**Atmospheric
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Mercury deposition in southern New Hampshire, 2006–2009

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Abstract

Mercury (Hg) is a global contaminant due to its toxicity and ubiquitous presence in the atmosphere. The primary source of Hg to terrestrial and aquatic ecosystems is atmospheric deposition. In an effort to understand the atmospheric cycling and depositional characteristics of Hg, event-based wet deposition samples were collected from July 2006 to September 2009 at Thompson Farm (TF), a near-coastal rural site in Durham, NH, part of the University of New Hampshire AIRMAP Observing Network. Total aqueous mercury exhibited seasonal trends in Hg wet deposition at TF. The lowest Hg wet deposition occurred in the winter with an average total seasonal deposition of $1.56\,\mu g\,m^{-2}$ compared to the summer average of $4.71\,\mu g\,m^{-2}$. Inter-annual differences are generally linked with precipitation volume, with the greatest deposition occurring in the wettest year. Comparisons of Hg wet deposition trends with meteorological data and ambient gas phase mixing ratios revealed weak correlations. The strongest correlation was observed between maximum hourly precipitation rate and Hg wet deposition, and the relationship was strongly driven by extreme events. Dry deposition of reactive gaseous Hg (RGM) was estimated based on continuous RGM measurements at TF from October 2006 to September 2009 using an order-of-magnitude approach. Comparisons between Hg wet deposition and RGM dry deposition suggest that the seasonal ratios of Hg wet deposition to RGM dry deposition vary by up to a factor of 80. Additional studies of seasonal differences in Hg deposition mechanisms (wet vs. dry) may provide a better understanding of the biogeochemical cycling of Hg.

1 Introduction

Mercury (Hg) is a naturally occurring contaminant of global concern due to its toxicity and ubiquitous presence in the atmosphere. It exists in diverse chemical forms comprised of gaseous elemental mercury (Hg°), reactive gaseous mercury (RGM = $HgCl_2$ + $HgBr_2$ + HgOBr + ...), and particulate mercury (Hg^P). Deposition of atmospheric

Hg, mainly the more soluble forms of RGM and Hg^P, is an important source of Hg to terrestrial (Rea et al., 2002; Bushey et al., 2008; Choi et al., 2008, Selvendiran et al., 2008) and aquatic ecosystems (Landis and Keeler, 2002; Ariya et al., 2004). Trace levels of Hg deposited through wet and dry mechanisms bioaccumulate in fish species, whose consumption is the major exposure route to humans (Downs et al., 2007).

Previous studies suggest that the magnitude of Hg wet deposition varies geographically and seasonally due to climatic conditions, atmospheric chemistry, and human influences (VanArsdale et al., 2005; Selin and Jacob, 2008; Prestbo and Gay, 2009). In North America seasonal trends are observed in both depositional flux and concentration with the highest values in the summer and lowest values in the winter (Sorensen et al., 1994; Mason et al., 2000; Guentzel et al., 2001; Keeler et al., 2005; VanArsdale et al., 2005; Choi et al, 2008; Prestbo and Gay, 2009). Explanations for this observation include more effective Hg scavenging by rain compared to snow (Sorensen et al., 1994; Mason et al., 2000; Keeler et al., 2005; Selin and Jacob, 2008), a greater availability of soluble Hg due to convective transport in summer events (Guentzal et al., 2001; Keeler et al., 2005), and a summer increase in Hg-containing soil derived particles in the atmosphere (Sorensen et al., 1994).

Geographic differences in Hg wet deposition may be explained in part by the proximity to atmospheric sources. Results from the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) sites in the Northeastern United States exhibit a geographic trend with southern and coastal sites receiving higher Hg concentrations and depositional fluxes (Prestbo and Gay, 2009; VanArsdale et al., 2005). The sites with elevated Hg deposition are nearer to the East coast megalopolis and downwind of anthropogenic emission sources such as coal burning power plants and waste incinerators. Contradictory results have been reported in studies comparing Hg deposition fluxes and/or concentrations between rural and urban sites. Some report elevated annual fluxes (Mason et al., 2000) and concentrations (Steding and Flegal, 2002) at urban locations while others report no significant differences in mean concentrations (Sorensen et al., 1994; Guentzel et al., 2001; Hall et al., 2005). Gaseous

evasion of Hg^o from marine waters is a significant global source of atmospheric Hg and may also contribute to elevated depositional fluxes in coastal regions. Elevated levels of Br in the marine boundary layer are suggested as an important contributor to the oxidation of Hg^o (Holmes et al., 2009).

Like many areas in New England, New Hampshire (NH) air quality is adversely affected by large power plants in the Midwest as well as urban areas located to the south along the East coast of the United States (NHDES, 2004). Two coal combustion power plants are also located in the southern portion of NH and are likely contributors to the local atmospheric load of Hg. Within the waterways of the Northeastern United States, including NH, biological species have been identified as containing elevated Hg levels (Chen et al., 2005; Evers, 2007) with atmospheric deposition considered the dominant source in undisturbed watersheds (Chen et al., 2005). Two MDN sites were previously located in NH, but sampling and analyses were terminated in 2002. This lack of Hg wet deposition information was filled using measurements conducted by the AIRMAP program (http://airmap.unh.edu) at the University of New Hampshire (UNH). Event-based wet deposition samples were collected over a 36-month time period from July 2006–August 2009.

Event-based precipitation sampling is necessary to elucidate relationships with meteorological and atmospheric chemical conditions. MDN sites predominantly collect weekly integrated samples and results indicate single weekly samples contribute significantly to the annual Hg load (VanArsdale et al., 2005). The relative Hg wet deposition contribution of single events and potential correlations with other factors can be obscured by integrated sampling methods. An event-based sampling site in Underhill, VT (MDN site VT99) reports discrete precipitation events with Hg deposition greater than 0.4 µg m^{-2} can account for 5–17% of the total annual deposition (Keeler et al., 2005). The event-based sampling at TF provides the opportunity to evaluate correlations between Hg wet deposition, meteorological conditions and gas phase species.

In this study, seasonal and annual variations of Hg wet deposition and concentration from a site in Southern NH are compiled and compared to contemporaneous results

from (MDN) sites in the adjacent state of Maine (ME). Meteorological conditions and gas phase indicators of anthropogenic air mass sources are briefly examined in relation to Hg wet deposition at TF. Long-term Hg wet deposition measurements exist at many locations within the United States and Canada as part of the MDN; however, long-term contemporaneous Hg gas phase and Hg wet deposition measurements are lacking. A recent study (Engle et al., 2010) reports Hg gas phase speciation data, Hg^P, and Hg wet deposition fluxes at nine sites located in the central and eastern United States and Puerto Rico, none of which had data for more than one year. To our knowledge, this is the first multi-year comparison of Hg wet deposition flux with the contribution from RGM dry deposition. These long-term coupled measurements provide insights into seasonal variations in Hg deposition pathways.

2 Sample collection and analysis

Precipitation samples were collected at Thompson Farm (TF) (43.11° N, −70.95° W, 24 m elevation) located in Durham, New Hampshire, USA (Fig. 1). The sample site is situated in a rural setting immediately surrounded by agricultural fields and mixed hardwood and pine forests. It is approximately 25 km from the Gulf of Maine. The UNH AIRMAP program maintains and collects numerous atmospheric chemistry measurements at TF (Chen et al., 2007; Darby et al., 2007; Mao et al., 2008; Sigler et al., 2009a). Meteorological data used in this study (temperature, solar radiation, precipitation amount, and precipitation rate) are from the NOAA Climate Reference Network (CRN) site co-located at TF. Information about CRN data measurement and collection techniques is available at (www.ncdc.noaa.gov/crn/instrdoc.html).

Wet deposition samples were collected using a modified Aerochem automated precipitation sampler, and sample collection bottles were manually changed on a primarily event-based schedule. In the winter months a heater placed in the bottom of the sampler prevented samples from freezing. The sampling train consisted of acid washed

polyethylene funnels placed directly into pre-acidified and acid washed fluorinated ethylene propylene (FEP) bottles.

Due to the ubiquity of Hg and its adhesion to plastic materials, sample bottles and funnels underwent stringent acid-cleaning procedures prior to deployment. Briefly, sampling vessels were first soaked in warm 7.5N trace metal grade nitric acid for a minimum of 12 h and subsequently soaked in warm 4N hydrochloric acid for a minimum of 12 h. Following each acid treatment, vessels were triple rinsed with 18 MΩ nanopure water. Sampling bottles were stored in warm dilute aqueous hydrochloric acid for a minimum of 5 days, then rinsed three times in 18 MΩ nanopure water, and finally stored in double polypropylene bags with dilute hydrochloric acid contained in the bottles. Prior to sample deployment in the field, bottle blanks were collected and sample bottles were treated with 1.25 mL of 6N HCl for sample preservation.

Upon collection, samples were preserved with the addition of trace metal grade hydrochloric acid and bromine monochloride to a final concentration of 0.5%. Prior to analysis hydroxochloroamine hydroxide was added to destroy any free halogens and the samples were reduced with the addition of stannous chloride. All samples were analyzed using a Tekran model 2600, a dual amalgamation cold vapor atomic fluorescence spectrometer. The average system blank value over all sample analyses was $0.45 \, \mathrm{ng \, L^{-1}}$ and the average method detection limit as determined by three times the standard deviation of the system blank was $0.08 \, \mathrm{ng \, L^{-1}}$. The average bottle blank abundance was 0.09 ng. ORMS-3 and ORMS-4 (National Research Council, Canada) were used as external standards. The average standard values of $12.04 \, \mathrm{ng \, L^{-1}}$ and $22.97 \, \mathrm{ng \, L^{-1}}$ for ORMS-3 ($n = 22$) and ORMS-4 ($n = 18$), respectively, are within range of the accepted values. Final concentration values were corrected for system and bottle blanks. Precipitation samples with a collected volume of less than 20 ml are excluded from this data set ($n = 21$). The Hg wet deposition data discussed in this study consist of 162 wet samples collected from 21 July 2006 to 30 August 2009.

RGM has been measured at TF since November 2006 using a KCl-coated denuder module attached to a cold vapor atomic florescence spectrometer (Tekran model

2537A; for details see Sigler et al., 2009a). From November 2006 to February 2009 the RGM sampling interval was 120 min. Due to the addition of in-line Hg[P] measurements in February 2009, the sampling interval increased to 175 min.

Other ambient gas phase measurements at TF include carbon monoxide (CO), total reactive nitrogen ($NO_y = NO + NO_2 + HNO_3 + PAN + RNO_2 + $ aerosol $NO_3^- + \ldots$) and sulfur dioxide (SO_2). These measurements have been collected at TF since 2001. Automated, one-minute time resolution measurements of CO and NO_y are made with modified Thermo Environmental Instruments. Measurements of SO_2 are made with a pulsed florescence analyzer (model 450C, Thermo Scientific Inc.). Mao and Talbot (2004) provide measurement and sampling details for CO and NO_y at TF. In this study, hourly averaged data for these species are used.

3 Seasonal trends and inter-annual variability

Precipitation samples were collected from 21 July 2006 to 30 August 2009 and represent 260 precipitation events. In this study, we define a precipitation event as a period of precipitation bordered by a twelve-hour time interval of no precipitation. Ninety-seven samples (60%) represent single events and 45 samples (28%) represent two precipitation events. Figures 2a–c show the measured concentration, calculated deposition, and total precipitation for each sample in the study period. The maximum Hg concentration was 65.09 ng L^{-1} occurring on 12 July 2007. The maximum single event deposition was 1.74 µg m^{-2} and occurred from 23 July to 24 July 2008. This single precipitation event constituted almost 6% of the total wet deposition at TF during this three-year study and 14% to the annual load for 2008. As shown in Fig. 2b, single precipitation events with elevated Hg deposition levels can account for a substantial portion of the total deposition. Similarly, Keeler et al. (2005) also report a single event contributing approximately 17% to the annual Hg wet deposition load from event-based sampling in Underhill, VT.

During the 37-month sampling period at TF, the cumulative Hg wet deposition was 30.78 µg m^{-2} and the total precipitation depth was 4.28 m. The seasonal and annual

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variations in Hg concentration and wet deposition are summarized in Table 1. In general, the summer and spring exhibited elevated Hg wet deposition with an unusually large value in 2008.

The seasonal volume weighted mean (VWM) concentrations of Hg in precipitation at TF are shown in Fig. 3a and listed in Table 1. The VWM concentrations are elevated during the spring and summer seasons in comparison to the fall and winter seasons. These seasonal variations in VWM Hg concentrations are annually repeatable. The greatest seasonal VWM Hg concentrations at TF occurred in both summer seasons (summer 2008 = 14.85 ng L^{-1}; summer 2007 = 12.48 ng L^{-1}), with the second highest seasonal concentrations occurring in the spring seasons of each year. The summer VWM Hg concentrations are 2.2–3.4 times greater than the fall and winter values. There is little variability in the VWM concentrations at TF for the same season from year-to-year. These seasonal variations are similar to previously reported trends at MDN sites within the northeastern United States (Keeler et al., 2005; VanArsdale et al., 2005; Prestbo and Gay, 2009).

Total seasonal Hg wet deposition at TF is shown in Fig. 3b and listed in Table 1. The Hg wet deposition is calculated as the product of the event concentration and amount of precipitation (Fig. 3c). Patterns in seasonal Hg wet deposition are less consistent than the VWM concentrations and are linked more closely to precipitation totals. In 2007 the highest seasonal deposition, 3.39 µg m^{-2}, occurred in the spring, while in 2008 it was observed in the summer with a value of 6.39 µg m^{-2}. The large deposition in summer 2008 reflects the combination of typically greater summer Hg concentrations and the above normal precipitation for that season (Fig. 3c). The total amount of precipitation received in summer 2008 was 180% above the 30 yr summer average in New Hampshire (http://www.nrcc.cornell.edu). Similarly, the elevated deposition at TF during the 2007–2008 winter, compared to other winters, is most likely due to the elevated amount of precipitation, which was 154% above the 30 yr winter average (http://www.nrcc.cornell.edu).

Non-parametric Wilcoxon rank sum tests were employed to determine statistically

significant differences between seasonal Hg wet deposition and concentration values at TF. When the data are grouped by season and not separated by year (e.g. fall 2006 + fall 2007 + fall 2008 = fall data), the summer and spring Hg concentration values are significantly different ($p <0.05$) than all other seasons, and the fall and winter concentrations are not significantly different from each other.

Statistically significant differences ($p <0.05$) were found for the Hg wet deposition fluxes between the summer and fall, and between the summer and winter. While the season with the greatest Hg wet deposition varies annually at TF, statistically significant differences between the same season for varying years only exist for the fall values. Based on the Wilcoxon rank sum test, both the Hg concentration and wet deposition values for fall 2007 are significantly different ($p <0.05$) than fall 2006 and fall 2008.

Annual Hg wet deposition fluxes varied over the duration of this study and were strongly linked to annual precipitation totals. During the calendar years 2007 and 2008 the Hg wet deposition fluxes at TF were $8.41\,\mu g\,m^{-2}\,yr^{-1}$ and $12.33\,\mu g\,m^{-2}\,yr^{-1}$, respectively with corresponding precipitation totals of 114.1 cm and 160.3 cm. Between these two years the amount of precipitation increased by 40% and the annual Hg wet deposition flux increased by 47%. These increases are similar in magnitude, indicating that the large annual Hg wet deposition flux for 2008 is primarily a consequence of enhanced precipitation. The amount of precipitation in New Hampshire during 2008 was 43% above the 30 yr normal and the highest annual amount of precipitation based on a 114 yr record (http://www.nrcc.cornell.edu). In contrast, the amount of precipitation at TF during 2007 was only 11% above the normal. To put the annual Hg wet deposition fluxes in context, the typical annual fluxes reported for MDN sites in the northeastern United States from 1996–2005 were $4–8\,\mu g\,m^{-2}\,yr^{-1}$ (Prestbo and Gay, 2009). The Hg annual wet deposition flux at TF for 2007 is slightly above this range, whereas the annual flux for 2008 is >50% higher. This comparison in annual Hg wet deposition fluxes is made to emphasize the elevated flux measured at TF during 2008. Comparisons between different time periods and locations should be made with caution due to the numerous conditions affecting deposition that may also change with time and location.

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4 Comparison with Maine MDN sites

Patterns in seasonal VWM concentrations and Hg wet deposition are generally consistent between TF and the MDN sites (Fig. 3a and b) with elevated levels during spring and summer seasons. The greatest seasonal VWM concentration during this sampling period occurred at all locations for summer 2007. The 2006–2007 winter had the lowest seasonal VWM Hg concentration at TF and all Maine MDN sites with the exception of ME02. Similarly, all sites had the highest total seasonal Hg wet deposition in summer 2008 and low wet deposition totals during the winter seasons.

The seasonal VWM Hg concentrations and seasonal deposition at TF are typically greater than the Maine MDN sites (Fig. 3a and b), possibly due to a combination of elevated Hg concentrations and precipitation. First, the elevated VWM concentrations at TF indicate that more Hg is available in the atmosphere to be deposited than at the Maine MDN sites. TF is the most southerly of the sites resulting in slightly warmer temperatures compared to the MDN sites and is also located nearer large urban pollution sources such as Boston and New York. Thus it is reasonable to hypothesize that TF receives more Hg due to anthropogenic emissions. Second, the amount of precipitation recorded at TF is consistently second highest amongst these sites with MDN site ME98 regularly receiving the most precipitation.

5 Influence of meteorological conditions

Relationships were examined between Hg wet deposition, Hg concentration, and meteorological parameters including temperature, solar radiation, and precipitation intensity at the TF site. Previous studies attribute regional and seasonal differences in Hg wet deposition to temperature differences (Keeler et al., 2005). On an event basis there is weak correlation between the average daily temperature and Hg wet deposition and Hg concentration ($r = 0.23$ and 0.28, respectively, $p < 0.05$). On a monthly timescale the correlation increases between total Hg wet deposition and av-

erage monthly temperature ($r = 0.48$). Keeler et al. (2005) reported similar results for event based sampling and a more direct relationship between monthly averaged temperature and Hg deposition.

Additionally, studies suggest photochemistry is important in the production of RGM (Lin and Pehkonen, 1999; Sigler et al., 2009a) implying a relationship with Hg wet deposition (Selin and Jacob, 2008). In this study we looked into relationships between solar radiation and Hg wet deposition. At TF, Hg concentration and Hg wet deposition were correlated with total daily solar radiation ($r = 0.23$ and $r = 0.25$, respectively, $p < 0.05$). As with the temperature data, the correlation between Hg wet deposition and total solar radiation increases on a monthly timescale ($r = 0.41$). The lack of strong correlations on an event basis between temperature, solar radiation and Hg wet deposition indicates that effects from these parameters are not directly related to Hg wet deposition.

Wet deposition can be greatly affected by precipitation intensity and scavenging (Seinfeld and Pandis, 1998), therefore relationships between precipitation intensity and Hg concentration and wet deposition were investigated. The NOAA CRN at TF records the average hourly and maximum hourly precipitation rate. Correlations between the Hg concentration, maximum hourly and average hourly rainfall rates were not statistically significant. However, there is a strong correlation between the maximum hourly precipitation rate and Hg deposition ($r = 0.62$, $p < 0.05$) (Fig. 4). This observed correlation is driven primarily by four extreme events with Hg deposition greater than $0.6\,\mu g\,m^{-2}$ and maximum precipitation rates greater than $23\,mm\,hr^{-1}$. Omitting these four events reduces the correlation coefficient ($r = 0.37$, $p < 0.0001$). Three of these four extreme precipitation events occur in the summer when precipitation events typically have the greatest maximum hourly precipitation rates and the greatest Hg wet deposition (Fig. 4).

6   Anthropogenic influence

To investigate anthropogenic contributions to Hg wet deposition, we examined links with Hg wet deposition and gas phase concentrations of carbon monoxide (CO), total reactive nitrogen (NO_y), and sulfur dioxide (SO_2), all commonly used indicators for an-
5 thropogenic influence (Mao et al., 2008). CO is emitted mainly from mobile combustion sources while NO_y includes compounds emitted directly from fossil-fuel combustion and oxidation products of such compounds. SO_2 is emitted primarily from coal-fired power plants, a significant anthropogenic source of gas phase Hg (Pacyna and Pacyna, 2002). This initial investigation of relationships between CO, NO_y, SO_2 and Hg con-
10 centration in precipitation did not suggest statistically significant correlations ($p < 0.05$). However, weak negative correlations ($|r| \sim 0.2$) exist between CO, NO_y, SO_2 and Hg wet deposition (Table 2).

7   Linkage between RGM and Hg wet deposition

RGM is more soluble than Hg^o and therefore important in contributing to both the wet
15 and dry deposition of Hg (Schroeder and Munthe, 1998; Selin, 2009). However, few studies report long-term concurrent measurements of RGM and Hg wet deposition (Engle et al., 2010). RGM has been measured at TF since October 2006 (Sigler et al., 2009a; Mao et al., 2011) and we compare these measurements with Hg wet deposition measurements during the nearly three-year period from October 2006 through
20 August 2009. Elevated RGM mixing ratios typically occur in winter and spring seasons at TF (Fig. 5), and the typical diurnal cycle for RGM is a minimum at night with a rapid increase during the morning to peak levels at midday (Sigler et al., 2009a; Mao et al., 2011).
   Relationships of Hg wet deposition and Hg concentration in precipitation versus daily
25 maximum RGM and RGM depletion during precipitation events were not statistically significant ($p < 0.05$). RGM mixing ratios typically decline during precipitation events

at TF. Sigler et al. (2009a, b) and Mao et al. (2011) observed RGM depletion during precipitation events at this site and others have made similar observations at diverse locations (Lindberg and Stratton, 1998; Laurier and Mason, 2007; Yatavelli et al., 2006).

In this study, ineffective scavenging of RGM by snow is evidenced by the less frequent depletion of RGM below the limit of detection (LOD, 0.1 ppqv) during winter precipitation events at TF. Seven of 19 winter precipitation events (37%) result in RGM mixing ratios below the LOD. RGM mixing ratios during summer precipitation events dip below the LOD at a much higher frequency; 17 of 20 events (85%). These seasonal variations in RGM removal efficiencies substantiate the hypothesis that seasonal variations in Hg wet deposition are due in part to less effective scavenging of gas phase Hg by snow (Keeler et al., 2005; Selin and Jacob, 2008).

It is important to gauge the relative contribution of Hg wet deposition in comparison with other atmospheric Hg sinks such as RGM dry deposition. To accomplish this we performed an order-of-magnitude estimate for RGM dry deposition flux using long-term continuous measurements of RGM mixing ratios. Estimates of RGM dry deposition velocity and deposition fluxes at TF were calculated based on nighttime depletion events, which are most common during warm season (May to September) nocturnal inversions in the planetary boundary layer. The method has been employed in Talbot et al. (2005), Mao et al. (2008), and Sigler et al. (2009a), and the step-by-step estimate is elucidated in Russo et al. (2010). A brief explanation of this method is given here. Nocturnal inversions at TF are evidenced by the depletion (<5 ppbv) of atmospheric ozone and Hg$^{\text{o}}$ (Mao et al., 2008). Concurrent depletions were also observed in RGM. To obtain a robust estimate we used the diurnal cycle average over all days from the warm season with the occurrence of nocturnal inversions. The average rates of RGM depletion and RGM concentration during these inversions were calculated to solve for the deposition velocity in the following equation:

$$V_{\text{d}} = \frac{dC}{dt} \cdot \frac{H}{C} \tag{1}$$

where V_{d} is the deposition velocity, dC/dt is the rate of change in RGM concentration

from the average diurnal cycle in RGM over all inversion events, $\overline{C}$ is the average RGM concentration over the depletion period, and H is the boundary layer height. In these calculations a constant boundary layer height of 125 m is applied (Talbot et al., 2005; Mao et al., 2008; Russo et al., 2010). This calculation also assumes that during the nocturnal inversions dry deposition is the only loss mechanism of RGM and there is no RGM production, therefore the calculated V_d should be considered a maximum due to the potential for RGM loss due to aerosol uptake.

Nocturnal inversion events were identified by the nighttime depletion of ozone to less than 5 ppbv with a corresponding decrease in RGM to less than 0.1 ppqv. The number of inversion events per warm season varied from 17 to 21 during 2007 to 2009. The average RGM concentration over the depletion period varied annually from 0.13 to 0.20 ppqv however, the RGM depletion based on the average diurnal cycle was always complete in the time window of 00:00 to 03:00 UTC. Using Eq. (1) the average RGM dry deposition velocity at TF is estimated to be 2.31 cm s^{-1}. This estimate is within the range of RGM dry deposition velocities reported in the literature (0.5 to 7.6 cm s^{-1}) from a variety of measurement methods, surface compositions, locations, and seasons (Zhang et al., 2009 and references therein).

RGM dry deposition fluxes at TF were further estimated using RGM mixing ratios and a dry deposition velocity of 2.31 cm s^{-1}. The seasonal and annual estimated RGM dry deposition fluxes and ratios to wet deposition fluxes are listed in Table 3. There was distinct variation in seasonal dry deposition loss of RGM. The greatest seasonal RGM dry deposition fluxes, which were greater than 0.6 µg m^{-2} occur in the winter and spring (excluding winter 2007), following the seasonal pattern in RGM mixing ratios. Summer and fall exhibit low RGM dry deposition values, all below 0.4 µg m^{-2} (Fig. 5).

The estimated RGM dry deposition fluxes are less than the measured Hg wet deposition fluxes for all seasons and on an annual basis. Our results suggest that the relative contribution of Hg wet deposition and RGM dry deposition to the total Hg deposition flux at TF varies greatly by season and is opposite in phase with ratios of Hg wet deposition to RGM dry deposition ranging from 1.6 in the winter to 80 during sum-

mer 2008. Large Hg wet deposition and low RGM dry deposition typically occurs in summer. The greatest ratio occurred in summer 2008 reflecting the exceptionally large amount of precipitation and Hg wet deposition and the lowest RGM dry deposition estimate of all summers. On an annual basis the ratios of Hg wet deposition to RGM dry

5 deposition are moderate in comparison to the large seasonal variations at TF. The ratio for annual year 2008 is more than double the ratio for 2007 (8.5 and 3.5, respectively) and the large ratio likely reflects the record amount of precipitation in 2008.

We can compare our calculations to only a few studies from the literature reporting both Hg wet deposition and RGM dry deposition. Annual ratios of Hg wet deposition

10 to RGM dry deposition for eight sites located in the eastern United States and Puerto Rico were calculated from measurement data in Engle et al. (2010) (Table 4). Miller et al. (2005) estimate higher annual fluxes of RGM dry deposition than Hg wet deposition for New Hampshire. In comparison the TF ratio for 2007 is within the range of values from Engle et al. (2010) for rural and coastal sites and the TF ratio for 2008 is slightly

15 greater (excluding Puerto Rico). In contrast to the findings of Miller et al. (2005), results from our study, as well as those of Engle et al. (2010), demonstrate that annual Hg wet deposition fluxes are typically greater than RGM dry deposition fluxes. The observations hold across many different sites, with the exception of one urban site of Engle et al. (2010), in spite of differences in geographic location and sampling years.

20 **8 Summary and conclusions**

Total aqueous Hg in precipitation samples collected at TF in Durham, NH from July 2006 to September 2009 demonstrate seasonal Hg wet deposition and VWM concentration patterns consistent with previous observations for the northeastern United States with elevated values during the summer and spring seasons. Wet deposition

25 samples from regional MDN sites collected during the same sampling interval exhibit similar seasonal patterns. Comparisons of the relative Hg precipitation concentrations

and wet deposition fluxes between the TF and MDN sites suggest that the proximity to anthropogenic Hg sources may partially explain observed differences.

The quantity of precipitation also contributes to the seasonal and annual variations in Hg wet deposition. As observed at TF, the winter 2007–2008 and summer 2008 had above normal precipitation amounts and high Hg wet deposition fluxes. This relationship is also exhibited on an annual basis with the anomalously high amount of precipitation that fell during 2008 contributing to the very high annual Hg wet deposition flux for the year. While this observation may seem rudimentary (i.e. more precipitation equates to more wet deposition), it warrants noting as observed and predicted increases in precipitation amount and intensity in the mid-latitudes due to climate change (Easterling et al., 2000) imply Hg wet deposition fluxes will also increase.

The elevated amounts of precipitation during 2008 likely influence our ratios of Hg wet to dry deposition. However, our results show these ratios differ greatly by season with Hg wet deposition exceeding the RGM dry deposition by up to a factor of 80. The seasonality in the atmospheric Hg depositional mechanisms (wet vs. dry) may subsequently affect the fate and transport of Hg in aquatic and terrestrial ecosystems. Improved quantification of Hg wet and dry deposition, via long term simultaneous measurements and advances in measurement technology, will lead to a better understanding of the biogeochemical cycle of Hg.

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Table 1. Seasonal and annual total precipitation, Hg wet deposition, and concentration summary statistics for Thompson Farm.

Season	Precipitation	Deposition ($\mu g\,m^{-2}$)				Concentration ($ng\,L^{-1}$)			VWM concentration
	Total (cm)	Total	Mean	Median	Range	Mean	Median	Range	$ng\,L^{-1}$
7/21/06 to 9/20/06	22.46	1.16	0.116	0.089	0.027–0.263	6.16	5.05	1.39–12.51	5.23
Fall 2006	42.02	2.85	0.190	0.139	0.058–0.600	9.63	8.10	2.28–23.06	6.71
Winter 2006–2007	24.58	1.12	0.125	0.121	0.016–0.274	10.50	5.90	0.96–47.50	4.76
Spring 2007	40.13	3.39	0.339	0.379	0.030–0.561	18.14	10.57	0.99–47.89	8.69
Summer 2007	20.59	3.02	0.275	0.234	0.090–0.548	22.84	14.24	4.24–65.09	14.85
Fall 2007	30.26	0.99	0.083	0.061	0.023–0.231	3.39	2.71	0.75–8.94	3.67
Winter 2007–2008	47.53	2.17	0.135	0.117	0.055–0.399	5.79	5.36	1.41–10.88	4.33
Spring 2008	19.97	1.79	0.162	0.107	0.066–0.553	12.49	8.64	3.48–25.81	8.84
Summer 2008	52.52	6.37	0.354	0.112	0.015–1.737	15.29	14.74	4.21–37.72	12.48
Fall 2008	37.00	1.76	0.125	0.114	0.039–0.256	7.55	6.77	2.24–19.21	4.60
Winter 2008-2009	29.86	1.49	0.149	0.133	0.050–0.339	9.04	4.50	2.72–34.83	5.67
Spring 2009	27.37	2.23	0.172	0.137	0.020–0.452	9.52	7.86	3.57–17.76	8.18
6/21/09 to 8/30/09	37.36	2.62	0.202	0.168	0.042–0.565	9.94	9.70	3.34–20.62	7.02
Year 2007	114.1	8.41	0.205	0.155	0.016–0.561	13.68	6.88	0.75–65.09	7.97
Year 2008	160.3	12.33	0.209	0.115	0.015–1.74	10.41	8.41	1.66–37.72	8.09

Table 2. Pearson's r correlation co-efficients and significance levels for Hg wet deposition and Hg concentration with meteorological conditions and gas phase measurements at Thompson Farm.

	Hg wet deposition		Hg concentration	
	r	p	r	p
Daily average temperature	0.23	0.0033	0.28	0.0003
Daily total solar radiation	0.25	0.0014	0.23	0.0030
Hourly maximum precipitation rate	0.62	< 0.0001	−0.31	0.0372
Daily average CO	−0.19	0.0154	−0.02	0.8459
Daily average NO_y	−0.20	0.0229	−0.10	0.2592
Daily maximum SO_2	−0.05	0.6510	0.04	0.7263
Daily maximum RGM	0.01	0.9050	0.07	0.5461
RGM depletion during precipitation event	0.18	0.1352	−0.01	0.9543

Table 3. Seasonal and annual Hg wet deposition and RGM dry deposition fluxes, ratios of Hg wet deposition to RGM dry deposition, and the sum of Hg wet deposition and RGM dry deposition at TF. The asterisks indicate seasons missing more than 3 days of RGM measurements. The seasonal daily average RGM was used to fill gaps in the data and calculate a total RGM flux.

Season	Hg wet deposition ($\mu g\,m^{-2}$)	RGM dry deposition ($\mu g\,m^{-2}$)	Hg wet deposition/ RGM dry deposition	Wet plus RGM dry deposition ($\mu g\,m^{-2}$)
Winter 2006–2007	1.12	0.68	1.65	1.80
Spring 2007	3.39	1.23	2.76	4.62
Summer 2007	3.02	0.26	11.6	3.28
Fall 2007	0.99	0.30	3.3	1.29
Winter 2007-2008	2.17	0.36	6.03	2.53
Spring 2008	1.79	0.75	2.39	2.54
Summer 2008	6.37	0.08*	79.6	6.45
Fall 2008	1.76	0.16*	11.0	1.92
Winter 2008-2009	1.49	0.93*	1.60	2.42
Spring 2009	2.23	0.78	2.86	3.01
6/21/09 to 8/30/09	2.44	0.17	13.2	2.61
Year 2007	8.41	2.43	3.46	10.84
Year 2008	12.33	1.45	8.50	13.78

Table 4. A comparison between annual Hg wet deposition and RGM dry deposition values reported in the literature and calculated in this study.

Location	Dates	Hg wet deposition ($\mu g\, m^{-2}\, yr^{-1}$)	RGM dry deposition ($\mu g\, m^{-2}\, yr^{-1}$)	Hg wet dep./ RGM dry dep.	Reference
Alabama	12 Apr 2005–11 Apr 2006	10.9	2.2	4.95	Engle et al. (2010)
Illinois	1 Jan 2004–31 Dec 2004	11.0	51.8	0.21	Engle et al. (2010)
Massachusetts	5 Feb 2008–3 Feb 2009	2.9	1.0	2.9	Engle et al. (2010)
New Hampshire	None given	5.8	7.5	0.77	Miller et al. (2005)
New Hampshire	1 Jan 2007–31 Dec 2007	8.41	2.43	3.46	This study
New Hampshire	1 Jan 2008–31 Dec 2008	12.33	1.45	8.50	This study
North Dakota	1 Jan 2004–12 Dec 2004	3.3	1.7	1.94	Engle et al. (2010)
Puerto Rico	1 Jan 2006–31 Dec 2006	29.5	0.5	59	Engle et al. (2010)
South Carolina	23 May 2006–22 May 2007	6.5	1.8	3.61	Engle et al. (2010)
Virginia	1 Jan 2006–12 Dec 2006	9.0	1.4	6.43	Engle et al. (2010)
Wisconsin	28 Jun 2004–6 Jun 2005	6.7	5.3	1.26	Engle et al. (2010)
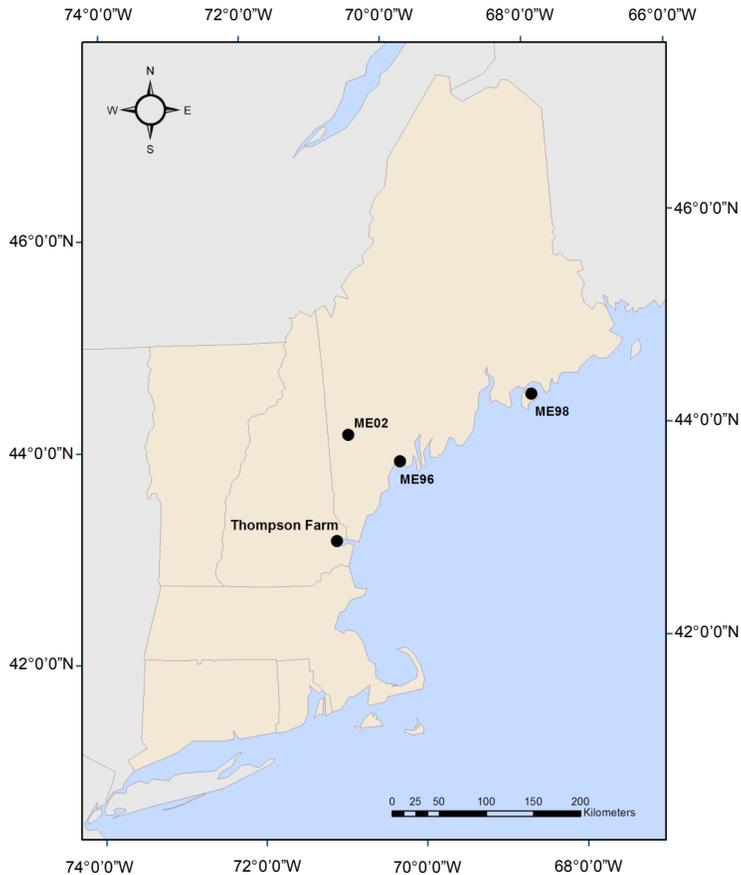
Fig. 1. Thompson Farm location and Mercury Deposition Network locations in Maine.
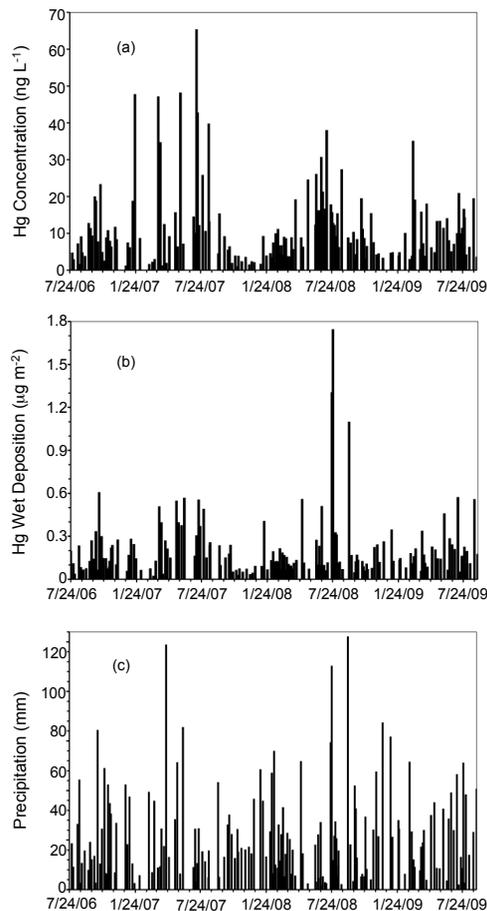
Fig. 2. Time series of wet deposition samples from Thompson Farm; **(a)** Hg concentration, **(b)** Hg wet deposition, **(c)** Precipitation amount.

Fig. 3. Seasonal Hg volume weighted mean concentrations **(a)**, Hg wet deposition **(b)**, and precipitation amount **(c)**, at Thompson Farm and Mercury Deposition Network sites located in Maine.

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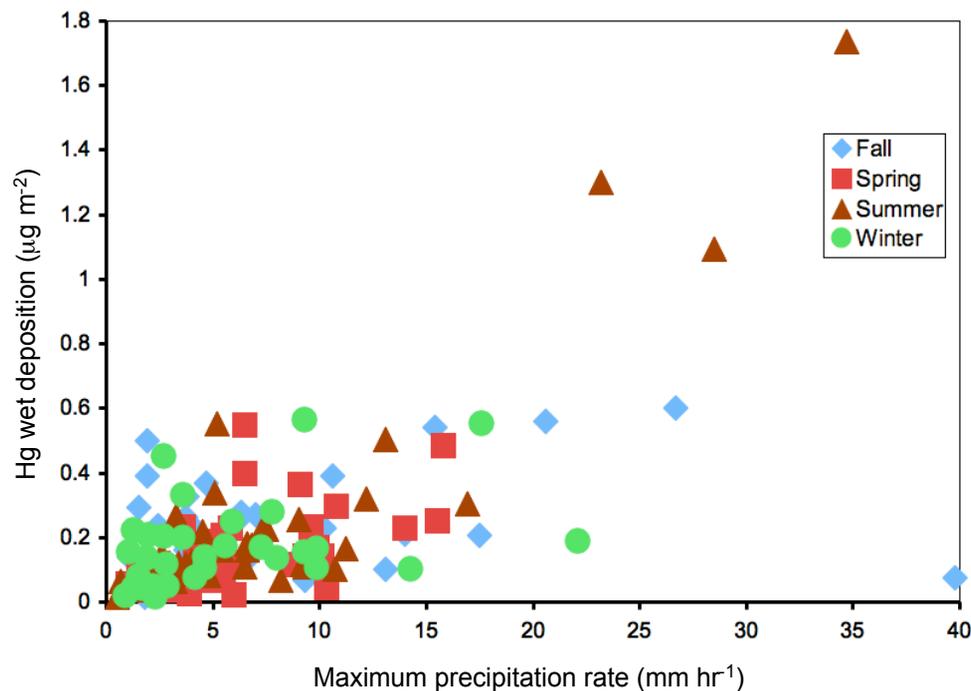
Fig. 4. Hg wet deposition as a function of maximum hourly precipitation rate per sample identified by season. The correlation between these variables is largely driven by the four samples with Hg wet deposition greater than $0.6\,\mu g\,m^{-2}$.
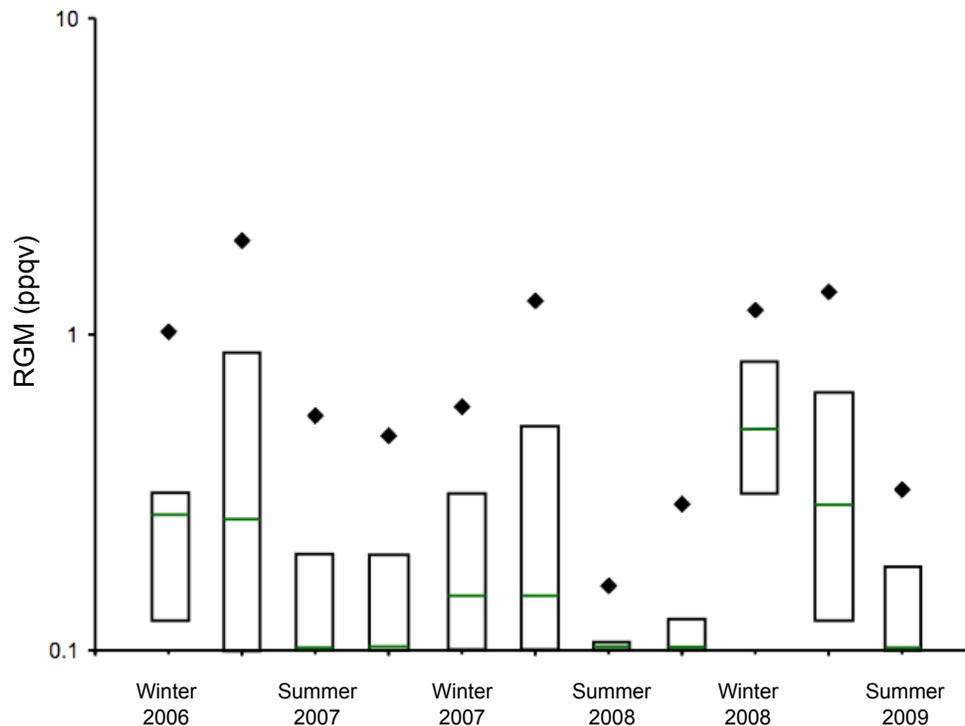
Fig. 5. Seasonal variations in RGM at TF. Each box encompasses the 25th to 75th percentiles and the solid horizontal line within each box represents the median value. The black diamonds indicate the 90th percentile.

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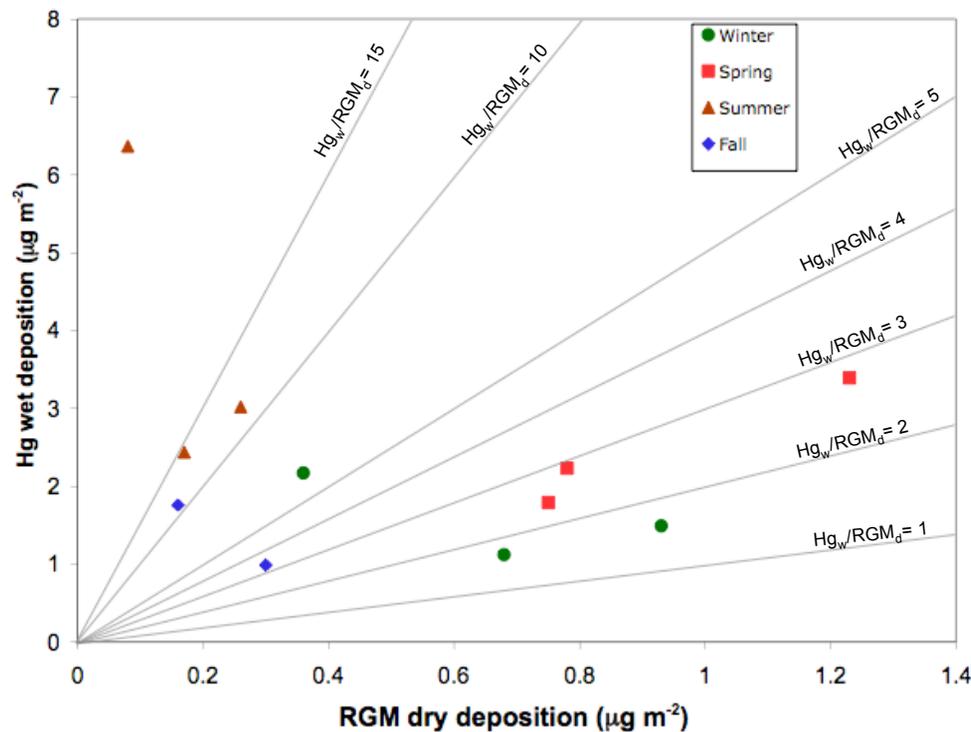
Fig. 6. Seasonal Hg wet deposition fluxes and estimated RGM dry deposition fluxes at TF. Contour lines represent wet to dry deposition (Hg_w/RGM_d) ratios.