# Land-Atmosphere Dynamics of Mercury and Ecological Implications for Adirondack Forest Ecosystems

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# Land-Atmosphere Dynamics of Mercury and Ecological Implications for Adirondack Forest Ecosystems

*Final Report*

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# Abstract

Despite the dominance of forest land cover in North America, there has been limited detailed research on the deposition, transport, and fate of mercury within forested ecosystems. The objective of this research was to quantify the numerous pathways of mercury deposition in forested sites in the Adirondack region of New York State and to examine spatial and geographic patterns of mercury deposition and fate.

The research was conducted in three phases. In Phase 1, at Huntington Wildlife Forest in the Adirondacks, mercury deposition and transport processes and mercury soil pools were compared at a deciduous hardwood plot and a coniferous plot for 2009 and 2010. Mercury deposition due to litterfall was similar between the two stands, but total mercury deposition was greater in the coniferous plot due to larger fluxes of throughfall mercury. Soil evasion losses of mercury were significantly higher in the hardwood plot. Despite the greater mercury deposition and lower evasion losses, soil mercury pools in the conifer plot were smaller than in the hardwood plot. The loss mechanism of mercury in the conifer stand is not clear. Annual variability in climate conditions was substantial between 2009 and 2010, and changes in mercury deposition quantities appear to be related to variation in temperature and precipitation quantity.

In Phase 2 of the study, the effects of elevation and landscape position on atmospheric mercury deposition were evaluated. Two transects were established along the eastern and western sides of Whiteface Mountain in the Adirondacks. The 24 sample sites ranged from approximately 450–1450 meters (m) above sea level and covered three distinct forest types: deciduous/hardwood forest, spruce/fir conifer forest, and stunted growth alpine/fir forest. Throughfall mercury inputs and mercury accumulation in organic soils were greater in the spruce/fir and alpine areas than the deciduous forest areas. Estimates of cloud water mercury deposition demonstrate that cloud water is an important contributor to total mercury fluxes in alpine environments. Total mercury deposition was correlated to mercury concentrations in organic soil layers. Variation in both physical orographic effects and biological forest types appear to drive mercury deposition processes along this mountainous elevation gradient.

Finally, in Phase 3, spatial patterns of mercury deposition were assessed by collecting canopy foliage and organic soils from 45 different plots across the Adirondack Park. The results showed species-specific differences in foliar uptake of mercury with the lowest concentrations found in first-year growth conifer needles and the highest concentrations found in black cherry (*Prunus serotina*). Latitude and longitude were negatively correlated with mercury concentrations in foliage and humus layer soils, while elevation

was positively correlated with mercury concentrations in foliage and humus layer soils. Elemental analysis of foliage and soil also showed strong, positive correlations between mercury concentrations and nitrogen concentrations in foliage and soil. The spatial patterns of mercury deposition within the Adirondack Park are similar to patterns found for other atmospheric contaminants that originate largely from combustion sources, such as nitrogen and sulfur.

# Keywords

Adirondacks, atmospheric mercury deposition, foliar mercury, forest ecosystem, mercury, Whiteface Mountain

# Acknowledgments

# Table of Contents

# List of Figures

# List of Tables

# 1    Background and Project Design

## 1.1    Background and Project Goal

Mercury (Hg) contamination is an environmental issue that affects essentially every ecosystem on Earth. Despite its status as one of the top priority pollutants in the United States[1] approximately 24 tons of Hg are released annually through various industrial processes in the United States (National Emission Inventory 2019). Although Hg emissions and deposition in the U.S. have declined from 110 tonnes in 2002 to 24 tonnes in 2017, many ecosystems still experience symptoms of Hg contamination (Schmeltz et al. 2011, Drevnick et al. 2012). The Mercury and Air Toxics (MATS) rule was promulgated by the U.S. Environmental Protection Agency (EPA) in 2012 and went into effect in 2015 to control Hg emissions from electric utilities. MATS has greatly decreased emissions in the United States (Zhang et al. 2016). However, Hg emissions are increasing globally due to industrialization, particularly in East Asia (Amos et al. 2013, Streets et al. 2019). As a result, it is unclear to what extent domestic controls on emissions will mitigate elevated Hg concentrations in biota. Moreover, centuries of anthropogenic releases of Hg are currently cycling through Earth ecosystems due to reemissions (Amos et al. 2013; Driscoll et al. 2013). It is possible that deposition of Hg will continue to increase even if global controls are enacted to limit direct anthropogenic Hg emissions (Amos et al. 2013).

The global biogeochemical cycle of Hg is among the most dynamic and complex of any element. Production of methylmercury (MeHg) largely occurs in aquatic ecosystems, and it subsequently bioaccumulates and is biomagnified in aquatic food chains (Wiener et al. 2003). As human and wildlife exposure to Hg occurs primarily through consumption of MeHg contaminated fish and shellfish, past research has mainly focused on aquatic environments. However, freshwater ecosystems occupy less than 3% of the total land cover in North America. Forest is the predominant land cover category in North America and likely receives greater atmospheric Hg deposition than any other land cover category. Despite the potential for forests to act as receptors for a considerable mass of Hg, relatively few studies have examined Hg deposition and cycling in these ecosystems.

Previous studies that have examined Hg in forest ecosystems have consistently shown forests to enhance deposition of Hg relative to adjacent, unvegetated areas. Mercury accumulates in leaf and needle tissues, resulting in a large flux of Hg to the forest floor during litterfall (Risch et al. 2012, Bushey et al. 2008, Rea et al. 1996). Both field and experimental studies suggest that Hg deposited via litterfall is derived almost completely from atmospheric sources (Ericksen et al. 2003, Rea et al. 2001). In addition, leaf and needle surfaces adsorb reactive atmospheric Hg species that are washed off during rain events, leading to

elevated deposition of Hg in throughfall beneath a forest canopy compared to open precipitation samples (Graydon et al. 2008, Kolka et al. 1999, Rea et al. 2001). While there is agreement that forest cover influences Hg deposition processes, there has been little research on the variability of atmospheric Hg deposition across different forested landscapes. Evidence suggests that the biological structure of forest stands (hardwood, conifer) impacts Hg deposition processes (Demers et al. 2007, Sheehan et al. 2006). In addition, geography, landscape features, climate, and proximity to Hg emission sources have been shown to affect Hg deposition processes to forested ecosystems (Obrist et al. 2011, Driscoll et al. 2007, Nater and Grigal 1992).

The overall goal of this study is to characterize and quantify the dynamics of Hg deposition and cycling processes in forested ecosystems in order to improve understanding of the inputs and fate of this contaminant. The Adirondack Park in Upstate New York, which contains diverse forest stands and has highly variable landscape features, was used as the study area. The Adirondacks have been designated as a "biological Hg hotspot" (Evers et al. 2007) and there are fish consumption advisories for 65 waters in and around the Adirondack region.[2] Multiple methods were employed to accomplish the objectives, and three distinct research phases were developed and implemented to explore forest Hg processes. These phases include comparing Hg deposition processes in different forest types (hardwood versus conifer); examining the influence of mountainous landscapes on Hg deposition processes; and using spatial methods to study the impact of variation in geography landscape features on atmospheric Hg deposition. In addition, the data generated from this research can be used as a baseline to assess the effectiveness of upcoming legislation designed to decrease Hg emissions. With the Mercury and Air Toxics (MATS) rule in the United States (EPA 2012), Clean Air Regulatory Agenda in Canada,[3] and the Minamata Convention: United Nations Global Treaty on Mercury,[4] there will be a need for datasets that can be used to evaluate progress in Hg control programs. The data from this research will provide an extensive collection of measurements from forests of the Adirondack Park.

## 1.2   Project Design

There are three main research phases of this research program. Phase 1 (section 4) is a detailed comparison of Hg deposition processes and soil Hg accumulation in two different forest plots, one dominated by hardwoods (HW) and one by coniferous (Con) tree species. Both plots are located at Huntington Wildlife Forest in the Adirondack Park and are exposed to similar meteorological conditions and Hg deposition due to their proximity. Measurements of wet Hg deposition, litterfall Hg, throughfall

Hg, soil Hg concentrations, and soil Hg evasion allowed for detailed estimates of land-atmosphere Hg exchange and soil accumulation in each plot and a comparison of Hg deposition processes between conifer and hardwood stands. Atmospheric Hg and meteorological monitoring data are also available for Huntington Wildlife Forest and were used to examine relations to forest Hg deposition.

In Phase 2 (section 5), measurements were made along two elevation transects to study the impact of mountainous terrain on Hg deposition processes. The study site for Phase 2 was Whiteface Mountain, which is the fifth-highest peak in the Adirondacks. Like Phase 1, detailed Hg deposition estimates were made by monitoring litterfall Hg, throughfall Hg, and soil Hg concentrations. Additionally, measurements of cloud water Hg were made at the summit. The elevation gradient at Whiteface causes a shift in forest type from northern hardwood to spruce/fir coniferous forest to alpine vegetation near the summit. The data collected for Phase 2 were used to evaluate both orographic and biological effects of elevation on Hg deposition processes.

Phase 3 (section 6) is a spatial study of Hg deposition in Adirondack Park that uses 45 field sites located across the park. The field sites cover a variety of forest types including hardwood, mixed hardwood/conifer, spruce/fir conifer, and pine conifer. The geographic extent of the field sites also creates spatial variation in precipitation quantity, site elevation, and other landscape variables. In this research phase, live foliage samples and organic soil layers were used as indicators of Hg deposition for each of the field sites. Statistical analysis was used to examine spatial patterns of Hg deposition and the impact of biological and geographic variables on Hg deposition across the Adirondack Park.

The final section (section 7) of this report provides a synthesis of the three phases of experimental work and the relevant literature on land-atmospheric exchange of Hg and its fate across the Adirondack Park.

# 2    Literature Review

## 2.1   Mercury Emissions

Mercury emissions to the atmosphere are derived from multiple sources. Many natural processes emit Hg to the atmosphere, including volcanic activity, weathering, soil processes, ocean and freshwater gas exchange, and biomass burning (Gustin et al. 2008). Processes such as volcanic eruptions emit Hg that was stored within the Earth and previously inactive in global cycling, so these emissions represent direct, "new" emissions of Hg. Other processes, such as biomass burning or soil evasion, emit Hg that was previously deposited on the Earth's surface and incorporated into living or dead organic matter. These processes cause "old" Hg that was previously bound to become active once again in the Hg cycle. Quantifying natural emissions is a difficult task, and all such calculations have a high degree of associated uncertainty. One recent study estimated the global emissions of Hg from new and old natural sources to be 8,000 tons/year (UNE 2019). The single largest natural source of Hg was from oceans, which accounted for 62% of all-natural emissions. Only about 9% (500 tons/yr) of naturally emitted Hg is estimated to be from geogenic sources.

Anthropogenic activity is responsible for many modifications to the global Hg cycle. Processes such as coal and oil incineration, mining, cement production, and other human activities all release Hg to the atmosphere. Approximately two-thirds of all Hg that is currently cycled on Earth is derived from current and past anthropogenic processes (Pirrone et al. 2010, Mason et al. 1994). Historically, direct mining of Hg ore has led to localized Hg contamination around mines, but direct mining also emits Hg to the atmosphere. Today, artisanal gold mining, stationary combustion sources (largely coal incineration), cement and nonferrous metal production are the most significant source of anthropogenic Hg to the atmosphere (UNE 2019). Asia accounts for about 60% of all current global anthropogenic Hg emissions (Streets et al. 2019).

## 2.2   Atmospheric Forms and Transport of Mercury

Emissions of Hg to the atmosphere occur predominantly in three chemical forms: gaseous elemental Hg (GEM, $Hg^0$), reactive gaseous Hg (RGM), and particulate Hg ($Hg_p$). $Hg^0$ is stable in the atmosphere and has an estimated residence time in the atmosphere of approximately 0.5 to 1 year (Mason et al. 1994). As a result, emissions of $Hg^0$ can persist in the atmosphere and may be transported thousands of kilometers from the emission source (Fitzgerald et al. 1998). The dominant form of RGM is gaseous oxidized mercury ($Hg^{2+}$) and its associated compounds, the most common of which is $HgCl_2$. These

forms of Hg are volatile and tend to be deposited near emission sources (Carpi 1997, Driscoll et al. 2007). $Hg_p$ is mercury bound to particles and is currently the most difficult Hg fraction to characterize. It is thought to be largely composed of oxidized Hg ($Hg^{2+}$) that is bound to particles, and deposition characteristics depend largely on the size of the particles to which the Hg is bound (Lindberg et al. 2007). Measurements from industrial and urban areas indicate that $Hg_p$ concentrations are similar to concentrations of gaseous species near emission sources, but concentrations of $Hg_p$ from rural areas are up to an order of magnitude lower than concentrations near emission sources (Keeler et.al 1995). Average ratios of the three Hg forms in emissions are estimated at 53% $Hg^0$, 37% $Hg^{2+}$, and 10% $Hg_p$ (Pacyna and Pacyna 2002), but are highly variable from source to source.

Mercury contamination is a global problem because of the mobility of Hg in the atmosphere. Mercury, mostly as $Hg^0$, can remain in the atmosphere for extended periods (~0.5 yr) and be subsequently transported around the Earth by prevailing winds. Since industrialization, sediments from remote lakes, peat profiles, and surface soils have all shown increasing Hg deposition despite being remote from local Hg emission sources (Fitzgerald et al. 1998). Sediment records in the Great Lakes region and the remote Arctic show increases in Hg deposition from the mid-1800s through the late 1900s (Drevnick et al. 2012, Pirrone et al. 1998, Hermannson 1998). A number of studies have used global simulation models to determine the relative contributions of background (natural, re-emissions), global, and local, direct emissions to regional deposition, generally finding that background and global emissions are the major contributors. For example, Chen et al. (2014) found that for total, dry, and wet deposition to North America, background sources contributed 64%, 42%, 22%, global direct emissions contributed 27%, 18%, 9% and regional direct emissions contributed 9%, 11%, 6%, respectively. Jaffe and Strode (2008) found that approximately 7–20% of all Hg deposition in United States can be attributed to long-range transport of emissions from Asia. In contrast, emissions of oxidized Hg (RGM, $Hg_p$) are thought to be deposited near emission sources (Driscoll et al. 2007). Recent decreases in Hg deposition to sediments in the lakes of the Great Lakes region are thought to be due to recent controls on Hg sources in North America (Drevnick et al. 2012).

## 2.3    Deposition of Mercury

Gaseous and particulate Hg eventually adsorb to surfaces or are taken up by vegetation through deposition processes. Total deposition of Hg is the combination of two processes, wet and dry deposition. Wet deposition occurs as rain, snow, sleet, fog, cloud water, and dew. Wet Hg deposition is easier to measure than dry deposition, and as a result, more studies and monitoring programs focus on wet Hg deposition. Currently, the National Atmospheric Deposition Program (NADP) Mercury

Deposition Network (MDN) monitors wet deposition for approximately 93 sites across North America.[5] Ecological variables, such as forest type (Graydon et al. 2008, Witt et al. 2009), and geographic variables, such as proximity to Hg emission sources (Miller et al. 2005), can affect concentrations of Hg in wet deposition.

In forests, Hg inputs are partly associated with throughfall, which is precipitation that has passed through the forest canopy. Mercury that is deposited on the surface of leaves may be washed off during rain events, and as a result, throughfall Hg deposition is generally higher than wet (precipitation) Hg deposition (Rea et al. 2001, Kolka et al. 1999). On average, throughfall Hg concentrations are approximately twice as high as concentrations in precipitation (Kolka et al. 1999, Rea et al. 1996, Munthe et al. 1995). Coniferous foliage is thought to remove particulates from the atmosphere more efficiently than deciduous foliage, and as a result, throughfall Hg fluxes are greater in coniferous forests (Witt et al. 2009, Kolka et al. 1999). Canopy density also affects throughfall Hg concentrations, and samples gathered under thick forest canopies have higher Hg concentrations than samples from sparse canopies (Witt et al. 2009).

Mercury concentrations in wet deposition can also be affected by proximity to Hg sources and geographic variables. Throughfall Hg concentrations are higher in areas directly downwind from power plants than in areas that are much further from emission sources (Dutt et al. 2009). In south Florida, wet deposition Hg concentrations were measured in multiple storm events. Mercury concentrations in precipitation were significantly higher from storms that passed over known atmospheric Hg emission sources than from storms that traveled over rural areas with no point-source Hg emissions (Dvonch et al. 2005). In Ohio, it was determined that most Hg in wet deposition was derived from local and regional emission sources, with over 70% attributed to coal combustion (Keeler et al. 2006). Spatial patterns of Hg in wet deposition may be confounded by other factors such as climate and land cover variation, but regional patterns emerge. Based on analysis of MDN data, the southeastern United States has the highest wet Hg deposition, followed by the Ohio River Valley, the Midwest, and then Northeast (Prestbo and Gay 2009). Landscape factors such as elevation may have a significant effect on wet Hg deposition. At one high elevation site (Mt. Mansfield, VT), fluxes of Hg from cloud water at the summit were approximately twice as high as fluxes from throughfall at a nearby low-elevation site (Lawson et al. 2003). Mercury emissions in the United States have decreased in recent years, and many areas have shown a decrease in

Hg concentrations in wet deposition (Gratz et al. 2009, Prestbo and Gay 2009, Zhou et al. 2017; Mao et al. 2017). However, these decreases in Hg concentrations have been offset by increases in precipitation, so wet Hg deposition fluxes have remained unchanged at many locations despite decreases in emissions (Gratz et al. 2009, Risch et al. 2012).

Dry deposition includes adsorption of Hg species, uptake of Hg by vegetation, and any other Hg deposition process that takes place at times when precipitation events are not occurring. Dry deposition is more difficult to estimate than wet deposition. Dry deposition of Hg is a product of many variables, including concentrations of Hg species ($Hg^0$, $Hg^{2+}$, $Hg_p$) in the air, atmospheric reactions of Hg gases and particles, physical and meteorological conditions (temperature, wind speed, mixing height), and landscape variables (Pirrone et al. 1995, Wesely and Hicks 2000). Dry deposition estimates are further complicated by the lack of standard methods for estimating dry Hg deposition. Multiple methods have been used to estimate Hg dry deposition, including direct measurements to surrogate surfaces, meteorological models, calculations based on direct measurements of throughfall, litterfall, and wet deposition (dry deposition = throughfall Hg + litterfall Hg– wet Hg deposition), and combining models with direct measurements of Hg species in air (Zhang et al. 2009). Methods and combinations of these approaches have improved understanding of dry Hg deposition and revealed consistent patterns. Dry Hg deposition varies over time and demonstrates a seasonal pattern with the highest fluxes occurring in the summer (Lyman et al. 2007). Diurnal patterns are also evident, with the highest dry deposition fluxes occurring in the afternoon and lowest occurring at night (Lindberg and Stratton 1998, Caldwell et al. 2006, Lyman et al. 2007). Like wet deposition, dry Hg deposition appears to be greater in areas near emission sources (Keeler et al. 1995, Engle et al. 2010). Dry Hg deposition is also affected by vegetative cover, with deposition occurring at higher rates to vegetated areas than open areas (Lindberg et al. 2007).

Comparisons among different methods for measurement of dry Hg deposition remain difficult, as different methods can produce different results. Dry Hg deposition to surrogate surfaces can vary based on the shape of the surface (Huang et al. 2011) and the chemical coating of the surface (Lai et al. 2011). For static water surrogate surfaces, dry deposition varies depending on whether deionized or acidified water is used in the collector (Lai et al. 2011). Direct methods for determining dry deposition often measure higher deposition than indirect methods when compared side by side (Caldwell et al. 2006, Lyman et al. 2007, Marsik et al. 2007). There is also considerable uncertainty for how measurements to artificial surfaces actually relate to dry deposition to natural surfaces.

Live foliage has been used in many studies to estimate Hg dry deposition to forest ecosystems. Evidence from field studies suggests that Hg in foliage is almost entirely from atmospheric sources (Bushey et al. 2008, Rea et al. 2001), and experimental evidence has supported this conclusion (Fay and Gustin 2007, Ericksen et al. 2003, Frescholtz et al. 2003). Subsequent studies have concluded that litterfall following Hg accumulation in foliage represents the single largest input of Hg into hardwood forest ecosystems (Bushey et al. 2008, Rea et al. 2002). While $Hg^{2+}$ and $Hg_p$ can be deposited to the surface of the leaf, most of the Hg in foliage is $Hg^0$ that is taken up through the stomata (Lindberg et al. 2007). Mercury uptake varies with foliage age, and foliar Hg concentrations increase approximately linearly throughout the growing season (Bushey et al. 2008, Rea et al. 2002, Rasmussen 1995). Different species exhibit different rates of foliar Hg accumulation (Siwik et al. 2009, Bushey et al. 2008). Using foliage as a monitor for dry Hg deposition could be possible if temporal variation and species-specific differences are taken into account.

## 2.4    Mercury Contamination in the Adirondack Park

Although limited information is available, some studies have examined Hg deposition in the Adirondack Park. Sediment records from lakes west of Adirondack Park in central New York State indicate that total atmospheric deposition of Hg peaked in the 1970s for this region (Bookman et al. 2008). Lake sediment records from Adirondack Park were used to estimate a pre-industrial Hg deposition rate of 5.0 µg/m$^2$-yr, compared to a current deposition rate of 8.9 µg/m$^2$-yr (Lorey and Driscoll 1999). Estimates of Hg deposition to New York State attribute 9–25% to local sources, 25–50% to regional sources, and the remainder to emissions generated from global sources (Signeur et al. 2003). Other source attribution studies indicate that much of the Hg deposition to the park comes from sources in Pennsylvania, the Ohio Valley region, and as far away as Texas (Choi et al. 2008a). Modeling of total Hg deposition reveals a general gradient, the highest deposition in the southwest portion of the park and lowest deposition in the northeast park areas (Yu et al. 2013, Miller et al. 2005). Because of the large proportion of emissions that result from long-range transport, there is uncertainty on how regional controls on Hg emissions would affect deposition to the Adirondack Park.

# 3    Objectives and Hypotheses

## 3.1    Comparison of Mercury Dynamics between Hardwood and Conifer Forests

The objective of Phase 1 was to characterize the Hg deposition processes of a hardwood forest plot and a coniferous forest plot and calculate a mass balance of Hg input into the forest floor. The goal was to compare and contrast the pathways of deposition both qualitatively and quantitatively and to examine the effects of temporal climate variability on Hg deposition processes. The following hypotheses were evaluated for Phase 1:

- Dry Hg deposition contributes a larger fraction of total Hg deposition than wet Hg deposition in both hardwood and coniferous forest plots. Although wet deposition delivers large pulses of Hg to the forest floor during precipitation events, dry deposition occurs for a larger percentage of the time and accounts for the majority of Hg deposited to forests.
- Concentrations of Hg increase linearly with time (season) in foliar samples from both hardwood and coniferous plots. This pattern has been previously documented in hardwood forests (Bushey et al. 2008) but has not been examined in conifers.
- Throughfall concentrations are greater in conifer stands than hardwood stands. Conifer needles more effectively remove particulates and reactive Hg species from the atmosphere compared to hardwood leaves (Kolka et al. 1999), and as a result, rain events wash more Hg off needles and result in higher throughfall concentrations and deposition to the conifer stands.
- As Hg deposition is influenced by meteorological conditions, there is considerable temporal variation in Hg deposition that is driven by variation in meteorology.

## 3.2    Deposition of Mercury in Forests along an Elevation Gradient

The objective of Phase 2 was to evaluate the effects of an elevation gradient and mountainous terrain on Hg deposition processes. Elevation gradients influence both the abiotic (e.g., temperature, precipitation, solar radiation) and biotic (forest communities) characteristics of the environment, which in turn would be expected to affect the pathways and magnitude of Hg deposition. The following hypotheses were evaluated for Phase 2:

- Precipitation quantity, throughfall Hg concentrations, and foliar Hg concentrations all increase with increasing elevation. Evidence suggests that higher elevations receive higher Hg deposition than lower elevations (Lawson et al. 2003, Miller et al. 2005). Both wet Hg deposition and dry Hg deposition increase with increasing elevation.
- Because of increased deposition with elevation, organic soil horizons accumulate significantly higher Hg at higher elevations than at lower elevations. Soil horizons accumulate deposited Hg over time. High Hg deposition rates at higher elevations result in higher Hg pools in higher elevation soils.

- The distinct forest zones at Whiteface Mountain will have a significant effect on Hg deposition processes. The forest community abruptly shifts from hardwood to coniferous vegetation along the elevation gradient. Because the forest canopy influences both wet and dry Hg deposition processes, this forest community shift will lead to measurable differences in Hg deposition in different forest types.

## 3.3     Spatial Patterns of Mercury in Foliage and Organic Soils in Adirondack Park

The objective of Phase 3 was to assess the spatial patterns of Hg deposition across the Adirondack Park using live foliage and organic soil layers from 45 plots as indicators of present and historic Hg deposition. The variation in climate and forest communities across the park likely influences Hg deposition patterns and quantities. The goal of this portion of the study was to estimate Hg deposition and identify regions of the park that are susceptible to Hg contamination issues. The following hypotheses were evaluated for Phase 3:

- Foliar and soil concentrations of Hg decrease from the southwest portion of the park to the northeast portion of the park. A gradient in foliage has been observed for nitrogen (McNeil et al. 2007), and modeling suggests a similar gradient for Hg deposition (Miller et al. 2005).
- Elevation is positively correlated with Hg concentrations in soil samples and foliar samples. There is some evidence that suggests Hg deposition is higher at higher elevations (Lawson et al. 2003, Miller et al. 2005). This increased Hg deposition increases Hg concentrations in foliage and soil.
- Different tree species accumulate foliar Hg at significantly different concentrations. This pattern has been demonstrated by other studies (Bushey et al. 2008, Rea et al. 2002), and will be evident in the spatial survey. Phase 3 expands on knowledge of foliar Hg concentrations by sampling tree species that have not been previously documented.

# 4 Comparison of Mercury Dynamics between Hardwood and Conifer Forests

## 4.1 Methods

### 4.1.1 Study Site

This phase of the research was conducted at Huntington Wildlife Forest (HWF) in New York State (43.97° N, 74.22° W). The 6,000-hectare (ha) forest is operated by State University of New York College of Environmental Science and Forestry (SUNY-ESF) and is located in the central portion of the Adirondack Park near Newcomb, NY (Figure 1). The forest has been the site of numerous biogeochemical studies (e.g., Selvendiran et al. 2008, Mitchell et al. 1992, Johnson and Lindberg 1992), and serves as a monitoring station for the National Atmospheric Deposition Program (NADP) National Trends Network (NTN), Mercury Deposition Network (MDN), and EPA Clean Air Status and Trends Network (CASTNET) programs. For this study, two plots were established within the HWF, one dominated by hardwood and another dominated by coniferous trees. The hardwood plot is located within the Arbutus Lake watershed and contains species common to northern hardwood forests. The dominant canopy species within the hardwood plot are sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), and American beech (*Fagus grandifolia*), and the understory is dominated by American beech. This plot has served as a site for previous Hg studies (Bushey et al. 2008, Choi et al. 2008b, Choi and Holsen 2009). The conifer plot is located within the Rich Lake watershed and consists of a canopy dominated by white pine (*Pinus strobus*) with interspersed balsam fir (*Abies balsamea*) and eastern white cedar (*Thuja occidentalis*). The understory is relatively open due to the thick canopy with only occasional understory yellow birch and sugar maple. The two plots are approximately 2 kilometers (km) apart, and the conifer stand is directly adjacent to the NADP NTN and MDN sampling stations.

**Figure 1. Map of Forest Plot Areas at Huntington Wildlife Forest**
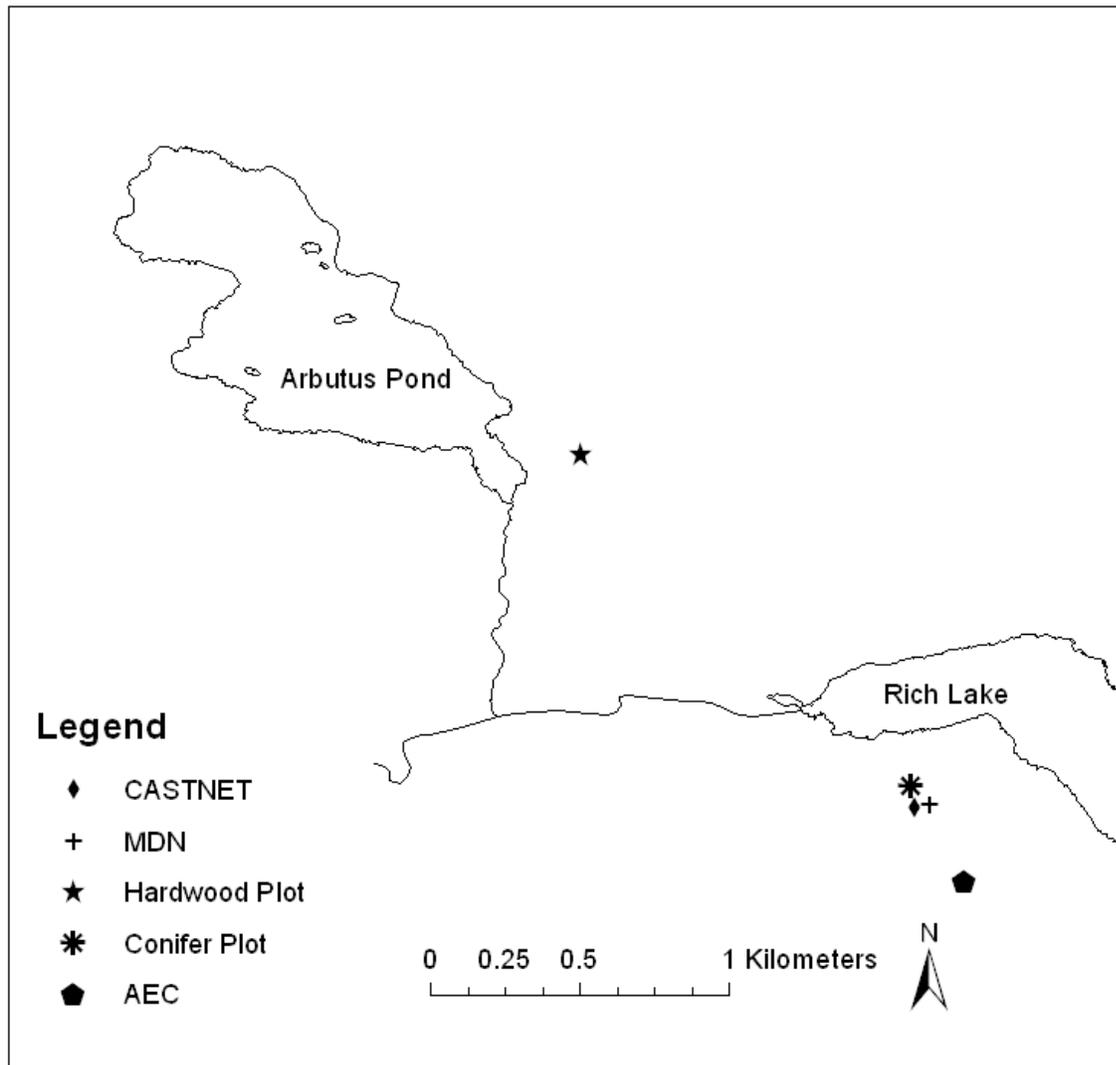


## 4.1.2 Foliar Sampling

Live foliage was sampled from dominant canopy species in both the conifer plot and hardwood plot
in 2009 and 2010. Canopy foliage, defined as foliage over 12 meters (m) in height in direct sunlight,
was sampled from three to five individual trees of each species on approximately a monthly basis
throughout the growing season. Foliage was collected by shooting canopy branches with steel shot
fired from a shotgun. Downed branches were gathered and placed in polyethylene zipper bags. All
samples were frozen within 24 hours. To avoid contamination, the shotgun operator did not gather
samples, but foliar samples were collected by an assistant wearing nitrile gloves. In 2010, foliage was

also collected from the mid-canopy (5–7 m, shaded) and understory (< 2 m). Mid-canopy foliage was collected using the same methods as canopy foliage. Understory foliage was collected using pruning shears. Within the hardwood plot, the only species present in the understory was American beech. There was little understory growth present in the conifer plot.

### 4.1.3  Litter Collection

Litter was collected from both plots using litter traps. The traps were constructed from plastic crates and were lined with plastic mesh. Five collectors were randomly deployed in both the conifer plot and hardwood plot. Hardwood traps were deployed only from May to December, and samples were collected from the traps between mid-September and early December. Conifer traps were deployed year-round but were elevated 1.5 m off the ground during the winter season so they would remain above the snowpack. Conifer litter samples were collected monthly between June and December and again in April and May of each sampling year.

### 4.1.4  Throughfall and Precipitation Sampling

Precipitation Hg was sampled weekly throughout the entirety of the project at the Huntington Wildlife Forest MDN station (NY20). This site contains a wet-only sampler in an open clearing that collects direct precipitation continuously and has operated since 1999.[6]

In addition to direct precipitation, throughfall samples were collected monthly during the growing seasons of 2009 and 2010. Throughfall collectors were constructed by attaching acid washed polyethylene funnels to Teflon collecting bottles using Teflon tubing. Bottles were placed in an opaque casing and charged with 10 milliliters (mL) of concentrated low-Hg HCl to prevent volatilization of Hg and microbial growth. Acid-washed watch glasses were placed in the opening of each funnel to prevent leaf litter and insects from entering the bottles. Five collectors were randomly placed in both the hardwood and conifer plots, and bulk throughfall samples were collected over a two- to three-week period. After collection, bottles were removed and stored at 4°C until time of analysis. Sampling funnels and tubing were rinsed with 10% low-Hg HCl between samplings to prevent carryover contamination.

Canopy interception was determined for the conifer plot by comparing throughfall collector volumes from within the plot to wet deposition volumes collected in a nearby clearing. This method was used for both rain and snow events. In addition, concentrations of Hg in throughfall and snowfall beneath the canopy were compared to concentrations in the open clearing. These data were used to calculate canopy

enrichment factors within the conifer plot. Calculations from Choi et al. (2008b) were used to calculate interception in the hardwood plot; note that the Choi et al. (2008b) research was conducted within the same hardwood stand used for this study, and their calculations for canopy interception compare well with other literature values of interception rates in northern hardwood forests (Risch et al. 2012, Demers et al. 2007, Rea et al. 2001). During the leaf-off period, hardwood interception rates and Hg enrichment factors were assumed to be zero.

### 4.1.5  Soil Profile and Evasion Sampling

Soil profiles were sampled, measured, and characterized by excavating two soil pits in each plot. The pits in the hardwood plot were excavated and characterized in 2004 (Driscoll, unpublished data). The soil pits in the conifer plot were excavated in October 2008. The soils from both plots are Spodosols (Typic Haplorthod) and have similar horizons (Oa, E, Bh, Bs1, Bs2, Bs3, C). Five replicate samples from each horizon were collected from the undisturbed wall of each soil pit, and horizon thickness was measured. Bulk density was estimated for each horizon based on averages from an extensive study of Adirondack soils that contained multiple hardwood and pine dominated plots (Bedison 2009). Soil pools were calculated by combining measurements of soil Hg concentrations, horizon thickness, and horizon bulk densities.

Soil Hg evasion was measured in the conifer plot in 2010 by researchers from Clarkson University (Thomas Holsen, John Maxwell, unpublished data). Soil Hg evasion was estimated in the conifer plot using dynamic flux chambers connected to a Tekran 2537A mercury autoanalyzer. This method has been discussed in detail in Choi and Holsen (2009). Choi and Holsen (2009) measured soil Hg fluxes in the same hardwood stand at HWF; however, they used polycarbonate flux chambers while the current study used Teflon flux chambers. Results from the conifer plot were compared to results from Choi and Holsen (2009) to explore differences in evasion processes between conifer and hardwood stands.

### 4.1.6  Meteorological and Hydrologic Variables

Meteorological (precipitation, air temperature, relative humidity, wind speed) and hydrologic measurements (flow, well height) were made continuously at the HWF.[7] The site for the meteorological measurements is immediately adjacent to the location of the hardwood plot for this study, while discharge is measured at Archer Creek in the Arbutus Pond watershed. Summary statistics of meteorological variables for the study years of 2009 and 2010 are presented in Table 1, and stream discharge is presented in Figure 2.

**Table 1. Monthly Averages of Meteorological Conditions during the Growing Season at Huntington Wildlife Forest Arbutus Monitoring Station (Precipitation Values are Monthly Totals)**

Precipitation quantity and relative humidity were greater during 2009. Air temperature was significantly higher in 2010.

| | Precipitation (mm) | | Air Temperature (°C) | | Relative Humidity (%) | | Wind speed (m/s) | |
|---|---|---|---|---|---|---|---|---|
| | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 |
| May | 137.2 | 47.5 | 10.9 | 13.3 | 65.1 | 61.5 | 1.8 | 1.4 |
| June | 82.3 | 169.7 | 14.3 | 15.7 | 78.3 | 80.0 | 1.1 | 1.2 |
| July | 101.6 | 91.9 | 15.9 | 19.4 | 82.7 | 76.4 | 1.3 | 1.0 |
| Aug | 106.9 | 70.1 | 17.3 | 17.6 | 83.8 | 76.4 | 1.0 | 1.2 |

**Figure 2. Flow Duration Curve for the Arbutus Pond Inlet during the Growing Seasons (May–September) of 2009 and 2010**
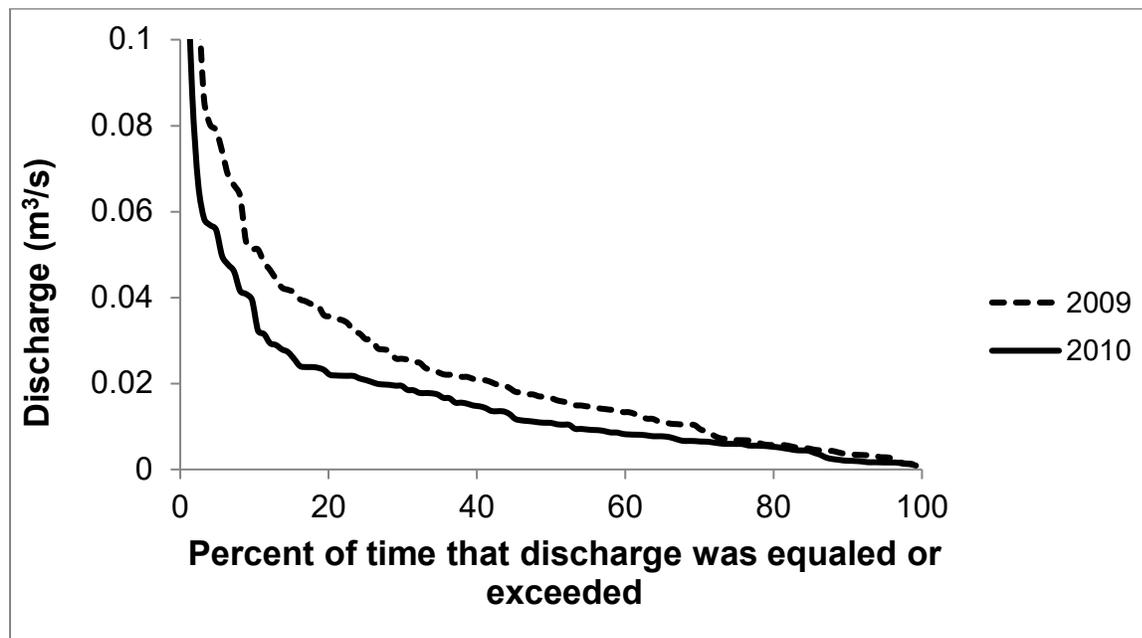


## 4.1.7  Laboratory Methods

All solid samples (foliage and soil) were transported to the laboratory at Syracuse University on ice and frozen until time of analysis. Before analysis, each sample was freeze-dried for at least 72 hours to remove moisture. Foliar samples were analyzed using a Milestone DMA-80 (Milestone, Shelton, CT), which utilizes EPA Method 7473 (EPA 1998). The instrument was calibrated using an apple leaf matrix standard (NIST 1515, 44±4 ng/g), and mussel tissue (NIST 2976, 61±3.6 ng/g) was used as an external check standard.

Soil samples were analyzed using a LECO AMA direct combustion analyzer (LECO Corp.), which also operates based on EPA Method 7473 (EPA 1998). It was calibrated using a fly-ash standard (NIST 1633b, 143±2 ng/g) and a marine sediment standard (NRC-Canada MESS-3, 91±9 ng/g) was used as an external check standard. Soil organic matter content was estimated using the loss-on-ignition method (ASTM 2000).

Aqueous samples were stored in the dark at 4°C until analysis. Samples were treated with bromine monochloride to oxidize Hg species and then analyzed using a Tekran 2600 (Tekran, Inc.) with a cold-vapor atomic fluorescence detector. The samples were analyzed according to EPA Method 1631 (EPA 2002). Calibration standards were prepared using a certified aqueous mercury reference stock solution (Ultra Scientific, 10 µg/mL) and a certified external mercury solution (NIST 1641-D). For foliage, soil, and aqueous samples, all calibration verification standards and external check standards were within 10% of the expected concentration.

## 4.1.8  Deposition Calculations and Statistics

Throughfall, litterfall, and total deposition were calculated for each plot for 2009 and 2010. To simplify calculations, each study year was established at the beginning of the growing season, which was defined as May 15. In this study, references to 2009 indicate the time period from May 15, 2009 to May 14, 2010 and references to 2010 indicate May 15, 2010 to May 14, 2011. Total Hg deposition is defined as the sum of the throughfall Hg deposition plus the sum of litter Hg deposition. Throughfall Hg deposition was calculated by multiplying throughfall Hg concentrations (ng/L) by the interception rate (%) and then by the measured precipitation quantity (cm). To account for differences in precipitation type (rain versus snow) and the presence or absence of leaves, the study year was also divided by season: spring (March 15–May 15), summer growing season (May 16–October 15), fall (October 16–December 1), and winter (December 2–March 14), and the totals from all seasons were summed to calculate annual total deposition. For the months that throughfall data were collected, monthly deposition was computed based on measured Hg concentrations. For the months that throughfall was not collected, precipitation quantity and Hg concentrations measured at the MDN station were multiplied by interception factors and enrichment factors to calculate approximate deposition to each plot.

Litterfall Hg was calculated based on litterfall mass and foliar Hg concentrations for each tree species. Because litter could not be feasibly collected from traps regularly and because rain, dew, and snow could increase Hg concentrations in litter samples (Demers et al. 2007), litter Hg concentrations were determined from regressions of foliar Hg accumulation as a function of time over the growing season.

Foliar Hg accumulation in hardwoods has been shown to be approximately linear throughout the growing season (Bushey et al. 2008, Rea et al. 2002), so foliar Hg concentrations were estimated using linear regression. For hardwood species, the growing season was approximated to be 155 days from bud-break to litterfall. Because white pine typically carries two age classes of needles, the period of foliar Hg exposure was assumed to be two years (730 days). The contribution of different age classes to litter from balsam fir and eastern white cedar is not well understood, so an exposure period of three years (1095 days) was used so that calculated litter Hg fluxes would represent conservative estimates.

Wet Hg deposition was assumed to be equivalent to the measured deposition at the MDN station. Dry Hg deposition was calculated by summing the throughfall Hg deposition and the litter Hg deposition and then subtracting the wet Hg deposition from the total. Dry Hg deposition was defined for each plot as $THg_{Throughfall} - THg_{Precipitation} + THg_{Litterfall}$. This approach has been used by previous studies to estimate dry Hg deposition (Graydon et al. 2008, Driscoll et al. 2007). For each plot, total Hg deposition was subdivided into percent wet deposition and percent dry deposition.

One-way ANOVA was used to test differences in foliar Hg concentrations among species and among different canopy heights. Student's t-test was used to examine differences in throughfall concentrations between the hardwood and conifer plot. For all tests, significance was determined at $\alpha \leq 0.05$. All statistical analyses were performed using IBM-SPSS Statistics 19.0.

## 4.2 Results

### 4.2.1 Foliar Mercury Accumulation and Litter Fluxes

Mercury concentrations in live foliage increased throughout the growing season for all species in both 2009 and 2010 (Figure 3). Increases in foliar Hg were relatively linear throughout the growing season for both years, indicating a consistent accumulation of Hg in foliage. The rate and pattern of foliar Hg accumulation were different for the two growing seasons, but in general, patterns showed that rates of Hg accumulation in deciduous species were over five times greater than conifer species (Table 2). Within the hardwood plot, all canopy species showed similar Hg uptake rates and patterns in 2010; however, in 2009, American beech had a higher Hg concentration than both sugar maple and yellow birch by the end of the growing season, although this difference was just outside the limits of statistical significance (*p=0.093*). Mercury accumulation rates in coniferous foliage were greatest in white pine (0.040 ng/day), followed by balsam fir (0.031 ng/day) and eastern white cedar (0.023 ng/day).

**Figure 3. Mercury Concentrations in Foliage of Hardwood Species over the Growing Seasons of 2009 and 2010**

AB—American Beech, SM—Sugar Maple, and YB—Yellow Birch
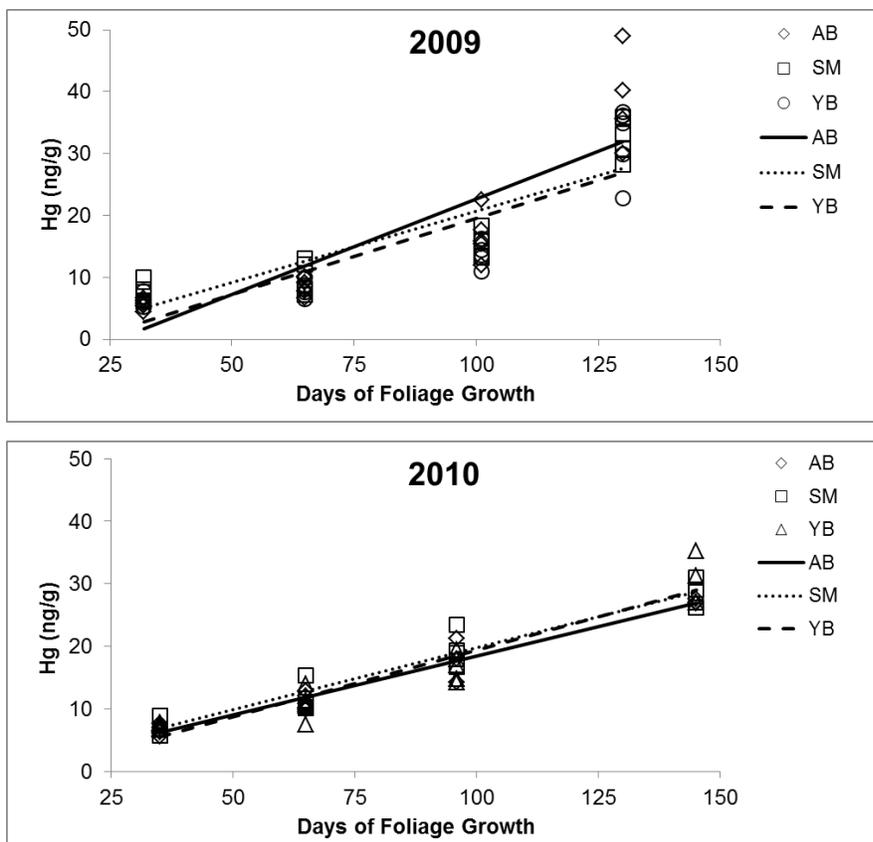


**Table 2. Mean Daily Hg Accumulation Rate (ng/g-d) and Litter Hg Concentration at Time of Senescence (ng/g) for Tree Species for 2009 and 2010**

Error measurements represent standard deviation.

| Species | Daily Hg Accumulation (ng/g-d) | Litter Hg Concentration (ng/g) |
|---|---|---|
| American Beech | 0.235±0.038 | 36.5±5.9 |
| Sugar Maple | 0.207±0.023 | 32.0±3.6 |
| Yellow Birch | 0.207±0.027 | 32.1±4.2 |
| Balsam Fir | 0.031±0.002 | 33.6±2.19 |
| White Pine | 0.040±0.002 | 29.4±1.46 |
| Eastern White Cedar | 0.023±0.002 | 24.7±2.21 |

Canopy position significantly influenced foliar Hg concentrations within the hardwood plot. Upper canopy foliage (sun leaves) had the lowest mean concentrations, although the differences were not significantly different from mid-canopy foliage. Because American beech was the only species present in the understory, it was the only species for which three heights were compared. Results of one-way ANOVA followed by Tukey's test revealed that understory Hg concentrations were significantly higher than both mid-canopy and upper-canopy samples. Canopy position did not have significant effect on foliar Hg concentrations early in the growing season, but the differences in Hg concentrations among the different heights were significant for both July ($F_{(2,8)}=24.9, p<0.001$) and August ($F_{(2,6)}=19.3, p=0.002$) (Table 3). Canopy position did not have a significant effect on foliar Hg concentrations in the conifer plot; however, there were limited understory trees present in the conifer plot.

**Table 3. Concentrations of Foliar Hg (ng/g) by Hardwood Species, Month, and Canopy Position in 2010**

* = significant difference from other canopy positions of the same species and month.

| Species | Canopy Position | June Hg (ng/g) | July Hg (ng/g) | August Hg (ng/g) |
|---|---|---|---|---|
| American Beech | Low | 17.3 | 28.6* | 38.5* |
| | Mid | 8.6 | 15.6 | 24.8 |
| | High | 6.6 | 11.2 | 17.8 |
| Sugar Maple | Low | ----- | ----- | ----- |
| | Mid | 7.7 | 13.9 | 21.5 |
| | High | 7.6 | 11.7 | 19.6 |
| Yellow Birch | Low | ----- | ----- | ----- |
| | Mid | 7.7 | 13.4 | 16.0 |
| | High | 7.2 | 10.8 | 16.7 |

Litterfall was measured for both the 2009 and 2010 growing seasons in the conifer and hardwood plots. Total litterfall mass in the hardwood plot was 294±38 g/m$^2$ and 230±16 g/m$^2$ for 2009 and 2010, respectively. The species contributions to litterfall were consistent between the two years with American beech contributing 59% and 62%, sugar maple contributing 24% and 22%, and yellow birch contributing 17% and 16%, respectively. Conifer litter mass was greater than hardwood litter mass in both sampling years, with averages of 325±22 g/m$^2$ and 289±84 g/m$^2$ in 2009 and 2010, respectively. Litterfall in the conifer stand was dominated by white pine, which contributed 70% of total litter mass. Mixed hardwoods that were interspersed throughout the conifer plot contributed an additional 22%, while balsam fir and eastern white cedar each contributed approximately 4% to litter mass.

Total litterfall Hg deposition to the forest floor was calculated for each plot and for each sampling year. For the 2009 and 2010 sampling years, total Hg litterfall deposition was similar between the two plots (Figure 4). Although the total litterfall Hg was approximately equal, litterfall contributed a significantly greater percentage of the total Hg deposition in the hardwood plot. Litter accounted for 65% and 47% of the total Hg deposition in 2009 and 2010 in the hardwood plot compared to 50% and 21% in the conifer plot.

**Figure 4. Contributions of Throughfall and Litterfall to Total Hg Deposition to Hardwood and Coniferous Plots at HWF for 2009 and 2010**
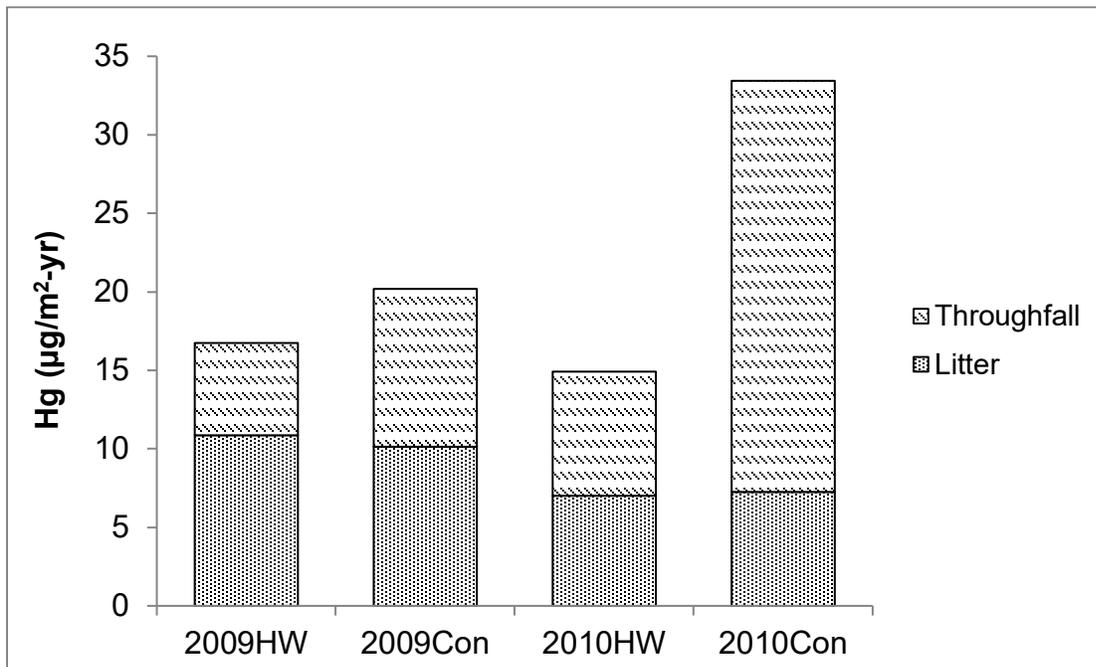


## 4.2.2  Precipitation, Snow, and Throughfall Mercury

Total Hg concentrations in throughfall were greater than in open precipitation samples in both the 2009 and 2010 growing seasons (Figure 5). Volume-weighted average Hg concentrations for throughfall were 2.0 and 3.7 times higher than precipitation in the conifer plot and 1.29 and 1.20 times higher in the hardwood plot in 2009 and 2010, respectively. When comparing throughfall concentrations between the conifer and hardwood plots, differences were statistically significant for every sampling period of both sample years.

**Figure 5. Mean Hg Concentrations in Wet Deposition, Hardwood Throughfall, and Coniferous Throughfall from 2009 and 2010**

Error bars represent standard errors. Wet Hg deposition measurements are taken from a single collector at the MDN station and have no error measurement.
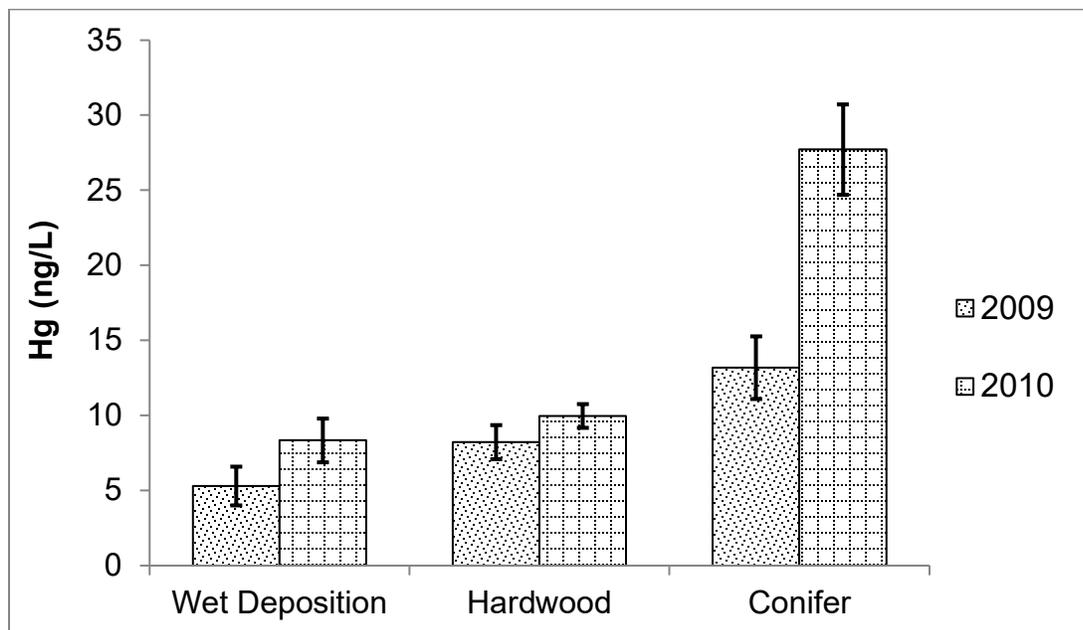


Total Hg concentrations in snow were measured twice beneath the canopy (throughfall) in the conifer plot and in a nearby open clearing. When compared to snow samples from the open clearing, snow throughfall Hg concentrations were enriched by 50% (1.49 vs. 2.24 ng/L) and 128% (0.7 vs. 1.6 ng/L). Interception of snow by the canopy was consistent for both sampling events, as snowfall volumes beneath the canopy were measured at 78% and 74% of volumes from the clearing.

Wet deposition was calculated for the MDN (direct precipitation), hardwood, and conifer plots for both sampling years. Wet deposition at the MDN station was 6.0 and 7.5 $\mu$g/m$^2$-yr for the 2009 and 2010 sampling years, respectively. Throughfall within the hardwood plot was nearly identical to wet deposition, with calculated Hg fluxes of 5.9 and 7.9 $\mu$g/m$^2$-yr in 2009 and 2010, respectively. Throughfall Hg within the conifer plot was considerably higher than both wet deposition and throughfall deposition in the hardwood plot. The calculated throughfall Hg flux of 10.1 $\mu$g/m$^2$-yr in the conifer plot in 2009 was about 72% higher than the calculated wet deposition and throughfall to the hardwood plot. The difference was even greater in 2010, due to effects of year-to-year meteorological variation (see discussion in section 4.3.4), as the conifer throughfall total of 26.2 $\mu$g/m$^2$-yr of wet deposition was over three times greater than throughfall Hg deposition in the hardwood plot.

### 4.2.3 Mercury in the Soil Profile

Total Hg concentrations in soil were measured from two soil pits that were excavated in the conifer plot. Conifer soil Hg concentrations were compared to concentrations in hardwood soil pits that were excavated in 2005 (Driscoll, unpublished data) (Figure 6). Soil samples were collected from Oa, Bh, Bs1, Bs2, Bs3, and C horizons in each soil pit. Total Hg concentrations were lower in the coniferous plot than in comparable horizons in the hardwood plot, although the differences were not significant. Both plots showed a pattern of decreasing total Hg concentrations with increasing depth from the surface organic layers downward through the mineral soil (Figure 6).

**Figure 6. Soil Horizon Profiles of Mean Total Hg Concentrations and Standard Deviations from the Hardwood and Conifer Plots**
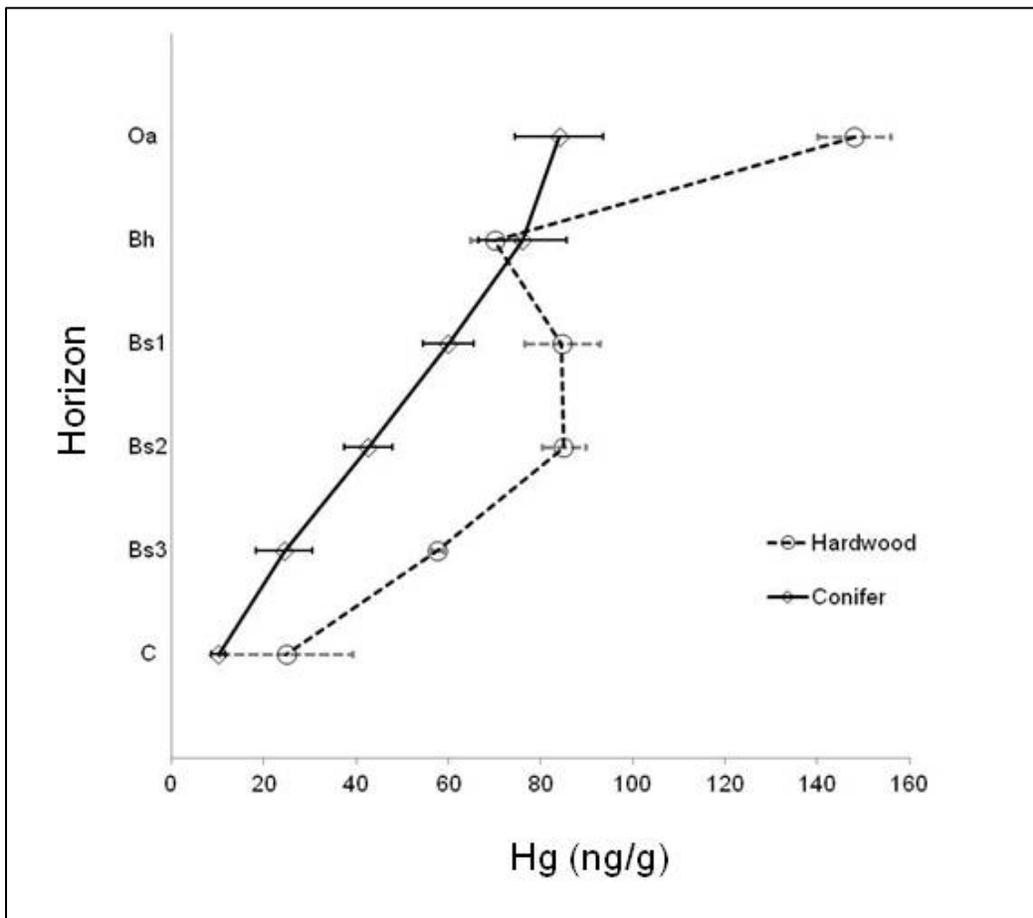
Estimated Hg pools were calculated based on estimated bulk densities and horizon thickness to an assumed depth of 1 m. The total Hg pools in the top three horizons (Oa, Bh, Bs1) were similar between the two plots, with a total of 13.9 mg/m$^2$ in the conifer plot and 12.5 mg/m$^2$ in the hardwood plot (Table 4). Mercury pools in the Oa horizon were approximately 25% greater in the hardwood plot than the conifer plot (3.7 vs. 2.8 mg/m$^2$), but Bh horizon pools in the conifer plot were approximately double hardwood pools (5.5 vs. 2.7 mg/m$^2$). Overall, hardwood soils had greater pools of Hg (40.6 vs. 33.8 mg/m$^2$) due to the higher concentrations of Hg in the Bs3 and C horizons, which despite having the lowest concentrations of any horizons, contribute substantially to the overall pool of soil Hg due to their large mass. Note that error estimates were not calculated for soil pools, but because of high variability in soil Hg concentrations, horizon thickness, and bulk density, calculated soil pools from this study have a high degree of uncertainty.

**Table 4. Soil Hg Concentrations and Pools for Different Horizons**

Soil profiles were calculated on an assumed total depth of 1 m. Bulk density values are estimated from measurements of Bedison (2009). Error measurements are standard deviation.

| Horizon | Hardwood | | | | Conifer | | | |
|---|---|---|---|---|---|---|---|---|
| | Hg (ng/g) | Bulk Density (g/cm$^3$) | Thickness (cm) | Pool (mg/m$^2$) | Hg (ng/g) | Bulk Density (g/cm$^3$) | Thickness (cm) | Pool (mg/m$^2$) |
| Oa | 148±8 | 0.28 | 9 | 3.7 | 84±20 | 0.39 | 8.5 | 2.8 |
| Bh | 70±5 | 0.54 | 7 | 2.7 | 76±15 | 0.73 | 10.0 | 5.5 |
| Bs1 | 85±8 | 0.60 | 12.0 | 6.1 | 59±7 | 0.80 | 12.0 | 5.6 |
| Bs2-C | 56±15 | 0.75 | 72 | 28.1 | 34±10 | 0.83 | 69.5 | 19.9 |
| Total | --- | --- | --- | 40.6 | --- | --- | --- | 33.8 |

## 4.2.4  Soil Hg Evasion

Gaseous emissions of elemental mercury (Hg$^0$) from the soil surface to the atmosphere were monitored during the fall of 2009 and the spring and summer of 2010, and these results were compared to the rates at the hardwood plot at the HWF described in Choi and Holsen (2009) (Table 5). Soil evasion was considerably lower in the conifer plot than the hardwood plot, with the summer being the only season that Hg$^0$ showed net release from the soil. The negative net evasion values for the fall and spring sampling suggest that the soil at the conifer site was not a net source of Hg$^0$ but absorbed Hg$^0$ during these sampling periods. Hg$^0$ emission fluxes were positively correlated with air temperature and solar radiation in both plots but were negatively correlated with relative humidity for most sampling periods.

**Table 5. Seasonal and Annual Hg⁰ Evasion Fluxes from the Soil Surface in the Hardwood and Conifer Plots**

Hardwood fluxes were determined by Choi and Holsen (2009).

| Season | Hardwood | | | | Conifer | | | |
|---|---|---|---|---|---|---|---|---|
| | Spring $(ng/m^2\cdot h)$ | Summer $(ng/m^2\cdot h)$ | Fall $(ng/m^2\cdot h)$ | Annual $(\mu g/\ m^2\text{-yr})$ | Spring $(ng/m^2\cdot h)$ | Summer $(ng/m^2\cdot h)$ | Fall $(ng/m^2\cdot h)$ | Annual $(\mu g/\ m^2\text{-yr})$ |
| Mean | 1.55 | 1.46 | 0.82 | 7.0 | -0.04 | 0.39 | -0.68 | -1.0 |
| Maximum | 27.10 | 5.26 | 4.12 | --- | 4.20 | 6.65 | 3.63 | --- |
| Minimum | -2.49 | -1.34 | -1.92 | --- | -2.09 | -3.20 | -2.44 | --- |

## 4.2.5 Total Net Hg Fluxes

Based on results from 2009 and 2010, the mean total Hg deposition into the hardwood plot was 15.9 µg/m²-yr, while the mean total deposition to the conifer plot was 26.8 µg/m²-yr (Figure 4). This difference was largely due to the greater throughfall inputs in the conifer plot in 2010. Dry deposition was the dominant pathway of Hg deposition to the conifer plot in both 2009 and 2010 (71% and 78% of total) (Figure 7). For the hardwood plot, dry deposition was the dominant Hg deposition pathway in 2009 (69%), but wet and dry deposition were essentially equal in 2010 (51% wet, 49% dry). For the leaf-on period only (May-October), dry deposition was the dominant Hg pathway to the hardwood plot, accounting for 79% of total deposition in 2009 and 68% in 2010.

**Figure 7. Dry and Wet Mercury Deposition for Hardwood and Conifer Plots for 2009 and 2010**

Dry deposition was calculated as $Hg_{Throughfall} - Hg_{Precipitation} + Hg_{Litterfall}.$
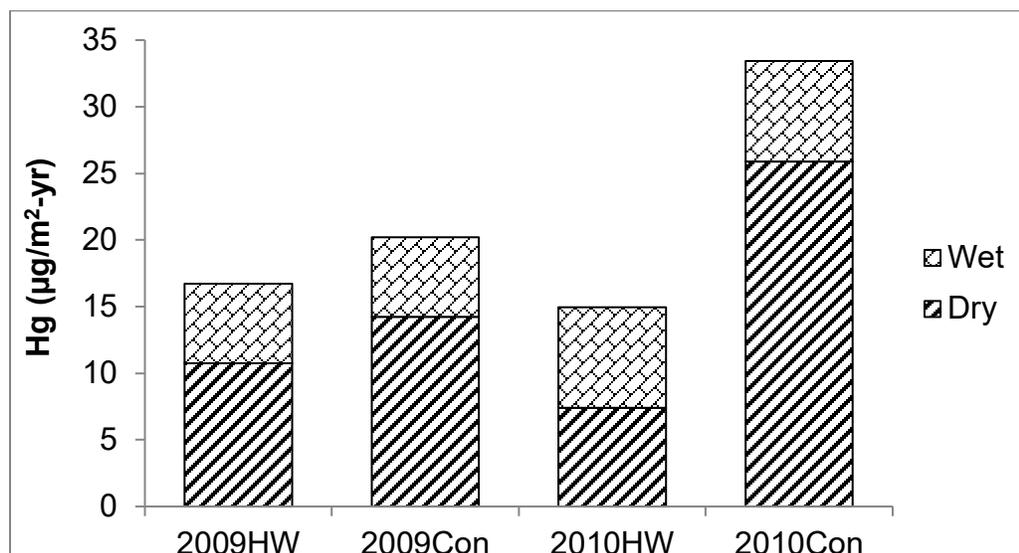
When combining fluxes with net soil evasion, the difference in net Hg deposition between the plots becomes even more evident (Figure 8). The hardwood plot released an estimated 7 $\mu g/m^2$-yr of $Hg^0$ through soil evasion, resulting in net total Hg deposition for the plot of 8.9 $\mu g/m^2$-yr. In contrast, the conifer plot had net deposition of $Hg^0$ rather than evasion, resulting in an estimated net total Hg deposition of 27.8 $\mu g/m^2$-yr.

**Figure 8. Conceptual Illustration of Hg Inputs ($\mu g/m^2$-yr), Evasion ($\mu g/m^2$-yr), and Soil Hg**
**Pools ($mg/m^2$) in Hardwood Plot and Conifer Plot at Huntington Wildlife Forest**



| | Soil Pools | |
|---|---|---|
| 3.7 | Oa | 2.2 |
| 2.7 | Bh | 5.5 |
| 34.2 | Mineral Soil | 25.5 |
| 40.6 | Total Soil Pool | 33.2 |
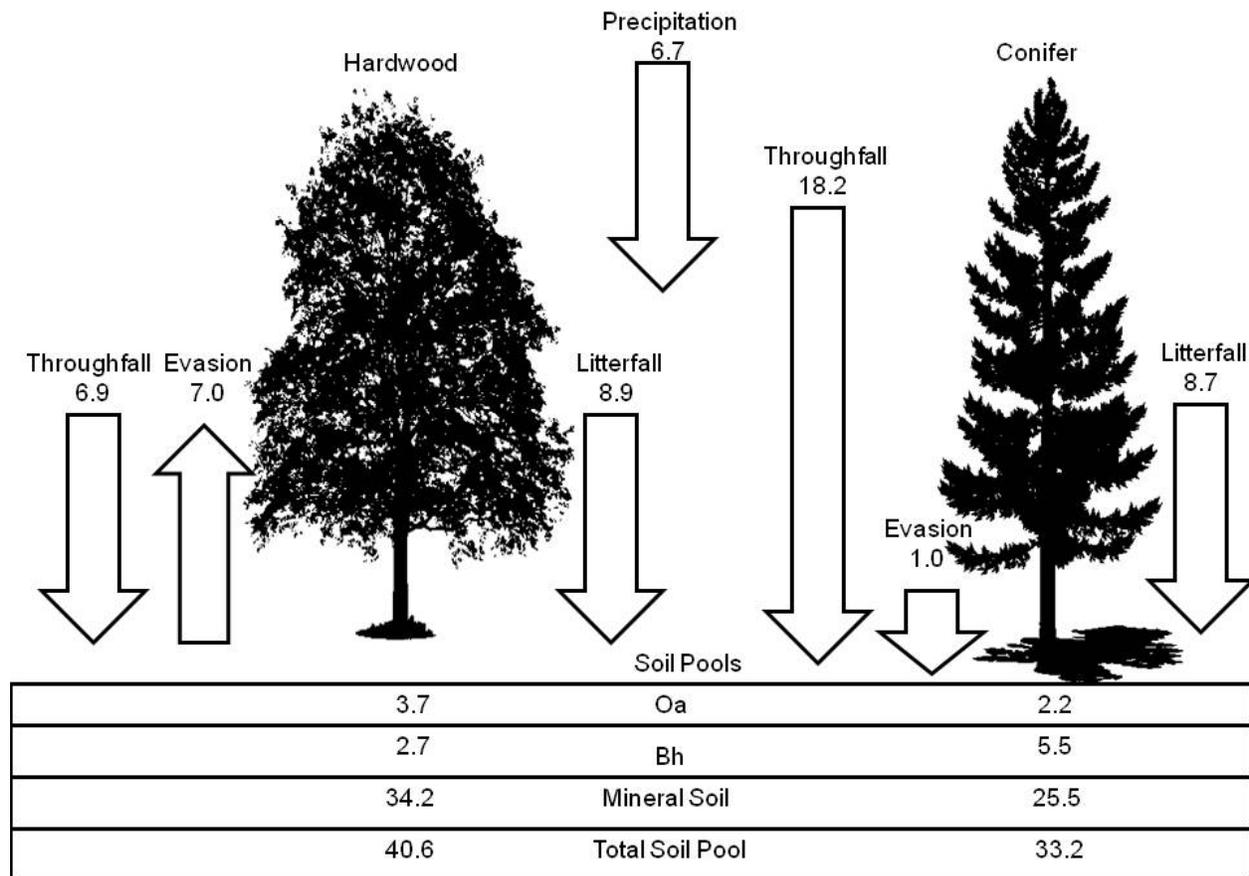
A simple comparison of Hg deposition via throughfall and litterfall relative to total deposition provide an approximate estimate of relative contributions of reduced ($Hg^0$) and oxidized ($Hg^{2+}$) Hg to ecosystem deposition. Throughfall is thought to be largely $Hg^{2+}$ inputs (Rea et al. 2001), and 68% of Hg in the conifer plot in 2009–2010 was deposited via throughfall, indicating the majority of Hg was deposited

as $Hg^{2+}$. In contrast, only 43% of Hg deposition in the hardwood plot was due to throughfall, while the remainder was due to litterfall. Litter is assumed to contribute mostly $Hg^0$, suggesting that the majority of deposition (57%) in the hardwood plot was likely deposited as $Hg^0$ through litterfall.

## 4.3 Discussion

### 4.3.1 Foliar Mercury and Litter Dynamics

Foliar Hg concentrations and uptake rates varied among different tree species. Previous studies have documented that the majority of Hg that accumulates in foliage is of atmospheric origin (Bushey et al. 2008, Ericksen et al. 2003, Rea et al. 2001, Rasmussen 1995), although a fraction could be due to recycled Hg from recent soil Hg evasion (see below). Within the hardwood species, there were significant differences among tree species. American beech leaves had higher concentrations of Hg than other hardwood species in 2009, a pattern consistent with other studies (Bushey et al. 2008, Rea et al. 2002). Substantial differences were evident between hardwood and conifer species. Daily Hg accumulation rates in hardwood species were approximately five to seven times higher than conifer species. This finding is consistent with other studies that have measured lower Hg uptake in conifer species than in hardwood species (Hanson et al. 1995). Conifers generally fix carbon at a lower rate than deciduous species (Catovsky et al. 2002). Although values are highly variable among species, average stomatal conductance is also generally lower in conifers (Medlyn et al. 2001). These characteristics imply that at a uniform concentration of atmospheric Hg, hardwoods would cycle more $Hg^0$ through their leaves than conifers, effectively increasing their Hg exposure. This physiological difference could account for the large differences in Hg uptake between hardwood and conifer foliage.

Canopy position has a statistically significant effect on foliar Hg concentrations, as understory foliage has significantly higher Hg concentrations than overstory foliage. Previous studies have shown similar results (Bushey et al. 2008), and these differences have been attributed to differences in photo-volatilization due to attenuation of solar radiation through the canopy; physiological differences in overstory and understory leaves; and greater uptake of soil-evaded Hg by the understory. All these mechanisms are likely contributing factors to differences in Hg accumulation at different canopy positions.

Understory leaves are located nearer to the soil, and soil evasion could increase the concentration of $Hg^0$ near the soil surface. Previous research has shown that foliage exposed to higher atmospheric $Hg^0$ concentrations accumulates proportionally greater Hg concentrations (Ericksen and Gustin 2004). Other evidence from the Adirondack region shows a correlation between soil Hg concentrations and Hg

accumulation in understory foliage (Blackwell, unpublished data). Whether or not understory Hg concentrations are derived from local soil evasion is an important issue for the estimation of Hg deposition to forests, as evaded soil Hg from a forest stand would not represent a new source of Hg but rather recycling of previously deposited Hg. Although understory foliage contributes a relatively small quantity to the total litter mass, if the enhanced foliar concentrations are due to the efficiency of understory leaves capturing atmospheric Hg or lower photo-volatilization from understory leaf surfaces, the Hg from understory vegetation would be a source of "new" mercury, and Hg fluxes from this study and others would be incorrectly characterizing the true Hg deposition due to litterfall.

### 4.3.2  Throughfall Concentrations and Fluxes

Increased concentrations of Hg in hardwood throughfall compared to open precipitation have been documented in many studies (e.g. Choi et al. 2008b, Rea et al. 2001, Rea et al. 1996). However, few have examined throughfall enrichment by conifers (St. Louis et al. 2001, Kolka et al. 1999). In this study, throughfall in the conifer plot contained significantly higher Hg concentrations than both wet deposition and throughfall from the hardwood plot. Kolka et al. (1999) also measured throughfall Hg in conifers, finding that coniferous throughfall deposition was approximately double open precipitation deposition. This enrichment compares well with our measurements in 2009, but the difference was even greater in 2010 as conifer throughfall deposition was 3.7 times greater than wet deposition. Because forest canopies decrease the volume of precipitation that reaches the forest floor, the effect of throughfall Hg concentration enrichment is partially offset by water quantity losses due to interception. Deposition calculations from this current study suggest that canopy Hg enrichment and interception water losses essentially offset one another in the hardwood stand, which compared well with previous wet deposition estimates from Huntington Wildlife Forest (Choi et al. 2008b). Despite the conifer forests having a slightly higher interception rate than the hardwood forest, there was a much greater canopy enrichment effect resulting in significantly greater Hg throughfall flux compared to wet deposition.

Even though hardwood foliage apparently takes up greater amounts of atmospheric $Hg^0$, evidence indicates that conifers are more effective at removing $Hg^{2+}$ from the atmosphere than deciduous canopies (Kolka et al. 1999). This $Hg^{2+}$ is not immobilized by the canopy and is washed from the needles during precipitation events. Leached $Hg^{2+}$ may be complexed with DOC exuded from needle surfaces, as there is a strong correlation between DOC and Hg concentrations in throughfall samples (section 5; Kolka et al. 1999). $Hg^{2+}$ is estimated to make up only about 3% of total gaseous Hg concentrations in Upstate New York (Han et al. 2004), but it is thought to contribute substantially to dry Hg deposition (Lindberg and

Stratton 1998, Driscoll et al. 2007). Because of their solubility, $Hg^{2+}$ and DOC are readily leached from needle surfaces. The source of DOC in throughfall samples is likely to be from the canopy because DOC concentrations in throughfall are elevated over bulk deposition measurements for northeastern U.S. forests (Likens et al. 1983).

### 4.3.3 Accumulation of Mercury in the Soil Profile

Inputs of Hg from throughfall and litterfall are eventually deposited to the forest floor and potentially incorporated into the soil layers. Both stands showed enrichment of Hg from the litter layer (Oi/Oe) to the organic humus (Oa) layer, which is likely due to a combination of mass loss due to decomposition, soil surface Hg evasion, and sorption of Hg inputs from throughfall in the Oa horizon (Demers et al. 2007). Coincident with an increase in Hg, a decrease in the organic carbon content from Oi/Oe to the Oa horizon was observed. However, this mass loss of carbon is not sufficient to explain the increase in Hg from the Oi/Oe to the Oa layer. The balance of the increase is likely from Hg inputs due to throughfall percolation through the soil profile and subsequent adsorption of Hg. The mass-balance of Hg due to loss of litter mass and inputs from throughfall has been outlined in detail in Demers et al. (2007), and while throughfall Hg could sufficiently account for soil Hg enrichment within conifer plots, it was an insufficient source to totally account for Hg increases in hardwood soils (Demers et al. 2007).

The forest stands used in this study are on similar soils with common characteristics, and as a result, it would be expected that increased Hg fluxes to the conifer plot would result in greater accumulation of Hg in the soil profile than in the hardwood plot. However, soil Hg concentrations were not significantly different between the hardwood and conifer plots despite the substantially higher Hg loading of the conifer plot's forest floor. Calculated Hg pools within the upper soil layers (Oa, Bh, and Bs1 layers) were also similar between the two plots (Table 4). A similar pattern across hardwood and conifer plots was reported by Demers et al. (2007), and they hypothesized that this discrepancy may be offset by greater rates of $Hg^0$ evasion from soils under conifer stands. However, very low rates of $Hg^0$ evasion were observed in the conifer stand at the HWF. The lower soil $Hg^0$ emissions are likely partially due to the dense, year-round canopy of the conifer plot, since solar radiation and increased temperatures stimulate evasion of Hg from the soil surface (Choi and Holsen 2009). This discrepancy of greater Hg inputs but lower soil Hg storage and evasion than the hardwood stand suggests there is an additional loss mechanism of Hg from the conifer stand. Some of this loss might be due to uptake of Hg by woody

structures in trees. In western North America, some conifer species have been shown to store significantly more Hg in roots and stems than hardwood species (Obrist et al. 2012). If a similar pattern occurs for white pine and northern hardwood species, this mechanism could account for a portion of the discrepancy in Hg mass balance between the stands.

Another potential pathway is enhanced drainage losses through soil solutions. Drainage is generally considered to be a relatively minor loss mechanism of Hg in forest stands (Demers et al. 2007). Transport of Hg in soil solutions is correlated with DOC, and soil solutions from conifer stands have been shown to have significantly higher concentrations of DOC than hardwood stands (Kalbitz et al. 2000). Mercury concentrations in soil solutions are rare in the literature, but DOC concentrations in soil solutions are measured more frequently in biogeochemical studies. One of the most detailed studies of soil solution chemistry from forests of the Northeast has been conducted at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. One analysis of soil solutions from a 12-year period at HBEF found that DOC concentrations were substantially higher in soil solutions from coniferous plots than in hardwood plots (Oa, Bh, and Bs layer solutions), and nearby streams draining coniferous areas also exhibited elevated DOC (Dittman et al. 2007). This literature suggests that Hg losses by drainage could be greater in conifer stands than in hardwoods. During high-flow rain events or snowmelt, drainage fluxes are amplified further. Concentrations of DOC and Hg increase in streams and rivers as soil solutions rapidly drain from soil profiles (Demers et al. 2010, Schuster et al. 2008). Aquatic ecosystems that drain watersheds largely composed of coniferous forest species may be at a higher risk of Hg contamination than aquatic ecosystems in largely hardwood forested watersheds. Previous research has shown that a large portion of DOC in Adirondack lakes is derived from terrestrial sources (Canham et al. 2004). In addition, one landscape level study found a correlation between percent coniferous land cover and watershed export of DOC (Aitkenhead-Peterson et al. 2007), while another found elevated Hg concentrations in ecoregions that contain high percentages of coniferous land cover (Drenner et al. 2011). Coniferous land cover could potentially be an important variable in Hg availability to a watershed, and future landscape-level studies may benefit from exploring this connection.

Contributions of wet and dry deposition to total Hg deposition were similar between this study and others in similar forests. A regional model of Hg deposition projected approximately 67% dry deposition and 33% wet deposition in the Adirondack region (Miller et al. 2005). St. Louis et al. (2001) found that dry deposition was the most significant pathway of Hg inputs despite the low atmospheric $Hg^{2+}$ concentrations in the Experimental Lakes Area of Canada. Litterfall accounted for the majority of

dry Hg deposition and is an important source of Hg to the forest floor, especially in hardwood stands. Dry deposition during the leaf-on period accounted for an even greater percentage of total Hg deposition when compared to the entire year, suggesting that dry Hg deposition and litter Hg deposition could be greater at lower latitudes due to the prolonged growing season and leaf-on period.

Elemental $Hg^0$ and reactive $Hg^{2+}$ cycle differently through compartments of the forest ecosystem. In addition to estimating wet and dry components of Hg deposition, quantifying inputs of Hg species also contributes to our understanding of Hg cycling within the forest ecosystem. Over the entire study period, litterfall accounted for 56% of Hg deposition in the hardwood stand and 28% in the conifer. Deciduous litterfall Hg is assumed to be $Hg^0$ derived from the atmosphere that was retained by foliage during the growing season. Hanson et al. (1995) suggested that at atmospheric $Hg^0$ concentrations of less than 1.5 ng/m$^3$, foliage will re-emit $Hg^0$ to the atmosphere, but this re-emission mechanism was not supported by results of this study. Despite average atmospheric $Hg^0$ concentrations below 1.5 ng/m$^3$ at HWF (Yu et al. 2013), foliage steadily accumulated Hg throughout the growing season, indicating that Hg in foliage is bound and remains bound through litterfall until released through soil decomposition processes. This hypothesis is supported by research that shows that early stages of leaf decomposition do not readily release Hg from litter but rather accumulate Hg inputs (Demers et al. 2007). In contrast to the hardwood plot, the conifer plot received Hg largely via throughfall, which is likely in the form of $Hg^{2+}$. Because of its volatility and solubility, $Hg^{2+}$ is more readily leached from the soil profile or cycled through ecosystem processes. It is not clear if these contrasting pathways of Hg inputs have implications for pathways of Hg losses and subsequent effects on watersheds and aquatic ecosystems.

### 4.3.4  Meteorological Variation and Climate Influence

Considerable year-to-year variability in foliar and throughfall Hg concentrations was evident between the 2009 and 2010 sampling years. Foliar Hg concentrations from Huntington Wildlife Forest in 2004 and 2005 (Bushey et al. 2008) compared well to 2009 values, but 2010 concentrations were appreciably lower. This response might be explained by differences in meteorology between the 2009 and 2010 growing seasons. Precipitation totals were lower during the 2010 growing season than in 2009, and higher air temperatures in 2010 likely led to higher moisture deficits (Table 1). In addition, the Adirondack region was experiencing a period of abnormally dry conditions in the months of April and May 2010 (U.S. Drought Monitor, droughtmonitor.unl.edu). Stream discharges are closely related to soil moisture (Groffman et al. 2012), and stream discharge patterns indicate that 2009 was characterized

by more even precipitation and steadier discharges, while 2010 had high-intensity rain events followed by prolonged periods of dryness and low discharge, likely indicating lower soil moisture (Figure 2). The pre-growing season dryness coupled with lower precipitation totals and higher air temperatures during the 2010 growing season likely led to low-soil moisture and possible water stress in the forest plots. Both conifers and hardwoods show decreases in transpiration and stomatal uptake in response to moisture deficits (Maier and Teskey 1992, Irvine et al. 1998, Leuzinger et al. 2005). Foliar uptake of Hg is likely coupled with stomatal gas exchange, so decreases in gas uptake due to drought stress in 2010 likely contributed to the lower Hg accumulation in foliage.

Changes in foliar uptake in response to variation in meteorological conditions may have important implications for changes in Hg deposition and cycling due to $CO_2$-induced climate change. Climate change is expected to increase global temperatures and alter weather patterns. Increased $CO_2$ could potentially increase soil storage capacity of Hg through increases in soil organic matter (Natali et al. 2008). In the northeastern United States, climate change is also expected to increase precipitation quantity and variability, cause lower snowpack and earlier snowmelt, increase transpiration, and decrease soil moisture during the growing season (Hayhoe et al. 2008, Plummer et al. 2006). If such a decrease in soil moisture was sufficient to increase the occurrence of drought stress, the result could be an overall decrease in Hg litter deposition due to decreased foliar Hg uptake and subsequent litterfall deposition. This change would be particularly important in hardwood forests, where litter deposition is the primary input of Hg into the forest floor. Hg litter deposition in the hardwood plot in 2010 was about 30% less than in 2009 due to decreases in both litter mass and foliar Hg concentrations, indicating that climatic variability could have a demonstrable impact on Hg litterfall deposition.

The conifer plot also exhibited a decrease in litterfall Hg in 2010, but despite this decrease, dry Hg deposition in the conifer plot increased over 60% in 2010 versus 2009 due to higher Hg concentrations in throughfall. Concentrations of Hg in throughfall have shown positive correlation with the duration of dry weather preceding a rain event (Rea et al. 2002, Choi et al. 2008b), and the average period between rain events in 2010 was longer than 2009 (68 rain free growing-season days in 2010, 54 in 2009). Warm temperatures and dry weather also increase atmospheric $Hg^{2+}$ concentrations (Han et al. 2004), and ambient air measurements of $Hg^{2+}$ at Huntington Wildlife Forest in 2010 were much greater than in 2009 (RGM + $Hg_p$ was 1.7 and 6.0 $pg/m^3$ for 2009 and 2010, respectively; Yu et al. 2013). Conifer needles with high leaf area index are more efficient at collecting $Hg^{2+}$ from the atmosphere than hardwood leaves. The implications of this pattern are that an increased interval between precipitation

events and higher temperatures would likely increase Hg deposition to conifer forests by increasing $Hg^{2+}$ adsorption and wash-off, leading to increased throughfall Hg concentrations and deposition. Note that this variation in meteorological conditions, while apparently decreasing Hg inputs to the hardwood stand, increased Hg inputs to the conifer stand. This pattern suggests that there could be a shift in Hg input pathways and deposition quantities to forests under changing climatic conditions, and watershed composed largely of coniferous forests could receive greater Hg loading under the expected future climate conditions.

## 4.4   Conclusions

Overall, the results of this phase of the study demonstrate that both hardwood and coniferous forests receive substantial inputs of Hg through both litter and throughfall, with litter being the dominant flux in hardwood forests and throughfall being the dominant flux in conifer forests. Despite significantly greater Hg inputs to the forest floor and lower evasion losses in conifer stands, the concentrations of Hg in the soil of the conifer forests are lower than hardwood stands, suggesting there is a loss mechanism in coniferous forests that has not been adequately quantified. Aquatic ecosystems located in watersheds that are forested with a high percentage of conifers may be at an increased risk of greater Hg contamination compared to aquatic ecosystems in deciduous forested watersheds. Previous papers have referred to forest soils as a net sink of atmospheric mercury (Graydon et al. 2008, Kolka et al. 1999), but this sink for atmospheric Hg could potentially be a significant source of Hg to watersheds. Moreover, there was significant year-to-year variation in the magnitude and pathways of Hg deposition between stands, seemingly due to differences in precipitation and temperatures. Predicted changes in climatic conditions in the northeastern United States could shift Hg deposition pathways by decreasing litterfall Hg deposition and increasing throughfall Hg deposition in forested ecosystems.

# 5 Deposition of Mercury in Forests Along an Elevation Gradient

## 5.1 Methods

### 5.1.1 Study Site and Experimental Design

Whiteface Mountain (Whiteface) is located in the northeast portion of the Adirondack Park near Wilmington, NY (summit location 44.37°N, 73.90° W) (Figure 9). Whiteface has a prominence of over 1,000 meters, with a base elevation of approximately 400 m above sea level and a summit elevation of 1483 m. The mountain 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. It is also a monitoring site for the National Atmospheric Deposition Program (NADP) National Trends Network (NTN) and a site for cloud-chemistry monitoring for the NYS Department of Environmental Conservation. The NADP Mercury Deposition Network (MDN) stations are located approximately 50 km (Huntington Wildlife Forest, Newcomb, NY) and 80 km (Underhill, VT) from the summit of Whiteface. An alpine ski area occupies the southeastern slope, but the majority of the rest of the mountain is protected by either New York State wild forest or wilderness designation. There are hiking trails from the base to summit along the southwestern and northeastern faces, and a road runs to the summit along the northern side of the mountain.

**Figure 9. Map Showing Location of Whiteface Mountain within the Adirondack Park and Sampling Transects.**

The transects are along the Southwest (Black Symbols) and Northeast (Open-Dot Symbols) Sides of Whiteface Mountain. Square symbols represent hardwood plots, triangles represent spruce/fir plots, and circles represent alpine plots.
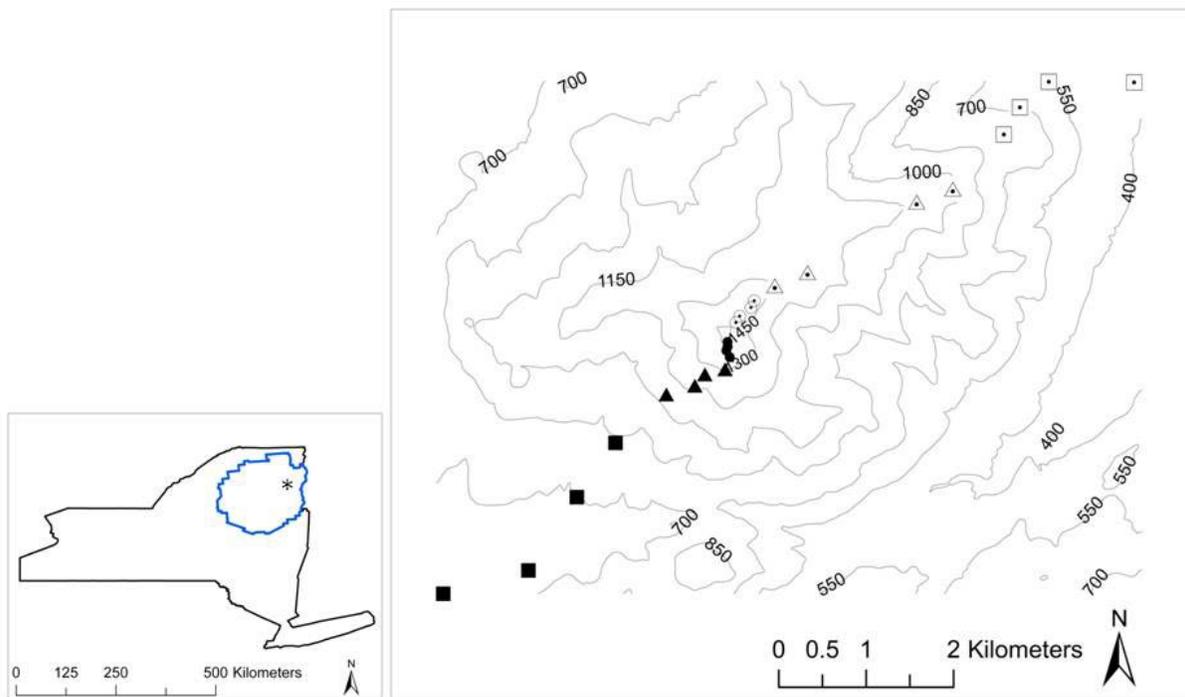


Forest communities of Whiteface Mountain are segregated into three distinct zones with small forest transition zones between. The lower elevations (hardwood zone) are characterized by northern hardwood forest dominated by sugar maple, yellow birch, red maple, and American beech, ranging from 400 m to approximately 900 m. The mid-elevations (spruce/fir zone) are thick stands of balsam fir and red spruce with interspersed paper birch that range from approximately 1000 m to 1300 m. The third zone is an alpine forest zone that is comprised almost entirely of sparse, stunted-growth balsam fir with occasional red spruce, paper birch, and mountain ash. The alpine zone ranges from approximately 1350 m to the summit.

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 the mountain (Figure 9). Each transect contained 12 study plots that span a range of

elevations and forest types, and plots were placed near major hiking trails to allow reasonable access. For both transects, four plots were established at regular elevation intervals in each of the three major vegetation zones (hardwood, spruce/fir, alpine). Sample collections from transects were made between June 1, 2009 and June 6, 2011.

## 5.1.2  Sample and Data Collection

After selecting plots, positions were recorded using a handheld global positioning system (GPS). Elevation was estimated using a combination of topographic maps, handheld GPS, and a digital elevation model of the Adirondack Park. Throughfall collectors were installed at each plot by inserting a 4-inch PVC pipe into the ground. A 1-liter (L) Teflon bottle charged with 10 mL of concentrated low-Hg HCl was placed inside the PVC pipe and connected to a 20 cm polyethylene funnel by Teflon tubing. Throughfall gauges were also constructed at each site by attaching a 15 cm polyethylene funnel to a 4-L collecting bottle. Throughfall was collected throughout the growing season and was sampled for an interval between 10–30 days depending on rainfall quantities over the collection period. Litterfall collectors were also deployed by placing two plastic crates lined with plastic mesh in each plot. Litterfall samples were collected twice per year, in late fall and late spring.

Organic soil and canopy and understory vegetation were also collected from each plot. Soil samples were collected in June, August, and September 2010. Soil was collected by inserting a split-PVC corer into the soil profile, extracting intact cores, and separating the horizons based on visual appearance. Two horizons were collected: the Oi/Oe litter layer and Oa humus layer. All soil samples were placed in plastic sample bags and frozen from collection until analysis. Canopy vegetation was sampled in September 2009 and 2010. Canopy vegetation was sampled from dominant species at each plot by using a shotgun to shoot high canopy branches from the trees. Steel-shot cartridges were used, and downed vegetation was collected by an assistant wearing nitrile gloves to prevent contamination of foliage samples. Understory foliage was collected from American beech and striped maple in the hardwood zone using pruning shears. All foliage samples were placed in plastic bags and frozen from the time of collection until analysis.

Cloud deposition is an important contributor to chemical inputs in montane landscapes (Weathers et al. 2006, Miller et al. 1993). A cloud collector was installed at the summit of Whiteface to collect and measure Hg concentrations in cloud water for the 2009 sampling season. The collector housing was constructed from acid-washed PVC pipe that was lined with Teflon coating. A cartridge inside the

housing held Teflon strings that condensed cloud water droplets and directed them to a collection bottle through a Teflon tube. The string collector was connected to a pneumatic pump and sensors that would close the collector during dry weather or precipitation events and only open the collector during cloud events. Samples from 19 cloud events were collected between July and September 2009.

Meteorological data were measured in 2009 and 2010 at the summit of Whiteface. Conditions at the summit are not necessarily representative of simultaneous conditions at other sampling sites, but the general meteorological trends can be summarized from these measurements. The meteorological measurements included air temperature, wind speed, cloud frequency, and precipitation quantity (Table 6).

**Table 6. Monthly Averages of Meteorological conditions during the Growing Season at the Whiteface Mountain Summit Monitoring Station**

Monitoring values are monthly totals.

| Month | Temperature (°C) | | Wind Speed (m/sec) | | Cloud Frequency (min/hr) | | Precipitation (mm) | |
|---|---|---|---|---|---|---|---|---|
| | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 |
| June | 8.8 | 9.4 | 6.9 | 8.8 | 17.2 | 20.3 | 134.6 | 158.5 |
| July | 10.0 | 13.3 | 8.3 | 9.5 | 24.1 | 18.4 | 132.8 | 76.5 |
| August | 11.7 | 12.0 | 8.5 | 9.0 | 25.0 | 18.6 | 90.4 | 88.9 |
| September | 7.6 | 8.1 | 7.6 | 9.9 | 18.9 | 19.9 | 77.0 | 118.6 |

## 5.1.3  Laboratory Analysis

Foliage and soil samples were freeze dried before analysis for at least 72 hours. Foliar samples were analyzed for Hg using a Milestone DMA 80 and soil samples were analyzed using a LECO AMA 254. Both instruments are based on EPA Method 7473 (EPA 1998) and analyzed solid samples without digestion or treatment. The DMA 80 was calibrated with NIST certified reference material 1515 (apple leaves, 44 ng/g), and NIST 2976 (mussel tissue, 61 ng/g) was used as an external reference. The LECO AMA 254 was calibrated with NIST 1633b (coal fly ash, 143 ng/g) and CNRC MESS-3 (marine sediment, 91 ng/g) was used as the external check standard. Both foliar and soil samples were

also analyzed for carbon (C) and nitrogen (N) using a Costech 4010 Elemental Analyzer calibrated with acetanilide. Atropine was used as an external check for elemental C and N analysis. All foliage and soil samples analyzed were over the detection limit of 0.2 ng Hg and calibration check and external check standards were all within 90–110% of certified values for Hg, C, and N.

Liquid samples were stored at 4°C from time of collection until analysis. Hg analysis was performed on all throughfall and cloud samples using EPA Method 1631-E (EPA 2002). Samples were treated with BrCl prior to analysis to oxidize all Hg to Hg (II), and then treated with $NH_2OH$ followed by SnCl during analysis to reduce Hg (II) to $Hg^0$. This analysis was performed on a Tekran 2600 which uses an atomic fluorescence detector. The instrument was calibrated using gravimetric dilution of a certified aqueous Hg standard (Ultra Scientific, 10 µg/mL) and was verified using a second source aqueous standard (NIST 1641-D). All calibration and check standards were between 85–105% of reported values. Fourteen cloud samples and 72 throughfall samples were also analyzed for $NO_3^-$ and $SO_4^{2-}$ using a Dionex ion chromatograph. Additionally, the 72 throughfall samples were analyzed for dissolved organic carbon (DOC) using a Teledyne Tekmar Apollo organic carbon analyzer. Both instruments were calibrated using certified reference standards (Ultra Scientific) and all reference standards were between 90–110% recovery.

## 5.1.4  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 sampling periods, both components were measured directly at each plot. Throughfall quantities measured at each plot during sampling periods were compared to precipitation quantities at the Whiteface NADP NTN station. Mercury concentrations at each site were compared to mean Hg concentrations from MDN stations near Newcomb, NY and Underhill, VT. Based on these comparisons, precipitation quantity factors and Hg enrichment factors were developed for 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 precipitation and Hg enrichment factors.

Litterfall Hg fluxes were calculated by multiplying litterfall mass per area by foliar Hg concentrations. Because litter could not be sampled shortly following deposition, and because throughfall Hg inputs increase the Hg concentrations of litter (Demers et al. 2007), litterfall Hg concentrations were estimated

based on foliar Hg concentrations. Hardwood foliar Hg concentrations at time of litterfall were estimated by assuming a 140-day growing season and extrapolating September foliage Hg concentrations to litterfall at the end of the growing season. For conifer needles, all litter was assumed to be three years old. Mercury concentrations from this age group of foliage were extrapolated from the September sampling period. Litterfall mass per unit area was estimated from litter trap collections.

Cloud fluxes were estimated by multiplying mean measured cloud Hg concentrations with a modified cloud water quantity model for Whiteface Mountain outlined in Miller et al. (1993). The model developed by Miller et al. (1993) is based on a model created by Lovett (1984), but it has been modified specifically for Whiteface Mountain. This model predicts annual cloud water quantity at different elevations. For the purpose of deposition calculations, cloud water Hg concentrations at all elevations were assumed to be equal to the cloud water Hg concentrations measured at the summit. To adjust for variations in cloud frequency, a 10-year data set (2001–2010) of cloud observations from Whiteface was used.[8] Total cloud volume captured by the collector was calculated for each year, and the average of 10 years of cloud monitoring was considered to be equivalent to the average cloud water flux calculated by Miller et al. (1993). A proportional correction factor was then applied based on the total volume of cloud water that was collected during the sampling year. This estimated cloud quantity was then multiplied by the volume-weighted cloud Hg concentration to estimate cloud Hg flux. Because the cloud collector was inoperable for the 2010 season, 2009 cloud Hg concentrations were applied to flux calculations for both years.

Total fluxes were estimated for each plot by summing throughfall, litterfall, and cloud water components. Although it is likely that cloud water did contribute a portion of the throughfall flux at higher elevations, throughfall and cloud water were assumed to be exclusive of each other for the purpose of flux calculations. Fluxes were reported by forest zone, with each forest zone Hg flux representing the mean of calculations for eight sites each year.

### 5.1.5  Statistical Analysis

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

## 5.1 Results

### 5.1.1 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 10). Results of one-way ANOVA of log-transformed throughfall Hg concentrations indicate that the differences among forest types were significant ($F_{(2,140)} = 10.3, p<0.001$). *Post-hoc* 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 the concentrations for open precipitation samples that were measured near Newcomb, NY and Underhill, VT (Figure 10). Cloud water 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 10).

**Figure 10. Average Concentrations of Hg in Precipitation, Throughfall, and Cloud Water**

Because precipitation concentrations were measured from a single collector, no standard error was calculated. Precipitation was measured at Mercury Deposition Network stations at Huntington Wildlife Forest near Newcomb, NY (HF) and a station near Underhill, VT (UH). Throughfall was collected in different forest zones at Whiteface Mountain. Cloud water was collected at the summit of Whiteface Mountain and was only collected in 2009.
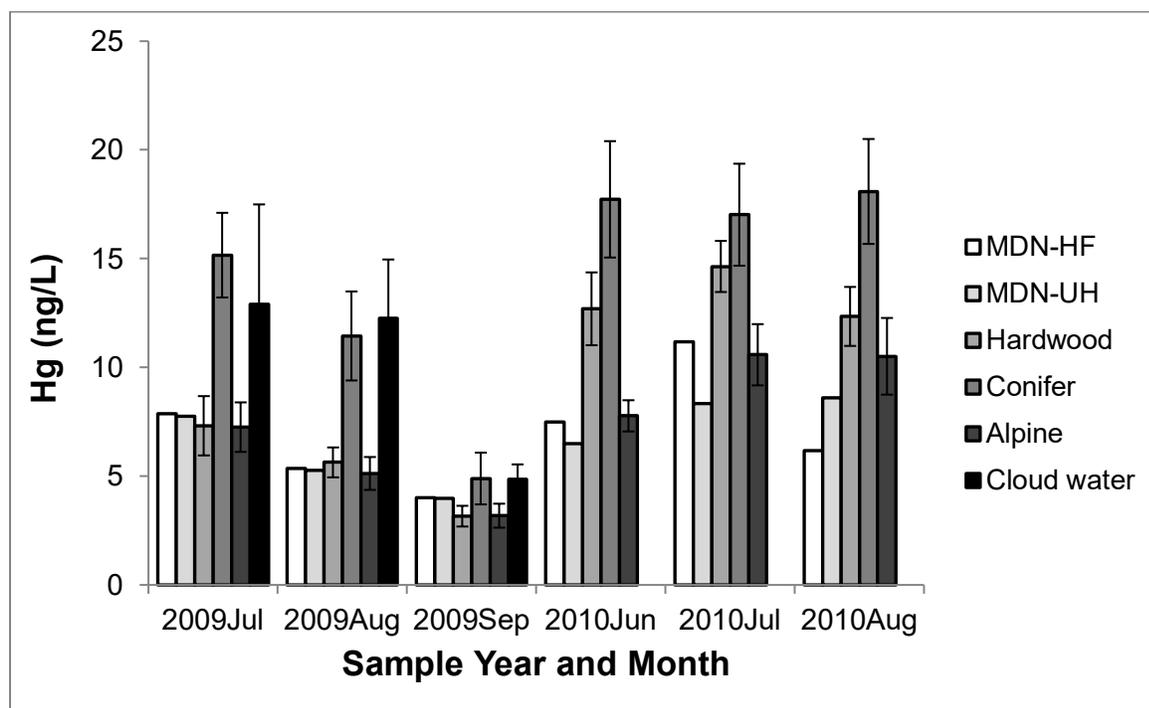
Chemistry measurements of a subset of 14 cloud samples and 72 throughfall samples showed that Hg concentrations were correlated with concentrations of other chemical species. Throughfall concentrations were strongly, positively related to DOC concentrations in all forest types (Figure 11) but were unrelated to $NO_3^-$ and $SO_4^{2-}$ concentrations. Cloud water Hg concentrations were positively related to both $NO_3^-$ and $SO_4^{2-}$ concentrations (Figure 12). Cloud samples were not analyzed for DOC. However, data from the Adirondack Lake Survey Corporation cloud water collector on the summit of Whiteface show that TOC is highly related to both $NO_3^-$ and $SO_4^{2-}$, so it is likely that DOC in cloud water is related to Hg as well.

**Figure 11. Regression Showing Relations between DOC Concentrations and Hg Concentrations in Throughfall Samples**

The relation appears to be independent of forest type. Triangles represent hardwood samples, circles represent spruce/fir samples, and squares represent alpine samples.
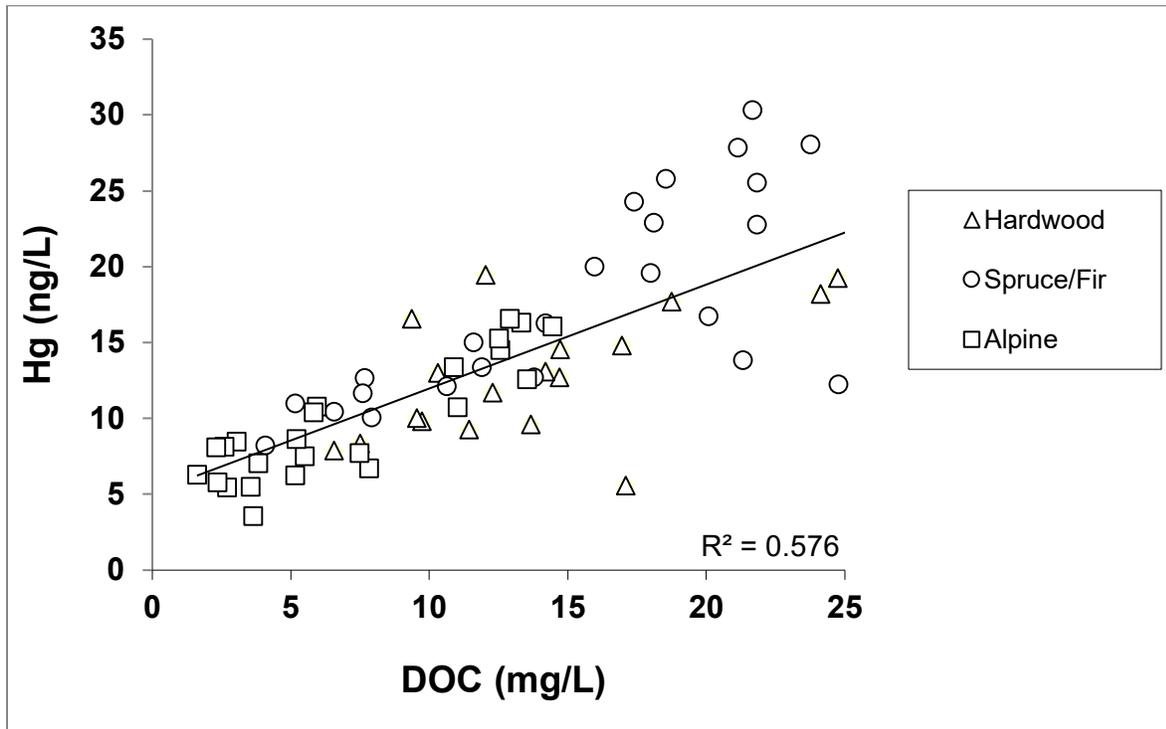
**Figure 12. Relations and Regression Lines between Concentrations of Hg and Strong Acid Ions (NO$_3^-$ and SO$_4^{2-}$) in Cloud Water Samples**
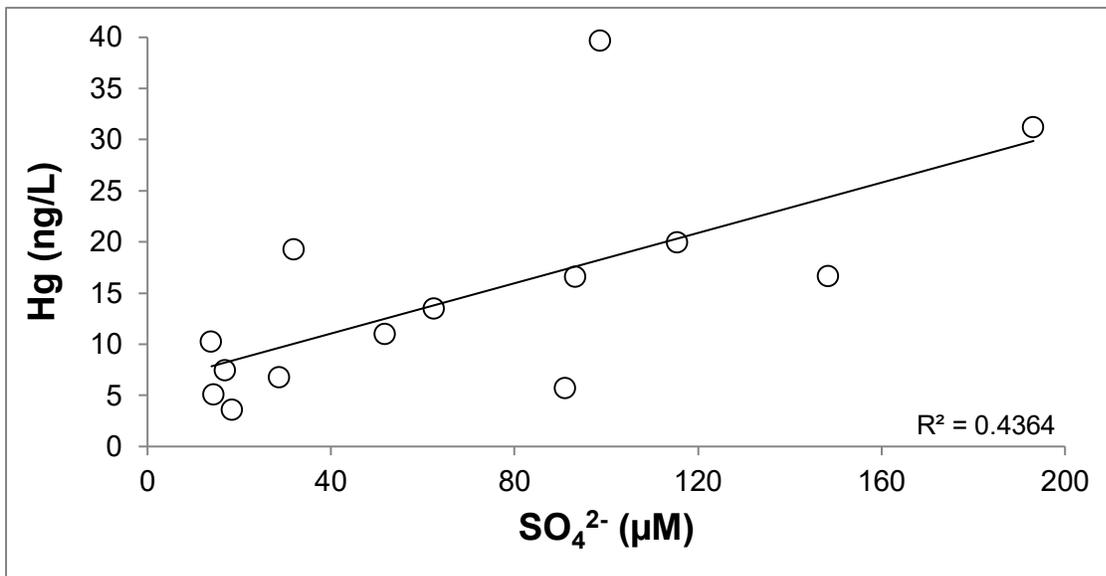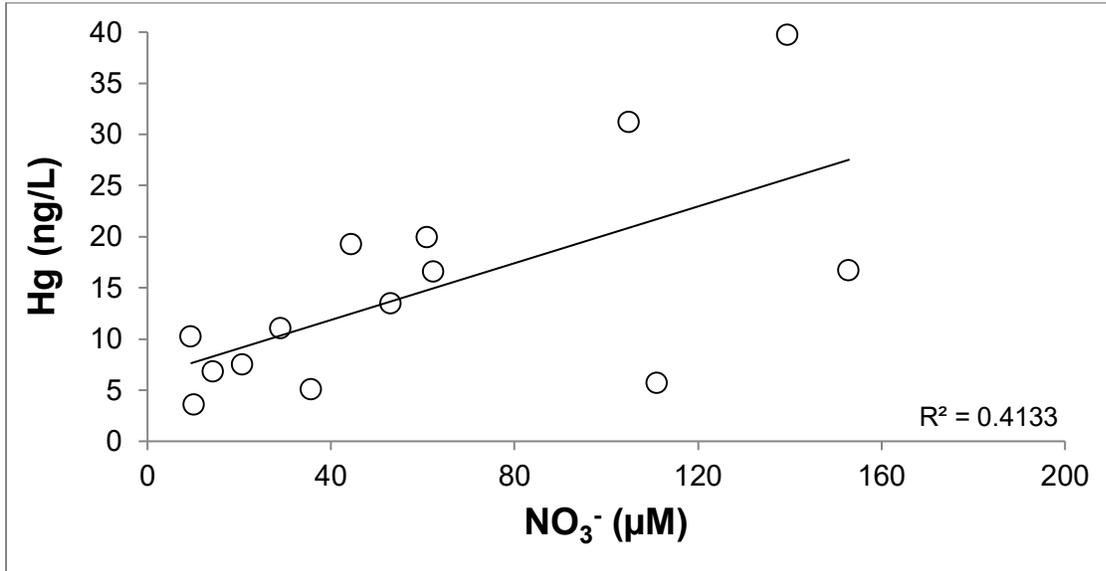


## 5.1.2 Hg in Organic Soils

Hg concentrations in the litter layer (Oi/Oe horizon) and humus layer (Oa horizon) were two to four times higher than Hg concentrations of the litterfall. In the profile, the humus layer Hg concentrations were significantly higher than litter layer Hg concentrations, with the difference being more pronounced in the spruce/fir and alpine zones (Figure 13). Linear regression revealed that humus layer Hg concentrations were positively related to both %N and %C. However, litter layer Hg concentrations were not related to

either %N or %C, and neither litter nor humus layer 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 litter to humus layers. Hg concentrations in both litter and humus layers showed a significant positive relation to elevation, but the stronger relation was observed in the Oa horizon (Figure 14).

**Figure 13. Soil Hg Concentrations in Litter (Oi/Oe) and Humus (Oa) Layers in Different Forest Zones**

Error bars represent standard error.
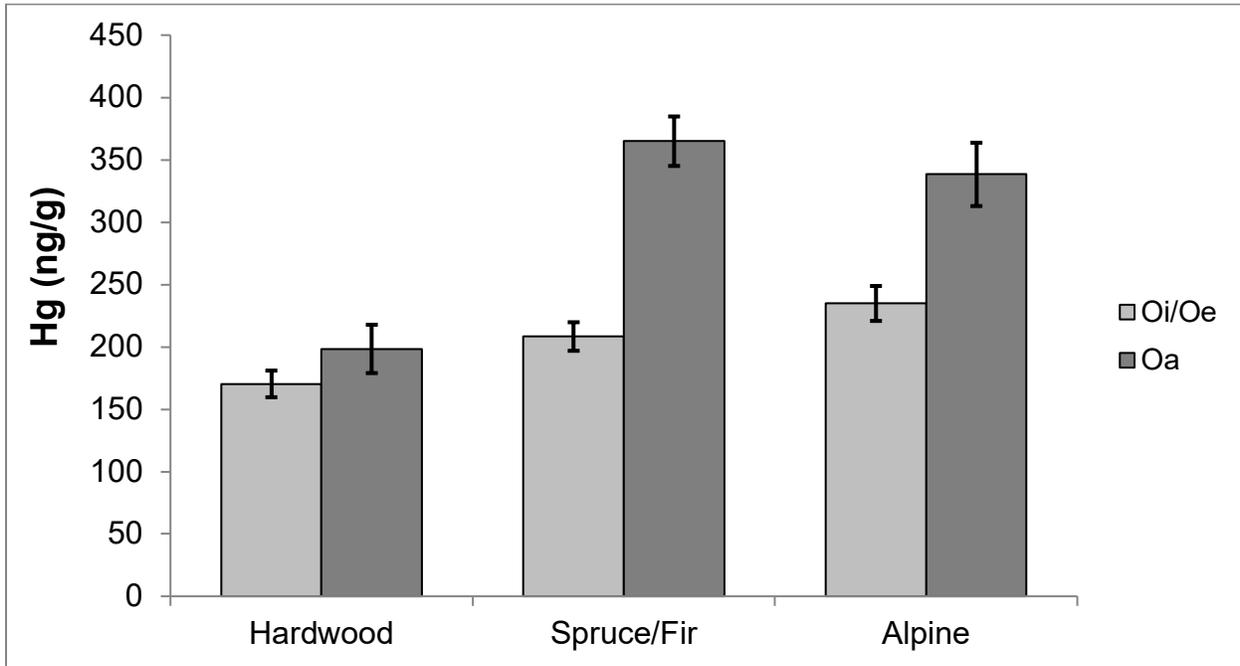
**Figure 14. Relations between Forest Floor Hg Concentrations and Elevation for both Litter (Oi/Oe) and Humus (Oa) Layers**

Regressions were statistically significant for both litter and humus layers.
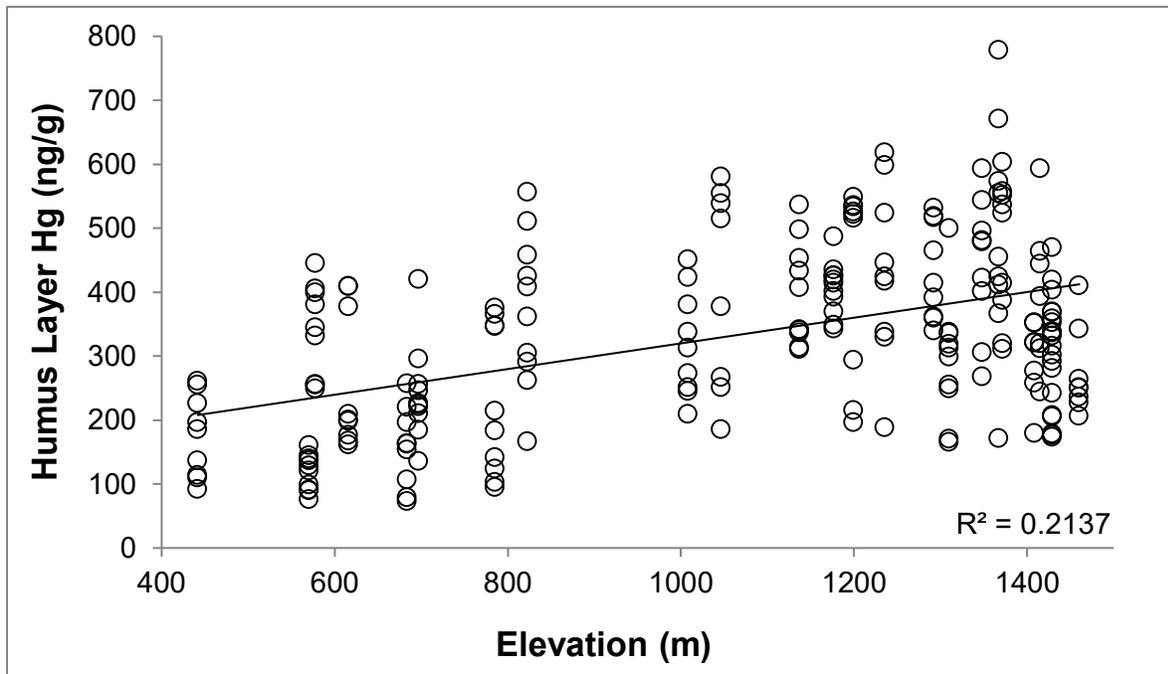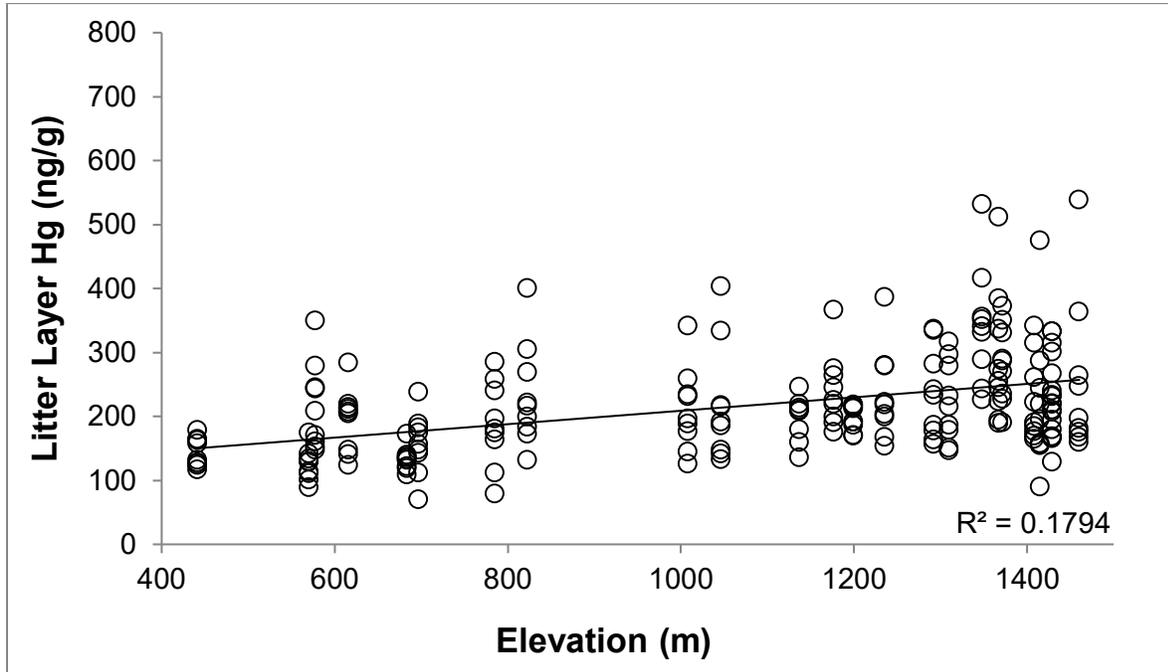
## 5.1.3 Foliar Hg

Foliage was collected from eight different species that were commonly found in multiple plots. These include the canopy hardwoods: sugar maple, yellow birch, red maple, and paper birch. Understory species included American beech and striped maple. Two species of conifer, balsam fir and red spruce, were the dominant species in the upper elevations. 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 15). Conifer foliage Hg concentrations were dependent on the age class of the needles, with concentrations in two-year-old needles > one-year old needles > current year needles. The increase in Hg concentration was consistent throughout the age classes. Estimated foliar Hg accumulations were approximately 10-15 ng/year for balsam fir and 4-6 ng/year for red spruce.

**Figure 15. 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.
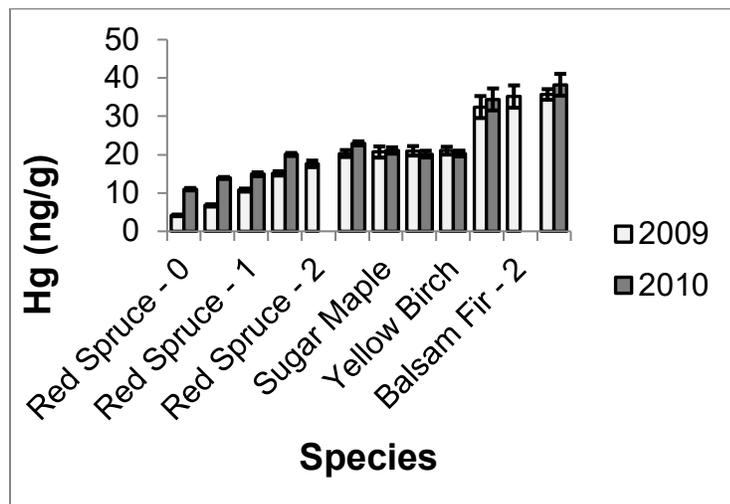


Effects of elevation on foliar Hg concentrations were evaluated using linear regression. In both 2009 and 2010, elevation had a significant, negative effect on foliar Hg concentrations (Figure 16). However, this pattern is partially confounded by the shift in species along the elevation gradient. To attempt to account for this, elevation effects were evaluated for paper birch, which is the only species that was found in all plots. The resulting regression was still negative and strongly significant for the 2009 samples (Figure 17). In 2010, the same pattern was not detectable, and paper birch foliage Hg concentrations were relatively homogenous along the entire elevation gradient.

**Figure 16. Regression between Foliar Hg Concentrations and Plot Elevation for 2009 and 2010**

All hardwood and age-0 conifer samples were included in the analysis. Regressions were significant for both 2009 an d2010 (*p<0.001* for both years).
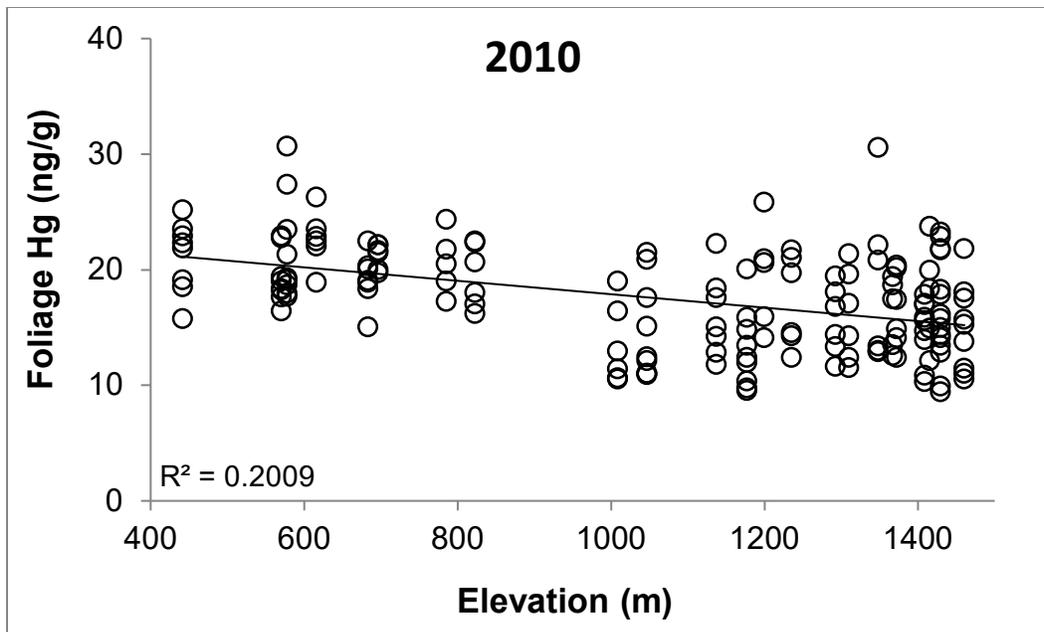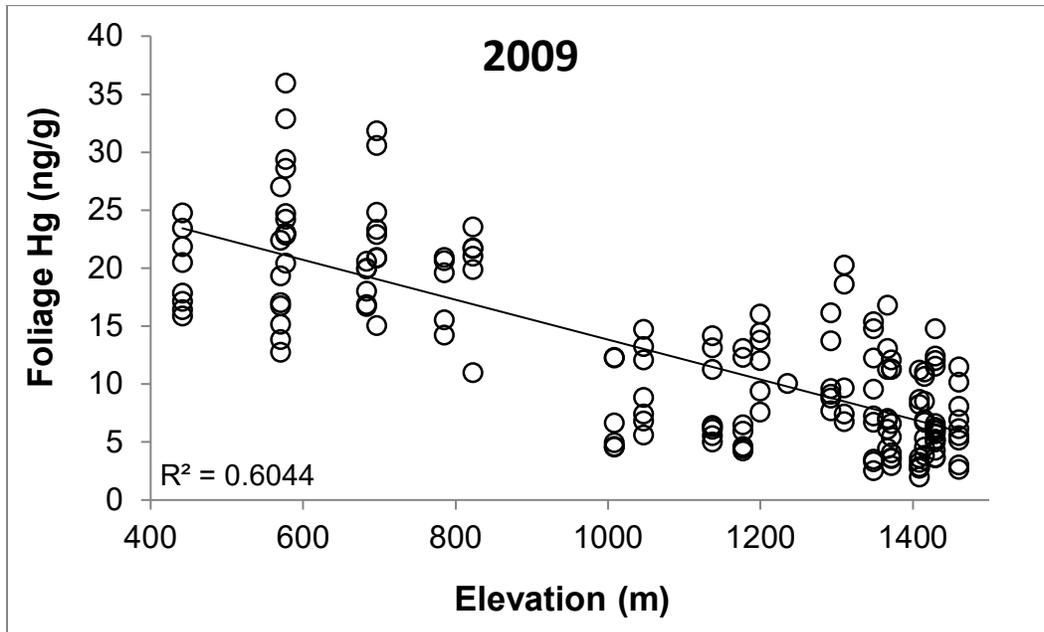
**Figure 17. Regression between Paper Birch Foliar Hg Concentrations and Plot Elevation**

Regression was significant for 2009 samples (*p<0.001*) but not for 2010.
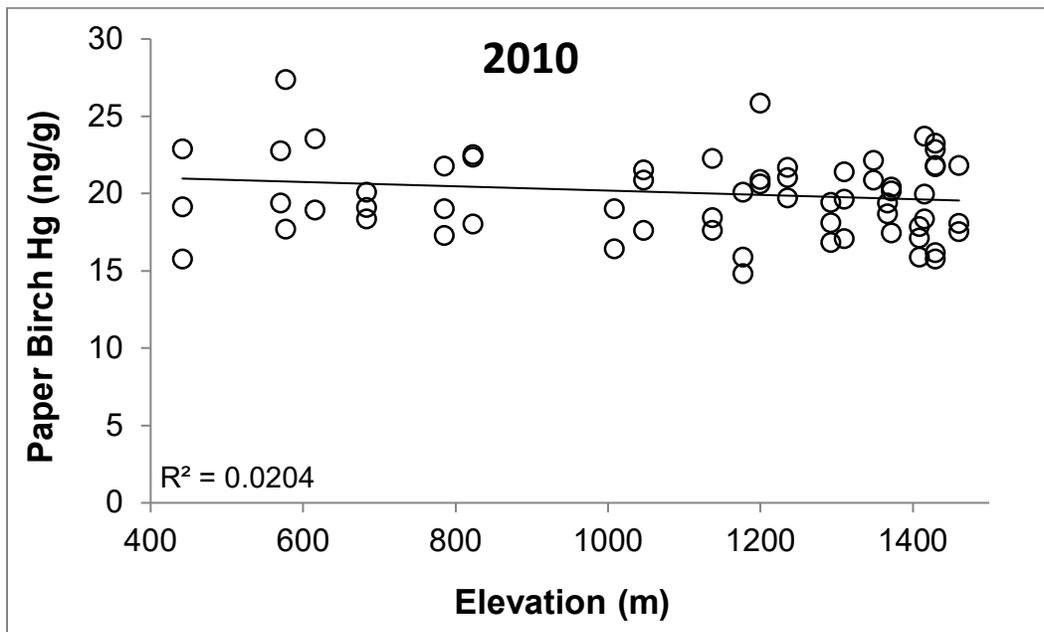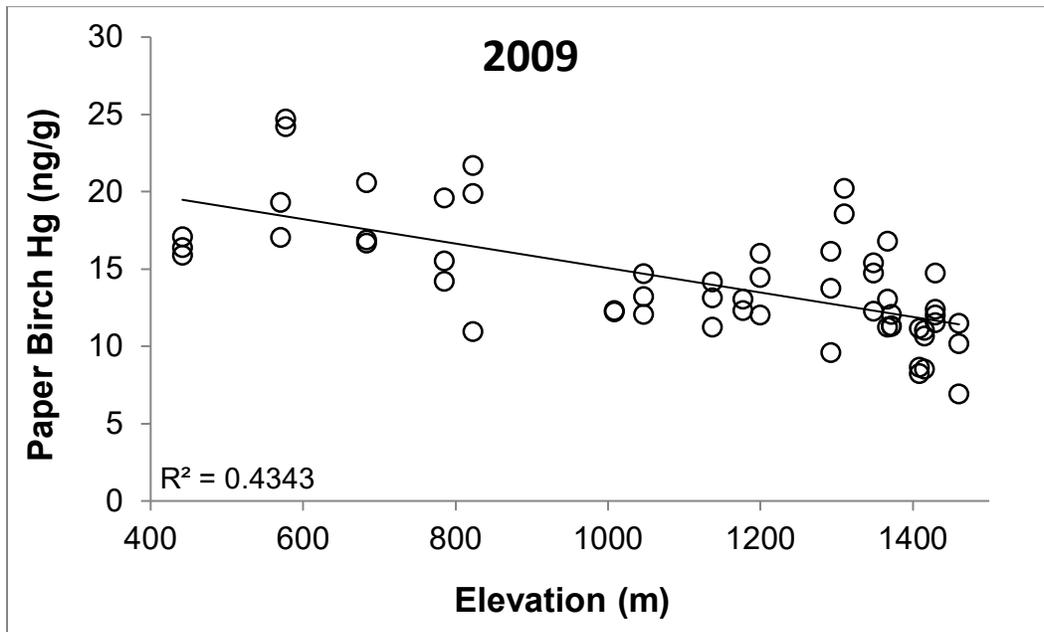
## 5.1.4 Mercury Deposition

Mercury deposition was highly variable across the three forest types, with the pathways of deposition (litterfall, throughfall, and cloud water) each contributing different proportions to total Hg deposition in the three forest types (Figure 18). The highest Hg fluxes in 2009 and 2010 were evident in the alpine zone (49.2 and 38.7 μg/m$^2$-yr), 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 7). 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 it was throughfall. The spruce/fir zone received most deposition from cloud water in 2009, but throughfall was the more important contributor in 2010. In the alpine zone, cloud water was the dominant contributor of Hg deposition in both 2009 and 2010.

**Figure 18. Proportional Contributions of Throughfall, Litterfall, and Cloud Water to Total Hg Fluxes in Each Forest Zone in 2009 and 2010**

HW = Hardwood, SF = Spruce/Fir, and Alp = Alpine
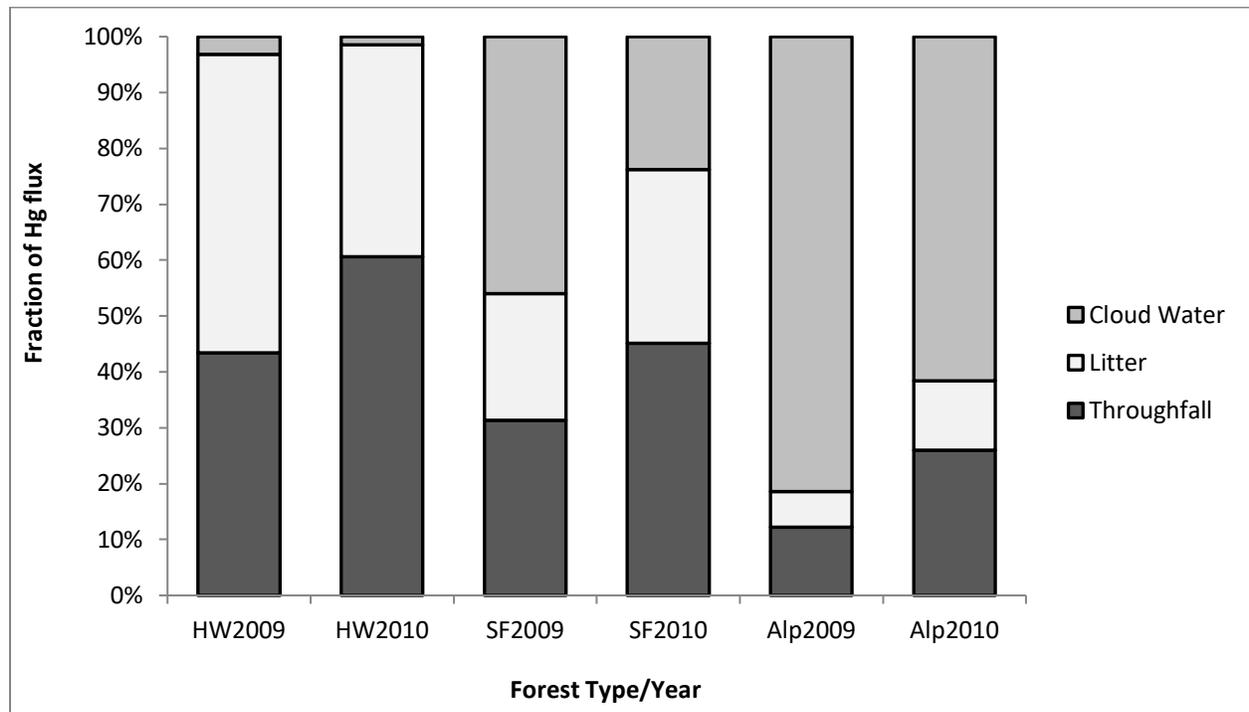
**Table 7. Estimated Hg Fluxes from Throughfall, Litterfall, and Cloud Water in Each Forest Zone in 2009 and 2010**

Measurements are µg/m²-yr. Measurements represent annual means estimated from eight plots in each forest zone, ± one standard deviation of those eight measurements.

|  | 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 |

## 5.2   Discussion

### 5.2.1   Comparison to Other Studies

While studies of Hg deposition along elevation transects are rare in the literature, there are two other investigations that corroborate these findings of increased Hg deposition at higher elevations. Neither Stankwitz et al. (2012) nor Townsend (2011) attempted to quantify total Hg fluxes, but both found that soil Hg concentrations increased by approximately a factor of four along elevation transects in the northeastern United States, a phenomenon they attributed to increased Hg deposition. Other studies have found that Hg concentrations in high-altitude lakes are often higher than low-altitude lakes (Krabbenhoft et al. 2002, Watras et al. 1995) and that Hg concentrations in fish are positively correlated with elevation (Blais et al. 2006). In addition, increased deposition of pollutants, mainly acidic deposition (N and S), has been documented in high-elevation forests across North America (Baron et al. 2011, Weathers et al. 2006, Nodvin et al. 1995, Miller et al. 1993, Lovett and Kinsman 1990). In this study, Hg in cloud water was correlated with both $NO_3^-$ and $SO_4^{2-}$ at the summit of Whiteface. Mercury, N, and S share common emission sources and are subject to long-range transport, so the fact that elevation gradients affect Hg similarly to N and S suggests that the same climate and landscape variables that control elevation patterns of acidic deposition also influence Hg deposition processes.

### 5.2.2   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 (sections 4 and 6; Bushey et al.

2008, Rea et al. 2002), and conifers accumulate Hg more slowly than hardwoods (Millhollen et al. 2006). 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 (Sheehan et al. 2006). The slower Hg uptake of conifers was evident through a comparison of Hg concentrations in leaves and needles from the current growing season (Figure 15). Tree species naturally partition along the elevation gradient at Whiteface, and high-elevation species are almost entirely coniferous. Upper-elevation conifers require more than two years on average to accumulate the same concentrations of Hg that lower-elevation hardwoods accumulate in a single growing season. However, on average, foliar Hg concentrations were higher in coniferous zones because conifers contain needles that are several years old. Higher average foliar Hg concentrations in coniferous zones were also found on a nearby mountain (Camel's Hump, VT) (Stankwitz et al. 2012). The authors attributed this pattern to enhanced Hg deposition (Stankwitz et al. 2012). However, this process of enhanced Hg deposition is likely not because of higher deposition of atmospheric Hg but rather because of longer exposure periods of coniferous foliage than deciduous foliage.

The foliar concentrations of Hg are likely the result of atmospheric $Hg^0$ that is taken into the leaf through the stomata (Milhollen et al. 2006, Ericksen et al. 2003, Rea et al. 2001), as foliar uptake of Hg is directly correlated with atmospheric $Hg^0$ concentrations (Ericksen and Gustin 2004). Paper birch was used to evaluate a potential $Hg^0$ gradient because it was found throughout the elevation range at Whiteface (Figure 17). Observations were inconclusive and varied between the two study years. Paper birch Hg concentrations were higher at lower elevations in 2009, suggesting a possible $Hg^0$ gradient. However, paper birch foliar Hg concentrations were relatively uniform in 2010. $Hg^0$ is relatively stable in the atmosphere and is often assumed to be homogenous across the landscape, but meteorological variables such as relative humidity (Choi and Holsen 2009) and wind speed (Fu et al. 2010) have been shown to be inversely correlated to atmospheric $Hg^0$ concentrations. Marked increases in elevation can cause variation in both humidity and wind speed over a short distance, leading to a greater likelihood that $Hg^0$ concentrations will vary across an elevation transect. While there was no evidence that wind conditions were significantly different between 2009 and 2010, differences in cloud frequency likely led to gradients in relative humidity along the elevation transects. In 2009, weather conditions were generally overcast, and the upper elevations of Whiteface were more frequently enveloped by clouds, while in 2010 cloud frequency was less and average temperatures were higher (Table 6). Based on these conditions, it would be expected that 2009 was a more favorable year for the formation of a relative humidity gradient along the elevation transect, which could partially explain the negative correlation between foliar Hg concentrations in paper birch and elevation.

### 5.2.3  Mercury in Throughfall and Cloud Water

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 throughfall concentrations in deciduous forests (section 4; Witt et al. 2009, Graydon et al. 2008) and that canopy density is positively correlated with throughfall concentrations (Witt et al. 2009). Throughfall Hg concentrations from the spruce/fir zone were significantly higher than open precipitation, hardwood, and alpine concentrations for every sampling period. 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 ionic $Hg^{2+}$ deposition that is adsorbed from the atmosphere by leaf and needle surfaces. $Hg^{2+}$ is soluble and is readily washed from leaf surfaces during rain or cloud events. Conifer species are believed to be more efficient at capturing $Hg^{2+}$ than deciduous species due to their greater leaf area index (Kolka et al. 1999). $Hg^{2+}$ concentrations in the atmosphere have also been shown to increase under warm, dry weather conditions. These hypotheses are supported by the throughfall patterns at Whiteface, as the coniferous spruce/fir zone had the highest throughfall Hg concentrations and fluxes of the three forest zones. Moreover, throughfall Hg concentrations and fluxes were higher in all forest zones in the sunnier, drier 2010 growing season (Table 7).

Cloud water Hg concentrations were highly elevated over precipitation concentrations and were comparable to concentrations in spruce/fir throughfall. Cloud water Hg concentrations and fluxes are difficult to measure, and few studies have attempted such measurements. The volume-weighted average concentration of 9.7 ng/L (range 3.5-38 ng/L) for cloud water samples from this study is lower but still comparable to a previous study at nearby Mt. Mansfield in 1998 which was conducted during a period of higher Hg emissions (mean 24 ng/L, range 7.5-71.8) (Malcolm et al. 2003; Schmeltz et al. 2011).

## 5.2.4  Relations between Mercury and Other Elements

Chemical relations between cloud water Hg and strong acid ions $NO_3^-$ and $SO_4^{2-}$ offer further evidence that emissions, transport, and deposition of these pollutants are related and that emission sources causing acid-deposition in the Adirondacks are also contributing to Hg contamination. There is also a strong relation between N and Hg in soils at Whiteface, so the environmental fate of these compounds may be similar as well. However, the relation between Hg and $NO_3^-$ and $SO_4^{2-}$ was not evident in throughfall, which indicates that the Hg canopy processes and ecosystem cycling that occur between the time of deposition and fate are not coupled with $NO_3^-$ and $SO_4^{2-}$ cycling. Mercury does, however, seem to be closely coupled with organic C throughout the deposition and cycling processes. Although DOC was not measured in cloud water samples, DOC in throughfall samples and C content of the humus layer soil samples were both strongly correlated with Hg concentrations. Other studies have shown a strong correlation between throughfall Hg and DOC (Kolka et al.1999) and Hg and DOC in streams and soil water (Demers et al. 2010, Dittman et al. 2010, Schuster et al. 2008). While it is generally accepted that Hg cycling is closely linked with C cycling within ecosystems, examining links between Hg and C in cloud water could provide further insight into the transport, deposition, and cycling processes of atmospheric Hg.

## 5.2.5  Magnitude and Fate 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 changes among the different forest types and with different meteorological conditions. Not surprisingly, the alpine region was dominated by cloud water deposition, and canopy processes of litterfall and throughfall contributed relatively small amounts of Hg. The lower frequency of clouds did decrease deposition in 2010 relative to 2009, but cloud deposition still accounted for over 60% of total Hg deposition in the alpine zone. The change in cloud frequency and weather conditions from 2009 to 2010 had more substantial impacts on Hg deposition in the spruce/fir and hardwood zones. In the spruce/fir zone, it was expected that the lower frequency of clouds would decrease cloud Hg deposition in 2010. However, what was unanticipated was that the dry, warm conditions of 2010 led to much higher throughfall Hg concentrations and fluxes, presumably through increased scavenging of $Hg^{2+}$ by the coniferous canopy associated with higher temperatures and higher air concentrations of $Hg^{2+}$. Litter Hg concentrations and mass were both higher in 2010 than 2009 in the spruce/fir zone as well, leading to a substantially higher litter Hg flux. The dry, warm conditions also increased throughfall Hg concentrations in the hardwood

zone and resulted in a larger throughfall Hg flux. However, both Hg concentrations and litter mass were lower in 2010 than 2009, resulting in considerably lower litter Hg deposition. Similar to observations of interannual shifts in the magnitude of Hg deposition pathways at Huntington Wildlife Forest over the same time period (section 4), the findings suggest meteorological variables play an important role in the deposition of Hg in mountainous regions. Several studies have demonstrated the importance of cloud water contributions to Hg fluxes at high elevations (Stankwitz et al. 2012, Lawson et al. 2003, Malcolm et al. 2003). However, in years of warm, dry weather conditions, the importance of cloud water Hg is diminished but may be compensated by increasing 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 (Pourmokhtarian et al. 2012, 2016, Hayhoe et al. 2008), the fraction of total Hg deposition that occurs via throughfall may become even more prominent.

The dry and wet deposited Hg is largely input to the forest floor where it is incorporated into the soil profile. At Whiteface, Hg concentrations in O-horizon soils increase with increasing elevation, an observation that is supported by other studies (Stankwitz et al. 2012, Szopka et al. 2011, Townsend 2011). 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 litter layer (Oi/Oe horizon) and humus layer (Oa horizon) showed a positive relation between total Hg deposition and Hg concentrations (Figure 19). However, total Hg deposition explained little of the variance in these models (14% in litter layer, 30% in humus layer). Soil processes are variable and difficult to predict even under fairly uniform conditions. Different forest types have been shown to influence soil decomposition processes (McClaugherty et al. 1985), and Hg transformation in soil following litterfall is not consistent between hardwood and conifer stands (Demers et al. 2007). The influence of forest type, soil temperatures, soil chemistry, precipitation, and a number of other variables make accurate predictions of soil Hg accumulation difficult, but results from this study suggest that Hg deposition does play an important role in soil Hg processes. The enrichment in Hg from the Oi/Oe to the Oa horizon was evident across all elevation zones but increased from the hardwood zone through both the spruce/fir and alpine zones (Figure 14). Investigations have suggested that litterfall Hg becomes enriched in the humus layer of the forest floor by retention of throughfall inputs (Smith-Downey et al. 2010, Demers et al. 2007). This enrichment in soil Hg by throughfall/cloud water retention is evident across the 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 characterized by large inputs of throughfall and cloud water Hg. Also, 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 (Garten and Hanson 2006). This slower C turnover at high elevations could lead to slower decomposition of molecules that bind Hg which, along with increased deposition rates, could also contribute to high soil Hg concentrations at higher elevations.

**Figure 19. Regression between Calculated Hg Deposition and Organic Soil Hg Concentrations**
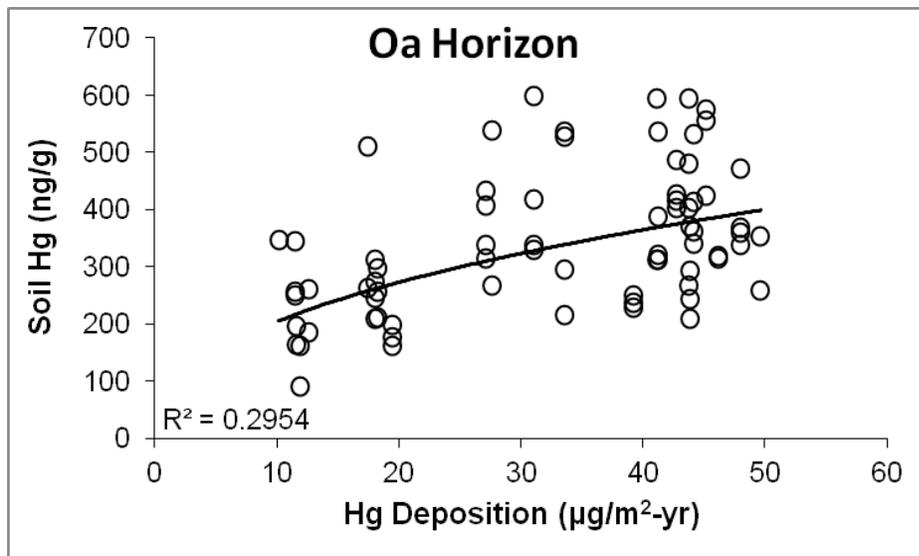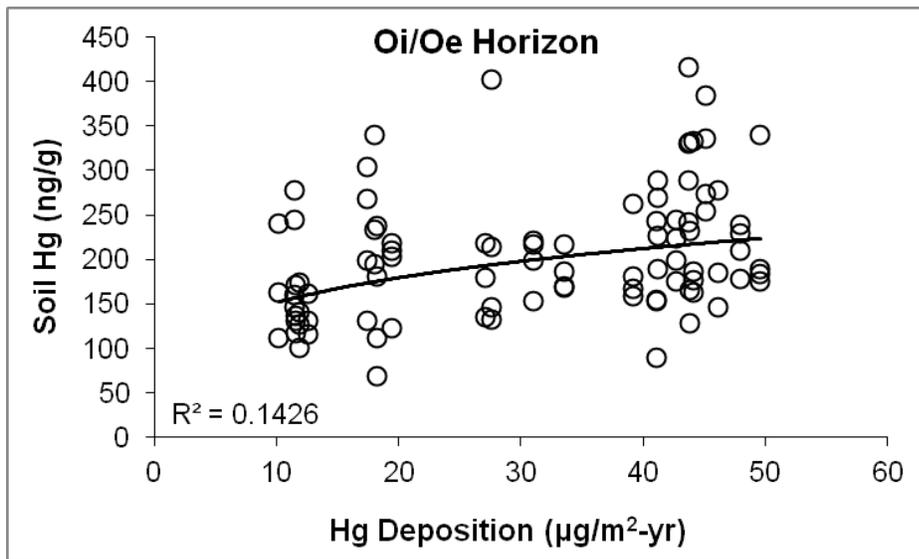
Recent studies have shown the magnitude of atmospheric Hg deposition, coupled with the complexity of climate and vegetation of the montane landscape influence spatial patterns of methylmercury formation at Whiteface Mountain (Gerson et al. 2017). Spatial patterns of methylmercury in soil coincide with methylmercury concentrations in the blood of species of thrush at Whiteface (Sauer et al. 2020), suggesting, as reported for Hg in aquatic ecosystems, that atmospheric Hg deposition is not the sole controller of biotic exposure. Landscape characteristics which mediate Hg deposition and loss and potential to methylate $Hg^{2+}$ are also important drivers (Driscoll et al. 2007).

### 5.2.6  Mercury Transport from High-Elevation Forests

Although this study did not quantify transport of Hg along the elevation transect, it is probable that significant portions of Hg deposited to high-elevation forests is transported to surface waters at lower altitudes. Hg transport in streams is closely coupled with DOC transport (Demers et al. 2010, Dittman et al. 2010, Schuster et al. 2008). Measured stream water DOC is higher in the higher-elevation coniferous forests than lower-elevation hardwood forests (Dittman et al. 2007, Cronan and Aiken 1985). Mercury transport is elevated during high-flow events such as snowmelt and thunderstorms (Demers et al. 2010, Dittman et al. 2010, Schuster et al. 2008). The combination of elevated precipitation, high Hg deposition, high soil Hg concentrations, and steep topographic gradients should facilitate the transport of both DOC and Hg from high-elevation watersheds to lower-elevation zones. Many headwater streams in the Adirondack Park originate in high-elevation forests and eventually flow into larger waterways that are used for recreational purposes. The area within and near to Adirondack region has 65 Hg-impaired waters[9] and is considered to be a biological hotspot of Hg contamination (Evers et al. 2007). The importance of fluvial Hg transport from high-elevation ecosystems warrants further study and could provide needed insight into the management of Hg-impacted waters in the Adirondack Park.

## 5.3    Conclusions

Mercury deposition is highly variable along elevation gradients in mountainous areas. In this phase of the study, Hg deposition increased by a factor of four in 2009 and 2.5 in 2010 from the low-elevation hardwoods to high-elevation alpine forests. This increase in Hg deposition with elevation appears to be linked to both orographic and biological components. Orographic effects of increased precipitation quantity and increased cloud water quantity at higher elevations led to substantial increases in Hg deposition, while shifts in forest communities from hardwood to coniferous led to higher throughfall Hg concentrations and higher litterfall Hg concentrations due to foliage age. While the orographic components of Hg fluxes may follow consistent patterns with elevation, forest

composition and characteristics shift abruptly along forest zones. Relations between total Hg deposition and soil Hg concentrations indicate that Hg deposition does affect Hg accumulation in the soil, but weak correlations suggest that additional factors such as climate and tree species also contribute to the observed variation. Contributions of throughfall, litterfall, and cloud water Hg deposition vary with different forest types. The dominant Hg deposition pathways were litterfall in low-elevation hardwoods, throughfall in the mid-elevation spruce/fir, and cloud water in the high-elevation alpine forest. Meteorological conditions also affected Hg deposition pathways, as the contributions of cloud water to Hg fluxes were diminished in 2010 (dry conditions) compared to 2009 (wet conditions). However, the dry conditions in 2010 led to significant increases in throughfall Hg fluxes compared to 2009. Overall, these findings suggest that elevation, forest characteristics, and meteorological conditions are all important drivers of Hg deposition in mountainous landscapes.

# 6 Spatial Patterns of Mercury in Foliage and Organic Soils in Adirondack Park

## 6.1 Methods

### 6.1.1 Study Area

The Adirondack Park is a 2.5 million ha forest preserve that is managed as a partnership between public agencies (New York State Department of Environmental Conservation, Adirondack Park Agency) and private landowners. The park has varying conservation approaches for different areas, so although there is some development within the park, many of its forests are highly protected and have been under conservation status for more than a century. Because of its size and location, the Adirondack Park spans a considerable geographic area covering multiple forest types and a range of elevations (37–1629 m). Two previous studies have established forest plots across the park to study nitrogen and calcium gradients (McNeil et al. 2007, Bedison and Johnson 2010). Using those previously established plots, 45 plots were selected as sample sites for this study (Figure 20). Plots included both hardwood and coniferous forests and were selected to maximize variation in latitude, longitude, elevation, and precipitation quantity.

**Figure 20. Map of Adirondack Park in Upstate New York, USA, with Locations of Study Plots Indicated**
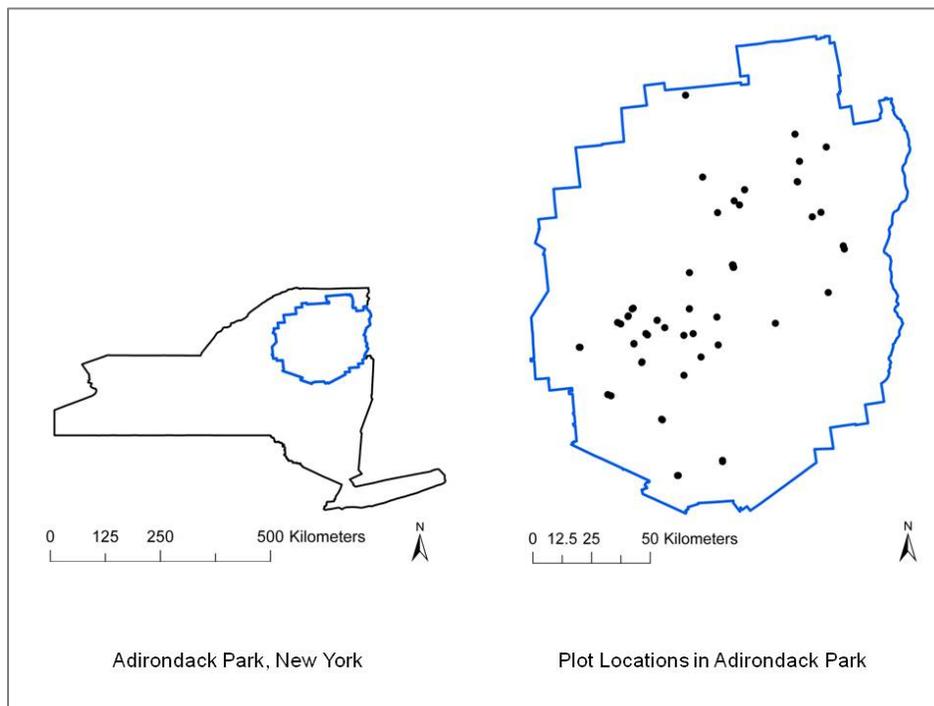
## 6.1.2  Sampling Methods

Foliar Hg concentrations in hardwoods increase throughout the growing season (section 4; Rea et al. 2002). As a result, all plots were sampled between August 4 and August 15, 2009 to reduce the impact of temporal variability on data analysis. At each plot, a random center point was selected, and latitude and longitude were recorded using GPS. Elevation for each plot was extracted from a digital elevation model of Adirondack Park. Percent cover was estimated using a densitometer at 10 points along four transects, and stem diameter at breast-height and density were recorded at five subplots (5 m radius around a center point) within the sample plot.

Dominant canopy species were selected for foliar sampling at each plot. Foliar samples were collected by shooting high canopy branches with steel-shot fired from a shotgun and allowing branches to fall to the forest floor. All downed branches were retrieved by an assistant wearing nitrile gloves to prevent contamination from the shotgun. Two to five individual trees of each dominant species were sampled per plot. Organic soil samples were also collected from each plot using PVC tubes. PVC tubes were hammered approximately 15 cm into the soil to extract the cores. The litter layers (Oi/Oe horizon) and humus layer (Oa horizon) were separated based on visual inspection and collected. All foliage and soil samples were placed in plastic zipper bags and frozen until analysis.

## 6.1.3  Laboratory Methods

To remove moisture, all soil and foliage samples were freeze dried for at least 72 hours prior to Hg analysis. Hg analysis was performed using a LECO AMA 254, which analyzes solid samples and conforms to EPA Method 7473 (EPA 1998). For foliar analysis, the analyzer was calibrated using a certified Hg standard made of apple leaves (NIST 1515, 44±4 ng/g), and calibration was verified during analysis by using certified mussel tissue (NIST 2976, 61±3.6 ng/g). For soil samples, calibration curves were created using a coal fly ash standard (NIST 1633b, 143±2 ng/g) and marine sediment (NRC-Canada MESS-3, 91±9 ng/g) was used as an external check. All samples analyzed were over the method detection limit of 0.2 ng.

Foliar and soil samples were also analyzed for C and N using a Costech 4010 elemental analyzer. Calibration curves were created using primary standard grade acetanilide, and curves were validated by using primary standard grade atropine as an external standard. For Hg, C, and N analyses, all calibration and external check standards were within ±10% of certified value.

## 6.1.4  Data Analysis

Differences in Hg concentrations among tree species were analyzed using one-way ANOVA. Relations between geographic variables and Hg concentrations in foliage and soil were analyzed using linear regression. Note that precipitation quantity was highly correlated to elevation in the sampling area (Table 8), so precipitation quantity was not used as a predictive variable. For comparisons of foliar Hg concentrations to literature litter values, foliar Hg concentrations were extrapolated to approximate concentrations at leaf senescence by assuming that Hg concentrations are 0 ng/g at bud-break and increased linearly throughout a 150-day growing season. Linear regression was also used to evaluate relations between C and N concentrations and Hg concentrations in foliage of dominant tree species and soil samples. Relations between soil fertility (characterized by C:N mass ratios) and Hg accumulation (characterized by Hg:C mass ratios) were examined using non-linear regression. Hg:C ratios were log-transformed to dampen outlier effects and to allow comparison to other studies. Stepwise regression was used to determine a best-fit model for predicting foliar Hg concentrations in the most widely distributed tree species (yellow birch) and soil Hg concentrations in the humus layer based on geographic and chemistry variables. All statistics were computed using IBM SPSS 19.0, and significance was determined at $\alpha \leq 0.05$.

**Table 8. Correlation Matrix of Geographic and Climate Variables Used for Regression Analysis**

Elevation was used as a predictive variable for regression in place of precipitation due to the strong correlation between elevation and precipitation.

|  | Longitude | Latitude | Elevation | Precipitation | Wet Hg Deposition | Dry Hg Deposition |
|---|---|---|---|---|---|---|
| **Longitude** | 1.00 | 0.57 | -0.15 | -0.36 | -0.64 | 0.22 |
| **Latitude** | 0.57 | 1.00 | -0.11 | -0.37 | -0.64 | 0.13 |
| **Elevation** | -0.15 | -0.11 | 1.00 | **0.91** | 0.31 | 0.20 |
| **Precipitation** | -0.36 | -0.37 | **0.91** | 1.00 | 0.46 | 0.20 |
| **Wet Hg Deposition** | -0.64 | -0.64 | 0.31 | 0.46 | 1.00 | -0.09 |
| **Dry Hg Deposition** | 0.22 | 0.13 | 0.20 | 0.20 | -0.09 | 1.00 |

## 6.2 Results

### 6.2.1 Species Differences and Ecosystem Mercury Enrichment

Fourteen different canopy tree species were present in more than one plot (Figure 21). These included red spruce (*Picea rubens*), red pine (*Pinus resinosa*), white pine (*Pinus strobus*), balsam fir (*Abies balsamea*), eastern hemlock (*Tsuga canadensis*), paper birch (*Betula papyrifera*), red oak (*Quercus rubra*), yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), bigtooth aspen (*Populus grandidentata*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia*), white ash (*Fraxinus americana*), and black cherry (*Prunus serotina*). Mercury was variable among the different species, and one-way ANOVA indicated that tree species had a strongly significant effect on foliar Hg concentrations ($F_{(13,260)} = 51.01, p<0.001$). *Post-hoc* testing using Tukey's HSD separated the species into six different homogenous subsets (Table 9). Age 0 (current growth) conifer needles had the lowest Hg concentrations (Subset 1). With the exception of paper birch and black cherry, all hardwood species were grouped into a single subset (subset 5). Black cherry foliar Hg concentrations were significantly greater than all other tree species. For conifer needles, Hg concentrations increased with needle age, with Age 1 needles containing approximately twice as much Hg as Age 0 needles (Table 10).

**Figure 21. Foliar Hg Concentrations among Canopy Tree Species of the Adirondacks**

Error bars represent ± one standard deviation. Note that concentrations reflect mid-growing season collections and are not maximum values.
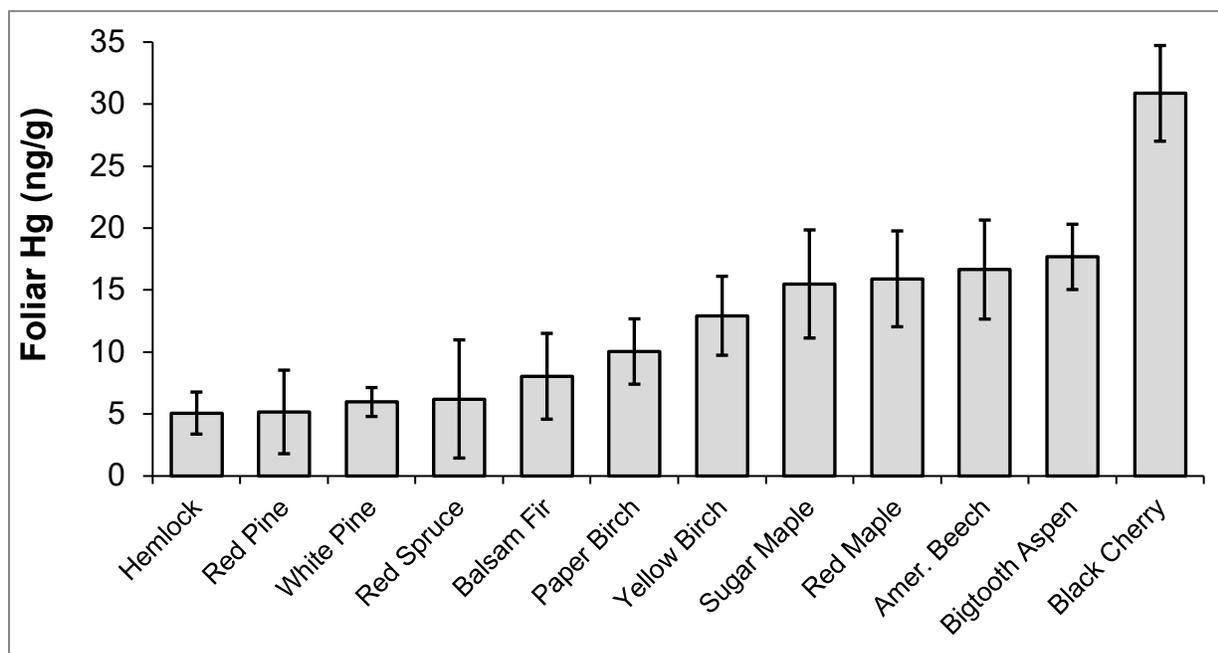
**Table 9. Homogenous Subsets of Tree Species Determined by One-Way ANOVA Using Tukey's HSD**

Values represent mean species Hg (ng/g) although the test was run on square-root transformed data to fit normality assumptions.

| Species | N | Subset for alpha = 0.05 | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| Red Spruce | 18 | 4.9 | | | | | |
| Red Pine | 8 | 5.2 | | | | | |
| White Pine | 19 | 6.4 | 6.4 | | | | |
| Balsam Fir | 23 | 7.5 | 7.5 | 7.5 | | | |
| Hemlock | 10 | | 8.6 | 8.6 | | | |
| Paper Birch | 12 | | 11.0 | 11.0 | 11.0 | | |
| Red Oak | 6 | | | | 12.8 | 12.8 | |
| Yellow Birch | 48 | | | | 12.8 | 12.8 | |
| Sugar Maple | 38 | | | | 15.1 | 15.1 | |
| Aspen | 8 | | | | 15.5 | 15.5 | |
| Red Maple | 29 | | | | | 16.4 | |
| Amer. Beech | 41 | | | | | 16.4 | |
| White Ash | 6 | | | | | 17.0 | |
| Black Cherry | 8 | | | | | | 29.9 |
| Significance | | 0.258 | 0.083 | 0.077 | 0.054 | 0.174 | 1.000 |

**Table 10. Mean Hg Concentrations (ng/g) and Standard Deviations in Coniferous Foliage of Different Age Classes**

| Species | Age 0 | Age 1 | Age 2 |
|---|---|---|---|
| Red Spruce | 5.5±3.0 | 13.9±5.4 | 18.9±5.3 |
| Red Pine | 5.2±1.5 | 18.0±2.5 | ------- |
| White Pine | 6.3±1.1 | 22.7±4.2 | ------- |
| Balsam Fir | 7.5±2.7 | 19.4±6.3 | 27.9±7.6 |

Within forest plots, Hg concentrations increased by a factor of approximately five to seven times between estimated foliage concentrations at litterfall and the soil litter layer (Oi/Oe horizon). This pattern was apparent in all plots regardless of differences in the dominant overstory species that contributed to the litterfall (Figure 22). Within the soil profile, Hg concentrations increased from the litter layer to the humus layer (Oa horizon) (litter layer mean Hg = 198±73 ng/g, humus layer

mean Hg = 282±127 ng/g). This pattern of increase was smaller than the enrichment between foliage and litter but still significant across most plot types. The one exception was in plots dominated by pine. Plots dominated by pine species (both white and red pine) showed a slight but statistically insignificant decline in Hg concentrations between the litter and humus layer.

**Figure 22. Mean Hg Concentrations in Foliage, Projected Litterfall, Soil Litter (Oi/Oe Horizon), and Soil Humus (Oa Horizon)**

Plots selected for this analysis had relative basal area of at least 50% for the dominant species, so species indicated likely comprise the majority of litterfall. Error bars represent standard errors.
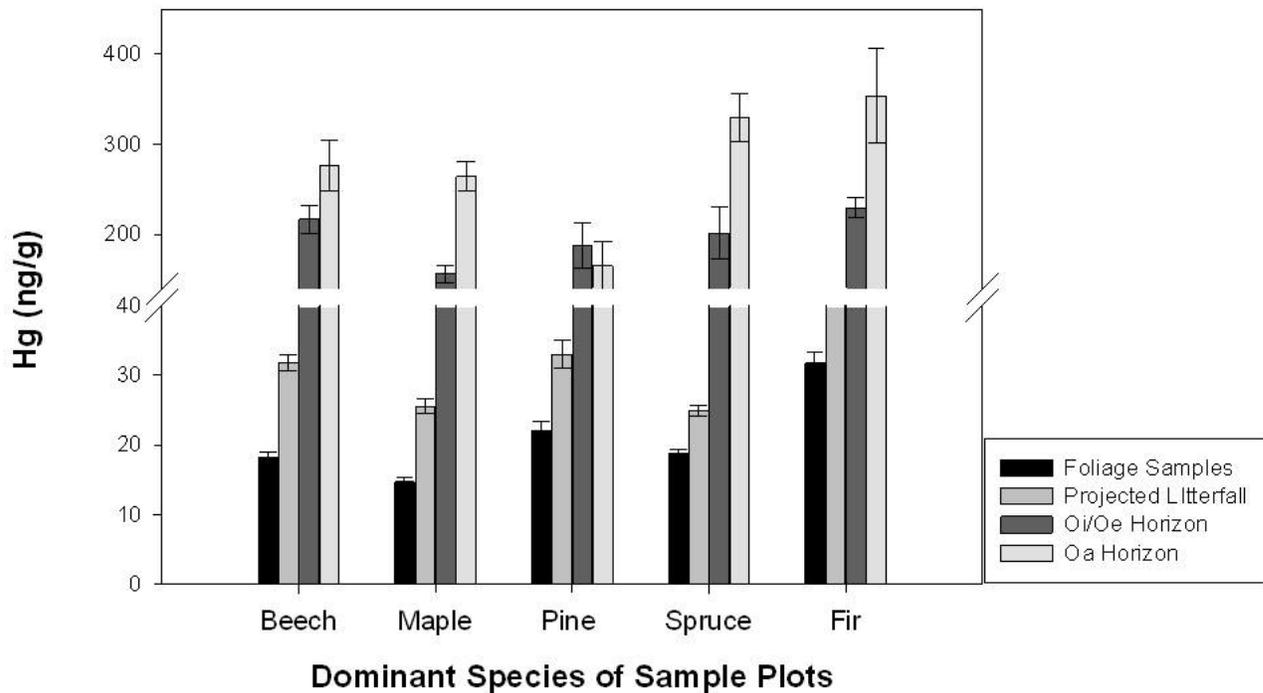


## 6.2.2  Spatial Patterns of Hg in Foliage and Soil

Regression analysis was used to examine relations between Hg concentrations in foliage and latitude, longitude, and elevation. Because of the species-specific differences in foliar Hg concentrations, regression analysis for the hardwood species was performed on the three most abundant species: yellow birch, sugar maple, and American beech. In general, all three hardwood species showed similar patterns of Hg decreasing from south to north, decreasing from west to east, and increasing with elevation (Figure 23). Yellow birch, which was present in the largest number of plots, showed the strongest relations between foliar Hg and geographic variables, with significant negative relations to latitude

($p<0.001$, $R^2 = 0.43$) and longitude ($p = 0.001$, $R^2 = 0.20$) and a significant positive relation to elevation ($p<0.001$, $R^2 = 0.25$). Sugar maple foliar Hg was also significantly, negatively correlated with latitude and longitude ($p =0.003$ and $0.003$, $R^2 = 0.22$ and $0.23$, respectively). The relation between sugar maple foliar Hg concentrations and elevation was positive but not statistically significant. American beech showed similar but weaker patterns than sugar maple, with significant relations to latitude ($p =0.03$, $R^2 = 0.12$) and longitude ($p = 0.04$, $R^2 = 0.10$) but an insignificant relation to elevation.

All conifer species were pooled together for geographic analyses due to smaller sample sizes and the fact that foliar concentrations among species were not significantly different. Separate regressions were run for Age 0 and Age 1 needle classes for conifers. Neither age class of conifer needles showed a significant relation to any of the geographic variables.

Geographic variables were also used to examine spatial relations in organic soil Hg. Regression analysis between litter layer (Oi/Oe) Hg concentrations and latitude, longitude, and elevation did not reveal any statistically significant patterns. Humus layer (Oa) regressions did reveal a weak yet statistically significant negative relation between Hg concentrations and latitude ($p=0.023$, $R^2 = 0.06$). The relation between humus layer Hg concentrations and latitude was also negative but was just outside the bounds of statistical significance ($p=0.07$). Elevation showed a stronger, positive relation to humus layer Hg concentrations ($p=0.01$, $R^2 = 0.17$).

### 6.2.3  Foliar Mercury and Leaf Chemistry

Regression analysis was used to determine relations between foliar Hg concentrations and foliar C and N concentrations. Like the geographic variables, regressions were run for the species yellow birch, sugar maple, and American beech. All conifer species were pooled together but separated by needle age class. There were no significant relations between foliar %C and Hg for any of the species or for the separate age classes of conifers. Stronger relations were found between foliar %N and Hg concentrations, with the strongest relation found in yellow birch ($p=0.005$, $R^2 = 0.43$). Similar but weaker patterns between %N and Hg were evident for sugar maple ($p=0.01$, $R^2=0.19$) and American beech ($p=0.04$, $R^2=0.12$) (Figure 24). There were no detectable relations between %N and Hg concentrations in conifer needles.

**Figure 23. Scatter Plots and Regression Analysis between Hg Concentrations in Hardwood Foliage or Soil Humus (Oa horizon) and Geographic Variables**
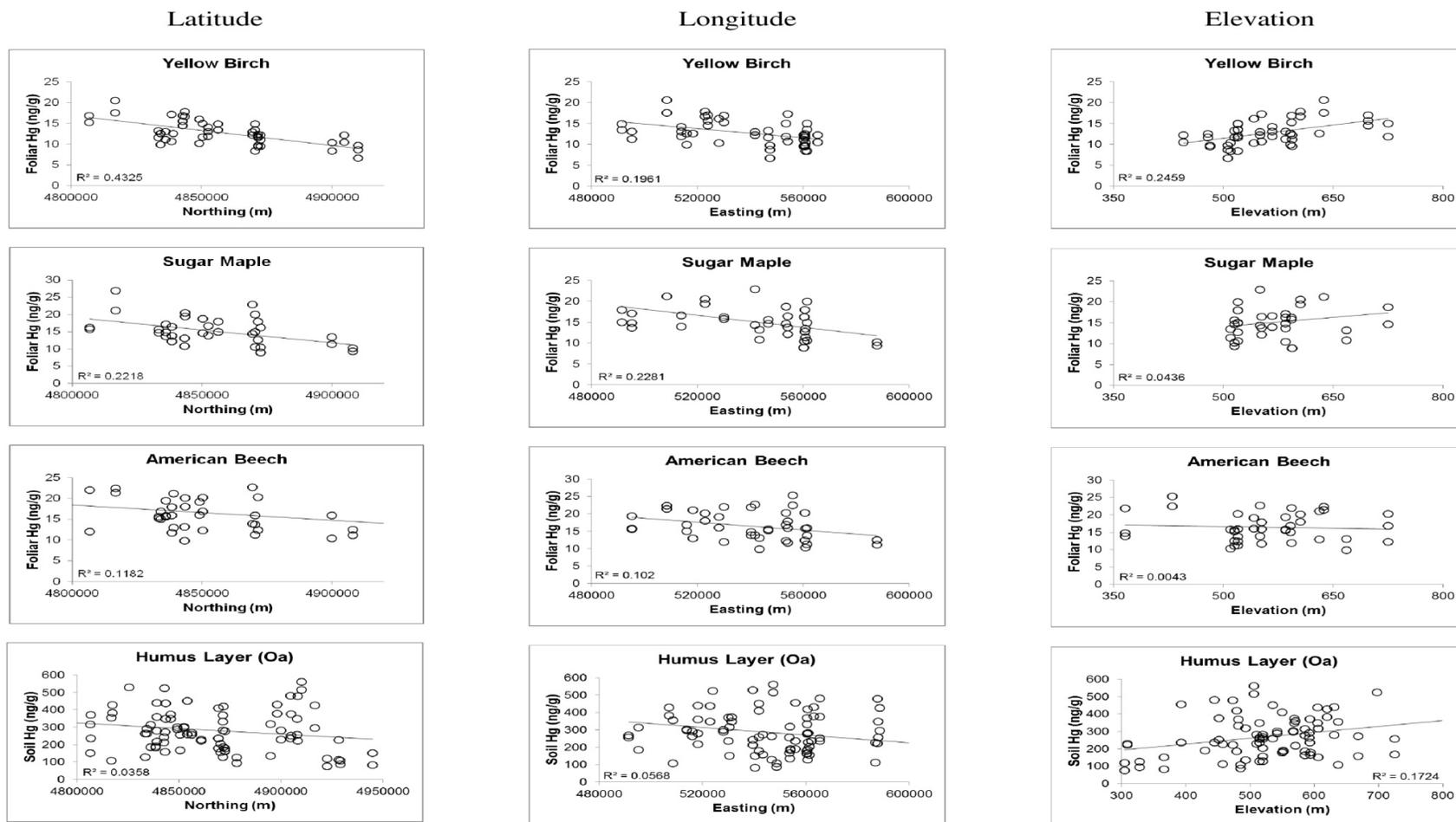
**Figure 24. Scatter Plots and Linear Regression Analysis**

The analysis is between N and C Concentrations and Hg Concentrations in Foliage and Humus Layer Samples from Forest Stands in the Adirondack Region
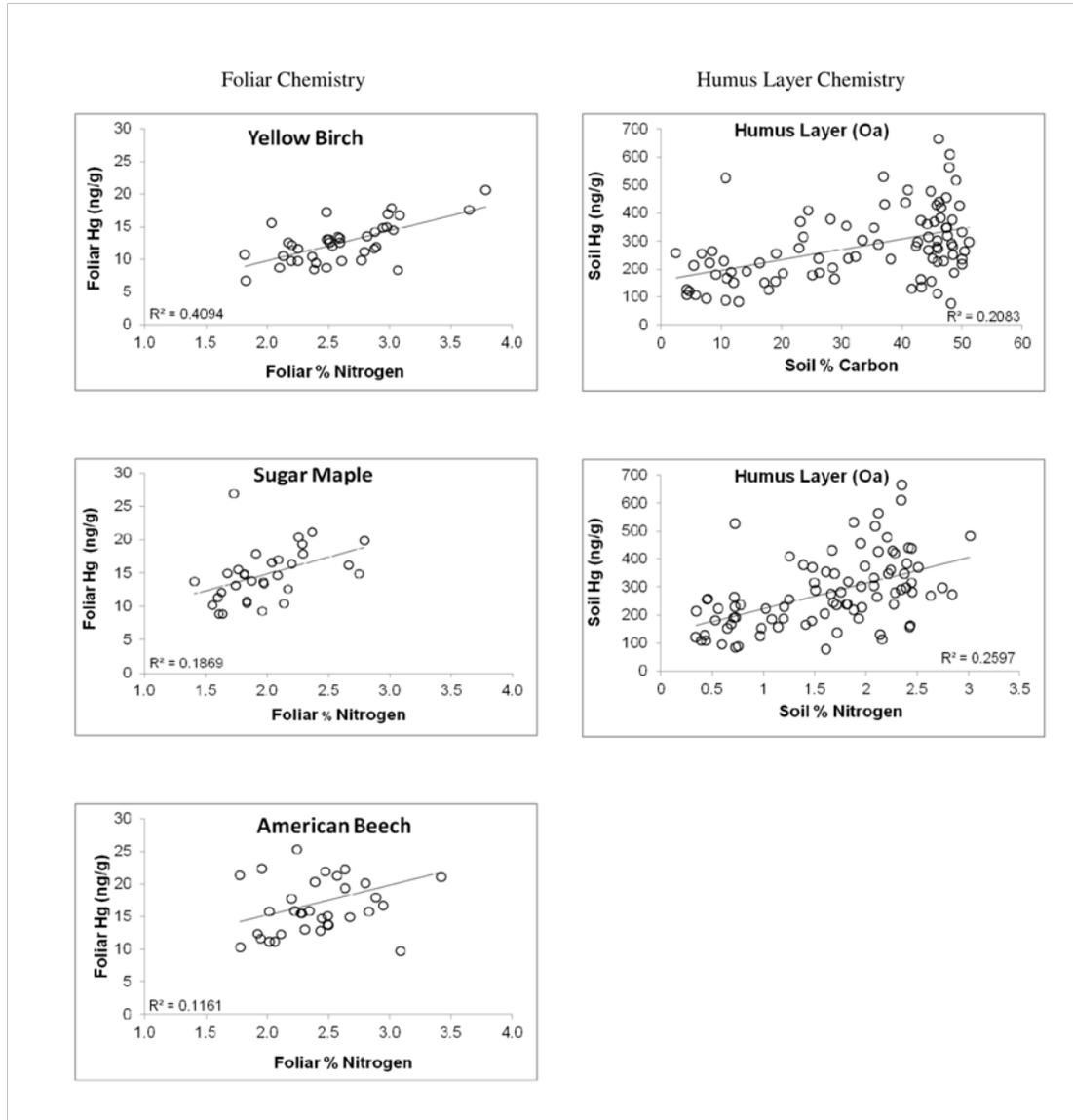


For organic soil samples, relations between %N and Hg and %C and Hg were not significant for the litter layer (Oi/Oe). Among humus layer (Oa) samples, relations between %C and Hg and %N and Hg were strongly positive *(p<0.001, $R^2$ = 0.21, p<0.001, $R^2$ = 0.26,* respectively). When all litter and humus layer samples were pooled together, there was a strong, negative relation between C:N mass ratios and Hg:C ratios, which were best fit by a log-function regression line (*$R^2$ = 0.36,* Figure 25).

**Figure 25. The Relation between C:N Ratios and Log-Transformed Hg:C Ratios in Organic Soils**

C:N ratios are expressed as C(g)/N(g) and Hg:C ratios are expressed as log [Hg(ng)/C(g)]. Triangles represent humus layer (Oa) samples and circles represent litter layer (Oi/Oe) samples.
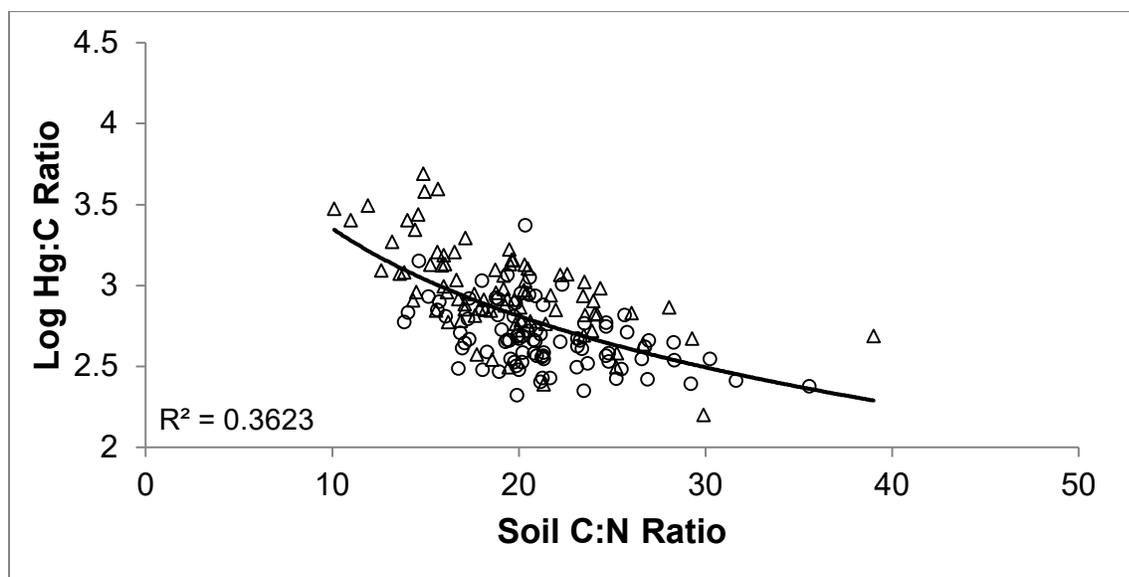


Stepwise regression was used to develop a best-fit multiple regression model for yellow birch foliar Hg concentrations and soil Hg concentrations in the Oa horizon. All geographic, chemistry, and forest characteristic variables were input, and for both foliage and soil, the most significant model used only two variables. For foliage, the two variables selected were N concentration and latitude, but the resulting $R^2$ value was only 0.56. For soil, the two predictor variables were N concentration and elevation, and the resulting $R^2$ was lower than in foliage at 0.38.

## 6.3   Discussion

### 6.3.1  Species Differences

The Hg concentrations measured in foliage during this study were lower than other values reported in the literature. However, this pattern is likely due to the time frame in which the collections occurred—in the middle of the growing season. Given rates of Hg accumulation in hardwood foliage, it would be expected that the measured Hg concentrations would increase approximately 75–100% by the end of the growing season (Figure 22). These extrapolated Hg concentrations are comparable to literature values of foliar Hg from the same species (Bushey et al. 2008, Rea et al. 2002). Species differences were responsible for a large portion of the variation in foliar Hg concentrations. The greatest differences in Hg concentrations were observed between hardwood and conifers, with average hardwood Hg uptake

exceeding conifer uptake by a factor of two to three for most species. Within hardwoods, previous studies have found American beech to accumulate significantly more Hg than other dominant northern hardwood species (section 5; Bushey et al. 2008). American beech also had the highest average foliar concentration among overstory dominant species in this study; however, black cherry, which was not commonly found in the study plots, had a significantly higher concentration than American beech and all other species. Previous studies have demonstrated a positive relation between foliar Hg and Hg concentrations in the atmosphere (Erickson and Gustin 2004). Differences in Hg uptake among tree species have been attributed to physiological differences (e.g., leaf mass per area differences, presence/absence of foliar pubescence) or differences in stomatal uptake (Bushey et al. 2008, Ericksen et al. 2003). These explanations may contribute to the high uptake rates of Hg in black cherry since the foliage does have pubescence on the leaf surface, and a previous study showed greater stomatal conductance in black cherry than all other tree species measured, including four species sampled in this study (Kubiske et al. 1996).

Species differences in foliar Hg accumulation indicate that presence/absence of species in a plot will impact the amount of Hg that can potentially be incorporated into the litter and the soil profile. Litter fluxes are important contributors of Hg in both hardwood (section 4; Bushey et al. 2008, Sheehan et al. 2006, Rea et al. 1996) and conifer stands (section 4; Demers et al. 2007). Among the hardwood species sampled, most species had similar foliar Hg concentrations, suggesting that Hg deposition via litterfall may be more heavily influenced by canopy biomass and litter mass than by species composition in hardwood forests.

The effect of species composition on litter Hg deposition in conifer forests is less predictable than in hardwood forests due to the different ages of the needle classes and year-round exposure to atmospheric Hg. Pine species sampled in this study (white pine and red pine) typically only have two age classes of needles, and they appear to take in Hg at similar rates in both age classes. Other species, such as balsam fir and red spruce, can contain many different needle classes spanning many years. Needles collected during this study were from a maximum of three age classes (0–2 years of age), and needles showed consistent increases in Hg over the three age classes. It is unclear whether this increase would continue throughout the life of the needles or whether Hg accumulation would eventually reach a maximum concentration. It is also unclear what age of needles make up the majority of the litter that falls in conifer plots. These unknowns could cause significant uncertainty when attempting to estimate litter fluxes in forest stands dominated by spruce and fir trees. Further research will be needed to allow better estimation of litter deposition in conifer forests, especially information characterizing the average age of needles at the time of litterfall.

Uptake of Hg via foliage will eventually be deposited to the forest floor as leaves senesce. As a result, a relation between foliar Hg concentrations and soil litter Hg concentrations might be expected. However, no relation was observed between foliar and Oi/Oe horizon Hg concentrations. This lack of a pattern would suggest that there are other sources of Hg to the litter layer or differences in evasion and transport of Hg from the litter among different forest stands. Forest throughfall can contain elevated concentrations of Hg (section 4; Graydon et al. 2008, Rea et al. 2001, Kolka et al. 1999) that could adsorb to leaf litter or humus, increasing concentrations in the soil profile. This process likely explains some of the Hg enrichment effect among the foliage, litter, and humus (Figure 22). Demers et al. (2007) found that throughfall could explain the enrichment in Hg from litterfall to the litter layer in conifer forests but was insufficient to completely account for the enrichment in hardwood forests. The lack of a relation between foliar Hg concentrations and soil litter Hg concentrations would suggest that processes other than litterfall Hg deposition may play an important role in determining the amount of Hg that is retained within the soil of a particular forest.

## 6.3.2 Geographic Patterns

All three dominant hardwood species showed similar regional patterns of uptake of Hg by foliage, which strengthens the likelihood that these patterns represent a true geographic gradient of Hg accumulation. Several studies have suggested that atmospheric $Hg^0$ is the primary form of Hg that is incorporated into leaf tissue (Bushey et al. 2008, Ericksen et al. 2003, Rea et al. 2002). Elemental mercury ($Hg^0$) is estimated to make up almost 60% of anthropogenic atmospheric emissions in the northeastern United States (Denkenberger et al. 2012, Driscoll et al. 2007). Elemental mercury is also stable in the atmosphere and capable of being transported long distances from sources (Fitzgerald et al. 1998). Because there is a demonstrated relation between Hg concentrations in the atmosphere and Hg uptake by foliage (Ericksen and Gustin 2004), it is possible that the observed longitudinal and latitudinal relations represent an atmospheric gradient of $Hg^0$. A spatial gradient of $Hg^0$ has been documented in at least one previous study, with $Hg^0$ concentrations decreasing from urban areas to suburban areas to rural regions (Zhang et al. 2012). Urban areas and electric utility Hg emission sources are located to the west and to the south of the Adirondack Park, which is consistent with the spatial pattern of Hg concentrations in foliage. Also, the predominant wind pattern is from the southwest of the Adirondacks toward the northeast portions of the park and could transport $Hg^0$ from the industrial sources in the Midwest. Back-trajectory modeling of Hg in the Adirondacks has indicated that sources in the Midwest are important contributors

to Hg deposition in the Adirondack Park (Choi et al. 2008a). The spatial pattern of Hg in foliage is also similar to the observed pattern of N concentrations in tree foliage in the Adirondack region, a pattern that has been attributed to gradients in atmospheric N deposition due to long-range transport of N (McNeil et al. 2007).

Positive relations between elevation and Hg concentrations were detected in yellow birch foliage and in the soil humus layer. Elevation effects are particularly difficult to elucidate in foliage because forest species tend to shift from northern hardwood to spruce/fir forests as elevation increases. This shift in forest type limits the range of elevation that can be used for comparisons within a single tree species, and species-specific differences in foliar Hg concentrations make evaluating multiple species simultaneously impractical. In this study, elevation effects are also confounded by the strong correlation with precipitation. The differences in forest types along the elevation gradient will also have an impact on Hg concentrations in soil horizons, so it is not clear whether correlations between elevation and humus layer Hg concentrations are driven by differences in Hg deposition or by differences in cycling and storage of Hg among different forest types. Other research has indicated that both factors could play a role in regulating soil Hg concentrations (section 5). As elevation increases, cloud frequency also increases (Miller et al. 1993), and Hg concentrations in cloud water are generally considerably greater than concentrations in precipitation (section 5; Lawson et al. 2003, Malcolm et al. 2003). Cloud water is rarely considered as an ecosystem input of Hg, and cloud water Hg fluxes increase with increasing elevation. However, cloud water is not likely to be an important input of Hg for most of the sites in this study which were below 1000 m asl. However, the shift to conifer forests with higher elevation also increases Hg deposition via throughfall, as throughfall Hg fluxes under conifers are generally higher than under hardwoods in the Adirondacks (section 4, section 5). It is likely that increases in humus layer Hg with elevation are also mediated by the shift from hardwood to conifer trees with increasing elevation.

While large spatial studies of Hg in foliage and soil are rare in the literature, the patterns observed for the Adirondacks do not correspond to the observations from a study that collected samples from 14 sites ranging from California to Maine (Obrist et al. 2011). Note that half of the sites in that study were located on the West Coast, and large portions of the United States were unsampled. That study failed to detect spatial patterns within foliage which, by the researcher's own admission, is likely because they did not control for tissue age or tree species in their analyses. The study found both litter and soil Hg concentrations increase with latitude, the opposite pattern observed for the Adirondacks. The differences between the two studies are likely based on the scale of the observations, as this study was conducted entirely within a single ecoregion (the Adirondacks), while Obrist et al. (2011) spanned

several different ecoregions. This discrepancy likely demonstrates that large-scale patterns Obrist et al. (2011) observed are controlled by differences in Hg accumulation and cycling among the many different forest types they sampled, while the results from this current study are more likely governed by differences in Hg deposition across the more homogeneous Adirondack landscape.

### 6.3.3  Chemistry Patterns

Multiple studies have linked Hg dynamics to organic C accumulation and processing both in aquatic (Ullrich et al. 2001, Driscoll et al. 1995) and terrestrial environments (Obrist et al. 2012, Pant and Allen 2007, Kolka et al. 1999). However, in this study, there were no significant relations between Hg and C in foliage and litter. This is likely due to the limited variation in C concentration of the samples, with all litter and foliage samples falling in the 47-51% carbon range. Carbon concentrations in the humus layer were more variable, and there was a significant relation between humus layer Hg concentrations and %C. Despite the lack of variation in carbon concentration, there was wide variation in Hg concentrations in the litter layer, indicating that carbon dynamics do not control variation in Hg concentrations in organic soils but that other processes are important drivers, such as the rate of Hg evasion.

Links between N concentrations and Hg concentrations in both foliage and the humus layer are interesting in that both N and Hg are derived from similar sources (such as industrial atmospheric emissions) and are subject to potential long-range transport. Because of the importance of N as a nutrient in ecosystems, there is also a large biological component to N cycling, especially in soils. Nitrogen is strongly retained within terrestrial ecosystems, so C:N ratios tend to decrease as litter is decomposed and processed (Melillo et al. 1989). For this reason, Obrist et al. (2011) used C:N ratios to indicate the relative age of a soil and compare these values with Hg concentrations (normalized as Hg:C ratios). Their relation shows that organic soils with low C:N ratios have the highest Hg:C ratios. This analysis was repeated for the study (Figure 25), and a similar pattern was evident. Obrist et al. (2011) hypothesized that this relation is likely due to differences from centuries of Hg inputs known as "legacy" Hg. However, because the Adirondacks is a region with relatively uniform soil age, disturbance history, and Hg deposition history, it would appear that soil decomposition processes and soil nutrient status are regulating this pattern, and Hg enrichment within the profile seems to be driven more by ecosystem processes than by deposition patterns and "legacy" Hg.

### 6.3.4 Model Comparison

Due to limitations in resolution, most spatial models of Hg deposition are not precise when applied to a relatively small region such as the Adirondack Park. However, Yu et al. (2013) developed a Hg deposition model for the Adirondack region that estimates wet, dry, and total deposition of Hg. There were no significant correlations between foliar or soil Hg concentrations and the model predictions of Hg deposition across the study plots. Obrist et al. (2011) also found that there was little correlation between Hg in litter and soil and estimates of deposition of atmospheric Hg. While this could be due to the accuracy of the models, the lack of correlation could also suggest that landscape processes and biological variation among forest stands are more influential in soil accumulation of Hg than Hg deposition. Multiple regression models built from the data collected from this study were only able to explain a maximum of 56% and 38% of the variance in foliar and soil humus Hg concentrations, respectively. This analysis suggests that a substantial amount of variation in Hg concentrations in foliage and organic soils in the Adirondack region is likely contained in variables that were not considered by this study. Future studies should focus on identifying factors that could be controlling soil Hg accumulation, because soil Hg is a legacy of historical deposition and could become mobilized to the atmosphere or surface waters in the future under conditions of lower atmospheric Hg deposition or changing climate.

### 6.3.5 Foliage and Soil as a Bioindicator of Hg Contamination

It appears that hardwood foliage is sensitive to variations in atmospheric Hg and could be a useful tool in assessing spatial patterns of Hg deposition, even in relatively small geographic areas that have seemingly homogenous forest cover and deposition. The observable, repeatable geographic patterns of Hg in foliage and organic soil from this study indicate that current atmospheric models may not accurately capture fine-scale variation in atmospheric Hg concentrations. Moreover, subtle changes in the landscape or climate may potentially affect Hg uptake by foliage (section 4, section 5). Tree species composition has a strong influence on Hg uptake by foliage, so regions that contain a common hardwood species or a suite of species that accumulate similar Hg concentrations in foliage would be the most suitable for using foliage to assess spatial Hg patterns. Unlike hardwood foliage, conifer needles in this study were not sensitive to changes across the landscape and do not appear to be a suitable indicator of atmospheric Hg gradients. The results from this study also provide observations that support the value of a new program launched by the Mercury Deposition Network of the National Atmospheric Deposition Program in 2012 to monitor Hg in litterfall. Data from this study suggest it would be useful to expand this program to as many sites as possible, as litterfall Hg data are relatively inexpensive to obtain and could

provide useful information about dry deposition of Hg to forested areas. Hg patterns in the soil litter layer were not correlated to spatial or soil chemistry variables, and humus layer Hg concentrations were only weakly correlated with geographic variables. At current environmental levels of contamination, it appears that variation in soil processes, climate, and landcover is too great to allow detection of Hg spatial patterns across similar soil types.

## 6.4   Conclusions

Foliar Hg concentrations vary widely among canopy tree species, but if species differences are considered, hardwood foliage in the Adirondack Park appears to be sensitive to variation in atmospheric Hg, suggesting that atmospheric Hg concentrations decrease from the southwest to the northeast portion of the park. This pattern demonstrates a decrease in atmospheric Hg concentrations with increasing distance from Hg source areas and is consistent with previous findings for other anthropogenic atmospheric pollutants. Foliar and soil concentrations of Hg were related to N concentrations. This consistency suggests that the two contaminants may originate from similar sources and follow similar trajectories before deposition and/or be related through ecosystem processes. Correlations between spatial variables and foliar Hg indicate that foliage sampling is potentially an affordable, simple method for examining spatial Hg patterns, even in remote settings with low-background Hg and relatively homogenous landscape features. Spatial patterns indicate that regional Hg sources could be significantly contributing to foliar Hg concentrations, a finding that suggests atmospheric Hg controls through the Mercury and Air Toxics rule could immediately decrease Hg deposition to forested ecosystems via litterfall.

# 7 Synthesis and Future Recommendations

## 7.1 Effect of Forest Type on Mercury Deposition

The results from all three phases of this research demonstrate that forest type plays an important role in the deposition of Hg to forested areas within the Adirondack Park. This role is complex and not only affects the quantity of Hg deposition but also deposition pathways. Previous studies have hypothesized that conifer needles adsorb reactive Hg more efficiently than hardwood leaves due to higher leaf area indexes (Witt et al. 2009, Kolka et al. 1999). Results from both Phase 1 and Phase 2 support this hypothesis, as throughfall Hg concentrations and fluxes were significantly higher in coniferous forests than in hardwood forests. Results from all three phases found significant differences in foliar Hg concentrations among tree species, with the greatest differences detected between conifer and hardwood species. While the mass of litterfall was similar between hardwood and conifer plots, uptake of atmospheric Hg in conifer foliage occurred at a much slower rate than in hardwood foliage. However, the Hg exposure period is much longer because conifers retain foliage for multiple years. How this factor affects litter Hg fluxes is largely determined by the age of the foliage at the time of senescence. In species such as white pine and red pine, the majority of the litterfall is from needles that are two years old. Concentrations of Hg in pine foliage after two full years are similar to concentrations of Hg in deciduous leaves after a single growing season, so litter fluxes between pine-dominated and hardwood plots are also similar. Other species, such as balsam fir, have needles that are up to seven years old. Balsam fir needles generally need two to three years to accumulate Hg concentrations that are similar to hardwood Hg concentrations at the time of litterfall. While the precise age distribution of needles that make up balsam fir litterfall is not known, field observations of multiple branches from many individual trees indicate that the majority of balsam fir litter is at least three years old, suggesting that litter Hg fluxes in balsam fir stands will potentially be higher than both hardwood and pine dominated stands.

Demers et al. (2007) compared Hg deposition and soil pools between conifer (balsam fir, red spruce) and hardwood plots in the Adirondacks, finding that despite higher inputs of Hg, soil pools were lower in the conifer stand. They speculated this discrepancy was due to elevated evasive losses of $Hg^0$ from the conifer stand. This hypothesis was inconsistent with results from observations in section 4. While similar patterns were evident at Huntington Wildlife Forest in terms of deposition and soil pools for conifer and hardwood stands, evasion of $Hg^0$ was very low in the conifer stand compared to the hardwood stand. As a result, it appears as though coniferous forest stands have another (unmeasured) pathway of Hg loss compared with hardwood stands.

## 7.2   Effect of Landscape and Geography on Mercury Deposition

Sections 5 and 6 of this study showed that many landscape variables were correlated with Hg deposition, and this landscape effect appears to be the result of both physical and biological processes. Observations at Whiteface Mountain suggest that steep elevation gradients affect Hg deposition processes. Mercury deposition increased at higher elevations due to increases in precipitation quantity, increased throughfall and litter Hg concentrations from the presence of coniferous vegetation, and cloud water inputs. The increases in Hg deposition with elevation at Whiteface coincided with increases in Hg concentrations in organic soil layers. In section 6, spatial methods were used to show that increased elevation was also related to higher foliar and organic soil Hg concentrations across the Adirondack Park. The mechanism explaining the relation between elevation and Hg concentrations was less apparent in the park-wide spatial assessment, but overall, the results suggest that elevation plays an important role in Hg deposition processes.

In addition to elevation, the regional survey data (section 6) suggest that both latitude and longitude can significantly affect Hg concentrations in canopy foliage. The mechanism that leads to this pattern is not clear, but it could be related to proximity to sources of atmospheric Hg emissions. The highest foliar Hg concentrations were found in the western and southern portions of the park, which are closest to urban and industrial emission sources. Air concentrations of Hg have been shown to increase along a rural to urban gradient (Zhang et al. 2012), and elevated soil Hg concentrations coincide with areas of elevated industrial activity and atmospheric Hg deposition in the midwestern United States (Nater and Grigal 1992). Although not definitive, the relations of foliar Hg concentrations to latitude and longitude suggest that there is a regional gradient in atmospheric concentrations of $Hg^0$ which reflect regional emissions of atmospheric Hg that are potentially impacting nearby "remote" forest ecosystems. This finding suggests that controls on regional Hg emissions through the implementation of the MATS rule (EPA 2012) could immediately decrease Hg uptake by foliage and lead to lower Hg litter fluxes in forested ecosystems.

## 7.3   Effect of Climate Variability on Mercury Deposition

The role that climate change may play in the global Hg cycle is not well understood. Although some research has addressed this issue, most of it has focused on Arctic ecosystems, where climate change effects are expected to be the most severe (reviewed in AMAP 2011). By noting observations over multiple growing seasons, this current study was able to examine effects of temporal meteorological variability on Hg deposition processes. The results of this study provide some of the only field

observations of climate effects on Hg deposition within the scientific literature. Compared to the cool and moist conditions of 2009, the warmer, drier conditions in 2010 resulted in increased precipitation Hg fluxes, throughfall Hg fluxes, and litterfall fluxes. This difference was particularly pronounced in low- and mid-elevation coniferous forests, as throughfall concentrations were significantly higher throughout 2010. There is considerable land area of temperate deciduous and boreal forest in the northeastern United States and eastern Canada that is similar to the study sites used in this study. If future changes in climate result in shifts in Hg deposition processes that are comparable to observations from this research, total Hg deposition may increase in forested ecosystems of the northeastern United States and eastern Canada. Conversely, the drier conditions of 2010 did decrease total Hg deposition to high-elevation alpine forests. Climate models predict rising temperatures and little change in summer precipitation over the next century (Hayhoe et al. 2008, Plummer et al. 2006, USGCRP 2017), which will likely lead to higher evapotranspiration and drought stress (Pourmokhtarian et al. 2016). These conditions could decrease cloud frequency in high-elevation forests of the eastern United States and Canada, which would presumably decrease total Hg deposition within these forests. Despite this decrease, total Hg deposition to the landscape would likely increase with warming climates because low- and mid-elevation forests occupy a much greater percentage of the landscape than high-elevation montane forests.

## 7.4  Future Research

While the results of this research provide insight into Hg deposition processes and fate, there are still many areas of uncertainty regarding Hg transformations and transport within forested ecosystems. The following research suggestions could provide needed contributions to the overall understanding of Hg deposition and cycling in forests and their watersheds.

- Further investigation into Hg transport in soil solutions, groundwater, and stream water could provide useful information on how deposition of Hg to terrestrial surfaces impacts interconnected aquatic environments. Evidence from this study suggests that the presence of coniferous or deciduous vegetation could impact the magnitude of Hg fluxes and the mechanisms of Hg transport from the soil profile to aquatic systems.
- Examine the physiological effects of tree communities on Hg cycling in forest plots. Obrist et al. (2012) found that uptake of Hg by plant roots and stems differed between coniferous and hardwood species. Mass balances of Hg from section 4 of this research were unable to explain smaller Hg pools in the coniferous plot compared to the hardwood plot. Exploring how tree physiology impacts the Hg cycle could further explain Hg cycling processes in forests.

- Examine linkages between cycling of nutrients (C and N) and cycling of Hg within terrestrial ecosystems. Results from all three phases of this study revealed relations between nutrient and Hg concentrations in foliage, soil, throughfall, and cloud water samples. The strength of these relations was not consistent among different research phases, and they appeared to be dependent on the spatial scale of investigation. Further research that focuses on intensive examination of cycling processes of C, N, and Hg in differing forest plots could produce useful knowledge on how these elements are linked.
- Monitor dry deposition throughout the forested regions of the United States using foliage and fresh litter samples. Measurements of dry deposition of Hg are not standardized and are problematic for calculating Hg deposition fluxes. Foliage and litter sampling provide an inexpensive method for monitoring dry deposition and direct estimates of Hg fluxes due to litterfall. Furthermore, long-term measurements of foliar Hg concentrations should provide a useful record for evaluating the effectiveness of legislation that limits atmospheric Hg emissions.
- Integrate Hg measurements into more of the long-term research sites throughout the United States. Evaluation of slow, constant changes to ecosystems (such as climate change) requires data from multiple years and study sites. Adding Hg measurements to both aquatic and terrestrial long-term research monitoring would result in more robust data sets that would allow for better analysis of long-term trends in Hg cycling.

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# Endnotes

1  http://www.atsdr.cdc.gov/SPL/index.html

2  https://www.health.ny.gov/environmental/outdoors/fish/health_advisories/regional/adirondack.htm#advisorymap

3  http://www.ec.gc.ca

4  mercuryconvention.org/

5  nadp.slh.wisc.edu/mdn/

6  Visit nadp.slh.wisc.edu/mdn for more information about the sampling methods of the MDN network.

7  http://www.esf.edu/hss/em/index.html

8  Adirondack Lakes Survey Corporation, http://www.adirondacklakessurvey.org/

9  www.health.ny.gov/environmental/outdoors/fish/health_advisories/regional/adirondack.htm#advisorymap

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