this is unlikely due to changing atmospheric deposition rates (cf. Streets et al., 2011) and forest maturation, it allows for an approximation of Hg retention in forest soils. We calculated organic horizon MRT as the organic horizon pool divided by the sum of the input fluxes, atmospheric deposition, and litterfall rates (Eq. 1). The input flux to the mineral horizons was calculated as the atmospheric deposition and litterfall inputs from the organic horizons minus losses to volatilization (Eq. 2).[¶]

Eq. (1) $\text{MRT}_{\text{Organic horizons}} = \text{Pool}_{\text{Organic horizons}} / (\text{F}_{\text{litterfall}} + \text{F}_{\text{atmdep}})$ [¶]

Eq. (2) $\text{MRT}_{\text{Mineral horizons}} = \text{Pool}_{\text{Mineral horizons}} / (\text{F}_{\text{litterfall}} + \text{F}_{\text{atmdep}} - \text{F}_{\text{volatilization}})$ [¶]

We assumed the weathering input and root uptake of Hg in the organic and mineral horizons to be zero.

Moved up [1]: Annual litterfall fluxes of Hg from deciduous vegetation were assumed to be the entire foliar biomass. Annual litterfall fluxes from balsam fir and eastern hemlock was assumed to be 1/3 the foliar biomass because Barnes and Wagner (1981) observed average needle longevity to be 3 yr. Similarly, litterfall fluxes from spruce species, red spruce, was assumed to be 1/5 the foliar biomass because Barnes and Wagner (1981) the observed average time needle longevity to be 5 yr. The annual litterfall for each stand was calculated as the summed litterfall contribution for each tree at stand. Leaves from trees may fall beyond the boundaries of the 707-m² stand; thus, our litterfall values are likely overestimates (Ferrari and Sugita, 1996).

Deleted: Annual atmospheric deposition of Hg (wet + dry deposition) at the 16 stands was interpolated from Miller et al. (2005) and Yu et al. (2014) and ranged from 0.06 to 0.26 g ha⁻¹ yr⁻¹. Values fell into the typical atmospheric deposition rates in the northeastern US and New England (Grigal, 2002; Chalmers et al., 2014). Annual volatilization rates of Hg from organic horizons at the eight sites were interpolated from Yu et al. (2014). We ran Eq. (1) and (2) under the assumption of equal atmospheric deposition and volatilization rates for coniferous and deciduous stands. This assumption may not be true because coniferous and deciduous stands have been found to have significantly different atmospheric deposition and volatilization rates (Demers et al., 2007; Blackwell et al., 2014) due to greater canopy density and leaf density for coniferous vegetation (Weathers et al., 2006).

Deleted: The Hg flux from coarse woody debris was not included due to the wide variation in contribution at stands (twigs and branches to whole trees; cf. Fahey et al., 2005). The values for fluxes and model outputs are given in Supplemental Table 2.

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, Bh_s, 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 Bh_s (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 Bh_s 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

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

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

Deleted: E, Bs,

341

342 3.2 Hg concentrations and pools in forest soils

343 3.2.1 Total Hg in forest soils

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

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

Deleted: litterfall inputs (discussed in Section 3.3) or

365 were regressed with soil C, pH, % clay, latitude, and longitude using stepwise linear regressions
366 and multiple regressions. Concentrations of THg in the organic horizons were weakly explained
367 by soil C and pH, accounting for only 24 % of the variation (Table 2). These weak to poor
368 correlations suggest other processes are responsible for THg. Based on the vertical THg
369 distribution in the organic horizons shown in Figure 2, the THg concentrations are dependent on
370 the vegetation type and degree of decomposition. Of the explanatory variables examined by
371 stepwise linear regressions, only soil C, pH, and % clay were significant for mineral horizons
372 (Table 2). For the mineral soil, soil C had the greatest explanatory power, and when multiple
373 regressed with % clay and pH, the variables explained 56 % of the variation in THg (Table 2).

374 This correlation suggests that accumulation of Hg is primarily driven by sorption, which is
375 controlled by soil C, % clay, and pH, and matches observations by Obrist et al. (2011), Juillerat
376 et al. (2012), Richardson et al. (2013), and Yu et al. (2014). However, nearly 40% of the
377 variation in the mineral soil and 76 % of the variation in the organic horizons remains
378 unexplained and could be due to other unconstrained variables; hydrology and sesquioxides are
379 two prime examples. Sesquioxides, Al and Fe oxy-hydroxides, are important inorganic surfaces
380 that may sorb Hg directly, or provide surfaces for organo-mineral complexation (Garbriel and
381 Williamson, 2004; do Valle et al., 2005). These are particularly of interest for the Bhs horizons,
382 which have accumulations of both sesquioxides and SOM.

383 It is possible that soils under coniferous vegetation at the most southern sites would
384 accumulate more Hg than at the most northern sites due to a longer growing season. In addition,
385 the soils of the White Mountains of New Hampshire may receive more atmospheric deposition of
386 Hg than the Green Mountains in Vermont (Miller et al., 2005). However, we did not find a
387 significant correlation for THg with longitude or latitude. This suggests that longitude and

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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

Deleted: Spruce-Fir

Deleted: ~7000 ha

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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](#)

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

453

454 3.3 Hg concentrations and pools in aboveground biomass

455 3.3.1 Total Hg in foliage

456 Previous studies have shown that Hg concentration in foliage varies among tree genera
457 (e.g., St. Louis et al., 2001; Grigal, 2002; Bushey et al., 2008; Juillerat et al., 2012). We expected
458 THg concentrations to be greater in coniferous needles due to their longevity, which coincides
459 with observations of higher Hg concentrations in conifer needles (Rasmussen et al., 1991; Hall
460 and Louis, 2004; Obrist et al., 2012). We instead found that [Abies balsamea](#) and [Fagus](#)
461 [grandifolia](#) had higher THg concentrations than [Picea rubens](#), [Acer spp.](#), and [Betula spp.](#) (Fig.
462 4). Our results match the rankings of THg concentrations by Rea et al. (2002), Bushey et al.
463 (2008), Juillerat et al. (2012), and Blackwell and Driscoll (2015). This suggests that differences

Deleted: balsam fir

Deleted: American beech

Deleted: red spruce, maples, and birches

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).

Deleted: Spruces, Maples, and Birches

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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

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

496 3.3.2 Total Hg in bole wood

497 Bole wood had significantly lower THg concentrations ($8 \pm 4 \mu\text{g kg}^{-1}$) than foliar (35 ± 9
498 $\mu\text{g kg}^{-1}$). Wood THg concentrations ranged from 10 to 50 % of their respective foliar
499 concentrations. Wood THg concentrations were greater for coniferous genera ($11.7 \pm 0.8 \mu\text{g}$
500 kg^{-1}) than for deciduous genera ($5.3 \pm 0.7 \mu\text{g kg}^{-1}$) (Fig. 4). These values are similar to bole
501 wood Hg concentrations in other studies (e.g., Obrist et al., 2012). The greater concentrations of
502 Hg in coniferous tissue are likely due to ecophysiological properties, such as growth rate and
503 root uptake (Rea et al., 2002). Although root uptake of Hg is generally considered a small
504 contribution (Aastrup et al., 1991; Grigal, 2002; Rea et al., 2002; Schwesig and Krebs, 2003), it
505 could differ among genera (Beauford et al., 1977) and could possibly be greater for coniferous
506 vegetation. In addition, retention in the xylem could also vary for each genus (Bishop et al.,
507 1998).

508 3.3.3 Aboveground biomass total Hg estimation

509 The foliar and woody biomass was calculated using 2012 basal area measurements for all
510 trees within the 707-m² stands and allometric equations for each species (TerMikaelian and
511 Korzukhin, 1997). It must be noted that these values are approximations, and biomass can vary
512 with canopy geometry, tree morphology, and individual fitness of each tree (Ferrari and Sugita,
513 1996; Luyassaert et al., 2002; Bushey et al., 2008). From the allometric equations, we estimated
514 that coniferous stands had significantly less foliar biomass ($1650 \pm 360 \text{ kg ha}^{-1}$) than deciduous
515 stands ($5680 \pm 610 \text{ kg ha}^{-1}$). Similarly, coniferous stands had significantly less woody biomass
516 ($9070 \pm 2220 \text{ kg ha}^{-1}$) than deciduous stands ($24,500 \pm 5480 \text{ kg ha}^{-1}$). The difference in foliar

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

520 Mercury pools in the aboveground biomass (foliage and wood) were calculated using
521 averaged 2012, 2013, and 2014 THg concentration data with biomass estimates from allometric
522 equations. Our results in Figure 5 show that coniferous and deciduous stands do not have
523 significantly different foliar pools of THg despite significantly more foliar biomass at deciduous
524 stands. However, woody biomass at coniferous stands has a significantly larger THg pool ($0.30 \pm$
525 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
526 biomass at coniferous stands than deciduous stands, wood biomass THg pools at coniferous
527 stands were greater than deciduous stands. Foliar and wood biomass Hg concentrations can vary
528 annually due to precipitation and temperatures (Risch et al., 2011; Obrist et al., 2012). Moreover,
529 Hg concentrations can vary with the type of wood sampled (twigs, branches, bark, and bole
530 wood), and vertical location in the canopy can also affect Hg estimates (Risch et al., 2011; Obrist
531 et al., 2012). However, we believe our estimates of foliar Hg pools are representative values. For
532 example, the calculated litterfall rates, based on foliar Hg biomass at the 16 stands, was $0.13 \pm$
533 $0.04 \text{ g ha}^{-1} \text{ yr}^{-1}$, which matched litterfall rates measured by Risch et al. (2011) ($0.12 \pm 0.01 \text{ g}$
534 $\text{ha}^{-1} \text{ yr}^{-1}$) and Rea et al. (2002) ($0.16 \pm 0.02 \text{ g ha}^{-1} \text{ yr}^{-1}$). [The litterfall fluxes at coniferous stands](#)
535 [\(~10 % of the total Hg deposited\) and deciduous stands \(~45% of the total Hg deposited\) are](#)
536 [similar to observations by Blackwell and Driscoll \(2015\) in the northern hardwood forest and](#)
537 [Picea spp./Abies spp. forests.](#) The litterfall rates were significantly lower for coniferous stands
538 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 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 coniferous stands. Proposed mechanisms for this difference include litter quality, sorption

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We estimated Hg residence time in the organic and mineral horizons using a simple two-box model system (see Section 2.5 for details). The calculated Hg MRTs in the organic horizons were significantly longer at coniferous stands ($183 \pm 44 \text{ yr}$) than deciduous stands ($65 \pm 15 \text{ yr}$) (Supplemental Table 2). Similarly, the Hg MRT in the mineral soil was significantly longer for coniferous stands ($386 \pm 57 \text{ yr}$) than for deciduous stands ($188 \pm 27 \text{ yr}$) ($p < 0.05$; Supplemental Table 2). The organic horizon MRT was similar to estimates by other Hg studies conducted in this region (e.g., Demers et al., 2007; Yu et al., 2014). Moreover, organic horizons MRTs matched values for other pollutant toxic metals, specifically Pb (Miller and Friedland, 1994; Kaste et al., 2003; Richardson et al., 2013; Richardson et al., 2015). The Hg MRT in organic horizons at deciduous stands was very similar to the Pb residence time estimated by Kaste et al. (2003) and Richardson et al. (2014), which was 61 yr. Our results suggest that the MRT may be significantly longer at coniferous stands due to the larger organic horizons Hg pool. The opposite result was predicted by Demers et al. (2007) on the basis of smaller organic horizon Hg pools under coniferous vegetation. Mineral horizons MRTs were at least a 1000 years shorter than Yu et al. (2014), in which they calculated 1800 yr MRT for mineral soils across the northeastern US. The difference likely arose from the method used to estimate Hg leaching: Our study used the steady-state assumption with fluxes based on litterfall and atmospheric deposition, whereas Yu et al. (2014) used soil solutions.¶ The MRT values offer rough approximations of Hg cycling in forest soils under coniferous and deciduous stands, but the estimates are limited by data and assumptions used in our methods. First, the assumption of steady state is unlikely to be true because loadings have been increasing due to coal combustion and artisanal gold mining (Kamman and Engstrom, 2002; Streets et al., 2011; Tipping et al., 2011). Second, our volatilization rates and atmospheric deposition loads of Hg are interpolated values. The true volatilization and atmospheric deposition at each site can vary due to aspect, local topography, and many other properties not taken into account. Moreover, weathering of meta-sedimentary rocks may contribute a non-negligible amount of Hg on the order of centuries. The simple box models demonstrate that pollutant Hg can be retained by soils in the region for decades to centuries, and a change from coniferous to deciduous vegetation may affect the sequestration of Hg in forest soils. Additional information on deposition, litterfall, and sequestration of Hg in organic matter from different vegetation types is needed to constrain the role of vegetation in Hg biogeochemistry.¶ Mercury transport and accumulation in forest soils has been noted as strongly linked with the biogeochemistry of C in soils (Smith-Downey et al., 2010; Obrist et al., 2011; Demers et al., 2013; Zhou et al., 2015). We used a similar simple box model approach to estimate the MRT of C in the organic horizons as the C pool divided by the litterfall C flux. We assumed that the primary source of C to the organic horizons was via litterfall and that the C system is roughly in steady state. The MRT of C in the organic horizons was calculated to be significantly longer for coniferous stands ($12.0 \pm 3.2 \text{ yr}$) than for deciduous stands ($2.1 \pm 0.6 \text{ yr}$) ($p < 0.05$). Our estimates matched those by Fassnacht and Gower (1999), who calculated SOM MRT in the organic horizons of forests in Wisconsin to be 3.2–10.3 yr under coniferous stands and 0.8–4.7 yr under deciduous stands. The MRT was much longer at coniferous stands because the organic horizon C pools are greater and litterfall fluxes of C are smaller than at deciduous stands. The longer C residence time may increase the time Hg can be sequestered to SOM. However, the sequestration of Hg may be influenced by other SOM processes ...

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699 capacity of SOM, and susceptibility for microbial decomposition. Mineral soil THg
700 concentrations and pools did not significantly differ with vegetation type. Instead, soil C, % clay,
701 and pH explained 56 % of the variation in total Hg concentrations in the mineral soil. The
702 mobility of Hg did not vary significantly with vegetation type and was weakly explained by soil
703 physicochemical properties. Our empirical data indicate that coniferous vegetation accumulate
704 more Hg in their underlying soils, primarily in their organic horizons. We calculated a 28 %
705 lower (12 g ha^{-1}) Hg accumulation in soils at deciduous stands than at coniferous stands. When
706 extrapolated to the predicted ~2.2 million-ha loss of coniferous forests, the vegetation shift could
707 represent ~27 Mg kg less Hg sequestered in the organic horizons across the region. Further
708 investigations should evaluate the effect of vegetation type on Hg volatilization, atmospheric
709 deposition, and leaching rates to constrain landscape and regional changes. This will better aid
710 regional and global Hg models in implementing the effect of shifting vegetation type on future
711 Hg pools in soils.

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721 6. References

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Deleted: The effect of lower Hg storage is unclear: Hg may be volatilized to the atmosphere or lost to leaching and enter downslope water bodies at faster rates. We estimated the MRT of Hg in organic and mineral horizons underlying coniferous and deciduous stands to range from 65 to 515 years. The organic horizons MRT may be longer for coniferous stands than deciduous stands, whereas mineral horizons MRTs were similar for both vegetation types.

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955

956 **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)	957
	m			stems ha ⁻¹	m ² ha ⁻¹	%	%		958
VT 1	601	Conifer	A,B,C,E,G,H	257	8	63	56	Frigid Oxyaquic Haplorthod	959
		Deciduous	A,B,C,E,G	329	14	4	22	Frigid Typic Haplorthod	960
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	961
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	962
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	963
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	964
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	965
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	966
NH 4	640	Conifer	C,G,H,I	314	9	89	73	Frigid Typic Haplorthod	967
		Deciduous	C,E,F,G,H	279	12	1	11	Frigid Oxyaquic Haplorthod	

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

970

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**

[†]Decimal degrees

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