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Deposition of Mercury in Forests along a Montane Elevation Gradient

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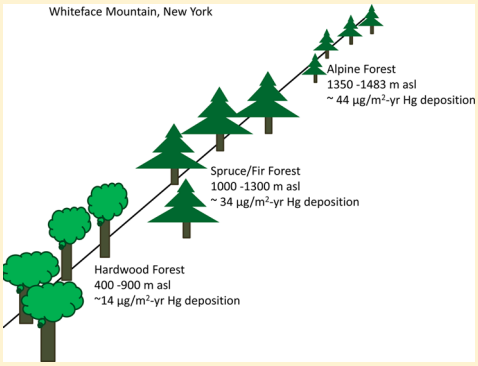
Supporting Information

ABSTRACT: Atmospheric mercury (Hg) deposition varies along elevation gradients and is influenced by both orographic and biological factors. We quantified total Hg deposition over a 2 year period at 24 forest sites at Whiteface Mountain, NY, USA, that ranged from 450 to 1450 m above sea level and covered three distinct forest types: deciduous/hardwood forest (14.1 μg/m^2-yr), spruce/fir forest (33.8 μg/m^2-yr), and stunted growth alpine/fir forest (44.0 μg/m^2-yr). Atmospheric Hg deposition increased with elevation, with the dominant deposition pathways shifting from litterfall in low-elevation hardwoods to throughfall in midelevation spruce/fir to cloudwater in high-elevation alpine forest. Soil Hg concentrations (ranging from 69 to 416 ng/g for the Oi/Oe and 72 to 598 ng/g for the Oa horizons) were correlated with total Hg deposition, but the weakness of the correlations suggests that additional factors such as climate and tree species also contribute to soil Hg accumulation. Meteorological conditions influenced Hg deposition pathways, as cloudwater Hg diminished in 2010 (dry conditions) compared to 2009 (wet conditions). However, the dry conditions in 2010 led to increased Hg dry deposition and subsequent significant increases in throughfall Hg fluxes compared to 2009. These findings suggest that elevation, forest characteristics, and meteorological conditions are all important drivers of atmospheric Hg deposition to montane forests.



INTRODUCTION

Mercury (Hg) contamination is a major environmental issue for remote ecosystems that receive elevated deposition from long-range atmospheric transport. Anthropogenic activities have increased the global pool of available Hg by approximately a factor of 3.[1] Although Hg emissions have decreased in North America and Europe, activities in Asia have resulted in overall increases in global Hg emissions.[1,2] Mercury deposition is difficult to estimate on a global basis because many factors can influence its land−atmosphere exchange. Land cover has been shown to impact Hg deposition, as forested areas enhance Hg deposition processes.[3−6] Differences in forest type also impact Hg deposition.[7−9] Additionally, geographic features such as latitude, longitude, and elevation have been correlated to Hg deposition.[10−12]

Previous studies have shown that high-elevation forests receive elevated atmospheric deposition of anthropogenic pollutants.[13−15] Mercury concentrations in soils increase with increases in elevation,[16,17] and two montane areas of the northeastern United States (the Adirondack and Catskill Mountains) are considered to be "biological Hg hotspots".[18] The steep elevation gradients found in mountainous regions create abrupt changes in climate, which in turn lead to shifts in forest communities from low-elevation hardwood forest to high-elevation conifer forest. As both meteorological and biological factors influence Hg deposition, there is potential for marked variability in Hg deposition processes along mountain gradients, even over relatively small distances. Mountainous areas are also likely to experience more severe changes in meteorological conditions driven by human-induced climate change than low-elevation areas.[19] Mountainous areas have shallow soils, harbor sensitive plant and wildlife species, and serve as recharge areas for down gradient water resources. As a result, there is a critical need to characterize and quantify atmospheric deposition to montane landscapes.

The purpose of this study was to quantify Hg deposition over a 1000+ m elevation gradient in the Adirondack Mountains of New York State, USA, and to evaluate the role of physical factors (precipitation quantity, solar radiation, etc.) and biological factors (forest type) in Hg deposition processes. We estimated deposition through both wet and dry processes and measured Hg concentrations in organic soil horizons. As this study spanned two growing seasons, we also examined effects of meteorology on Hg deposition by comparing Hg deposition calculations from a wet, cool, predominantly overcast growing season (2009) with Hg deposition calculations from a warm, dry, and predominantly sunny growing season (2010). In addition, this study could serve as a baseline for monitoring both reductions in Hg emissions in North America and long-term variation in Hg deposition as a result of climate change.

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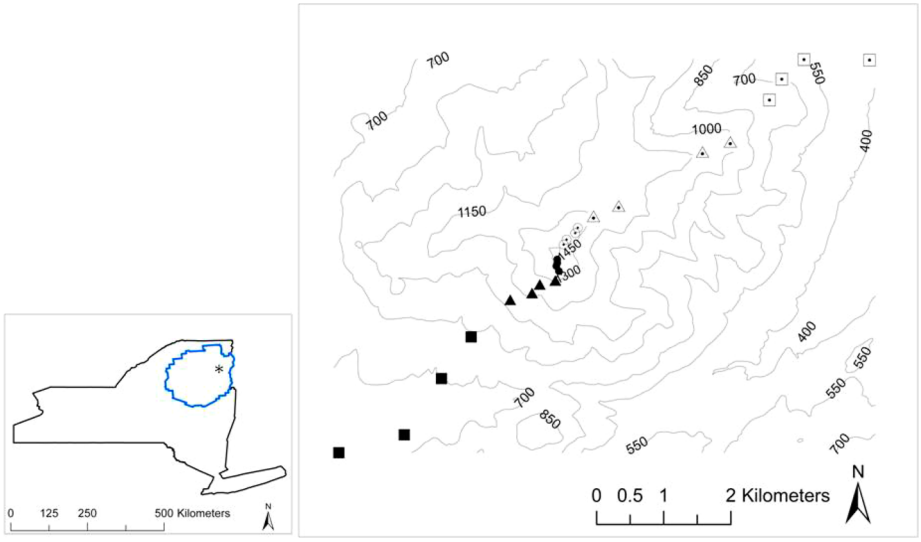

Figure 1. Map showing location of Whiteface Mountain within the Adirondack Park and sampling transects along the southwest (black symbols) and northeast (open-dot symbols) sides of Whiteface Mountain. Square symbols represent hardwood plots, triangles spruce/fir plots, and circles alpine plots.

MATERIALS AND METHODS

Study Site and Experimental Design. Whiteface Mountain is located in the northeast portion of the Adirondack Park near Wilmington, NY (summit location 44.37°N, 73.90° W) (Figure 1). The mountain has a prominence of over 1000 m, with a base elevation of approximately 400 m above sea level and a summit elevation of 1483 m. Whiteface is home to the State University of New York Atmospheric Science Research Center (ASRC) and has atmospheric monitoring stations located at approximately 610 m and at the summit. There is also a monitoring site for the National Atmospheric Deposition Program National Trends Network (NADP NTN) and a site for cloud-chemistry monitoring operated by the NY Department of Environmental Conservation. Mercury Deposition Network (MDN) stations are located approximately 50 km (Huntington Forest, NY; NY20) and 80 km (Underhill, VT; VT99) from the summit of Whiteface.

Forest communities of Whiteface Mountain are segregated into three distinct zones with small transition zones between. Lower elevations (hardwood zone) are characterized by northern hardwood forest dominated by sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), red maple (*Acer rubrum*), and American beech (*Fagus grandifolia*) and range from 400 m to approximately 900 m. Canopy heights in the hardwood forest range from 10 to 20 m on average, and the understory is relatively open. Midelevations (spruce/fir zone) are thick stands of balsam fir (*Abies balsamea*) and red spruce (*Picea rubens*) with interspersed paper birch (*Betula papyrifera*) and range from approximately 1000 to 1300 m. The canopy heights of the midelevations range from 5 to 10 m, and the understory ranges from open to extremely dense growths of young evergreens. The third zone is an alpine forest zone that is composed almost entirely of sparse, stunted-growth balsam fir with occasional red spruce, paper birch, and mountain ash (*Sorbus americana*). The alpine zone ranges from approximately 1350 m to the summit. The canopy height in this area rarely exceeds 2 m, and much of the "canopy" is less than 1 m in height.

This study was designed to estimate atmospheric Hg deposition along the entire elevation gradient of Whiteface Mountain. This goal was accomplished by establishing transects along both the southwest and northeast sides of Whiteface (Figure 1). Each transect contained 12 study plots that spanned a range of elevations and forest types. For both transects, four plots were established at regular elevation intervals in each of the three major vegetation zones (hardwood, spruce/fir, alpine). Samples were collected from the transects between June 1, 2009 and June 6, 2011.

Sample and Data Collection. After selecting plots, we recorded latitude and longitude using a hand-held global positioning system (GPS). Elevation was estimated using a combination of topographic maps, hand-held GPS, and a digital elevation model of the Adirondack Park. Throughfall collectors were installed at each site, and throughfall was collected every 10−30 days during the growing season. Green canopy foliage was collected from high canopy trees in late September of both 2009 and 2010. Senesced litter was collected in plastic crates at each site throughout the year. Organic soil samples were collected from each plot. Two subsamples were taken from the horizons of each soil core. The Oi and Oe horizons, which are made up of slightly to intermediately decomposed leaf litter and organic matter, were combined into a single sample. The Oa horizon, made up of highly decomposed organic matter, was also collected. In addition, a cloudwater collector was installed at the summit to estimate deposition via cloudwater. Detailed information about the methods used to collect samples can be found in Supporting Information. Meteorological data, which included air temperature, wind speed, cloud frequency, and precipitation quantity, were measured at the summit of Whiteface and are included in Supporting Information (Table S1).

Laboratory Analysis. All solid samples (foliage, litter, soil) were freeze-dried for at least 72 h to remove moisture and were then analyzed for total Hg using EPA Method 7473 (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf). A subsample of solid samples was also analyzed for total carbon and total nitrogen content. Aqueous samples (throughfall, cloudwater) were fixed with hydrochloric acid and stored at 4 °C before analysis for total Hg using EPA Method 1631e (http://water.epa.gov/scitech/methods/cwa/metals/mercury/

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upload/2007_07_10_methods_method_mercury_1631.pdf). Throughfall samples collected in 2010 were also analyzed for NO_3^-, SO_4^{2-}, and dissolved organic carbon (DOC). Detailed information on laboratory analysis, including quality control, is included in Supporting Information.

Deposition Calculations. Sampling years were designated as beginning June 1 of each year to simplify flux calculations. Sampling year 2009 was defined as June 1, 2009 to May 31, 2010, and sampling year 2010 was defined as June 1, 2010 to May 31, 2011. Throughfall Hg fluxes were calculated by multiplying throughfall concentrations by throughfall quantities. During the growing season, both components were measured directly at each plot. For periods when samples were not collected directly, wet Hg deposition was estimated at each plot using the NTN and MDN data and multiplying those data by the average precipitation and Hg enrichment factors for each plot. See Supporting Information for further explanation of this method.

Litterfall Hg fluxes were calculated by multiplying litterfall mass per unit area by foliar Hg concentrations. Cloud fluxes were estimated by multiplying mean measured cloud Hg concentrations with a modified cloudwater quantity model for Whiteface Mountain outlined in Miller et al.[14] This model was optimized specifically for Whiteface Mountain and predicts annual cloudwater quantity at different elevations. Mercury deposition fluxes were calculated for litterfall, throughfall, and cloudwater at each plot. These deposition pathways were assumed to be independent of each other, and total Hg fluxes were assumed to be the sum of the three components. Deposition of Hg in each forest zone was estimated by averaging calculated fluxes from all eight plots within each zone. Refer to Supporting Information for more detailed explanations of calculation of deposition estimates.

Statistical Analysis. Regression analysis was used to examine patterns in elevation with measured chemistry variables and estimated Hg deposition. One-way ANOVA was used to determine statistically significant differences among the different forest zones. Data that were not normally distributed were log-transformed before analysis. Statistical significance was defined at $\alpha < 0.05$. All data analysis was performed using IBM SPSS Statistics 19.0.

RESULTS

Meteorological Variables. Weather patterns in 2009 were markedly different from weather patterns in 2010, as 2009 was generally cool and overcast with regular rain showers, while 2010 was warmer with less cloud cover and precipitation. A substantially greater proportion of the rainfall in 2010 was the result of storm events. Although it was not possible to collect meteorological data at each site, data were collected at the summit and are summarized in Table S1 of Supporting Information.

Throughfall and Cloud Hg Concentrations. Concentrations of Hg in throughfall varied among the different forest types, with the lowest concentrations found in the alpine zone and highest concentrations found in the spruce/fir zone (Figure 2). Results of one-way ANOVA of log-transformed throughfall Hg concentrations indicate that the differences among forest types were significant ($F_{(2,140)} = 10.3$, $p < 0.001$). Posthoc testing using Tukey's HSD showed that throughfall Hg concentrations in the spruce/fir zone were significantly higher than both the hardwood and alpine zone ($p < 0.01$ for both), but differences between the hardwood and alpine zones were not significant ($p = 0.286$). Throughfall Hg concentrations in the alpine zone were similar to concentrations for open precipitation samples that were measured near Newcomb, NY and Underhill, VT (Figure 2). Cloudwater Hg concentrations were comparable to spruce/fir throughfall concentrations and were higher than alpine and hardwood throughfall concentrations for all three months of measurement (Figure 2).

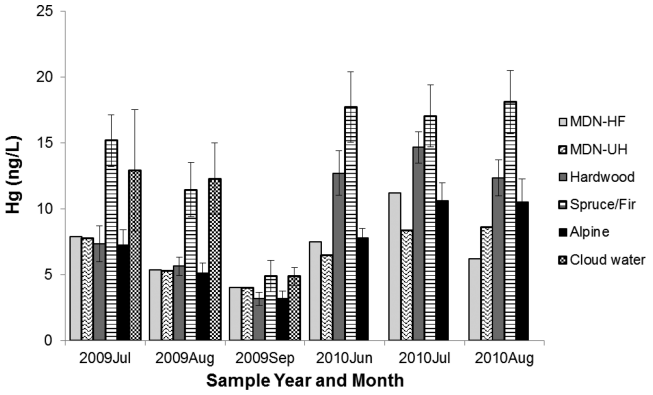

Figure 2. Average concentrations of Hg in precipitation, throughfall, and cloudwater. Error bars represent standard errors. Because precipitation concentrations were measured from a single collector, no standard error was calculated. Precipitation was measured at Mercury Deposition Network (MDN) stations at Huntington Forest near Newcomb, NY (HF) and a station near Underhill, VT (UH). Throughfall was collected in different forest zones at Whiteface Mountain. Cloudwater was collected at the summit of Whiteface Mountain and was only collected in 2009.

Chemistry measurements of a subset of 14 cloud samples and 72 throughfall samples showed that Hg concentrations were correlated with concentrations of other chemical species. Throughfall concentrations, however, were strongly, positively related ($r^2 = 0.58$, $p < 0.001$, Figure S1, Supporting Information) to DOC concentrations in all forest types but were unrelated to NO_3^- and SO_4^{2-} concentrations. Cloudwater Hg concentrations were positively related to both NO_3^- and SO_4^{2-} concentrations (Figure S2, Supporting Information). Cloud samples were not analyzed for DOC. However, data from Adirondack Lake Survey Corporation cloudwater collector on the summit of Whiteface show that DOC is highly related to both NO_3^- and SO_4^{2-}, so it is likely that DOC in cloudwater is related to Hg as well.

Foliar Hg. One-way ANOVA indicated that tree species had a significant effect on foliar Hg concentrations in both 2009 ($F_{(8,101)} = 34.4$, $p < 0.001$) and 2010 ($F_{(8,176)} = 137.8$, $p < 0.001$). In general, hardwood foliage accumulated more Hg than current-year conifer foliage (Figure 3). Conifer foliage Hg concentrations were dependent on the age class of the needles, with concentrations in 2 year old needles >1 year old needles > current year needles. The increase in Hg concentration was consistent throughout the age classes. Estimated rates of foliar Hg accumulation were approximately 10−15 ng/g-yr for balsam fir and 4−6 ng/g-yr for red spruce.

Effects of elevation on foliar Hg concentrations were evaluated using linear regression. In both 2009 and 2010, elevation had a significant, negative effect on foliar Hg concentrations ($r^2 = 0.62$ and 0.20, respectively, $p < 0.001$ for both years, Figure S4, Supporting Information). However, this pattern is partially confounded by the shift in species along the elevation gradient. To attempt to account for this, elevation effects were evaluated for paper birch, which is the only species

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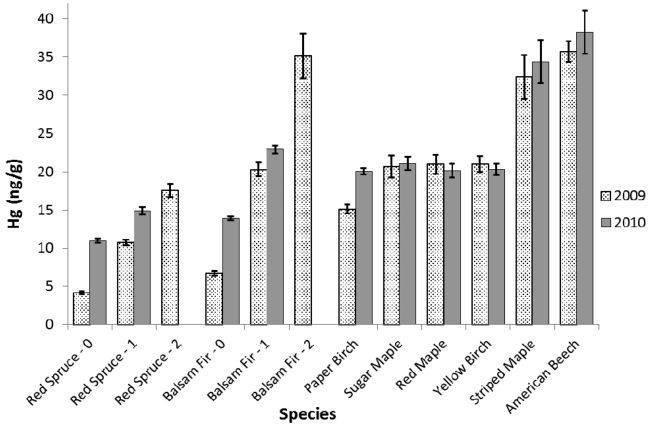

Figure 3. Mean foliar Hg concentrations of tree species at Whiteface Mountain. Numbers following names of conifer species represent age of needles in years. Values represent mean Hg concentrations at time of sampling in mid-September 2009 and 2010. Error bars represent standard errors.

that was found in all plots. The resulting regression was still negative and strongly significant for the 2009 samples (r^2 = 0.43, $p < 0.001$, Figure S5, Supporting Information). In 2010, the same pattern was not significant, and paper birch foliage Hg concentrations were relatively homogeneous along the entire elevation gradient.

Hg in Organic Soils. Hg concentrations in the soil organic Oi/Oe horizon and Oa horizon were 2−4 times higher than Hg concentrations of the litterfall. Within the profile, the Oa horizon Hg concentrations were significantly higher than Oi/Oe horizon Hg concentrations, with the difference being more pronounced in the spruce/fir and alpine zones (Figure 4).

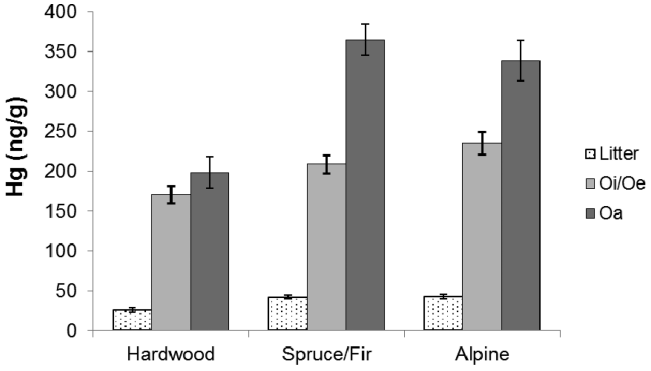

Figure 4. Mercury concentrations in fresh litter, Oi/Oe horizon, and Oa horizon samples from different forest zones. Error bars represent standard error.

Linear regression revealed that Oa horizon Hg concentrations were positively related to both %N and %C. However, Oi/Oe horizon Hg concentrations were not related to either %N or %C, and neither Oi/Oe nor Oa horizon Hg were related to C:N ratios. Like Hg, %C was highest in the spruce/fir zone. But unlike Hg, both C and N concentrations decreased significantly from the Oi/Oe horizon to the Oa horizon. Hg concentrations in both Oi/Oe and Oa horizons showed a significant positive relationship with elevation, but the stronger relationship was observed in the Oa horizon (Figure S3, Supporting Information).

Mercury Deposition. Mercury deposition was highly variable across the three forest types, with the pathways of deposition (litterfall, throughfall, and cloudwater) each contributing different proportions to total Hg deposition in the three forest types (Figure 5). The highest Hg fluxes in 2009

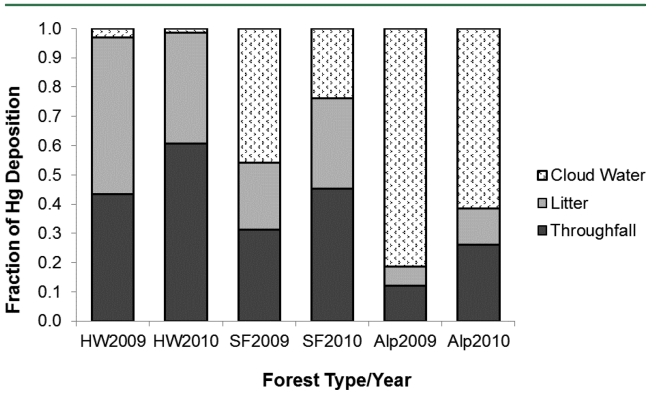

Figure 5. Fractional contributions of throughfall, litterfall, and cloudwater to total Hg deposition in each forest zone in 2009 and 2010. HW = Hardwood, SF = spruce/fir, and Alp = alpine.

and 2010 were evident in the alpine zone (49.2 and 38.7 μg/m^2-yr, respectively), followed by the spruce/fir zone (31.5 and 36.1 μg/m^2-yr), and then hardwood zone (12.2 and 16.0 μg/m^2-yr) (Table 1). There were marked differences in Hg fluxes between the two sampling years. In the hardwood zone, the dominant form of deposition in 2009 was litterfall, while in 2010 throughfall was the largest Hg input pathway. The spruce/fir zone received most deposition from cloudwater in 2009, but throughfall was the more important contributor in 2010. In the alpine zone, cloudwater was the dominant contributor of Hg deposition in both 2009 and 2010.

DISCUSSION

Comparison to Other Studies. While studies of Hg deposition along elevation transects are rare in the literature, there are two other investigations that corroborate our findings of increased Hg deposition at higher elevations. Neither Stankwitz et al.[16] nor Townsend et al.[17] attempted to quantify total Hg fluxes, but both found that soil Hg concentrations increased by approximately a factor of 4 along elevation transects in the northeastern United States, a phenomenon attributed to increased Hg deposition. Other studies have found that Hg concentrations in high-altitude lakes are often higher than low-altitude lakes[20,21] and that Hg concentrations in fish are positively correlated with elevation.[22,23] In addition, increased deposition of pollutants, mainly acidic deposition (N and S), has been documented in high-elevation forests across North America.[13−15,24,25] Acidic deposition can play an important role in the mercury cycle, as poorly buffered, acidic surface waters may exacerbate bioaccumulation of Hg in food webs.[26] In this study, Hg in cloudwater was correlated with both NO_3^- and SO_4^{2-} at the summit of Whiteface. Mercury, N, and S are emitted largely through the combustion of coal and are subject to long-range transport,[26] suggesting that Hg deposition and acidic deposition could be derived from similar sources. Our data suggest elevation gradients affect Hg similarly to N and S, and the same climate and landscape variables that control elevation patterns of acidic deposition also influence Hg deposition processes.

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Table 1. Estimated Hg Fluxes from Throughfall, Litterfall, and Cloudwater in Each Forest Zone (hardwood, HW; spruce-fir, S/F; alpine, Alp) in 2009 and 2010[a]

	2009			2010		
	HW	S/F	Alp	HW	S/F	Alp
throughfall	5.3 ± 2.4	9.9 ± 4.2	6.0 ± 2.5	9.7 ± 3.9	16.3 ± 6.6	10.1 ± 4.1
litter	6.5 ± 1.8	7.1 ± 2.9	3.2 ± 2.4	6.1 ± 1.4	11.2 ± 2.6	4.8 ± 2.5
cloud	0.4 ± 0.4	14.5 ± 8.1	40.1 ± 2.1	0.2 ± 0.2	8.6 ± 4.8	23.8 ± 1.3
total	12.2 ± 3.2	31.5 ± 12.3	49.2 ± 2.7	16.0 ± 4.5	36.1 ± 8.1	38.7 ± 5.0

[a]Measurements are $\mu g/m^2$-yr. Measurements represent annual means estimated from eight plots in each forest zone, ± one standard deviation of those eight measurements.

Mercury in Foliage. Tree species distribution is clearly important in mediating Hg deposition. Species composition affected foliar Hg concentrations, litter quantity, and throughfall Hg concentrations, all of which influence dry deposition fluxes of Hg. Observations of foliar Hg concentrations from this study were consistent with previous studies: different tree species accumulate Hg at different rates,[5,27] and conifers accumulate Hg more slowly than hardwoods.[28] The slower Hg uptake of conifers was evident through a comparison of Hg concentrations in leaves and needles from the current growing season (Figure 3). Despite slower uptake of Hg, conifer needles are exposed to atmospheric Hg for several years, and as a result, conifer needle Hg concentrations are higher than hardwood leaves at the time of litterfall.[29] Tree species naturally partition along the elevation gradient at Whiteface, and high elevation forests consist almost entirely of coniferous species. On average, foliar Hg concentrations were higher in coniferous zones because conifers contain needles that are several years old. High foliar Hg concentrations in coniferous zones were also found on nearby Camel's Hump, VT.[16] The authors attributed this pattern to enhanced deposition of Hg at higher elevations; however, this process of enhanced Hg deposition is likely not because of greater deposition rates of atmospheric Hg but is due to multiyear exposure periods of coniferous foliage compared to single-year exposure of deciduous foliage.

Recent studies of isotopic signatures of Hg along elevation gradients suggest that the proportion of Hg that is derived from the atmosphere is greater at higher elevations.[30] The foliar concentrations of Hg are likely the result of atmospheric Hg^0 that is taken into the leaf through the stomata,[3,28,31] as foliar uptake of Hg is directly correlated with atmospheric Hg^0 concentrations.[32] Foliar Hg concentrations from dominant species along the elevation gradient at Whiteface do not offer a useful indication of atmospheric Hg^0 concentrations because of the different rates of Hg uptake between deciduous and conifer species. Although it is not a dominant species, paper birch trees were found in all 24 plots along the elevation transects. Attempts to use paper birch as an indicator of atmospheric Hg^0 concentrations were inconclusive as patterns varied between the two study years. Paper birch Hg concentrations were higher at low elevations in 2009, suggesting that Hg^0 concentrations decrease with elevation. However, paper birch foliar Hg concentrations were relatively uniform in 2010 (see Supporting Information). Hg^0 is relatively stable in the atmosphere and is often assumed to be homogeneous across the landscape, but meteorological variables such as relative humidity[33]and wind speed[34] have been shown to be inversely correlated to atmospheric Hg^0 concentrations. Orographic effects can cause variation in both humidity and wind speed over a short distance, leading to a high likelihood that Hg^0 concentrations will vary across an elevation transect. Due to the remoteness and ruggedness of the mountain, we were unable to measure humidity and wind speed at our plot locations. Further investigation is needed to determine if paper birch (or another tree species distributed along an elevation gradient) could be a reliable indicator of variation in atmospheric Hg^0 concentrations along elevation transects.

Mercury in Throughfall and Cloudwater. Like foliar Hg concentrations, throughfall Hg concentrations were significantly influenced by forest composition. Other studies have found that Hg concentrations in throughfall from coniferous forests are higher than in deciduous forests[4,7,9,35] and that canopy density is positively correlated with throughfall concentrations.[35] Throughfall Hg concentrations from the spruce/fir zone were significantly higher than open precipitation, hardwood, and alpine concentrations for every sampling period (Figure 2). Hardwood throughfall Hg concentrations were only significantly higher than precipitation in 2010, and alpine throughfall Hg was not significantly different from precipitation in either 2009 or 2010. This lack of Hg enrichment by the alpine canopy can likely be explained by canopy height and tree density because the predominantly balsam fir "canopy" of the alpine zone is only 1−1.5 m in height on average and is relatively sparse in many areas due to exposed bedrock and rocky soils.

Unlike foliar Hg concentrations, throughfall Hg concentrations most likely represent gaseous and particulate Hg(II) deposition that is adsorbed from the atmosphere by leaf and needle surfaces.[3,5,36] Hg(II) is relatively soluble and is readily washed from leaf surfaces during rain or cloud events.[3] Conifer species are believed to be more efficient at removing Hg(II) from the atmosphere than deciduous species, but they readily leach the captured Hg(II) during rain events.[3,6,9] This hypothesis is supported by the throughfall patterns at Whiteface, as the coniferous spruce/fir zone had the highest throughfall Hg concentrations of the three forest zones. In addition, precipitation was greater at the higher elevations, resulting in significantly larger volumes of throughfall in the spruce/fir zone compared to low-elevation hardwood forests. This combination of high concentrations and large throughfall volumes leads to Hg fluxes that are significantly greater in the conifer regions of mountains, and this would contribute to the observation that atmospherically derived Hg is greater at higher elevations.[30] Throughfall fluxes are also influenced by meteorology, as Hg(II) concentrations in the atmosphere are positively correlated with temperature and solar radiation,[37] so dry deposition to the forest canopy is likely to be greater under warm, dry weather conditions. Observations from the present study support this hypothesis, as the warmer, drier season of 2010 resulted in much higher throughfall Hg concentrations and deposition compared to 2009.

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Cloudwater Hg concentrations were highly elevated over precipitation concentrations and were comparable to concentrations in spruce/fir throughfall. Cloudwater Hg concentrations and fluxes are difficult to measure, and while several studies have demonstrated the importance of cloudwater contributions to Hg fluxes at high elevations, there is little information on the magnitude of Hg deposition due to cloudwater.[16,38,39] Results from this present study measured volume-weighted average Hg concentration of 9.7 ng/L (range 3.5−38 ng/L) for cloud samples, which is lower but still comparable to a previous study at nearby Mt. Mansfield in 1998 before recent decreases in Hg emissions (mean 24 ng/L, range 7.5−71.8).[38] Orographic effect can cause large differences in cloud frequency between the base and summit of a mountain, and modeling of cloudwater Hg fluxes indicated a strong elevation gradient due to much larger volumes of cloudwater at higher elevations (Figure 5 and Table 1). Cloudwater contributions to Hg fluxes were essentially nonexistent in the hardwood forest but were significant in the spruce/fir zone and were by far the most dominant Hg flux to the alpine zone of Whiteface. Meteorological conditions have a substantial effect on cloud Hg fluxes and were an important driver of differences in cloud Hg deposition between 2009 and 2010 at Whiteface Mountain. The wetter conditions and increased cloud frequency in 2009 resulted in Hg fluxes that were nearly double the fluxes from 2010 (Table 1). Although estimates of cloud deposition are not exact and subject to error, our results indicate that deposition of Hg through cloudwater was the most significant pathway of Hg deposition at Whiteface during the study period. Future studies should focus on accurately estimating cloud deposition to mountainous terrain, as this is an imperative component of quantifying Hg deposition along elevation gradients.

Mercury in Soil. The majority of dry and wet deposited Hg is supplied to the forest floor where it is incorporated into the soil profile. At Whiteface, Hg concentrations in O-horizon soils increase with increasing elevation (Figure S3, Supporting Information), an observation that is supported by other studies.[16,17,40] Soil processing of Hg is complex and not well understood, but one simple hypothesis is that increasing Hg deposition leads to increases in soil Hg concentrations and pools. While soil pools were not estimated in this study, both the Oi/Oe horizon and Oa horizon showed a positive relationship between total Hg deposition and Hg concentrations (Figure 6). However, total Hg deposition explained little of the variance in these models (14% in the Oi/Oe layer, 30% in Oa layer). Different forest types have been shown to influence soil decomposition processes,[41] and Hg transformation in soil following litterfall is not consistent between hardwood and conifer stands.[7] The influence of forest type, soil temperatures, soil chemistry, precipitation, and a number of other variables challenge predictions of soil Hg accumulation. However, results from this study suggest that Hg deposition does play an important role in soil Hg processes (Figure 6). Investigations have suggested that litterfall Hg becomes enriched in the humus layer of the forest floor by retention of throughfall inputs.[7,42] Variations in this enrichment in soil Hg by throughfall/cloudwater retention was evident across the forest landscape at Whiteface. There were limited increases in Hg concentrations from the Oi/Oe horizon to the Oa horizon in the hardwood zone. In contrast, there were relatively large increases in Hg concentrations from the Oi/Oe horizon to the Oa horizon in the conifer and alpine zones, both of which are

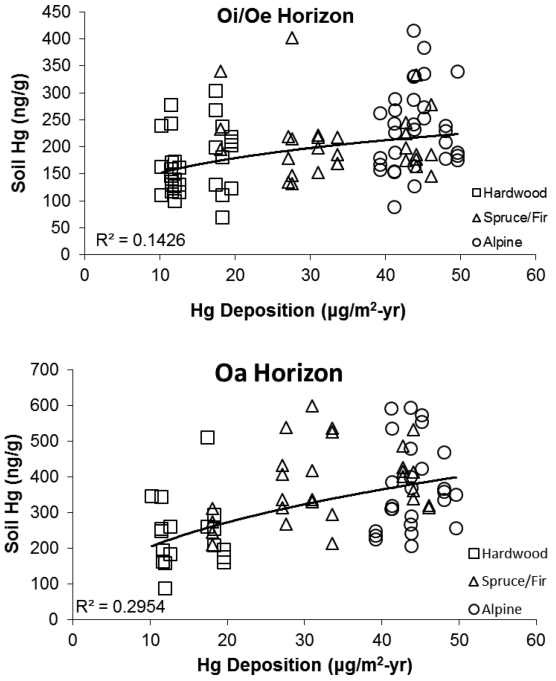

Figure 6. Regression relationships between calculated Hg deposition and organic soil Hg concentrations ($p < 0.001$ for both regressions).

characterized by large inputs of throughfall and cloudwater Hg. Also, although carbon contents were similar in foliar samples, slight increases in forest floor carbon content were observed from the hardwood to spruce/fir and alpine zones, which would indicate the cooler, wetter upper elevations were cycling C more slowly. Slower C turnover at high elevations has been documented previously, with turnover times at high elevations estimated to be three times longer than base elevations.[43] This slower C turnover at high elevations could lead to slower decomposition of detrital organic matter that binds Hg and slower rates of Hg respiration loss[42] which, coupled with increased deposition rates, likely contribute to high soil Hg concentrations at high elevations.

Magnitude of Mercury Fluxes at Whiteface. Litterfall, throughfall, and cloud deposition of Hg all play important roles in Hg inputs and soil accumulation at Whiteface, but the relative importance of each component of Hg deposition shifts among the different forest types. The alpine region had the greatest Hg deposition and was dominated by cloudwater deposition, with canopy processes of litterfall and throughfall contributing relatively small amounts of Hg (Table 1). In the spruce/fir zone, although throughfall was the dominant Hg deposition pathway over the course of the study, litterfall and cloudwater both contributed significant portions to the total Hg flux. The hardwood forest zone received approximately equal contributions from throughfall and litterfall pathways and only negligible Hg deposition from cloudwater.

Comparison between differences in annual Hg deposition estimates and meteorological conditions suggest that the magnitude of the deposition pathways is largely dependent on meteorological variables. The litter deposition pathway was the most consistent between 2009 and 2010 and is likely the pathway that is least influenced by meteorological variation. Warmer temperatures reduced cloud frequency in 2010 compared to 2009. The lower frequency of clouds decreased total Hg deposition in 2010 relative to 2009, but cloud

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deposition still accounted for over 60% of total Hg deposition in the alpine zone. The change in cloud frequency and meteorology from 2009 to 2010 had more substantial impacts on Hg deposition in the spruce/fir zone. Cloudwater Hg deposition decreased in 2010 in the spruce/fir zone, and although throughfall volumes also decreased, throughfall Hg concentrations increased substantially, resulting in overall higher deposition. Presumably, the dry, warm conditions of 2010 led to increased scavenging of Hg(II) from the atmosphere by the coniferous canopy. The dry, warm conditions of 2010 also increased throughfall Hg concentrations in the hardwood zone and led to a larger throughfall Hg flux compared with 2009. These are similar to observations of interannual shifts in the magnitude of Hg deposition pathways at Huntington Forest in the Adirondacks over the same period[9] and suggest that meteorological variables play an important role in the deposition of Hg in mountainous regions. In years of warm, dry weather conditions, the importance of cloudwater Hg is diminished substantially, but nearly all benefits of low cloudwater Hg deposition may be offset by increases in throughfall Hg. Considering the warm temperatures and dry conditions (due to early loss of snowpack and increased evapotranspiration) that are predicted for the approaching decades,[44,45] the fraction of total Hg deposition that occurs via throughfall may become a more prominent component of total Hg fluxes.

Overall, this study demonstrates the influence that elevation gradients have on Hg deposition processes. Orographic effects of increased cloud frequency at higher elevations drive much of the variability in Hg deposition along elevation gradients, but the composition of forests plays a significant role in predicting Hg deposition to the landscape. Higher elevation coniferous forests receive greater Hg deposition than lower elevation hardwood forests because of increased volumes of throughfall and cloudwater in conjunction with increased scavenging of Hg from the atmosphere by the coniferous canopy. These processes lead to greater Hg deposition to the forest floor, and when coupled with slower C turnover and reduced Hg evasion due to cooler temperatures at higher elevation, Hg concentrations in high-elevation soils are significantly greater than low-elevation soils. In addition, at high elevations, a greater proportion of Hg deposition is in the form of throughfall and cloudwater. As a result, when compared to hardwood forests, high elevation conifer forests receive most Hg deposition in the active form of Hg(II) as opposed to Hg^0. This suggests that a greater percentage of Hg deposited to high elevation forests is available for transport, and surface waters that drain high elevation watersheds may be at an increased risk of developing Hg contamination issues.

We anticipate the information from this study will be useful as a reference condition to inform the potential recovery of ecosystems from contamination due to elevated atmospheric Hg deposition. In the U.S., plans are underway to implement the Mercury and Air Toxics Rule and other rules to limit Hg emissions from electric utilities and other sources.[46] The UNEP-led Minamata Convention is intended to limit Hg releases at the global level. We anticipate that overall decreases in Hg deposition to montane ecosystems will be manifested differently across deposition pathways. National and regional control programs should result in relatively rapid future decreases in Hg(II) emissions and associated decreases in throughfall and cloud Hg deposition. In contrast, decreases in the atmospheric Hg^0 pool will likely be realized over longer time scales due to the importance of secondary Hg^0 emissions,[47] and the contribution of litterfall Hg may increase in relative importance to total Hg deposition.

■ ASSOCIATED CONTENT

Supporting Information

Additional detailed descriptions of field methods, meteorological conditions, and deposition calculations. Six figures and two tables with related chemistry and meteorological information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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