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CLOUD WATER CHEMISTRY AND MERCURY DEPOSITION
IN A HIGH ELEVATION SPRUCE-FIR FOREST

A Thesis Presented

by

Sean T. Lawson

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements
for the Degree of Master of Science
Specializing in Forestry

October, 1999

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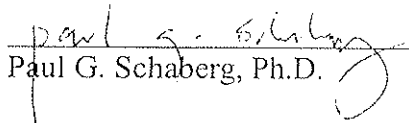
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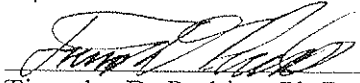
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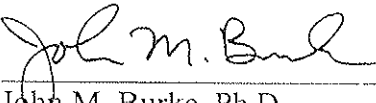
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Abstract

As part of the Lake Champlain Basin watershed study of mercury (Hg) and pollutant deposition, cloud water and cloud throughfall collections were conducted at the south summit (1204m) of Mt. Mansfield, Vermont between August 10 and October 16, 1998, for multi-element chemical analysis. A passive strand-type Teflon collector was deployed during non-precipitating events to sample cloud/fog water at timberline, while three sets of paired funnels collected cloud throughfall under the red spruce-balsam fir canopy. Samples were analyzed for pH, conductivity, and concentrations of Hg, major ions (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+), and 28 trace elements. Ultra-clean sampling and analysis techniques were utilized throughout the study.

Six events were sampled for cloud water alone, and four events were sampled for both cloud water and cloud throughfall. Cloud water pH values were highly acidic, with a volume-weighted mean of 3.0 and a range of 2.1 to 4.4. Cloud throughfall chemistry showed substantial modification with a mean increase in pH of 1.2 units. Much higher concentrations of Hg (2.3x), base cations (Ca^{2+} , K^+ , Mg^{2+} 3-18x) and certain trace metals (Al, Ni, Cu, Mn, Rb, Sr; 2-34x) were observed in throughfall than in cloud water. These results suggest that despite recent reductions in S inputs to the atmosphere, cloud water remains highly acidic and can leach important nutrients from tree foliage. Cloud water deposited an average of $0.42 \pm 0.12 \text{ mm H}_2\text{O hr}^{-1}$ and a total of 279 ng m^{-2} Hg to the forest floor during three non-precipitating cloud events. Estimated cloud water deposition of Hg was $7.4 \mu\text{g m}^{-2}$ for the period August 1 - October 31. Cloud events likely deposit significant annual amounts of water, mercury, and other pollutants to the high elevation ecosystem at Mt. Mansfield.

Acknowledgments

This study has been a cooperative effort that would not have been possible without the participation of many people from the University of Vermont and the University of Michigan. While I was the principal field investigator, Elizabeth Malcolm at University of Michigan Air Quality Laboratory (UMAQL) performed all of the mercury analyses, hosted me during a visit to Ann Arbor, and trained me in the techniques and use of the ICP-MS equipment for analyses of trace metals. Elizabeth has been an invaluable cooperator. Jennifer Larson at the University of Vermont Environmental and Agricultural Testing Lab performed all of the major ions analyses.

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During the course of my research and writing, I learned an incredible amount about clouds and how they interact with the high elevation forests of the Green Mountains in Vermont. It has been an amazing experience, and I will never forget the days of sampling, high on the mountain top, with the wind blowing fiercely at times, immersed in the clouds that had sent everyone else scrambling for the valleys. This study, in particular, and my entire experience as a graduate student have given me a new perspective on the world. As my knowledge of the natural world grows, I am continually humbled by the awesome power of the earth and her ever-changing weather. As I look towards the mountains and up to the sky, I will never see clouds in the same way again!

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Chapter 1 - Cloud Water Chemistry and Ecology

1.1 Introduction

Cloud water has been shown to be ecologically significant and important in the deposition of atmospheric pollutants to high elevation forests (Vogelmann et al., 1968; Lovett et al., 1982; Scherbatskoy and Bliss, 1984; Miller et al., 1993b). On a landscape scale, ecologists have suggested that fog water plays an important role in the development and spatial distribution of coniferous forests. Along the coast of Maine (Davis, 1966), on the slopes of Isle Royal adjacent to Lake Superior, Michigan (Linn, 1957), and in the Green Mountains of Vermont (Siccama, 1974), researchers have observed a sharp transition between spruce-fir and deciduous forests that coincides very closely with the frequent occurrence of fog or cloud moisture.

The deposition of cloud water on exposed surfaces occurs during periods when mountains are immersed in clouds and may represent a large portion (30-50%) of the total water input (rain + snow + cloud water + rime ice) to ecosystems above 1000m elevation in eastern North America (Leedy, 1972; Lovett 1984; Vong et al., 1991; Miller et al., 1993b). Research has consistently shown lower pH and higher concentrations of major ions and other atmospheric pollutants in cloud water than in precipitation collected at the same location (Mrose, 1966; Falconer and Falconer, 1980; Scherbatskoy and Bliss, 1984; Weathers et al., 1988; Miller et al., 1993b; Mohnen and Vong, 1993). The ecological importance of cloud water can be attributed to the following three factors: 1) the

influence of cloud water on the distribution and persistence of plant communities; 2) the greater magnitude of both water and chemical inputs to high-elevation forests relative to lower elevations; and 3) the detrimental effects and possible toxicity to ecosystems that can result from the high levels of pollutant deposition by clouds.

1.2 High Elevation Forest Ecology

Mountainous locations in the northeastern United States between approximately 800 m and 1200 m in elevation are dominated by a coniferous forest ecosystem of balsam fir [*Abies balsamea* (L.) Mill.] and red spruce [*Picea rubens* Sarg.] trees (Siccama, 1974). The climate at this elevation is characterized by a short frost-free growing season, prolonged and sometimes extreme cold in winter, frequent occurrence of high wind speeds, frequent moisture interception via both precipitation and cloud immersion, and much greater inputs of water and chemical species than lower elevations (Voglemann et al., 1968; Leedy, 1972; Siccama, 1974; Scherbatskoy and Bliss, 1984). Shallow, naturally acidic, and nutrient poor soils combine with a harsh climate to make high elevations an inhospitable environment for vegetation. Boreal mountain forests in the Northeast U.S. are island ecosystems which survive at high elevations in a microclimate that is similar to sea-level climate many hundreds of miles to the north. These ecosystems bear the additional stresses of anthropogenic changes in the atmospheric and terrestrial environment such as acid precipitation, pollutant deposition, acidic leaching of nutrients from soils and tree foliage, increased mobility of micronutrients and potential toxins such

as Al in the soil system, increased ultraviolet (UV) light, increased ozone (O₃) exposure, and climate change (Lovett and Kinsman, 1990; Lovett, 1994).

Mountains cause air masses to rise, resulting in orographically enhanced precipitation that is twice as great at high elevations than at valley locations in Vermont (Cummings and Scherbatskoy, 1997; NCDC, 1999). Clouds likely add a significant amount of water to high elevation ecosystems in addition to annual precipitation (Vong et al., 1991; Miller et al., 1993b). Increased total water inputs through both precipitation and cloud moisture cause greater loading of atmospheric pollutants to montane forests.

A progressive decline of high elevation forests in the northeastern U.S. in recent decades has been well documented (Johnson and Siccama, 1983; Scott et al., 1984; Vogelmann et al., 1985; see reviews by Unsworth and Fowler, 1988; Eager and Adams, 1992; and NAPAP, 1992). In Vermont, high elevation red spruce forests have experienced extensive mortality and significantly reduced densities and basal area of trees over the last 40 years (Klein and Perkins, 1992; Johnson et al., 1996). Similar declines have been observed in spruce forests of the southern Appalachian mountains (Bruck et al., 1989) and Europe (Huttl, 1989). Numerous studies conclude that acidic deposition is one of the causal factors leading to this recent decline in high elevation forests (Unsworth and Fowler, 1988; McLaughlin et al., 1990, 1991; DeHayes, 1992; DeHayes et al., 1999).

1.3 Cloud Water Ecology

Researchers have long recognized that cloud and fog moisture play an important ecological role in the coastal and high elevation forests of North America (Nichols, 1918; Kittredge, 1948; Siccama, 1974). In the mountains of California, Kittredge (1948) demonstrated that artificial collectors designed to simulate tree foliage captured much greater quantities of combined cloud and rain water than precipitation-only collectors. Twomey (1956) documented the same phenomenon in Quebec, while Vogelmann et al. (1968) found that rain gauges equipped with wire screen cloud collectors captured on average 67% more water than unscreened gauges at 1100 m in the Green Mountains of Vermont. In recent decades, researchers have continued to employ artificial collecting devices to measure the chemical composition and volume of cloud water deposited (Schlesinger and Reiners, 1974; Weathers et al., 1988; Miller et al., 1993a).

Due to the physical nature of cloud droplet deposition to a forest canopy, direct measurement of total cloud water interception is not possible (Lovett et al., 1982). Therefore, researchers have relied upon modeling the transfer of water from clouds to forests and comparison of these results to field collections of cloud water dripping from the forest canopy to estimate total cloud water inputs (Lovett, 1984; Mueller et al., 1991). Visual observations and research findings confirm that there is a high incidence of cloud immersion and moisture presence at high elevations (Mohnen, 1988; Miller et al., 1993b). However, estimates of total cloud water deposition have relied upon extrapolation of artificial collector rates to a heterogeneous forest canopy, which results in considerable uncertainty.

Measurement of net cloud deposition involves the collection of water dripping from trees (throughfall) and flowing along the main bole of the tree (stemflow), and requires an estimate of interception loss (water evaporation and retention in the canopy) in order to quantify total input of water to a forest (Lovett et al., 1982; Lovett, 1984). Estimated evaporative losses during cloud immersion are usually less than 30% of incident cloud water deposition, but may be much higher during thin, intermittent cloud immersion or very low wind speeds (Lovett, 1984, 1988). In addition, cloud water throughfall amounts are highly variable over short distances and can increase by an order of magnitude where trees or forest edges are exposed to ambient air flow and higher wind speeds (Dasch, 1988; Weathers et al., 1995). Thus, there remains considerable uncertainty associated with estimating cloud water inputs to high elevation forests.

1.4 Cloud Water Chemistry

Comprehensive monitoring of precipitation in recent decades has shown that rain and snow are quite acidic (Lynch et al., 1995; Cummings and Scherbatskoy, 1997) and carry a significant load of pollutants as major ions and heavy metals (Barnes et al., 1982; Lindberg and Turner, 1988; Miller and Friedland, 1999). Investigations of cloud chemistry in the northeast have documented the high acidity and significant loading of potentially toxic metals such as lead, cadmium, and copper in cloud water events (Scherbatskoy and Bliss, 1984; Miller et al., 1993a; Weathers et al., 1995).

Recent studies of cloud water chemistry in North America include the Cloud Water Project (Weathers et al., 1988), two projects by the U.S. Environmental Protection

Agency: the Mountain Cloud Chemistry Project (MCCP) from 1986 to 1989 (Mohnen, 1988) and the Clean Air Status and Trends Network (CASTNET) Mountain Acid Deposition Program (MADPro) from 1994 to present (ESE, 1997). These studies documented significantly higher concentrations of major ions and pollutants in cloud water than in rain and concluded that clouds are responsible for the majority of acidic deposition to high elevations. Measurements of cloud water pH have been as low as 2.4 during single events (Weathers et al., 1988). At all study locations, sulfates (SO_4^{2-}), nitrates, (NO_3^-) and hydrogen ions (H^+) were the major ionic constituents of cloud water.

Cloud chemistry in the eastern United States reflects changes in the atmosphere caused by anthropogenic emissions of pollutants and a myriad of other chemical substances over the last 150 years. In remote southern Chile, precipitation chemistry is thought to be one of the closest approximations to pre-industrial conditions in the world (Hedin et al., 1995; Galloway et al., 1996). Weathers and Likens (1997) measured cloud chemistry at the southern tip of Chile from 1987-1994 and found much lower acidity than in the U.S., with a mean pH of 4.8 (median, 5.2) and a range of pH 4.2-6.3. Interestingly, clouds here were also many times more concentrated in major ions (20-80x) than rain water, showing a greater disparity (cloud vs. rain) than many locations in the U.S. (Weathers et al., 1988). These results suggest that unpolluted cloud water is more acidic and concentrated than theoretically "pristine" rain water (pH~5.6), due to the physical properties of cloud droplets (e.g., size, volume/surface area ratio, scavenging efficiency).

Whiteface Mountain, located in upstate New York approximately 65 km west of Mt. Mansfield, Vermont, is a site of continuous long-term atmospheric monitoring and measurement of cloud water chemistry in the non-freezing months of the year (Miller and

Friedland, 1999), Falconer and Falconer (1980) reported that mean pH in non-precipitating cloud events for the summers of 1977 and 1979 was 3.5, a range of 2.2 to 6.0 and that 90% of the observations were in the pH interval between 2.66 and 4.66. During the 10-year period from 1986-1996 the monthly volume-weighted mean pH of cloud water at Whiteface ranged from 3.2 to 4.2 with a median of 3.9 (Miller and Friedland, 1999). Cloud water at this site contains significantly higher concentrations of H^+ , NO_3^- , SO_4^{2-} , and NH_4^+ than precipitation, and is responsible for about 50% of the total atmospheric deposition (wet + dry + cloud) of both N and S to the high elevation forest (Miller and Friedland, 1999).

Cloud chemistry was monitored at Madonna Mountain, Vermont, several kilometers northeast of Mt. Mansfield, during the summers of 1981 and 1982. Scherbatskoy and Bliss (1984) found that cloud water at this site had a mean pH of 3.8 compared to the mean rain pH of 4.2, and that clouds contained higher concentrations of SO_4^{2-} , NO_3^- , Cd, Cu, Pb, and Zn than rain. Hemmerlein and Perkins (1993) measured the pH and conductivity of cloud water during the 1991 growing season at 900 m on Camels Hump mountain, about 24 km south of Mt. Mansfield. They found that clouds were highly acidic at Camels Hump, with a mean pH of 3.2 (range of 2.9-4.5) and mean conductivity of $467 \mu S cm^{-1}$ (range of 74-997) during seven events. During three of these events, pH averaged only 2.9, a level of acidity that is likely to have significant ecological effects on high elevation forests (DeHayes et al., 1991; Johnson et al., 1996).

Highly acidic cloud water may contribute to red spruce forest decline directly by affecting foliage physiology (Joslin et al., 1988; Adams et al., 1991; DeHayes et al., 1991; DeHayes et al., 1999) or indirectly by altering soil chemistry (Klein and Perkins,

1992; Likens et al., 1996). Low pH clouds leach important plant nutrients (e.g., Ca and Mg) from the foliage of spruce trees (Joslin et al., 1988; Thornton et al., 1994). Foliar leaching of calcium leads to decreased cold tolerance of red spruce foliage and is likely one of the physiological factors contributing to the observed decline of this tree species (DeHayes et al., 1999).

1.5 Cloud Water Deposition

The deposition of cloud water on exposed surfaces that occurs during both precipitating and non-precipitating cloud events may represent a large portion of total water deposition (rain + snow + cloud water + rime ice) in high elevation ecosystems above 1000 m. (Vogelmann et al., 1968; Lovett et al., 1982; Scherbatskoy and Bliss, 1984; Vong et al., 1991; Miller et al., 1993b). Estimated and modeled cloud water inputs are equivalent to 50-100% of precipitation inputs above 1000m (Lovett, 1984; Mosher, 1989; Lovett and Kinsmann, 1990).

High elevation forests are immersed in clouds for significant periods of time over a year (Thornton et al., 1994; Miller and Friedman, 1999). Cloud immersion time increases significantly with elevation. Average cloud base in the northeastern U.S. is around 800 m (Siccama, 1974), where cloud presence is less than 10% (Miller et al., 1993b). At Whiteface Mtn., NY, average cloud frequency is 21% at 1000 m, and 45% at 1450 m (Miller et al., 1993b). The summit of Mt. Washington, NH (1920m) has clouds present 50-60% of the time (Mosher, 1989). High elevation coniferous forests are efficient scavengers of cloud droplets, both as liquid moisture during the growing season,

and as rime ice during sub-freezing months of the year (Vogelmann et al., 1968; Siccama, 1974; Lovett and Kinsmann, 1990).

Lovett (1984) developed a two-part model to simulate cloud water fluxes in a high elevation balsam fir forest. The first part of the model simulates the turbulent diffusion of cloud droplets into the forest and their deposition onto tree surfaces. Lovett divided the forest canopy into multiple strata taking into account a number of different canopy structure details to model the surface area of each layer. Then, using micrometeorological data, his model calculates the transfer of water droplets by both impaction and sedimentation to the canopy in each layer, using a turbulent diffusivity constant, wind speed, boundary layer and aerodynamic resistances, cloud liquid water content, and three different droplet size classes. Cloud water fluxes from each of the droplet size classes are summed for each canopy layer, then each layer is summed to yield the total flux.

The second part of Lovett's model simulates the evaporation/condensation processes during cloud immersion conditions in the forest. Although cloud immersion usually coincides with conditions of atmospheric saturation, evaporation has potentially significant effects. The model predicted that 5 to 30% of intercepted cloud water is lost to evaporation, but this amount may increase to near 100% when light clouds/fog or low wind speeds occur (Lovett, 1984, 1988). Condensation of water onto tree surfaces during cloud events may be important when temperatures drop below the dew point (Shuttleworth, 1977). Lovett (1984) incorporated net radiation and energy flow into the model described above to develop the second sub-model to predict the rates of evaporation or condensation during cloud events.

In a short-term study, Lovett tested his model against field data consisting of hourly deposition rates of water, measured by collecting throughfall in a balsam fir forest at Mt. Moosilauke, NH, during non-precipitating cloud events. Lovett found good agreement between modeled predictions of net cloud water deposition and measured net deposition in the high elevation forest, ranging from 0.1 to over 0.4 mm hr⁻¹. He also found that most cloud deposition takes place in upper 3 m of the canopy, which is the most exposed and receives the highest wind speeds. The total annual deposition of cloud water at Mt. Moosilauke, NH (1200m) was estimated at 84 cm, which is equivalent to about 50% of the precipitation inputs for the year, and thus would account for one-third of the total hydrological budget (rain + snow + cloud water) at this elevation.

Lovett's model has been widely accepted and used as a useful tool in estimating cloud water deposition to high elevation forests. At Whiteface Mtn., NY, Miller et al., (1993b) used a modified version of Lovett's model to estimate cloud water fluxes in a high elevation forest quite similar to that at Mt. Mansfield, VT. They estimated an annual input of 81.1 cm of cloud water at 1225 m, which represents 57% of precipitation (rain + snow) at that elevation. Closer to the summit (1350 m), they found that cloud water input is likely equal to precipitation at 153 cm yr⁻¹. Scherbatskoy and Bliss (1984) measured cloud water interception with an artificial collector at Madonna Mtn., VT (1110 m) over two growing seasons. Using weekly cloud collection rates, they estimated annual cloud water deposition to be 154 cm yr⁻¹ at this location, just northeast of Mt. Mansfield, VT. Table 1 summarizes the estimates of cloud water deposition to high elevation sites across the eastern United States.

Table 1a - Summary of cloud water deposition research at mountain locations in the eastern United States.

Site	Elevation (meters)	Year	Cloud H ₂ O (cm yr ⁻¹)	Cloud (%) frequency	Reference
Mt. Mansfield, VT	1204	1998	92 ± 26 ^a	25 ^b	Lawson et al. (1999)
Whiteface Mt., NY	1225	1986-90	81.1	23	Miller et al. (1993b)
Mt. Moosilauke, NH	1220	1990	40.5	--	Schaefer and Reiners (1990)
Mt. Moosilauke, NH	1220	1980-81	84.0	40	Lovett et al. (1982)
Madonna Mt., VT	1110	1980-81	154.0	--	Scherbatskoy and Bliss (1984)
Camels Hump, VT	1110	1970	76.0	--	Leedy (1972)
Whiteface Mt., NY	1483	1987	127.0	42	Mohnen (1988)
Whiteface Mt., NY	1050	1986-89	28.4	10	Miller et al. (1993a)
Mt. Mitchell, NC	2000	1986	35-77	25-62	Saxena et al. (1989)
Mt. Mitchell, NC	2000	1986-88	59.0	29	Mohnen et al. (1990)
Whitetop Mt., VA	1686	1986-88	90.0	30	Mohnen et al. (1990)
Whiteface Mt., NY	1350	1986-89	153.5	36	Miller et al. (1993b)

- a. Annual cloud water deposition estimated in this study from three non-precipitating cloud events, where mean cloud water flux (not accounting for canopy retention or evaporation) was measured at 0.42 ± 0.12 mm hr⁻¹, extrapolated to annual basis using cloud frequency.
- b. Cloud frequency estimate based on lower limit of visual and meteorological observations at Mt. Mansfield summit station (NCDC, 1999).

One inherent problem with any estimate of cloud water flux is that researchers rely on short-term field measurements during the growing season and then extrapolate the results to an entire year. Due to the high variability of weather conditions and cloud immersion during and between years and the different dynamics of rime ice deposition during the freezing months compared to liquid cloud water deposition in the summer, there remains a considerable degree of uncertainty about estimates of annual cloud water deposition (Lovett and Kinsman, 1990; Miller and Friedland, 1999).

To further compound the complexities of estimating cloud deposition, high elevation forest canopy structure is extremely heterogeneous over small spatial scales. It has been demonstrated that exposed forest edges collect much higher quantities of cloud

water than a homogeneous canopy (Dasch, 1988; Weathers et al., 1995). Cloud water deposition models are based on a homogenous forest canopy, which does not accurately represent the montane forests in steep terrain where cloud interception may be important. Furthermore, the models are quite sensitive to small changes in the input parameters of wind speed, cloud liquid water content, droplet size distribution, cloud immersion frequency, and forest canopy structure, all of which exhibit extreme spatial variability in mountain landscapes (Lovett, 1984; Lovett and Reiners, 1986; Lovett, 1994).

The temporal and spatial variability of cloud deposition make estimates of annual cloud water inputs to an entire forest ecosystem highly uncertain. More accurate quantification of annual cloud water fluxes will require a labor-intensive and continuous measurement of water and rime ice deposition to forest canopies over longer periods of time and at a diversity of mountain locations.

1.6 Pollutant Deposition by Clouds

The subalpine high-elevation forests of the northeastern U.S. receive some of the greatest loads of air pollutants in North America (Lovett and Kinsmann, 1990; Miller et al., 1993a; Miller and Friedman, 1999). The high rate of atmospheric pollutant transfer to montane forests is due to a combination of high frequency of cloud immersion, high wind speeds, orographic enhancement of precipitation, and the large surface area of coniferous trees (Miller et al., 1993b, Lovett, 1994). The ecological effects of atmospheric pollutants on high elevation forests will be a result of total annual loading (wet, dry, and cloud) and transient events with highly concentrated cloud water (Lovett, 1994).

Calculations of ecosystem loading of pollutants which rely solely on estimates derived from rainfall have underestimated total pollutant deposition because they did not include inputs from cloud moisture. Only in recent years have the total atmospheric inputs to high elevation ecosystems been estimated by intensive measurements combined with deposition modeling (Lovett and Kinsman, 1990; Miller et al., 1993b, Miller and Friedland, 1999). These studies indicate that cloud water deposits a majority of the total load of major pollutants to high elevation forests. Murthy and Aneja, (1990) indicated that cloud water can be the primary pathway (~60%) for atmospheric pollutant deposition at high elevations, as compared with rainfall and dry deposition (~20% each). Numerous other studies estimate that cloud deposition contributes 40-80% of total fluxes of the ions that cause acidity and is the primary vector for pollutant loading to high elevations (Lovett et al., 1982; Scherbatskoy and Bliss, 1984; Waldman et al., 1985; Mohnen, 1988; Mueller and Weatherford, 1988; Saxena et al., 1989).

Recent trends of atmospheric pollutant concentrations in precipitation include significant decreases in SO_4^{2-} , Pb, Ca^{2+} , and Mg^{2+} , and a slight increase in NO_3^- (Hedin et al., 1994; Miller and Friedland, 1994; Lynch et al., 1995; Miller and Friedman, 1999). The Clean Air Act Amendments of 1990 placed new restrictions on sulfate emissions in the U.S. and were intended to reduce acidic precipitation in the eastern part of the country. However, despite recent reductions in SO_4^{2-} deposition, the acidity of rain water has remained about the same or slightly increased at most locations in the U.S. (Lynch et al., 1995; Pembroke, 1998). Possible explanations for the lack of improvement in acidic deposition include the decreased buffering capacity in precipitation due to declines in base cations, and increased nitrate emissions, which are not regulated as strictly under the

Clean Air Act (Lynch et al., 1995). Clearly, the continued acidity of precipitation and cloud water deserves attention in both pollution research and regulation.

One pollutant of great concern that has received little attention in studies of cloud water deposition is mercury (Hg). There are no published studies to date in North America that document cloud water concentrations of Hg. Very few measurements of Hg in cloud water have been made anywhere in the world. Researchers in India measured the chemistry of "yellowish fog precipitation" and found that the mean Hg concentration of nighttime fogs at four locations ranged from 19 to 125 ng L⁻¹ (Patel et al., 1998). A study in the mountains of Germany found that Hg in cloud water had a median concentration of 130 ng L⁻¹, with a range of 100-350 ng L⁻¹ (Wrzensinsky et al., 1998). Neither of these studies used the rigorous clean sampling and analysis techniques that are now recognized as essential to prevent contamination of the minute concentrations of Hg present in environmental samples (Fitzgerald, 1993; Keeler et al., 1995). As such, there is some uncertainty about the accuracy of these results and an urgent need for quantification of Hg in cloud water in North America. Given the magnitude of cloud water and pollutant inputs, cloud events at mountainous locations may deposit a considerable load of Hg to high elevations.

Chapter 2 - Mercury as an Environmental Pollutant

2.1 Introduction

Mercury (Hg) has long been recognized as an environmental pollutant of concern (Hunter et al., 1940; Tsubaki, 1968; Takizawa, 1979; Fitzgerald, 1993; Hamasaki et al., 1995; Scherbatskoy et al., 1998). The toxicity of mercury to humans, wildlife, and plants has been well documented (Nriagu, 1979a; Weiner and Spry, 1996; USEPA 1997). Research in recent decades has documented increasing levels of mercury in various environmental media (air, water, soils, vegetation) (Nriagu and Pacyna, 1988; Beauchamp et al., 1997) that has been attributed to increasing anthropogenic emissions of Hg to the atmosphere over the last 150 years (Johansson et al., 1991; Fitzgerald et al., 1998).

Mercury is a highly toxic environmental pollutant that is of concern in North America, Europe, and globally. In Vermont, elevated levels of Hg have been measured in lake water and tissues of fish species in the Lake Champlain Basin (Watzin, 1992). Hg contamination of the lake has been attributed to atmospheric deposition through direct wet and dry inputs and the export of Hg from the watershed area in surface waters (Scherbatskoy et al., 1998). Subsequent bioaccumulation of Hg in the aquatic food chain occurs as Hg is absorbed by organisms directly from lake waters and magnified several orders of magnitude by transfers in trophic level (Lindqvist et al., 1991).

2.2 The chemistry of mercury

Mercury is a complex element which is present at ambient temperatures as a gas, a liquid, and a particle. Pure elemental mercury is a heavy, silver-white liquid (density 13.5 g L^{-1} at 20°C), with a melting point of -38.9°C and a boiling point of 357°C . (Andren and Nriagu, 1979). Mercury is characterized by high electrical and thermal conductivity, high surface tension, and a uniform volume expansion over the temperature range of its liquid phase. Purified mercury tends to readily vaporize, and its vapor pressure increases significantly with temperature, from 14 mg m^{-3} at 20°C to 72 mg m^{-3} at 100°C (Grier, 1968). Liquid Hg has a strong tendency to break into tiny droplets, which increases both the rate of vaporization and the vapor pressure. However, Hg is rarely found in the environment as a pure liquid, but rather as part of inorganic salts, complex organic compounds, and metal amalgams (Nriagu, 1979a).

Elemental Hg is only slightly soluble in water, while many inorganic Hg compounds are highly soluble and mobile. Unlike other metals, Hg tends to form covalent rather than ionic compounds (Andren and Nriagu, 1979). Mercury has a strong affinity for organic compounds which tend to immobilize Hg (Shuster, 1991). Mercury does not readily react with air, oxygen, oxide compounds, hydrogen sulfide, phosphorus, or organic solvents. However, Hg is highly reactive towards ozone, halogens, hydrogen peroxide, nitric and sulfuric acids, and chlorides (Andren and Nriagu, 1979).

Mercury forms a myriad of chemical compounds and can be present in several ionization states [Hg^0 (elemental), Hg^{1+} (mercurous), and Hg^{2+} (mercuric)] (Horvat, 1996). Mercury is most commonly found as mercuric (Hg^{2+}) salts such as HgS and HgCl_2 .

(Carty and Malone, 1979). Many mercuric compounds are highly soluble in water (except HgS, which is highly insoluble) and thus tend to be quite mobile in the environment (Horvat, 1996). Organic mercury compounds, especially methylmercury (MeHg), are highly toxic forms of Hg. Monomethyl- (CH_3Hg^+) and dimethylmercury (CH_3HgCH_3) compounds occur in nature most commonly as methylmercuric chloride (CH_3HgCl) and methylmercuric hydroxide (CH_3HgOH) (Shuster, 1991). MeHg compounds are of the greatest concern, since these are the most toxic forms of mercury. Methylmercury is highly mobile and readily biomagnifies in food webs.

2.3 Sources of Mercury

Mercury has both natural and anthropogenic sources in the global biogeochemical cycle. Mercury is known to cycle and deposit to various ecosystems mainly via atmospheric processes, which also have the most critical role in the global dispersal of Hg (Pacyna, 1996; Fitzgerald et al., 1998). Natural sources of mercury emissions include degassing from the earth's mantle and oceans, volcanoes, geothermal vents, landscape fires, and vaporization of mercury from soils and mineral deposits near the earth's surface (Andren and Nriagu, 1979).

Since the advent of the industrial revolution in the mid 1800's, anthropogenic emissions of mercury have been on the rise. In the last century, mercury has been widely utilized for its unique properties and tendency to form amalgams. Commercial use of Hg has included heavy industry (smelting and ore production), the manufacture of electronics, batteries, fluorescent lamps, thermostats, switches, fungicides and pesticides,

paints, and in chlor-alkali (simultaneous production of chlorine and caustic soda) (Nriagu, 1979b).

Estimates of global Hg emissions vary widely. Globally, combustion of fossil fuels for the production of heat and electricity is considered the largest source of mercury emissions (Pacyna, 1996); (700-3800 tons/yr; Nriagu and Pacyna, 1988). Municipal and medical waste incineration are estimated to be the second largest source of Hg emission globally (200-2100 tons/yr; Nriagu and Pacyna, 1988) and the largest source in the United States (118 tons/yr; USEPA, 1997). Industrial processes (chlor-alkali plants, smelters) are the third largest contributor to global atmospheric Hg (100-200 tons/yr; Nriagu and Pacyna, 1988).

Industrial and combustion processes liberate gaseous elemental mercury (Hg^0) from other materials. Hg concentrations in coal range from 0.01 to 1.5 ppm (Gluskoter et al., 1977) and in crude oil from 0.01 to 30.0 ppm (Pacyna, 1987). During emissions, a substantial portion of mercury is oxidized to Hg^{2+} , which can readily dissolve and react to form mobile salts and organic compounds. Pacyna (1996) estimates that roughly half of emitted Hg to be oxidized (Hg^{2+}), and half elemental (Hg^0), with higher proportions of Hg^{2+} in incinerator releases due to the greater content of chlorine in wastes compared to fossil fuels. Capri (1997) states that mercury in emissions is partitioned as follows: coal combustion sources - 20-50% Hg^0 and 50-80% Hg^{2+} ; waste incinerators - 10-20% Hg^0 , and 80-90% Hg^{2+} . The emitted species of Hg will have a significant effect on the resultant transport and deposition of Hg, as the large fraction of soluble Hg^{2+} will be scavenged and deposited locally, while Hg^0 will tend to contribute to the global Hg cycle.

Information on the global fluxes of mercury remain quite uncertain and incomplete. Researchers have estimated that anthropogenic sources have elevated atmospheric and fresh water Hg concentrations by a factor of 2 to 5 over the historical background levels (Mason et al., 1994). Recent inventories of the global release of mercury to the atmosphere from human activities estimate that 50 to 75% of the total yearly input are due to anthropogenic sources (Nriagu, 1989; Fitzgerald and Clarkson, 1991) The scale of natural emissions processes and the lack of available information from many parts of the world make accurate determinations of worldwide emissions very difficult.

2.4 Mercury in the Atmosphere

Almost all atmospheric mercury is found as a gas (98%) with a small fraction present as a particles (2%) (Mason et al., 1994). Air concentrations generally range from 0.5 to 10 ng/m³ and are partitioned as follows: Hg⁰ - 90 to 99%; Hg²⁺ - 0.1 to 5%; MeHg - 0.1 to 5%; (Horvat, 1996). Elemental mercury has a high vapor pressure, low solubility and low reactivity, thus it has a long residence time in the atmosphere (a year or more). Hg⁰ is transported and cycled globally (Capri, 1997; Fitzgerald et al., 1998). However, reactive (Hg²⁺ and MeHg) and particulate (Hg_p) mercury are short-lived in the atmosphere and have a residence time of only a few hours to several months. Reactive mercury is transported and cycled both locally and regionally (Capri, 1997; Fitzgerald et al., 1998). Mercury is distributed fairly evenly in the troposphere, except near local sources. During

atmospheric transport, Hg is subject to a myriad of complex transformations which are poorly understood by scientists.

2.5 Mercury Deposition

The regional and long-range transport and subsequent deposition of atmospheric mercury result in contamination of ecosystems which may be far removed from sources (Iverfeldt, 1991; Fitzgerald et al., 1998). Deposition of Hg is a function of speciation, meteorological conditions, and atmospheric chemistry. Removal of mercury from the atmosphere occurs through bulk precipitation (including rain, snow, ice, cloud/fog deposition) and dry deposition of Hg vapor and particles (Lindqvist et al., 1991). In forested ecosystems, wet and dry deposition are both significant. Dry deposition is the dominant pathway of Hg deposition to forests when gaseous uptake of Hg into foliage and litterfall is included (Lindberg, 1996; Rea et al., 1996). In open field sites and marine ecosystems, wet deposition is likely to be dominant (Horvat, 1996).

Wet deposition of Hg occurs through the wash-out of soluble and particulate forms of Hg and the oxidation of Hg^0 . Deposited mercury may occur as Hg^{2+} , inorganic salts, organic compounds, and MeHg (up to 5%) (Bloom and Watras, 1988). Atmospheric reactions and Hg oxidation will have an influence on the rate of Hg deposition. It is theorized that elemental mercury in the atmosphere gradually converts to reactive mercury through oxidation processes with ozone, SO_2 , and OH^\cdot , forming HgCl_2 and HgO (Galperin et al., 1995). Oxidized Hg is then transferred to cloud and rain droplets. Acidic conditions and a high availability of chloride ions in clouds tend to

increase this reaction (Galperin et al., 1995). In rain water, Hg is present both in particulate and dissolved forms, with total concentrations ranging from 1 to 100 ng L⁻¹ (Peterson et al., 1996) and averaging in the 1 to 10 ng L⁻¹ range (Lindberg, 1996; Scherbatskoy et al., 1997). The total wet Hg flux for northern temperate systems is in the range of 7 to 12 μg m⁻² yr⁻¹ (Beauchamp et al., 1997; Scherbatskoy et al., 1997).

Dry deposition of Hg includes a number of potential pathways. Particulate Hg may collect on and adsorb to surfaces, gaseous Hg⁰ may oxidize upon contact with surfaces and be adsorbed, and Hg^{II} (gas) uptake can occur in the foliage of living plants (Rea et al., 1996). Forested ecosystems are particularly impacted by dry deposition, since leaf surfaces present an area (available for Hg deposition) that is 4 to 8 times greater than the surface area of the ground. Throughfall measurements and leaf washing experiments indicate that dry deposited Hg washes off of surfaces, transporting Hg to the soil, soil water, and surface waters (Iverfeldt, 1991; Rea, 1998). Hg that is retained by foliage will then be deposited as litterfall. Litterfall in forests may contain high levels of Hg and represent a significant annual input of Hg, estimated to be 13 to 30 μg m⁻² yr⁻¹ for deciduous forests (Rea et al., 1996; Lindberg, 1996). The total flux of atmospherically deposited mercury to forest ecosystems in the Eastern U.S. is estimated to be 40 to 50 μg m⁻² yr⁻¹ (Lindberg, 1996; Scherbatskoy et al., 1998). The rate of gaseous re-emission (via volatilization) of previously deposited Hg is largely unknown, but is also thought to represent a significant flux (Lindberg, 1996).

2.6 Mercury in Forest Ecosystems.

Seasonal patterns and biogeochemistry of Hg vary considerably in temperate forests, as the presence/absence of deciduous vegetation significantly affects the deposition and cycling of Hg. In forested ecosystems, litterfall and throughfall represent the two largest deposition pathways for Hg (Lindberg, 1996; Rea et al., 1996). Dry deposition can contribute a significant fraction to both of these fluxes. During the growing season, forests present a large surface area for dry deposition and foliar uptake of Hg. Deciduous forests in the northeast have a leaf area index (LAI, the ratio of surface area of leaves per unit area of ground) of about 4 (Rea, 1998) whereas coniferous forests have an LAI of approximately 8 (Miller et al., 1993b). The persistent (year-round) foliage and greater surface area of high elevation coniferous forests allow for greater loading of dry deposited Hg than in deciduous forests (Lindberg, 1996). Dry deposition of Hg to forest canopies can be estimated using net throughfall concentration of Hg (total throughfall - precipitation) (Lindberg et al., 1994; Rea, 1998). In general, total throughfall Hg concentration is about twice as high as ambient precipitation (Munthe, 1995; Rea, 1998), suggesting that wet and dry deposition are roughly equal.

Both coniferous and deciduous forests exhibit a strong seasonal trend in wet and dry Hg deposition that is highest during the growing season (May-October) (Lindberg et al., 1994; Munthe et al., 1995). Precipitation inputs of Hg to forests are highest in the summer and fall months, vapor Hg concentrations in the air are relatively constant, while suspended particulate Hg concentrations are highest in the winter (Scherbatskoy et al., 1997). The absence of foliage in temperate deciduous forest significantly reduces dry

deposition during the winter. Coniferous forests also exhibit reduced dry deposition in the winter, and researchers have speculated that this due to less favorable conditions for deposition (e.g., temperature, reduction/oxidation reaction rates, atmospheric chemistry) (Munthe et al., 1995; Iverfeldt et al., 1996). Forest ecosystems may act as sinks for atmospheric mercury deposition. However, even the small fraction of Hg that is exported from forest soils to surface waters represents an important source of mercury loading to watershed systems (Lee et al., 1994; Kolka, 1996).

2.7 Mercury Cycling in Forests

Mercury inputs to forests occur through bulk precipitation, throughfall, dry deposition, and gaseous uptake of Hg^0 through living foliage. Rea (1998) found that Hg concentrations in foliage and litterfall could be largely attributed to gaseous uptake of Hg^0 , while the translocation of Hg in soil water to foliage contributed less than 15% of Hg in litterfall. Others have found that uptake of dissolved Hg in soil water accounts for <10% of Hg in litterfall (Lindberg, 1996; Bishop et al., 1998). Mercury in soil water is primarily in the elemental form (Hg^0), as a dissolved gas (Bishop et al., 1998). As soil water is taken up by trees and lost to the atmosphere by transpiration, only a small fraction (<10%) of the Hg is retained in tree foliage (Bishop et al., 1998). Foliar emission of Hg^0 through evapotranspiration could be a significant mechanism for transfer of soil-based Hg to the atmosphere (Hanson et al., 1995; Lindberg, 1996; Lindberg et al., 1998). Mercury concentrations in the woody tissues of trees are generally low, indicating that

storage of Hg in forest biomass is relatively insignificant (Lindberg, 1996; USEPA, 1997).

2.8 Mercury Accumulation in Forest Soils

It is thought that forest ecosystems and soils, in particular, act as a strong sink for atmospherically deposited mercury. Studies of Hg transport in forested watersheds based on surface water outflows indicate that greater than 90% of deposited Hg is retained and accumulated in forest ecosystems (Lindberg, 1996; Scherbatskoy et al., 1998). The ultimate fate of this atmospherically deposited Hg remains highly uncertain. It is not clear if most of the Hg remains in soils or if a large fraction is revolatilized to the atmosphere. Gaseous re-emission of Hg^0 may account for some or most of the deposited Hg (Lindberg, 1996; Lindberg et al., 1998). However, it is clear that enough Hg is retained in forested catchments to result in the accumulation of Hg in forest soils (Anderssen, 1979; Johansson et al., 1991; Bishop et al., 1998; Donlon 1999).

Mercury is strongly retained by forest soils, particularly in the litter and organic layers, with decreasing concentrations found at increasing depths (Lindberg, 1996; Donlon, 1999). Mercury is found in a wide range of species in the soil environment, including the most toxic form, methylmercury (MeHg). It has a tendency to form inorganic complexes with Cl^- , OH^- , S^{2-} and has a strong affinity for organic matter, especially humic and fulvic acids (Schuster, 1991). Mercury that is complexed with organic compounds or sulfur is generally immobilized, insoluble, and stable (McBride, 1994). The coupling of Hg and organic matter in biogeochemical cycles has been well

documented (Andersson, 1979; Lindqvist et al., 1991; Kolka, 1996). The vast majority of atmospherically deposited mercury is immobilized in the surface layers of soil systems, while a small fraction (<10%) is exported in surface waters (Scherbatskoy et al., 1998).

The gaseous emission of Hg^0 from soils (and other environmental surfaces) may play an important role in Hg cycling (Lindberg et al., 1998), but has been the subject of limited research. At an Hg contaminated site in Tennessee, Lindberg (1996) found that an average of $65.7 \mu\text{g Hg}^0 \text{ m}^{-2} \text{ yr}^{-1}$ was volatilized from the soil, which is close to the annual Hg input at this site. Measurements of the Hg vapor flux here were highly variable and bi-directional, indicating that the soils here may act either as a sink or a source of Hg. At an uncontaminated site in Sweden, the volatile loss of Hg from soils was measured at only $9.0 \mu\text{g Hg}^0 \text{ m}^{-2} \text{ yr}^{-1}$, far less than the annual input of Hg, indicating that soils here were a strong Hg sink (Schroeder et al., 1989). It remains unclear if Hg^0 emissions are a major or minor part of the soil cycle, however, these emissions are an important consideration in any Hg budget.

Mercury accumulation in forested ecosystems is an area of great concern because 1) forest soils contain the highest media-specific concentrations of Hg; 2) the movement of mercury to surface waters largely is through forested catchments; and 3) soils appear to store the vast majority atmospherically deposited Hg. Although the wet and dry deposition of mercury and forest processing of Hg have been thoroughly studied, the transformation, methylation, bioaccumulation, and ultimate fate of Hg in terrestrial ecosystems remains poorly understood.

As anthropogenic emissions continue to add to the burden of Hg accumulation in soils around the earth, volatilization of previously deposited atmospheric Hg may become

increasing important in Hg cycles. The vast pool of Hg that is now present in surface soils is of great concern and may become an even more serious problem if future conditions were to permit increased or rapid mobilization of Hg into biological systems. There is little information available to determine if natural soils will reach a saturation point for Hg or whether changing climatic conditions may increase the export of Hg from soils to surrounding compartments. Widespread contamination of soils by mercury may represent an ominous indicator of pervasive environmental toxicity.

2.9 Conclusions

The scientific literature indicates that both cloud water deposition and mercury pollution are important considerations for high elevation ecosystems and watersheds as a whole. In Vermont, little research has addressed the chemistry or amount of cloud water deposition to montane forests. It is clear from long-term studies that atmospheric chemistry and deposition are highly variable over time, and that current research is needed to address these inputs at high elevations. Because the volume of cloud water inputs are often high for mountain ecosystems, the potential exists for cloud water to be a major source of Hg and other pollutants in mountainous landscapes.

In order to improve quantification of pollutant loading to the LCB watershed, I measured cloud water and cloud throughfall chemistry and quantified deposition rates to the high elevation spruce-fir forest on Mt. Mansfield, Vermont during the late summer/early fall of 1998. The objectives of the field study were as follows: 1) to measure the acidity and concentrations of 8 major ions and 28 trace metals in cloud

water; 2) to measure the chemistry of cloud water which has collected on and dripped through the canopy of the high elevation spruce-fir forest (cloud throughfall); 3) to assess the canopy processing of cloud water; and 4) to perform the first quantification of mercury concentrations in cloud water in North America

The results of this field study are presented in two journal articles (to be submitted to Environmental Science and Technology). Chapter 3, "Cloud water deposition and throughfall chemistry in a high-elevation forest at Mt. Mansfield, Vermont", compares the chemistry of ambient cloud water to cloud throughfall, assesses the canopy processing of deposited cloud water, and quantifies the deposition of mercury, water, and pollutants by clouds to the high elevation forest at Mt. Mansfield. Appendix B, "Mercury and trace metals in cloud water and precipitation at Mt. Mansfield, Vermont", quantifies the short-term concentrations of mercury and other pollutants in cloud water, compares these concentrations to precipitation, and discusses the air mass history and possible emissions sources. In combination, the data collected in this study significantly adds to our understanding of the transfer of mercury and other pollutants high-elevation ecosystems.

Cloud Water Deposition and Throughfall Chemistry in a High Elevation Spruce-Fir Forest at Mt. Mansfield, Vermont.

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Abstract

As part of the Lake Champlain Basin watershed study of mercury (Hg) and pollutant deposition, cloud water and cloud throughfall collections were conducted at the south summit (1204m) of Mt. Mansfield, Vermont between August 10 and October 16, 1998, for multi-element chemical analysis. A passive strand-type Teflon collector was deployed during non-precipitating events to sample cloud/fog water at timberline, while three sets of paired funnels collected cloud throughfall under the red spruce-balsam fir canopy. Samples were analyzed for pH, conductivity, and concentrations of Hg, major ions (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+), and 28 trace elements. Ultra-clean sampling and analysis techniques were utilized throughout the study.

Six events were sampled for cloud water alone and four events were sampled for both cloud water and cloud throughfall. Cloud water pH values were highly acidic, with a volume-weighted mean of 3.0 and a range of 2.1 to 4.4. Cloud throughfall chemistry showed substantial modification with a mean increase in pH of 1.2 units. Much higher concentrations of Hg (2.3x), base cations (Ca^{2+} , K^+ , Mg^{2+} 3-18x) and certain trace metals (Al, Ni, Cu, Mn, Rb, Sr; 2-34x) were observed in throughfall than in cloud water. These results suggest that despite recent reductions in S inputs to the atmosphere, cloud water remains highly acidic and can leach important nutrients from tree foliage. Cloud water deposited an average of $0.42 \pm 0.12 \text{ mm H}_2\text{O hr}^{-1}$ and a total of 279 ng m^{-2} Hg to the forest floor during three non-precipitating cloud events. Estimated cloud water deposition of Hg was $7.4 \mu\text{g m}^{-2}$ for the period August 1 - October 31. Cloud events likely deposit significant annual amounts of water, mercury, and other pollutants to the high elevation ecosystem at Mt. Mansfield.

1. Introduction

Cloud water has been shown to be ecologically significant and important in the deposition of water and atmospheric pollutants in high elevation forests (Vogelmann et al., 1968; Lovett et al., 1982; Scherbatskoy and Bliss, 1984; Lovett and Kinsman, 1990). The deposition of cloud water droplets on exposed surfaces occurs during both precipitating and non-precipitating cloud events and may represent a large portion (30-50%) of total water inputs (rain + snow + cloud) in high elevation ecosystems above 1000m. (Lovett, 1984; Leedy, 1972; Vong et al., 1991; Miller et al., 1993b). Research has consistently shown lower pH and higher concentrations of major ions and other atmospheric pollutants in cloud water compared to precipitation collected at the same site (Mrose, 1966; Falconer and Falconer, 1980; Scherbatskoy and Bliss, 1984; Weathers et al., 1988; Miller et al., 1993b; Mohnen and Vong, 1993). Previous studies in the northeast U.S. have documented high acidity and significant loading of toxic metals such as lead, cadmium, and copper in cloud water events (Scherbatskoy and Bliss, 1984; Miller et al., 1993a; Weathers et al., 1995). However, concentrations of mercury (Hg) in cloud water have not yet been reported in the literature.

Mercury is a naturally occurring element that is also considered a highly toxic environmental pollutant of global concern, due to additions of Hg to the atmosphere by anthropogenic emissions. In Vermont, elevated levels of Hg have been measured in lake water and tissues of fish species in the Lake Champlain Basin (Watzin, 1992). Mercury contamination of the lake has been attributed to direct wet and dry atmospheric deposition and the transport of Hg in surface waters to the lake (Scherbatskoy et al.,

1998). Previous estimates of Hg loading to this watershed (Rea et al., 1996; Scherbatskoy et al., 1997) have not accounted for cloud water inputs of Hg to high elevations and likely underestimated total Hg deposition. The input of Hg to high elevation sites is likely much greater than low elevations due to orographically enhanced precipitation and the additional contribution from clouds.

A progressive decline of high elevation forests in the northeastern U.S. in recent decades has been well documented (Johnson and Siccama, 1983; Scott et al., 1984; Vogelmann et al., 1985; see reviews by Eager and Adams, 1992; and NAPAP, 1992). In Vermont, high elevation red spruce forests have shown extensive mortality and significantly reduced density and basal area over the last 40 years (Klein and Perkins, 1992; Johnson et al., 1996). Acidic deposition has directly contributed to the observed decline of red spruce in the Northeast (Unsworth and Fowler, 1988; DeHayes, 1992; NAPAP, 1992). Highly acidic cloud water has been found to leach important plant nutrients (e.g., Ca and Mg) from the foliage of spruce trees (Joslin et al., 1988; Thorton et al., 1994; DeHayes et al., 1999) and increase the the risk of damage to foliage by freezing injury during the winter (DeHayes et al., 1991; Vann et al., 1992)

Cloud water can be an important source for the loading of chemicals to mountains and entire watersheds. In order to improve quantification of pollutant inputs to the Lake Champlain watershed, we measured cloud water and cloud throughfall chemistry in the high elevation spruce-fir forest on Mt. Mansfield, Vermont, from August 10 to October 16, 1998. Our cloud water research was divided into two studies. The first paper (Lawson et al., 1999) quantifies the deposition of water, mercury, and other pollutants due to cloud immersion at Mt. Mansfield, and characterizes the chemistry of

cloud throughfall, providing a detailed assessment of a forest canopy processing of cloud water in a high elevation ecosystem. The second paper (Malcolm et al., 1999) quantifies mercury and trace metal concentrations in clouds and precipitation and identifies source regions and other factors that may affect the observed concentrations.

2. Methods and Materials

2.1 Site description

The study site is at the south summit of Mount Mansfield (1204 m), located along the spine of Green Mountains in north-central Vermont. The site is located ~35 km northeast of Burlington, Vermont, ~120 km south of Montreal, Quebec and ~28 km east Lake Champlain. Mt. Mansfield has been a site for meteorological measurements and long-term ecological study since 1954.

The high elevation forest at this site is predominately balsam fir [*Abies balsamea* (L.) Mill.] with a lesser component of red spruce [*Picea rubens* Sarg.]. The canopy is characterized by a highly variable mix of mature trees, regenerating clumps of young trees, and open gaps created by wind throw or forest dieback. The average canopy height is approximately 7-10 m which decreases rapidly near the elevational limit of this forest at about 1200 m. Meteorological measurements are made in an open area adjacent to several buildings which service radio and television transmitter towers at the summit. The site receives an annual average of 173.5 cm of precipitation (1955-1998) which is about twice the annual average of 87.2 cm (1955-1994) at Burlington, Vermont, a low elevation site (101 m) located on the eastern shore of Lake Champlain (NCDC, 1999). The

meteorology during our sampling period (August 10 - October 16, 1998) was fairly representative of average conditions during this time of the year at Mt. Mansfield.

2.2 *Cloud water and throughfall collection*

The cloud water collector was installed just above timberline on the western slope of Mt. Mansfield, near the summit, allowing direct interception of ambient clouds. Cloud water was collected and analyzed as described in Malcolm et al. (1999). Three pairs of funnel collectors (each pair consisting of one glass and one polypropylene funnel; 182.4 and 167.55 cm² collection area, respectively) were randomly placed under the canopy of the mature spruce-fir forest with the funnel opening 0.5m above the ground. The throughfall collection site is approximately 10 m lower in elevation and 100 m southwest of the cloud collector in an area with a gentle slope (<5%) and a western aspect.

Throughfall collection was initiated during periods when non-precipitating clouds were present, after a "loading-up" period of at least 2 hours, which allowed the trees to become saturated with cloud water. When the forest was saturated, throughfall closely approximated net cloud deposition and the drip rate was sufficient to collect the volume required for sample analyses. This method slightly underestimates total deposition, since there is some evaporation of water from the canopy (inception loss) and some water moves to the forest floor as stemflow. However, inception loss is likely to be small under the high humidity conditions that were sampled, and stemflow has been found to be very low (~ 2% of water deposited) in coniferous stands (Lindberg and Owens, 1993).

Ultra-clean sampling techniques were utilized in all phases of collection and handling of samples. Funnels and bottles were subjected to a rigorous, multi-day acid

washing process and stored in triplicate zip-lock bags, as described by Malcolm et al. (1999). Particle-free gloves were worn at all times during handling of equipment or sample bottles. Polypropylene funnels and bottles were used to collect cloud water throughfall for pH, conductivity, major ions and trace metals analyses, while glass funnels and Teflon bottles (with 20 ml 0.08 M HCL acid preservative) were used for mercury analysis. After collection, sample bottles were sealed with Teflon tape and triple bagged for storage.

The passive collector used in this study does not exclude precipitation, thus sampling was only conducted during non-precipitating cloud events. The fog collector and funnels were deployed during appropriate cloud conditions and then dismantled and acid washed after each cloud event. Two to three sequential samples were obtained for cloud water in each event when sample volume was sufficient, while three replicates of cloud throughfall were obtained in each event. Due to event frequency and logistical considerations, only four events were sampled for both cloud water and drip water concurrently.

2.3 *Sample analyses*

Collected samples were immediately transported to the Proctor Maple Research Center (PMRC) in Underhill Center, Vermont. Sub-samples were poured-off in a portable class 100 HEPA filtered air chamber. Measurement of pH and conductivity was performed at PMRC within two hours of the conclusion of field sampling, as described by Malcolm et al. (1999). Bulk samples were stored at 4°C and packaged for overnight shipment to University of Michigan Air Quality Laboratory (UMAQL) for trace metal

and mercury analysis. Sub-samples were refrigerated until transport to the University of Vermont Environmental Testing Laboratory in Burlington, Vermont, where they were stored frozen (-20°C) until major ion analyses (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+) were performed as described by Malcolm et al. (1999).

A series of field blanks were collected by pouring ~500 ml of de-ionized water through a funnel, washing all sides, into a sample bottle (n=6) following protocol by Landis and Keeler (1997). Concentrations of Hg, trace metals, and major ions in blanks were below machine detection limits. All field blanks and laboratory standard check samples tested within +/- 0.05 and +/- 0.10 pH units of control, respectively. QA/QC procedures for all other data analyses are described by Malcolm et al. (1999).

3. Results and Discussion

3.1 Cloud acidity

Cloud water was sampled in nine non-precipitating cloud events (n=17) and one cloud event (n=3) that contained brief showers of both rain and snow which could not be excluded from collection (10/1/98). Sequential cloud samples and replicate throughfall samples were volume-weighted to determine mean concentrations. The chemistry of collected cloud water is presented in Malcolm et al. (1999). Cloud events at Mt. Mansfield were found to be highly acidic with a volume-weighted mean pH of 3.0 and conductivity of $487 \mu\text{S cm}^{-1}$. Event-based mean pH and conductivity ranged from 2.38 to 3.44, and 181 to $1842 \mu\text{S cm}^{-1}$, respectively, while individual sequential samples ranged

from pH 2.11 to 4.38 and conductivity of 21 to 3360 $\mu\text{S cm}^{-1}$. Figure 1 shows the pH results for all cloud water samples with the volume collected and duration of collection. The lowest pH values were observed during low volume events.

Clouds sampled in this study had some of the lowest pH measurements for cloud water reported in the literature. Other reports of extremely low cloud pH values include 2.26 at Whiteface Mtn., NY (Falconer and Falconer, 1980), 2.3 and 2.4 at Mt. Mitchell, NC (Holden, 1986). The Vermont Acid Precipitation Program, initiated in 1980, monitors the pH of precipitation year-round. Mt. Mansfield consistently receives the lowest pH precipitation in Vermont (Pembroke, 1998). Volume-weighted annual mean pH (1980-1994) ranged from 3.86 to 4.49, and single low-volume precipitation events at Mt. Mansfield have been as acidic as pH 3.0 (Pembroke, 1998). Precipitation pH tends to be lowest during the summer months at Mt. Mansfield. Physiological damage to red spruce foliage can be severe at or below pH 3.0 (Dehayes et al., 1999).

The cloud events sampled in this study are a small subset of all possible cloud events at Mt. Mansfield and these non-precipitating clouds may represent the driest events with the lowest liquid water content (LWC). Estimated LWC was not higher than 0.25 g m^{-2} in any sampling period, and estimated mean LWC was 0.12 g m^{-2} for all cloud events. This result is much lower than the seasonal average LWC (1994-1996) of about 0.55 g m^{-2} at nearby Whiteface Mtn., NY, where non-precipitating clouds were continuously monitored from June to October (ESE, 1997). The seasonal mean pH at Whiteface ranged from 3.5 to 3.8, reflecting the broader range of cloud conditions sampled and the higher LWC values observed there.

Visual observations during this study indicate that the cloud base elevation was frequently within 100 m of the study site. The edge or bottom of a cloud generally contains smaller droplets and lower LWC than to the middle of the cloud (Leitch et al., 1983; Mohnen, 1988). Ionic concentrations show the reverse pattern and are highest at the cloud edge, where droplets have the highest concentrations and the lowest pH values. The proximity of the cloud base would suggest that our measurements sampled the most highly concentrated portions of the clouds. The low LWC of sampled clouds and the low pH of precipitation observed at the summit of Mt. Mansfield help to explain the high acidity and ionic strength of cloud water in our study.

3.2 *Cloud water deposition*

Total cloud water deposition is defined as canopy throughfall (TF) + stemflow (water flowing along the main stem of trees) + canopy retention (the amount of water required to saturate the canopy) - evaporation. Net cloud water deposition is defined as the quantity of water that reaches the forest floor, measured here as cloud throughfall, and slightly underestimates total deposition. Cloud deposition rates (Figure 2) were calculated by dividing the volume of water collected in the funnel collectors (ml) by the collecting surface area of the funnels (cm^2) and the duration of collection (hr). A mean deposition rate of $0.42 \pm 0.12 \text{ mm H}_2\text{O hr}^{-1}$ was observed for three non-precipitating cloud events.

These results agree closely with the mean deposition rate (0.45 mm hr^{-1}) measured at Whitetop Mtn., VA (Mueller et al., 1991), and are slightly higher than the rates observed and modeled ($0.1\text{-}0.4 \text{ mm hr}^{-1}$) at Mt. Moosilauke, NH (Lovett, 1984). Miller et al. (1993b) used a modified version of Lovett's model to calculate cloud water deposition

at Whiteface Mt., NY. They reported an estimated annual water deposition of 81.1 cm at 1225 m elevation and an observed cloud frequency of 23.2%. These results yield an average annual deposition rate of 0.39 mm hr^{-1} , which is very close to our short-term mean. Based on visual observations and meteorological records (NCDC, 1999), the summit of Mt. Mansfield is estimated to be immersed in both precipitating and non-precipitating clouds a minimum of 25% of the year. Using our measured deposition rate, we estimate annual cloud water inputs of $92.0 \pm 26 \text{ cm yr}^{-1}$ at 1204 m (Table 1). A comparison to estimated deposition rates at similar elevations in the northeastern U.S. is shown in Table 1.

Cloud water interception in high elevation ecosystems is highly variable over short distances, as a function of micrometeorology, wind speed, liquid water content, droplet size distribution, and forest canopy structure (Lovett 1984, 1994). Exposed forest edges and individual trees which protrude from the canopy will collect much greater quantities (up to 10x) of cloud water than a homogeneous canopy (Weathers et al., 1995; Dasch, 1988). Because high-elevation forests are quite heterogeneous and cloud immersion changes dramatically with elevation (Miller et al., 1993b), cloud deposition will vary widely across different elevations and years in these ecosystems. As such, any estimate of annual cloud water deposition involves a considerable degree of uncertainty.

3.3 Throughfall chemistry

3.3.1 Acidity

Cloud throughfall was collected for three non-precipitating cloud events ($n=13$) and one precipitating event on 10/1/98 ($n=6$), with a volume-weighted mean pH of 4.17.

Acidity decreased significantly ($p < 0.015$) as cloud water passed through and was modified by the coniferous forest canopy, with a mean increase of +1.17 pH units. The greatest change in acidity occurred during low volume deposition of cloud water (8/26, 9/10), where cloud droplets had the longest contact time with foliage and the greatest opportunity for chemical interaction.

Few other studies have collected throughfall during non-precipitating cloud events. Bruck et al. (1989) found that mean cloud pH increased from 3.5 to 3.9 as it passed through the foliage of a spruce forest at Mt. Mitchell, NC, while Dasch (1988) found an mean increase of +0.65 pH units in throughfall compared to cloud water in a fir forest at Clingmans Dome, NC. Cronan and Reiners (1983) found that incoming strong acids in precipitation at Mt. Moosilauke, NH, were neutralized by base cation exchange and Bronstead base leaching. Cation exchange in tree tissues occurs when H^+ ions are removed from solution by tree foliage, displacing base cations and releasing neutral salts of K, Ca, Mg, or Mn, resulting in a net neutralization of acidic inputs.

3.3.2 *Major ions*

Major ion chemistry was altered considerably in cloud throughfall relative to ambient cloud water. Base cation concentrations were much higher in throughfall, with an increase of 3.4x for Ca^{2+} , 4.2x for K^+ , and 18.1x for Mg^{2+} (Table 2). Enrichment of these cations may be due to leaching from foliage, wash-off of dry deposition, or evaporation in the forest canopy. Sulfate, ammonium, and sodium ions showed a slight increase in throughfall concentrations. Chloride and nitrate concentrations were lower in throughfall,

indicating net retention of these ions in the canopy. No statistically significant differences were detected ($p < 0.1$) probably because of the small sample size.

It is likely that much of the increase in base cation concentrations observed in TF are due to foliar leaching. Evaporation is generally low during cloud immersion (Lovett, 1984; Shuttleworth, 1977). Concentrations of base cations in the atmosphere have declined significantly in recent years, with the steepest declines in the northeast U.S. (Hedin et al., 1994; Lynch et al., 1995), making dry deposition an unlikely source of the increased TF concentrations of these elements. It is well known that foliar loss of cations increases significantly as pH of water inputs decreases (Evans et al., 1981; Scherbatskoy and Klien, 1983; Joslin et al., 1988; DeHayes et al., 1999). Joslin et al. (1988) found large increases of base cations in cloud throughfall in a spruce forest, with Ca, Mg and K concentrations 8x, 4x, and 7x higher than in cloud water, respectively. Foliar Ca and Mg losses were markedly intensified by increased acidity. DeHayes et al. (1999) demonstrated that leaching by acidic clouds causes significant loss of Ca from red spruce needles, leads to foliar membrane instability, and decreases foliar cold tolerance by 3-10°C. Depletion of foliar calcium by acidic cloud water is one of the physiological mechanisms that helps to explain the observed decline in high elevation red spruce in Vermont over the last 40 years (DeHayes, 1992).

The decrease in NO_3^- concentrations in cloud throughfall likely indicates an uptake of nitrogen by the foliage. Lower concentrations of nitrogen in throughfall compared to cloud or rain water have also been observed in the southern Appalachians (Lindberg et al., 1986; Joslin et al., 1988; Dasch, 1988; Shubza et al., 1995). Grennfelt et al., (1986) suggested that N-deficient ecosystems will utilize N from wet deposition,

while N-saturated systems will release N. Our results suggest there is considerable uptake of nitrogen in cloud water by tree foliage at high elevations on Mt. Mansfield.

3.3.3 *Mercury and trace metals*

Throughfall (TF) concentrations of mercury and certain trace metals (Table 3) were considerably higher than in cloud water. Due to the small size of the data set, it is difficult to detect statistically significant differences, however, a paired t-test revealed significantly higher TF concentrations of Ni ($p < 0.06$) and Cu ($p < 0.04$).

Mean TF concentration of Hg ($17.5 \pm 6.6 \text{ ng L}^{-1}$) was 2.3x higher than in cloud water ($7.5 \pm 2.7 \text{ ng L}^{-1}$) collected concurrently (Table 4). Increased Hg found in cloud TF for the high elevation spruce-fir forest is similar to that observed in precipitation TF (1.85x) by Rea et al. (1996) in a lower elevation (400m) hardwood forest on the western slope of Mt. Mansfield. The increased Hg concentrations in TF can be attributed to wash-off of dry deposited Hg from tree foliage (Lindberg et al., 1994, Rea et al., 1996). Increases of Hg and Al (also dry-deposited) in TF at Mt. Mansfield were larger for the two events (8/18 and 10/1) preceded by a dry period of > 48 hr than in the event (9/10) preceded by two days of cloud immersion and intermittent rain showers (Figures 3 & 4), supporting this conclusion.

Increased Hg concentrations in TF are remarkably similar across different forest types and years. At Walker Branch, TN, precipitation throughfall had a mean concentration of Hg about 2x higher than rainwater in a deciduous forest (Lindberg et al., 1994). In a coniferous forest in Sweden, annual mean throughfall Hg concentration was 1.8x to 2.3x higher than precipitation over three study years (Munthe et al., 1995).

The trace elements selected for this study were chosen due to their toxicity (Hg, Al, Cr, Ni, As, Cd, Pb), importance as plant nutrients (Mg, Mn, Cu) or behavior similar to essential plant nutrients (Rb, Sr). One group of trace elements (Cu, Mn, Rb, Sr) is subject to leaching from the leaves of plants (Tukey, 1970; Heinrichs and Mayer, 1980; Evans et al., 1981; Lindberg, 1989; Rea, 1998). Foliar leaching may be an important source of the enrichment observed in the throughfall concentrations at Mt. Mansfield. Mean concentrations of Mn and Rb were 24x and 38x higher in throughfall, respectively, indicating the strong influence of foliar leaching on these elements. Sr was enriched 4x in throughfall, close to the 3.5x increase in Ca which has similar behavior in plants.

A second group of elements (Hg, Al, Cr, Ni, As, Cd, Pb) have known emission sources to the atmosphere such as combustion of fossil fuels, smelters, and incineration (Milford and Davidson, 1985) and are generally not leached from foliage (Rea, 1998). These elements are deposited by both wet and dry processes. Cloud events which follow periods without precipitation can wash dry deposited materials from foliar surfaces, as observed for Hg and Pb in precipitation throughfall (Iverfeldt, 1991; Rea et al., 1996). Similar increases in throughfall concentrations were observed for other dry deposited metals at Mt. Mansfield (Al, Cr, Ni, Cd).

Aluminum is a crustal element, often soil derived, and is generally not subject to leaching. Aluminum can provide a useful reference point in identifying the source of elements in throughfall. By comparing the ratio of an element to Al in cloud water to the ratio (element:Al) in cloud throughfall at Mt. Mansfield, the relative influence of dry deposition and foliar leaching becomes evident. Much higher ratios in throughfall than in cloud water indicate that Mn, Rb, Mg^{2+} , Ca^{2+} , K^+ were strongly influenced by foliar

leaching, while similar cloud and throughfall ratios indicate that Hg, Cr, Ni, Cu, and Cd were most influenced by dry deposition. In a leaf washing study to determine the relative importance of foliar leaching and dry deposition of trace metals in precipitation throughfall in a hardwood forest at Mt. Mansfield, Rea (1998) found the following: 1) increases in throughfall concentrations of Hg, Pb, and Al could be attributed to wash-off of dry deposition; 2) Mn and Rb were strongly influenced by foliar leaching; and 3) Mg, Zn Cu, As, Cd, Sr were influenced by both processes.

3.4 *Mercury and chemical deposition*

Deposition of Hg, trace metals, and major ions by cloud water was calculated for four events using mean cloud water concentration data from the passive string collector and the mean volume of throughfall collected (Tables 5-7). Total throughfall deposition was calculated using the mean throughfall concentration data and the total volume of throughfall. Net throughfall deposition was calculated as total TF minus cloud.

Mercury and chemical deposition by clouds (Tables 6 & 7) was estimated for the three month period (August 1 - October 31, 1998) using the mean deposition rate (0.42 mm hr^{-1}) and an estimated cloud frequency of 35% for this period of time, based on visual observations and meteorological records (NCDC, 1999). Mercury deposition by cloud water was estimated at 7.4 ug m^{-2} for the three month period. This result is nearly twice the measured deposition of Hg in precipitation (3.9 ug m^{-2}) for the same period at the lower elevation monitoring site (PMRC ~ 400m) on Mt. Mansfield. Wet deposition of Hg shows a strong seasonal trend and is highest in the summer (Munthe et al., 1995; Scherbatskoy et al., 1997). We expect cloud deposition to exhibit a similar seasonal trend.

Assuming that the long-term mean Hg concentration in precipitation at 1200m is similar to the 400 m site (8 ng L⁻¹; Malcolm et al., 1999), we can make a conservative estimate of the relative contributions of precipitation and cloud water to the annual input of Hg to the high elevation forest. Using the volume-weighted mean Hg concentration in all cloud events (15 ng L⁻¹), estimated annual cloud water deposition (92 cm), and the average annual precipitation (174 cm) at the summit of Mt. Mansfield, we estimate that clouds deposit 14 ug Hg m⁻² yr⁻¹ and precipitation an additional 14 ug Hg m⁻² yr⁻¹, for total wet inputs of 28 ug m⁻² yr⁻¹ at 1200 m. Wet deposition of Hg to low elevation forests in Vermont is estimated at 7 ug m⁻² yr⁻¹, using the mean precipitation Hg at PMRC (8 ng L⁻¹) and the long-term average annual precipitation (87 cm) at Burlington, Vermont. These results suggest that high elevations in the Green Mountains may be subject to wet loading of Hg that is four times higher than surrounding lowlands. This 4x increase in deposition at high elevations has been observed for other pollutants. Forests in the Adirondack Mountains, NY, where precipitation and cloud water account for over 90% of the annual deposition, receive up to five times more N and four times more S than surrounding low-elevation forests (Miller et al., 1993b).

The additional fluxes of Hg in litterfall and throughfall must be considered in estimating total mercury deposition to high elevation forests. In Sweden, long-term monitoring of Hg deposition in spruce forests provides the most complete record to compare to our site. Long-term atmospheric and precipitation concentrations of Hg are similar in Vermont and Sweden (Iverfeldt et al., 1996; Malcolm et al., 1999). Coniferous litterfall in Sweden was found to add an additional flux of 23 µg Hg m⁻² yr⁻¹ and throughfall about 17 µg Hg m⁻² yr⁻¹, with wet and dry inputs totaling ~40 µg Hg m⁻² yr⁻¹.

Assuming that the litterfall flux of Hg in the coniferous forest at Mt. Mansfield is similar to that in Sweden and that throughfall Hg concentrations are generally twice as high as precipitation and cloud water, we expect that total Hg deposition (precipitation $\sim 14 \mu\text{g} +$ cloud $\sim 14 \mu\text{g} +$ dry (measured as TF) $\sim 30 \mu\text{g} +$ litterfall $\sim 23 \mu\text{g}$) to high elevations in Vermont may be over $80 \mu\text{g Hg m}^{-2} \text{ yr}^{-1}$.

4. Ecological Implications

Cloud water has been shown to be highly acidic at Mt. Mansfield and more concentrated in pollutants than precipitation. The ecological effects of acidic deposition by these clouds may include direct damage to trees, leaching of soils, and mortality of biota in terrestrial soils and surface waters. The low pH of clouds at Mt. Mansfield results in substantial leaching of base cations from the foliage of trees and is linked to forest decline at high elevations. Despite the recent reductions in sulfate emissions, that were mandated by the USEPA Clean Air Act, there has been no observed reduction in the acidity of precipitation in Vermont (Pembroke, 1998) or the eastern United States (Lynch et al., 1995). Although short-term in duration, our results suggest that nitrates, which have not been as strictly regulated, are now contributing to the bulk of acidity in cloud water at Mt. Mansfield. Substantial reductions in the acidity of clouds and precipitation are necessary if damage by acidic deposition to Vermont's high elevation forests is to be abated.

Cloud water is likely a significant source of Hg deposition to high-elevation ecosystems. The toxicity of Hg is well known for humans and certain fauna, however, the

possible toxic effects of Hg deposition to high elevation forests and other alpine biota are largely unknown. Cloud water may deposit an equivalent amount of Hg as precipitation at elevations above 1000m. Cloud throughfall washes off dry deposited Hg from tree foliage, increasing Hg deposition to the forest floor by a factor of more than two. Total atmospheric deposition of Hg and other pollutants at Mt. Mansfield is likely to be at least 2x to as much as 4-5x higher than at surrounding low elevation sites. Mount Mansfield may receive a high proportion of the annual water budget directly from clouds. As such, interception of cloud water by mountains must be included in estimating pollutant deposition to the Lake Champlain Basin and other watersheds which contain landscapes subject to cloud immersion. Cloud interception by the high elevation forest at Mt. Mansfield results in enhanced inputs of both water and pollutants to this ecosystem.

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Table 1 - Estimated annual cloud water deposition at mountain locations in the northeastern United States.

Site	Elevation (meters)	Year	Cloud H ₂ O (cm yr ⁻¹)	Cloud (%) frequency	Reference
Mt. Mansfield, VT	1204	1998	92 ± 26 ^a	25 ^b	Lawson et al. (1999)
Whiteface Mt., NY	1225	1986-90	81.1	23	Miller et al. (1993a)
Mt. Moosilauke, NH	1220	1990	40.5	--	Schaefer and Reiners (1990)
Mt. Moosilauke, NH	1220	1980-81	84.0	40	Lovett et al. (1982)
Madonna Mt., VT	1110	1980-81	154.0	--	Scherbatskoy and Bliss (1984)
Camels Hump, VT	1110	1970	76.0	--	Leedy (1972)
Whiteface Mt., NY	1050	1986-89	28.4	10	Miller et al. (1993b)
Whiteface Mt., NY	1350	1986-89	153.5	36	Miller et al. (1993a)
Whiteface Mt., NY	1483	1987	127.0	42	Mohnen (1988)

- a. Annual cloud water deposition estimated in this study from three non-precipitating cloud events, where mean cloud water input was measured at 0.42 ± 0.12 mm hr⁻¹ and extrapolated to annual basis using cloud frequency.
- b. Cloud frequency estimate based on lower limit of visual and meteorological observations at Mt. Mansfield summit station (NCDC, 1999).

Table 2 - Mean (volume-weighted) concentrations of major ions in three paired cloud water and throughfall collections at Mt. Mansfield, Vermont.

Ion (mg L ⁻¹)	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺
<u>Cloud water (n=7)</u>								
Mean	0.17	0.26	0.009	0.08	1.46	0.86	9.80	0.75
Std. dev.	0.12	0.12	0.007	0.04	1.55	0.53	13.76	0.44
Median	0.15	0.29	0.014	0.10	1.43	0.56	3.40	0.48
Maximum	0.32	0.52	0.020	0.12	4.45	1.77	34.60	1.42
Minimum ^b	<0.005	<0.05	<0.005	<0.005	<0.33	0.29	0.40	0.13
<u>Throughfall (n=9)</u>								
Mean	0.57	1.10	0.168	0.11	0.65	1.33	0.29	0.88
Std. dev.	0.62	0.66	0.196	0.05	0.49	1.39	0.22	1.36
Median	0.21	1.00	0.040	0.14	0.57	0.57	0.40	0.11
Maximum	2.04	2.56	0.557	0.26	1.84	4.52	0.63	4.25
Minimum ^b	0.09	0.50	0.010	<0.005	0.37	0.33	<0.05	0.04
Net Throughfall	0.40	0.84	0.16	0.03	-0.81	0.47	-9.50	0.13
Enrichment factor ^a	3.4	4.2	18.1	1.4	0.4	1.5	0.03	1.2

- a. Enrichment factor calculated as mean throughfall divided by mean cloud water.
b. Some sample concentrations were below machine detection limits.

Table 3 - Mean concentrations (volume-weighted) of trace metals in four paired cloud water and throughfall collections at Mt. Mansfield, Vermont.

Element (ug L ⁻¹)	Al	Cr	Mn	Ni	Cu	Zn	As	Rb	Sr	Cd	Pb
Cloud water (n 9)											
Mean	7.92	0.09	1.73	0.24	0.51	5.52	0.13	0.07	0.30	0.03	0.58
Std. dev.	31.60	0.19	5.33	0.58	1.11	12.08	0.68	0.34	1.42	0.16	2.56
Median	6.82	0.10	1.52	0.24	0.56	4.06	0.18	0.13	0.51	0.03	0.93
Maximum	101.31	0.63	17.30	1.90	3.64	30.27	2.12	1.08	4.61	0.52	8.17
Minimum	2.01	0.01	0.29	0.05	0.12	0.68	0.04	0.03	0.04	0.01	0.11
Throughfall (n 10)											
Mean	17.32	0.11	40.93	0.64	0.99	6.91	0.18	2.53	1.18	0.07	0.76
Std. dev.	13.79	0.08	52.30	0.57	0.36	6.76	0.12	3.14	1.73	0.09	0.49
Median	15.94	0.13	50.66	0.64	1.03	3.74	0.13	2.06	0.53	0.04	0.62
Maximum	55.58	0.23	172.14	2.11	1.61	23.94	0.39	10.26	4.62	0.27	1.54
Minimum	7.10	0.00	4.98	0.26	0.54	2.94	0.07	0.52	0.17	0.01	0.27
Net throughfall	9.40	0.02	39.20	0.40	0.48	1.39	0.05	2.46	0.88	0.05	0.18
Enrichment factor ^a	2.2	1.2	23.7	2.7	1.9	1.3	1.4	38.3	4.0	3.0	1.3

a. Enrichment factor calculated as mean throughfall divided by mean cloud water.

Table 4 - Mean (volume-weighted) mercury concentrations in three paired cloud water (CW) and throughfall (TF) collections at Mt. Mansfield, Vermont.

Hg (ng L ⁻¹)	Paired collections	
	Cloud water (n=7)	Throughfall (n=9)
Mean	7.51	17.49
Std. dev.	2.73	6.62
Median	6.18	16.47
Maximum	11.81	33.30
Minimum	3.74	9.95
Net Throughfall (TF-CW)		9.97
Enrichment factor (TF/CW)		2.3

Table 5 - Mean Hg concentrations and estimated deposition in four paired cloud water and cloud throughfall (TF) collections at Mt. Mansfield, Vermont.

	Date	8/18	8/26	9/10	10/1 ^a	Total	units
Hg Concentration	Throughfall	15.02	*	13.47	19.58		
	Cloud	7.52	33.98	11.81	4.83		ng L ⁻¹
	Net Throughfall	7.50	*	1.66	14.75		
Hg Deposition	Cloud ^b	37.12	31.67	15.32	37.21	125.32	
	Net Throughfall ^c	37.03	*	2.71	113.79	153.53	ng m ⁻²
	Total	74.15	31.67	22.03	151.00	278.85	
Cloud Deposition Rates	Hg	3.91	9.74	3.86	6.47		ng m ⁻² hr ⁻¹
	Water	0.52	0.29	0.33	1.34 ^d		mm hr ⁻¹

- a. Cloud event on 10/1 contained some precipitation in brief showers which could not be excluded from collection. All data for 10/1 reflects cloud + precipitation.
- b. Hg deposition calculated as mean cloud Hg concentration x mean TF volume and does not account for evaporation or retention of water in the canopy, and thus underestimates total deposition.
- c. Net throughfall deposition calculated as difference of cloud and total throughfall deposition.
- * Volume obtained in 8/26 throughfall sample (17ml) too small for Hg analysis.

Table 6 - Cloud water and throughfall deposition of major ions to the forest floor during three cloud events and estimated deposition by cloud water for the three month period (August 1 - October 31, 1998) at Mt. Mansfield, Vermont.

Deposition (mg m ⁻²)	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺
Cloud water	2.06	2.65	0.15	0.65	20.04	9.24	134.71	7.67
Total throughfall	7.99	15.45	2.50	1.47	9.04	18.25	4.38	11.64
Net throughfall	5.93	12.80	2.35	0.82	-11.00	9.01	-130.33	3.97
Estimated deposition (g m ⁻²)								
August 1 - October 31, 1998	0.09	0.10	0.04	0.05	0.64	0.64	4.18	0.92

Table 7 - Cloud water and throughfall deposition of trace metals to the forest floor during four cloud events and estimated deposition by cloud water for the three month period (August 1 - October 31, 1998) at Mt. Mansfield, Vermont.

Deposition ($\mu\text{g m}^{-2}$)	Al	Cr	Mn	Ni	Cu	Zn	As	Rb	Sr	Cd	Pb
Cloud water	107.26	1.49	30.58	2.95	8.24	90.50	4.42	1.55	6.49	0.54	9.89
Net throughfall	181.12	0.35	662.93	7.49	7.12	4.18	-1.65	40.34	12.55	0.60	1.77
Total throughfall	288.38	1.84	693.51	10.44	15.36	94.68	2.77	41.89	19.04	1.14	11.66
Estimated cloud water deposition (mg m^{-2})											
(August 1 - October 31, 1998)	4.18	0.05	1.04	0.20	0.55	5.49	0.19	0.07	0.27	0.05	0.82

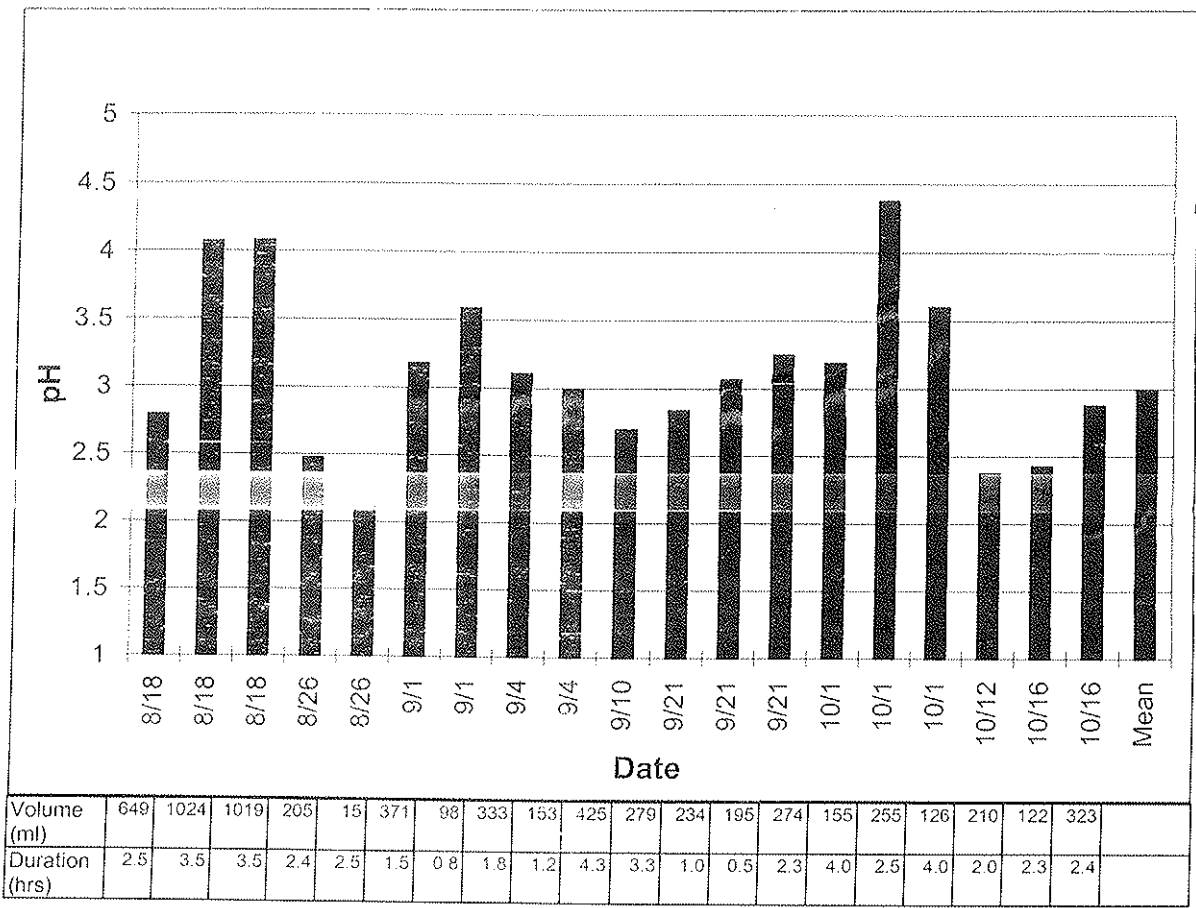


Figure 1 - pH values, volume, and duration of collection for all collected cloud water samples at Mt. Mansfield, Vermont, August 10 to October 16, 1998.

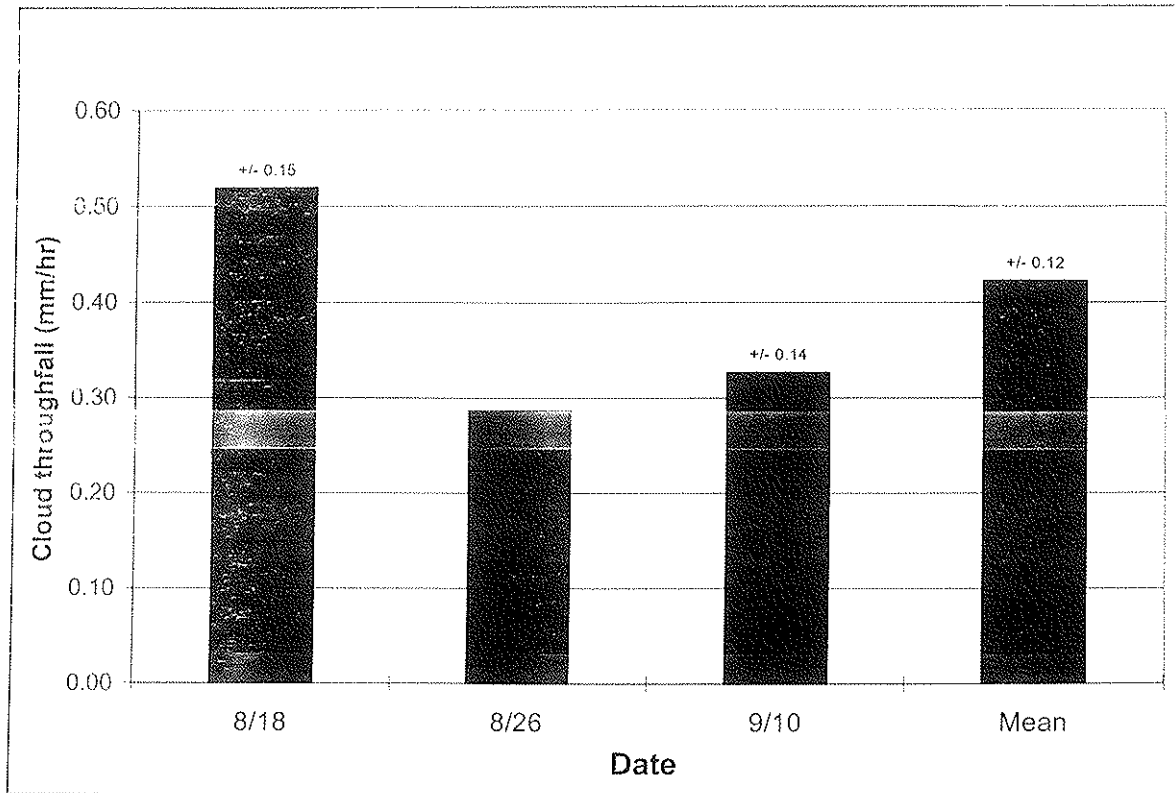


Figure 2 - Net cloud water deposition measured as throughfall under the spruce-fir canopy during three non-precipitating cloud events at Mt. Mansfield, Vermont.

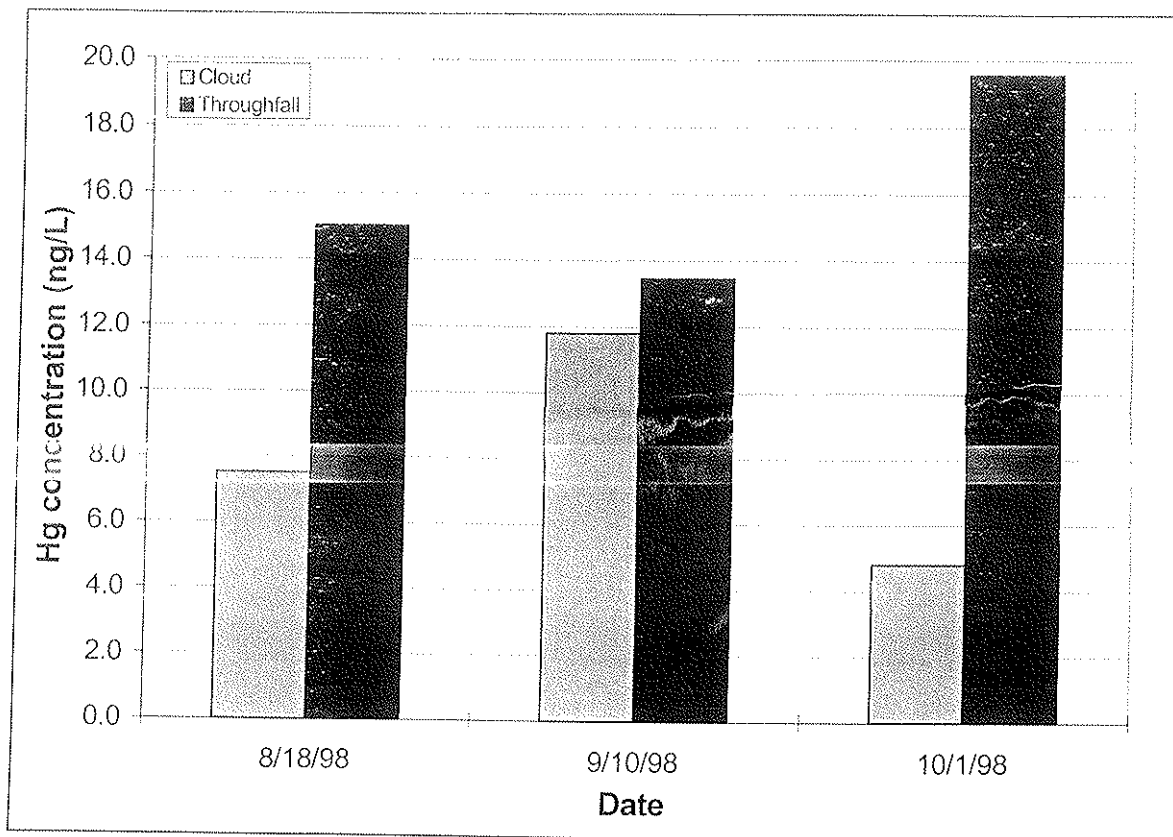


Figure 3 - Concentrations of mercury (Hg) in cloud water compared to throughfall during three cloud events at Mt. Mansfield, Vermont.

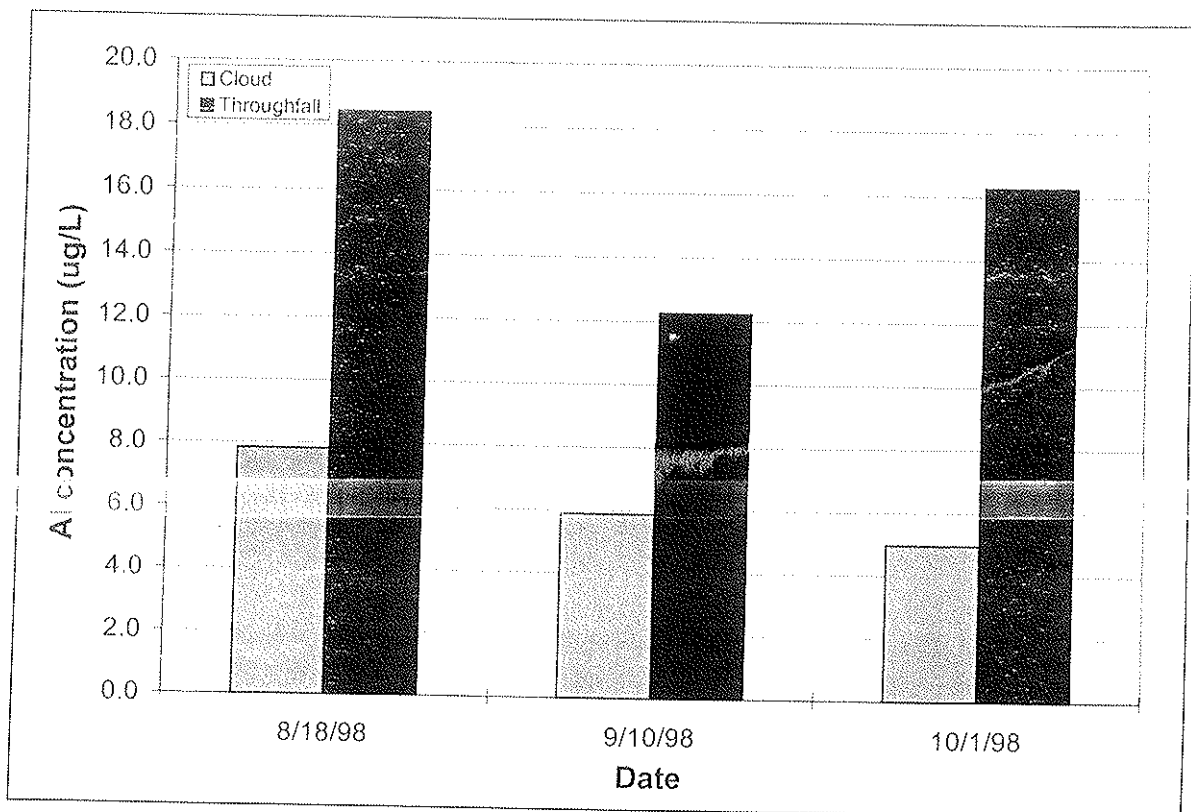


Figure 4 - Concentrations of aluminum (Al) in cloud water compared to throughfall during three cloud events at Mt. Mansfield, Vermont.

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Appendices

Appendix A

**Mercury and trace elements in cloud water and precipitation
collected on Mt. Mansfield, Vermont**

MERCURY AND TRACE ELEMENTS IN CLOUD WATER AND
PRECIPITATION COLLECTED ON MT. MANSFIELD, VERMONT

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A cloud and fog water collector was designed and tested for sequential mercury and trace metals sampling. Cloud water was collected during nine non-precipitating cloud events on Mt. Mansfield, VT between August 10 and October 16, 1998. Sequential samples were collected during six of these events. Mercury cloud water concentrations ranged from 7.5 to 71.8 ng/L, with a mean of 22.8 ng/L. Twenty-nine event precipitation samples were collected during the cloud sampling period near the base of Mt. Mansfield. The range of mercury concentrations in precipitation was similar to, but lower, than that of the cloud water, with a lower mean (10.4 ng/L). Cloud and precipitation samples were analyzed for sixteen trace metals including Mg, Cu, Zn, As, Cd and Pb using ICP-MS. Mean concentrations were higher in cloud water than precipitation for all metals investigated. Meteorological analysis revealed that the lowest mercury concentrations were associated with transport from the north and highest concentrations with transport from the west and southwest, consistent with known source regions of anthropogenic mercury. Interesting patterns in trace element concentrations were also observed with northwesterly flows.

Introduction

Mercury is a known toxin to humans, animals, and plants with both natural and anthropogenic origins (Clarkson, 1992; Meyer *et al.*, 1995; Facimire *et al.*, 1995; Panda *et al.*, 1992). One of the primary pathways by which Hg enters watersheds is through atmospheric deposition. Understanding the sources, atmospheric transport, chemistry, and deposition of Hg is crucial to finding a solution to this problem (Expert Panel, 1994). Clouds and fog are expected to play an important role in the transport and deposition of mercury, but little research has investigated this phenomenon.

Clouds affect atmospheric transport of mercury by acting as a reaction vessel for aqueous chemistry. In-cloud chemistry will influence the rates at which atmospheric Hg is incorporated into raindrops and deposited via precipitation. Since gas phase reactions appear to be of little importance to Hg (Petersen *et al.*, 1995), aqueous chemical reactions in clouds will be the primary factor that affects atmospheric Hg speciation. Mercury species will also interchange between the elemental gas, divalent (reactive) gas, and particle adsorbed forms within clouds. Each of these Hg species has a very different reactivity, which will determine atmospheric removal rates of Hg and ultimately affect the transport and deposition of mercury (Lin and Pehkonen, 1999).

Chemical species are often more concentrated in cloud droplets than in precipitation collected at the same location, and some major ions have been found to be up to two orders of magnitude greater than in corresponding precipitation events (Weathers *et al.*, 1988; Dawei *et al.*, 1994; Igawa, *et al.*, 1998). Consequently, cloud water deposition onto surfaces such as trees, plants, and man made structures is known to be a major source of pollutants to many watersheds (Weathers *et al.*, 1988; Miller *et al.*,

1998). Evans and Hutchinson (1996) found evidence of mercury deposition by cloud water when using moss and lichens to assess Hg accumulation at high elevations.

Despite the importance of clouds to chemical cycling, measurements of Hg in cloud water have not been reported in the literature. This paper aims to provide a more complete understanding of the Hg cycle through direct atmospheric measurements. Mt. Mansfield, VT, in the Lake Champlain watershed, was chosen as the cloud sampling site. Atmospheric mercury concentrations and deposition have been extensively studied in this watershed, which is known to contain fish and sediment contaminated by mercury (Scherbatskoy *et al.*, 1998; Rea *et al.*, 1996; Burke *et al.*, 1995; McIntosh, 1994). The first objective of our research, presented in Lawson *et al.* (1999), was to estimate and determine the relative importance of direct water, mercury, and pollutant deposition from clouds to a high elevation forest. Our second objective, presented in this paper, was to quantify the amount of mercury in clouds, characterize cloud chemistry at a high-elevation site, and understand the factors that affect the observed concentrations.

Methods

Cloud Collector Design. The cloud collector designed for this study was modeled after the strand collectors utilized by many researchers and monitoring programs including the Atmospheric Science Research Center (Mohnen and Kadlec, 1989), the U. S. Mountain Cloud Chemistry Project (Mohnen and Vong, 1993), and the Canadian Chemistry of High Elevation Fog Program (Schemenauer, 1986). Several modifications were necessitated to use this collector for mercury and trace element sampling. Most collectors are constructed of either polypropylene, which is known to adsorb mercury, or

out of metal, which cannot be acid cleaned. This collector is made entirely of Teflon, the material of choice for trace mercury sampling, with the exclusion of three Techtron PPS (Polyphenylene Sulfide) supporting rods. TFE Teflon rods were originally used but contracted more than the PTFE Teflon strands in cold conditions, causing the strands to become slack. The Teflon funnel at the base of the collector attaches to a Teflon bottle by an adapter containing a glass vapor lock preventing sample volatilization (Landis and Keeler, 1997). The adapter also includes a Teflon slide valve, providing easy bottle switching during sequential sampling without loss of liquid from the funnel.

Site Description. The south summit of Mt. Mansfield has an elevation of 1204 m and is located approximately 35 km east of Burlington, VT and Lake Champlain, in the Northeastern US. A sampling site was selected just above the tree line near the summit of the mountain to allow direct interception of ambient clouds. A red spruce-balsam fir forest covers the upper slopes of the mountain to an elevation of ~ 1200 m. At an elevation of 400 m on the western slope of the mountain, a mercury monitoring station located at Proctor Maple Research Center (PMRC) has been in operation since December 1992 (Burke *et al.*, 1995). Concentrations measured at PMRC are comparable to those measured at rural and remote sites in the Great Lakes Region of North America (Hoyer *et al.*, 1995; Pirrone *et al.*, 1995) and in Sweden (Iverfelt *et al.*, 1995). The mean concentration of mercury measured at PMRC was 8.0 ng/L in event precipitation (volume-weighted; standard deviation = 8.5 ng/L, n=538), 1.6 ng/m³ for vapor phase mercury (standard deviation = 0.3 ng/m³, n=305) and 9.3 pg/m³ for total particulate phase mercury (standard deviation = 6.6 pg/m³, n=346) from January 1993 through December

1997. NRG Systems, INC provided wind data from a Maximum # 40 Anemometer operated on at tower at 15 m above the summit.

Sample Collection, Preparation, and Analysis. Cloud events were sampled from August 10-October 16, 1998. A maximum of three sequential samples was collected per event, dependent on event duration and sample volume collection rate. At the conclusion of field collection, samples were immediately transported to PMRC. A sub-sample for pH and major ion analysis was poured off from each bulk sample in a portable class 100 HEPA filtered air chamber. Bulk samples were refrigerated (4°C) and shipped overnight to the University of Michigan Air Quality Laboratory (UMAQL), then acidified with HNO₃ (to 0.2% v/v solutions) to prevent retention of metals on the bottle wall. After the sample was acidified for a minimum of twenty-four hours, a sub-sample was poured off into an acid-cleaned polypropylene bottle for trace metal analysis. The remaining sample, in the original Teflon bottle, was oxidized with BrCl (to 1% v/v solutions) for mercury analysis.

Clean techniques are required for trace level mercury and metals research and were employed throughout sampling and analysis. This included the use of particle free gloves, storage of all cleaned supplies and samples in triple zip lock bags, and the use of Teflon tape to seal sample bottles. All sample preparation and analysis was conducted in a class 100 clean room for mercury and a class 1000 clean room for trace metals, both at UMAQL. All bottles and glassware used for mercury or metals samples were cleaned using a modified version of procedure developed by Rossmann and Barres (1992). The long acid soaks in the procedure were changed to six hour heating first in 3 M HCl and then 3.5 % (by volume) HNO₃. All bottles and supplies were rinsed at least five times

with MilliQ ultrapure water (18.2 M Ω •cm resistivity; Millipore Corp., Bedford, MA) after acid cleaning. The collector was cleaned by soaking in HCl and then HNO₃ (each 10% by volume) for a minimum of twenty-four hours each. Within four hours of sampling, the collector was removed from the HNO₃ and rinsed thoroughly (10-15 minutes) with Milli-Q water.

Analysis of pH and conductivity were performed within two hours of the end of the cloud event, using an Orion EA920 digital pH meter with a Broadley-James probe and a VWR Scientific EC meter, model 2052 with a 515 AU dip cell following the National Acid Deposition Program protocol (Penden, 1986). Major ion analyses were performed at the University of Vermont Environmental Testing Laboratory. Ammonium was quantified by flow injection analysis using a Lachat Quick-Chem AE Automated Ion Analyzer. All other cations were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer Optima 3000DV). Anions were analyzed by ion chromatography using a Dionex IC 2010i. At the UMAQL, trace metal samples were analyzed in a class 1000 clean room by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer ELAN 5000). Mercury concentrations were determined by analysis in a wet analysis protocol developed by the UMAQL with a Tekran 2537 utilizing cold vapor atomic fluorescence and gold trap amalgamation (Fitzgerald and Gill, 1979).

Results and Discussion

Liquid Water Content. Liquid water content (LWC) was calculated based on the collector size and efficiency, and the wind speed (Dudkiewicz and Husain, 1998). LWC ranged from 0.005 to 0.24 g/m³, with a mean of 0.12 g/m³. Results indicate that clouds sampled at Mt. Mansfield had lower LWC than those typically sampled on nearby Whiteface Mountain (Mohnen and Kadlecek, 1989). Based on visual observations, the sampling location was often within 100 m of the cloud base, a region which typically has low LWC. The low LWC is consistent with the type of cloud events sampled, since only non-precipitation clouds were collected, which are known to be drier than precipitating clouds (Mohnen and Kadlecek, 1989).

Cloud Chemistry. Ten cloud events were sampled on Mount Mansfield from August 10-October 16, 1998. Two or three sequential samples were collected from six of these events. The only event during which there was precipitation is treated separately in all statistical descriptions and analysis. Concentrations of mercury varied by an order of magnitude among cloud-only events, ranging from 7.5 to 71.8 ng/L (Figure 1). The mean (arithmetic) cloud water concentration was 22.8 ng/L, with a median of 12.5 ng/L.

Precipitation was collected during the study period at PMRC, located at 400 m elevation on the western slope of the mountain. Since primarily non-precipitating cloud events were sampled, precipitation sampling was not simultaneous to cloud sampling. Although only a small number of cloud events were sampled, and variability in concentrations was high, our results suggest that Hg and trace metal concentrations in cloud water often exceed those typically found in precipitation (Figure 2). This finding is

consistent with other research comparing cloud and precipitation chemistry (Weathers *et al.*, 1988; Dawei *et al.*, 1994; Igawa, *et al.*, 1998).

The event on October 1 included rain, snow, and ice pellets, in addition to cloud water. The three sequential samples collected on 10/1 were lower in Hg concentrations than all non-precipitating cloud samples collected during this study. One reason for the low concentrations is the inclusion of precipitation, which was generally lower in Hg concentration than cloud water. Additionally, snow has significantly lower Hg concentrations than rain (Hoyer, 1995; Landis and Keeler, 1999). Further research on the Hg chemistry of clouds that produce snow will be necessary to fully understand causes of lower snow Hg concentrations. The low concentration of the mixed snow/cloud sample may indicate that clouds that produce snow are typically lower in Hg concentration than clouds that produce rain.

Table 1 presents the mean (arithmetic), median, and range of metal concentrations measured in cloud only events and precipitation events sampled from August 6 through October 16, 1998. The ranges of trace metal concentrations overlap between cloud and precipitation, but mean and median concentrations were higher in cloud samples, as observed for Hg. Three studies have measured concentrations of specific trace metals at nearby Whiteface Mountain in New York (Table 2). Concentrations measured at Mt. Mansfield were quite similar to those measured during summer and fall seasons at Whiteface Mountain, especially considering the small number of events sampled in all investigations.

Regression analysis showed that nearly all trace elements and mercury in cloud water were highly correlated with each other, typically at $R^2 > 0.6$ and $p < 0.001$. Very

distinct trace element ratios or “signatures” in individual samples would have indicated the influence of different and diverse sources or strong local sources. The homogeneity of trace metal profiles suggests that cloud concentrations measured were influenced by multiple regional sources. Many regional mercury and metals emission sources affect Mt. Mansfield, and aerosol reaching the site has aged and been influenced by multiple source types. Determining individual source contributions to a particular event typically involves statistical methods that require a large number of samples. Although only 17 cloud samples were collected for this study, some sources signatures are identifiable and are discussed below as case studies. The high variability in Hg and metals concentrations, despite good correlation between different metals, indicates that other factors, in addition to sources, are influencing cloud concentrations. These factors likely include changes in LWC and cloud microphysics that affect concentrations without changing the relative ratios of one element to another.

Liquid water content was inversely correlated to mercury concentrations of sequential cloud water samples (Figure 3). Similar relationships have been observed in studies of major ion cloud chemistry (Mohnen and Kadlec, 1989) and would be expected if LWC differences result from droplet growth or evaporation. Although LWC is one factor that influences concentrations, it only explains about 30% of the variability in the mercury concentrations ($R^2 = 0.3$, $p = 0.03$). Similar inverse relationships exist between LWC and measured concentrations of V, Mn, Ni, As, and Sr. Correlations with other metals were not as strong ($R^2 < 0.2$).

Meteorological Analysis. Forty-eight hour back trajectories were calculated using the National Oceanic and Atmospheric Administration Air Resources Laboratory’s

HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Hess, 1998). Meteorological data is input into this lagrangian dispersion model to predict the most probable trajectory of air reaching the sampling location. A strong directional trend becomes evident when sequential samples are categorized by source region (Figure 4). Cloud water associated with air masses from the north of Mt. Mansfield was lower in concentration than in air masses from the west and southwest of the site. Liquid water content does not explain this trend, as there was no dependence of LWC on air mass history. The high mercury concentrations, however, correspond with locations of known Hg sources (EPA, 1998). Mercury emissions sources are more numerous in the Mid-Atlantic and Ohio Valley regions, where air masses with the highest Hg originated, indicating that the Hg cloud water concentrations are strongly influenced by sources upwind of Mt. Mansfield. These sources include incineration, coal fired power plants, and metals processing including such as smelting and refining. Similar results were obtained for most metals, one notable exception discussed below.

Case Studies. One sequential sample was collected on August 10, 1998 from 13:15 to 19:15 local time. The cloud event was intermittent and preceded precipitation. This event had the highest measured concentrations for mercury and all the trace elements sampled. The lowest LWC (0.005 g/m^3) of all sequential samples also occurred on this day, likely contributing to high concentrations. Due to the low LWC, insufficient volume was collected for pH or major ion analysis. This was the only sample associated with flow from the southwest and south of the site (Figure 5), an area with many industrial and urban sources of mercury and other metals (EPA, 1998).

On September 21 from 12:10 to 21:00, three sequential samples were collected during an orographically enhanced cloud event, produced as a cold front passed by the mountain. Prior to the event haze reduced visibility. The three sequential samples collected (Figure 1) were high in mercury, with concentrations decreasing from 50 to 23 ng/L over the sampling period. At the start of the event, pH was quite low at 2.5, and increased to 3.1 and then 3.5. Several ions were elevated in cloud water on this day compared to other events, including Ca^{2+} , Na^+ , SO_4^{2-} and NH_4^+ , the latter three of which were more than double the cloud water means for the study. The highest concentrations, with the exception of August 10, were measured on this day for Pb, V, Ni, As, Mg and Sr. This event was associated with west-southwest flow and high metals concentrations are likely the result of the influence of industrial regions of Lake Erie and Ontario. Although the back trajectory remained constant, LWC increased over the event from 0.05 to 0.14 to 0.24 g/m^3 , resulting from a nearly ten degree Fahrenheit drop in temperature accompanied by a much smaller drop in the dew point. Most ions and all metals decreased steadily over the event. Ratios of metals concentrations (i.e. Hg/Pb, Zn/Cd) however, were nearly constant across all three sequential samples. This suggests that the change in concentrations over the course of the event resulted from increasing LWC and not from varying source influences or changing aerosol composition of the feeder air.

The elements that were enhanced during event on 9/21 (e.g., As, Cd, Sb, and Mo) and the trajectory path of this air mass are both characteristic of what Olmez et al. (1998) refer to as a "U.S. regional source." This source was identified by factor analysis of 20 months of aerosol data collected at four upstate New York locations. The major influence on mercury and metals concentrations in this source is attributed to aged

emissions related to coal combustion, originating from the Midwestern US. Elements typical of this source were not as elevated in cloud water collected on other days with west or southwesterly trajectories (8/10, 8/26, 9/4)

An orographically enhanced cloud event was sampled on September 1 from 7:35 to 9:45 AM. Two sequential samples were obtained from this event. The mercury concentration was moderate, increasing from 10.8 to 18.9 during the morning. Flow remained constant from the northwest (Figure 6). The second sequential sample had the highest mercury concentration of all sequential samples associated with flow from north or northwest of Mt. Mansfield. Although mercury was not particularly high compared to other events associated with flow from the west and southwest, Zn, Cu, Pb, Cd and As were elevated relative to their concentrations for other events and the sample profiles for other metals (Figure 7). Liquid water content was relatively high compared to other events sampled and decreased by 30% from the first to second sample. This decrease in LWC likely contributed to the increase in concentrations in most elements including mercury, Mn, Cu, As, Sb, and Pb during the event. Trajectory analysis and trace metal data suggest that this event was influenced by emissions from Canadian smelters and/or refineries which emit Zn, Cu, Pb, As and Cd (Skeaff and Dubreul, 1997).

Conclusions

Non-precipitating cloud events sampled on Mt. Mansfield, VT were found to have mercury concentrations that varied by an order of magnitude. Sequential sampling revealed that concentrations changed by as much as a factor of two from the start to end of the event. Concentrations of Hg and trace metals in cloud water were similar to, but slightly higher, than those measured in precipitation near the base of the mountain. LWC,

which is inversely related to concentration, explained about 30% of the variability in cloud Hg concentrations. Cloud events associated with air mass transport from north and north west of Mt. Mansfield generally had the lowest concentrations of mercury and trace metals, while transport from the west and southwest resulted in the highest concentrations. Meteorological analysis and trace metal data indicate that cloud water concentrations were influenced by exposure to sources in the Great Lakes, Ohio Valley and Mid-Atlantic regions.

Low Hg concentrations in a mixed snow/cloud event may indicate that mercury levels are quite low in clouds which produce snow, resulting in the low concentrations of snow which have been reported in North America and Europe. Although mercury, unlike all other metals, occurs in both a gas (>90% of total) and particle phase, comparisons between cloud and precipitation were similar for mercury and metals. Future research on the relative importance of aerosol and gas phase Hg scavenging and in-cloud chemistry will be necessary for predicting wet deposition and transport of mercury and determining the cause of differences between snow and rain concentrations.

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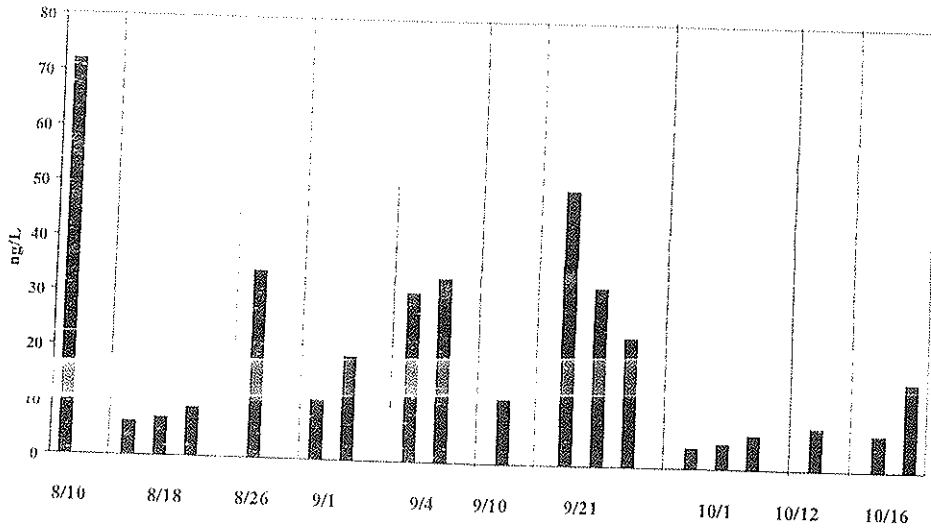


Figure 1. Concentrations of mercury (ng/L) in sequential cloud samples collected on Mt. Mansfield, VT.

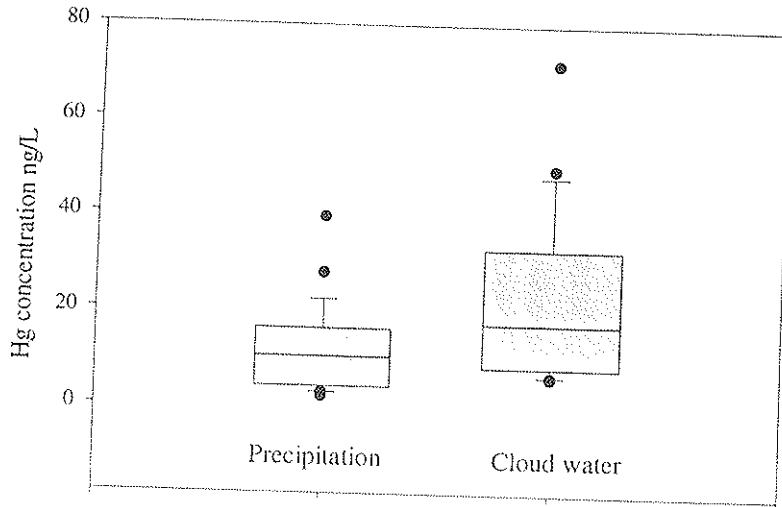


Figure 2. Box and whisker plot comparison of mercury concentrations measured in precipitation and cloud water events, Mt. Mansfield, VT. Box delineates median, 25 and 75 percentiles. Bar extends to 10 and 90 percentiles, outliers represented by points.

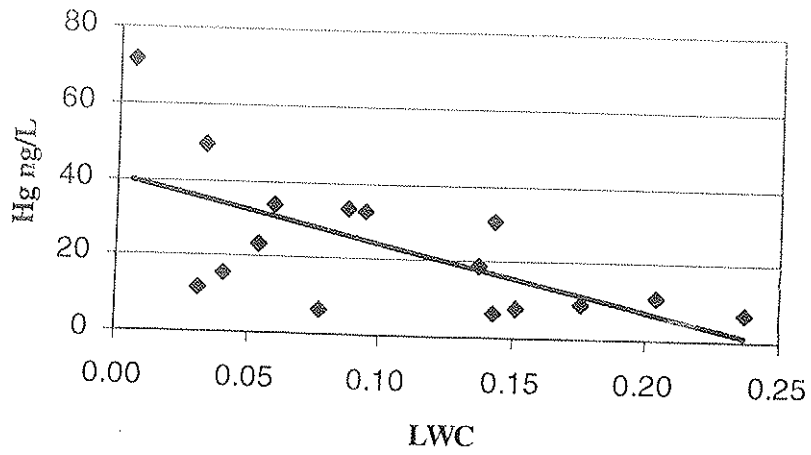


Figure 3. Liquid water content (LWC) versus mercury cloud concentration (ng/L).

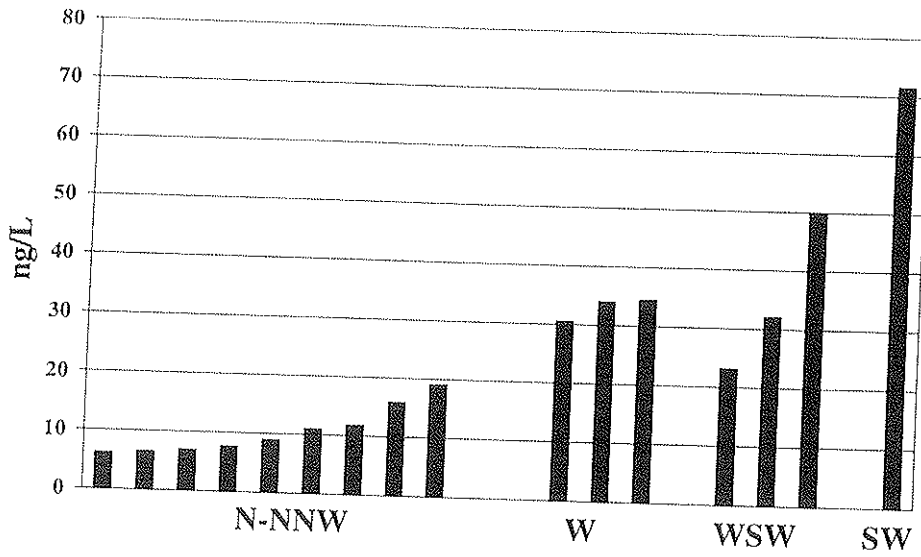


Figure 4. Mercury cloud water concentration in sequential samples categorized by air mass source region.

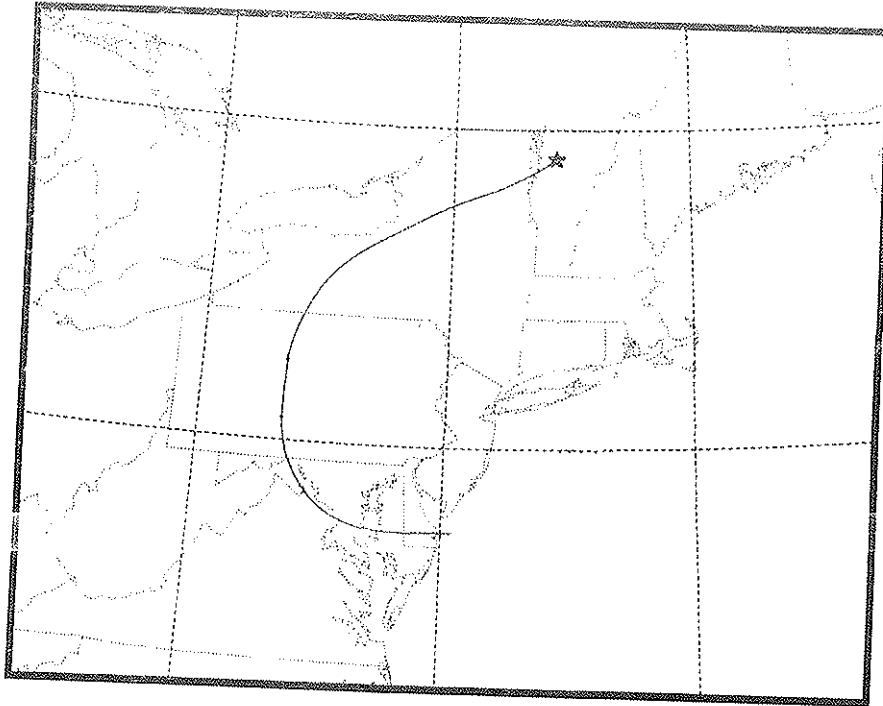


Figure 5. HYSPLIT 48 hour back trajectory for cloud sample on August 10, 1998.

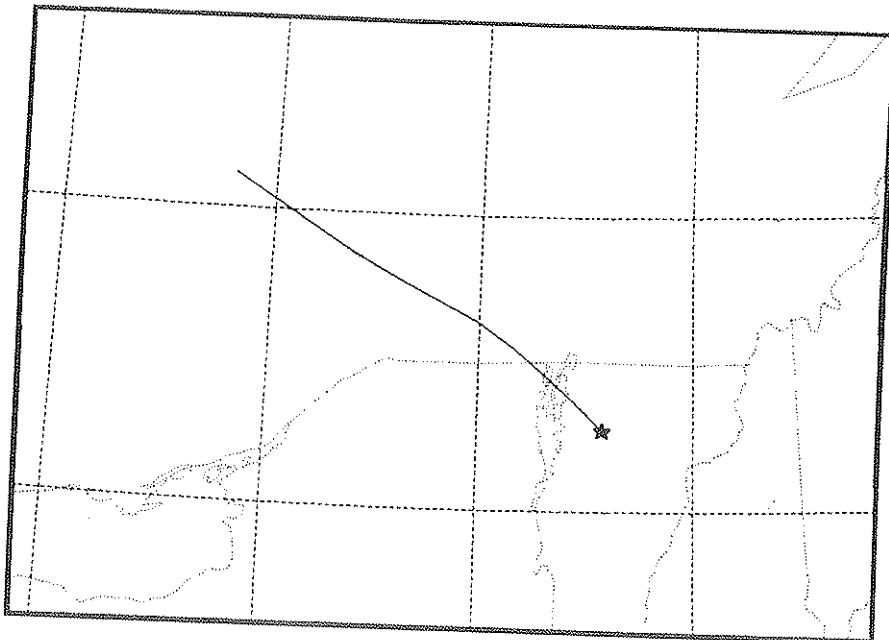


Figure 6. HYSPLIT 10 hour back trajectory for cloud sample on September 1, 1998.

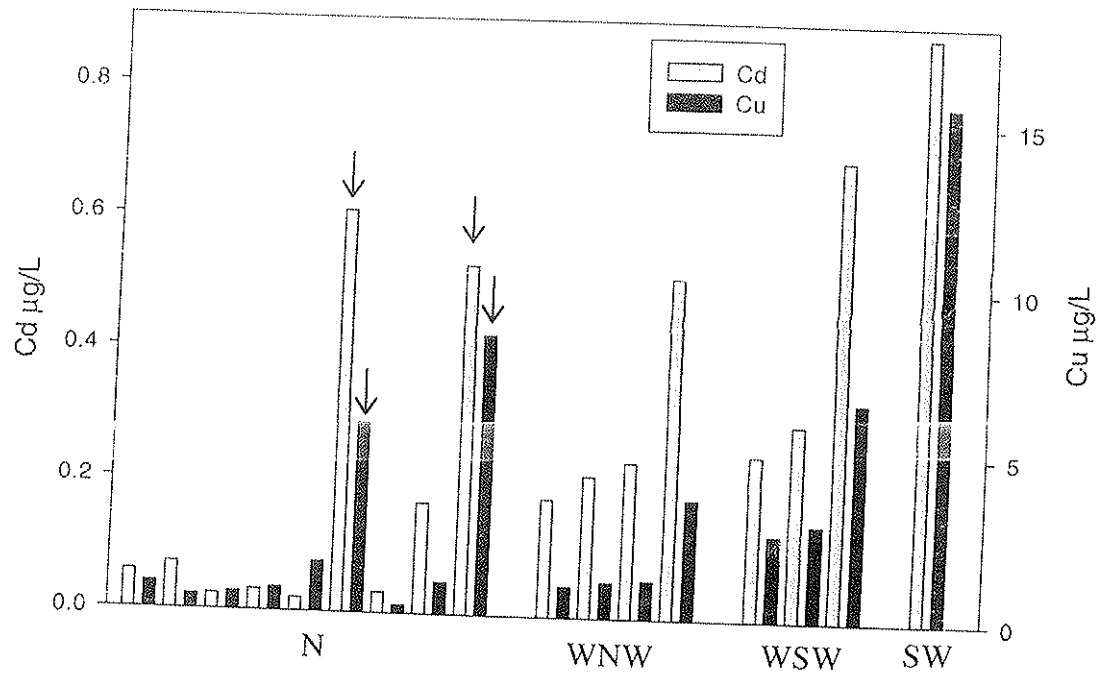


Figure 7. Concentrations of metals were typically low for samples associated with transport from north of the sampling location. Certain metals however, including Cd and Cu shown here, were found in high concentration in the two sequential samples from September 1 (indicated by arrows).

Table 1. Arithmetic mean, median, minimum and maximum concentrations of metals measured in cloud water and precipitation, Mt. Mansfield, VT.

		Hg	Mg	V	Mn	Ni	Cu	Zn	As	Sr	Mo	Cd	Sb	Pb
Cloud (n=9)	Mean	22.8	183.85	3.76	6.98	1.67	3.11	31.13	1.04	2.13	0.11	0.25	0.39	4.98
	Med.	12.16	22.63	1.13	2.08	0.42	0.95	12.59	0.55	0.53	0.04	0.14	0.14	1.87
	Min.	7.5	9.26	0.33	0.83	0.10	0.25	3.40	0.04	0.20	0.01	0.02	0.05	0.10
	Max.	21.0	189.13	33.27	39.95	11.07	15.62	156.38	4.34	14.00	0.56	0.88	2.21	27.23
Rain (n=29)	Mean	11.82	22.3	0.35	1.53	0.44	0.67	4.01	0.11	0.40	0.03	0.05	0.05	0.54
	Med.	10.39	14.7	0.24	1.12	0.15	0.42	2.52	0.10	0.26	0.03	0.03	0.05	0.46
	Min.	2.04	2.58	0.01	0.88	0	0.04	0.31	0.01	0.03	0	0	0	0.03
	Max.	35.35	94.91	1.19	5.69	4.01	4.50	16.33	0.26	1.30	0.06	0.31	0.12	1.45

Table 2. Comparison of concentrations of trace metals measured in this study at Mt. Mansfield and by others at nearby Whiteface Mountain.

Location	n ^a	Concentration $\mu\text{g/L}$				
		Mn	Cu	Zn	As	Pb
Mt. Mansfield	9	0.8 - 40 7.0	0.3 - 16 3.1	3.4 - 156 31	0.04 - 4.3 1.0	0.1 - 27 5.0
Whiteface Mountain ^b	3	5.5 - 29 13	<2.0 - 7.7 3.9	<10 - 43 18	—	4.3 - 13 7.7
Whiteface Mountain ^c	7	0.2 - 30 5.7	<0.07 - 24 4.1	—	—	—
Whiteface Mountain ^d	14	—	—	—	0.29 - 3.4 0.72	—

- a. n = number of events sampled
b. Khwaja *et al.*, 1995.
c. Siefert *et al.*, 1998.
d. Dutkiewicz and Husain, 1996.

Appendix B

Summary statistics and raw data

Table A1 - Summary of water deposition in non-precipitating cloud events at Mt. Mansfield, Vermont, August - September, 1998.

Date	Total volume of water collected (ml)	Number of collectors	Area ^a of collector surface (cm ²)	Mean event deposition (mm m ⁻²)	Length of collection (hours)	Deposition rate (mm hr ⁻¹)
8/18	274	3	167.55	5.45	9.5	0.57
8/26	17	1	182.4	0.93	3.25	0.29
9/10	79/93	3/3	167.55/182.4	1.64	5	0.33
Totals				8.02	17.75	0.45

a. Two types of funnels collectors were used: glass for Hg analysis (182.4 cm²) and polyethylene for trace metals analysis (167.55 cm²).

Table A2 - Summary statistics for major ion concentrations in all cloud water samples at Mt. Mansfield, Vermont, August 10 to October 16, 1998.

Ion	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺
(8 events, n=16)								
Mean (volume-weighted)	0.26	0.32	0.13	0.14	1.96	1.97	12.87	2.82
Median	0.24	0.30	0.02	0.12	1.21	1.15	10.60	0.91
Maximum	1.06	0.77	1.89	0.81	7.50	8.45	71.41	24.93
Minimum	0.01	0.05	0.01	0.01	0.33	0.29	0.40	0.13
Estimated annual cloud deposition (kg ha ⁻¹ yr ⁻¹)	2.58	3.13	1.28	1.38	19.38	19.48	127.28	27.89

Table A3 - Summary statistics for trace metals concentrations in all cloud water samples at Mt. Mansfield, Vermont, August 10 to October 16, 1998.

All cloud samples (ug L ⁻¹) (10 events, n=20)	Al	Cr	Mn	Ni	Cu	Zn	As	Rb	Sr	Cd	Pb
Mean (volume-weighted)	12.89	0.16	3.21	0.62	1.70	16.92	0.59	0.23	0.84	0.15	2.52
Median	10.02	0.21	3.00	0.47	1.02	18.52	0.54	0.22	0.66	0.17	2.22
Max.	101.31	2.91	39.98	11.07	15.62	156.83	4.34	1.89	14.00	0.88	27.23
Min.	2.01	0.01	0.29	0.05	0.12	0.68	0.04	0.03	0.04	0.01	0.10
Estimated annual deposition ^a via cloud water (mg m ⁻² yr ⁻¹)	11.86	0.15	2.95	0.57	1.56	15.57	0.54	0.21	0.77	0.14	2.32

a. Annual deposition estimated from mean concentrations and estimated annual cloud water deposition of 92 cm yr⁻¹.

Raw data - pH values, conductivity, H+ ions for all cloud water and cloud throughfall samples

Cloud water samples				Throughfall samples					
Date	Cloud-pH	Conductivity	Volume	Time of collection	H+ ions	Date	Drip-pH	conductivity	H+ ions
8/18/98	2.79	802	649	630	900	8/18/98	3.87	56.9	0.00013490
8/18/98	4.07	45	1024	1000	1330	8/18/98	4.01	53.8	0.00009772
8/18/98	4.08	50.2	1019	1330	1700	8/18/98	4.05	92.3	0.00008913
8/26/98	2.48	1523	205	938	1200	8/26/99	3.86	84.0	0.00013804
8/26/98	2.11	3360	15	1200	1430	9/10/98	4.19	36.1	0.00006457
9/1/98	3.18	341	371	735	900	9/10/98	4.53	16.3	0.00002951
9/1/98	3.59	128	98	900	945	9/10/98	4.24	27.9	0.00005754
9/4/98	3.11	389	333	700	845	9/10/98	4.2	35.6	0.00006310
9/4/98	3.00	505	153	845	1005	9/10/98	4.25	30.2	0.00005623
9/10/98	2.7	944	425	1115	1530	10/1/98	4.54	17.9	0.00002884
9/21/98	2.84	950	279	1610	1930	10/1/98	4.26	29.4	0.00005495
9/21/98	3.07	514	234	1930	2030	10/1/98	4.37	22.1	0.00004266
9/21/98	3.25	360	195	2030	2100				
10/1/98	3.19	323	274	2030	2100				
10/1/98	4.38	20.8	155	945	1200				
10/1/98	3.61	126	255	1200	1600				
10/12/98	2.38	1842	126	1600	1830				
10/16/98	2.43	1767	210	1530	1930				
10/16/98	2.88	657	122	1030	1230				
	pH	uS/cm	ml		eq/L		pH	uS/cm	eq/L

Raw data - Major ion concentrations in all cloud water (fog) and throughfall (drip) samples

sample ID	Date	Ca	K	Mg	Na	Cl	SO4	NO3	NH4
Cloud water samples									
LKC-02-FOG-HG	8/18/98	0.048	0.267	<0.005	0.089	4.452	1.768	15.470	1.419
LKC-03-FOG-HG	8/18/98	0.312	0.272	0.007	0.118	0.380	0.555	0.853	0.480
LKC-04-FOG-HG	8/18/98	0.147	0.312	0.020	0.116	0.422	1.058	0.203	0.992
LKC-5-FOG-HG	8/26/98	0.376	0.406	0.055	0.124	3.163	4.061	5.160	2.932
LKC-9-FOG-HG	9/1/98	0.011	0.341	<0.005	0.134	2.094	0.740	1.502	0.470
LKC-10-FOG-HG	9/1/98	0.040	0.322	0.018	0.202	1.215	1.238	0.380	0.834
LKC-11-FOG-HG	9/4/98	0.381	0.400	0.044	0.124	7.496	1.737	10.702	2.002
LKC-12-FOG-HG	9/4/98	0.502	0.658	0.053	<0.005	5.022	2.087	15.627	2.543
LKC-13-FOG-HG	9/10/98	0.119	0.521	0.008	<0.005	2.587	0.385	34.600	0.488
LKC-14-FOG-HG	9/21/98	1.060	0.774	0.799	0.810	1.157	8.436	12.835	24.927
LKC-15-FOG-HG	9/21/98	0.550	0.220	1.890	0.305	1.204	8.448	9.167	11.683
LKC-16-FOG-HG	9/21/98	0.719	0.296	<0.005	0.343	0.812	8.448	5.838	9.326
LKC-19-FOG-HG	10/1/98	<0.005	<0.05	<0.005	<0.005	1.100	0.293	10.839	0.308
LKC-20-FOG-HG	10/1/98	<0.005	<0.05	<0.005	<0.005	<0.33	0.300	0.397	0.132
LKC-21-FOG-HG	10/1/98	0.322	<0.05	0.019	0.025	1.750	0.717	3.398	0.433
LKC-22-FOG-HG	10/12/98	0.173	<0.05	0.023	0.019	1.207	0.426	71.410	0.620
Throughfall samples									
LKC1-DRP-MT1	8/18/98	0.710	1.320	0.133	0.168	0.448	2.238	0.561	4.248
LKC1-DRP-MT2	8/18/98	0.496	1.001	0.095	0.166	0.572	1.762	0.604	0.498
LKC1-DRP-MT3	8/18/98	2.035	2.563	0.385	0.263	0.776	4.518	0.627	0.618
LKC3-DRP-MT1	9/10/98	0.197	1.650	0.040	0.105	1.838	0.567		0.563
LKC3-DRP-MT2	9/10/98	0.110	0.552	0.010	0.112	1.361	0.347	0.164	0.106
LKC3-DRP-HG2	9/10/98	0.088	0.502	0.013	0.140	0.369	0.334		0.053
LKC-DRP-4-MT1	10/1/98	0.205	1.120	0.024	<0.005	0.487	0.539	<0.05	0.044
LKC-DRP-4-MT2	10/1/98	0.204	0.888	0.024	<0.005	0.812	0.670	0.180	0.041
LKC-DRP-4-MT3	10/1/98	0.731	0.520	0.557	0.115	0.489	0.497	0.245	0.047

Raw data - Mercury and trace metal concentrations for all cloud water and cloud throughfall samples

Date	Site	Sample Type	Volume (ml)	Hg (ng/L)	start time	stop time	Li7 (ug/L)	Be9 (ug/L)	Mg26 (ug/L)	Al27 (ug/L)	Ti47 (ug/L)	V51 (ug/L)	Cr53 (ug/L)	Mn55 (ug/L)	Co59 (ug/L)
8/18/98	LKC	1-MT1 DRIP	124	12.22	700	1630	0.083	0.000	120.484	15.831	0.329	0.556	0.142	83.859	0.054
8/18/98	LKC	1-MT2 DRIP	80	18.03	700	1630	0.103	0.000	95.406	14.047	0.359	0.542	0.140	62.187	0.052
8/18/98	LKC	1-MT3 DRIP	70	15.28	700	1630	0.162	0.000	359.392	28.106	0.247	0.773	0.184		0.148
9/10/98	LKC	2-HG1 DRIP	12				0.000	0.000	300.154	55.578	0.402	1.910	0.234	172.140	0.101
9/10/98	LKC	3-MT1 DRIP	26	17.01	1030	1530	0.049	0.000	52.426	19.899	0.121	0.505	0.180	50.663	0.025
9/10/98	LKC	3-MT2 DRIP	36	14.32	1030	1530	0.035	0.000	22.737	9.148	0.000	0.396	0.000	14.515	0.010
9/10/98	LKC	3-MT3 DRIP	17	9.95	1030	1530	0.053	0.000	17.041	7.104	0.000	0.367	0.000	6.954	0.018
10/1/98	LKC	4-MT1 DRIP	124	33.30	1015	1600	0.000	0.022	52.050	17.176	0.349	0.273	0.118	51.283	0.017
10/1/98	LKC	4-MT2 DRIP	109	18.13	1015	1600	0.000	0.001	37.495	15.493	0.280	0.372	0.046	25.852	0.018
10/1/98	LKC	4-MT3 DRIP	116	16.47	1015	1600	0.000	0.032	19.180	16.040	0.570	0.447	0.058	4.981	0.015
8/10/98	LKC	1 FOG	30	71.82	1315	715	0.446	0.019	1441.153		6.125	23.269	2.906	39.983	0.883
8/18/98	LKC	2 FOG	649	6.18	630	900	0.264	0.000	31.611	16.463	0.753	0.976	0.188	2.144	0.034
8/18/98	LKC	3 FOG	1024	6.96	1000	1330	0.054	0.000	9.265	3.378	0.093	0.326	0.008	0.827	0.007
8/18/98	LKC	4 FOG	1019	8.93	1330	1700	0.033	0.000	18.663	6.819	0.298	0.993	0.073	1.521	0.019
8/26/98	LKC	5 FOG	205	33.98	938	1200	0.072	0.000	55.425	16.325	0.549	1.521	0.223	4.099	0.036
8/26/98	LKC	6 FOG	15				0.016	0.000	329.377	101.307	3.097	3.500	0.634	17.298	0.205
9/1/98	LKC	9 FOG	371	10.82	735	900	0.172	0.000	13.554	10.020	0.613	0.368	0.092	1.141	0.010
9/1/98	LKC	10 FOG	98	18.86	900	945	0.443	0.000	28.933	22.350	1.394	0.769	0.073	1.857	0.022
9/4/98	LKC	11 FOG	333	30.70	700	845	0.068	0.000	50.655	16.891	0.913	1.689	0.247	4.124	0.035
9/4/98	LKC	12 FOG	153	33.49	845	1005	0.073	0.000	63.520		0.793	2.251	0.227	5.176	0.047
9/10/98	LKC	13 FOG	425	11.81	1115	1530	0.203	0.019	25.923	5.883	0.066	0.425	0.072	1.361	0.009
9/21/98	LKC	14 FOG	279	49.75	1610	1930	0.100	0.000	293.692	97.372	3.310	9.026	0.681	18.233	0.326
9/21/98	LKC	15 FOG	234	32.22	1930	2030	0.173	0.000	113.938		2.004	4.462	0.254	7.353	0.143
9/21/98	LKC	16 FOG	195	23.22	2030	2100	0.158	0.000	94.406	41.651	1.828	3.979	0.264	6.255	0.123
10/1/98	LKC	19 FOG	274	3.74	945	1200	0.025	0.003	3.281	3.624	0.051	0.107	0.102	0.285	0.004
10/1/98	LKC	20 FOG	155	4.56	1200	1600	0.043	0.002	4.802	2.009	0.037	0.142	0.032	0.879	0.004
10/1/98	LKC	21 FOG	255	6.16	1600	1830	0.370	0.011	32.174	8.222	0.051	0.368	0.137	4.985	0.012
10/12/98	LKC	22 FOG	126	7.67	1530	1930	0.000	0.000	11.176	6.775	0.188	0.428	0.010	1.698	0.015
10/16/98	LKC	23 FOG	210	6.47	1030	1230	0.435	0.000	12.361		0.164	1.478	0.237	0.891	0.016
10/16/98	LKC	24 FOG	122	15.87	1230	1450	0.975	0.000	36.809		1.019	4.311	0.279	3.863	0.058

Raw data - Mercury and trace metal concentrations for all cloud water and cloud throughfall samples

Date	Site	Sample	Type	Ni60 (ml)	Cu65 (ng/L)	Zn66 time	As75 time	Rb85 (ug/L)	Sr88 (ug/L)	Mo95 (ug/L)	Ag107 (ug/L)	Cd' 11 (ug/L)	In115 (ug/L)	Sb121 (ug/L)	Ba137 (ug/L)	La139 (ug/L)
8/18/98	LKC	1-MT1	DRIP	0.762	1.009	9.328	0.249	3.420	1.797	0.000	0.000	0.109	0.000	0.132	2.238	0.023
8/18/98	LKC	1-MT2	DRIP	0.515	1.050	7.306	0.249	2.628	1.125	0.000	0.000	0.096	0.000	0.150	1.497	0.034
8/18/98	LKC	1-MT3	DRIP	1.315	1.478	23.944	0.348	7.339	4.624	0.000	0.000	0.268	0.000	0.162	5.937	0.021
8/1/98	LKC	2-HG1	DRIP	2.105	1.605	1408.944	0.390	10.260	4.491	0.051	0.005	0.215	0.002	0.163	7.883	0.041
9/10/98	LKC	3-MT1	DRIP	0.669	0.855	3.635	0.095	2.744	0.554	0.000	0.000	0.036	0.000	0.051	0.632	0.014
9/10/98	LKC	3-MT2	DRIP	1.162	1.304	3.163	0.073	1.373	0.297	0.032	0.000	0.031	0.001	0.065	0.383	0.023
9/10/98	LKC	3-MT3	DRIP	0.501	0.879	3.738	0.072	1.037	0.171	0.038	0.000	0.025	0.001	0.067	0.221	0.023
10/1/98	LKC	4-MT1	DRIP	0.614	1.354	4.300	0.102	1.498	0.497	0.020	0.000	0.044	0.001	0.053	0.606	0.016
10/1/98	LKC	4-MT2	DRIP	0.261	0.542	2.940	0.131	1.386	0.410	0.020	0.000	0.015	0.001	0.098	0.600	0.026
10/1/98	LKC	4-MT3	DRIP	0.258	0.575	3.362	0.128	0.522	0.178	0.012	0.000	0.008	0.001	0.070	0.392	0.041
8/10/98	LKC	1	FOG	11.070	15.617	156.383	4.198	1.885	14.003	0.557	0.006	0.883	0.006	2.121	16.322	0.676
8/18/98	LKC	2	FOG	0.424	0.805	30.271	0.329	0.144	0.513	0.046	0.002	0.057	0.001	0.115	1.103	0.037
8/18/98	LKC	3	FOG	0.103	0.555	4.063	0.043	0.041	0.254	0.074	0.003	0.023	0.002	0.056	0.479	0.013
8/18/98	LKC	4	FOG	0.243	1.516	5.493	0.057	0.060	0.541	0.142	0.006	0.019	0.005	0.159	0.556	0.029
8/26/98	LKC	5	FOG	0.585	0.922	10.049	0.832	0.380	1.073	0.037	0.002	0.179	0.001	0.175	2.331	0.019
8/26/98	LKC	6	FOG	1.899	3.642	31.930	2.116	1.080	4.614	0.081	0.009	0.515	0.001	0.456	8.069	0.142
9/1/98	LKC	9	FOG	0.225	5.755	54.682	0.579	0.178	0.202	0.009	0.001	0.609	0.007	0.125	0.578	0.037
9/1/98	LKC	10	FOG	0.406	8.492	51.977	0.953	0.271	0.366	0.017	0.003	0.528	0.014	0.174	0.895	0.046
9/4/98	LKC	11	FOG	0.595	1.082	21.117	0.411	0.435	0.784	0.050	0.001	0.216	0.001	0.145	2.166	0.037
9/4/98	LKC	12	FOG	0.995	1.163	34.629	0.508	0.558	0.907	0.039	0.002	0.238	0.002	0.146	2.501	0.048
9/10/98	LKC	13	FOG	0.249	0.248	3.798	0.097	0.162	0.431	0.015	0.001	0.031	0.000	0.056	0.423	0.010
9/21/98	LKC	14	FOG	3.712	6.622	48.576	4.337	1.175	4.812	0.270	0.005	0.695	0.009	1.420	10.389	0.169
9/21/98	LKC	15	FOG	1.761	2.918	20.181	1.965	0.496	1.983	0.201	0.010	0.297	0.011	0.632	5.152	0.118
9/21/98	LKC	16	FOG	1.601	2.584	16.851	1.406	0.406	1.733	0.221	0.003	0.250	0.006	0.540	4.262	0.102
10/1/98	LKC	19	FOG	0.083	0.214	3.110	0.051	0.031	0.041	0.039	0.002	0.015	0.004	0.022	0.116	0.010
10/1/98	LKC	20	FOG	0.047	0.122	0.684	0.177	0.031	0.071	0.020	0.001	0.008	0.001	0.015	0.161	0.004
10/1/98	LKC	21	FOG	0.149	0.381	3.064	0.821	0.132	0.771	0.018	0.001	0.033	0.001	0.070	0.655	0.008
10/12/98	LKC	22	FOG	0.189	0.694	3.404	0.259	0.128	0.287	0.039	0.003	0.032	0.004	0.094	0.574	0.013
10/16/98	LKC	23	FOG	0.521	0.438	10.644	0.471	0.137	0.268	0.025	0.001	0.070	0.002	0.074	0.496	0.011
10/16/98	LKC	24	FOG	1.371	0.965	20.467	1.024	0.306	1.252	0.105	0.000	0.163	0.001	0.263	1.270	0.024

Raw data - Mercury and trace metal concentrations for all cloud water and cloud throughfall samples

Date	Site	Sample	Type	Ce140 (ml)	Nd146 (ng/L)	Sm147 time	W182 time	Tl205 (ug/L)	Pb208 (ug/L)
8/18/98	LKC	1-MT1	DRIP	0.041	0.018	0.003	0.000	0.051	0.723
8/18/98	LKC	1-MT2	DRIP	0.057	0.023	0.003	0.000	0.038	1.206
8/18/98	LKC	1-MT3	DRIP	0.045	0.021	0.002	0.000	0.111	1.540
8/1/98	LKC	2-HG1	DRIP	0.100	0.050	0.007	0.027	0.166	1.387
9/10/98	LKC	3-MT1	DRIP	0.027	0.011	0.001	0.000	0.043	0.370
9/10/98	LKC	3-MT2	DRIP	0.039	0.015	0.004	0.045	0.017	0.269
9/10/98	LKC	3-MT3	DRIP	0.039	0.016	0.002	0.046	0.016	0.268
10/1/98	LKC	4-MT1	DRIP	0.028	0.012	0.002	0.002	0.054	0.316
10/1/98	LKC	4-MT2	DRIP	0.045	0.019	0.001	0.013	0.031	0.519
10/1/98	LKC	4-MT3	DRIP	0.073	0.033	0.003	0.004	0.013	0.960
8/10/98	LKC	1	FOG	0.984	0.456	0.086	0.193	0.150	27.233
8/18/98	LKC	2	FOG	0.063	0.032	0.007	0.049	0.007	1.170
8/18/98	LKC	3	FOG	0.018	0.010	0.003	0.053	0.003	0.975
8/18/98	LKC	4	FOG	0.036	0.018	0.007	0.063	0.004	0.927
8/26/98	LKC	5	FOG	0.037	0.017	0.003	0.013	0.013	2.430
8/26/98	LKC	6	FOG	0.266	0.101	0.015	0.030	0.038	8.166
9/1/98	LKC	9	FOG	0.062	0.028	0.003	0.009	0.012	2.670
9/1/98	LKC	10	FOG	0.088	0.033	0.003	0.009	0.011	5.685
9/4/98	LKC	11	FOG	0.079	0.034	0.005	0.009	0.011	2.016
9/4/98	LKC	12	FOG	0.092	0.040	0.006	0.012	0.013	2.785
9/10/98	LKC	13	FOG	0.015	0.007	0.000	0.010	0.002	0.208
9/21/98	LKC	14	FOG	0.303	0.138	0.030	0.073	0.110	16.902
9/21/98	LKC	15	FOG	0.200	0.098	0.025	0.106	0.051	8.253
9/21/98	LKC	16	FOG	0.178	0.076	0.015	0.064	0.044	6.798
10/1/98	LKC	19	FOG	0.018	0.008	0.004	0.042	0.002	0.245
10/1/98	LKC	20	FOG	0.006	0.003	0.002	0.016	0.000	0.105
10/1/98	LKC	21	FOG	0.013	0.007	0.003	0.017	0.001	0.357
10/12/98	LKC	22	FOG	0.023	0.011	0.001	0.050	0.011	0.312
10/16/98	LKC	23	FOG	0.016	0.010	0.003	0.005	0.014	0.846
10/16/98	LKC	24	FOG	0.039	0.018	0.005	0.016	0.030	2.592