Assessing Biological Mercury Hotspots in Montane Ecosystems of the Northern Forest

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Methylmercury concentrations at Whiteface Mountain in the Adirondack region in New York are highest in the coniferous zone. These patterns are consistent with patterns of methylmercury in thrush species. Methylmercury accumulating in biota appears to be disproportionately derived from Hg in precipitation, as opposed to litterfall. Altogether, this suggests that future declines in both regional and global mercury emissions could be important in reducing mercury inputs to terrestrial systems and thus concentrations of mercury in montane avian species of the Northern Forest.

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http://www.nsrcforest.org

Project Summary

- Mercury is a potent neurotoxin that can be transported far from emission sources to remote areas. Once deposited to the ecosystem, mercury can form methylmercury which strongly bioaccumulates across the food chain and poses risks for humans and wildlife. Though methylmercury can form in the atmosphere, the majority of methylmercury is formed by sulfate-reducing bacteria in the soil. We examined precipitation and soil samples collected across an elevational gradient on Whiteface Mountain in the Adirondack region of New York State to determine spatial patterns in methylmercury concentrations across a forested montane landscape. We used mercury isotope techniques to trace mercury from atmospheric sources (precipitation and litterfall) to soil and into biota. We found that soil methylmercury concentrations were highest in the mid-elevation coniferous zone compared to the alpine and deciduous zones, while the percent mercury as methylmercury in soils decreased linearly with elevation. These findings for methylmercury concentrations are consistent with patterns of mercury concentrations in terrestrial bird species. Mercury isotope analysis suggests that methylmercury accumulating in biota is disproportionately derived from precipitation (rather than litterfall) mercury inputs. Altogether, this suggest that future declines in both local-regional and global mercury emissions that reduce mercury inputs to terrestrial systems could be important to reducing concentrations of mercury in montane avian species of the Northern Forest.

Background and Justification

- Mercury contamination results predominantly from direct atmospheric emissions into the atmosphere
- Atmospheric deposition has increased nearly 3.5 times since industrialization, primarily as a result of anthropogenic activities
- Mercury can be transformed into the neurotoxic form of methylmercury
- Methylmercury can bioaccumulate across the food chain, resulting in high concentrations in large fish and bird species
- Mercury can cause neurological, physiological, and behavioral impacts on wildlife and humans when consumed

Background and Justification

- The Adirondacks are a “biological mercury hotspot” with relatively high levels of mercury inputs and high concentrations of methylmercury found in fish
- Patterns in mercury have been based upon studies of aquatic systems, with relatively little understood about mercury accumulation in terrestrial species

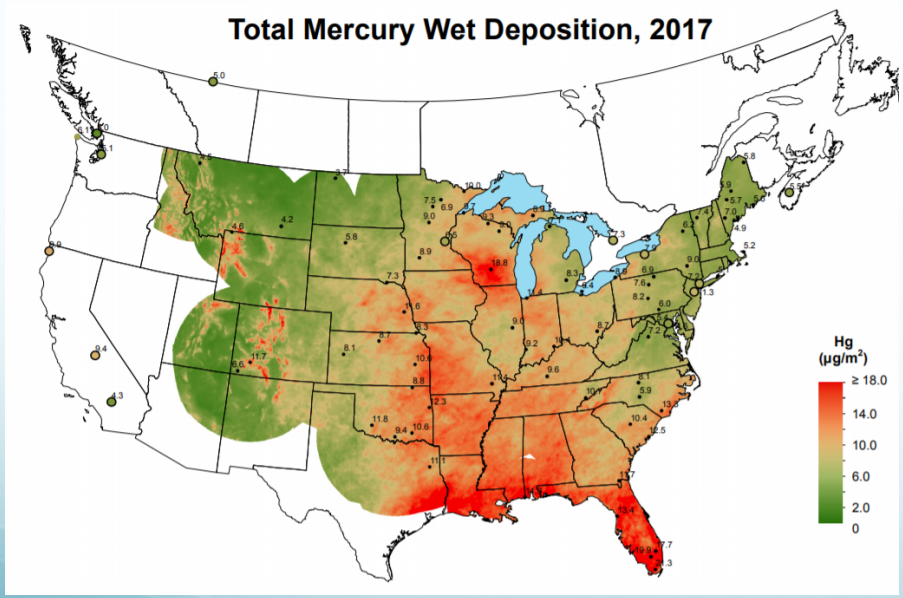
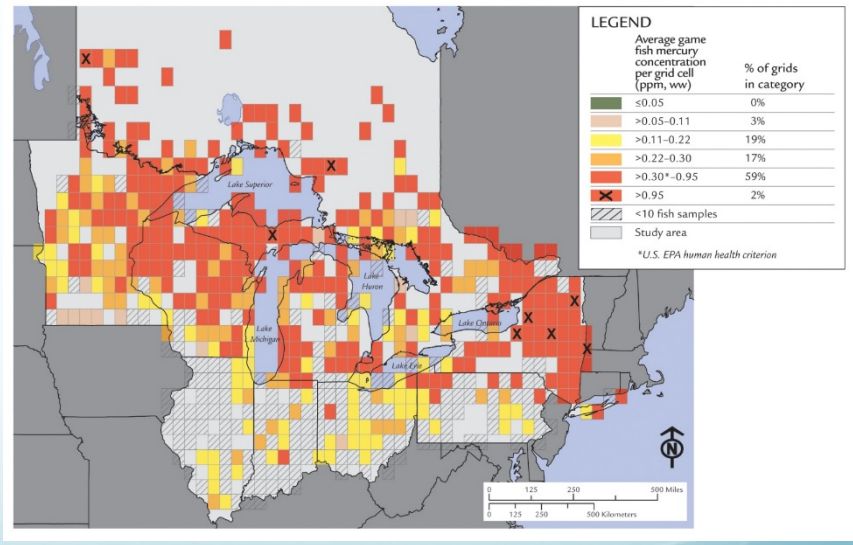


Figure 1: Patterns in wet mercury deposition across the US



Source: Evers et al, 2011

Figure 2: Biological mercury hotspots in the Northeast

Background and Justification

- High elevation mountain zones (sub-alpine and alpine) that receive high inputs of air pollutants (including mercury), are highly sensitive to air pollution and other stresses, and represent unique habitats that are often in protected areas.

- The overarching goals of our research were to: (1) evaluate the similarities and differences in patterns of increasing soil mercury concentrations with elevation at Whiteface Mountain; and (2) assess the factors driving the formation of biological mercury hotspots in these sensitive, unique and protected high elevation habitats of the Northern Forest.

- We sought to improve understanding of the mechanisms underlying the transfer of elevated soil mercury to mountain biological species of concern (e.g., Bicknell's thrush), thus supporting biodiversity and protected area management of the Northern Forest.

- This research improves projections of the impact of recent regional and national policy regarding controls on mercury emissions on these sensitive high elevation ecosystems.

Objectives

This project had two major research components. The first was a regional multi-mountain assessment of mercury accumulation in soils across New York, Vermont, New Hampshire, and Maine. The second was an intensive study of methylmercury (MeHg) transformation and bioaccumulation along an elevation gradient at Mount Whiteface in New York State, which included mercury isotope analysis to track atmospheric sources deposited to soil and accumulated in biota.

1. **Regional Multi-Mountain Assessment**.

   Objective: Evaluate elevational patterns of mercury in soils across the Northern Forest by comparing mountain transects in New York (Whiteface Mountain), Vermont (Mount Mansfield), New Hampshire (Mount Washington), and Maine (Saddleback Mountain).

2. **Methylmercury Transformation and Bioaccumulation at Whiteface Mountian.**

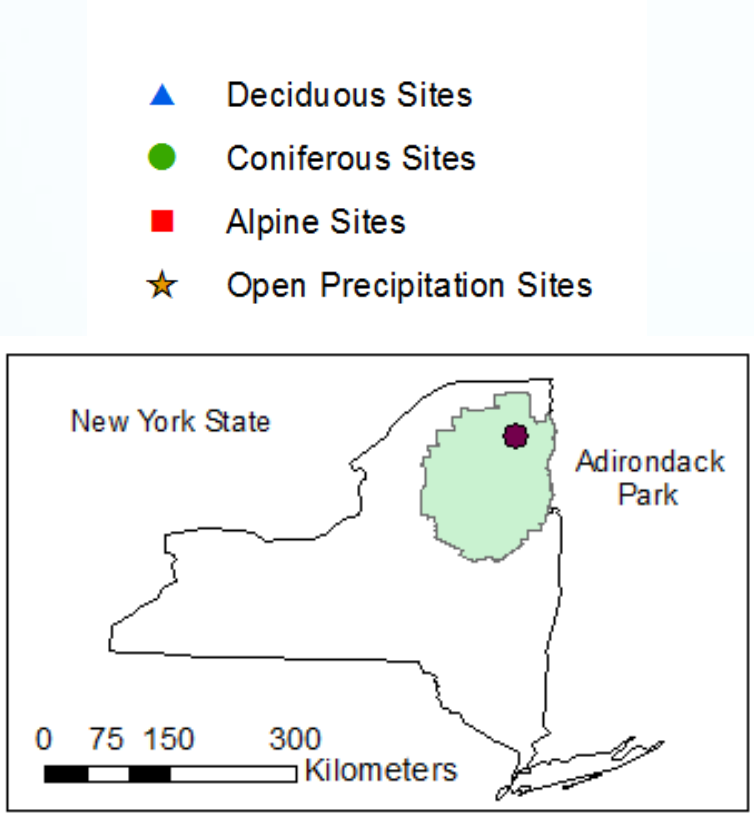
   Objective: Quantify differences in pathways of Hg deposition across elevational zones and the efficiency of its transfer to biota by: (i) measuring MeHg in soil and biota along a mountain transect (Whiteface Mountain, NY) and (ii) coupling MeHg data with Hg isotopes to trace sources of atmospheric Hg into terrestrial food webs.

Methods

Sample Collection: Whiteface Mountain Intensive

- Whiteface Mountain was divided into 3 zones by forest cover type:
  - Deciduous zone: 400-900 m; dominated by beech, birch, and maple trees
  - Coniferous zone: 1000-1300 m; dominated by spruce and fir trees
  - Alpine zone: 1350-1483 m; dominated by stunted-growth spruce and fir trees
- 12 sites were established across Whiteface Mountain:
  - 4 sites under tree cover were established equally spaced within each zone
  - 1 site in the open was established within each zone
- During May-October 2015, throughfall (precipitation passing through the canopy) and open precipitation samples were collected monthly from each site and cloudwater was collected during cloud-dominated events at the summit.
- Litterfall baskets were placed at all sites in May 2015 and collected in October 2015.
- Archived soil samples (Oi/Oe and Oa horizons) were collected during summer 2010.
- Archived invertebrate and songbird blood samples were collected during summer 2010.

Methods



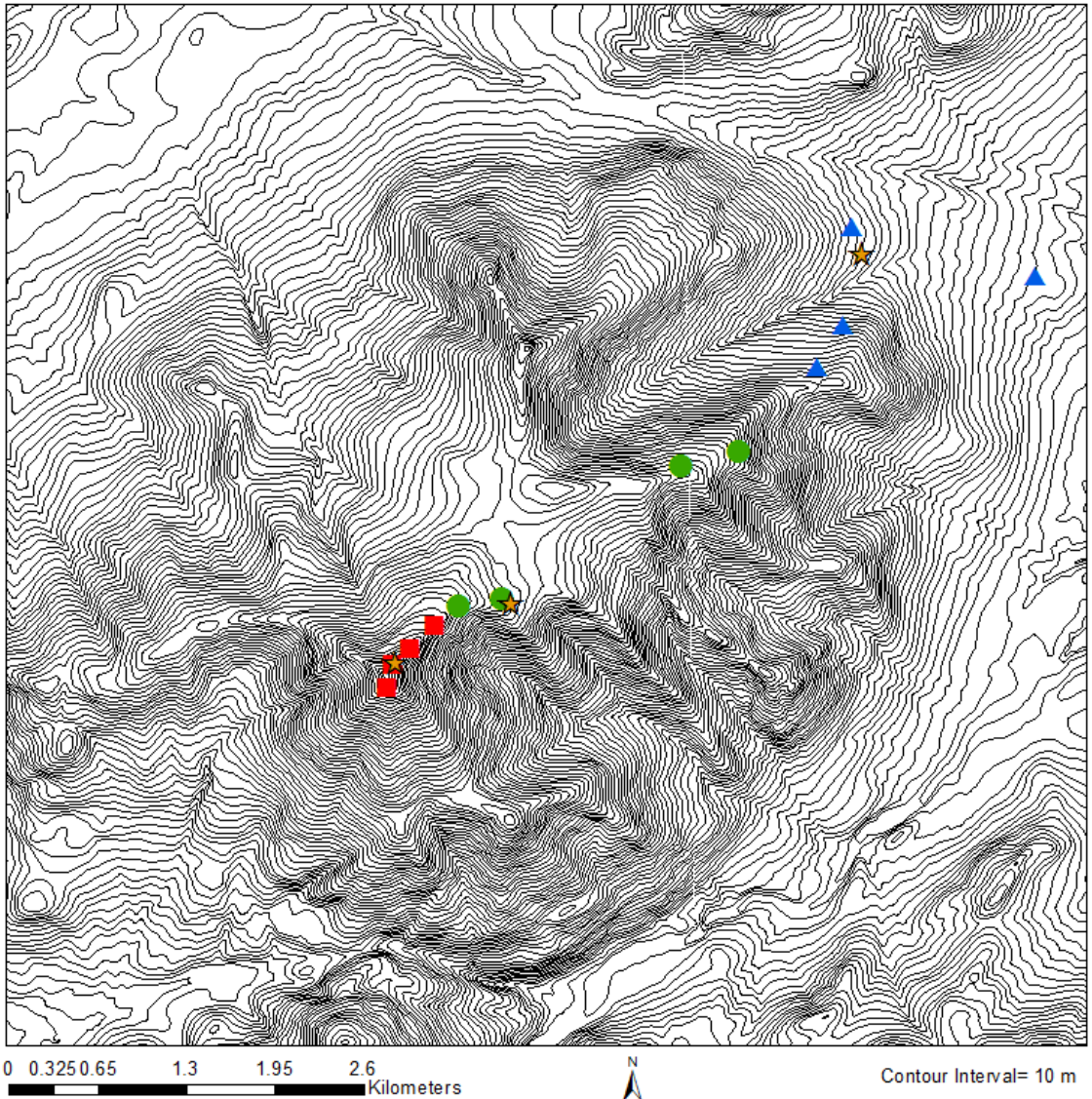


Figure 3: Location of study sites at Whiteface Mountain in the Adirondack Park in New York

Methods

Concentration Analyses:

- Throughfall, open precipitation, and cloudwater samples
  - MeHg – cold-vapor atomic fluorescence spectrometer (CVAFS)
  - THg – CVAFS
  - DOC – organic carbon analyzer
  - Sulfate – ion chromatograph
- Soil and litter samples
  - MeHg – acid digestion, CVAFS
  - THg – direct mercury analyzer
  - C – elemental analyzer
  - N – elemental analyzer
  - S – elemental analyzer

Methods

Mercury Isotope Analyses:

- Soil and Biota Samples
  - Dual stage combustion, matrix separation by purge and trap, CV-MC-ICP-MS (Cold Vapor Multi-Collector Ion-Coupled Plasma Mass Spectrometry)
- Precipitation, Throughfall, and Cloudwater Samples
  - There was insufficent mercury collected for isotopic analysis of precipitation, throughfall, and cloudwater. However, atmospheric sources of Hg in relatively rural areas have relatively consistent isotopic compositions and thus a synthesis of literature values of atmospheric sources was able to provide a contextual basis for understanding the sources of mercury depositing to soils and accumulating in biota in this study.

Results/project outcomes

- Total mercury concentrations in throughfall were highest in the coniferous zone, suggesting increased scavenging of atmospheric mercury by coniferous trees.
- No patterns were noted by forest cover for methylmercury concentrations or percent mercury as methylmercury, suggesting that methylmercury inputs do not differ by forest cover type.
- There was no difference between open precipitation and throughfall for methylmercury concentrations or percent mercury as methylmercury, suggesting that foliar surfaces do not increase methylmercury deposition.

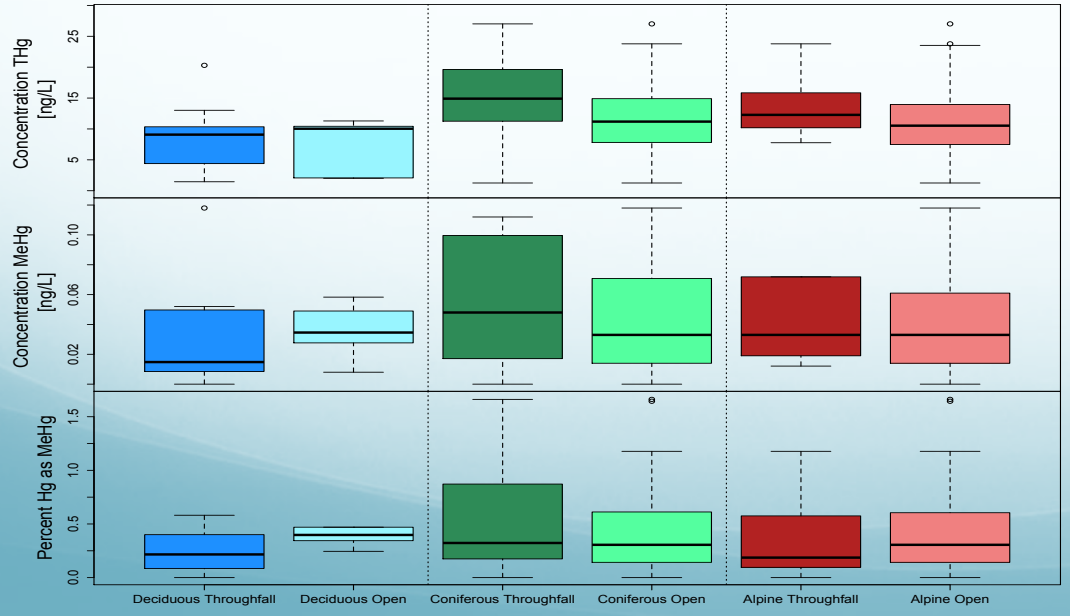


Figure 4. Concentrations of total mercury, methylmercury, and percent mercury as methylmercury in wet deposition (throughfall and open precipitation) across different forest covers at Whiteface Mountain.

Results/project outcomes

- Highest concentrations of soil mercury were found during the month of July when temperatures are warmer and precipitation is greater.
- Soil total mercury concentrations were greatest in the alpine zone, suggesting increased storage of mercury at higher elevations.
- Soil methylmercury concentrations were greatest in the coniferous zone, suggesting differential methylmercury production by forest cover.

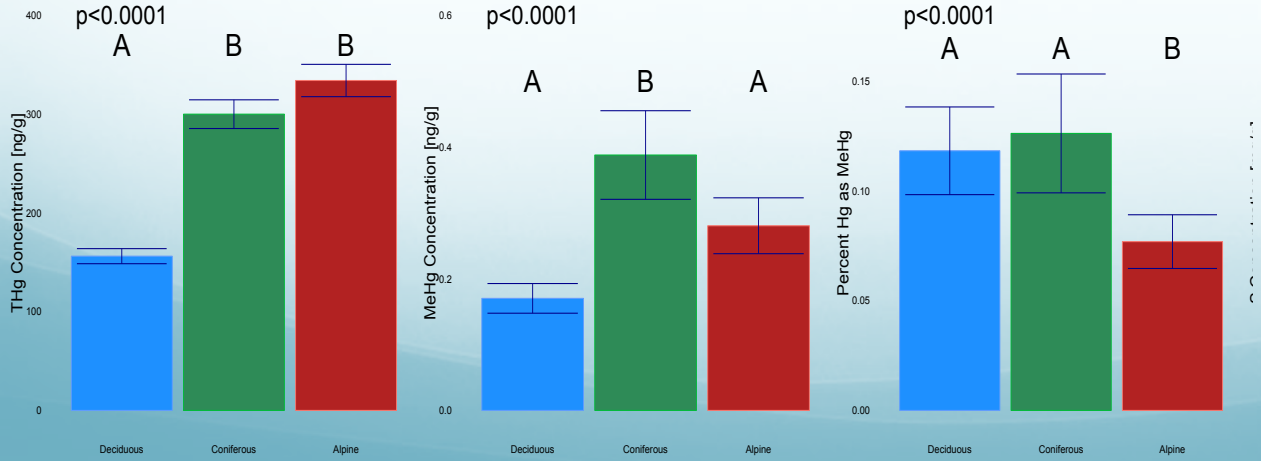
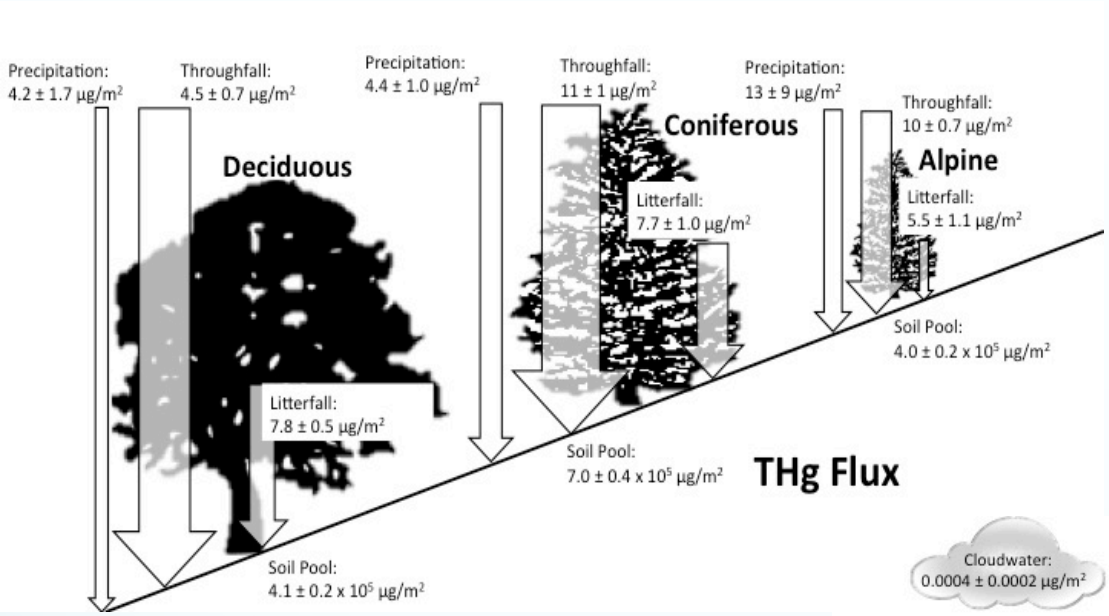


Figure 5. Soil concentrations of total mercury, methylmercury, and percent mercury as methylmercury at Whiteface Mountain.

Results/project outcomes



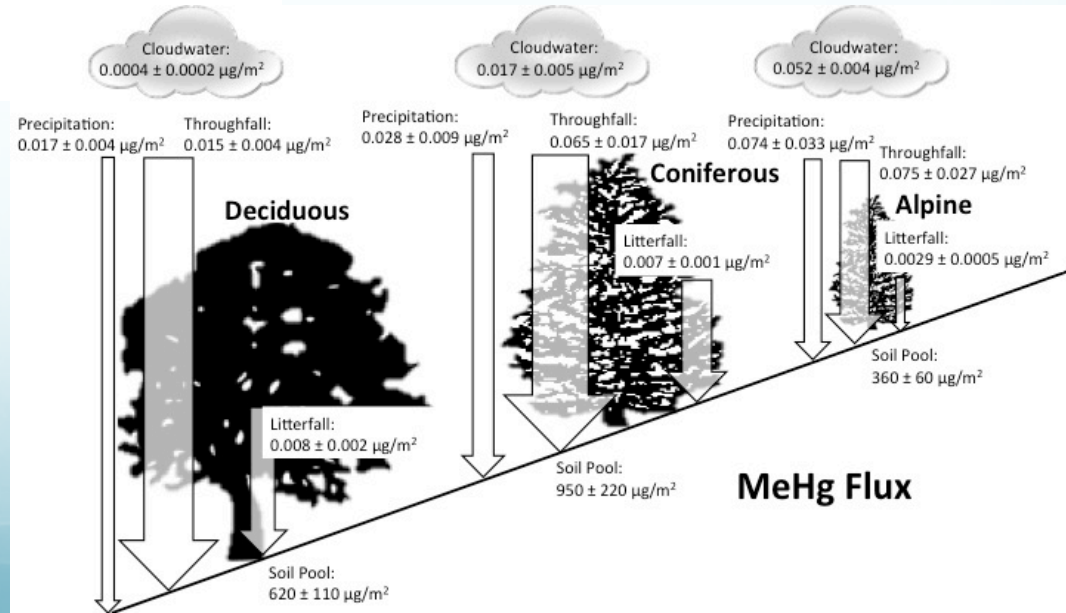


Figure 6. Comparison of total mercury and methylmercury inputs and soil storage at Whiteface Mountain.

Results/project outcomes

- Total mercury concentrations in soil are dependent upon elevation, with higher concentrations found at higher elevations
- Methylmercury concentrations in soil are dependent upon forest cover, with higher concentrations found in coniferous forests
- Percent mercury as methylmercury decreases across an elevational gradient
- Differing external inputs of methylmercury by forest cover are driven predominantly by differences in litterfall and cloudwater, but these external contributions are small
- The majority of methylmercury is produced within soils, likely by sulfate-reducing bacteria.

Results/project outcomes

- Hg isotope analysis indicates that soil Hg at Whiteface Mountain is predominantly derived from foliar uptake of gaseous Hg that is deposited with litterfall. This is consistent with other forest Hg isotope studies (e.g., Demers et al. 2013), but is somwhat in contrast to mass balance results indicating throughfall inputs dominate in the coniferous and alpine zones.
- Photo-volatilization of Hg associated with thiol ligands is greater in conifer and alpine forests than in deciduous forests, as inidicated by the lower Δ^{199}Hg values in coniferous and deciduous forest soil.

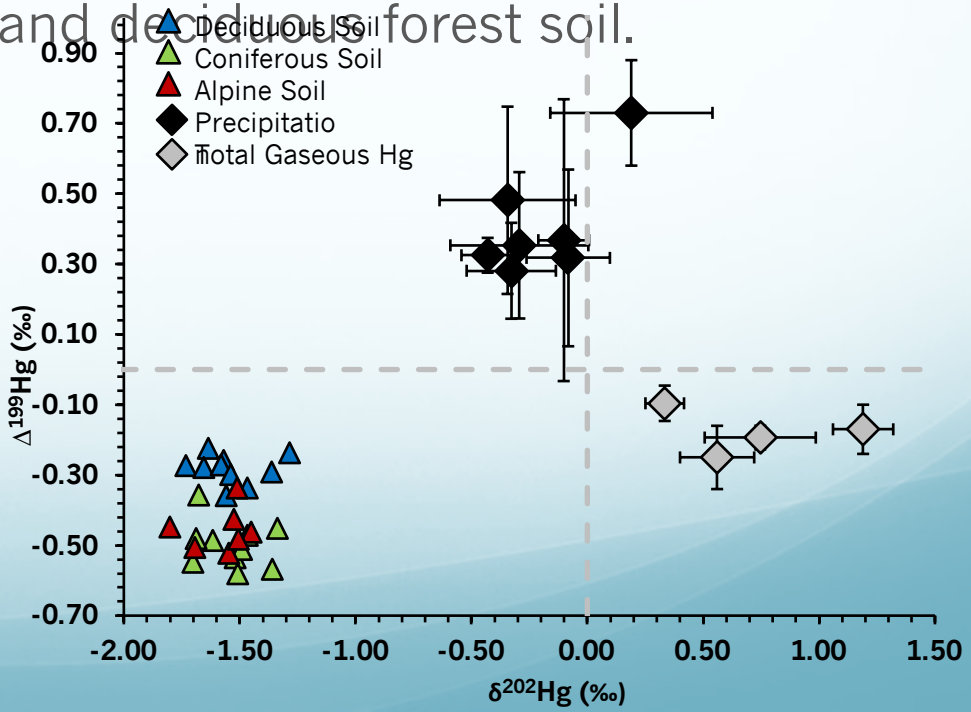


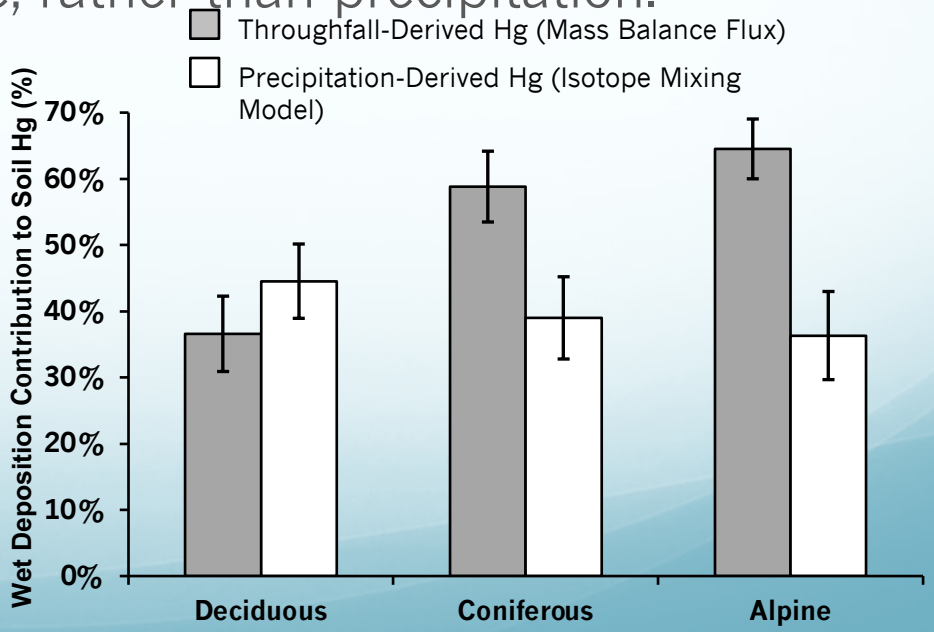
Figure 7. Mercury isotopic composition of soils at Whiteface Mountain. Typical literature values of precipitation and total gaseous mercury (TGM) from rural locations are shown for context.

Results/project outcomes

- Precipitation-derived Hg accumulating in forest soils (based on isotope mixing model) was similar to throughfall flux estimates in deciduous forests, but lower than throughfall flux estimates in coniferous and alpine zones.

- This is consistent with increased Hg volatilization suggested by Hg isotope signatures within coniferous and alpine soils, and may also suggest that a larger component of throughfall inputs in coniferous and alpine zones is derived from foliage, rather than precipitation.

Figure 8: Comparison of precipitation-derived total mercury accumulating in forest soils based on mass balance vs. isotope mixing model approaches at Whiteface Mountain.



Results/project outcomes

- Soil invertebrates accumulate Hg that is a mixture of sources from forest soil and precipitation. Low trophic level invertebrates with low %MeHg resemble the inorganic Hg signatures of forest soils, whereas higher trophic level invertebrates with high %MeHg have an isotopic composition similar to precipitation Hg that has been partially photochemically reduced prior to methylation.
- Songbird Hg isotopic signatures do not completely overlap with soil invertebrate Hg isotope signatures, suggesting that songbirds accumulate MeHg from additional source(s).

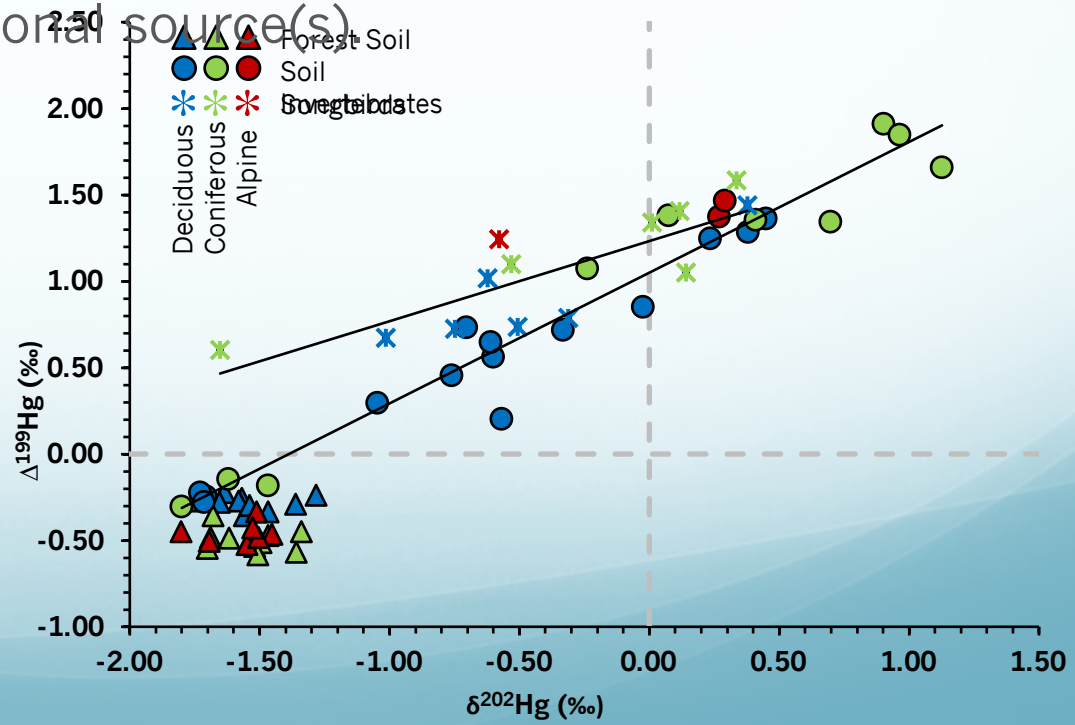


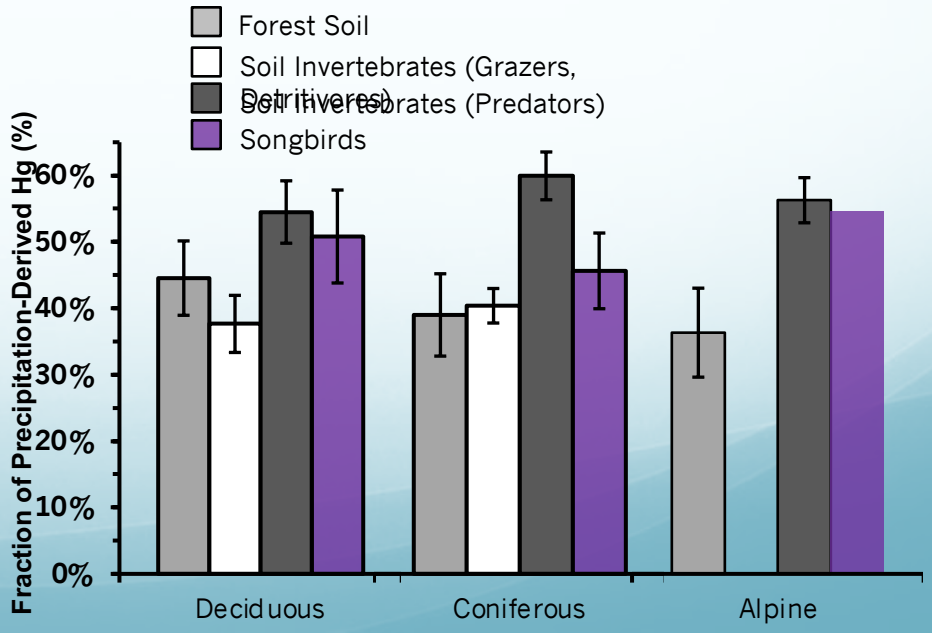
Figure 9: Mercury isotopic composition in forest soils, soil invertebrates, and songbird blood at Whiteface Mountain.

Results/project outcomes

- The fraction of precipitation-derived Hg was similar in forest soil and low trophic level soil invertebrates with low %MeHg. High trophic level soil invertebrates with high %MeHg typically had a greater fraction of precipitation-derived Hg. This suggests that precipitation-derived Hg is preferentially transformed to MeHg and bioaccumulated in soil biota.

- The relative fraction of precipitation-derived Hg in songbird blood was more variable, again suggesting that birds obtain MeHg from multiple source(s).

Figure 10: Fraction of precipitation-derived Hg in forest soil, soil invertebrates, and songbird blood at Whiteface Mountain. Error bars show ±1SD of mean for each component within each forest type. There was only one composite songbird blood sample available from the alpine zone.



Implications and applications in the Northern Forest region

- Elevational and forest cover patterns in total mercury and methylmercury deposition are evident at Whiteface Mountain and likely at other mountains in the Northeast.
- Patterns in methylmercury concentration drive patterns in bird blood mercury concentrations.
- Precipitation-derived Hg is disproportionately transformed to toxic methylmercury and accumulated in biota.
- Rules such as the Mercury and Air Toxics Standard (MATS) that decrease methylmercury concentrations to montane ecosystems could lead to reductions in bird blood mercury concentration and reduce stress to vulnerable populations.

Future directions

- Perform methylmercury analyses for invertebrates
- Perform an inter-mountain comparison from samples collected at four mountains in the Northeast

Journal Articles

- Gerson JR, Driscoll CT, Demers JD, Sauer AK, and Montesdeoca MR. 2017. Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape of Whiteface Mountain in the Adirondack Region of New York. *Environmental Science and Technology.*
- Gerson JR. 2016. Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape of Whiteface Mountain in the Adirondack Region of New York. *Syracuse University Master's Thesis.*
- Sauer, A. K., C. T. Driscoll, D. C. Evers, E. M. Adams, and Y. Yang. In review. Mercury exposure in songbird communities along an elevational gradient on Whiteface Mountain, Adirondack Park (New York, USA). Ecotoxicology.

Reports

- Driscoll, C., and A. Sauer. 2015. Methylmercury bioaccumulation within terrestrial food webs in the Adirondack Park of New York State. NYSERDA Report 16-06.

Presentations

- Gerson JR, Driscoll CT, Demers JD, Sauer AK, and Montesdeoca MR. Apr 2016. "Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape of Whiteface Mountain in the Adirondack Region of New York," Syracuse University Civil and Environmental Engineering Department Seminar. Oral Presentation. Syracuse, NY.

- Gerson JR, Driscoll CT, Demers JD, Sauer AK, and Montesdeoca MR. Apr 2016. "Montane Mercury Patterns at Whiteface Mountain in the Adirondack Park of New York, " NUNAN Research Day. Poster Presentation. Syracuse, NY.

- Gerson JR, Driscoll CT, Demers JD, Sauer AK, and Montesdeoca MR. Mar 2016. "Biological Mercury Hotspots Across an Elevational Gradient at Whiteface Mountain in the Adirondacks," Adirondack Research Forum. Poster Presentation. Old Forge, NY.

- Gerson JR. Feb 2016. "Assessing Biological Mercury Hotspots in Montane Ecosystems of the Northern Forest," Syracuse University Three Minute Thesis Competition. Oral Presentation. Syracuse, NY.

- Gerson JR, Driscoll CT, Demers JD, Sauer AK, Montesdeoca MR, Blackwell BD, Shanley JB, and Ross DS. Jun 2015. "Assessing Biological Mercury Hotspots in a Montane Ecosystem of New York, USA," International Conference on Mercury as a Global Pollutant. Poster Presentation. Jeju, South Korea.

Presentations

- Demers, JD, Blackwell, BD, Gerson, JR, Montesdeoca, MR, Ross, D, Sauer, A, Shanley, J, Driscoll, CT. Using mercury isotopes to identify sources of mercury accumulating is forest soils and biota along a montane elevational gradient. Presented at the 14th International Conference on Mercury as a global Pollutant, Krakow Poland 8-13 September 2019.