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Long-term relationships between mercury wet deposition and meteorology

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ABSTRACT

Daily-event precipitation samples collected in Underhill, VT from 1995 to 2006 were analyzed for total mercury and results suggest that there were no statistically significant changes in annual mercury wet deposition over time, despite significant emissions reductions in the Northeast United States. Meteorological analysis indicates that mercury deposition has not decreased as transport of emissions from major source regions in the Midwest and East Coast have consistently contributed to the largest observed mercury wet deposition amounts over the period. In contrast, annual volume-weighted mean (VWM) mercury concentration declined slightly over the 12-years, and a significant decrease was observed from CY 2001 to 2006. An increase in the total annual precipitation amount corresponded with the decline in annual VWM mercury concentration. Analysis suggests that the increase in precipitation observed was strongly related to changes in the amount and type of precipitation that fell seasonally, and this departure was attributed to a response in meteorological conditions to climate variability and the El Niño-Southern Oscillation (ENSO) cycle. Increased amounts of rainfall and mixed precipitation (mixture of rainfall and snowfall), particularly in the spring and fall seasons, enhanced annual precipitation amounts and resulted in declining VWM mercury concentrations during these periods. Thus, declines in concentration at the more remote Underhill site appear to be more directly linked to local scale meteorological and climatological variability than to a reduction in emissions of mercury to the atmosphere.

1. Introduction

Mercury is a hazardous air pollutant and bioaccumulative neurotoxin. It is a naturally occurring element in the earth's crust released to the atmosphere by natural and anthropogenic sources. Anthropogenic emissions, including combustion, manufacturing, agricultural burning, and mobile sources (U.S. EPA, 1997), are the most significant source of mercury to the environment (Schroeder and Munthe, 1998). In the United States, fossil fuel combustion is the most significant anthropogenic source of atmospheric mercury (U.S. EPA, 1997).

Mercury exists in three main forms in the atmosphere: gaseous elemental mercury (Hg^0), fine particle bound mercury (Hg(p), and divalent reactive gaseous mercury (RGM). Hg^0, the primary form of mercury in the atmosphere, is not very water soluble (Carpi, 1997; Schroeder and Munthe, 1998). Hg(p) and RGM (collectively Hg(II)), however, are very water soluble and much more reactive than Hg^0. Hg(II) is removed readily through wet and dry deposition (Lin and Pehkonen, 1999) whereas Hg^0 can travel long distances before being oxidized to Hg(II) and depositing (Schroeder and Munthe, 1998).

Oxidation of gaseous Hg^0 through photochemistry or reactions with ozone (O_3), hydroxyl radical (OH), and reactive halogens is likely the first step in mercury removal from the atmosphere (Lin et al., 2006). Dry deposition of Hg^0 may also be an important removal mechanism (Schroeder and Munthe, 1998; Lin et al., 2006). Reduction of Hg(II) to Hg^0 leads to additional transport away from sources but is dependent on the particular Hg(II) species involved, given that each has its own kinetic properties. The relative predominance of these reactions varies based on the availability of the oxidizing and reducing species, as well as meteorological conditions and source emissions (Lin et al., 2006). Therefore, the relative amounts of Hg^0 and Hg(II) in the atmosphere vary seasonally and geographically, impacting the amount of mercury available to be removed through wet deposition.

Given the continued growth in worldwide industrialization and energy use, quantification of mercury emissions, transport, and deposition is vital to understanding the impact of mercury pollution on the environment and society. Currently, most states in the United States have fish consumption advisories due to mercury contamination in lakes and rivers. Consequently, the Great Waters Program was created under the Clean Air Act Amendments of 1990 to mandate measurements of mercury wet deposition in the Great Lakes, Lake Champlain, the Chesapeake Bay and other selected

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coastal waterways (U.S. EPA, 1994). This program prompted the initial monitoring efforts in Underhill, VT.

In 1998, the Northeast Governors and Eastern Canadian Premiers formed a task force to eliminate regional anthropogenic sources of mercury. Mercury emissions in the northeastern United States consequently declined from 15.9 ton yr^{-1} to 4.7 ton yr^{-1} from 1998 to 2002 (NESCAUM, 2005). These reductions occurred primarily due to the nationwide U.S. EPA rule that required 95% reductions in municipal and medical waste combustion emissions, previously two of the largest anthropogenic sources of mercury in the Northeast. Municipal waste combustion currently comprises 22% of all mercury emissions in the Northeast. Other major emitters in the Northeast include electric utility boilers, residential heating, and sewage sludge incinerators; however, emissions from these sources have not declined as significantly (NESCAUM, 2005).

Mercury emissions across the United States also decreased throughout the 1990s by approximately 100 tons, primarily due to reductions in waste incineration emissions (Cohen et al., 2007), and more substantial declines occurred in the Northeast than the Midwest (Butler et al., 2008). Emissions from utility coal boilers, industrial boilers, and other major anthropogenic sources in the United States remained relatively constant from the early 1990s to 2002 (Cohen et al., 2007; Butler et al., 2008). Today, elevated levels of mercury in fish and wildlife remain a persistent problem in the Northeast states, with much of the contamination attributed to atmospheric deposition (Hammerschmidt and Fitzgerald, 2006; Evers et al., 2007). Therefore, despite regulatory achievements, there is still much to be understood about mercury emissions, transport, and deposition in the United States.

Mercury wet deposition measurements at Underhill represent one of the longest running mercury records to date. An earlier analysis from 1993 to 2003 showed no statistically significant linear trend in mercury deposition, and identified important seasonal and meteorological relationships with mercury wet deposition. In addition, the highest deposition events were largely associated with air mass transport from the Ohio River Valley Region (Keeler et al., 2005).

The present manuscript examines long-term patterns in precipitation, mercury concentration and wet deposition at Underhill from 1995 to 2006. Relationships between mercury in precipitation and local meteorology, including temperature, precipitation amount, and precipitation type, are used to interpret the observations. In light of recent studies showing the impact of climate variability and large scale meteorological phenomena on precipitation in the Northeast (Barlow et al., 2000; Patten et al., 2003; Hungtington and Hodgkins, 2004; Griffiths and Bradley, 2007), seasonal and local scale climate variability are also examined at Underhill in conjunction with mercury deposition measurements. Through these analyses, the unique Underhill precipitation record is used to examine the influence of meteorological parameters on mercury deposition over time.

2. Methodology

2.1. Site description

The Underhill site is located on the west slope of Mount Mansfield at the Proctor Maple Research Center (PMRC) (elevation 399 m), approximately 25 km east of Lake Champlain (Fig. 1). Daily-event wet-only precipitation samples were collected for mercury and trace elements in collaboration with the Vermont Monitoring Cooperative (VMC) using a modified MIC-B (MIC, Thornhill, Ontario) automatic precipitation collector (Landis and Keeler, 1997). Sample collection commenced at Underhill in December 1992 and continued through September 2007.

2.2. Sampling and analysis

When sample collection began in 1992, precipitation was collected into 10 L borosilicate glass bottles through a Teflon-coated funnel in the MIC-B wet-only collector. In September 1994, the sampling train was redesigned and replaced with separate sampling trains for mercury and trace elements, as described in Landis and Keeler (1997). The sampling trains minimized enrichment of trace elements in precipitation samples, and reduced effects caused by the absorptive behavior of trace metals to the walls of the sampling bottles (Church et al., 1984). The mercury sampling train consisted of a borosilicate glass funnel (collection area 191 $\pm$ 9 cm^2), a Teflon adapter with a glass vapor lock to prevent loss of mercury from the samples, and a 1 L Teflon bottle. The trace element sampling train consisted of a polypropylene funnel (collection area 167 $\pm$ 7 cm^2), a polypropylene adapter, and a 1 L polypropylene bottle. Due to the change in sample collection technique in 1994, only data from the 12

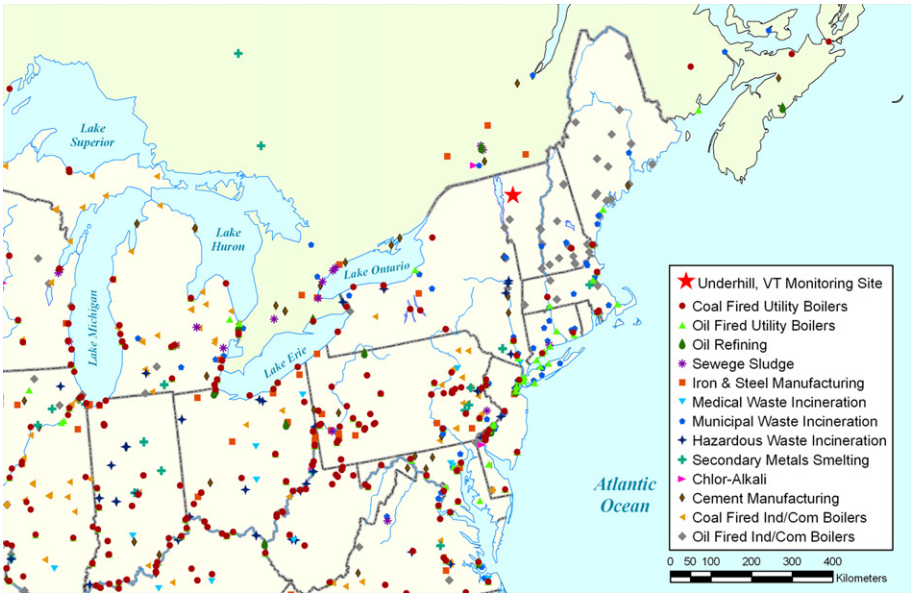

Fig. 1. Location of the Underhill, VT monitoring site and major mercury point sources emitting $\geq$ 0.1 kg $year^{-1}$ (U.S. EPA NEI, 2005; Environment Canada NPRI, 2007).

complete years of consistent sample collection (1995–2006) will be discussed in this manuscript.

All field supplies were rigorously prepared at the University of Michigan Air Quality Laboratory (UMAQL), and after collection samples were shipped back to the UMAQL for processing and analysis. The sampling trains were prepared in an 11-day acid-cleaning procedure (Landis and Keeler, 1997) and were replaced after individual precipitation events. Precipitation samples were processed at the UMAQL using clean techniques and were analyzed for mercury using cold-vapor atomic fluorescence spectrometry (CVAFS) (Keeler et al., 2005).

Precipitation amounts derived from samples collected at Underhill were compared with the on-site National Weather Service standard 8-inch rain gauge, and results indicated that the MIC-B precipitation collection agreed with the NWS rain gauge to within 1% (Miller et al., in preparation), confirming that the MIC-B is effective in collecting precipitation. In this study event precipitation depths were calculated using MIC-B measured sample volumes and the average recorded funnel area. All precipitation samples greater than 0.10 cm were included in this data analysis. Only 81 of 1236 (6.5%) samples collected were excluded, and no statistically significant trends were observed in the concentration or deposition for these low volume samples.

2.3. Statistical analysis

Precipitation samples collected at Underhill were examined on annual and seasonal time scales for the 12-year period (1995–2006) and the recent six-year period (2001–2006). Seasons were determined using true dates of solstice and equinox for each year. The statistical significance of changes in annual and seasonal precipitation depth, VWM mercury concentration, and mercury wet deposition were determined using linear regression and ANOVA tests (SPSS V16.0). Wilcoxon and Kruskal–Wallis tests were also used to determine if mercury deposition was significantly different among individual meteorological clusters (SAS V9.1).

2.4. Meteorological data

Meteorological data for the Underhill site, including ambient temperatures and tipping bucket rain gauge data, was provided by the PMRC Basic Meteorological Monitoring program. Data was recorded on hourly intervals prior to July 1998, and every 15 min from July 1998 onward. The hour of maximum precipitation for each event was determined from the tipping bucket rain gauge. Belfort rain gauge charts were used when tipping bucket data was unavailable. Precipitation type was categorized as rain, snow, or mixed precipitation (mixture of rainfall and snowfall) by an on-site operator.

Air mass transport to the Underhill site was modeled using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model Version 4.8 (Draxler and Hess, 1997). HYSPLIT back trajectories were calculated using the National Weather Service's National Center for Environmental Prediction (NCEP) Nested Grid Model (NGM) for 1995–1996 and the Eta Data Assimilation System (EDAS) for 1997–2006. Data was obtained from the National Oceanic and Atmospheric Administration's Air Resources Laboratory (NOAA-ARL). The hour of maximum precipitation was used as the starting time for each trajectory. The starting height was set to one-half of the mixed-layer height, as determined from upper-air soundings, in order to best represent air mass transport within the boundary layer. Cluster analysis was performed using Ward's Minimum-Variance method (Ward, 1963; Moody and Samson, 1989; Landis et al., 2002). Clusters were determined using trajectory endpoints as well as the mean on-site temperature on the day of the event, the total precipitation amount, and the precipitation type associated with each event. While three-day back trajectories are often used to represent regional transport regimes, two-day back trajectories were used here due to the frequency of missing data points associated with three-day back trajectories which would have reduced the number of precipitation samples used in the cluster analysis. A comparison of the calculated two- and three-day clusters resulted in equivalent transport regimes and thus, the choice of trajectory length did not have a significant impact on the findings discussed in the next section.

3. Results and discussion

3.1. 1995–2006

There were 1155 daily-event precipitation samples collected at Underhill from 1995 to 2006. The annual VWM mercury concentration and total wet deposition for 1995–2006 are shown in Fig. 2. Error bars were calculated using 8.1% uncertainty in the measured concentration (Landis and Keeler, 1997) and 5% uncertainty in the

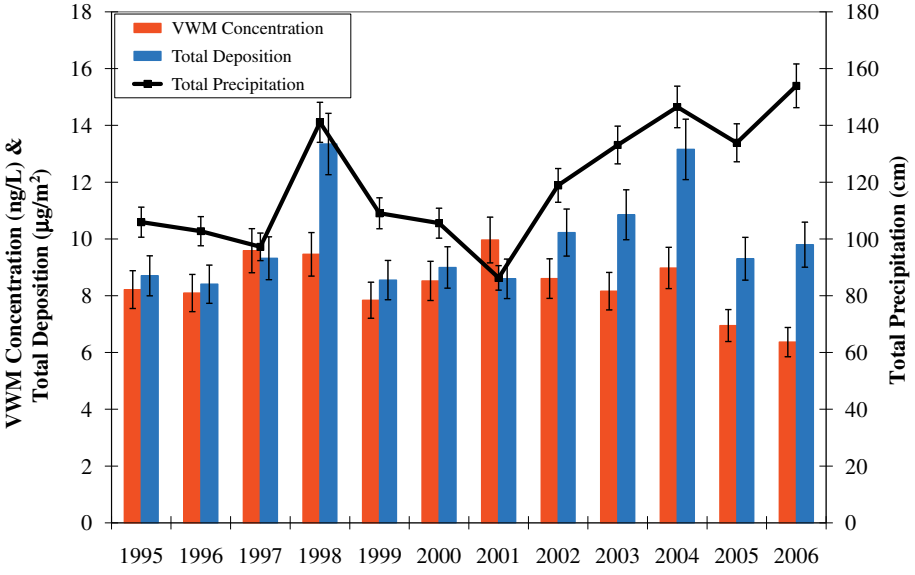

Fig. 2. Annual mercury and precipitation measurements.

precipitation depth (Keeler et al., 2006). The VWM mercury concentration for 1995–2006 was 8.3 ± 0.7 ng L^{-1} and the mean event mercury wet deposition was 0.10 ± 0.01 μg m^{-2}. The range in sample concentration was 0.9–90.5 ng L^{-1}. On average 96 samples were collected each year, and the average event precipitation depth was 1.24 ± 0.06 cm. The highest annual mercury deposition occurred in 1998 and 2004. These were two of the wettest years of the period as well, partially explaining the elevated deposition. CY 1998 also had the greatest number of events collected ($n = 124$) and the highest average annual temperature (8.1 °C for the entire year; 10.0 °C on days when precipitation occurred). In both years, approximately 80% of the total precipitation fell as rain, whereas for the other 10 years only 70% of the total precipitation was in the form of rain, on average. This suggests that meteorological parameters, including temperature, precipitation amount, and precipitation type were important in controlling the wet removal of mercury from the atmosphere.

From 1995 to 2006, annual precipitation amount at Underhill increased significantly by 3.9 cm yr^{-1} (4.2% yr^{-1}; $r^2 = 0.43$; $p = 0.02$). Annual VWM mercury concentrations declined slightly by 0.1 ng L^{-1} yr^{-1} (1.4% yr^{-1}) from 1995 to 2006 but the relationship was not significant ($r^2 = 0.21$; $p = 0.14$). Total annual deposition measured at Underhill did not change significantly over the 12-year period ($r^2 = 0.08$, $p = 0.36$).

Analysis of weekly precipitation samples collected by the Mercury Deposition Network (MDN) indicated a decline in VWM concentration at four of 12 sites in New England from 1998 to 2005 (Butler et al., 2008). A significant 1.7% per year decline in concentration was observed (14 ± 4% over the eight-year period) (Butler et al., 2008). Although the decline in concentration at Underhill was not significant from 1995 to 2006, or from 1998 to 2005, a statistically significant decline of 0.6 ng L^{-1} yr^{-1} (6% yr^{-1}) was observed during the second half of the study (2001–2006).

A significant decline in mercury wet deposition was not observed at the MDN sites (Butler et al., 2008) or at Underhill. The coincident decrease in VWM concentration and increase in precipitation amount at Underhill suggests that a relatively constant amount of mercury was available for scavenging in an increasing amount of precipitation, resulting in declining annual concentrations. This observation begs the question of why mercury wet deposition was approximately constant during a period of reported emission reductions for waste incinerators (USEPA, 2005). Because mercury emissions from waste incineration are primarily Hg(II) (Carpi, 1997; Dvonch et al., 1999), and Hg(II) is readily deposited (Lin and Pehkonen, 1999; White et al., 2009), it is logical to predict that a substantial emissions reduction in New England Region would have had a measurable impact on mercury deposition in many of the Northeast States. However, such a decline was not observed in northern Vermont based upon analysis of the daily-event deposition data from Underhill. Analysis of the prevailing flow regimes and upwind history of air masses associated with the largest mercury deposition events suggests that the consistent annual deposition may be due to the dominance of regional transport from mercury sources in high-density source regions where there are numerous source types that have not reported declines as significant as the waste incineration sector over the course of the study.

Studies of mercury deposition in the northeastern United States have identified major source regions as the Midwest and East Coast (Han et al., 2005; Choi et al., 2008), demonstrating the importance of transport on mercury deposition. To elucidate the impact of source regions on the Underhill site, cluster analysis was performed on HYSPLIT two-day back trajectories from 1995 to 2006. Sixteen clusters were computed, explaining 76% of the variance in the data. Wilcoxon and Kruskal–Wallis tests indicated that the mercury deposition was significantly different among individual clusters ($p < 0.0001$). The clusters with the highest mean and median wet deposition at the Underhill site represented transport from the Midwest and East Coast in conjunction with rainfall and average temperatures ranging from 4.9 °C to 27.2 °C (Fig. 3a–c; Table 1). The clusters with the lowest mean and median event wet deposition

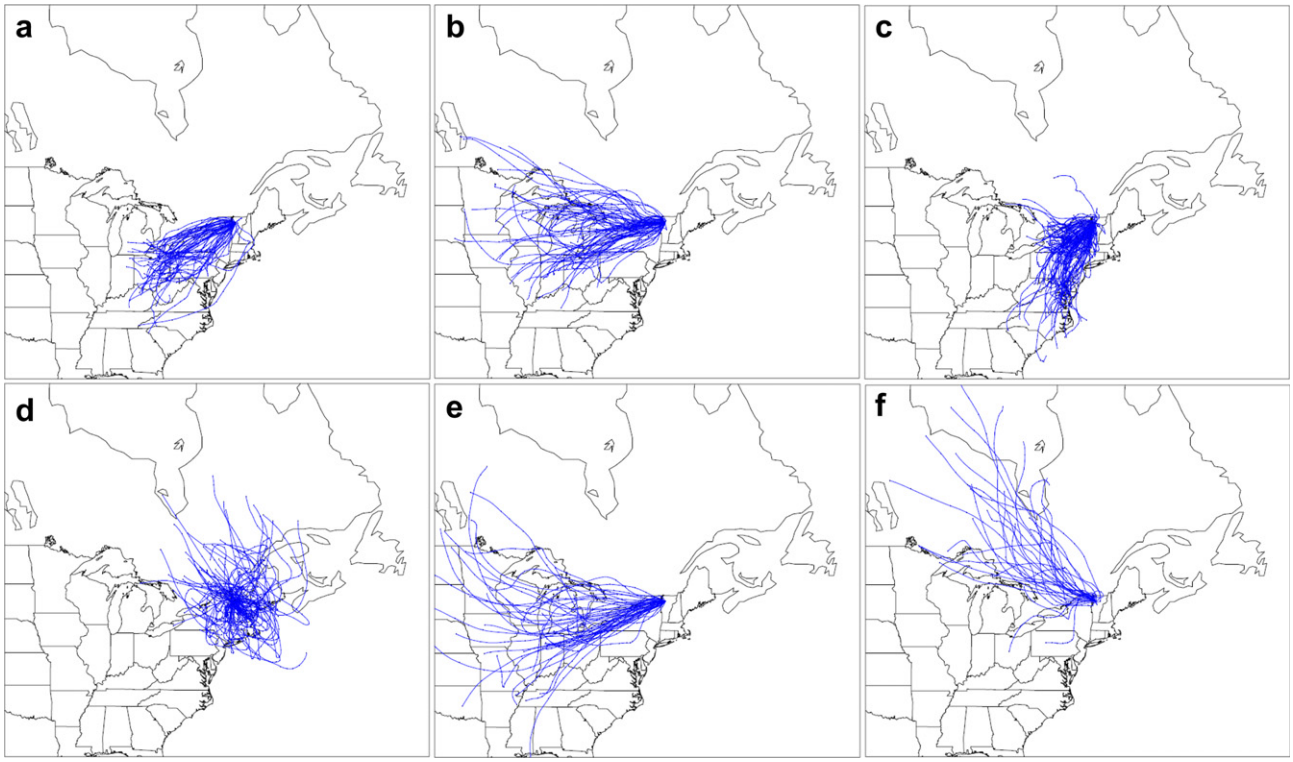

Fig. 3. Back-trajectory clusters for highest (3a–c) and lowest (3d–f) mean and median mercury wet deposition events.

Table 1
Summary of daily-event mercury measurements and on-site meteorological conditions associated with back-trajectory clusters.

Cluster	VWM Hg Concentration (ng L^{-1})	Mean Hg Deposition (μg m^{-2})	Median Hg Deposition (μg m^{-2})	Mean Temperature (°C)	Median Temperature (°C)	Temperature Range (°C)	Mean Precipitation Amount (cm)	Median Precipitation Amount (cm)	N Rain	N Snow	N Mix
a	11.1	0.18	0.13	14.4	14.9	4.9–21.3	1.6	1.3	47	0	5
b	11.3	0.15	0.12	19.2	19.4	12.5–26.5	1.4	0.9	95	0	2
c	12.4	0.15	0.11	20.5	20.4	10.2–27.2	1.2	0.8	64	0	0
d	4.6	0.04	0.03	−5.2	−4.9	−15.1–1.6	0.9	0.5	3	56	25
e	10.0	0.04	0.03	−3.1	−3.1	−13.8–6.7	0.4	0.3	3	34	6
f	6.3	0.02	0.02	−6.9	−6.9	−22.4–5.9	0.4	0.2	3	23	4

displayed transport from the northwest and southwest when average temperatures were between −22.4 °C and 6.7 °C and predominantly snowfall or mixed precipitation was recorded (Fig. 3d–3f; Table 1). Although southwest transport was observed in both the highest and lowest deposition clusters, lower wet deposition was accompanied with advection of cold air and snowfall. Similar to earlier studies (Hoyer et al., 1995), the cluster analysis indicates that the meteorological conditions leading up to and during precipitation events are critical factors for understanding deposition amounts. These results also demonstrate the importance of regional transport to Underhill from sources south and southwest of the site.

To statistically determine whether the largest mercury deposition amounts were consistently associated with transport from these major source regions over time, cluster analysis of back trajectories was performed on individual years. In each year from 1995 to 2006, the meteorological clusters with the highest mean deposition were associated with precipitation falling as rainfall, average on-site temperatures above 10 °C, and transport from the Midwest or East Coast. The clusters with the lowest mean deposition were associated primarily with northwesterly flow, average on-site temperatures below 5 °C and snowfall or mixed precipitation. Thus, the dominant transport regimes and air mass history associated with the highest deposition events at Underhill did not change appreciatively from year to year, and consequently, the annual deposition amounts did not decrease.

Finally, cluster analysis was also performed on individual seasons to further examine the effect of meteorological conditions on deposition patterns. In all seasons, the clusters with the highest mean mercury deposition occurred with southerly or southwesterly flow and warm air advection to the region. In winter the highest deposition clusters had average temperatures at the site above 0 °C, southwesterly transport, and either rainfall or mixed precipitation. The lowest deposition clusters displayed temperatures less than −4 °C, northerly flow, and either snowfall or mixed precipitation. In the summertime, when all precipitation was in the form of rainfall, the highest deposition clusters had average temperatures between 12 °C and 24 °C with southerly or southwesterly flow, and the lowest deposition occurred with temperatures between 8 °C and 20 °C with either easterly or northwesterly transport. The mean mercury deposition for the summertime clusters was three times greater than the clusters with the highest mean deposition in winter. Therefore, the combined effects of temperature, transport regime (upwind history including pathway and air mass characteristics), and precipitation type were critical in determining wet deposition amounts at Underhill. These factors are also important when considering the physicochemical transformations that occur en route between source and receptor.

Relationships between temperature, precipitation type, and mercury wet deposition at this site were reported previously (Keeler et al. 2005). Temperature is a critical parameter in the atmospheric chemistry of mercury and plays a major role in determining the speciation and amount of mercury that reaches the site (Han et al., 2004; Lynam and Keeler, 2006). Temperature appears weakly correlated to deposition on an event basis, but is more strongly correlated on monthly time scales ($r^2 = 0.50$; Fig. 4), indicating that the temperature at the site on the day of each event may not be as important as the regional, upwind meteorology in determining total deposition amounts. Mercury wet deposition is also highly seasonal, with greater wet deposition observed during the warmer months (Fig. 4), suggesting the importance of both mercury speciation and the removal efficiency of different precipitation types.

RGM is typically higher when temperatures are warm and during periods of increased photo-oxidation of Hg^0 (Liu et al., 2007; Lynam and Keeler, 2006). RGM is also readily removed by precipitation (Lin and Pehkonen, 1999; White et al., 2009). In contrast, during cold winter months particulate mercury is somewhat elevated at Underhill (Burke et al., 1995), and VWM mercury concentrations and wet deposition are noticeably lower. The relationship between precipitation type and mercury wet deposition is, in part, due to the fact that rain is more efficient than snow in scavenging mercury from the atmosphere (Hoyer et al., 1995; Landis et al., 2002; Keeler et al., 2006). Over 80% of the mercury wet deposition at Underhill was in the form of rain, with only 5% depositing as snow, and 12% as mixed precipitation. Fig. 5 shows the VWM mercury concentration and number of samples collected for different ranges of precipitation amount for each precipitation type. For a given precipitation amount, rain appears more efficient at removing mercury from the atmosphere than mixed precipitation or snowfall, further suggesting that precipitation type is one of many important factors determining the concentration of mercury in precipitation, and ultimately the amount of mercury that will deposit to the surface during a given event.

3.2. 2001–2006

The 12-year record from Underhill was divided into two six-year segments (1995–2000 and 2001–2006) to further examine changes in mercury deposition and meteorology over time and determine the cause for the recently observed increase in annual precipitation amount. The first six-years of data (1995–2000) did not show any significant variability in precipitation amount, VWM mercury concentration, or total mercury wet deposition. However, from 2001 to 2006 there was an approximately 0.6 ng L^{-1} yr^{-1} decline in VWM concentration (6% yr^{-1}; $r^2 = 0.79$; $p = 0.02$) and an 11.3 cm yr^{-1} increase in total precipitation amount (12% yr^{-1}; $r^2 = 0.78$; $p = 0.02$). The decline in VWM concentration coincided with the increase in precipitation amount starting in 2001, and both changes were significant. There was no significant change in the annual total deposition from 2001 to 2006. The highest concentrations were typically observed with low precipitation amounts (Fig. 5), suggesting that at this remote site most of the mercury was removed during the onset of precipitation, and additional precipitation acted

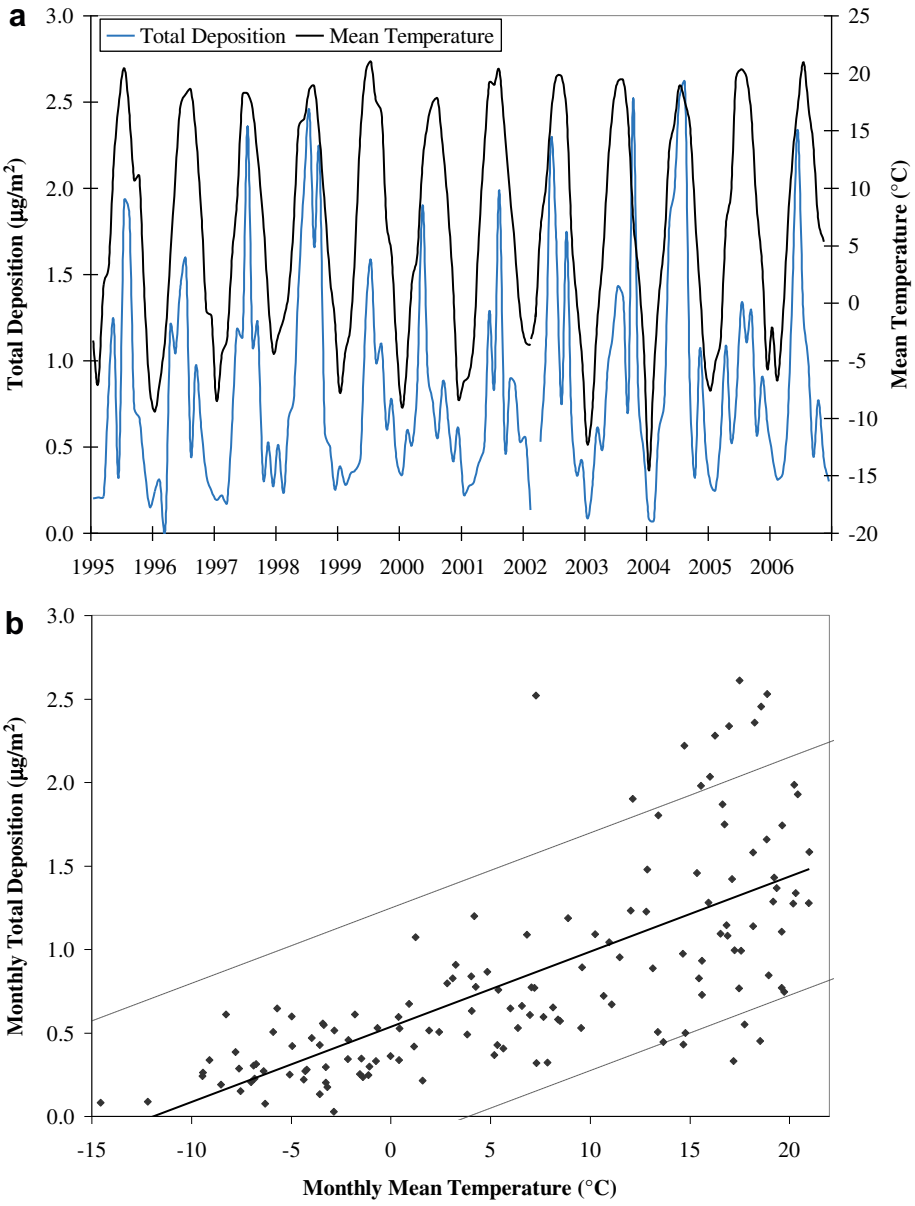

Fig. 4. (a) Seasonal relationship and (b) linear regression between monthly total deposition and monthly mean temperature with 90% confidence intervals shown.

to dilute samples throughout the remainder of the event. This relationship was consistent among all precipitation types (Fig. 5), suggesting that the observed decline in concentration from 2001 to 2006 was likely caused by the increase in annual precipitation amount.

To determine whether the increase in annual precipitation amount from 2001 to 2006 was isolated to the Underhill site or was in fact a regional phenomenon, annual precipitation totals from the PMRC and five regional airports (NCDC) were examined (Fig. 6). These airports were chosen because of their proximity to Underhill and the availability of data for the time period of interest. All sites showed an increase in annual precipitation amount from 2001 to 2006 of 10.8 cm yr^{-1} on average ($r^2 = 0.92$). This rate of change was equivalent to the change observed at Underhill (11.3 cm yr^{-1}) considering the 5% uncertainty in the precipitation depth measurement. Precipitation measurements from the other sites indicate that the increase was prevalent throughout the Northeast (Fig. 6). Further examination demonstrates that the greatest increase occurred in spring (April–May) and fall (October–November) months, indicating a possible change in the form and duration of precipitation during these seasons. This analysis was extended to airports across the Midwest and East Coast, and results indicate that the increase in precipitation from 2001 to 2006 was primarily isolated to the Northeast states. Although annual precipitation increased slightly at stations in New Jersey and eastern Pennsylvania (6.9 cm yr^{-1}; $r^2 = 0.55$) primarily in spring and fall, on average there was no change in annual precipitation for the Midwest or other East Coast locations examined here. Therefore, the decline in concentration at Underhill cannot be attributed to an increase in upwind wet removal of mercury in the high emission source regions.

A significant increase in the frequency of large volume precipitation samples collected at Underhill may further explain the increase in annual precipitation amount (Fig. 7). The precipitation sampling train was capable of collecting up to 2 inches (5.08 cm) of precipitation into a 1 L bottle. While the mean sample volume for the 12-year period was 237 mL (0.5 in; 1.27 cm), from 2001 to 2006,

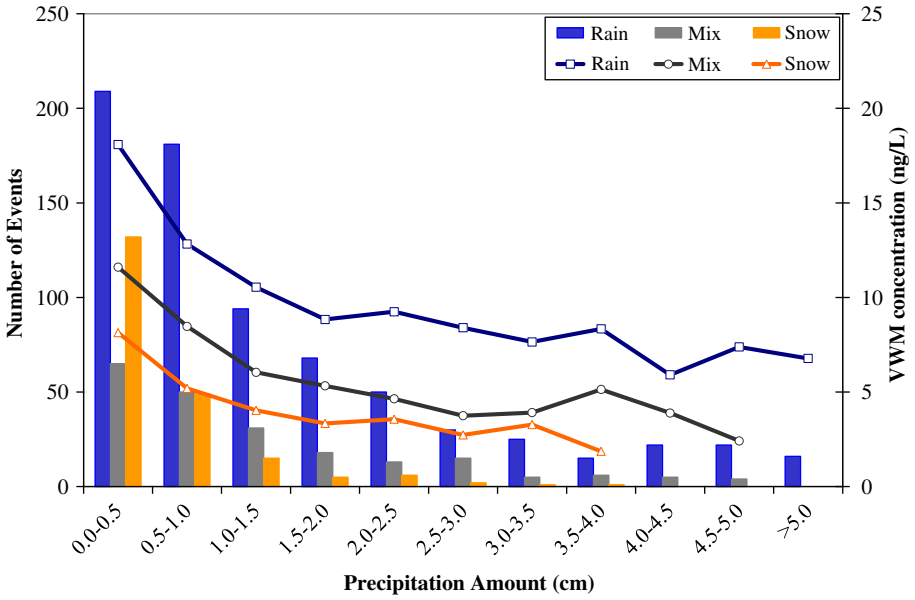

Fig. 5. VWM mercury concentrations (lines) and number of daily-events (bars) for different precipitation amount ranges based on precipitation type for 1995–2006.

there was a nearly three-fold increase in the number of daily-event samples with at least 500 mL (1 inch; 2.54 cm) of precipitation. The number of samples collected each year from 1995 to 2006 did not change significantly, potentially indicating longer duration periods of precipitation that lead to larger volumes being collected into individual daily-event samples. Because large volume events at Underhill typically lead to equivalent amounts of mercury diluted within a given sample, the decline in annual VWM mercury concentration was more likely influenced by an increase in the number of large precipitation events rather than a decline in atmospheric mercury available to be removed by precipitation.

Changes in precipitation type were also examined from 2001 to 2006 (Fig. 8). While there were no statistically significant changes in the annual amounts of rainfall or snowfall from 1995 to 2006, the annual mixed precipitation amount increased significantly by 1.7 cm yr^{-1} ($r^2 = 0.75$; $p = 0.0003$) from 1995 to 2006. From 2001 to 2006, rainfall increased by 9.0 cm yr^{-1} ($r^2 = 0.58$; $p = 0.082$), mixed precipitation increased by 3.1 cm yr^{-1} ($r^2 = 0.89$; $p = 0.005$), and both changes were statistically significant. Snowfall did not change significantly from 2001 to 2006. While additional years of data may be required to detect a statistically significant trend in annual snowfall, the increase in mixed precipitation and rainfall may indicate important changes in meteorology both seasonally and annually.

3.3. Observations of local climate variability

Changes in the form and amount of precipitation received at a given site may signal changes in the local or regional climate (Hungtington and Hodgkins, 2004; Griffiths and Bradley, 2007). To investigate the presence of local scale climate variability at the Underhill site, precipitation amounts were examined with respect to precipitation type and season. Not unexpectedly, there were no significant year to year changes in any precipitation type during

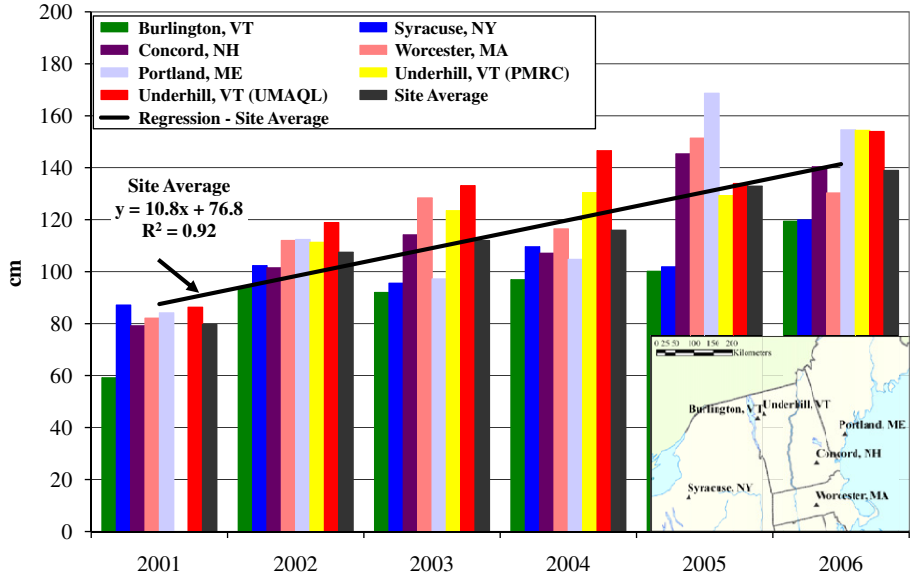

Fig. 6. Annual total precipitation from regional airports and Underhill, VT. PMRC rain gauge data from 2001 was omitted due to missing data.

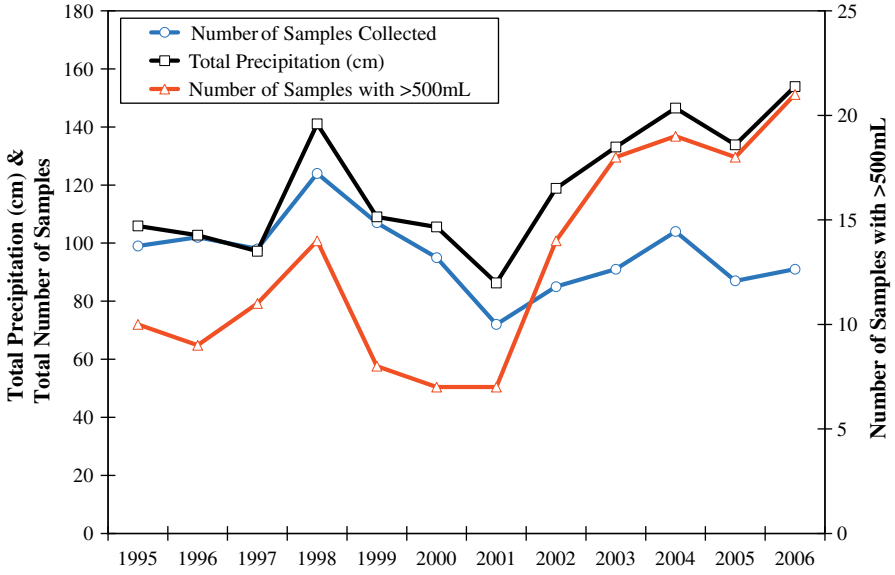

Fig. 7. Annual precipitation depth and number of daily-event samples collected.

summer or winter, but spring and fall showed interesting variability (Fig. 9).

From 1995 to 2006, spring rainfall amount increased significantly by 1.8 cm yr^{-1} ($r^2 = 0.43$; $p = 0.02$) (Fig. 9a). From 2001 to 2006, this change was more extreme with an increase of 5.4 cm yr^{-1} ($r^2 = 0.83$; $p = 0.012$). There were no significant springtime patterns for mixed precipitation or snowfall amounts from 1995 to 2006 or from 2001 to 2006. However, it is interesting to note that there was no springtime snowfall observed in 2003, 2005, and 2006. A lack of recorded spring snowfall did not occur in any year prior to 2003. In the fall from 1995 to 2006, mixed precipitation amount increased significantly by 1.3 cm yr^{-1} ($r^2 = 0.82$; $p = 0.0001$; Fig. 9b). There was an even greater increase in mixed precipitation amount of 1.5 cm yr^{-1} ($r^2 = 0.69$; $p = 0.04$) from 2001 to 2006. However, there were no significant changes in fall snowfall or rainfall amounts.

Significant changes in VWM concentration were observed from 1995 to 2006 and 2001–2006. From 1995 to 2006 the spring VWM concentration for rainfall declined significantly by 0.6 ng L^{-1} yr^{-1} ($r^2 = 0.65$; $p = 0.002$) (Fig. 9c). From 2001 to 2006, the spring VWM concentration declined for rainfall (0.9 ng L^{-1} yr^{-1}; $r^2 = 0.75$; $p = 0.08$) and mixed precipitation (1.5 ng L^{-1} yr^{-1}; $r^2 = 0.59$; $p = 0.07$) (Fig. 9c). Fall VWM also decreased for rainfall (1.1 ng L^{-1} yr^{-1}; $r^2 = 0.59$; $p = 0.07$) from 2001 to 2006 (Fig. 9d).

Changes in total mercury deposition from 1995 to 2006 and 2001 to 2006 for any precipitation type or season were not significant (Fig. 9e–f), with the exception of fall mercury deposition from mixed precipitation, which increased significantly from 1995 to 2006 by 0.05 μg m^{-2} yr^{-1} ($r^2 = 0.44$; $p = 0.02$).

This analysis shows that changes in seasonal precipitation type and amount from year to year may have in part contributed to the observed increase in annual precipitation amount and the

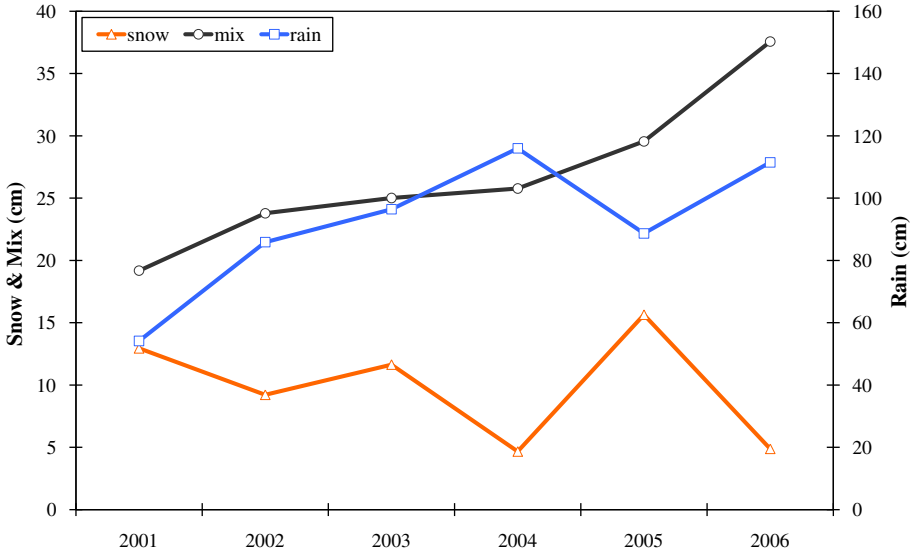

Fig. 8. Annual precipitation depth by precipitation type for 2001–2006.

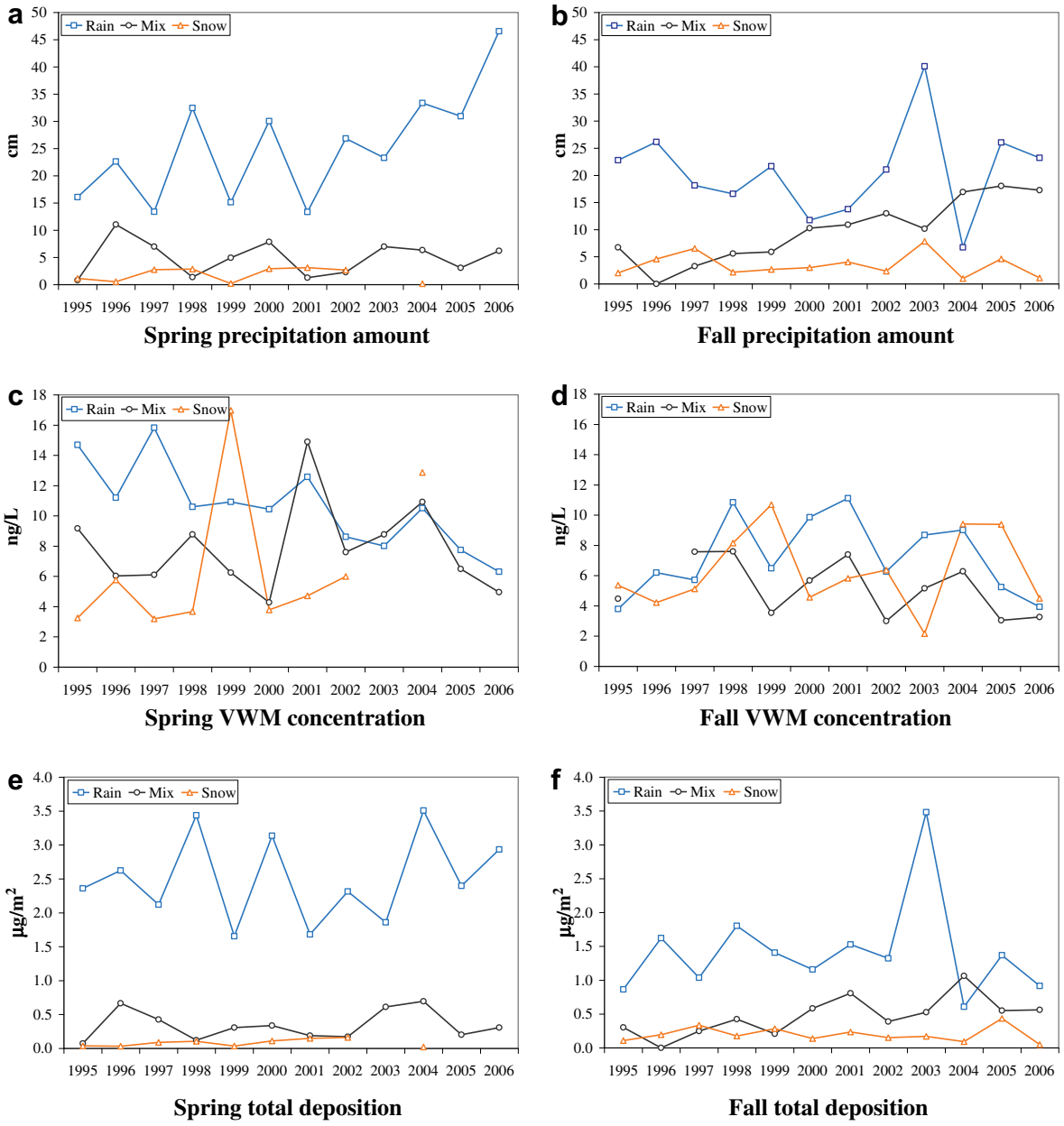

Fig. 9. Spring and Fall precipitation amount, VWM mercury concentration, and total mercury deposition for each precipitation type.

subsequent decline in VWM concentration. Further analysis demonstrates that in addition to local scale climate variability, other large scale meteorological phenomena may also be influencing changes in annual precipitation as well as the duration and volume of individual daily-events.

3.4. *Impacts of the* ENSO *cycle on precipitation*

Changes in annual precipitation associated with the El Niño-Southern Oscillation (ENSO) cycle are an indication of climate variability on a larger scale (Barlow et al., 2000; Patten et al., 2003). The increased frequency of El Niño in recent years is a possible explanation for the increase in annual precipitation amount and large volume events from 2001 to 2006 at Underhill. Acknowledging that there is limited data from this study to perform a long-term analysis, the data available does allow us to hypothesize on the relationship between ENSO and the observed increase in precipitation amount at Underhill.

ENSO is a phenomenon associated with changes in sea surface pressure that alter the general circulation of the equatorial Pacific and significantly impact global weather patterns. El Niño events typically occur every 3–7 years. During this time, some regions of the world experience increased precipitation while others experience increased drought (Rohli and Vega, 2008). The meteorological impacts of ENSO vary across the United States (Meehl et al., 2007). Although the relationship to El Niño is not as strongly observed in the Northeast as in the southern and central United States, stronger events can alter the jet stream flow enough to have a noticeable impact on the Northeast (Rohli and Vega, 2008).

Research on ENSO is often focused on wintertime variability because this is when ENSO conditions are most extreme; however there is potential for ENSO to impact summertime meteorology as

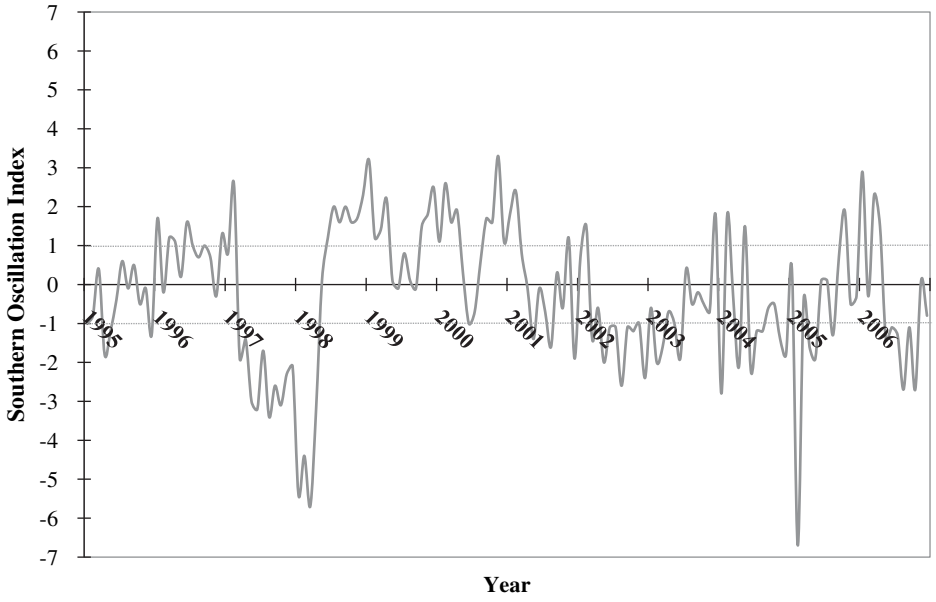

Fig. 10. SOI for 1995–2006.

well (Barlow et al., 2000). This may be due to a significant lag time between the peak of El Niño and the time at which the meteorological patterns in the Northeast United States are most strongly impacted. During El Niño years in the Northeast, there is often increased precipitation in June, with slightly drier conditions in July and very dry conditions in August (Barlow et al., 2000). As the frequency and intensity of El Niño vary over time, there is an apparent general shift in the El Niño teleconnections, or the large scale impacts of this climatological anomaly, toward the north and east in the United States (Meehl et al., 2007).

The ENSO cycle for 1995–2006 was quantified using the Southern Oscillation Index (SOI), where an SOI less than −1 represents El Niño and an SOI larger than +1 represents La Niña (NOAA Climate Prediction Center; Rohli and Vega, 2008). By this analysis, a powerful El Niño occurred in 1997–1998, which had a significant impact on global weather patterns. Following this event, there was an extended La Niña from mid 1998 through early 2001. Although El Niño episodes typically occur every 3–7 years, an El Niño occurred every other year from 2001 to 2007 (NOAA Climate Prediction Center) (Fig. 10). These periods coincide with the variability in precipitation from 1995 to 2006 at Underhill, both in the annual precipitation amount (Fig. 2) and the annual frequency of large volume daily-event samples (Fig. 11). Fig. 11 shows the number of large volume daily-events (sample volume >500 mL) occurring each month from 1995 to 2006, with El Niño years (red) distinguished from La Niña (blue) and neutral years (black; no fill),

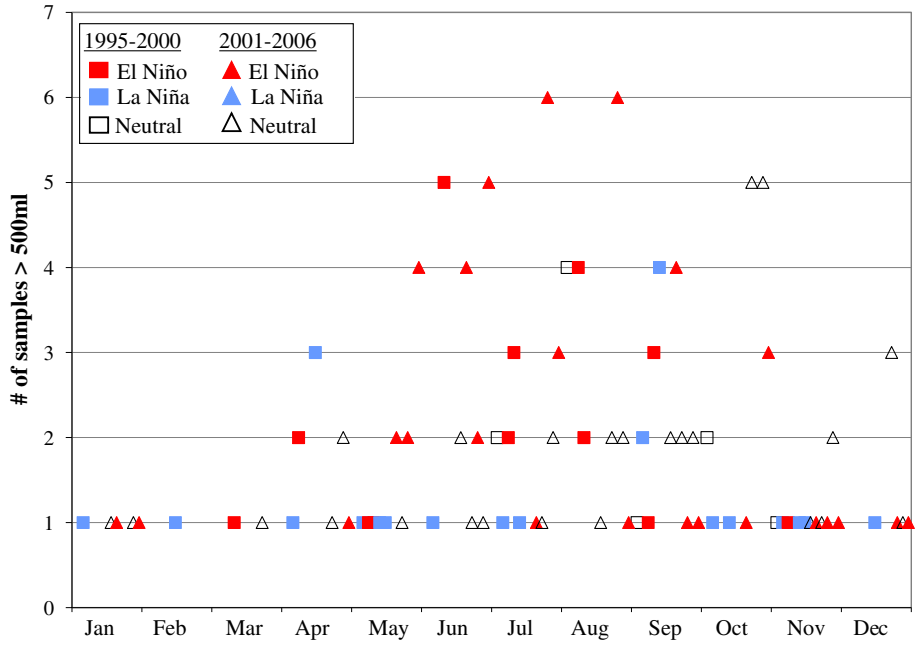

Fig. 11. Frequency of large volume daily-event samples by month for 1995–2006.

and 1995–2000 (squares) distinguished from 2001 to 2006 (triangles). Note that during La Niña and neutral years, Underhill typically experienced 1–2 large volume daily-events. During El Niño years, Underhill often received 2–6 large volume daily-events, especially from 2001 to 2006. These events mostly occurred from May to September. Additionally, *t*-tests showed that significantly more summer rainfall was recorded during El Niño years as compared to La Niña or neutral years ($p = 0.07$). While more extensive analysis is necessary in order to identify a clear linkage between ENSO and the precipitation patterns observed at Underhill, the data does indicate that more extended periods of rain and/or higher rainfall amounts occurred in the summer months of El Niño years, which consequently contributed to the increase in annual precipitation and the decline in VWM concentration.

4. Conclusions

Analysis of 12-years of daily-event precipitation samples shows that although the VWM mercury concentration has declined at Underhill, VT, there has not been a significant change in mercury wet deposition. Meteorological transport analysis suggests that the largest contributors to mercury wet deposition at Underhill are sources in the Midwest and East Coast Regions, and the influence of these source regions has not changed significantly over the years studied. This apparently consistent atmospheric input from the high emission source areas is likely responsible for the observed lack of decline in mercury wet deposition at Underhill. Changes in the type and amount of precipitation at the Underhill site are also playing a critical role in determining mercury concentrations in precipitation.

While the decline in mercury concentration at Underhill could be attributed to a combination of emission reductions and increased precipitation over time, this analysis indicates that changes in the local meteorological factors are a more dominant influence in this decline. Since mercury is a persistent, bioaccumlative toxic pollutant only a decline in the total mercury deposition can demonstrate the efficacy of any reduction in atmospheric mercury emissions. Thus, investigating trends in precipitation concentration data must be performed with great care as to not falsely ascribe variability in concentration to changes in pollutant emissions. Future receptor modeling of daily-event trace element deposition data at Underhill will identify the major source types contributing to mercury measured in precipitation, and elucidate how these source influences have changed over time, the results of which will aid in further explaining the observed patterns in mercury wet deposition.

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