Atmospheric transport of speciated mercury across southern Lake Michigan: Influence from emission sources in the Chicago/Gary urban area

Lynne E. Gratz *, Gerald J. Keeler, Frank J. Marsik, James A. Barres, J. Timothy Dvonch

University of Michigan Air Quality Laboratory, 1415 Washington Heights, SPH 1, Ann Arbor, MI 48109-2029 USA

HIGHLIGHTS

► We measured speciated atmospheric Hg in Chicago, IL and Holland, MI in summer 2007.
► Transport from Chicago/Gary resulted in elevated Hg concentrations in Holland.
► Primary RGM emissions and Hg^0 oxidation both influenced elevated RGM in Holland.
► Chicago/Gary source emissions significantly impact receptors along Lake Michigan.

ARTICLE INFO

ABSTRACT

Quantifying the local and regional impacts of speciated mercury (Hg) emissions from major urban and industrial areas is critical for understanding Hg transport and cycling in the environment. The Chicago/Gary urban area is one location where Hg emissions from industrial sources are significant and the regional transport of emissions may contribute to elevated ambient Hg concentrations at downwind locations. From July to November 2007, we collected semi-continuous measurements of gaseous elemental Hg (Hg^0), fine particulate bound Hg (Hg_p), and divalent reactive gaseous Hg (RGM) in Chicago, IL and Holland, MI to characterize the impact of Chicago/Gary source emissions on Hg concentrations in southwest Michigan and to improve our overall understanding of speciated Hg transport and deposition. The mean (and median) concentrations of Hg^0, Hg_p, and RGM in Chicago were 2.5 ng/m³ (1.9 ng/m³), 9 pg/m³ (5 pg/m³), and 17 pg/m³ (6 pg/m³), respectively. In Holland the mean (and median) concentrations were 1.3 ng/m³ (1.3 ng/m³), 6 pg/m³ (6 pg/m³), and 8 pg/m³ (2 pg/m³), respectively. Cluster analysis of 24-hour HYSPLIT back-trajectories associated with the semi-continuous Hg measurements indicated that southwest transport from Chicago/Gary to Holland occurred during approximately 27% of the study. In Holland, under this transport regime, we observed a five-fold increase in RGM relative to the median concentration of the other transport clusters. We applied the HYSPLIT dispersion model to two case study periods to further quantify the impact of Chicago/Gary sources on southeast Michigan and investigate the role of direct transport and dispersion of speciated Hg emissions. Results suggested that more than 50% of the maximum RGM concentrations observed in Holland during the selected periods could be attributed to direct transport of primary RGM emissions from Chicago/Gary. The remaining RGM fractions are believed to be associated with Hg^0 oxidation during transport over Lake Michigan.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is a hazardous, bioaccumulative neurotoxin that threatens both human and environmental health (U.S. EPA, 1997). Atmospheric deposition has been widely linked to the levels of Hg in terrestrial and aquatic ecosystems (U.S. EPA, 1997; Landis and Keeler, 2002; Orihel et al., 2007; Harris et al., 2007). Therefore, to mitigate the impact of Hg on the environment, it is critical to understand atmospheric Hg emissions, chemistry, and transport prior to its removal through wet or dry deposition.

Mercury is present in the atmosphere primarily as gaseous elemental Hg (Hg^0), divalent reactive gaseous Hg (RGM), and fine particulate bound Hg (Hg_p). Elemental Hg comprises >90% of atmospheric Hg (Lin and Pehkonen, 1997) and can be transported regionally and globally due to its high volatility and low water solubility (Schroeder and Munthe, 1998). In contrast, RGM is highly reactive and water-soluble and therefore readily removed through wet deposition and dry deposition (Schroeder and Munthe, 1998). Particulate-bound Hg, which exists predominantly in the fine fraction (<2.5 μm), can be transported on large spatial scales prior to wet or dry removal (Keeler et al., 1995). Atmospheric reactions that convert Hg between its elemental, reactive,

* Corresponding author at: CNR-Institute of Atmospheric Pollution Research, CNR-IIA c/o UNICAL-Polifunzionale, 87036 Rende, Italy. Tel.: +1 734 931 6109.
E-mail addresses: lgratz@umich.edu, l.gratz@iia.cnr.it (L.E. Gratz).

and particulate forms (Seigneur et al., 1994; Lin and Pehkonen, 1997, 1999), as well as the deposition and re-emission of Hg from terrestrial and aquatic surfaces (Schroeder and Munthe, 1998; Gustin et al., 2008) add further complexity to Hg chemistry, transport, and biogeochemical cycling on various spatial scales.

The U.S. Great Lakes were targeted under the 1990 Clean Air Act Amendments' Great Waters Provision for monitoring of atmospheric Hg due to elevated Hg levels in the aquatic ecosystem (U.S. EPA, 1994). The Lake Michigan Mass Balance Study (LMMBS) and the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS) commenced in 1994 to identify major regional Hg sources and quantify Hg deposition to the Lake Michigan Basin (Landis and Keeler, 2002; Landis et al., 2002b; Vette et al., 2002; McCarty et al., 2004). Results suggested that atmospheric deposition was responsible for approximately 84% of total annual Hg inputs to Lake Michigan while the Chicago/Gary urban area alone contributed approximately 20% of the annual atmospheric Hg deposition to Lake Michigan (Landis and Keeler, 2002). The highest levels of Hg deposition in southwest Michigan also occurred with transport from Chicago/Gary, particularly with rapid transport where less Hg was deposited close to sources (Landis et al., 2002b).

The Chicago/Gary urban area lies on the southwest shore of Lake Michigan (Fig. 1). Major Hg emission point sources in Chicago/Gary include secondary metal smelters, iron-steel manufacturers, and coal- and oil-fired utility boilers. Coal combustion is the largest anthropogenic emitter of total Hg, both in Chicago/Gary and nationally (U.S. EPA NEI, 2005). In Chicago/Gary, coal-fired utility boilers (CFUBs) contribute approximately 76% (nearly 3 tons per year (tpy)) of the total Hg point source emissions from the urban/industrial area (U.S. EPA NEI, 2005). Nationally, CFUBs emit an estimated 50 tpy of Hg (U.S. EPA, 1997; Cohen et al., 2007; Butler et al., 2008). CFUB Hg emissions are typically 50–80% Hg(II) and 20–50% Hg⁰ (Carpi, 1997; Seigneur et al., 2006). Given that Hg_p is more easily removed by filters and other stack

controls, it generally comprises <5% of total Hg emissions from combustion; therefore, Hg(II) emissions from combustion should be predominantly RGM (Carpi, 1997). These speciated source emissions directly influence the fraction of emitted Hg that is deposited locally and transported regionally within the Lake Michigan basin.

In addition, unique meteorological conditions are occasionally observed over Lake Michigan, during which Chicago/Gary source emissions can be transported across the lake with minimal loss or dispersion due to suppressed vertical atmospheric mixing (Lyons and Cole, 1975; Sillman et al., 1993; Dye et al., 1995). As a result, Chicago/Gary source emissions can have a measurable impact on downwind receptors along the lake. For example, under increased photochemical activity and stable atmospheric transport over the lake, significantly elevated ozone concentrations often occur along the Lake Michigan shoreline (Lyons and Cole, 1975; Sillman et al., 1993; Dye et al., 1995). Similarly, emitted Hg species may also be contained within the stable layers over the lake and undergo chemical reactions during transport. There is strong evidence for RGM production under relatively elevated ozone concentrations (>60 ppb) (Keeler and Dvonch, 2005; Liu et al., 2007, 2010), while anthropogenic NO_x and VOCs were also shown to significantly influence RGM production from Hg⁰ in the Great Lakes (Sillman et al., 2007). Further defining the spatial impacts of speciated Hg emissions from the Chicago/Gary urban area and investigating the influence of atmospheric transport and chemistry is critical to improving our understanding of the sources and fate of atmospheric Hg in the Great Lakes region.

Since the LMMBS and AEOLOS, the development of speciated Hg measurement systems has made it possible to continuously monitor Hg⁰, Hg_p, and RGM, offering new insights into atmospheric Hg chemistry and an ability to differentiate between local and regional emission source impacts (Lynam and Keeler, 2005; Liu et al., 2007, 2010). Using these techniques, we continuously monitored speciated atmospheric Hg in Chicago, IL and Holland, MI from July to November 2007. We used HYSPLIT back-trajectories to model the dominant air
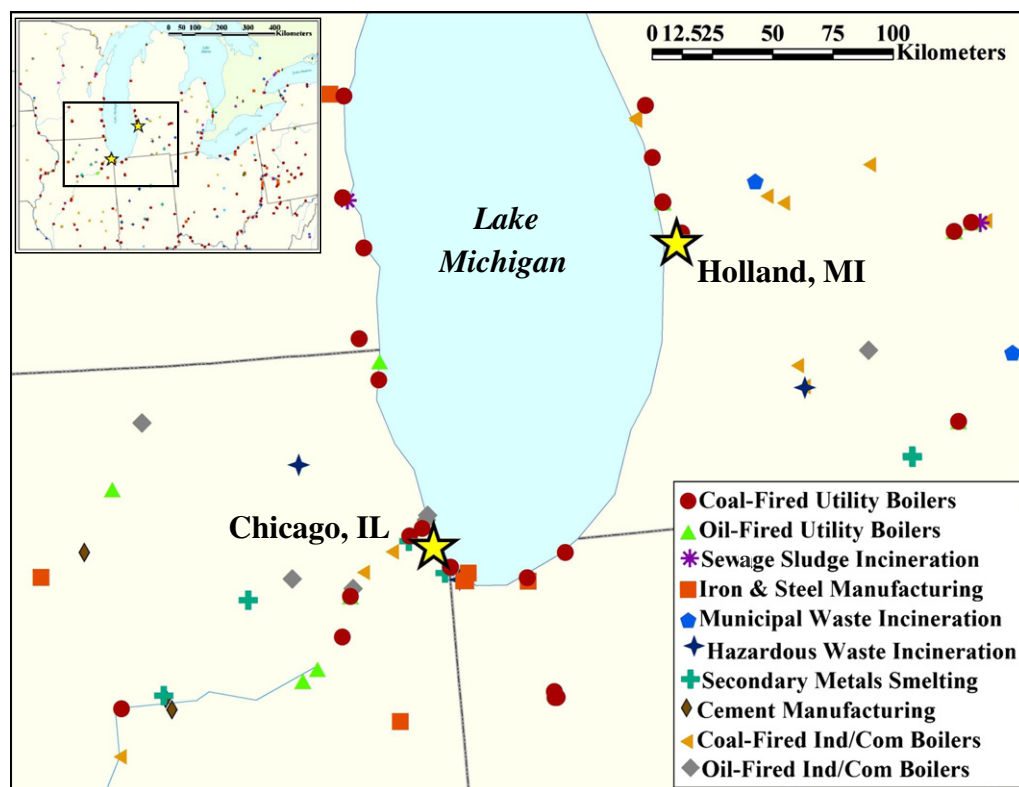

Fig. 1. Location of the Chicago, IL and Holland, MI monitoring sites and major Hg point sources emitting ≥0.1 kg (≥0.0001 tons) of Hg per year (US EPA NEI, 2005; Environment Canada NPRI, 2007).

Table 1

Summary statistics for speciated ambient Hg measurements at Chicago, IL and Holland, MI (Jul 1–Nov 8, 2007).

	Hg^0 (ng/m^3)		RGM (pg/m^3)		Hg_p (pg/m^3)	
	Chicago	Holland	Chicago	Holland	Chicago	Holland
Mean	2.5	1.3	17	8	9	6
SD	1.5	0.3	87	15	20	4
Median	1.9	1.3	6	2	5	6
25%	1.6	1.2	3	0	3	3
75%	2.8	1.4	13	9	8	8
Max	16.5	6.0	2707	137	401	31
N	1339	1489	1339	1489	1339	1489

mass transport patterns to the sites. We then applied the HYSPLIT dispersion model to two case studies (July 29–August 3, 2007 and August 26–29, 2007) to (a) support the upwind air mass history suggested by the measurements, and (b) estimate the fraction of primary RGM emissions directly transported from Chicago/Gary sources to the downwind Holland site relative to that which was produced through Hg^0 oxidation during transport.

2. Materials and methods

2.1. Site descriptions

The Chicago, IL site was located at the University of Chicago Kersten Physics building (41.791 N, 87.602 W) in southern downtown Chicago, approximately 2 km west of Lake Michigan. The speciated Hg sampling inlet was positioned on the roof of the Kersten building (approximately 20 m above ground level (AGL)). This site was in close proximity to emission point sources along southern Lake Michigan in the Chicago/Gary industrial region (Fig. 1). For the purposes of this study, we defined the Chicago/Gary urban area as the 16-county Chicago–Naperville–Joliet combined statistical area. This defined area encompasses all major emission point sources within 100 km of the Chicago monitoring site that reportedly emit > 0.1 kg of Hg (approximately 0.0001 tons) per year (U.S. EPA NEI, 2005; Fig. 1).

The Holland, MI site was located at the Michigan Department of Environmental Quality (MDEQ) monitoring station (42.768 N, 86.149 W) in an open area of a residential park that is approximately 5 km east of Lake Michigan and 162 km northeast of the Chicago site (Fig. 1). The speciated Hg sampling inlet was positioned on the roof of
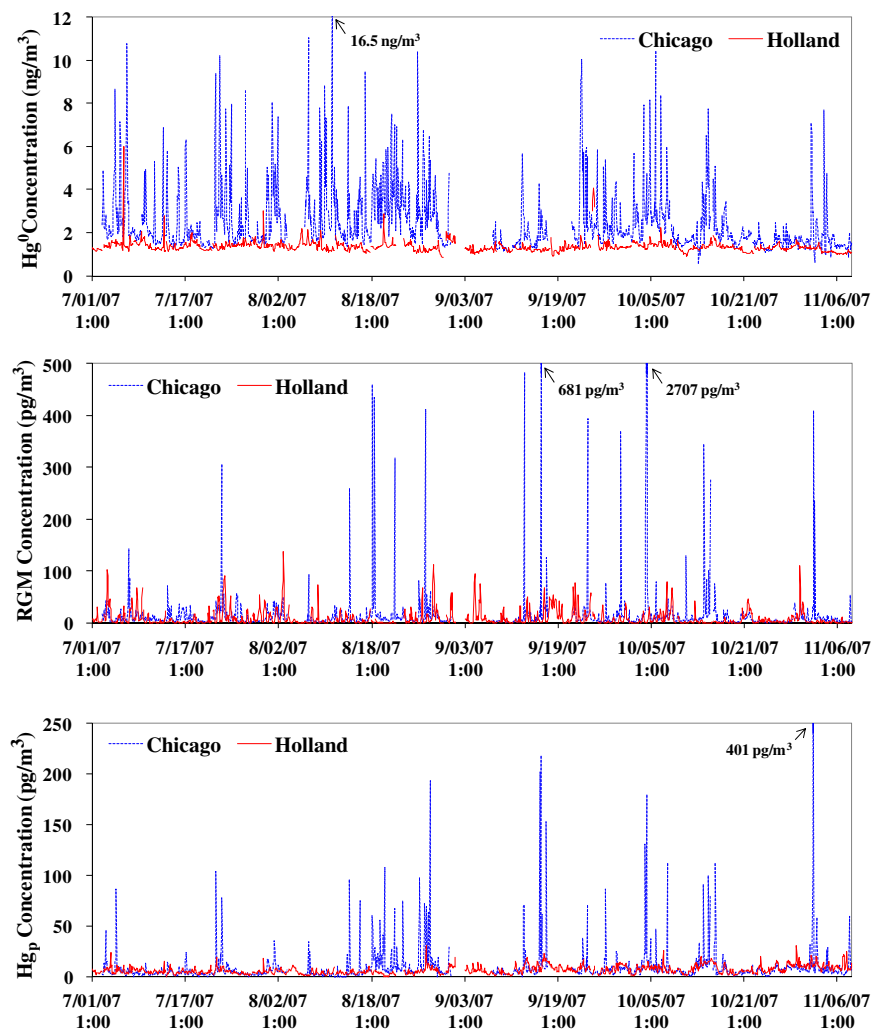

Fig. 2. Time series of semi-continuous Hg^0, RGM, and Hg_p concentrations at Chicago and Holland from July 1 to November 8, 2007. All times are reported in Eastern Standard Time (EST).
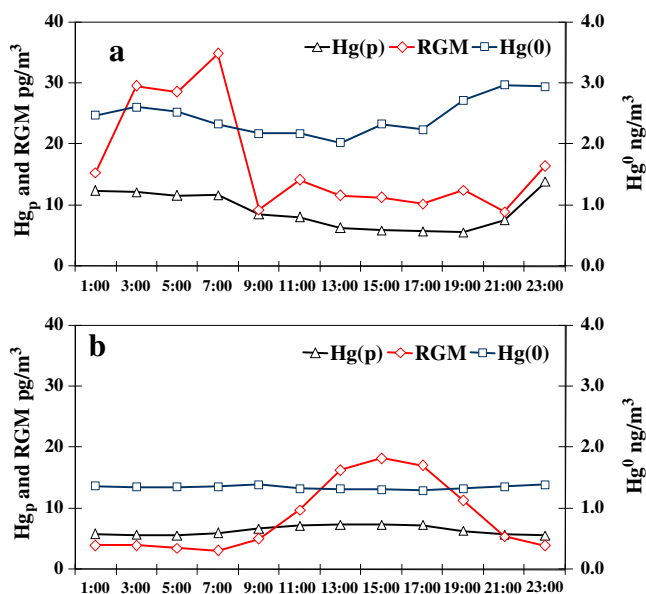
Fig. 3. Hourly average speciated ambient Hg concentrations at the (a) Chicago and (b) Holland sites.

Hg_p has been defined as three times the standard deviation of the system blank over the course of the study (Landis et al., 2002a), where for the speciated Hg system the system blank is the third zero air flush at the start of the analysis period (Liu et al., 2007, 2010). We determined accordingly that the method detection limit for RGM and Hg_p was 1.7 pg/m^3 in Chicago and 0.6 pg/m^3 in Holland.

In analyzing and reporting the speciated Hg data, we operationally defined the timing for speciated Hg measurements as the hour at which the 1-hour sampling period concluded and the 1-hour analytical cycle began. The summary statistics for Chicago and Holland demonstrated that speciated ambient Hg concentrations at both sites were not normally distributed; thus in any comparative statistical analyses of Hg concentrations and auxiliary data we used primarily non-parametric statistics, including median values and Spearman correlation coefficients (R_S).

We collected continuous meteorological data in Chicago using the Vaisala® Weather Transmitter WXT510. Hourly ozone concentrations in Chicago were measured by the Illinois EPA Cook County Branch using a Dasibi 1008-RS ozone analyzer. The MDEQ provided meteorological data from the Holland site for the entire monitoring period and ozone data from July 1 to September 30, 2007. At the Holland site we additionally collected ozone measurements from October 1 to November 8, 2007 and SO$_2$ measurements from July 28 to November 8, 2007 using TEI 49C and TEI 43C analyzers, respectively.

2.3. Meteorological back-trajectories

We modeled air mass transport to the two sites using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model Version 4.8 (Draxler and Hess, 1998). We computed 24-hour HYSPLIT back-trajectories using the National Weather Service's National Center for Environmental Prediction (NCEP) Eta Data Assimilation System (EDAS) 40 km gridded meteorological data, which was provided by the National Oceanic and Atmospheric Administration's Air Resources Laboratory (NOAA-ARL). The 24-hour back-trajectories were adequate for describing the transport between the sites while also accounting for transport from other major regional urban areas (e.g. St. Louis, MO and Detroit, MI). We computed trajectories starting every 2 h corresponding to the same times assigned to the speciated ambient Hg measurements. The starting height was set to one-half of the mixed layer depth, as determined by the HYSPLIT model, to best represent transport within the boundary layer. We performed cluster analysis of trajectories using Ward's Minimum-Variance method (Ward, 1963; Landis et al., 2002b). Nine clusters were determined for each site, explaining 80% of the variance in each dataset. Wilcoxon and Kruskal–Wallis tests indicated that the Hg^0, Hg$_p$, and RGM concentrations at each site were significantly different by cluster.

the MDEQ trailer (approximately 5 m AGL). A few Hg emission sources are located near the site, including one CFUB in Holland that emits approximately 0.004 tpy of Hg (U.S. EPA NEI, 2005) and three other CFUBs along the Lake Michigan shoreline north of Holland that collectively emit approximately 0.3 tpy of Hg (U.S. EPA NEI, 2005). The Holland site was south and west (i.e. upwind) of these major local sources so that there was minimal influence from those sources during west–southwest transport from the Chicago/Gary area (Fig. 1).

2.2. Data collection and analysis

Atmospheric monitoring at the Chicago and Holland sites began on July 1, 2007 and continued through November 8, 2007. We simultaneously measured Hg^0, RGM, and Hg$_p$ (<2.5 μm) at the two sites using the Tekran® 2537A/1130/1135 automated Hg sampling system. Data was collected semi-continuously on 2-hour intervals, consisting of a one-hour sampling period followed by a one-hour desorption and analysis period. The Tekran 1130/1135 inlet flow rate was 10 L/min. The Tekran 2537A flow rate was 1 L/min and the sampling interval was 5 min. We implemented the sampling method for the Tekran speciation systems, including instrument settings, temperatures, and flow rates according to previously reported techniques (Liu et al., 2010). We also prepared all materials for the Tekran system in the University of Michigan Air Quality Laboratory following previously reported clean techniques (Liu et al., 2010). We conducted routine weekly maintenance on the Tekran systems, including performing internal permeation source calibrations of the 2537A, replacing inlet filters, and changing the KCl-coated annular denuder. We changed the 1130 inlet assembly bi-weekly and replaced the 1135 regenerable particulate filter (RPF) every two months.

The precision of the Tekran 2537A is 2%, and the average method detection limit reported for the Tekran 2537A Hg^0 measurements is 0.06 ng/m^3 (Poissant et al., 2005; Liu et al., 2007, 2010). The precision of the Tekran 1130 and 1135 is not well known due to the lack of an available standard reference source for testing these instruments. However, Landis et al. (2002a) demonstrated through collection of collocated samples that the precision of manual KCl-coated annular denuders was $15.0 \pm 9.3\%$. The method detection limit for RGM and

Table 2
Median and maximum speciated Hg concentrations computed in 24-hour HYSPLIT back-trajectory clusters for Chicago, IL.

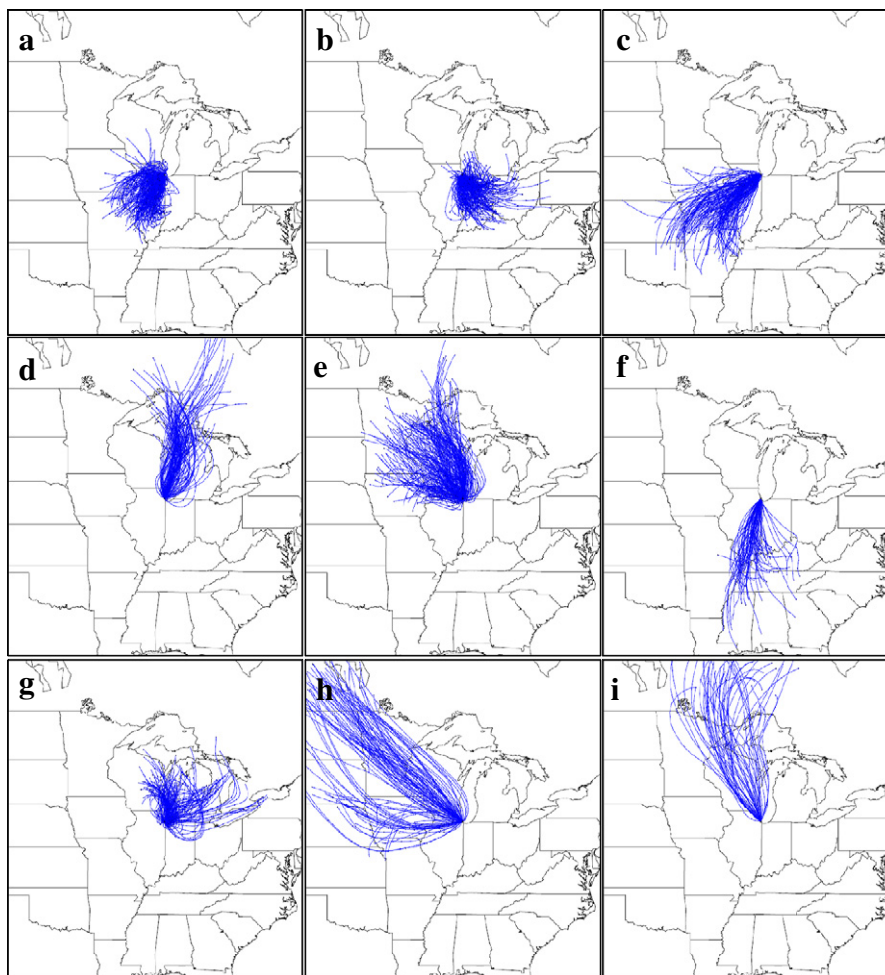| Cluster	Frequency	Hg^0 (ng/m^3)		RGM (pg/m^3)		Hgp (pg/m^3)	
		Median	Max	Median	Max	Median	Max
4a	19%	2.1	11.1	8	344	6	131
4b	17%	2.7	10.4	14	2707	10	218
4c	11%	2.0	8.7	6	36	4	29
4d	9%	1.6	10.4	3	43	2	29
4e	16%	1.8	9.5	3	409	4	401
4f	5%	1.9	3.4	7	43	5	15
4g	11%	2.2	16.5	6	460	4	202
4h	7%	1.5	7.1	4	28	5	31
4i	3%	1.4	5.3	3	130	3	11

Fig. 4. Cluster analysis of HYSPLIT 24-hour back-trajectories corresponding to the semi-continuous speciated ambient Hg measurements in Chicago, IL.

2.4. Dispersion modeling

We also used the HYSPLIT model to calculate the dispersion and deposition of Hg emissions from the Chicago/Gary source region during the two case studies. HYSPLIT uses the gridded meteorological data to calculate atmospheric advection and dispersion of pollutants released from a given location (Draxler and Hess, 1998). Plume dispersion was modeled using horizontal top-hat puff and vertical particle equations (Draxler and Hess, 1998). We used the model default parameters for puff splitting/merging and puff/particle release limits. We examined the plume dispersion from 0 m to 500 m AGL. Concentrations within the plume were calculated over a horizontal grid of 0.1° latitude by 0.1° longitude (approximately 10 km) using a 2-hour averaging interval. Atmospheric reactions during transport were not included in the model.

Given that CFUBs contribute approximately 76% of the total Hg point source emissions from the Chicago/Gary industrial area, to provide geographical reference for emissions from Chicago/Gary we released the modeled puffs from the location of a CFUB that is approximately 50 km southwest of the Chicago site and is the largest Hg emission point source in the defined Chicago/Gary area (41.495 N, 88.125 W) (U.S. EPA NEI, 2005). We released the modeled puffs continuously at one mass unit per hour from the stack height for this facility (137 m AGL; also the average stack height for all CFUBs in Chicago/Gary). We then used the annual total Hg emission rate reported for all CFUBs in the defined Chicago/Gary area (2558 kg/year; U.S. EPA NEI, 2005) and assumed continuous emissions (24 h/day, 365 days/year) to calculate an hourly total Hg emission rate

from the source location of 0.292 kg/year. Although this emission rate does not include the Hg emissions from various other point sources in the area, the relative fractions of speciated Hg emissions vary by source type and, unlike CFUBs, the speciated emissions for most other point source categories are not reported in the 2005 NEI. Furthermore, the average stack heights of other Hg point sources in Chicago/Gary are substantially lower than the average CFUB stack height. Consequently, these other source types may be more likely to have local scale impacts, whereas Hg emissions from the much taller CFUB stacks are more capable of being transported regionally. For these reasons, in this study we focused our attention on the speciated Hg emissions from Chicago/Gary CFUBs. We further assumed the fraction of RGM in Hg emissions from a typical CFUB as a

Table 3
Median and maximum speciated Hg concentrations computed in 24-hour HYSPLIT back-trajectory clusters for Holland, MI.

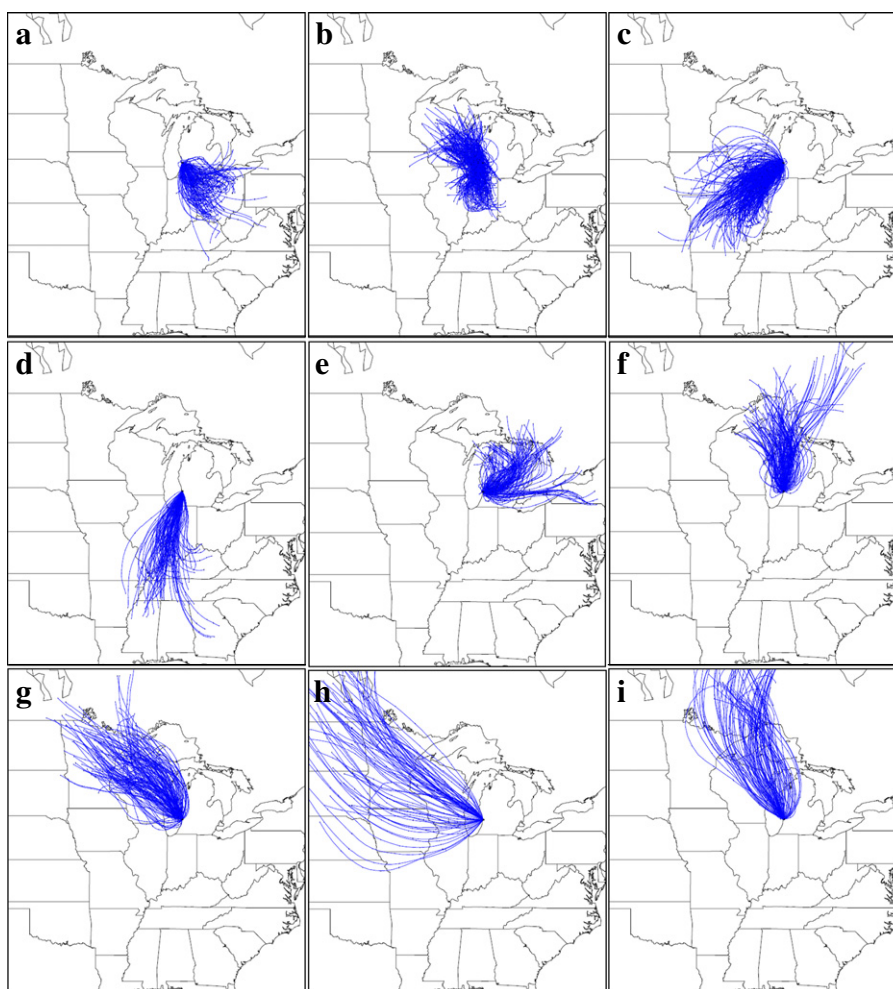|	Max	Max	Hg^0 (ng/m^3)		RGM (pg/m^3)		Hg$_p$ (pg/m^3)	
			Median	Max	Median	Max	Median	Max
5a	8%		1.4	2.9	2	90	8	30
5b	25%		1.4	3.0	1	103	5	23
5c	20%		1.4	4.1	6	137	6	31
5d	7%		1.3	4.1	14	112	6	15
5e	9%		1.3	1.9	2	53	4	19
5f	10%		1.2	6.0	1	68	4	24
5g	9%		1.3	2.8	2	43	5	18
5h	5%		1.3	1.6	1	54	7	21
5i	6%		1.2	1.5	1	72	4	22

Fig. 5. Cluster analysis of HYSPLIT 24-hour back-trajectories corresponding to the semi-continuous speciated ambient Hg measurements in Holland, MI.

reasonable first approximation. We assumed that 50% of total Hg emissions were RGM, but acknowledged that RGM could constitute anywhere from 25% (the average fraction of RGM in Chicago/Gary CFUB emissions reported in the U.S. EPA NEI (2005)) to 80% (Carpi, 1997) of total CFUB Hg emissions.

Dry deposition occurs in the HYSPLIT model only when the puff or particle is within the surface layer (the lowest above-ground layer and the model's second meteorological level; approximately 75 m) (Draxler and Hess, 1998). We selected a deposition velocity of 0.006 m/s to represent a typical RGM deposition velocity under relatively stable atmospheric conditions (Marsik et al., 2007). Although dry deposition velocity can fluctuate diurnally and over land and water due to variability in atmospheric turbulence and stability (Malcolm and Keeler, 2002; Zhang et al., 2003; Marsik et al., 2007), we used a constant dry deposition velocity as a reasonable first approximation because transport through the stable atmosphere over Lake Michigan was of the greatest interest. We did not include wet deposition in the model because it did not rain during the case study periods.

3. Results and discussion

3.1. Speciated ambient Hg summary statistics and temporal variability

Differences in the distribution and range of observed speciated ambient Hg concentrations at the two sites provide evidence for the impact of urban/industrial sources on the Chicago monitoring site

and the relative dearth of local sources impacting the Holland site (Table 1; Fig. 2). The semi-continuous concentrations of Hg^0, Hg_p, and RGM were significantly different between Chicago and Holland (Kruskal–Wallis, $p < 0.001$). The median Hg^0 and RGM concentrations in Chicago were 1.4 and 2.7 times greater, respectively, than in Holland. Although the median Hg_p concentrations were similar in Chicago and Holland, the range in concentrations measured in Chicago was noticeably larger.

Elemental Hg concentrations in Holland displayed a relatively narrow distribution, with a maximum concentration of 6.0 ng/m³ but a 75th percentile value of only 1.4 ng/m³. In contrast, Hg^0 in Chicago had a much wider distribution with concentrations up to 16.5 ng/m³. Although the median Hg^0 concentration in Chicago (1.9 ng/m³) was only marginally above the suggested global background in the Northern Hemisphere (1.5–1.7 ng/m³) (Lindberg et al., 2007), the semi-hourly concentrations were extremely variable, suggesting that local source emissions impacted the site frequently (Fig. 2).

Local source emissions in Chicago were also evident in the RGM concentrations, where interestingly the mean was larger than the 75th percentile as numerous peaks in RGM concentration were well above the median (Fig. 2). Similarly, the mean Hg_p in Chicago was also greater than the 75th percentile. The impact of a local source was particularly evident in the maximum RGM concentration at Chicago (2707 pg/m³), which occurred in the early morning hours in conjunction with elevated Hg^0 (4.8 ng/m³) and Hg_p (180 pg/m³). In contrast, RGM concentrations in Holland displayed a much narrower distribution with a maximum concentration of 137 pg/m³.
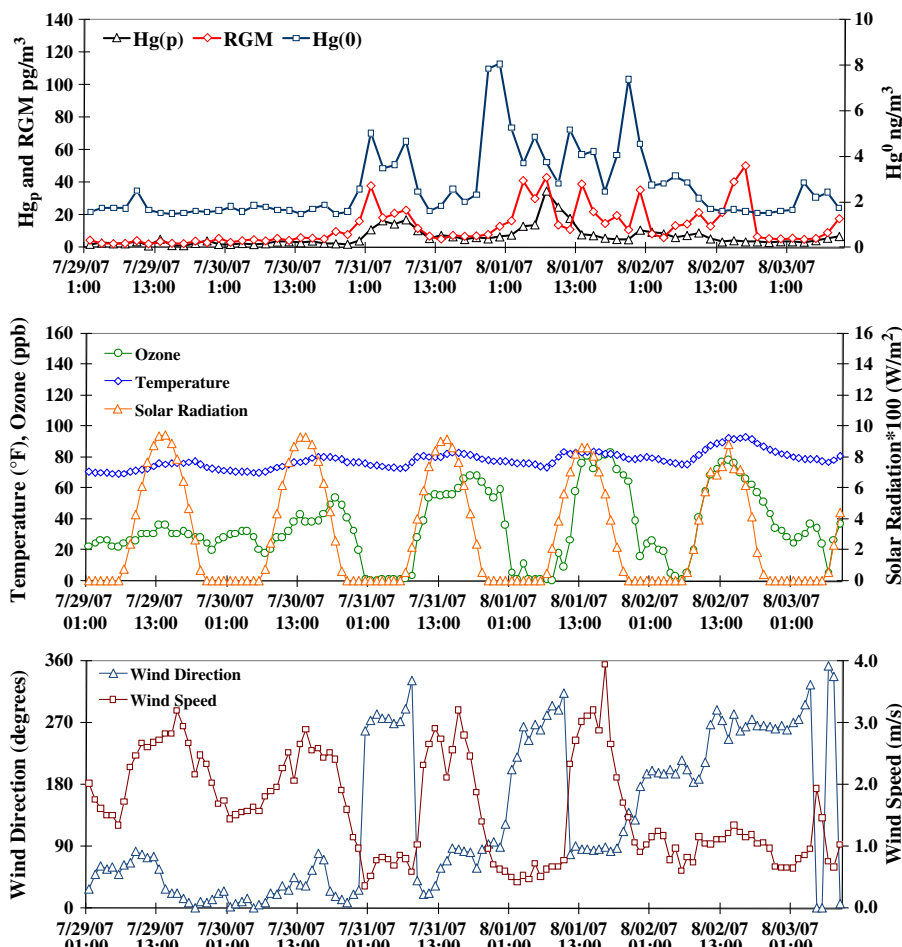
Fig. 6. Speciated Hg, ozone and meteorological measurements in Chicago, IL on July 29–August 3, 2007.

We observed a much greater range and variability in RGM concentrations at both Chicago and Holland relative to Hg$_p$ (Table 1; Fig. 2). In Chicago, this was likely due, in part, to the dominance of RGM over Hg$_p$ in combustion emissions (Carpi, 1997). At both sites, this observed pattern during our summertime study appears consistent with past observations suggesting that Hg(II) tends to exist primarily in the gas phase (RGM) when ambient temperatures are elevated and increased photochemical activity can result in the conversion of Hg^0 to RGM by ozone and other oxidants (Liu et al., 2010). In colder winter months, as well as in high humidity situations, there is a greater propensity for reactive Hg to partition into the condensed phase and bind to particles (Hg$_p$) (Lynam and Keeler, 2005; Liu et al., 2010).

Consistent with this hypothesis, over the course of the study we observed that RGM in Holland was significantly (p<0.0001) positively correlated with ozone (R$_S$=0.61), temperature (R$_S$=0.53), and solar insolation (R$_S$=0.45), and negatively correlated with relative humidity (R$_S$=−0.67). In Chicago, RGM was also positively correlated with ozone (R$_S$=0.09, p<0.001), temperature (R$_S$=0.31, p<0.0001), and solar insolation (R$_S$=0.16, p<0.0001), and negatively correlated with relative humidity (R$_S$=−0.37, p<0.0001); however, the weaker relationships between RGM and these parameters in Chicago (relative to the correlation coefficients for Holland) may reflect the more dominant impact from local source emissions on observed Hg concentrations.

Speciated Hg concentrations also displayed varying diurnal patterns between the two sites. In Chicago the largest peaks in Hg^0, RGM, and Hg$_p$ occurred predominantly during the evening and early morning (19:00–7:00 EST) (Fig. 3). This may suggest the effect of reduced vertical mixing in the stable nighttime boundary layer, which

allowed for a buildup of the atmospheric burden of the three species due to local source emissions. Daytime RGM and Hg$_p$ peaks also occurred at Chicago, but typically in sudden sharp increases under southeasterly flow.

Elevated Hg^0 concentrations in Holland occasionally occurred during the night and early morning hours under northerly or easterly flow, which may have transported emissions from local sources. Peak Hg$_p$ concentrations at Holland occurred during both day and nighttime hours, but more noticeable was the increased frequency of elevated Hg$_p$ concentrations during October and November (Fig. 2) with temperatures<20 °C, perhaps suggesting the increased preference for Hg(II) to bind to particles under cooler temperatures.

Unlike Hg^0 and Hg$_p$, elevated RGM concentrations in Holland occurred almost entirely during daytime hours (11:00–19:00 EST) (Fig. 3). These concentrations typically occurred with southwesterly winds and temperatures>15 °C. Hourly ozone concentrations in Holland were also typically elevated during the afternoon hours, likely due to transported precursor species and daytime photochemical activity. These conditions suggest that elevated RGM concentrations in Holland were strongly related to daytime photochemistry as well as transport from the Chicago/Gary region.

3.2. Meteorological back-trajectory cluster analysis

In Chicago, the highest median Hg concentration occurred in a cluster representing southeasterly flow from the highly industrialized local urban area (Table 2; Fig. 4b). In this transport regime the median Hg^0 concentration was 49% greater while Hg$_p$ and RGM were each
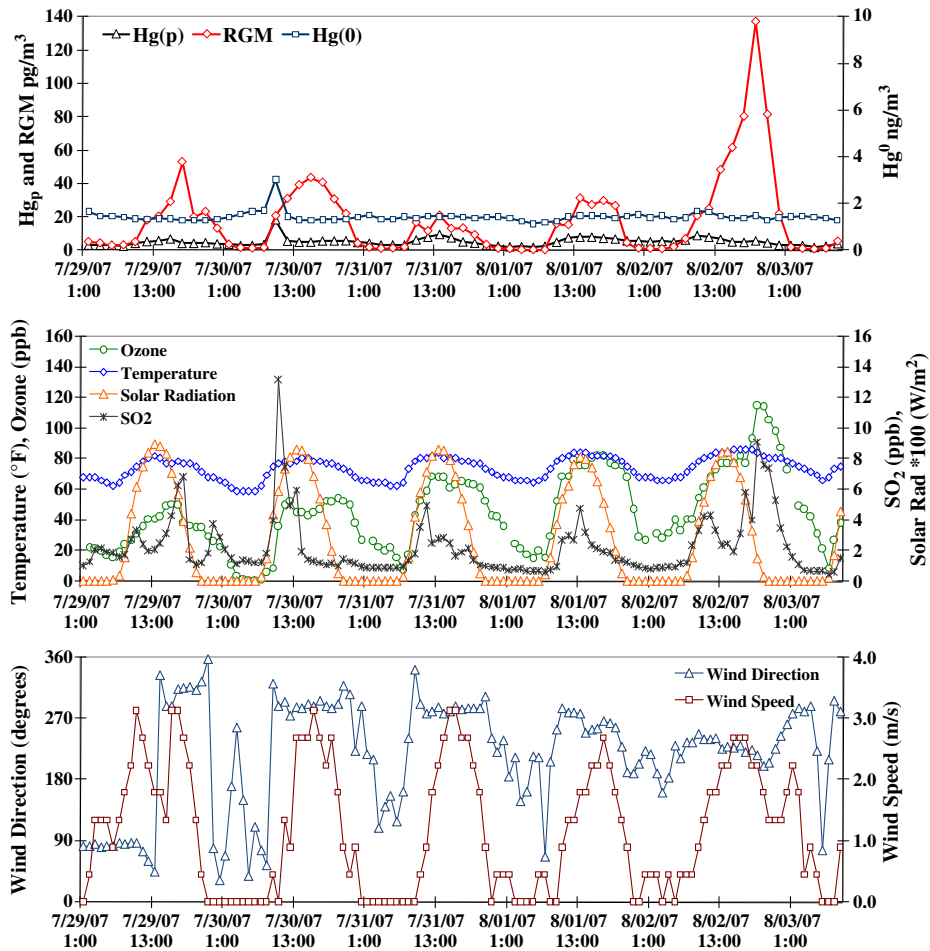
Fig. 7. Speciated Hg, ozone, SO₂, and meteorological measurements in Holland, MI on July 29–August 3, 2007.

more than two times greater than the median concentrations in the other eight clusters. All three Hg species were significantly positively correlated in this southeasterly cluster ($R^S_{Hg-RGM} = 0.16$, $p = 0.02$; $R^S_{Hg-Hg_p} = 0.20$, $p = 0.003$; $R_{S\ RGM-Hg_p} = 0.46$, $p < 0.0001$). A positive correlation between Hg^0 and RGM has been predicted for locations under the influence of direct source emissions, given that the chemical conversion between Hg^0 and RGM is thought to be fairly slow (Sillman et al., 2007). The lowest median Hg concentrations occurred with northerly transport, often with flow across the lake (Table 2; Fig. 4d and 4i).

In Holland, the highest Hg concentrations occurred under south-southwesterly flow (Table 3; Fig. 5c and 5d). The median Hg^0 and Hg_p concentrations across these two clusters were 6% and 8%, greater, respectively, than the median concentrations of Hg^0 and Hg_p observed across the other modeled transport regimes. However, the Hg_p enhancement was not statistically significant. Most interestingly, the median RGM concentration under south-southwesterly flow was five times greater than the median RGM concentration of the other modeled transport regimes. It is has been predicted that Hg^0 and RGM should be anti-correlated when RGM is formed primarily through photochemical oxidation of Hg^0 (Sillman et al., 2007). Furthermore, elevated RGM may also be observed together with persistently elevated ozone due to the production of these two species from similar photochemical mechanisms (Sillman et al., 2007). In this study, the median ozone concentration under south-westerly flow was 39 ppb, while the median ozone concentration for all other clusters was 23 ppb. Under south-southwesterly flow at Holland, RGM was significantly positively correlated with ozone ($R_{S\ 5c} = 0.54$; $R_{S\ 5d} = 0.48$; $p < 0.0001$). In cluster 5c Hg^0 was not significantly correlated with RGM or ozone, whereas in cluster 5d, Hg^0 was negatively
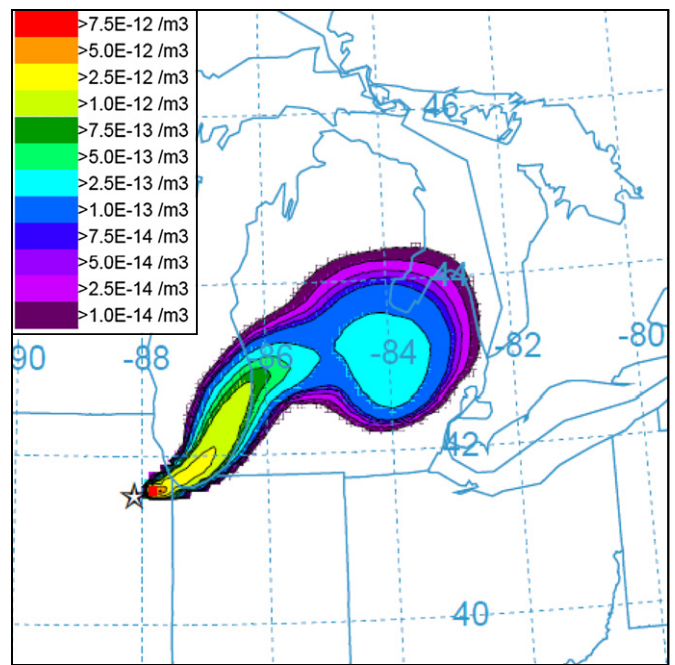

Fig. 8. HYSPLIT dispersion model output integrated from 18:00 EST on August 2, 2007 to 20:00 EST August 2. Contours represent the concentration in g/m³ (averaged between 0 and 500 m AGL) of continuous emissions dispersed from the source location (41.495 N, 88.125 W; 137 m AGL).
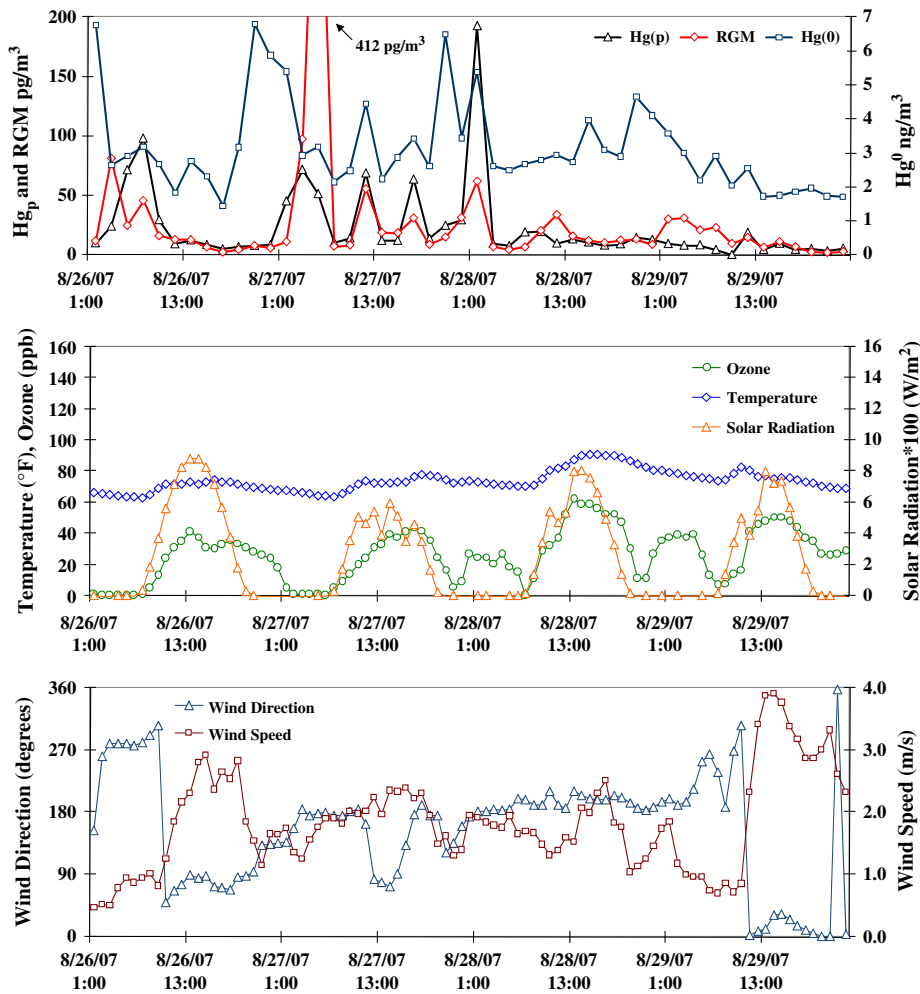
Fig. 9. Speciated Hg, ozone, and meteorological measurements in Chicago, IL on August 26–29, 2007.

correlated with both RGM ($R_S = -0.32$, $p = 0.001$) and ozone ($R_S = -0.24$, $p = 0.02$). These varying relationships may suggest a combination of direct transport of emissions and photochemical activity affecting speciated Hg concentrations in Holland under south-southwesterly flow.

Under northerly flow at Holland (Table 3; Fig. 5f and 5i), the median concentrations of Hg^0, Hg_p, and RGM were significantly less (11%, 32%, and 83%, respectively) than the median concentrations observed under southwest flow. In these clusters a positive correlation between RGM and Hg^0 ($R_{S \, 5f} = 0.18$, $p = 0.04$; $R_{S \, 5i} = 0.29$, $p = 0.006$) may suggest an impact of direct Hg emissions from sources north of the site (Fig. 1; Sillman et al., 2007).

3.3. Case studies and HYSPLIT dispersion modeling

3.3.1. Case study #1: July 29–August 3, 2007

In this case study we examined the passage of a high pressure center over Lake Michigan and the impact of the associated clockwise flow on ambient Hg concentrations at the monitoring sites. Figs. 6 and 7 display the speciated Hg and auxiliary measurements from Chicago and Holland, respectively, during the case study period. On July 29–30, the high-pressure system was northwest of Chicago, at which time northeasterly flow over the lake resulted in relatively low Hg concentrations at the site. In Holland, we observed predominantly easterly transport during evening and early morning hours, and north-northwesterly transport

during the day. RGM concentrations varied diurnally with wide daytime peaks suggesting the impact of photochemical activity and RGM production. The occasional influence of local source emissions was evidenced by concurrent peaks in speciated Hg and SO_2 under northerly flow. The high-pressure system progressed eastward over southern Lake Michigan between July 31 and August 1. In Chicago, diurnally varying wind speed and direction coincided with fluctuating speciated Hg concentrations, with elevated levels observed predominantly in the evening and early morning when local emissions were contained within the boundary layer.

By the morning of August 2, the high-pressure system moved east of southern Lake Michigan, generating southwesterly flow behind it. In Holland on the afternoon of August 2, under consistent south-southwesterly flow, RGM concentrations reached the maximum for the period (137 pg/m³). Hourly ozone and SO_2 concentrations simultaneously increased in relatively sharp peaks (115 ppb and 7.6 ppb, respectively). The RGM peak in Holland was approximately 2.5 times greater than the largest RGM peak observed during the previous four days.

We applied the HYSPLIT dispersion model for 48 h from 8:00 EST on August 1 to 8:00 EST on August 3. Initially, the modeled plume gradually expanded northward with little east–west dispersion until approximately 22:00 EST on August 1 when it began to disperse over the lake following the eastward movement of the high pressure system. The plume first intercepted the Holland site at approximately
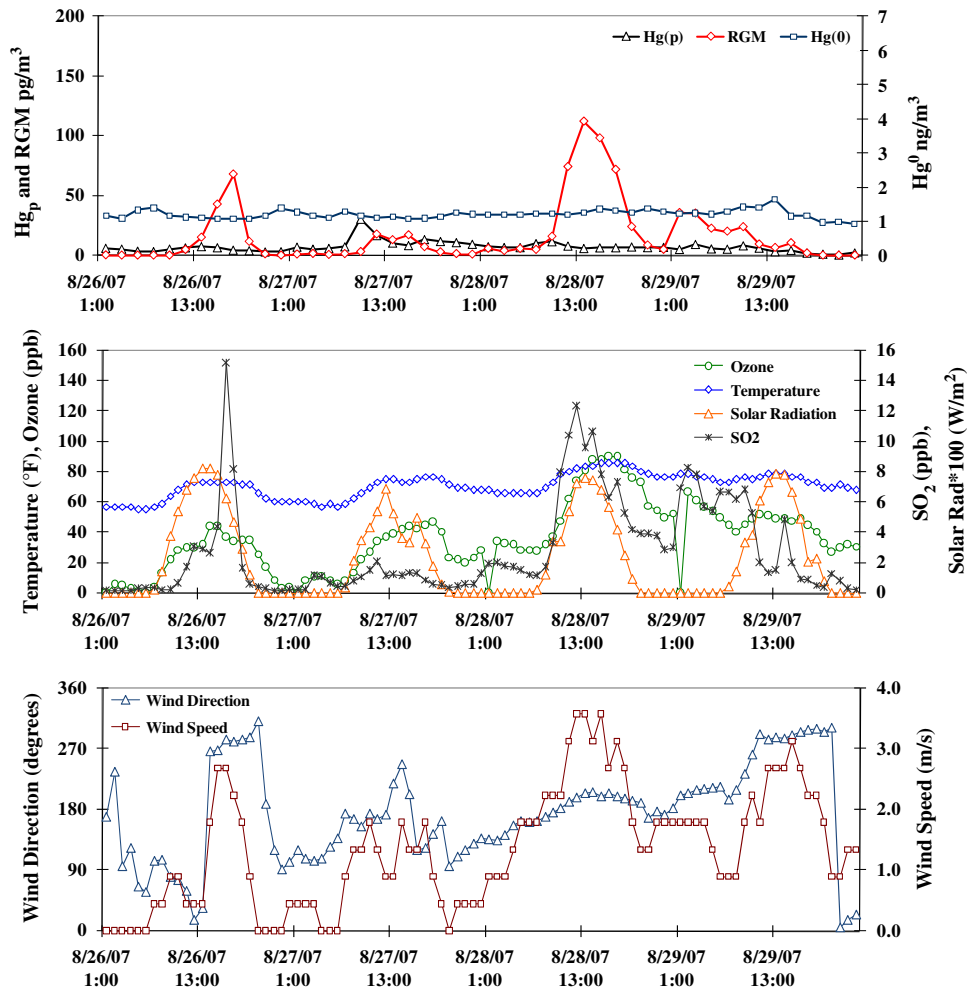
Fig. 10. Speciated Hg, ozone, SO₂, and meteorological measurements in Holland, MI on August 26–29, 2007.

6:00 EST on August 2 and continued on a northeast trajectory. Fig. 8 displays the plume contours at the time of the RGM maximum in Holland.

Using the grid-to-station feature (con2stn) of the HYSPLIT model, we determined that the model-predicted two-hour average concentration at the Holland site from 18:00 to 20:00 EST on August 2 was 0.91 pg/m³. Given that this model-estimated concentration was based upon a modeled emission rate of 1 g/h, we calculated that the emission rate required to produce the observed RGM peak concentration (137 pg/m³) through direct transport of RGM source emissions was 151 g/h (0.151 kg/h).

Using the continuous total Hg emission rate from Chicago/Gary of 0.292 kg/h (obtained from the reported annual total Hg emissions from Chicago/Gary CFUBs; U.S. EPA NEI, 2005), and assuming that 50% of these emissions are RGM, we determined an RGM emission rate of 0.146 kg/h. Comparing this value to the required emission rate (0.151 kg/h) calculated from the model results, we determined that direct transport and dispersion of RGM emissions from Chicago/Gary CFUBs could potentially account for 97% of the observed RGM peak in Holland on August 2. The remainder can be attributed to RGM production en route through Hg⁰ oxidation. Acknowledging that RGM may constitute anywhere from 25% (U.S. EPA NEI, 2005; 0.073 kg/h) to 80% (Carpi, 1997; 0.234 kg/h) of total CFUB Hg emissions, then primary RGM emissions from Chicago/Gary CFUBs could account for between 48% and 100% of the observed RGM peak in Holland.

The sharp nature of the observed RGM peak in Holland is consistent with a large estimated contribution from direct transport of RGM source emissions. However, the observed speciated Hg concentrations in Chicago prior to the RGM peak in Holland actually showed relatively low RGM concentrations and greater levels of observed Hg⁰, indicating that perhaps RGM production from Hg⁰ oxidation during transport was important in producing the RGM peak in Holland than the HYSPLIT model suggests; therefore, in this case the lower end of the calculated fraction due to direct RGM emissions transport may be more representative of the actual conditions.

3.3.2. Case study #2: August 26–29, 2007

Here we examined the influence of rapid southwest flow in advance of a frontal passage on the transport of Chicago/Gary source emissions to Holland. Figs. 9 and 10 display the speciated Hg and auxiliary measurements from Chicago and Holland, respectively, during this case study period. From the afternoon of August 26 until the morning of August 28, relatively consistent southeasterly flow brought local source emissions to the Chicago site, producing large and variable peaks in Hg⁰, RGM, and Hg_p. On August 26 in Holland, north-northwesterly winds during the day were associated with elevated levels of RGM in conjunction with ozone and SO₂. In particular, a sudden substantial rise in SO₂ and RGM under northwesterly flow was suggestive of local combustion source emissions.

On August 28, rapid southwesterly transport occurred throughout the afternoon in advance of an ensuing cold front from the northwest. In Chicago, RGM and Hg_p concentrations decreased while Hg⁰ remained steady. In contrast, the RGM concentration in Holland rose to 112 pg/m³, the maximum for this three-day period. Ozone and SO₂ increased in Holland (90 ppb and 11 ppb, respectively) in
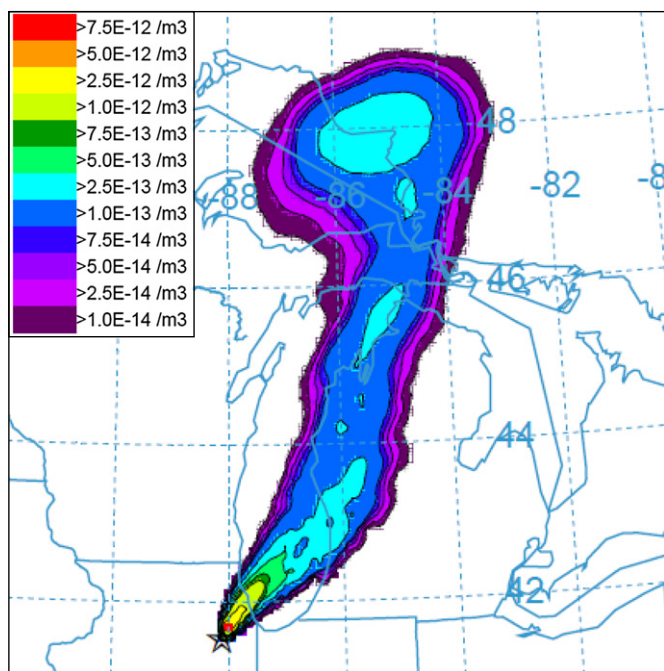
Fig. 11. HYSPLIT dispersion model output integrated from 12:00 EST on August 28, 2007 to 14:00 EST on August 28, 2007. Contours represent the concentration in g/m^3 (averaged between 0 and 500 m AGL) of continuous emissions dispersed from the source location (41.495 N, 88.125 W; 137 m AGL).

conjunction with RGM. The smaller SO_2 peak on August 28 under southwesterly flow from Chicago/Gary (relative to that observed under local source influences on August 26) likely reflects the difference in transport distance between the source and receptor in these two situations. However, the coinciding RGM peak on August 28 was approximately 1.6 times larger than the RGM peak observed on August 26, suggesting that a combination of greater Hg emissions from Chicago/Gary sources and/or the chemical production of RGM during transport influenced the concentration of RGM at the site.

We applied the HYSPLIT model for 48 h from 8:00 EST on August 27 to 8:00 EST on August 29. In this simulation, puff splitting was turned off by the model at the point when the limit for the maximum number of puffs was reached. The modeled plume behavior again appeared consistent with the observed air mass transport between Chicago and Holland during this period. Initially the plume traveled north–northwestward along the lakeshore before shifting eastward over Lake Michigan in the early morning on August 28. The plume was transported over Holland between 10:00 EST and 16:00 EST on August 28. From 16:00 EST on August 28 to 0:00 EST on August 29, the plume shifted slightly northward, and then moved steadily southward again, passing over the Holland site a second time. Fig. 11 displays the plume contours at the time of the RGM peak maximum in Holland on August 28.

Using the grid-to-station (con2stn) feature of the HYSPLIT model, we determined that the model-predicted two-hour average concentration at the Holland site from 12:00 EST to 14:00 EST on August 28 was 0.45 pg/m^3. Considering this value, and following the same calculation used in Case study #1, we determined that the emission rate required to produce the observed RGM peak concentration (112 pg/m^3) through direct transport of RGM source emissions was 0.251 kg/h. We again assumed the continuous total Hg emission rate from Chicago/Gary CFUBs (0.292 kg/h; U.S. EPA NEI, 2005) and 50% emission as RGM (0.146 kg/h). Comparing this emission rate to the model-estimated required emission rate (0.251 kg/h), we determined that direct transport and dispersion of RGM emissions from Chicago/Gary CFUBs could account for 58% of the observed RGM peak in Holland

on August 2. Acknowledging again the range in reported RGM fractions in total Hg emissions from combustion (25–80%), direct transport and dispersion could account for between 29% and 93% of the maximum RGM peak measured in Holland on August 28.

While these estimated fractions of RGM due to direct transport of source emissions are slightly lower than those calculated in the first case study, the half-width of the RGM peak on August 28 was noticeably larger than that observed on August 3. Furthermore, warm temperatures during transport and elevated ozone at the time of the RGM peak in Holland on August 28 were conducive to chemical reactions occurring within stable layers over the lake, lending support to the idea that perhaps a larger contribution to RGM came from Hg^0 oxidation than from direct dispersion in this case study period.

HYSPLIT also predicted the subsequent RGM peak observed on August 29 at 1:00 EST (Fig. 10). The model-predicted concentration in Holland at that time for a 1 g/h emission rate was 0.45 pg/m^3, the same as that predicted for the August 28 peak. In contrast, the observed nighttime peak in Holland on August 29 (36 pg/m^3) was nearly 70% less than the daytime peak on August 28 (112 pg/m^3), further indicating that daytime photochemistry was important in producing the elevated RGM concentration on August 28. In both case studies, a more complex modeling analysis including atmospheric chemistry mechanisms is needed to better understand the observed variability in speciated Hg concentrations; however, our estimates provide a useful first approximation for the fraction of observed RGM concentrations associated with transport of primary RGM source emissions.

4. Conclusions

These speciated Hg measurements from Chicago, IL and Holland, MI reveal substantial differences in ambient Hg concentrations at the urban and rural locations and provide valuable insight into the fate and transport of speciated Hg emissions. The corresponding air mass back-trajectory analysis suggests that ambient Hg concentrations, particularly RGM, in Holland were significantly enhanced under southwesterly flow from the Chicago/Gary urban area. The dispersion model analysis further elucidated the relative importance of direct dispersion of Chicago/Gary Hg source emissions versus the production of RGM via Hg^0 oxidation en route. Results suggest that both mechanisms substantially influence RGM concentrations at downwind receptors, and their relative importance likely depends on meteorological conditions, photochemical activity, and the presence of atmospheric oxidants. It is evident from these analyses that the emissions from an urban/industrial location such as Chicago/Gary can have a measurable impact on atmospheric Hg concentrations not only near emission sources, but also at downwind receptors. Therefore, regulating Hg emissions from major industrial sources should substantially reduce the amount of Hg available for deposition to both local and regional ecosystems.

References

Butler TJ, Cohen MD, Vermeylen FM, Likens GE, Schmeltz D, Artz RS. Regional precipitation mercury trends in the eastern USA, 1998–2005: declines in the Northeast and Midwest, no trend in the Southeast. Atmos Environ 2008;42:1582–92.

Carpi A. Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. Water Air Soil Pollut 1997;98:241–54.

Cohen MD, Artz RS, Draxler RR. Report to Congress: mercury contamination in the Great Lakes. Silver Spring, MD: NOAA Air Resources Laboratory; 2007.

Draxler RR, Hess GD. An overview of the HYSPLIT_4 modeling system for trajectories, dispersion and deposition. Aust Meteorol Mag 1998;47:295–308.

Dye TS, Roberts PT, Korc ME. Observations of transport processes for ozone and ozone precursors during the 1991 Lake Michigan Ozone Study. J Appl Meteorol 1995;34:1877–89.

Environment Canada. National Pollutant Release Inventory (NPRI) 2007. www.ec.gc.ca/inrp-npri/. site visited: 3-March-2010; site updated: 11-June-2012.

Gustin MS, Lindberg SE, Weisberg PJ. An update on the natural sources and sinks of atmospheric mercury. Appl Geochem 2008;23:482–93.

Harris RC, Rudd JWM, Amyot M, Babiarz CL, Beaty KG, Blanchfield PJ, Bodaly RA, Branfireun BA, Gilmour CC, Graydon JA, Heyes A, Hintelmann H, Hurley JP, Kelly CA, Krabbenhoft DP, Lindberg SE, Mason RP, Paterson MJ, Podemski CL, Robinson A, Sandilands KA, Southworth GR, St. Louis VL, Tate MT. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proc Natl Acad Sci 2007;104(42):16586–91.

Keeler GJ, Dvonch JT. Atmospheric mercury: a decade of observations in the Great Lakes. In: Pirrone N, Mahaffey K, editors. Dynamics of mercury pollution on regional and global scales: atmospheric processes and human exposures around the world. Kluwer Ltd.; 2005.

Keeler GJ, Glinsorn G, Pirrone N. Particulate mercury in the atmosphere: its significance, transport, transformation and sources. Water Air Soil Pollut 1995;80:159–68.

Landis MS, Keeler GJ. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan Mass Balance Study. Environ Sci Technol 2002;36:4518–24.

Landis MS, Stevens RK, Schaedlich F, Prestbo EM. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. Environ Sci Technol 2002a;36:3000–9.

Landis MS, Vette AS, Keeler GJ. Atmospheric mercury in the Lake Michigan Basin: influence of the Chicago/Gary urban area. Environ Sci Technol 2002b;36:4508–17.

Lin C, Pehkonen SO. Aqueous free-radical chemistry of mercury in the presence of iron oxides and ambient aerosol. Atmos Environ 1997;31:4125–37.

Lin C, Pehkonen SO. The chemistry of atmospheric mercury. Atmos Environ 1999;33:2067–79.

Lindberg S, Bullock R, Ebinghaus R, Engstrom D, Feng X, Fitzgerald W, Pirrone N, Prestbo E, Seigneur C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio 2007;36(1):19–32.

Liu B, Keeler GJ, Dvonch JT, Barres JA, Lynam MM, Marsik FJ, Taylor-Morgan J. Temporal variability of mercury speciation in urban air. Atmos Environ 2007;41:1911–23.

Liu B, Keeler GJ, Dvonch JT, Barres JA, Lynam MM, Marsik FJ, Taylor-Morgan J. Urban–rural differences in atmospheric mercury speciation. Atmos Environ 2010;44(16):2013–23.

Lynam MM, Keeler GJ. Automated speciated mercury measurements in Michigan. Environ Sci Technol 2005;39:9253–62.

Lyons WA, Cole HS. Photochemical oxidant transport: mesoscale lake breeze and synoptic-scale aspects. J Appl Meteorol 1975;15:733–43.

Malcolm EG, Keeler GJ. Measurements of mercury in dew: atmospheric removal of mercury species to a wetted surface. Environ Sci Technol 2002;36:2815–21.

Marsik FJ, Keeler GJ, Landis MS. The dry-deposition of speciated mercury to the Florida Everglades: measurements and modeling. Atmos Environ 2007;41:136–49.

McCarty HB, Miller K, Brent RN, Schofield J, Rossman R. Results of the Lake Michigan Mass Balance Study: mercury data report. . EPA 905 R-01-012Chicago, IL: U.S. EPA Great Lakes National Program Office; 2004 [http://www.epa.gov/greatlakes/lmmb/results/mercury/lmmbhg.pdf].

Orihel DM, Paterson MJ, Bodaly RA, Hintelmann H. Experimental evidence of a linear relationship between inorganic mercury loading and methylmercury accumulation by aquatic biota. Environ Sci Technol 2007;41:4952–8.

Poissant L, Pilote M, Beauvais C, Constant P, Zhang HH. A year of continuous measurements of three atmospheric mercury species (GEM, RGM, and Hg_p) in southern Quebec, Canada. Atmos Environ 2005;39:1275–87.

Schroeder WH, Munthe J. Atmospheric mercury — an overview. Atmos Environ 1998;32:809–22.

Seigneur S, Wrobel J, Constantinou E. A chemical kinetic mechanism for atmospheric inorganic mercury. Environ Sci Technol 1994;28:1589–97.

Seigneur C, Lohman K, Vijayaraghavan K, Jansen J, Levin L. Modeling atmospheric mercury deposition in the vicinity of power plants. J Air Waste Manage Assoc 2006;56:743–51.

Sillman S, Samson PJ, Masters JM. Ozone production in urban plumes transported over water: photochemical model and case studies in the Northeastern and Midwestern United States. J Geophys Res 1993;98:12,687–99.

Sillman S, Marsik FJ, Al-Wali KI, Keeler GJ, Landis MS. Reactive mercury in the troposphere: model formation and results for Florida, the northeastern United States, and the Atlantic Ocean. J Geophys Res 2007;112:D23305.

U.S. Environmental Protection Agency (U.S. EPA). An introduction to the issues and the ecosystems. . EPA-453/B-94/030Durham, NC: Office of Air Quality Planning and Standards; 1994.

U.S. Environmental Protection Agency (U.S. EPA). Mercury study report to Congress. . EPA-452/R-97-003Washington DC: Office of Air Quality Planning and Standards, Office of Research and Development; 1997.

U.S. Environmental Protection Agency (U.S. EPA). National Emissions Inventory (NEI) Data and Documentation 2005. www.epa.gov/ttnchie1/net/2005inventory.html. site visited: 3-March-2010; site updated: 11-December-2008.

Vette AS, Landis MS, Keeler GJ. Deposition and emission of gaseous mercury to and from Lake Michigan during the Lake Michigan Mass Balance Study (July, 1994–October, 1995). Environ Sci Technol 2002;36:4525–32.

Ward JH. Hierarchical grouping to optimize objective function. J Am Stat Assoc 1963;58:236–44.

Zhang L, Brook JR, Vet R. A revised parameterization for gaseous dry deposition in air-quality models. Atmos Chem Phys 2003;3:2067–82.