Mercury Wet Deposition and Speciated Air Concentrations from Two Urban Sites in New York State: Temporal Patterns and Regional Context

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ABSTRACT

Since 2008, ambient speciated mercury (Hg) concentrations and weekly Hg wet deposition have been measured at two urban locations in New York – Rochester and New York City (borough of Bronx). These measurements were initiated to establish ambient Hg baselines ahead of anticipated emissions reductions, as well as characterize air concentrations and deposition at two different urban settings. In this paper seasonal and regional patterns in Hg wet deposition are presented, as well as seasonal, day of week and diurnal patterns in ambient Hg species at these two sites. The mean (and median) Hg concentration in precipitation was 9.56 ng/L (8.37 ng/L) at the Bronx site, and 9.95 ng/L (8.30 ng/L) at Rochester. Mean ambient air concentrations of gaseous elemental Hg (GEM), reactive gaseous Hg (RGM), and particle-bound Hg (PBM) at the Bronx and Rochester sites were 1.52 and 1.40 ng/m^3, 6.26 and 8.24 pg/m^3, and 7.96 and 13.48 pg/m^3, respectively. Conditional probability function analysis was used to examine potential source regions impacting these two sites. Using these data we were able to examine monthly and diurnal patterns in speciated ambient Hg; however, more research is needed to more fully characterize potential emission sources that impact these sites.

Keywords: Gaseous elemental mercury; Reactive gaseous mercury; Particle-bound mercury; Urban air monitoring; Precipitation.

INTRODUCTION

Mercury (Hg) is a highly toxic compound present in many consumer products (e.g., fluorescent lighting) and is predominantly released into the atmosphere through combustion of coal, cement production, metal smelting and medical and municipal incineration processes (e.g., Pirrone *et al.*, 2010). Other sources may include mining, gold production, crematoria, wood combustion, oil refineries and paper manufacturing (e.g., Pacyna *et al.*, 2006). Mercury can also be reemitted from soils and aquatic environments (e.g., Pirrone *et al.* 2010 and references within). Consumption of fish and seafood containing methylmercury continues to be a major public health issue in many regions. In New York more than 130 water bodies, many of which have no known direct inputs of Hg other than atmospheric deposition, have specific sport fish consumption advisories (NYSDOH, 2013). To address this problem, several states – including New York – have implemented rules for reducing Hg emissions from coal-fired electric generating units (EGUs). By 2015, emissions from this sector in New York are expected to be 90% lower than 1999 levels (see http://www.dec.state.ny.gov/chemical/8519.html). At the federal level, the United States Environmental Protection Agency (USEPA) recently finalized the first-ever rules for Hg and other hazardous air pollutants from EGUs (Mercury and Air Toxics Standards (MATS); see http://www.epa.gov/mats). To characterize baseline levels and eventually track the effectiveness of such emission reduction programs of this toxic pollutant, in 2008 New York began monitoring Hg in ambient air and wet deposition at two urban locations in New York State – Rochester and New York City.

In ambient air, Hg exists in three forms: gaseous elemental mercury (GEM), divalent or reactive gaseous mercury (RGM), and particle-bound mercury (PBM) (e.g., Schroeder and Munthe, 1998). Since the precise chemical forms of RGM (also referred to as gaseous oxidized mercury, GOM) and PBM are not known (e.g., Lindberg *et al.*, 2007), they are considered method-dependent definitions. The predominant form of ambient Hg is GEM (usually accounts for > 90% of the total atmospheric Hg), which is relatively insoluble and has a lifetime on the order of months (e.g., Holmes *et al.*, 2010). Because of its relatively long atmospheric lifetime, GEM is considered a global pollutant, with average concentrations of ~1–2 ng/m^3 even in remote Arctic regions (e.g., Berg *et al.*, 2013). Except near emission sources, RGM and PBM account for a much smaller percentage of ambient Hg in the eastern US; however, these more reactive forms

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of Hg are more water soluble and readily removed from the atmosphere through wet or dry deposition. Thus the majority of Hg in wet deposition is believed to arise from the scavenging of ambient RGM and PBM.

There have been numerous short-term ambient Hg monitoring efforts in New York and the surrounding region, focused on urban areas, and only a few studies are mentioned here. Cheng *et al.* (2009) used multiple source apportionment techniques to analyze ambient Hg data from Toronto, Ontario, finding that industrial and chemical processes were more important than coal combustion in contributing to ambient Hg. Huang *et al.* (2010) characterized seasonal variations and used principle components analysis (PCA) to investigate sources affecting Hg levels at Rochester over the 2007–2009 period. They found that, among other things, melting snow was a potential source of GEM in winter, whereas GEM oxidation and coal-fired facilities were potential sources of RGM at this site. Wang *et al.* (2013) attributed a 25% decrease in GEM and approximately 70% decrease in RGM and PBM at Rochester to the closure of a nearby coal-fired EGU. Closer to New York City, Aucott *et al.* (2009) compared speciated Hg data from two sites in New Jersey – New Brunswick and Elizabeth. Levels of GEM were dependent on surface wind direction at both sites, but the authors were unable to reconcile all of their findings using known Hg sources in the region.

The studies summarized above represent a small sample of urban Hg measurements in the region, and this area of study is still evolving. In an effort to understand ambient and wet deposited Hg levels across New York State, measurements were performed at two different sites; one in the western region and the other in the southeastern end of the state. This paper describes the ambient speciated Hg and wet deposition Hg measurements for more than five years. We show temporal patterns in the Hg data from these two urban sites, present exploratory co-pollutant analysis to investigate potential sources and fates of ambient Hg at these sites, and compare our data with observations of ambient and wet deposition data from urban and rural sites across the region.

SITE DESCRIPTIONS

The Rochester site (43°08′36″N, 77°32′52″W; USEPA site ID 36-055-1007) is located in a metropolitan area of about 1 million people, along the southern shore of Lake Ontario. The site is on the eastern edge of the city within ~1 km of two state highways (Routes 590 and 490), downwind of numerous coal-fired facilities in western New York and the Midwestern US. The equipment is mounted atop or housed within an air conditioned shelter in a clearing bounded by trees, train tracks, a Rochester Gas & Electric electrical substation, and residential areas within ~100–200 m. A suite of other pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), ozone (O_3), fine particulate ($PM_{2.5}$) mass and species, black carbon (BC) and meteorological parameters are also measured. The site is a USEPA Chemical Speciation Network (CSN) site for fine particulate speciation, a National Air Toxics

Trends Station (NATTS), and a National Atmospheric Deposition Program/National Trends Network (NADP/NTN) acid deposition site. Prior to joining the NADP/NTN in 2013, the NYSDEC operated an independent wet deposition network of 20 sites, including Rochester, that collected similar anions and cations, nominally on the same weekly schedule as the NADP.

The New York City site (40°52′05″N, 73°52′42″W; USEPA site ID 36-005-0133) is located on the roof of the Pfizer Plant Resource Laboratory at the New York Botanical Garden in the north Bronx (hereafter "Bronx"). The 100 ha New York Botanical Garden is surrounded by highways and mixed residential and commercial areas. New York City is a metropolitan area with > 19 million people and the region has a long manufacturing, petrochemical, and industrial legacy that includes contamination from Hg and other toxic compounds. Similar to the Rochester site, continuous meteorological parameters and various trace gas and toxic air pollutants are collected at this site. The Bronx site is also an NADP/NTN site (and was part of the NYSDEC wet deposition network no longer in operation), as well as a Photochemical Assessment Monitoring Station (PAMS) site for various hydrocarbons. The reader is referred to the NYSDEC ambient air monitoring plan (NYSDEC, 2013) for additional details on these two sites.

MEASUREMENT METHODS

In addition to being NADP/NTN acid deposition sites, both locations have participated in the NADP's Mercury Deposition Network (MDN) since January 2008. Weekly Hg wet deposition samples are collected in an N-CON 00-125-2 automatic precipitation sampler (N-CON Systems Co., Inc., Crawford GA), and precipitation is monitored with an ETI NOAH IV total precipitation gauge (ETI Instrument Systems, Inc., Fort Collins CO), as per MDN protocols. Each Tuesday the wet deposition samples are collected and shipped to the MDN analytical laboratory (Frontier Global Sciences, Seattle WA) for total Hg analysis. Additional details on the MDN sampling may be found in Prestbo and Gay (2009) and references within. The NADP quality assures and makes publicly available the data within approximately 6–9 months (http://nadp.sws.uiuc.edu/mdn). For comparison with these two urban sites, we also examined the MDN data from two rural sites – Huntington Wildlife in the Adirondack Mountains of northern New York, and Biscuit Brook in the Catskill Mountains of southeastern New York – over the entire data record. To provide additional regional context, we also examined the 2012 MDN data from 42 additional sites across the northeastern US and eastern Canada.

An identical set of continuous ambient Hg speciation instruments was operated at both sites since the summer of 2008. The reader is referred to earlier papers by Landis *et al.* (2002) and Gay *et al.* (2013) for additional details. The measurement system consists of a Tekran (Toronto, ON) model 2537B cold vapor atomic fluorescence (CVAF) analyzer for GEM; model 1130 unit with a KCl-coated glass annular denuder for RGM; and model 1135 unit with a regenerable quartz filter to collect PBM with an

aerodynamic cutoff of 2.5 µm. GEM is measured every 5 minutes, while RGM and PBM are collected every 2 hours, heated and vaporized, and detected by CVAF in the 2537B analyzer. Sample inlets and the 1130/1135 units were positioned about 2 m above the rooftop at the Bronx site and about 2 m above the shelter roof at Rochester, with sample air brought to the analyzers through a heated 50°C line. For most of the study period, the instrument at the Bronx site was calibrated daily with an internal permeation source, while the Rochester analyzer was calibrated every three days. The analyzer has a nominal detection limit of < 0.1 ng/m^3. Both Tekran systems are operated according to standard operating procedures outlined by the NADP's Atmospheric Mercury Network (AMNet). The AMNet site liaison performs annual site visits, which include manual injections to verify the internal permeation source, and is responsible for quality assurance of the data. In this paper we used the 2-hour average data reported on the AMNet website (http://nadp.sws.uiuc.edu.amn). The minimum detection limits for RGM and PBM of 0.46 pg/m^3 and 1.1 pg/m^3, respectively, reported by Huang *et al.* (2010) as three times the standard deviation of the system blanks, were used. Data from these two sites have been used in recent studies to estimate dry and total depositional Hg loadings (Zhang *et al.*, 2012a) and evaluate predictions of speciated air concentrations from photochemical models (Baker and Bash, 2012; Zhang *et al.*, 2012b). Although there is evidence that the Tekran instruments may underestimate ambient RGM and PBM by as much as a factor of 2–3 (e.g., Gustin *et al.*, 2013), no attempt was made to adjust the data in any way, but we acknowledge this may be an important source of uncertainty.

RESULTS AND DISCUSSION

Wet Deposition
Statistical Summary and Seasonal Variations

Table 1 presents a statistical summary of the weekly precipitation, Hg concentration, and Hg wet deposition data from the two urban sites in New York. At the Bronx site about 8% (23 of 281) of the weekly samples collected from January 2008 through August 2013 were precipitation-free or reported trace precipitation, while at Rochester, dry or trace precipitation samples accounted for about 7% (18 of 264) of the total valid samples. The minimum, median, mean, and maximum values presented in Table 1 only

cover the periods of non-dry and non-trace precipitation samples. In general, median and mean weekly precipitation and wet deposition are lower at the Rochester site, whereas Hg concentrations are similar at both sites over this time period. From 2008–2012, the annual average volume-weighted Hg concentrations ranged from 5.70–8.90 ng/L at the Bronx and 6.58–9.32 ng/L at Rochester, while Hg wet deposition ranged from 6.83–10.92 µg/m^2 and 6.45–8.54 µg/m^2 at the two sites, respectively.

The three panels in Figs. 1(a)–1(c) from top to bottom display the time series of average precipitation, volume-weighted Hg concentration, and Hg wet deposition by season at the Rochester (triangles) and Bronx (squares) sites. Season 1 is winter, defined as December, January, and February; each successive season comprises the next three months. For comparison, the data from two rural MDN sites in New York (Huntington Wildlife and Biscuit Brook) are also shown in the panels of Fig. 1 (http://nadp.sws. uiuc.edu/mdn). Precipitation (Fig. 1(a)) varies considerably from year to year; in general Rochester receives the least amount of precipitation while Biscuit Brook, an elevated (634 m MSL) site in the western Catskill Mountains receives considerable orographically-driven precipitation. Visual inspection of the seasonal precipitation data suggests that there is no clear seasonal pattern in precipitation observed at these sites over these five years. Note that the high precipitation amounts at the Bronx and Biscuit Brook sites in the summer of 2011 is largely attributed to the passage of tropical storms Irene and Lee through the region.

Concentrations of Hg in precipitation (Fig. 1(b)) are generally higher at the two urban sites in New York, since these sites are impacted by regional and local emissions sources. The highest Hg concentrations tend to occur during the summer followed by spring. This seasonal variation was similar to that observed at a rural coastal site in New Hampshire (Lombard *et al.*, 2011) and four sites in the eastern US (Huang *et al.*, 2013). Relatively high Hg concentrations at the Rochester and Bronx sites occurred in the spring and summer of 2008, but as with precipitation there is considerable year to year variability in Hg concentrations. We examined the relationship between Hg wet deposition and precipitation depth, and between Hg wet deposition and RGM + PBM (the fraction of atmospheric Hg most readily scavenged by precipitation) at each site, to assess which factor was more likely to dominate wet deposition levels. Figs. 2(a) and 2(c) compare weekly wet Hg deposition

Table 1. Statistical summary of weekly precipitation, Hg concentration, and Hg wet deposition at the Bronx and Rochester sites, January 2008–August 2013.

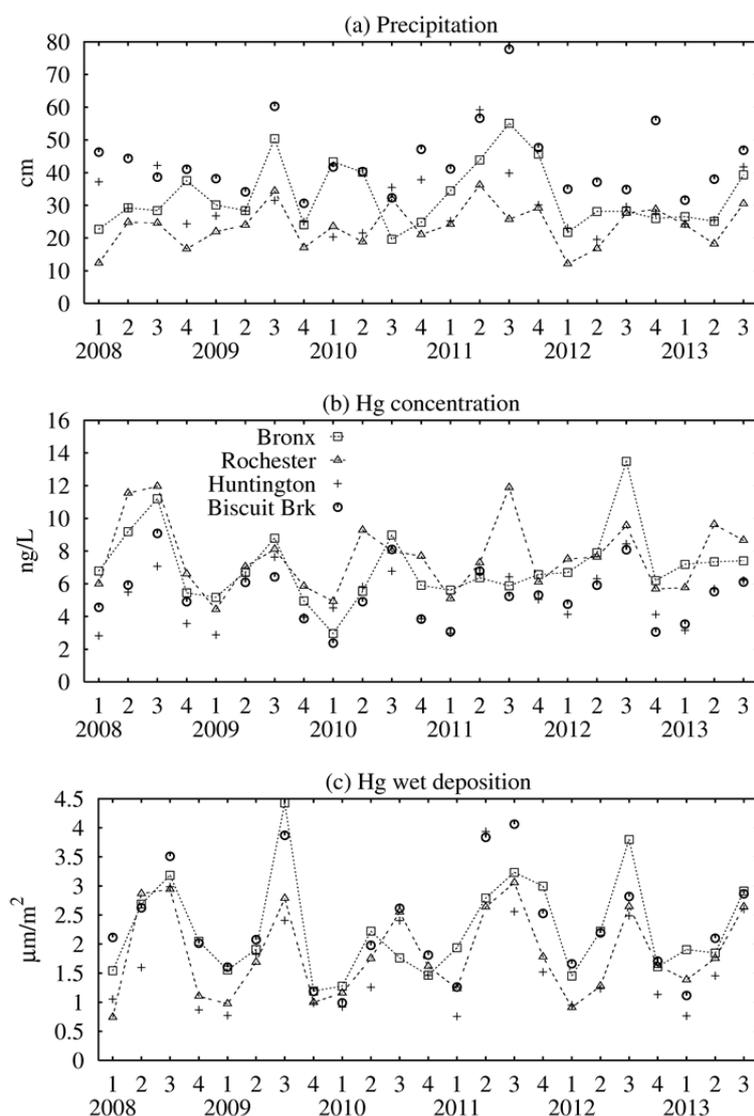| Site	# valid samples/ # non-dry or non-trace samples	Parameter, units	Minimum	Median	Mean	Maximum
Bronx	281/258	Precip., cm	0.05	2.13	2.88	17.27
		Hg conc., ng/L	1.33	8.37	9.56	41.75
		Hg wet dep., ng/m^2	3.6	165.8	199.1	829.8
Rochester	264/246	Precip., cm	0.03	1.51	2.11	9.30
		Hg conc., ng/L	1.72	8.30	9.95	48.91
		Hg wet dep., ng/m^2	1.9	115.3	162.1	1214.1

Fig. 1. Seasonal average (a) precipitation, (b) volume-weighted Hg concentration, and (c) Hg wet deposition at the two urban (Bronx and Rochester) and two rural NADP/MDN sites (Huntington Wildlife and Biscuit Brook) in New York included in this analysis.

and precipitation at the Bronx and Rochester sites, respectively, while Figs. 2(b) and 2(d) compare weekly wet deposition with RGM + PBM averaged over the MDN sampling weeks. There appears to be a strong relationship between wet Hg deposition and precipitation amount at both sites ($r^2 > 0.5$), whereas there is essentially no relationship between wet deposition and reactive atmospheric Hg on a weekly basis. Over a week, RGM and PBM can vary substantially and are scavenged differentially (e.g., Huang *et al.* (2013) and references within), and a weekly wet deposition sample can encompass precipitation events of differing intensity, duration, and possibly phase (rain, snow, ice). Despite these uncertainties, it appears that precipitation amount is a better predictor of wet Hg deposition at these two urban sites.

Wang *et al.* (2013) attributed significant decreases in ambient Hg concentrations to the closure of the Russell Station coal-fired EGU in early 2008. Two other EGU

facilities in western New York – Huntley Station, ~100 km west of Rochester, and Dunkirk Station, ~160 km southwest of Rochester – decreased coal usage by about 17% and 25%, respectively, from 2008 to 2009, based on emission reports to the NYSDEC. Without a longer data record, it is unclear whether the changes in wet Hg concentrations observed at Rochester can be attributed to these changes in emissions or if 2008 was an anomalous year. The only MDN site in New York with more than a decade of data is Huntington Wildlife, and there are indications that this and some other long-term sites in the northeastern US may be experiencing declines in Hg deposition (Butler *et al.*, 2008; Prestbo and Gay, 2009). However, Hg wet deposition has not significantly decreased at a rural site in northern Vermont (Gratz *et al.*, 2009; Gratz and Keeler, 2011), suggesting that it is important to continue tracking these pollutants over the coming years.

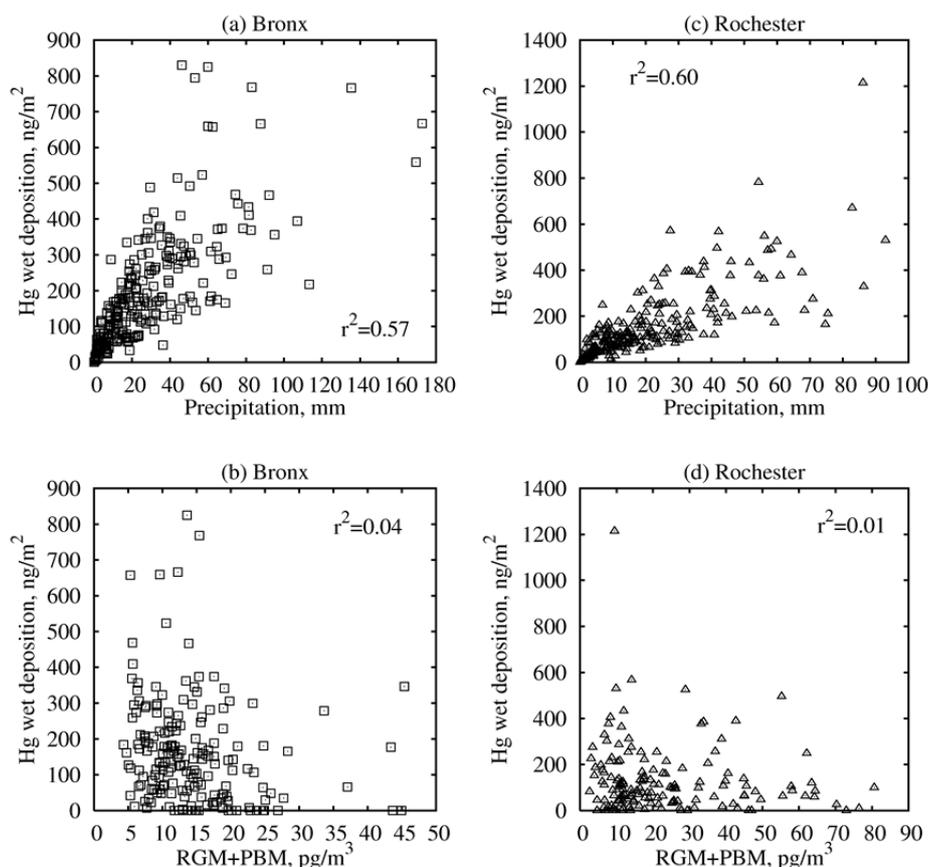Year to year changes in Hg wet deposition are significantly

Fig. 2. Weekly Hg wet deposition at Bronx versus (a) precipitation and (b) ambient RGM + PBM, September 2008 through June 2013. The corresponding data at Rochester are shown in panels (c) and (d).

impacted by changes in precipitation amount, which in New York have tended to be larger than the year to year changes in Hg concentrations in precipitation. Wet deposition exhibits a similar seasonality as Hg concentrations, with higher wet deposition tending to occur during the spring and summer months, consistent with the findings of Huang *et al.* (2013). While the Bronx (with generally high Hg concentrations) and Biscuit Brook (with generally high precipitation amounts) sites tend to have the highest wet deposition amounts, 2010 was a relatively low deposition year at all sites in New York. The Huntington Wildlife site is the most remote site in New York and most distant from upwind sources, and generally experiences the lowest wet deposition levels of all four sites.

Coal combustion from EGUs and other sources has long been known to be a source of sulfate (SO_4) in addition to Hg; hence, it is expected that these two pollutants might co-vary. Using the SO_4 data from the NYSDEC wet deposition samplers no longer operating, we can examine this relationship. From 2008–2010, weekly Hg and SO_4 concentrations in wet deposition were positively correlated at both sites (r^2 ~0.5 at both sites). These results are consistent with earlier findings from a rural site in northern Vermont (Burke *et al.*, 1995).

Regional Context

To provide regional context for the precipitation, volume-

weighted Hg concentration, and Hg wet deposition data observed at the Bronx and Rochester sites, the 2012 data from sites in surrounding states and provinces are shown in Table 2 and the panels of Fig. 3. All data were obtained from the NADP/MDN website (http://nadp.sws. uiuc.edu.mdn). In 2012 there were 46 NADP/MDN monitoring sites in the western Great Lakes region (11 sites in Minnesota, Wisconsin, and Illinois), eastern Great Lakes region (15 sites in Indiana, Michigan, Pennsylvania, and Ontario), mid-Atlantic US (10 sites in New York, New Jersey, Maryland, Virginia, and West Virginia), and New England and eastern Canada (10 sites in Massachusetts, Vermont, Maine, Quebec, and Nova Scotia). These sub-groups were chosen to have similar numbers of sites in each sub-group, with all four New York sites included with the other mid-Atlantic states. Over this region, there is more than a two-fold range in annual precipitation and wet deposition, and more than a three-fold range in Hg concentration. In 2012 the precipitation, volume-weighted Hg concentration, and Hg wet deposition amounts at the Bronx site were slightly above the regional mean values, while the corresponding values at Rochester were below the regional means. For precipitation, the 2012 values at both sites were within the 95% confidence interval of regional mean values (94.3–107.8 cm). At the Bronx site, the 2012 Hg wet deposition value of 9.42 $\mu g/m^2$ was above the 95% confidence interval of the regional mean values (7.69–8.71 $\mu g/m^2$), whereas both the Hg concentration

Table 2. Annual precipitation, volume-weighted Hg concentration, and Hg wet deposition at the Bronx and Rochester sites in 2012 compared to the minimum, mean, and maximum values across the other sites in the northeastern US and eastern Canada.

Parameter, units	Bronx	Rochester	Region Minimum	Region Mean	Region Maximum
Precip., cm	105.8	96.8	61.9	101.1	163.3
Hg conc., ng/L	8.90	6.97	4.73	8.58	17.54
Hg wet dep., $\mu g/m^2$	9.42	6.75	5.30	8.20	12.08
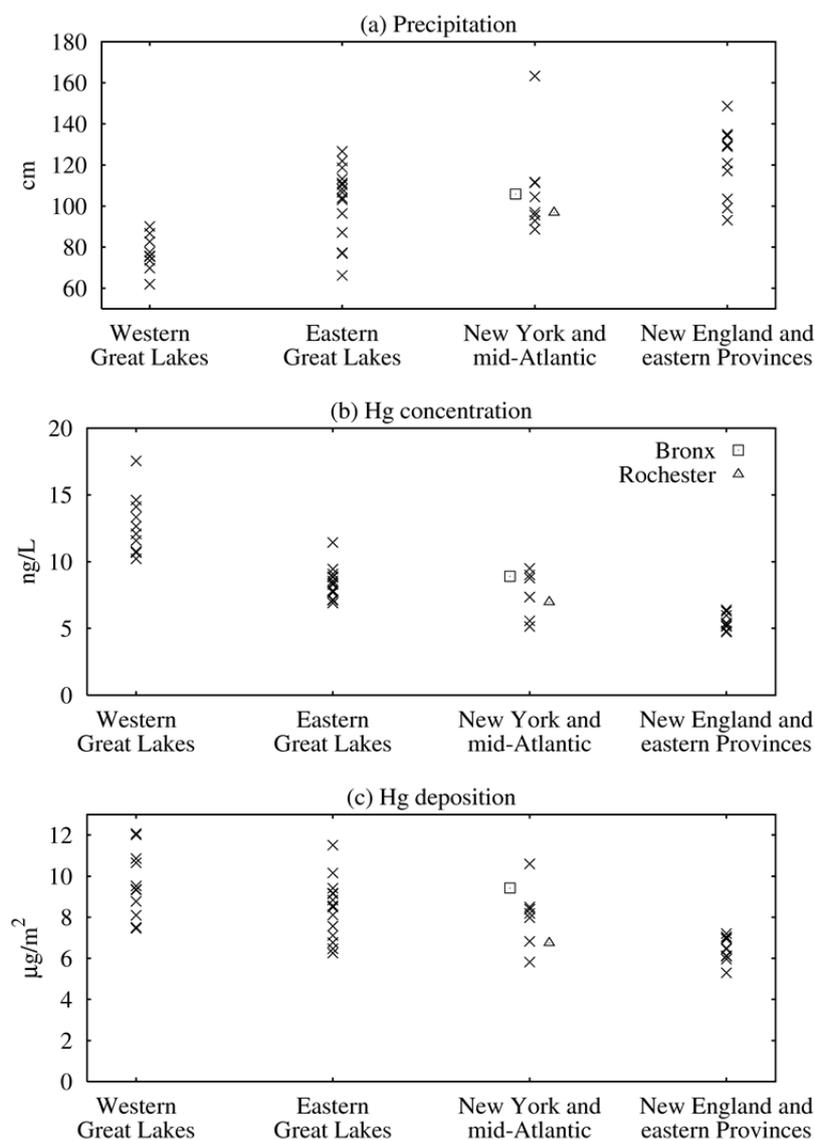
Fig. 3. 2012 annual (a) precipitation, (b) volume-weighted Hg concentration, and (c) Hg wet deposition at sites in the western Great Lakes states (n = 11), eastern Great Lakes states (n = 15), New York and US mid-Atlantic states (n=10), and New England states and eastern Canadian provinces (n = 10). The Bronx (squares) and Rochester (triangles) sites are shown with different symbols as a visual aid.

and wet deposition values Rochester were lower than the respective 95% confidence intervals. Similar regional patterns were observed in 2011, but these results are not shown here.

The panels in Figs. 3(a)–3(c), from top to bottom, display the 2012 total precipitation, mean volume-weighted Hg concentration, and Hg wet deposition at the 46 sites across the region. The sites are grouped according to the four sub-groups listed above, which are arranged roughly west to east. In general precipitation totals increase from west to east, while Hg concentration and Hg deposition decrease from west to east in this region, consistent with earlier findings in the Great Lakes area (Risch *et al.*, 2012) and northeastern US/eastern Canada (Miller *et al.*, 2005; Huang *et al.*, 2013).

Speciated Air Concentrations

Statistical Summary

Table 3 lists the 10th percentile, median, mean, and 90th percentile concentrations of ambient GEM, RGM, and PBM at the two sites, as well as the standard deviation and number of valid 2-hour data points from 2008 through June 2013. The average GEM concentration at the Bronx site (1.52 ng/m³) was slightly higher than that at the Rochester site (1.40 ng/m³), but this difference is not statistically significant. The average GEM concentration at the Bronx was somewhat lower than average concentrations measured at Elizabeth, NJ (2.25 ng/m³) and New Brunswick, NJ (2.15 ng/m³) during the mid-2000 s (Aucott *et al.*, 2009), while the average GEM concentration at Rochester was slightly lower than the average GEM in 2007–2009 from the same site – 1.4 ng/m³ compared to 1.6 ng/m³ (Choi *et al.*, 2013). Over this same period, the average GEM concentration at the rural Huntington Wildlife site was about 1.3 ng/m³ (Choi *et al.*, 2013), which is indicative of the regional GEM levels impacting all sites.

Unlike GEM, concentrations of RGM and PBM show more variability with higher values at Rochester compared to the Bronx site. This is likely due to Rochester's proximity to coal-burning sources in western New York and upwind states. However, RGM in particular was high at Rochester from the fall of 2009 through spring of 2010; this will be discussed in further detail in the next section. The average RGM and PBM concentrations at the Bronx site – 6.26 and 7.96 pg/m³, respectively – are similar to, but perhaps slightly less than, those from the two urban New Jersey sites (RGM, 6.04 and 8.93 pg/m³; PBM, 8.21 and 10.73 pg/m³; Aucott *et al.*, 2009). Both urban sites in New York have higher average RGM and PBM concentrations than Huntington Wildlife, where both Hg species are less than 2 pg/m³ (Lan *et al.*, 2012; Choi *et al.*, 2013). Using the estimated RGM and PBM detection limits reported by Huang *et al.* (2010), approximately 13% of the Rochester and 5% of the Bronx RGM data were below the detection limit of 0.46 pg/m³, whereas 4% of the Rochester and 7% of the Bronx PBM data were below the detection limit of 1.1 pg/m³.

Monthly Variations

The panels in Figs. 4(a)–4(c) display the monthly median concentrations of GEM, RGM, and PBM at the Bronx and Rochester sites. The error bars denote the 10th percentile to 90th percentile range each month. Most months the median GEM concentrations (Fig. 4(a)) are higher at the Bronx site, as is the range in the data over the month. An exception to

this is October 2012 when the Rochester site had numerous concentrations that exceeded 3 ng/m³. In general the Rochester site exhibits peak GEM concentrations during the winter and spring months and minimum GEM concentrations through the summer and fall. This is less clear at the Bronx site, which tends to exhibit more year to year variability in GEM. This seasonal pattern is generally consistent with that observed at other sites in the northeastern US (Mao *et al.*, 2008; Lan *et al.*, 2012; Choi *et al.*, 2013), and is likely due to seasonal patterns in emissions (i.e., coal and/or wood combustion associated with space heating); a more shallow planetary boundary (PBL) during the colder months; emissions from ground surfaces and melting snow (Choi *et al.*, 2013); and enhanced photochemical oxidation of GEM during the warmer months.

Fig. 4(b) displays the monthly RGM values at both sites. In general, RGM exhibits a spring maximum at both sites, consistent with photochemical oxidation of GEM released from ground surfaces as snow cover diminishes and temperatures increase, although there is substantial year to year variability in RGM. At Rochester, RGM levels were consistently high from the fall of 2009 through spring of 2010. A review of other air quality parameters (BC, CO, SO_2, and $PM_{2.5}$) did not suggest levels of those pollutants were anomalously high, nor were temperatures unusual during this period. Unfortunately, Hg data loss at the Bronx site was considerable during this time, so it is unclear if this was an unusual period that only impacted Rochester. Precipitation should efficiently scavenge RGM, but precipitation was not particularly unusual during that period (see Fig. 1(a)). There have been reductions in Hg emissions in recent years in the EGU sector in the eastern US as electrical generation switches from coal to natural gas. Two facilities mentioned earlier – Huntley Station and Dunkirk Station– have seen reductions from a combined high of ~180 kg in 2006 to ~75 kg in 2010. Additional monitoring may be helpful to better understanding these changes; however, the absence of a longer data record prior to these emissions reductions makes it difficult to assess the impacts of emissions at these facilities on RGM levels at Rochester.

Fig. 4(c) displays the monthly variations in PBM at both sites. Concentrations of PBM are generally higher during the colder seasons, attributable to emissions related to space heating, a tendency for reactive Hg to partition from the gas-phase to particle phase at lower temperatures (Rutter and Schauer, 2007), and more shallow PBL depths. Wood smoke is a potential source of PBM in this region of the

Table 3. Statistical summary of 2-hour GEM, RGM, and PBM concentrations at the Bronx and Rochester sites, September 2008–June 2013. The values in parentheses denote ± one standard deviation about the mean concentrations.

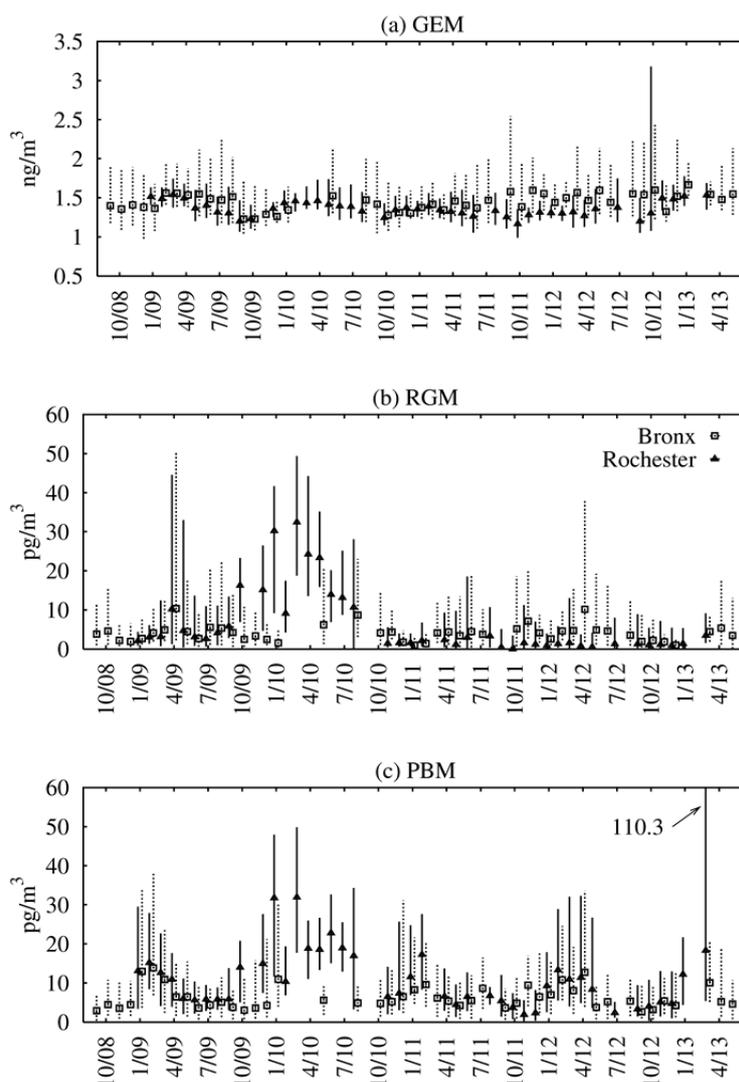|	GEM, ng/m³		RGM, pg/m³		PBM, pg/m³	
	Bronx	Rochester	Bronx	Rochester	Bronx	Rochester
10th %ile	1.20	1.17	0.78	0.29	1.42	2.36
Median	1.45	1.37	3.60	3.27	5.67	9.40
Mean (std. deviation)	1.52 (0.36)	1.40 (0.26)	6.26 (15.85)	8.24 (12.94)	7.96 (12.13)	13.48 (21.01)
90th %ile	1.92	1.61	13.53	23.25	15.82	27.32
N	10,719	9,835	10,003	9,144	10,110	8,942

Fig. 4. Monthly concentrations of (a) GEM, (b) RGM, and (c) PBM, September 2008 through June 2013. Symbols denote median values and the error bars denote the 10th and 90th percentile ranges at Bronx (squares) and Rochester (triangles).

US (e.g., Choi *et al.*, 2008; Huang *et al.*, 2011), and this will be discussed in a later section. In the latter half of March 2013 PBM levels were exceptionally high at Rochester, with five 2-hour concentrations that exceeded 200 pg/m^3 on March 16, 17, and 24; the 90th percentile value for this month was 110.3 pg/m^3. During this period, PBM was only weakly correlated with a number of combustion-related pollutants – SO_2, CO, BC, and NO_x. Overnight from March 17 to 18, wind speeds diminished to ~3 km/hr and surface pressure increased, reflective of stable conditions which allowed for general pollutant accumulation, including PBM. On the highest PBM days in March 2013, 48-hour back trajectories (not shown here) tended to originate from northern Canada, but we are not aware of any large forest fires that were occurring in this region. Hence, the high PBM concentrations from this period are likely attributed to regional EGU and other sources.

Day of Week Variations

In addition to monthly variations in ambient Hg, it may

be instructive to examine day of week patterns in the data related to the work activity. The panels in Fig. 5 display the average concentrations of (a) GEM, (b) RGM, and (c) PBM by day of week and season at the Bronx site, while Figs. 5(d)–5(f) display the corresponding concentrations at Rochester. During the spring and summer months at the Bronx site, GEM appears to be slightly higher during the work week except for Mondays; however, these differences are within the 95% confidence intervals about the day of week average concentrations. There is less of a contrast across seasons at Rochester. Huang *et al.* (2010) used PCA to investigate sources impacting Hg concentrations at Rochester, and found a weak association between ambient GEM and mobile sources. However, it is not clear from our data that mobile source emissions associated with weekly commuting patterns are an important source of GEM during the colder months at these two sites.

The two sites appear to exhibit different day of week patterns for RGM during the spring months. At the Bronx site, RGM is slightly higher on weekend days during the
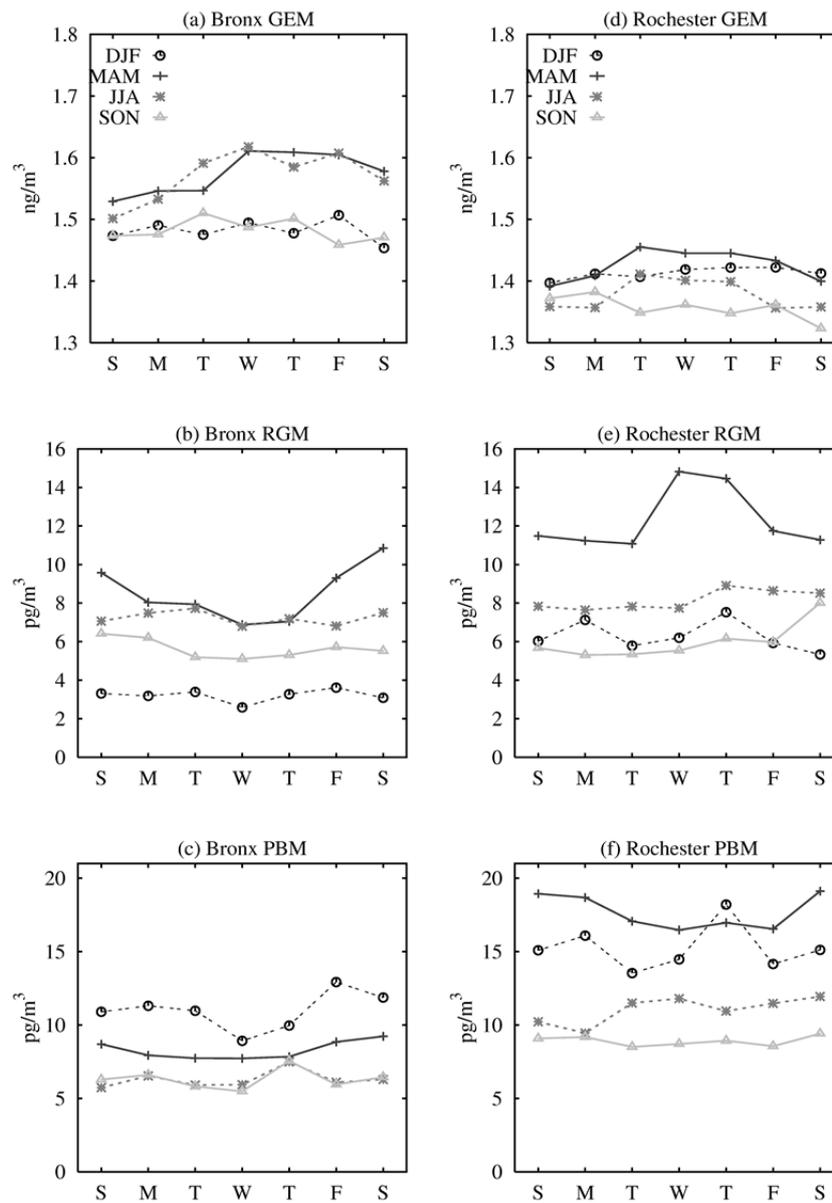
Fig. 5. Mean day-of-week concentrations of (a) GEM, (b) RGM, and (c) PBM at Bronx. The corresponding data at Rochester are shown in panels (c)–(f). Seasons are winter (circles), spring (+), summer (asterisks), and fall (triangles).

spring months, but at Rochester RGM exhibits a mid-week maximum. During the other seasons RGM exhibits a slight mid-week minimum at the Bronx site; this slight depression is also apparent in PBM levels. At Rochester, there is some indication in the summer and fall of slightly higher RGM concentrations later in the week, but this enhancement is not statistically significant. The PBM levels at Rochester during the spring appear elevated on weekend days, perhaps associated with residential wood combustion. Whether there are additional sources that are more likely to be associated with specific weekday/weekend activities warrants further study in this region.

Diurnal Variations

Figs. 6(a)–6(f) displays the diurnal variations of each Hg species at both sites, again by season. Both sites exhibit

little diurnal variation in GEM (Figs. 6(a) and 6(d)) during the winter months. During the spring, summer, and fall seasons, GEM exhibits a nighttime maximum and daytime minimum, which is more pronounced at the Bronx site. During the summer at the Bronx site the nighttime GEM values are ~25–30% higher than midday values, while during the spring and fall seasons the nighttime values are ~10–15% higher than midday values. During the non-winter seasons at Rochester, the nighttime GEM values are only ~10% higher than those during daylight. In addition to the Bronx site's proximity to the ocean, which can be a source of halogens to oxidize GEM, the PBL dynamics are different between the two sites. The panels in Fig. 7 show the average diurnal variation of the PBL heights at both sites during the winter and summer, estimated from a model-based air quality forecast platform (Doraiswamy *et al.*, 2010),
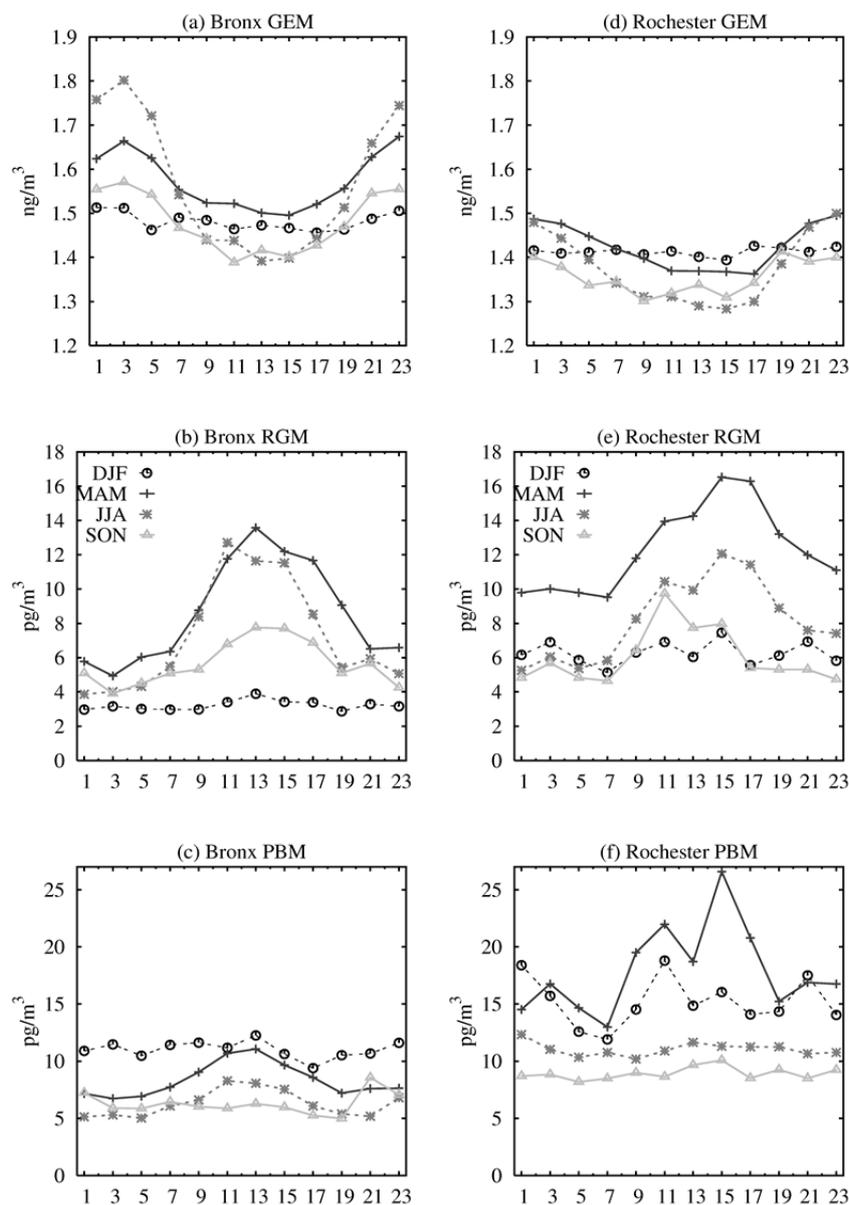
Fig. 6. Average diurnal variations of GEM, RGM, and PBM at the Bronx and Rochester sites by season, in EST. Symbols are the same as in Fig. 5.

as well as the diurnal variation in air temperature. The Bronx site exhibits a larger winter-summer contrast in afternoon PBL heights, with summertime afternoon PBL heights nearly a factor of four higher than nocturnal PBL heights (compared to a factor three at Rochester) due to a stronger heat island and more complex land/water circulation patterns. Temperatures on average are ~2–3°C higher at the Bronx site, but the winter-summer differences in temperatures are similar at the two sites. Lan *et al.* (2012) also noted contrasting diurnal patterns in GEM at sites across the US, which they attributed to local-scale meteorology (e.g., PBL dynamics, land-water breezes).

Figs. 6(b) and 6(e) display the diurnal variations of RGM, which in contrast to GEM exhibits a nocturnal minimum and daytime maximum, except during the winter months when there is much less variation over the diurnal cycle. This

pattern is most distinct during the spring and summer months when photochemistry is most pronounced, with afternoon maxima on average ~2–3 times higher than nighttime minima at both sites. Vertical mixing of RGM from the free troposphere during the morning hours, as well as enhanced dry deposition at night, may play important roles in the diurnal variation of RGM (Lan *et al.*, 2012; Nair *et al.*, 2012). This pattern is similar to photochemically-produced pollutants like ozone (O$_3$), and a case study at the Bronx site will be discussed in a later section.

The bottom panels if Fig. 6 display the diurnal variations of PBM at the two sites. During the spring months there is some evidence of a daytime maximum, suggesting that PBM may be produced photochemically, but this variation exhibits a smaller amplitude compared to RGM. The diurnal pattern in PBM is more variable in the winter and spring at
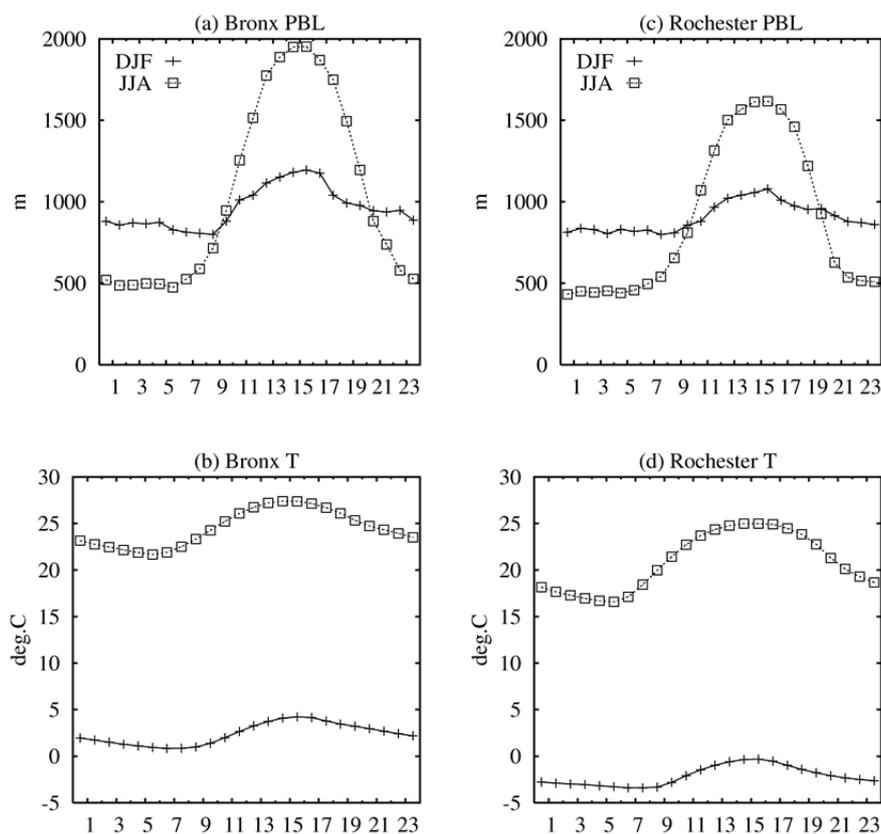
Fig. 7. Diurnal variation (EST) in (a) photochemical model-based PBL height and (b) measured ambient air temperature at Bronx in winter (+) and summer (squares). The corresponding data at Rochester are shown in panels (c) and (d).

Rochester than the Bronx site. During the spring, daytime maxima at the Bronx site are ~1.5 times the nocturnal minima, while at Rochester the daytime maxima can be a factor of 2 higher than the corresponding nocturnal minima. The PBM concentration tends to be higher in the colder months, and the variation from day to day can be substantial. The winter-summer contrast in PBM is larger at the Rochester site, consistent with additional sources during the heating season.

Conditional Probability Function Analysis

In an effort to characterize potential nearby source directions that impact ambient Hg levels at the Bronx and Rochester sites, we used conditional probability function (CPF) analysis with surface winds available from each site (e.g., Bae *et al.*, 2011). For a given wind direction, the CPF is the probability that a pollutant will exceed a predetermined threshold. For this analysis, we defined the thresholds of GEM, RGM, and PBM as concentrations exceeding the respective 75th percentiles (Kim and Hopke, 2004). The ambient GEM, RGM, and PBM data were binned and averaged into 45 degree wind direction sectors, with calm periods (wind speed < 1.6 km/hr) excluded from the analysis. As with the various temporal analyses, we generated each CPF as a function of season.

The panels in Fig. 8 display the average GEM, RGM, and PBM concentrations by wind direction and season for both sites. The Bronx site exhibits a clear GEM peak when surface winds are from the southwest during all seasons. The lowest average GEM concentrations are associated with more northerly winds. This is may be due to the large number of current and legacy sources of Hg in this region, including steel manufacturing, coal-fired utilities, crematoria, and incinerators (e.g., Aucott *et al.*, 2009) southwest of the Bronx site. In contrast, average GEM at Rochester exhibits less of a directional dependence than the Bronx site. This may be due to the smaller urban center with a less diverse "mix" of potential sources impacting Rochester, and is reflective of the regional nature of GEM. During the winter months, there is a GEM peak at Rochester when winds are from the northwest; the directional dependence is less pronounced during the other seasons.

At the Bronx site, RGM and PBM concentrations tend to be elevated when the winds are from the southwest and northwest. There is a stronger contribution from the southwest for RGM, most evident during the fall and winter months, while for PBM this is highly pronounced in the fall months. During the spring months, slightly higher RGM and PBM are associated with northwest winds. The patterns at Rochester are somewhat different. In general, elevated RGM and PBM at Rochester are associated with north/northwest winds, which may be indicative of nearby sources in those directions. The area in the immediate vicinity of the Rochester site is generally residential, and emissions from wood combustion for recreational use occasionally impact the monitoring site (e.g., Rattigan *et al.*, 2013).
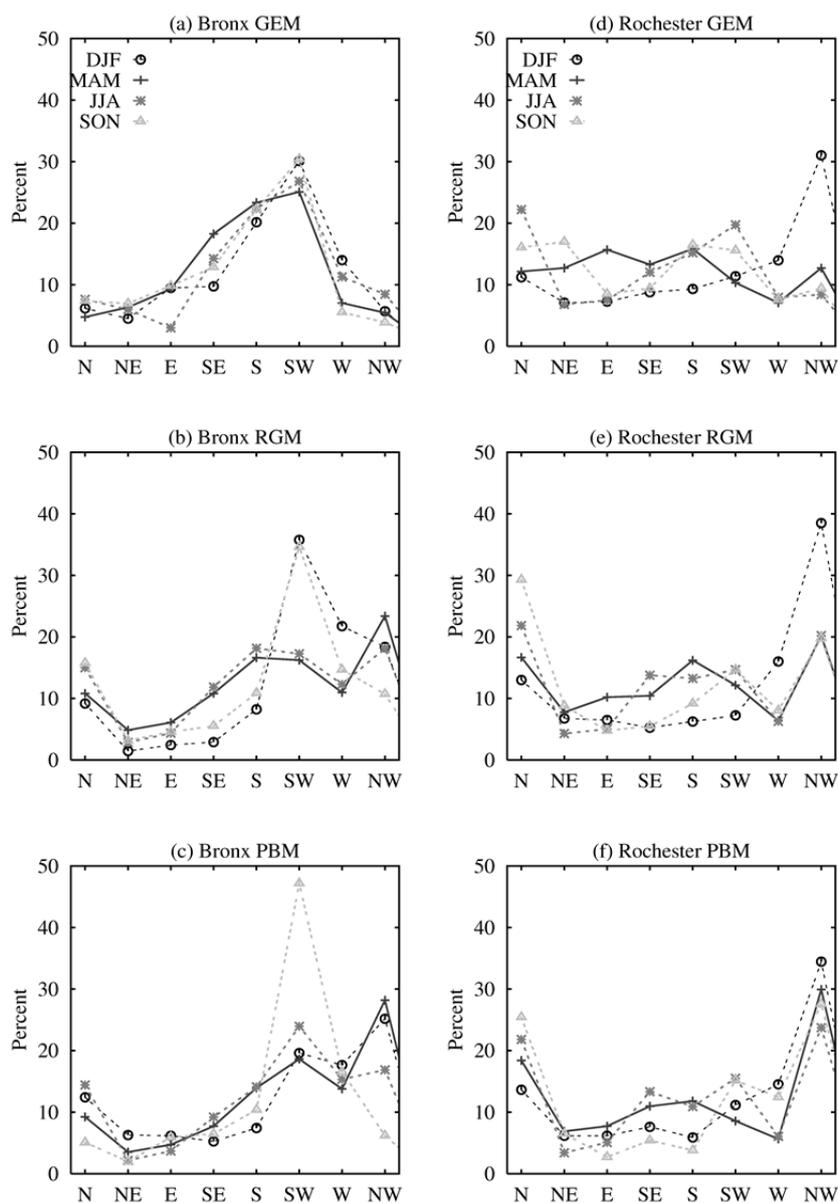
Fig. 8. Conditional probability functions of GEM, RGM, and PBM at the Bronx and Rochester sites by season. Symbols are the same as in Fig. 5.

Case Studies at Both Sites

To further investigate possible sources and fates of ambient Hg concentrations at these two sites, we examined relationships with co-pollutants in different seasons. An example of co-pollutant analysis at each site is presented here to preliminarily explore such relationships. The first example appears to be consistent with GEM oxidation during the summer at the Bronx site. The panels in Fig. 9 display the time series of (a) GEM and RGM, and (b) O_3 and temperature at the Bronx site over a nine-day period in August 2009. During most of this period, RGM is generally anti-correlated with GEM and generally correlated with O_3, which is also a product of photochemical reactions. Approximately 0.25 cm of rainfall mid-day on August 13 and ~0.6 cm of rainfall the afternoon of August 21 helped keep RGM and O_3 concentrations relatively low during

this period. On other days during the daytime hours, as O_3 increases from vertical mixing of precursors and enhanced solar activity, the Hg species exhibit behavior consistent with GEM oxidation by photochemically-active oxidants to RGM (e.g., Huang *et al.*, 2010; Choi *et al.*, 2013).

As noted earlier, smoke from residential wood combustion can impact the Rochester site during the colder months when wind speeds are low. A previous laboratory combustion chamber and field study found that combustion of wood or wood pellets can be an important source of GEM and PBM in northern climates in the winter (Huang *et al.*, 2011). The panels in Fig. 10 show (a) PBM and GEM, (b) wind speed and direction, and (c) temperature from the Rochester site during a six-day period in November 2010. The Rochester site also has a two-wavelength Aethalometer®; the difference between the 370 nm channel and the 880 nm
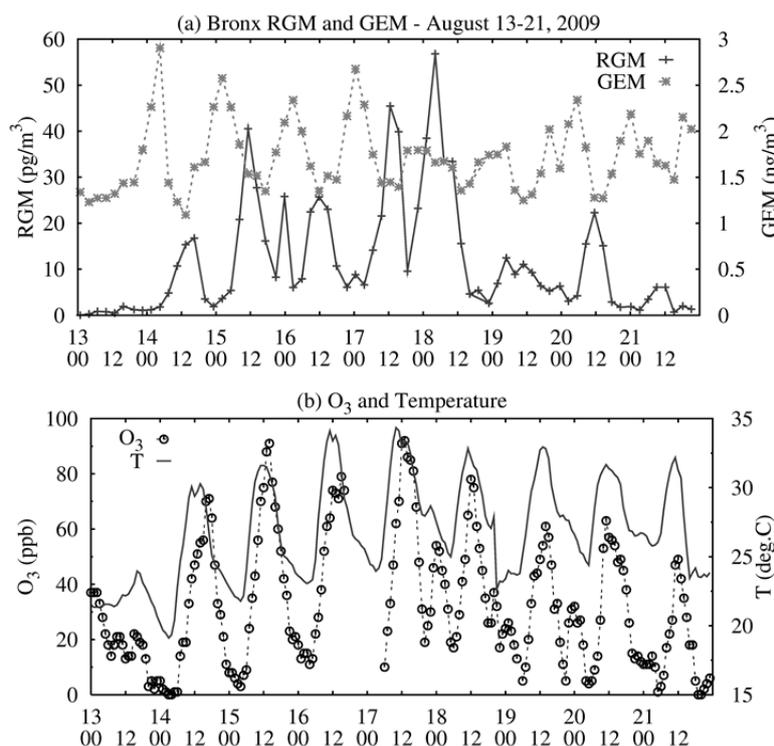
Fig. 9. Time series of (a) GEM (asterisks) and RGM (+), and (b) O$_3$ (circles) and ambient air temperature (solid lines) at the Bronx site, August 13–21, 2009.

channel, referred to as "Delta-C," has been shown to track levoglucosan, a wood smoke marker (e.g., Wang *et al.*, 2011), and is included in Fig. 10(a). Rattigan *et al.* (2013) showed that residential wood smoke events can be observed at Rochester, especially on cold weekend nights. During this period nighttime wind speeds were generally low, and overnight minimum temperatures were near or below 0°C. Late on the nights of Friday the 12th and Saturday the 13th the Delta-C signal exceeded 2 µg/m³. Although not shown here, elevated concentrations of PM$_{2.5}$ and CO were also observed overnight from the 12th to the 13th as well; this is consistent with stagnation allowing for the build-up of combustion-related pollutants. GEM concentrations were also somewhat elevated on those two nights, and PBM remained high during the second half of Friday through early morning on Saturday. Although Delta-C and PBM do not track each other exactly, the general tendency of high nighttime pollutant concentrations is consistent with a wood smoke signal.

SUMMARY

More than five years of wet deposition and ambient speciated Hg measurements are used to characterize temporal patterns at two urban locations. While this is not a long enough period to infer long-term trends in the data, it is more than sufficient to infer baseline levels and explore short-term temporal patterns and regional trends. Overall, the mean (and median) Hg concentration in wet deposition is 9.56 ng/L (8.37 ng/L) at the Bronx site, and 9.95 ng/L (8.30 ng/L) at the Rochester site. Wet Hg concentrations are currently similar to median levels across the Great Lakes region, northeastern US, and eastern Canada. In terms of ambient speciated Hg, GEM levels on average are higher at the Bronx site, whereas average RGM and PBM levels are higher at Rochester. Ambient GEM concentrations are only slightly higher than regional levels, but both sites exhibit higher RGM and PBM concentrations than a rural site in the Adirondack Mountains of northern New York. The two sites exhibit similar diurnal and monthly variations, but day-of-week and CPF analysis suggest that more work is needed to understand local and regional sources that potentially impact each site. Finally, an example of a GEM oxidation event at the Bronx site and potential impacts of wood combustion at the Rochester site illustrate the value of having co-pollutant data at each site to better understand sources and fates of Hg at these contrasting urban locations.

DISCLAIMER

Although this manuscript was reviewed internally, it does not necessarily reflect the views or policies of the NYSDEC or supporting agencies.
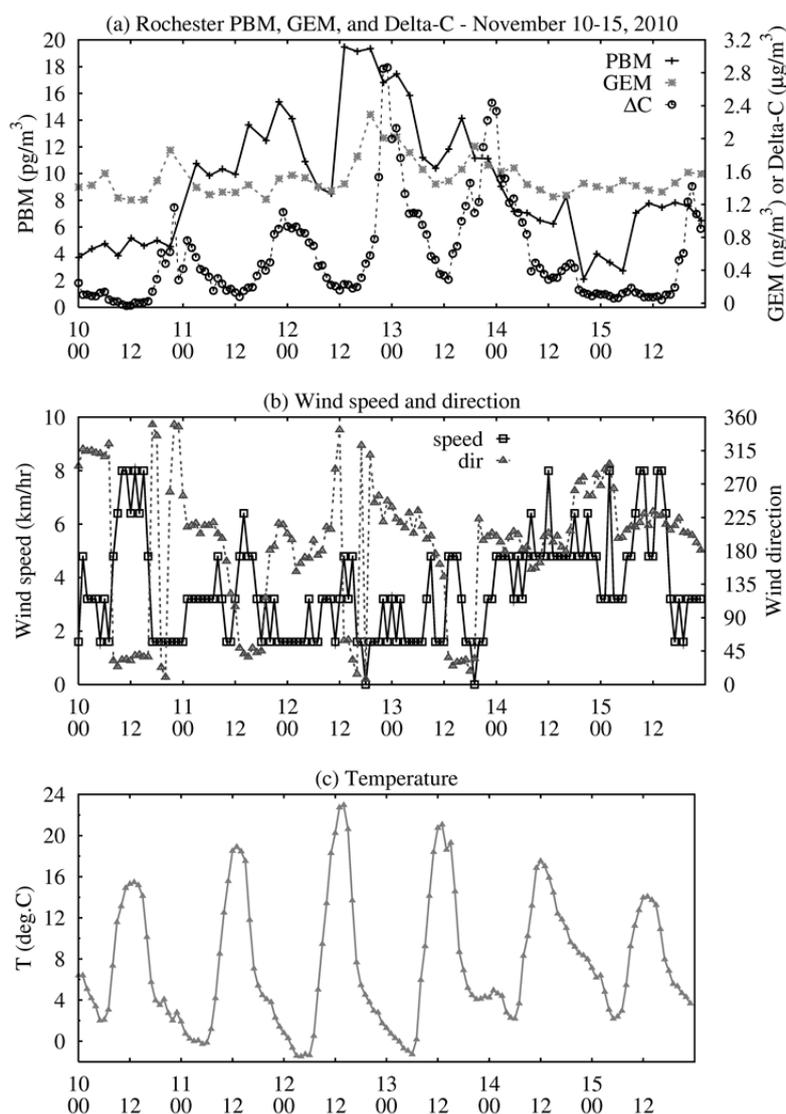
Fig. 10. Time series of (a) PBM (+), GEM (asterisks), and Delta-C (circles); (b) wind speed (squares) and direction (triangles); and (c) ambient air temperature at the Rochester site, November 10–15, 2010.

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