Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape of Whiteface Mountain in the Adirondack Region of New York

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Abstract

Global mercury contamination results from direct primary atmospheric and secondary legacy emissions, which can be deposited to ecosystems, converted to methylmercury, and bioaccumulated along food chains. I examined 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. I found that soil methylmercury concentrations were highest in the mid-elevation coniferous zone (0.39 ± 0.07 ng/g) compared to the alpine (0.28 ± 0.04 ng/g) and deciduous zones (0.17 ± 0.02 ng/g), while the percent mercury as methylmercury in soils decreased linearly with elevation. In multivariate linear analysis, soil sulfur concentrations had the greatest positive influence on soil MeHg concentrations, although they only explained 3.2% of the variability in soil MeHg concentrations. Soil MeHg concentrations appear to be driven by internal processing of Hg and not by deposition of MeHg to the forest floor and vary seasonally. These findings for methylmercury concentrations are consistent with patterns of mercury concentrations in terrestrial bird species and suggest that future declines in mercury emissions could be important to reducing concentrations of mercury in montane avian species.
Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape
of Whiteface Mountain in the Adirondack Region of New York

by

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Introduction

Mercury (Hg) is a potent neurotoxin that impacts the health of both humans and wildlife, even in remote areas (Driscoll et al. 2007, Evers et al. 2007). Atmospheric deposition of Hg has increased nearly 3.5 times since industrialization, primarily as a result of anthropogenic activities (Driscoll et al. 2013, Fitzgerald et al. 1998, Lorey and Driscoll 1999). Total Hg (THg) enters ecosystems via wet or dry deposition, with inputs varying by forest cover type and atmospheric Hg speciation. Dry deposition can occur as the adsorption of reactive gaseous Hg (RGM, Hg$^{2+}$) and particulate Hg (PHg) to the leaf surface (Lovett and Lindberg 1984, Rea et al. 2000, 2001). Mercury from dry deposition can enter soils via throughfall, which leaches Hg from the leaf surface (Choi et al. 2008, Fu et al. 2010). Additionally, Hg can enter forested ecosystems via the scavenging of gaseous elemental Hg (GEM, Hg$^0$) from the atmosphere by the stomata of canopy foliage, followed by deposition to the soil in litterfall (Demers et al. 2013, Graydon et al. 2008, Rea et al. 2000, 2002; Risch et al. 2012, Rutter et al. 2011). Many studies have found litterfall to be the dominant input of THg to deciduous forest ecosystems. Conversely, coniferous forests have higher throughfall and THg deposition than deciduous forests due to a greater scavenging efficiency driven by waxy cuticles, surface roughness, and high leaf surface area (Blackwell et al. 2014, Bushey et al. 2008, Demers et al. 2007, Fisher and Wolfe 2012, Graydon et al. 2008, Johnson et al. 2007, Kolka et al. 1999, Rea et al. 2002). Methylmercury (MeHg), the form of Hg that drives human and wildlife exposure, has the potential to form abiotically in the atmosphere via oxidative methylation of Hg or decomposition of dimethyl Hg or to enter the atmosphere via evasion from terrestrial or aquatic ecosystems (Conaway et al. 2010, Fu et al. 2010); however, these atmospheric processes of MeHg formation and transport are typically limited, and most MeHg is produced directly within terrestrial or aquatic ecosystems (Grigal 2003).
While many studies have examined the transport and fate of Hg in the environment, most have focused on aquatic ecosystems since MeHg bioaccumulation in fish is the dominant transfer pathway to humans (Dellinger et al. 2012). Nevertheless, MeHg bioaccumulation also occurs in terrestrial ecosystems; several studies have found altered physiological, behavioral, and reproductive functions resulting from high MeHg concentrations in terrestrial songbirds, invertebrates, and land biota (Evers et al. 2007, Rimmer et al. 2005, Townsend et al. 2014). While it is evident that MeHg concentrations increase with higher trophic levels (Rimmer et al. 2010), the pathway of Hg from the atmosphere to terrestrial biota is not fully understood. In fact, though several forested mountain environments in the northeastern United States (including the Adirondacks) have been identified as “biological Hg hotspots” (Evers et al. 2007), these classifications are based predominantly upon the contamination of aquatic ecosystems due to limited observations for terrestrial ecosystems.

Previous studies have shown that once Hg has been deposited, soils act as a net sink for Hg and a source of MeHg (Hojdová et al. 2007). Methyl Hg is produced in soils predominantly by sulfate reducing bacteria (SRB) under reducing conditions (Compeau and Bartha 1985), though investigations have also shown the methylation of Hg by iron reducing bacteria (IRB) (Kerin et al. 2006). Storage capacity of Hg within soils is enhanced by organic matter (OM) content, but the exact role of elevation remains poorly characterized (Townsend et al. 2014, Yu et al. 2011). Based upon soil characteristics, tree species, precipitation patterns, and expected Hg inputs, ecosystems at higher elevations are thought to receive higher Hg deposition and support greater methylation (Lawson et al. 2003, Yu et al. 2014). Findings of increased Hg concentrations in invertebrates, salamanders, and birds (Blais et al. 2006, Townsend et al. 2014), along with higher concentration of other contaminants (Lawson et al. 2003, Lovett and Kinsman
1990, Miller et al. 1993, Reiners et al. 1975), with increases in elevation support this hypothesis. Moreover, several studies have also reported higher concentrations of soil THg in coniferous compared to deciduous forests (Fisher and Wolfe 2012, Graydon et al. 2008, Kolka et al. 1999). Given that coniferous trees are often found at higher elevations, this forest cover type may also contribute to higher concentrations of Hg in sub-alpine zones. Nonetheless, to my knowledge, no studies have investigated forest ecosystem MeHg concentrations, fluxes, or pools along an elevational gradient.

In this study, I seek to understand the inputs and fate of Hg and MeHg in a montane forested ecosystem of the Adirondack region in New York State. To achieve this objective, open precipitation, cloudwater, throughfall, litterfall, and soil samples were examined across a 1000m gradient on Whiteface Mountain throughout the growing season. Specifically, my research questions are: 1) What are the relative contributions of various sources of THg and MeHg to the forest ecosystem? 2) How do THg and MeHg concentrations, fluxes, and pools vary across an elevational gradient and among different forest cover types (deciduous, coniferous, alpine)? 3) How do THg and MeHg concentrations, fluxes, and pools vary across the growing season (May-September)?

Methods

Study Area and Sample Plots

Whiteface Mountain is located in the northeastern Adirondacks of New York State (44.37°N, 73.90°W at the summit; Supplementary Figure 1). With a summit elevation of 1483 m, it is the fifth highest peak in the Adirondacks, and the most westerly peak of the 46 High Peaks in the region. Atmospheric chemistry and physics as well as forest ecology have been
monitored at Whiteface Mountain since the 1980s as part of the State University of New York at Albany Atmospheric Science Research Center (ASRC) (Dukett et al. 2011, Lovett and Kinsman 1990, Miller et al. 1993). Atmospheric monitoring stations are located at 610 m and at the summit, and cloudwater collection occurs at the summit. Both stations on Whiteface Mountain are managed by the New York State Department of Environmental Conservation (NYSDEC) as part of the Clean Air Status and Trends Network (CASTNet) and National Atmospheric Deposition Program National Trends Network (NADP NTN). There are two Mercury Deposition Network (MDN) sites located nearby at Huntington Forest in the Adirondacks (NY20, 50 km distance) and Underhill, VT (VT99, 80 km distance).

Forest communities on Whiteface Mountain consist of three major zones: deciduous, coniferous, and alpine (Blackwell and Driscoll 2015, Miller et al. 1993). The deciduous forest zone is located at low elevations of 400 to 900 m, has a mean canopy height ranging from 8.3 to 11.8 m, and is dominated by sugar maple (Acer saccharum), yellow birch (Betula alleghaniensis), red maple (Acer rubrum), and American beech (Fagus grandifolia). The coniferous forest zone is located at mid-elevations of 1000 to 1300 m, has a mean canopy height ranging from 6.0 to 8.1 m, and is dominated by balsam fir (Abies balsamea) and red spruce (Picea rubens). The alpine forest zone is located at high elevations of 1350 m to the summit at 1483 m, has a mean canopy height generally less than 2 m, and is dominated by sparse, krummholz-form balsam fir mixed with alpine tundra. Across Whiteface Mountain, the maximum mean canopy height occurs at 825 m and decreases linearly at higher elevations (Miller et al. 1993). Leaf area index (LAI) reaches its maximum at low- to mid-elevation (800 to 1220 m).
Fifteen plots were established across an elevational gradient on the eastern slope of Whiteface Mountain. Plot location, sample collection methodology, and sample analysis followed the approach of Blackwell and Driscoll (2015). Five plots were established within each forest cover type: four plots under the canopy (twelve total canopy plots) and one in an open area (three total open plots). The four under-canopy plots were equally spaced by elevation within each forest cover type.

Sample Collection

Soil samples were previously obtained in June, July, and September 2010 from twelve canopy plots, as described in Blackwell and Driscoll (2015). Soil samples were collected with a split-PVC corer and divided visually into Oi/Oe (containing slightly decomposed leaf litter and organic matter) and Oa (highly decomposed organic matter) horizons. In 2015, litterfall was collected from each canopy plot in two plastic mesh-lined crates that were deployed in May and retrieved in October. Samples were handled with clean nitrile gloves, placed in plastic bags, transported on ice to the laboratory, and frozen until processed.

Throughfall and open precipitation samples were collected monthly from May through September 2015 at each canopy and open plot, respectively. Two sample trains were established in the field: one for Hg analyses and one for ancillary chemical analyses (dissolved organic carbon [DOC] and sulfate [SO$_4^{2-}$]), with each open plot containing duplicate Hg sample trains. Mercury sampling trains were placed at plots and collected monthly using clean-hands protocols (EPA Method 1669). Briefly, Hg sample trains consisted of a glass funnel connected to two 500 mL Teflon bottles via perfluoroalkoxy (PFA) tubing and styrene-ethylene-butadiene-styrene (SEBS) block polymer (i.e., C-Flex) tubing with a loop as a vapor lock. Glass funnels contained
glass wool to prevent debris and insects from entering the sample train. Prior to deployment, glass funnels, PFA tubing, and Teflon bottles were pre-rinsed with 18.2 MΩcm Milli-Q water, immersed for a minimum of 24 hours in 10% nitric acid (HNO₃), rinsed three times with 18.2 MΩcm Milli-Q water, allowed to dry in a clean room, and double-bagged. Teflon bottles were stored until deployment with 10% trace metal grade hydrochloric acid (HCl) containing less than 0.1% Hg. At the time of deployment, all 500 mL Teflon bottles were acidified with two mL of trace metal grade HCl. C-flex tubing used to connect the glass funnels with the PFA tubing were pre-washed six times with 18.2 MΩcm Milli-Q water. New pre-rinsed C-flex tubing and glass wool were utilized at each deployment. Each Hg sampling train was replaced monthly at the time of sample collection. Teflon bottles were double-bagged, transported to Syracuse University, and stored at 4°C until analysis. Laboratory blanks (n=4) of the Hg sampling train had THg concentrations below the detection limit, and sample train standard spikes (5 ng/L) had recoveries of 90-110%. Ancillary chemistry sample trains consisted of a polyethylene funnel connected to a 1L polyethylene bottle via polyvinyl chloride tubing and C-flex tubing with a loop as a vapor lock. Prior to deployment, plastic funnels and one L bottles were pre-rinsed with deionized water, filled overnight with 10% HCl, and rinsed six times with deionized water. Polyvinyl chloride tubing was rinsed six times with deionized water. Mercury and ancillary chemistry method blanks were collected during each deployment.

Cloudwater was collected at the summit of Whiteface Mountain during 22 precipitation-free cloud events from July through September 2015. Cloudwater was collected with a passive sampler consisting of a Teflon-coated steel cartridge strung with 0.035 inch Teflon filament that condensed cloud water and mounted on the roof of the facility. Each sample was collected in a polypropylene funnel lined with Teflon and connected to a 500 mL polyethylene terephthalate
copolyster glycol (PETG) bottle via PFA tubing. The sampler was housed between sampling events in a PVC pipe lined with Teflon and covered with a stainless steel cap. Prior to the first deployment, Teflon strings and PFA tubing were pre-rinsed with 18.2 MΩ cm Milli-Q water, immersed for a minimum of 24 hours in 10% HNO₃, rinsed three times with 18.2 MΩ cm Milli-Q water, allowed to dry in a clean room, and double-bagged. Samples were acidified to 0.4% using trace metal grade HCl, transported to Syracuse University, and stored at 4°C until analysis.

Laboratory Analyses: Soil and Litterfall Samples

Of the 216 soil samples, 95% were previously analyzed for THg, percent carbon (%C), and percent nitrogen (%N), as reported in Blackwell and Driscoll (2015). I have supplemented these THg data with additional samples, as well as performed MeHg and percent sulfur (%S) analyses on all 2010 soil samples (n=216). Litterfall samples (n=24) were analyzed for THg, %C, %N, and %S.

Soil samples and litterfall samples were freeze-dried to a constant weight and analyzed for THg with a Leco AMA 254 via thermal decomposition, catalytic reduction, amalgamation, desorption, and atomic absorption spectroscopy (EPA Method 7473). The instrument was calibrated using National Institute of Standards and Technology (NIST) certified reference material 1633b (coal fly ash, 143 ng/g) and Canadian National Research Council (CNRC) certified reference material MESS-3 (marine sediment, 91 ng/g) with a detection limit of 0.2 ng Hg. Continuous calibration verification (CCV) and matrix spikes (MS) were performed using NIST 1633b, and quality control standard (QCS) was performed using MESS-3. All samples were run in duplicate. All CCV had recoveries within 90-110% (mean of 97%), all QCS had recoveries within 89-105% (mean of 96%), all MS had recoveries within 89-116% (mean of
95%), all duplicates had a relative percent different (%RPD) of 0.02-10% (mean of 4%), and all calibration blanks were below the detection limit.

For MeHg analyses, soil samples were microwave digested with trace metal grade HNO₃ and frozen until analysis (Hammerschmidt and Fitzgerald 2005); litterfall samples were digested with 2% potassium hydroxide in methanol at 55°C for a minimum of 48 hours (Horvat et al. 1993). Digested samples were analyzed via direct aqueous ethylation with sodium tetraethylborate, purge and trap, and cold vapor atomic fluorescence spectroscopy (CVAFS, EPA Method 1630) on a Tekran 2500 spectrometer. Calibration, CCV, on-going precision and recovery (OPR), laboratory control standard (LCS), and method detection limit (MDL) were performed using Frontier Geosciences certified laboratory MeHg standards. The method detection limit was 0.02 ng/L. All CCV had recoveries of 81-120% (mean of 95%), all OPR had recoveries of 96-111% (mean of 101%), all LCS had recoveries of 87-108% (mean of 92%), all MDL had recoveries of 78-123% (mean of 101%), and all calibration blanks were below the detection limit.

Percent C, %N, and %S were measured on freeze-dried soil and litterfall samples with a Costech 4010 Elemental Analyzer. Calibration and CCV for %C and %N analyses were performed using acetanilide (10.36% N, 71.09% C), and QCS was performed using atropine (4.84% N, 70.56% C). NIST certified reference sample 2709 (San Joaquin soil, 1.40% C) was used as an external standard for %C, and NIST 1515 was used as an external standard for %N (apple leaves, 2.25% N). Calibration and CCV for %S analyses were performed using sulfanilamide (18.62% S), and QCS was performed using BBOT (7.44% S). NIST 1515 (apple leaves, 0.18% S) was used as an external standard. For %C, all CCV had recoveries within 100-102% (mean of 101%), all QCS had recoveries within 99-102% (mean of 101%), all standards
had recoveries within 94-95% (mean of 95%), and all calibration blanks were below the
detection limit. For %N, all CCV had recoveries within 97-101% (mean of 99%), all QCS had
recoveries within 98-101% (mean of 99%), all standards had recoveries within 98-100% (mean
of 99%), and all calibration blanks were below the detection limit. For %S, all CCV had
recoveries within 90-112% (mean of 105%), all QCS had recoveries within 95-112% (mean of
103%), all standards had recoveries within 96-104% (mean of 102%), and all calibration blanks
were below the detection limit.

Laboratory Analyses: Throughfall, Open Precipitation, and Cloudwater Samples

Throughfall (n=57) and open precipitation samples (n=15) were analyzed for THg,
MeHg, SO$_4^{2-}$, and DOC. Cloudwater samples (n=22) were analyzed for MeHg and THg.
Throughfall, precipitation, and cloudwater samples were analyzed for THg via oxidation with
bromine chloride for a minimum of 24 hours, purge and trap, and CVAFS (EPA Method 1631
revision E) on a Tekran 2600 Automated Total Mercury Analyzer. Note that prior to analysis,
cloudwater samples were filtered at 0.45 µm to remove insects and particulate black carbon
residues. Calibration, CCV, MDL, and MS were performed using Ultra Scientific certified
aqueous Hg standard (10 µg/L); QCS and OPR were performed using NIST certified reference
material 1641D (Mercury in Water, 1.557 mg/kg). The method detection limit was 0.2 ng/L. All
CCV had recoveries within 87-115% (mean of 101%), all MDL had recoveries within 102-115%
(mean of 109%), all QCS had recoveries within 92-97% (mean of 94%), all OPR had recoveries
within 97-113% (mean of 98%), all MS had recoveries within 86-117% (mean of 100%), all
duplicates had RPD of 0.4-11% (mean of 6%), and all calibration blanks were below the
detection limit. Four of the six method blanks analyzed had THg concentrations below the
detection limit; the others had THg concentrations of 0.25 and 0.33 ng/L. In comparison, the
lowest THg concentration measured in a sample was 0.41 ng/L, while all other samples had THg
concentrations above 1.0 ng/L.

Samples were analyzed for MeHg via direct aqueous ethylation with sodium
tetraethylborate, purge and trap, and CVAFS (EPA Method 1630, Hammerschmidt and
Fitzgerald 2006) on a Tekran 2500 spectrometer. Calibration, CCV, MDL, and OPR were
performed using Frontier Geosciences certified laboratory MeHg standards. The method
detection limit was 0.02 ng/L. All CCV had recoveries of 86-115% (mean of 100%), all MDL
had recoveries of 87-100% (mean of 93%), all OPR had recoveries of 98-110% (mean of 102%),
and all calibration blanks were below the detection limit.

Water samples were analyzed for DOC via persulfate-ultraviolet oxidation (EPA Method
5310C) with a Teledyne Tekmar Apollo organic carbon analyzer and anions (SO$_4^{2-}$) via ion
chromatography (IC) with chemical suppression of eluent conductivity (EPA Method 4110B)
with a Dionex ion chromatograph. For DOC, all CCV had recoveries of 90-110% (mean of
99%), and all calibration blanks were below the detection limit. For IC, all CCV had recoveries
of 100-109% (mean of 107%), and all calibration blanks were below the detection limit.

**Flux Calculations**

Precipitation scaling factors were used to calculate open precipitation and throughfall
fluxes at each elevation based upon elevational scaling factors previously determined for
Whiteface Mountain (Miller et al. 1993), according to:

$$SF_P = 0.0746 \times (elev) + 51.718$$  \[[1]\]
where $SF_P$ is the precipitation scaling factor and $elev$ is the elevation of the plot in meters. Precipitation scaling factors were then multiplied by 2015 Hg concentrations and monthly precipitation volume from the NADP NTN to calculate monthly THg and MeHg fluxes. To calculate litterfall fluxes at each elevation, 2015 litterfall concentrations were multiplied by the average litterfall mass collected in 2009 and 2010 since 2015 litterfall was measured only for concentrations and not for fluxes.

Cloudwater THg and MeHg fluxes at each elevation were calculated using measured cloudwater Hg concentrations at the summit in an elevational cloudwater model (Miller et al. 1993). In this model, cloudwater THg and MeHg concentrations at the summit were assumed to represent cloudwater concentrations at other elevations, and the average cloudwater moisture flux employed for calculations in the model was estimated from the average of a ten-year record of annual cloudwater volumes. Scaling factors for each elevation were determined, according to:

$$SF_{CW} = 3 \times 10^{-20} \ (elev)^{6.9434}$$

where $SF_{CW}$ is the cloudwater moisture flux scaling factor and $elev$ is the elevation of the plot in meters. Cloudwater THg and MeHg concentrations were multiplied by the average cloudwater moisture flux and scaling factor to determine cloudwater THg and MeHg fluxes at each elevation. Total Hg and MeHg fluxes at each elevation were defined as the sum of throughfall, litterfall, and cloudwater inputs.

Organic (Oi/Oe and Oa horizons) soil Hg pools were calculated using the relationship between soil %C and bulk density reported in Huntington et al. (1989):

$$\ln(BD_i) = 0.263 - 0.147 \ln(%C_i) - 0.103(\ln%C_i)^2$$

where $BD_i$ is bulk density. Calculated bulk density values for each sample were then used to determine organic layer Hg pools, according to:
\[ \text{SP}_i = C_i \times BD_i \times T \]  

where \( \text{SP}_i \) is the organic soil Hg pool (mg/m\(^2\)), \( C_i \) is the Hg concentration (ng/g), and \( T \) is the horizon thickness (cm). To calculate the average soil pool at Whiteface Mountain, I used an average Oi/Oe horizon thickness of 3 cm for the deciduous and coniferous zones and 2 cm for the alpine zone and an average Oa horizon thickness of 7 cm for the deciduous and alpine zones and 4 cm for the alpine zone, based on field measurements. Average organic soil Hg pools were calculated as the sum of the average Oi/Oe and Oa horizon Hg pools.

**Statistical Analyses**

Statistical analyses were performed using SAS version 9.4 (SAS Institute). When necessary, data were log-transformed before applying statistical analyses to satisfy distributional assumptions. Ordinary least square and multivariate regression analyses across the elevational gradient were performed using a general linear model with PROC REG via step-wise regression. Influential datapoints determined using Cook’s D and outliers determined as values greater than 3 on the studentized residual plot were removed when performing regression analyses. All model residuals were tested for normality using the Shapiro-Wilk test, homogeneity of variance using the White test, and autocorrelation using the Durbin-Watson test. Three-way Analysis of Variance (ANOVA) factorial design analyses were performed with PROC GLM Type III sum of squares and Tukey’s post-hoc adjustment to compare soil concentrations in soil horizons (2 levels), across the growing season (3 levels), and among forest cover types (3 levels). Two-way ANOVA factorial design analyses were performed with PROC GLM Type III sum of squares and Tukey’s post-hoc adjustment to compare throughfall and open precipitation concentrations and fluxes across the growing season (5 levels) and among forest cover types (3 levels). One-
way ANOVA analyses were performed with PROC GLM Type III sum of squares and Tukey’s post-hoc adjustment to compare between throughfall and open precipitation concentrations (2 levels) and to compare cloudwater, litterfall, and soil Hg fluxes and pools by forest cover type (3 levels). Reported p-values reflect main effect comparisons within factors ($H_0 = $ all means within a factor are equal) at an alpha value of 0.05 and a marginal significance alpha value of 0.1. Comparisons within factors reflect simple effect differences within the factor using Tukey’s post-hoc adjustment at an alpha value of 0.05. Correlations among variables were performed using PROC CORR and Spearman Rank Correlation coefficients at an alpha value of 0.05. All concentrations below the detection limit were assigned a concentration of 0. Based upon my sampling design, sample sizes were as follows: n=216 for soils (n=72 per forest cover type, n=108 per horizon, n=72 per month), n=12 for litterfall (n=4 per forest cover type), n=57 for throughfall (n=19 per forest cover type, n=12 for August and September, n=11 for all other months), n=15 for precipitation (n=3 per month), and n=22 for cloudwater. Due to limited sample quantities, not all samples were analyzed for all chemical species; sample sizes for statistical analyses were adjusted accordingly, with ANOVA comparisons made using Type III analyses accounting for the unbalanced design. Data are presented as the arithmetic mean ± 1 standard error.

Results

Mercury in Wet Deposition: Throughfall, Precipitation, and Cloudwater

Average THg concentration in open precipitation was $8.1 \pm 1.9$ ng/L, MeHg concentration was $0.047 \pm 0.012$ ng/L, and percent Hg as MeHg (%MeHg) was $0.88 \pm 0.28\%$ (Figure 1). Average throughfall THg concentration was $12.4 \pm 0.9$ ng/L, MeHg concentration
was 0.087 ± 0.019 ng/L, and %MeHg was 0.55 ± 0.085%. Throughfall concentrations were higher than open precipitation for THg and marginally higher for %MeHg (p<0.0001, p=0.074, respectively). However, there was no difference in MeHg concentrations between throughfall and open precipitation (p=0.48).

Throughfall concentrations on Whiteface varied seasonally (p=0.0001 for THg, p=0.011 for MeHg, p=0.095 for %MeHg). Highest concentrations of THg were found in July (15.2 ± 2.3 ng/L) and August (13.9 ± 1.9 ng/L) compared to May (7.7 ± 1.5 ng/L), June (10.4 ± 2.3 ng/L), and September (9.4 ± 1.7 ng/L). Marginally higher concentrations of MeHg and %MeHg occurred in July (0.13 ± 0.04 ng/L, 0.98 ± 0.30%) compared to the other months (May-September mean range of 0.026 to 0.077 ng/L, mean range of 0.21 to 0.84%, respectively).

Throughfall THg concentration also varied by forest cover type (p<0.0001), with the highest values found in the coniferous zone (15.7 ± 1.8 ng/L), followed by the alpine zone (13.3 ± 1.1 ng/L), with the lowest concentration found in the deciduous zone (8.3 ± 1.1 ng/L; Figure 1). There was no difference by forest cover type (p=0.3052) for throughfall concentrations of MeHg (0.082 ± 0.028 ng/L in the alpine zone, 0.086 ± 0.022 ng/L in the coniferous zone, and 0.092 ± 0.046 ng/L in the deciduous zone) and %MeHg (0.64 ± 0.19%, 0.67 ± 0.15%, 0.36 ± 0.10%, respectively).

Cloudwater concentrations were measured at the summit of Whiteface. The average THg cloudwater concentration was 4.3 ± 0.5 ng/L, with a range of 1.8 ng/L to 9.9 ng/L. The average MeHg cloudwater concentration was 0.023 ± 0.003 ng/L, with a range of 0.013 ng/L to 0.073 ng/L.

Sulfate and DOC concentrations in throughfall also exhibited marginal spatial patterns (p=0.0895, p=0.0597, respectively). Average throughfall SO₄²⁻ concentration was 9.2 ± 1.1
mg/L across Whiteface. Marginally higher SO$_4^{2-}$ concentrations were found in the alpine zone (12 ± 2.5 mg/L) compared to the coniferous (8.1 ± 1.6 mg/L) and deciduous zones (7.3 ± 0.94 mg/L). Average summer SO$_4^{2-}$ throughfall flux was 108 ± 9.8 kg/m$^2$. Sulfate flux also differed by forest cover type (p=0.0268), with highest summer SO$_4^{2-}$ flux found in the coniferous zone (138 ± 20 kg/m$^2$) compared to the deciduous (96 ± 11 kg/m$^2$) and alpine zones (88 ± 17 kg/m$^2$).

Average throughfall DOC concentration was 765 ± 97 mg/L across Whiteface. Marginally higher DOC concentrations were found in the alpine (1050 ± 230 mg/L) and coniferous zones (960 ± 154 mg/L) compared to the deciduous zone (630 ± 150).

**Mercury in Litterfall**

Mercury concentrations in litterfall varied by forest cover type for THg concentrations (p<0.0001) and varied marginally for MeHg concentrations and %MeHg (p=0.0832, p=0.0924, respectively; Figure 2). For THg, concentrations were highest in the alpine zone (67 ± 3.9 ng/g), followed by the coniferous zone (48 ± 3.9 ng/g), and lowest in the deciduous zone (31 ± 1.4 ng/g). For MeHg, concentrations were highest in the coniferous zone (0.052 ± 0.0060 ng/g), followed by the alpine zone (0.039 ± 0.0049 ng/g), and lowest in the deciduous zone (0.031 ± 0.0071 ng/g). For %MeHg, values were highest in the coniferous (0.10 ± 0.0063%) and deciduous zones (0.10 ± 0.021%), and lowest in the alpine zone (0.061 ± 0.0081%). Additionally, THg concentration and %MeHg were correlated with elevation (p<0.0001, p=0.0749, respectively).
Mercury in Soil

Soil concentrations of THg and MeHg showed spatial variations on Whiteface (p<0.0001 for both THg and MeHg; Figure 3). The pattern by forest cover type differed for THg and MeHg for the combined organic horizons. Total Hg concentrations were greatest in the alpine (337 ± 16 ng/g) and coniferous zones (298 ± 15 ng/g) compared to the deciduous zone (156 ± 8 ng/g). Methylmercury concentrations were highest in the coniferous zone (0.39 ± 0.068 ng/g) compared to the alpine (0.28 ± 0.042 ng/g) and deciduous zones (0.17 ± 0.022 ng/g; Figure 3). Soil MeHg concentrations were positively correlated with the ratio of THg/C (p<0.0001, r²=0.3252), as well as the ratio of THg/N (p<0.0001, r²=0.3048). Percent MeHg was marginally negatively correlated with S concentrations in soils (p=0.0809, r²=0.1294) and marginally positively correlated with the ratio of THg/C (p=0.0925, r²=0.1184).

Variation between organic soil horizons (Oi/Oe, Oa) showed similar patterns for THg, MeHg, and %MeHg, with higher values found in the Oa horizon (p<0.0001 for THg, p=0.023 for MeHg, p=0.017 for %MeHg; Supplementary Figure 2). The Oa horizon also displayed higher THg/C (p<0.0001) and THg/N ratios (p<0.0001) than the Oi/Oe horizon. The Oa horizon had a mean THg concentration of 313 ± 14 ng/g compared to 209 ± 8 ng/g for the Oi/Oe horizon, mean MeHg concentration of 0.30 ± 0.029 ng/g compared to 0.18 ± 0.026 ng/g for the Oi/Oe horizon, and mean %MeHg value of 0.12 ± 0.015% compared to 0.07 ± 0.010% for the Oi/Oe horizon. On average, the Oa horizon contained 1.5 times greater THg concentration, 1.7 times greater MeHg concentration, and 1.2 times greater %MeHg than the Oi/Oe horizon.

Several elevational patterns were evident for soil Hg concentrations across Whiteface. Soil THg concentrations increased with elevation (p<0.0001, r²=0.39 for Oi/Oe horizon; p<0.0001, r²=0.48 for Oa horizon; p<0.0001, r²=0.38 for combined model containing Oi/Oe and
Oa horizons), while %MeHg values decreased with elevation (p=0.0002, $r^2=0.17$ for Oa horizon; p=0.081, $r^2=0.060$ for Oi/Oe horizon; p<0.0001, $r^2=0.12$ for combined model; Figure 4). No elevational patterns were found for MeHg concentrations (p=0.1554), likely due to peak values occurring in the coniferous zone.

Soil THg, MeHg, and %MeHg also displayed seasonal variations on Whiteface (p=0.074, p<0.0001, p=0.019, respectively), with July displaying the highest values (Figure 5). For THg, July concentrations averaged 376 ± 18 ng/g for the alpine zone, 309 ± 27 ng/g for the coniferous zone, and 153 ± 12 ng/g for the deciduous zone. Lower THg concentrations were found in the alpine zone for June (306 ± 24 ng/g, 307 ± 28 ng/g, 165 ± 13 ng/g, respectively) and in the alpine and coniferous zones for September (310 ± 31 ng/g, 284 ± 21 ng/g, 150 ± 14 ng/g, respectively). For MeHg, July concentrations averaged 0.35 ± 0.080 ng/g for the alpine zone, 0.65 ± 0.17 ng/g for the coniferous zone, and 0.18 ± 0.039 ng/g for the deciduous zone. Lower MeHg concentrations were found for the alpine and coniferous zones in June (0.25 ± 0.069 ng/g, 0.26 ± 0.014 ng/g, 0.16 ± 0.043 ng/g, respectively) and September (0.18 ± 0.029 ng/g, 0.20 ± 0.047 ng/g, 0.16 ± 0.039 ng/g, respectively). July concentrations of %MeHg averaged 0.10 ± 0.027% in the alpine zone, 0.15 ± 0.031% in the coniferous zone, and 0.14 ± 0.039% in the deciduous zone. Lower %MeHg values were found in June (0.08 ± 0.022%, 0.07 ± 0.012%, 0.10 ± 0.033%, respectively) and September (0.05 ± 0.012%, 0.06 ± 0.012%, and 0.11 ± 0.033%, respectively). Soil C/N June ratios were marginally higher than July and September (p=0.055).

The average soil C/N ratio at Whiteface was 21 ± 0.3 g C/g N. Ratios of C/N varied by forest cover type (p<0.0001), with highest values in the coniferous zone (23 ± 0.4 g C/g N) compared to the deciduous (20 ± 0.5 g C/g N) and alpine zones (21 ± 0.4 g C/g N, Figure 3). The ratio of THg/C increased with soil horizon. In the alpine zone, average C/N ratios decreased
from 42 ± 2 g C/g N in the litter to 21 ± 3 g C/g N in the Oi/Oe and Oa horizons, representing a 49% decrease. In the coniferous zone, average C/N ratios decreased from 46 ± 8 g C/g N to 22 ± 3 g C/g N, respectively, representing a 46% decrease. In the deciduous zone, average C/N ratios decreased from 50 ± 17 g C/g N to 20 ± 4 g C/g N, respectively, representing a 39% decrease.

The average soil S concentration was 1.9 ± 0.05 mg S/g. Concentrations of S also varied by forest cover type (p=0.0324), with highest values in the alpine (1.9 ± 0.09 mg S/g) and coniferous zones (2.0 ± 0.09 mg S/g) compared to the deciduous zone (1.6 ± 0.09 mg S/g). Additionally, THg/C and THg/N soil ratios displayed spatial variation (p<0.0001 for both; Figure 4), with highest Hg/C ratios in the coniferous and alpine zones compared to the deciduous zone and THg/N ratios highest in the coniferous zone compared to the deciduous and alpine zones. The THg/C ratios increased with elevation (p<0.0001, r^2=0.11), as did THg/N ratios (p<0.0001, r^2=0.17) and C/N ratios (p=0.0032, r^2=0.04). The ratio of THg/C increased with soil horizon. In the alpine zone, average THg/C ratios increased from 1.25 ± 0.07 µg/g in the litter to 6.0 ± 0.4 µg/g in the Oi/Oe horizon to 11.0 ± 0.5 µg/g in the Oa horizons, representing a 880% increase. In the coniferous zone, average THg/C ratios increased from 0.88 ± 0.08 µg/g to 4.8 ± 0.3 µg/g to 11.0 ± 0.5 µg/g, respectively, representing a 1300% increase. In the deciduous zone, average THg/C ratios increased from 0.64 ± 0.03 µg/g to 4.5 ± 0.7 µg/g to 7.1 ± 0.5 µg/g, respectively, representing a 1100% increase.

Using multivariate linear regression, soil MeHg concentrations on Whiteface were best predicted by S concentrations; though this relationship was marginally significant (p=0.064), it only explained 3.2% of the variability in observed soil MeHg concentrations. Soil THg concentrations were best predicted by a model that included elevation, C, N, and S
concentrations (p<0.0001, r²=0.45). Soil %MeHg values were best predicted by a model that included THg and C concentrations (p<0.0001, r²=0.30).

Terrestrial Mercury Fluxes and Organic Soil Pools

Average monthly summer open precipitation Hg flux for all forest cover types was 7.3 ± 0.3 µg/m² for THg and 38 ± 12 ng/m² for MeHg. Methyl Hg open precipitation flux had much greater variation than THg flux. Average monthly summer open precipitation THg and MeHg fluxes did not vary by forest cover type (p=0.2071, p=0.1685, respectively; Figure 6). Conversely, average THg open precipitation flux for all forest cover types showed marginal spatial variation across the growing season (p=0.0649), with the highest fluxes in June (4.4 ± 2.6 µg/m²) compared to the other months (range of 0.44 to 0.98 µg/m²). Average MeHg open precipitation flux for all forest cover types did not vary by month (p=0.3514).

Average summer throughfall Hg fluxes for all forest cover types were highly variable, with fluxes of 8.5 ± 0.7 µg/m² for THg and 50 ± 11 ng/m² for MeHg. Methyl Hg throughfall flux had much greater variation than THg flux. Average summer throughfall THg fluxes varied by forest cover type and month (p<0.0001 for both), with highest fluxes in the alpine (10 ± 0.7 µg/m²) and coniferous zones (11 ± 1 µg/m²), compared to the deciduous zone (4.5 ± 0.7 µg/m²; Figure 6). Total Hg throughfall flux for all forest cover types was highest in June and July (2.0 ± 0.3 µg/m² and 2.5 ± 0.3 µg/m², respectively) compared to the other months (range of 1.1 to 1.6 µg/m²). Average summer throughfall MeHg flux did not vary by forest cover type (p=0.3801) or by month (p=0.1829).

Average modeled cloudwater THg flux was 4.3 ± 0.9 µg/m². Modeled cloudwater THg flux increased with elevation (p<0.0001) and varied by forest cover type (p<0.0001; Figure 6).
The highest modeled cloudwater THg flux was found in the alpine zone (9.7 ± 0.3 µg/m²), followed by the coniferous zone (3.1 ± 0.4 µg/m²), and lowest in the deciduous zone (0.07 ± 0.02 µg/m²). Average modeled cloudwater MeHg flux was 23 ± 5.0 ng/m². Modeled cloudwater MeHg flux increased with elevation (p<0.0001) and varied by forest cover type (p<0.0001; Figure 6). The highest modeled cloudwater MeHg flux was found in the alpine zone (52 ± 2 ng/m²), followed by the coniferous zone (17 ± 2 ng/m²), and lowest in the deciduous zone (0.38 ± 0.09 ng/m²).

Average litterfall flux was 7.0 ± 0.8 µg/m² THg and 6.0 ± 1.3 ng/m² MeHg. Total Hg litterfall fluxes did not display any significant trends by forest cover type (p=0.1730) or elevation (p=0.1400), whereas MeHg litterfall flux varied among forest cover types (p=0.0363; Figure 6). The highest litterfall MeHg flux was found in the deciduous zone (8.1 ± 2.1 ng/m²), followed by the coniferous zone (7.3 ± 1.1 ng/m²), and was lowest in the alpine zone (2.9 ± 0.5 ng/m²). Consequently, MeHg litterfall fluxes decreased with elevation (p=0.0217 and r²=0.2265).

Across the mountain, average summer total flux (litterfall + throughfall + cloudwater) was 18 ± 3 µg/m² THg was 80 ± 11 ng/m² MeHg. Relative contribution of litterfall inputs was 35% for THg and 7% for MeHg, relative contribution of throughfall inputs was 43% for THg and 64% for MeHg, and relative contribution of cloudwater inputs was 22% for THg and 29% for MeHg.

Across the entire mountain, average THg organic soil pools on Whiteface were 507 ± 18 mg/m², and average MeHg organic soil pools on Whiteface were 0.64 ± 0.10 mg/m². Average THg and MeHg organic soil pools across the mountain varied by soil horizon (p<0.0001 for both) and forest cover type (p<0.0001, p=0.0341, respectively; Figure 6). Average Hg organic soil pools were greater in the Oa horizon (410 ± 25 mg/m², 0.54 ± 0.15 mg/m², respectively) compared to the Oi/Oe horizon (97 ± 2 mg/m², 0.10 ± 0.03 mg/m², respectively). Total Hg
organic soil pools were greatest in the coniferous zone (700 ± 40 mg/m$^2$) compared to the deciduous (410 ± 20 mg/m$^2$) and alpine zones (410 ± 20 mg/m$^2$). Methyl Hg organic soil pools were greatest in the coniferous zone (0.95 ± 0.22 mg/m$^2$) compared to the alpine (0.36 ± 0.063 mg/m$^2$) and deciduous zones (0.62 ± 0.11 mg/m$^2$). Methyl Hg organic soil pools also differed by season, with the highest values found in July (p<0.0001).

Discussion

*Overall Soil Hg Patterns*

Several distinct patterns of soil Hg concentrations were found with elevation and forest cover type. As reported by Blackwell and Driscoll (2015), soil THg concentrations increased with elevation from the deciduous to alpine zone along Whiteface Mountain, which is comparable to other montane studies of Hg (Fisher and Wolfe 2012, Stankwitz et al. 2012, Townsend et al. 2014) and other contaminants introduced to forested systems by atmospheric deposition (Lovett and Kinsman 1990, Miller et al. 1993). In contrast, soil MeHg concentrations did not exhibit a linear pattern with elevation, as values were highest in the coniferous zone. This finding is consistent with other forest studies that have found higher MeHg concentrations in coniferous soils compared to deciduous soils (Witt et al. 2009), though no studies that I am aware of have compared MeHg concentrations along an elevational gradient. I found that soil %MeHg patterns were inconsistent with MeHg concentration patterns; %MeHg decreased along the elevational gradient.

Both THg and MeHg concentrations in soils were higher in the Oa horizon compared to the Oi/Oe horizon. This is consistent with some studies in both natural and manipulated forested ecosystems (Obrist et al. 2011, 2012), although other studies have shown THg and MeHg
concentrations to be highest in the Oi/Oe horizon (Demers et al. 2007, Hojdová et al. 2007). Higher concentrations of MeHg in the Oa horizon likely reflect vertical percolation associated with precipitation-derived THg and MeHg (Jiskra et al. 2014), as well as the greater degree of organic matter decomposition compared to the Oi/Oe horizon; as organic matter decomposes, associated Hg is available for microbial conversion to MeHg (Obrist et al. 2011). Moreover, the Oa horizon might be more prone to microsites of reducing conditions, which would facilitate the production of MeHg.

Atmospheric Deposition as a Driver of MeHg Concentrations in Soils

Direct inputs of MeHg concentrations from atmospheric deposition can influence MeHg concentrations and %MeHg within soils (Hojdová et al. 2007, Witt et al. 2009). Though atmospherically deposited Hg can be reemitted (evaded) or transported (i.e., through surface runoff), the majority of Hg is believed to be sequestered within soils (Driscoll et al. 2007). Atmospheric deposition has been shown to be an important source of THg to terrestrial systems (Grigal 2002), but much less is known about MeHg.

At Whiteface, spatial patterns in soil MeHg concentrations do not appear to be driven by MeHg in wet deposition. Methyl Hg in precipitation can originate from direct emissions and transport of MeHg, abiotic atmospheric oxidative processes that convert RGM to MeHg, and/or soil evasion (Conaway et al. 2010, Fu et al. 2010). However, these processes are not thought to be quantitatively significant, and thus the concentration of MeHg in atmospheric deposition is expected to be small (Bloom and Watras 1989). Accordingly, %MeHg values in wet deposition were <1% at Whiteface, similar to other montane Hg studies (Conaway et al. 2010, Fu et al. 2010). The lack of an elevational or forest cover type pattern for precipitation MeHg
concentrations suggests that wet MeHg concentrations are consistent across the mountain, though wet deposition MeHg flux is higher in the coniferous and alpine zones due to greater precipitation quantity. Interestingly, this lack of pattern in MeHg concentrations is inconsistent with the elevational pattern of THg concentrations in precipitation, which increases with elevation. Other studies have suggested that MeHg concentrations in wet deposition are independent of THg and are instead dependent upon atmospheric methylation processes and concentration of atmospheric methylating agents, both of which are extremely limited (Hammerschmidt et al. 2007, Lee and Iverfeldt 1991).

Atmospheric deposition of Hg on mountains also occurs via cloudwater. Due to orographic effects, cloudwater contributions of Hg can result in higher Hg deposition at higher elevations (Fisher and Wolfe 2012). Some studies have found that THg deposition from clouds at high elevations can be twice that of wet deposition (Dore et al. 1999, Lawson et al. 2003). The impact of cloudwater on Hg concentrations is particularly important in the coniferous and alpine zones of mountains; at these higher elevations, the base of the cloud, which contains the highest solute concentration, can contribute high levels of deposition via contact with leaf surfaces (Lovett and Kinsman 1990). At Whiteface, the summit has been estimated to be covered by cloud 40-45% of the year, with significant cloud coverage also found in the coniferous zone (Mohnen 1988). Consequently, previous studies of cloudwater contribution to THg deposition at Whiteface have found cloudwater to be the most important input of Hg to the alpine zone and a comparable input to throughfall Hg deposition in the coniferous zone (Blackwell and Driscoll 2015). In this study, I find that similar cloudwater depositional patterns are apparent for MeHg, with significant inputs of cloudwater MeHg flux occurring in the alpine
and coniferous zones. These results suggest the importance of characterizing cloudwater Hg when evaluating depositional and storage pathways in montane ecosystems.

Another potential source of atmospheric MeHg input to soils is dry deposition, which is manifested as throughfall. Reactive gaseous Hg and PHg can adsorb to the leaf through dry deposition; Hg is then leached by precipitation as throughfall (Lindberg et al. 1995). Throughfall inputs of THg have been shown to be 1.5 to 1.8 times that of open precipitation due to the wash-off of Hg from leaves (Choi et al. 2008). Additionally, coniferous trees are more efficient at filtering atmospheric Hg particles than deciduous trees due to greater surface roughness and a canopy structure that decreases air flow and thereby enhances particle adsorption (Johnson et al. 2007, Kolka et al. 1999, Rea et al. 2002, Witt et al. 2009). As a result, THg inputs via throughfall are typically the predominant source of THg to coniferous forests (Demers et al. 2007), which is consistent with my results and previous results at Whiteface (Blackwell and Driscoll 2015). Throughfall inputs of THg to alpine zones, however, are reduced due to lower total leaf area associated with sparse tree density and lower canopy height. Though differences in throughfall THg concentrations for coniferous and deciduous forests have been shown, MeHg concentration patterns exhibit mixed results (Graydon et al. 2008). The source of MeHg in throughfall could be either dry deposition of atmospheric MeHg or abiotic methylation of RGM to MeHg on foliar surfaces (Graydon et al. 2008). I did not find any difference in throughfall MeHg concentrations among forest cover types or across the elevational gradient at Whiteface. Additionally, throughfall MeHg concentrations at Whiteface were not different than open precipitation MeHg concentrations, suggesting minimal MeHg adsorption onto leaf surfaces or foliar surface production. Inconsistent results have been reported in the literature, with some noting similar findings of no difference between MeHg in throughfall and open precipitation.
(Johnson et al. 2007, Lee and Iverfeldt 1991, Munthe et al. 1995), and others noting higher MeHg concentrations in throughfall (Witt et al. 2009). Thus, throughfall does not appear to drive forest cover type patterns of MeHg concentration at Whiteface.

The final source of atmospheric MeHg inputs to terrestrial systems is litterfall, which I found to exhibit an identical spatial pattern to that observed in soil MeHg concentrations. Other studies have also found litterfall to be a major input of both THg and MeHg to forested ecosystems, with 30-70% of THg in forests originating from litterfall (Demers et al. 2007, Graydon et al. 2008, Hall and St. Louis 2004, Munthe et al. 1995, Rea et al. 1996, 2002). Total Hg in litterfall is derived from new atmospheric inputs of GEM through direct uptake by stomata (Rea et al. 2000, 2002; Risch et al. 2012, Rutter et al. 2011) as trees scavenge atmospheric Hg (Rea et al. 1996). Coniferous trees are particularly effective at scavenging Hg compared to deciduous trees because of the multi-year lifespan of needles (Fisher and Wolfe 2012, Mowat et al. 2011), which is consistent with my finding of greater THg concentrations in coniferous litterfall compared to deciduous litterfall at Whiteface. Since Hg accumulates in foliage throughout the growing season, litterfall is an important source of THg inputs to forests (Bushey et al. 2008). Though atmospheric inputs are a small fraction of the forest floor THg pool, these new inputs of THg are likely more biologically available than older THg stored within the soil and can therefore be readily methylated by SRB (Grigal 2003, Hintelmann et al. 2002). Additionally, I found that MeHg concentrations in litterfall were highest in the coniferous zone deriving either from uptake of MeHg by leaves through the stomata or the abiotic methylation of mercury on the foliar surface. In contrast, MeHg litterfall flux was highest in the deciduous zone, mirroring the trend of %MeHg in soils.
Though elevational patterns are apparent in MeHg deposition concentrations (litterfall) and fluxes (throughfall, open precipitation, cloudwater, and litterfall), the magnitude of these inputs are much smaller than the MeHg soil pool (Figure 6). Thus, it is likely that external inputs of MeHg are not the main driver of MeHg concentrations in soils, though external inputs of THg are likely important to the microbial formation of MeHg in soils.

*Internal Drivers of MeHg Formation in Soils*

I propose that soil microbial methylation of RGM to MeHg by SRB and IRB is the primary source of MeHg in soils. The activity of SRB in terrestrial systems can be driven by organic C concentration, $\text{SO}_4^{2-}$ supply, environmental conditions (i.e., redox conditions, temperature), and THg concentration and bioavailable THg (Gilmour et al. 1992, Warner et al. 2005, Watras et al. 2005).

The activity of SRB is dependent upon C and $\text{SO}_4^{2-}$ in soils for the metabolic process that results in Hg methylation (Grigal 2003, Shanley and Bishop 2012). Litterfall inputs and the organic horizon in soils provide the source of organic C for bacteria (Amirbahman and Fernandez 2012, Grigal 2003), with higher elevation forests containing a greater organic C pool than lower elevation forests (Bolstad and Vose 2001). However, previous research has found that there is no effect of C concentration on MeHg concentrations (Hojdová et al. 2007). At the same time, several studies have noted the importance of S concentrations in soils for controlling Hg methylation pathways (Shanley and Bishop 2012, Steffan et al. 1988). In previous studies, S inputs via $\text{SO}_4^{2-}$ in precipitation and throughfall have been shown to increase across an elevational gradient in montane systems (Lovett and Kinsman 1990, Miller et al. 1993). My results support this finding, with highest $\text{SO}_4^{2-}$ concentrations in wet deposition occurring in the
alpine zone and highest SO$_4^{2-}$ fluxes occurring in the coniferous zone. Accordingly, at Whiteface, the S concentration in soils was greatest in the coniferous and alpine zones. This may suggest that increased SO$_4^{2-}$ deposition at higher elevations is an important internal driver of SRB activity and thus the production of MeHg in these soils. In fact, I found S concentration in soils to be the most important factor for predicting MeHg concentrations across Whiteface, albeit soil S concentrations explained only a small percent of the variability in soil MeHg concentrations possibly due to high heterogeneity in soil MeHg, complexation of Hg with S ions in soils, and relative concentration of SO$_4^{2-}$-S compared to the reduced form (S$^2$-). Microbial utilization of SO$_4^{2-}$ is thus likely an important internal driver of the activity of SRB.

Increased anoxic conditions (associated with soil saturation) and increased temperature enhance SRB activity (Amirbahman and Fernandez 2012, Grigal 2003, Morel et al. 1998, Ullrich et al. 2001). Such dependence of SRB on environmental conditions was evident from seasonal patterns at Whiteface, with highest MeHg soil concentrations found in July when temperatures were warmer (Shanley and Bishop 2012) and increased precipitation (http://www.adirondacklakessurvey.org/wfc.shtml) contributed to wetter soils (Grigal 2003). Spatially, SRB dependence on temperature and reducing conditions was also apparent. Warmer temperatures at lower elevations likely explain the higher %MeHg in the deciduous zone and lower MeHg concentrations in the alpine zone compared to the coniferous zone. Seasonality in MeHg soil concentrations also suggests the importance of demethylation and soil evasion processes. During the early summer months from June to July, soil MeHg concentrations and soil pools increase, as SRB methylation of Hg increases. Conversely, during the late summer months from July to September, soil MeHg concentrations and soil pools decrease, as
demethylation processes become prevalent. Thus, it appears that the soil MeHg pool at Whiteface has high seasonal variability controlled by microbial activity.

Total Hg bioavailability, which is directly related to organic matter (OM) degradation, is also important to SRB activity. High rates of OM decomposition, manifested as lower C/N ratios (Obrist et al. 2011), can lead to higher MeHg concentrations in soils. I found the deciduous zone to have the lowest C/N ratios and greatest percent changes in C/N ratios between the litter and organic soil layers compared to the coniferous and alpine zones. This pattern suggests increased methylation in the deciduous zone, as shown by the higher %MeHg in this zone. Conversely, soil MeHg concentrations and soil pools were greater in the coniferous zone, which may be explained by increased demethylation and evasion of MeHg in the deciduous zone due to greater light penetration and warmer temperatures. Higher THg/C ratios in the coniferous zone as well as greater percent increases in THg/C ratios between the litter and organic layers in the coniferous zone compared to the deciduous zone support this hypothesis. Other studies in northeastern forests have also found increased soil Hg evasion in deciduous forests compared to coniferous forests (Blackwell et al. 2014, Choi and Holsen 2009), while elevational temperature gradients further increase soil evasion in the deciduous zone. Additionally, while SRB activity is likely elevated in the deciduous zone, lower THg soil concentrations and deposition in the deciduous zone could also contribute to the lower soil MeHg concentrations and soil MeHg pool found in this zone. Since new Hg derived from atmospheric sources is likely more readily methylated and thus more bioavailable than old Hg stored in the soil (Grigal 2003, Hintelmann et al. 2002), depositional THg fluxes may be important drivers of SRB activity and could contribute to the spatial pattern of MeHg observed at Whiteface.
Due to patterns in soil S concentration, C/N ratio, THg/C ratio, and temperature, it is likely that SRB activity drive the elevational and seasonal patterns in soil MeHg concentrations and %MeHg at Whiteface and the observed trend of increased soil MeHg concentrations and soil pools in the coniferous zone and decreasing soil %MeHg with elevation.

Implications of Soil MeHg Patterns

This assessment of MeHg patterns in deposition and soils across a montane environment may allow for a greater understanding of Hg cycling in terrestrial ecosystems. The finding of decreasing %MeHg with elevation might be interpreted to suggest that Hg concentrations in biota should be highest in the deciduous zone. However, in an assessment of Bicknell’s thrush (Catharus bicknelli), Swainson thrush (Catharus ustulatus), and Hermit thrush (Catharus guttatus) (obligate insectivores) across the deciduous and coniferous zones of Whiteface, Hg blood concentrations increased with elevation, with coniferous zone concentrations nearly twice that of the deciduous zone (Driscoll and Sauer 2015). Similar findings have been found at other mountains for thrushes and salamanders (Townsend et al. 2014). Thus, songbird Hg concentrations appear to follow patterns in absolute soil MeHg concentration, not relative soil MeHg concentrations (%MeHg), and absolute soil MeHg concentrations may be a better indicator of wildlife exposure to MeHg. Moreover, previous studies have reported correlations between regional Hg flux patterns and Bicknell’s thrush blood Hg and have accordingly suggested the bioavailability of terrestrial MeHg (Rimmer et al. 2005). The relationship between soil MeHg concentrations and songbird blood concentrations of Hg at Whiteface corroborates these speculations. Since birds can display physiological, behavioral, and reproductive effects from high Hg concentrations and are bioindicators of MeHg bioavailability for many species, it
is important to understand and reduce exposure of MeHg by these species by understanding external and internal drivers of MeHg in terrestrial environments (Evers et al. 2007, Rimmer et al. 2005).

At Whiteface Mountain, a montane forested environment, MeHg concentrations appear to be driven predominantly by internal processing of Hg by SRB. With Hg loading 2-5x higher in montane northeastern forests such as the Adirondacks compared to lower elevations and other regions (Miller et al. 2005, Rimmer et al. 2005), this study provides an improved understanding of Hg drivers in high elevation biological Hg hotspots. In addition to elevated Hg deposition, alpine wildlife are likely highly susceptible to the effects of climate change. Regulations such as the proposed Mercury and Air Toxics Standard (MATS) that decrease MeHg concentrations to montane ecosystems could lead to reductions in bird blood Hg concentration and reduce stress to vulnerable populations.
Figures

Figure 1: Map of Whiteface Mountain in the Adirondack region of New York State. Alpine (n=4), coniferous (n=4), deciduous (n=4), and open plot zones (n=3) are delineated across the eastern slope of Whiteface Mountain. Five plots were established within each forest cover type: four sites were established under canopy cover (n=12) and one in an open area (n=3) for each forest cover type.
Figure 2: Concentrations of total mercury, methylmercury, and percent mercury as methylmercury in wet deposition (throughfall and open precipitation) across different forest cover types at Whiteface Mountain. Box-and-whisker plots show median values, Q1, and Q3 within the boxes (n=19 for throughfall at each forest cover type, n=5 for open precipitation at each forest cover type). Only outliers within the given bounds are shown. Total mercury concentrations in throughfall were highest in the coniferous zone, followed by the alpine zone, and lowest in the deciduous zone. Total mercury concentrations were also greater in throughfall compared to open precipitation. No patterns were noted by forest cover type for methylmercury concentrations or percent mercury as methylmercury. There was no difference between open precipitation and throughfall for methylmercury concentrations or percent mercury as methylmercury.

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Figure 3: Concentrations of litterfall total mercury, methylmercury, and percent mercury as methylmercury across different forest cover types at Whiteface Mountain. Barplots show mean values, and error bars denote standard error (n=4 for each forest cover type). Reported p-values represent differences between all levels (H₀ = means for all forest cover types are equal). Letters denote significant differences using Tukey’s post-hoc adjustment at an alpha level of 0.05. Total mercury concentration was highest in the alpine zone. Methylmercury concentrations and percent mercury as methylmercury were highest in the coniferous zone.
Figure 4: Soil mercury and ancillary characteristics across different forest cover types at Whiteface Mountain. Barplots show mean values, and error bars denote standard errors (n=72 for each forest cover type). Reported p-values represent differences between all levels (H₀ = means for all forest cover types are equal). Letters denote significant differences using Tukey’s *post-hoc* adjustment at an alpha level of 0.05.
Figure 5: Concentrations of total mercury, methylmercury, and percent mercury as methylmercury in soil Oi/Oe and Oa horizons at Whiteface Mountain using composite data for all sampling dates and plots. Box-and-whisker plots show median values, Q1, and Q3 within the boxes (n=108 for each soil horizon). Only outliers within the given bounds are shown. Letters denote significant differences at an alpha level of 0.05. The Oa horizon contained higher total mercury, methylmercury, and percent mercury as methylmercury than the Oi/Oe horizon.
Figure 6: Percent mercury as methylmercury in soils across the growing season and soil horizons at Whiteface Mountain (n=36 for each soil horizon during each month). All concentrations shown as 0 occurred below the detection limit (BDL). Vertical dashed lines represent the border between forest cover types. Percent mercury as methylmercury decreased with elevation (p<0.0001, r²=0.12 for combined model of Oi/Oe and Oa horizons).
Figure 7: Concentrations of total mercury, methylmercury, and percent mercury as methylmercury in soils across the growing season at different forest cover types at Whiteface Mountain. Box-and-whisker plots show median values, Q1, and Q3 within the boxes (n=24 for each forest cover type in each month). Only outliers within the given bounds are shown. Total mercury concentrations were highest in the alpine zone. Methylmercury concentrations were highest in the coniferous zone and in the month of July. Percent mercury as methylmercury was highest in July.
Figure 8: Comparison of growing season (May-September) A) total mercury and B) methylmercury fluxes in different forest cover types at Whiteface Mountain. Values denote mean and standard error. Values are compared at an alpha level of 0.1. Throughfall total mercury fluxes were greatest in the coniferous and alpine zones. Precipitation total mercury fluxes were greatest in the alpine zone. Litterfall total mercury fluxes were greatest in the deciduous and coniferous zones. The organic soil total mercury pool was highest in the coniferous zone. For methylmercury, precipitation and throughfall methylmercury mercury
fluxes were not significantly different by forest cover type. Litterfall methylmercury flux was highest in the deciduous zone and lowest in the alpine zone. Cloudwater methylmercury flux was highest in the alpine zone and lowest in the deciduous zone. The organic soil methylmercury pool was highest in the coniferous zone and lowest in the alpine zone.
References


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


EDUCATION

College of Civil and Environmental Engineering, Syracuse University – Syracuse, NY
2016  M.S., Environmental Engineering Science
     Thesis: *Elevational and Seasonal Patterns in Methylmercury Production Across the Montane Landscape of Whiteface Mountain in the Adirondack Region of New York*  
     Advisor: Charles T. Driscoll

Colgate University – Hamilton, NY
2011  B.A. Biochemistry, Minor: Environmental Studies, *Magna Cum Laude*  
     Thesis: *The uptake of pyrene molecules onto NaCl and NaNO₃ aerosol particles*  
     Advisor: Ephraim Woods, III

HONORS, AWARDS, FELLOWSHIPS, SCHOLARSHIPS

2015-2020  *Graduate Research Fellowship* – National Science Foundation

2016  *Exploration Fund Grant: Mamont Scholar* – Explorer’s Club

2016  *Student Travel Award* – Northeast Geologic Society of America

2015-2016  *EMPOWER National Research Traineeship* – Syracuse University

2015-2016  *Selected Professions Fellowship* – American Association of University Women

2015  *Richard A. Herbert Memorial Scholarship* – American Water Resources Association

2015  *Nunan Graduate Student Travel Grant* – Syracuse University

2014-2016  *Syracuse University Graduate Fellowship* – Syracuse University

2011  *Honors in Biochemistry* – Colgate University

2011  *Award for Excellence in Environmental Studies* – Colgate University

2011  *Distinction in CORE Curriculum* – Colgate University

2007-2011  *Dean’s List* – Colgate University

2010-2011  *Konosioni Senior Honor Society* – Colgate University

2008  *Phi Eta Sigma Honor Society* – Colgate University

2008  *Maurice M. Eaton Endowed Scholarship* – Colgate University

2008  *Arthur Watson Endowed Fund for Career Planning* – Colgate University

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RESEARCH EXPERIENCE


2010-2011  Chemistry Department, *Atmospheric Chemistry Research Assistant* – Colgate University
2009-2011  Environmental Studies Department, *Environmental Justice Research Assistant* – Colgate University

Summer 2010  Huyck Preserve and Biological Research Center, *Ecology Research Intern* – Rensselaerville, NY

2007-2009  Chemistry Department, *Biochemistry Research Assistant* – Colgate University

**PROFESSIONAL EXPERIENCE**

**Summer 2014**  Wilderness Ventures, *Trip Leader* – Jackson, WY


Fall 2011  Nature’s Classroom, *Environmental Sciences Teacher* – Groton, MA

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2008-2011  Outdoor Education, *Orientation and Program Leader* – Colgate University

2008-2011  Writing and Speaking Center, *Peer Advisor* – Colgate University

**Summer 2008**  Global Volunteer Network, *French Teacher* – Dawhenya, Ghana

**SERVICE**


2015-present  Biogeochemistry Journal Group, *Coordinator* – Syracuse University

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2014-present  Big Brothers Big Sisters, *Mentor* – Syracuse, NY

2014-2015  Science Corps, *STEM Mentor* – Syracuse University

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2007-2011  Campus Ecology Group, *Activity Coordinator* – Colgate University

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**PROFESSIONAL MEMBERSHIP**

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