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Discussions

# *Interactive comment on* "Mercury in coniferous and deciduous upland forests in Northern New England, USA: implications from climate change" *by* J. B. Richardson and A. J. Friedland

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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 expanded Materials and Methods subsection 2.5 to fully detail the creation of the two box model. We have added the four equations used to create the box models. The organic horizon fluxes have been corrected and now include volatilization. The MRT values have been changed to reflect this correction. Because we only consider fluxes into the mineral soil, and since Hg leaching is dependent on fluxes form the organic horizon, it utilizes the same fluxes in. Hence, the fluxes into the mineral horizons are litterfall and atmospheric deposition minus the amount loss from volatilization. There are many limitations to our approach and they are explicitly stated in our assumptions. We have expanded the assumptions in the Material and Methods subsection 2.5 and Results and Discussion subsection 3.4.

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 added our previously omitted sensitivity analysis. In the analysis, we ran our model under three additional scenarios to test if coniferous and deciduous vegetation significantly affect the MRT in their soils. The three scenarios were: 1) unequal atmospheric deposition, 2) unequal volatilization rates; and 3) unequal atmospheric deposition and unequal volatilization rates. These are given in supplemental table 3. We found that organic and mineral horizons MRT in coniferous stands did not vary significantly. However, organic and mineral horizons MRT at deciduous stands did. The sensitivity analysis is described in Material and Methods subsection 2.5 and the findings are given in Results and Discussion subsection 3.4.

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: As described in the previous author response, we have added a sensitivity analysis to the Material and Methods subsection 2.5 and the added findings are given in Results and Discussion subsection 3.4. We focused our sensitivity analysis on the influence of vegetation type as opposed to changes in anthropogenic deposition, which we have discussed only in brief in our manuscript. A numerical model of changes in with anthropogenic deposition is possible since fluxes are given annually. However, this complexity of modeling requires changes in aboveground biomass and species composition through forest aggradation, which is beyond the scope of our 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. Giogeochem. 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 rsp. 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 pulses in regional deposition history. Deposition in the northeastern U.S. and southern Canada show a variable deposition history with a 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. The last point about discussing the vertical Hg profile with respect to soil age and organic carbon age is unclear. We currently compare the mean residence time of mercury and carbon in the Results and Discussion subsection 3.4. Because the vegetation history of each stand beyond the past century is unclear, discussion of vegetation effect through pedogenesis cannot be made.

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, longer MRT) to deciduous properties (higher pH, less % C, shorter MRT). 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 did not observe a significant difference in the mineral soil Hg pools between the two vegetation types. We have separated the parts of the sentence regarding retention and mean residence time to address it more accurately.



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.

Interactive comment on Biogeosciences Discuss., 12, 11463, 2015.