

## Evidence for short-range transport of atmospheric mercury to a rural, inland site

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### ABSTRACT

Atmospheric mercury (Hg) species, including gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate-bound mercury (Hg<sub>p</sub>), were monitored near three sites, including a cement plant (monitored in 2007 and 2008), an urban site and a rural site (both monitored in 2005 and 2008). Although the cement plant was a significant source of Hg emissions (for 2008, GEM:  $2.20 \pm 1.39$  ng m<sup>-3</sup>, RGM:  $25.2 \pm 52.8$  pg m<sup>-3</sup>, Hg<sub>p</sub>  $80.8 \pm 283$  pg m<sup>-3</sup>), average GEM levels and daytime average dry depositional RGM flux were highest at the rural site, when all three sites were monitored sequentially in 2008 (rural site, GEM:  $2.37 \pm 1.26$  ng m<sup>-3</sup>, daytime RGM flux:  $29 \pm 40$  ng m<sup>-2</sup> day<sup>-1</sup>). Photochemical conversion of GEM was not the primary RGM source, as highest net RGM gains ( $75.9$  pg m<sup>-3</sup>,  $99.0$  pg m<sup>-3</sup>,  $149$  m<sup>-3</sup>) occurred within 3.0–5.3 h, while the theoretical time required was 14–23 h. Instead, simultaneous peaks in RGM, Hg<sub>p</sub>, ozone (O<sub>3</sub>), nitrogen oxides, and sulfur dioxide in the late afternoon suggested short-range transport of RGM from the urban center to the rural site. The rural site was located more inland, where the average water vapor mixing ratio was lower compared to the other two sites (in 2008, rural:  $5.6 \pm 1.4$  g kg<sup>-1</sup>, urban:  $9.0 \pm 1.1$  g kg<sup>-1</sup>, cement plant:  $8.3 \pm 2.2$  g kg<sup>-1</sup>). Together, these findings suggested short-range transport of O<sub>3</sub> from an urban area contributed to higher RGM deposition at the rural site, while drier conditions helped sustain elevated RGM levels. Results suggested less urbanized environments may be equally or perhaps more impacted by industrial atmospheric Hg emissions, compared to the urban areas from where Hg emissions originated.

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### 1. Introduction

Mercury (Hg) is a global pollutant and a known neurotoxin (WHO, 1990, 1991). Approximately 50% of Hg in the environment is from anthropogenic sources, primarily coal burning power plants (Carpi, 1997; Mason and Sheu, 2002). In the atmosphere, Hg exists in three operationally defined forms: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM, comprised of Hg(II)-compounds), and particulate-bound mercury (Hg<sub>p</sub>) (Lindberg et al., 2007). Because of its high volatility, low chemical reactivity, and low solubility in water, GEM has a relatively long atmospheric lifetime (~1 yr) (Schroeder and Munthe, 1998). RGM and Hg<sub>p</sub> are more water-soluble and have relatively short atmospheric residence times (i.e., minutes-weeks) and may be deposited locally

(<100 km) through dry or wet deposition (Schroeder and Munthe, 1998). Following deposition, inorganic Hg(II) may be converted to methylmercury (MeHg), which is efficiently biomagnified in the aquatic food web (WHO, 1990).

Due to its relatively long atmospheric life, GEM may be oxidized and deposited far from emission sources, contaminating otherwise pristine locations. In the continental troposphere, the primary oxidants of GEM are ozone (O<sub>3</sub>) (Hall, 1995; Pal and Ariya, 2004a) and the hydroxyl radical (OH) (Bauer et al., 2003; Pal and Ariya, 2004b; Sommar et al., 2001), while bromine and chlorine are considered important oxidants in the marine boundary layer (Donohoue et al., 2005, 2006; Holmes et al., 2009). Ground level O<sub>3</sub> is a photochemical oxidant, produced through the reaction between nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), volatile organic compounds and sunlight, while OH is generated through photolytic production (Finlayson-Pitts and Pitts, 1986, 1993, 1997, 2000).

The fate of GEM is likely linked to processes that affect the production and distribution of O<sub>3</sub> and/or OH; however, these processes may differ between urban centers and downwind rural locations (i.e., NO<sub>x</sub>-limited environments). O<sub>3</sub> concentrations tend to be higher in rural areas due to transport of the O<sub>3</sub> air mass

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downwind from the urban center, when the time for O<sub>3</sub> formation and accumulation is lengthened, while destruction of O<sub>3</sub> by urban pollutants may be evaded (Finlayson-Pitts and Pitts, 2000). Transport of Hg species in the O<sub>3</sub> air mass may also lead to the production and relocation of RGM to more remote regions, although oxidation of GEM to RGM by O<sub>3</sub> and/or OH is considered slow (Calvert and Lindberg, 2005; Hynes et al., 2008; Poissant et al., 2005).

In this study, atmospheric Hg species (GEM, RGM, and Hg<sub>p</sub>) were characterized near an industrial Hg source (a cement plant) and two control sites (one urban and one rural) within the San Francisco Bay Area air basin (Fig. 1). The entire San Francisco Bay Estuary is included on the California 303(d) List of Water-Quality Impaired Segments for Hg due to elevated Hg levels in fish tissue (USEPA,

2009), resulting from historical Hg and gold mining (Conaway et al., 2003, 2004). Although newly deposited atmospheric Hg is more readily converted to MeHg than legacy or native Hg (e.g., Hg from mining) (Hintelmann et al., 2002), few studies address the potential importance of industrial Hg atmospheric emissions to the San Francisco Bay Estuary.

Near the cement plant atmospheric Hg species were monitored for approximately two weeks in the early winter in 2007, while monitoring occurred at the control sites in 2005 between August and September. All three sites were monitored sequentially between August 2008 and October 2008 (Table 1). Criteria pollutants (e.g., O<sub>3</sub>, NO<sub>x</sub>, sulfur dioxide (SO<sub>2</sub>)) and meteorological data were also measured, in order to assess associations between these parameters and atmospheric Hg species.

## 2. Site descriptions

### 2.1. Lehigh Hanson Permanente Cement Plant

Lehigh Hanson Permanente Cement Plant (hereafter referred to as “the cement plant”) (latitude/longitude: 37.322432/–122.079305, elevation: 183 m) operates one of the largest single preheater kilns in the USA, with a clinker capacity of  $1.451 \times 10^6$  metric tonnes (t) of cement per year (Appendix C from USEPA, 1997). Since May 2007, the kiln was fueled exclusively by up to 18 t petroleum coke h<sup>-1</sup> (Brian Bateman, BAAQMD, personal communication). In 2007, the year most recent data were available, the cement plant accounted for 29% of the total estimated Hg emissions in the San Francisco Bay Area air basin (61.4 kg/214 kg, from CARB, 2009). Other significant Hg sources in the air basin included five refineries located approximately 75 km north of the cement plant, which accounted for 63% of 2007 total estimated Hg emissions in the San Francisco Bay Area (134 kg/214 kg) (CARB, 2009). Atmospheric Hg species were monitored near the northern property line, within 0.5 km of the cement kiln.

### 2.2. Control sites

Atmospheric Hg concentrations (GEM, RGM, and Hg<sub>p</sub>) were monitored at one urban site (Moffett Field, 11 km northeast of the cement plant, latitude/longitude: 37.415/–122.04806, elevation: 11 m) and one rural site (Calero Reservoir, 32 km southeast of the cement plant, latitude/longitude: 37.18852/–121.77634, elevation 149 m) (Fig. 1).

## 3. Methods

### 3.1. GEM, RGM, and Hg<sub>p</sub>

Atmospheric Hg species (GEM, RGM, and Hg<sub>p</sub>) were monitored simultaneously using an automated Tekran 2537A/1130/1135 speciation unit (Landis et al., 2002). The Tekran speciation system includes sequential collection of RGM on a KCL-coated quartz annular denuder, Hg<sub>p</sub> on a quartz filter assembly, and GEM on gold

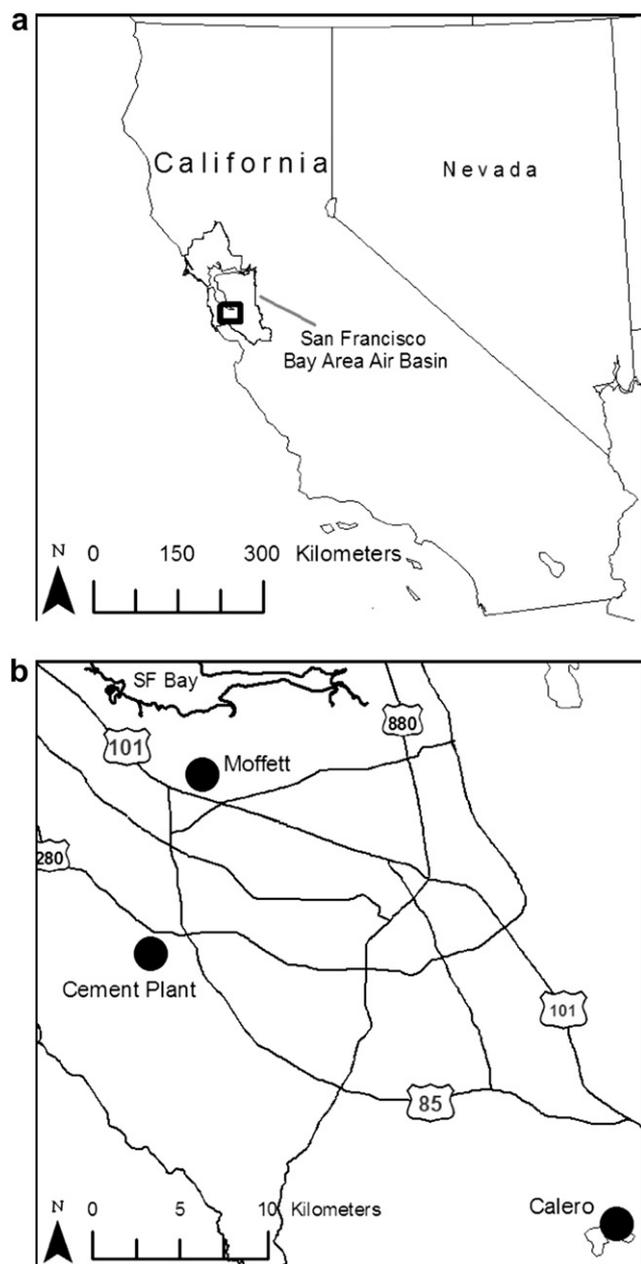


Fig. 1. Map of (a) San Francisco Bay Area air basin (b) sampling sites, including Lehigh Hanson Permanente Cement (the cement plant), Moffett Field (the urban site), and Calero Reservoir (the rural site).

Table 1  
Sampling dates for the cement plant, the urban site and the rural site.

	2005	2007	2008
Cement plant		17 days Nov. 26–Dec. 12	44 days Aug. 5–Sept. 17
Urban site	10 days Aug. 30–Sept. 9		11 days Sept. 19–Sept. 30
Rural site	18 days Sept. 9–Sept. 27		9 days Oct. 21–Oct. 30

traps within a model 2537A Mercury Vapor Analyzer. Sampling resolution was 5 min for GEM and 2 h for RGM and Hg<sub>p</sub>. Every 2 h the lines were flushed with Hg-free air, and for 1 h RGM and Hg<sub>p</sub> were each thermally desorbed and analyzed as GEM. The analyzer was programmed to sample air at a flow rate of 1 L min<sup>-1</sup> for GEM, and 8.5 L min<sup>-1</sup> for RGM and Hg<sub>p</sub>. The latter flow rate was lower than recommended by Landis et al. (2002) (i.e., 10 L min<sup>-1</sup>), and likely increased the cut point of the impactor from 2.5 to 3.0 μm (Lyman et al., 2007; USEPA, 1998), which possibly led to some Hg<sub>p</sub> quantified as RGM. Fresh denuders, which were cleaned and coated with KCl as described by Landis et al. (2002), were installed before monitoring at each site.

The model 2537A was automatically calibrated daily using an internal permeation source, and manual calibration checks of GEM were performed weekly and at the beginning and end of each deployment (average recovery: 99 ± 10%, *n* = 44). Precision and accuracy were determined by the relative percent difference (RPD) between parallel manual calibration checks (average RPD: 2.5 ± 2.3%, *n* = 20 pairs). The detection limit of the 2537A analyzer (for measurement of GEM) was 0.1 ng m<sup>-3</sup> (Tekran, 2002). The detection limit for RGM and Hg<sub>p</sub> was determined using *t* × σ of speciation system blanks, where *t* represented the level for specific sample size (*n*) at which there was less than a 1% chance of a Type 1 error (i.e., *p* < 0.01, from 40 CFR, Appendix B to Part 136). The system blank was defined as the last (i.e., third) reading during the Hg-free air flush prior to desorption of RGM and Hg<sub>p</sub>. In 2005, 2007 and 2008, the detection levels were 0.37 pg m<sup>-3</sup>, 0.75 pg m<sup>-3</sup>, and 4.7 pg m<sup>-3</sup>, respectively (for *n* > 31, *t* = 2.326). Based on the air intake rate of 8.5 L min<sup>-1</sup>, detection levels were 0.38 pg, 0.77 pg and 4.8 pg for each 2-h sampling period. All values for RGM and Hg<sub>p</sub> were blank corrected by subtracting the sum of the second and third readings during the Hg-free air flush prior to desorption. For all summaries and statistical analyses, half the detection level was imputed for RGM and Hg<sub>p</sub> values below the detection level. Aside from GEM data in Table 3 and Figs. 2, 4 and 5, all Hg data represented 2-h averages.

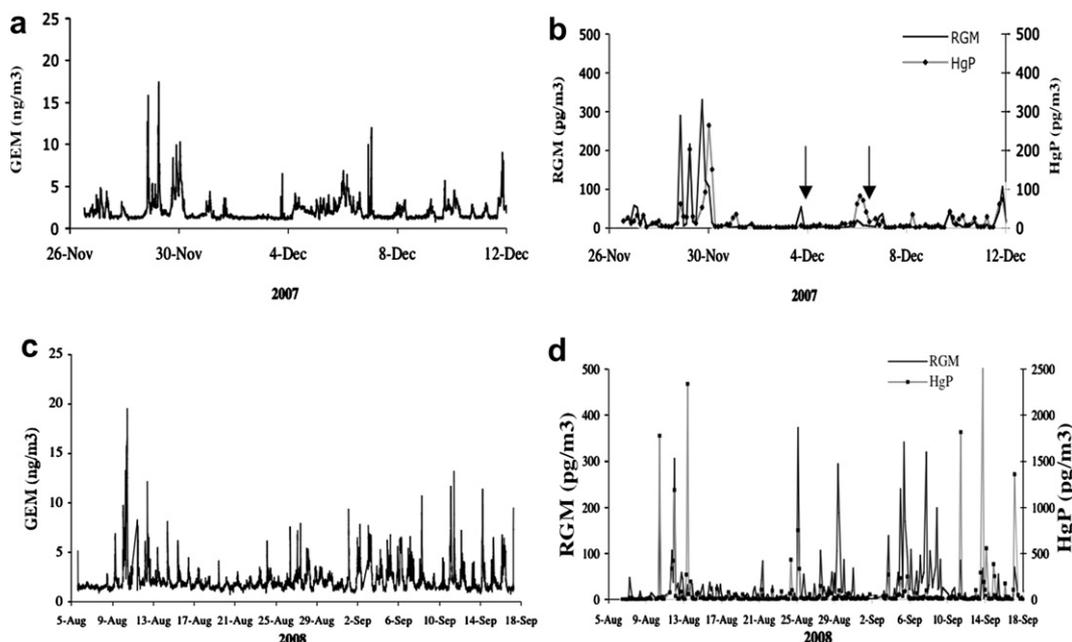
### 3.2. Criteria pollutants and meteorological data

Criteria pollutants were measured alongside Hg in 5-min intervals using the following USEPA certified methods: SO<sub>2</sub> (UV Fluorescence, EQSA-0495-100), NO and NO<sub>2</sub> (Chemiluminescence, RFNA-1194-099), and O<sub>3</sub> (Photometric Analysis, EQOA 0992-087). Manual calibration blanks for SO<sub>2</sub> and NO<sub>x</sub> averaged 102% and 101%, respectively (*n* = 8 for both). Meteorological parameters, including wind speed, solar radiation, relative humidity, pressure, and temperature, were measured simultaneously at 5-min intervals using MetOne instrumentation at all three sites in 2008, at the cement plant in 2007, and at Calero in 2005 (10 days out of 18 days). In 2005, onsite hourly-averaged data for temperature, wind speed, wind direction, pressure and relative humidity were obtained for Moffett Air Field from the National Oceanic and Air Administration (NOAA, 2009), while data for solar radiation were measured at the Los Altos climate station (~7 km east) and obtained from the Western Region Climate Center (WRCC, 2009). The water vapor mixing ratio (g kg<sup>-1</sup>) was calculated for each site using relative humidity, pressure and temperature, and the Clausius–Clapeyron relation. Table 2 summarizes meteorological data for the three sites.

## 4. Results

### 4.1. Seasonal differences

Atmospheric Hg was measured in 2005 and 2008 during the late summer/early fall. In 2007 the cement plant was monitored during the early winter (Table 1). From Table 2, temperature differences between deployments were not observed for the urban and rural sites, while the average temperature at the cement plant was 10 °C in 2007 and 20 °C 2008. Although partitioning between reactive Hg and aerosols is inversely correlated with temperature (Rutter and Schauer, 2007), average Hg<sub>p</sub> levels were >4 times higher in 2008 compared to 2007 (Table 3); therefore, differences in Hg<sub>p</sub> between 2007 and 2008 were not temperature-dependent. In 2007, 1.2 cm of



**Fig. 2.** Atmospheric Hg species measured at the cement plant in 2007 (a–b) and 2008 (c–d): (a) GEM (ng m<sup>-3</sup>), (b) RGM (pg m<sup>-3</sup>) and Hg<sub>p</sub> (pg m<sup>-3</sup>), (c) GEM (ng m<sup>-3</sup>), (d) RGM (pg m<sup>-3</sup>) and Hg<sub>p</sub> (pg m<sup>-3</sup>). GEM was measured semi-continuously every 5 min, while RGM and Hg<sub>p</sub> measurements represented 2-h averages. 1.2 cm of precipitation were measured on December 4, 2007 and December 6–7, 2007 (marked by arrows in b).

**Table 2**  
Meteorological data for the cement plant, Moffett Field (the urban site), and Calero Reservoir (the non-urban site), including temperature, relative humidity (RH), the water vapor mixing ratio (WV), wind speed (WS), wind direction and solar radiation. In all deployments, meteorological data were measured alongside Hg measurements, except at Moffett in 2005.

Site	Year	<i>n</i>	Temp (°C)	RH (%)	WV (g kg <sup>-1</sup> )	WS (m s <sup>-1</sup> )	Wind direction (degree)	Solar radiation (W m <sup>-2</sup> )
Cement Plant	2007	4162	10 ± 3.2 (3.6–18)	61 ± 20 (20–93)	4.8 ± 1.9 (1.9–12)	2.3 ± 1.0 (0.089–9.4)	200 ± 75 (0.40–360)	91 ± 160 (0–640)
	2008	9072	20 ± 5.9 (11–39)	60 ± 23 (4.5–92)	8.3 ± 2.2 (1.5–13)	1.9 ± 0.92 (0–6.0)	180 ± 120 (0–360)	130 ± 180 (0–630)
Urban	2005	268 <sup>a</sup>	18 ± 3.9 (12–34)	70 ± 15 (13–90)	8.8 ± 0.94 (4.5–11)	2.7 ± 1.7 (0–8.6)	270 ± 78 (0–360)	260 ± 340 <sup>b</sup> (0–905)
	2008	2962	18 ± 4.0 (10–28)	71 ± 13 (27–88)	9.0 ± 1.1 (5.5–12)	2.7 ± 1.7 (0–8.6)	250 ± 90 (0–360)	100 ± 150 (0–510)
Rural	2005	2813	18 ± 5.5 (8.2–30)	61 ± 22 (18–95)	7.3 ± 1.5 (3.9–11)	2.3 ± 1.2 (0–6.4)	200 ± 96 (0–360)	190 ± 281 (0–960)
	2008	2486	18 ± 6.2 (8.7–31)	48 ± 21 (12–92)	5.6 ± 1.4 (3.0–8.6)	1.9 ± 1.1 (0–4.9)	200 ± 90 (0–360)	86 ± 130 (0–380)

<sup>a</sup> In 2005, onsite hourly-averaged meteorological data were obtained for Moffett Air Field (the urban site) from the National Oceanic and Air Administration (NOAA, 2009).

<sup>b</sup> Data for solar radiation (*n* = 78 samples) were obtained from the Western Region Climate Center (WRCC, 2009).

precipitation were recorded near the cement plant on December 4, 2007 (0.6 cm) and December 6–7, 2007 (0.6 cm) (Fig. 2b). Both RGM and Hg<sub>p</sub> are scavenged by rain (Schroeder and Munthe, 1998), and therefore lower RGM and Hg<sub>p</sub> levels in 2007 may be due to washout; however, this effect was considered small due to the minimal amount of rain.

## 4.2. Cement plant

### 4.2.1. GEM

In 2007 and 2008, average GEM levels at the cement plant were 2.14 ± 1.47 ng m<sup>-3</sup> and 2.20 ± 1.39 ng m<sup>-3</sup>, respectively (Table 3, Fig. 2). Although the time frame was longer in 2008 (45 days versus 16 days), the range and distribution were similar (Table 3). Average GEM levels were slightly higher than the global background average (~1.5–1.7 ng m<sup>-3</sup>, Lindberg et al., 2007), but were lower than average values reported for other urban areas (Table 4). Comparatively lower GEM levels near the cement plant likely reflected fewer industrial Hg sources and proximity to the Pacific Ocean. Although long-range transport of Hg emissions from Asia is

a potential source of GEM to the western USA (Steding and Flegal, 2002), this effect is primarily observed in the spring due to lifting of cold fronts (Weiss-Penzias et al., 2006). Since all measurements for this study were made in the late summer or early winter, Hg inputs from Asia were considered negligible.

### 4.2.2. RGM and Hg<sub>p</sub>

In 2007 and 2008, RGM levels averaged 17.7 ± 49.0 pg m<sup>-3</sup> and 25.2 ± 52.8 pg m<sup>-3</sup>, respectively, and Hg<sub>p</sub> averaged 19.9 ± 37.4 pg m<sup>-3</sup> and 80.8 ± 283 pg m<sup>-3</sup>, respectively (Table 3, Fig. 2), which were significantly higher than other urban sites and reflected close proximity to a Hg source (Table 4). In 2008, four of eight Hg<sub>p</sub> spikes (>97th percentile, 555–2510 pg m<sup>-3</sup>) and five of six RGM spikes (>97th percentile, 240–373 pg m<sup>-3</sup>) occurred when the wind direction was from the southwest sector (195–270°), i.e., from the direction of the cement plant (Fig. 3a–c). Site-specific wind direction was unknown for three Hg<sub>p</sub> spikes and one RGM spike. Most events occurred between 12:30 am and 6:30 am when emissions from the cement kiln were typically released, and one event occurred at 10 am. One elevated Hg<sub>p</sub> event (555 pg m<sup>-3</sup>) occurred from the southeast sector (117°) and possibly reflected other regional sources.

## 4.3. Urban and rural control sites

### 4.3.1. GEM

In 2005 and 2008, urban site GEM averaged 1.74 ± 0.580 ng m<sup>-3</sup> and 1.76 ± 0.878 ng m<sup>-3</sup>, respectively (Table 3, Fig. 4). Like the cement plant, the range and distribution of GEM was similar between the two years (Table 3). Rural site GEM averaged 1.85 ± 0.446 ng m<sup>-3</sup> and 2.37 ± 1.26 ng m<sup>-3</sup>, respectively, which was comparable to GEM at other rural sites (Table 4, Fig. 5). In 2005 and 2008, average GEM levels were higher at the rural site compared to the urban site. In 2008, average GEM levels were highest at the rural site, although the rural site was more isolated from Hg point sources.

### 4.3.2. RGM and Hg<sub>p</sub>

At the urban site in 2005 and 2008, RGM averaged 1.81 ± 2.67 pg m<sup>-3</sup> and 2.58 ± 1.28 pg m<sup>-3</sup>, respectively, and Hg<sub>p</sub> averaged 3.06 ± 4.40 pg m<sup>-3</sup> and 3.17 ± 3.20 pg m<sup>-3</sup>, respectively (Table 3, Fig. 4). At the rural site in 2005 and 2008, RGM averaged 4.58 ± 6.92 pg m<sup>-3</sup> and 14.5 ± 30.2 pg m<sup>-3</sup>, respectively, and Hg<sub>p</sub> averaged 3.68 ± 3.08 pg m<sup>-3</sup> and 7.99 ± 6.74 pg m<sup>-3</sup>, respectively (Fig. 5). In both years, average RGM and Hg<sub>p</sub> levels at the rural site were lower than the cement plant, but higher compared to the urban site.

Unlike the cement plant, where most elevated RGM and Hg<sub>p</sub> levels occurred before dawn, the ten most elevated RGM spikes in 2008 (25.6–154 pg m<sup>-3</sup>) measured at the rural site occurred in the

**Table 3**

Hg speciation summary statistics, including sample size (*n*), average (avg) ± 1 standard deviation (sd), range, and 50th, 75th and 95th percentiles for all sampling campaigns: (a) GEM (ng m<sup>-3</sup>) (measured every 5 min), (b) RGM (pg m<sup>-3</sup>) (measured every 2 h), (c) Hg<sub>p</sub> (pg m<sup>-3</sup>) (measured every 2 h). Sampling occurred in 2005 and 2008 during the late summer, and in 2007 during the early winter.

Site	Year	<i>n</i>	Avg ± 1 sd (ng m <sup>-3</sup> )	Range (ng m <sup>-3</sup> )	50th	75th	95th
<i>a</i>							
Cement Plant	2007	3019	2.14 ± 1.47	0.827–17.4	1.58	2.45	4.49
	2008	7803	2.20 ± 1.39	0.749–19.5	1.76	2.39	4.66
Urban	2005	1849	1.74 ± 0.580	0.532–5.03	1.64	1.97	2.87
	2008	2051	1.76 ± 0.878	0.100–8.19	1.47	2.31	3.42
Rural	2005	3403	1.85 ± 0.446	0.837–4.42	1.73	2.03	2.76
	2008	1657	2.37 ± 1.26	0.100–11.7	2.37	3.05	4.20
<i>b</i>							
Cement Plant	2007	111	17.7 ± 49.0	0.375–330	2.57	11.9	106
	2008	290	25.2 ± 52.8	2.34–373	7.73	21.6	106
Urban	2005	76	1.81 ± 2.67	0.182–19.5	0.881	2.12	5.35
	2008	76	2.58 ± 1.28	2.34–10.4	2.34	2.34	2.34
Rural	2005	142	4.58 ± 6.92	0.182–39.7	1.50	5.83	16.7
	2008	63	14.5 ± 30.2	2.34–154	2.64	8.51	60.7
<i>c</i>							
Cement Plant	2007	111	19.9 ± 37.4	0.375–265	6.79	25.2	73.2
	2008	282	80.8 ± 283	2.34–2510	12.1	35.6	310
Urban	2005	76	3.06 ± 4.40	0.182–29.4	1.78	3.80	9.79
	2008	76	3.17 ± 3.20	2.34–23.1	2.34	2.34	7.55
Rural	2005	142	3.68 ± 3.08	0.182–13.9	2.83	5.01	9.64
	2008	63	7.99 ± 6.74	2.34–37.5	6.65	9.30	22.9

**Table 4**

Comparison between automated Hg measurements determined at other sites in North America and the 2008 results from this study.

	GEM ( $\text{ng m}^{-3}$ )	Hg <sub>p</sub> ( $\text{pg m}^{-3}$ )	RGM ( $\text{pg m}^{-3}$ )	Duration	Reference
<b>Urban and/or industrial</b>					
Detroit, MI, USA	2.2 ± 1.3	20.8 ± 30	17.7 ± 28.9	1 year	Liu et al., 2007
Tuscaloosa, AL, USA	4.1 ± 1.3	16.4 ± 19.5	13.6 ± 20.4	1 month	Gabriel et al., 2005
Downtown Toronto, Canada	4.5 ± 3.1	21.5 ± 16.4	14.2 ± 13.2	1 year	Song et al., 2009
Mexico City, Mexico	7.2 ± 4.8	187 ± 300	62 ± 64	17 days	Rutter et al., 2009
<b>Rural</b>					
Newcomb, NY, USA	1.4 ± 0.4	3.2 ± 3.7	1.8 ± 2.2	1 year	Choi et al., 2008
Devil's Lake, WI, USA	1.6 ± 0.3	8.6 ± 8.3	3.8 ± 8.9	1 year	Manolopoulos et al., 2007
St. Anicet, Québec, Canada	1.65 ± 0.42	26 ± 54	3 ± 11	1 year	Poissant et al., 2005
Cove Mountain, TN, USA	3.2 ± 0.7	9.7 ± 6.9	13.6 ± 7.4	1 month	Gabriel et al., 2005
Reno, NV, USA	1.6 ± 0.5	9 ± 10	26 ± 35	3 years	Peterson et al., 2009
San Francisco Bay Area, CA, USA (cement plant)	2.20 ± 1.39	80.8 ± 283	25.2 ± 52.8	44 days	This study
San Francisco Bay Area, CA, USA (urban)	2.28 ± 1.28	3.17 ± 3.20	2.58 ± 1.28	11 days	This study
San Francisco Bay Area, CA, USA (rural)	2.37 ± 1.26	7.99 ± 6.74	14.5 ± 30.2	9 days	This study

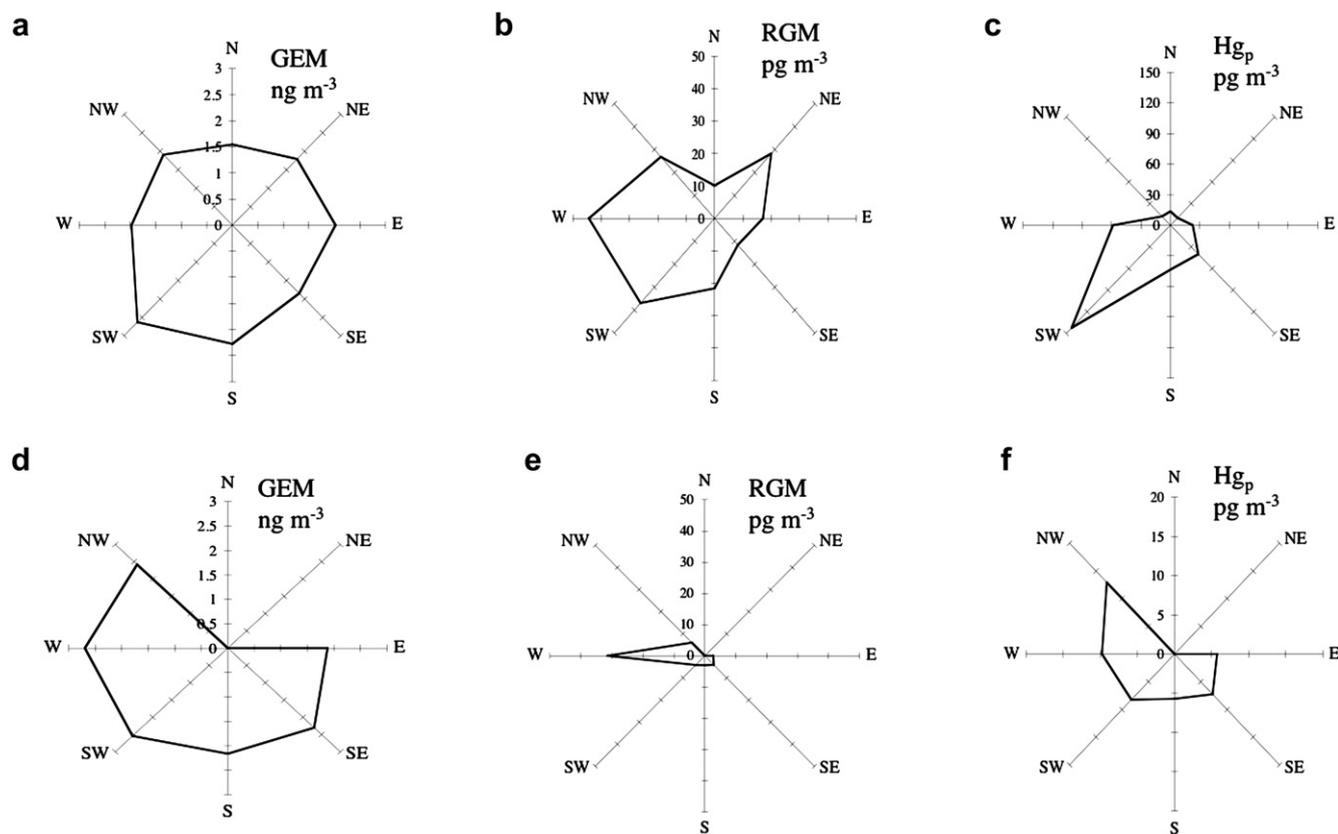
late afternoon (2:30 pm–6 pm). Likewise, the ten highest Hg<sub>p</sub> spikes in 2008 (12.9–37.5  $\text{pg m}^{-3}$ ) occurred between 12:30 pm and 9 pm. All RGM events and eight Hg<sub>p</sub> events originated from the west-southwest sector (wind direction: 230–300°), while two Hg<sub>p</sub> events originated from the eastern sector (wind direction: 90–135°) (Fig. 3d–f). All events originated from other regional Hg sources, as no significant events occurred from the northeast (i.e., the direction of the cement plant monitored for this study). The rural site was located about 70 km northeast of the Cemex Cement Plant in Davenport, CA, the nearest upwind Hg source (2007

estimated Hg emissions: Cemex: 79.4 kg = 98% of total estimated Hg emissions in the North Central Coast air shed, from CARB, 2009).

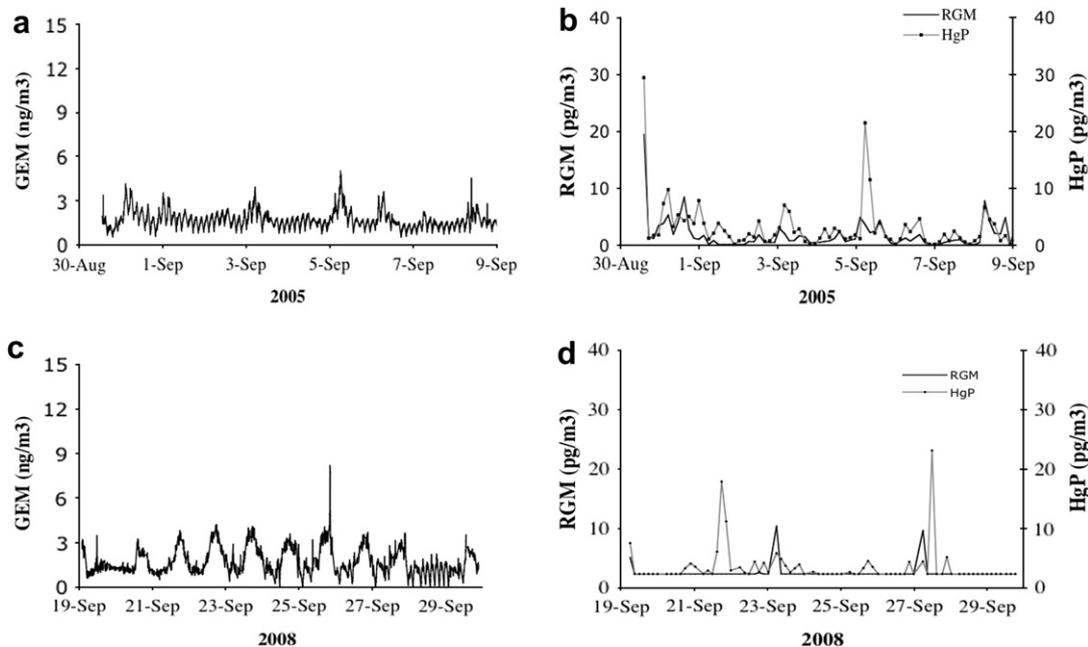
## 5. Discussion

### 5.1. Comparison with other urban and rural sites

Higher RGM and Hg<sub>p</sub> levels at the rural site compared to the urban site are the inverse of what is typically reported. Lynam and Keeler (2005) reported median RGM levels at an urban site



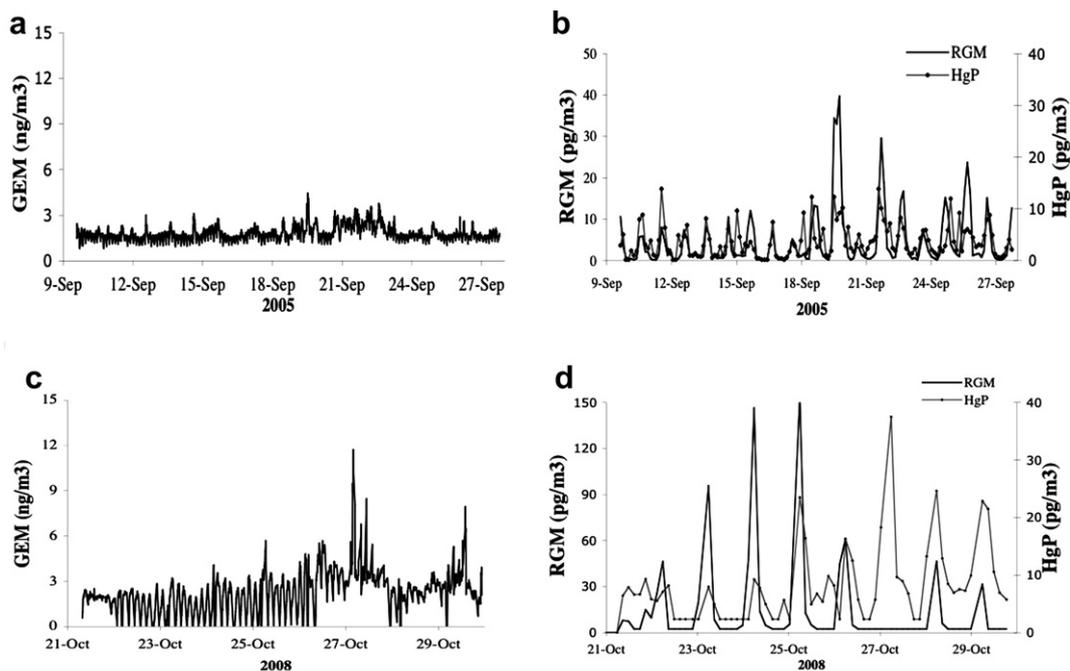
**Fig. 3.** Pollution roses for average Hg species at the cement plant in 2008: (a) GEM ( $\text{ng m}^{-3}$ ) (averaged over 2 h), (b) RGM ( $\text{pg m}^{-3}$ ), (c) Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ) and at the rural site in 2008, (d) GEM ( $\text{ng m}^{-3}$ ) (averaged over 2 h), (e) RGM ( $\text{pg m}^{-3}$ ), (f) Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ). Wind frequencies for the cement plant were 0.47% (N), 5.2% (NE), 17% (E), 10% (SE), 25% (S), 34% (SW), 4.2% (W) and 3.8% (NW). Wind frequencies for the rural site were 0% (N), 0% (NE), 21% (E), 9.5% (SE), 13% (S), 16% (SW), 40% (W) and 1.6% (NW). Additional pollution roses for prior years and the urban site are in Supplementary information.



**Fig. 4.** Atmospheric Hg species measured at the urban site in 2005 (a–b) and 2008 (c–d): (a) GEM ( $\text{ng m}^{-3}$ ), (b) RGM ( $\text{pg m}^{-3}$ ) and Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ), (c) GEM ( $\text{ng m}^{-3}$ ), (d) RGM ( $\text{pg m}^{-3}$ ) and Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ). GEM was measured semi-continuously every 5 min, while RGM and Hg<sub>p</sub> measurements represented 2-h averages.

(Detroit, Michigan, USA) were 3–11 times higher than levels at a rural site (Dexter, Michigan, USA), located 83 km west of Detroit. Laurier and Mason (2007) reported higher concentrations of Hg species (GEM, RGM) at Baltimore, MD, USA (urban), compared to a coastal site (rural, but near Hg sources); the ratio of average RGM levels at the non-urban and urban sites for two sets of RGM data was 0.57 ( $=9.7/16.9$ ) and 0.47 ( $=7.9/16.9$ ). Rutter et al. (2008) reported Hg species for one urban site and one upwind rural site

(i.e., not impacted by urban sources), both located in Wisconsin, USA, and the ratio of rural to urban levels for RGM and Hg<sub>p</sub> was 0.51 and 0.77, respectively. Gabriel et al. (2005) reported Hg species for one urban (Tuscaloosa, AL, USA) and one rural (Cove Mountain, TN, USA), and the ratios for average values were 1.00 and 0.59 for RGM and Hg<sub>p</sub>, respectively. The previous study was the only one in which comparable RGM levels were observed at an urban site and a non-urban site. The authors attributed elevated



**Fig. 5.** Atmospheric Hg species measured at the rural site in 2005 (a–b) and 2008 (c–d): (a) GEM ( $\text{ng m}^{-3}$ ), (b) RGM ( $\text{pg m}^{-3}$ ) and Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ), (c) GEM ( $\text{ng m}^{-3}$ ), (d) RGM ( $\text{pg m}^{-3}$ ) and Hg<sub>p</sub> ( $\text{pg m}^{-3}$ ). GEM was measured semi-continuously every 5 min, while RGM and Hg<sub>p</sub> measurements represented 2-h averages.

**Table 5**

Comparison between actual time observed and theoretical time required for greatest RGM spikes at the rural site in 2008, calculated using the following reaction rates:  $K_{\text{Hg}+\text{O}_3} = 7.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Pal and Ariya, 2004a);  $K_{\text{Hg}+\text{OH}} = 9.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Pal and Ariya, 2004b).

Date and time	Actual time (h)	RGM created ( $\text{pg m}^{-3}$ )	Starting GEM ( $\text{ng m}^{-3}$ )	Starting $\text{O}_3$ ( $\times 10^{12} \text{ molecules cm}^{-3}$ )	Theoretical time (h)
October 23, 2008 12:25–17:45 pm	5.3	75.9	1.52	1.23	13.7
October 24, 2008 14:45–17:45 pm	3.0	99.0	1.44	1.45	16.2
October 25, 2008 12:25–17:45 pm	5.3	149	1.30	1.74	22.9

daytime Hg levels (GEM, RGM, and  $\text{Hg}_p$ ) at the non-urban site to boundary layer effects, ambient photochemistry and air–surface exchange of Hg (Gabriel et al., 2005).

## 5.2. Photo-oxidation of GEM

RGM production by photo-oxidation was investigated by correlating GEM, RGM and  $\text{O}_3$ , and calculating the theoretical time required to produce spikes in RGM similar to those observed at the rural site. Sillman et al. (2007) modeled transport and photochemistry of Hg species and reported a strong positive correlation between GEM and RGM was associated with anthropogenic emissions (e.g., in the northeastern USA), while a negative correlation was associated with photochemical oxidation of GEM to form RGM (e.g., in southern Florida). Several studies reported GEM and RGM were inversely correlated in remote areas, including the Arctic (Lindberg et al., 2002; Schroeder et al., 1998), the marine boundary layer (Laurier et al., 2003; Laurier and Mason, 2007), and in the Pacific Northwest, USA (the latter reference for nighttime air in which RGM was  $>50 \text{ pg m}^{-3}$ , from Swartzendruber et al., 2006). In the previous studies, the primary source of RGM was photo-oxidation of GEM rather than anthropogenic emissions.

For this study, RGM and GEM were positively correlated at all three sites (after  $\log_{10}$ -transformation of both variables), although the strength of the relationship differed. At the cement plant the correlation was strongest (2007:  $r^2 = 0.50$ ,  $p < 0.0001$ ; 2008:  $r^2 = 0.27$ ,  $p < 0.0001$ ), indicating release and/or formation of RGM near the cement plant. GEM and RGM were also positively correlated at the urban site (2005:  $r^2 = 0.23$ ,  $p < 0.001$ ; 2008: not enough RGM data  $>$  MDL), but least correlated at the rural site (2005:  $r^2 = 0.083$ ,  $p < 0.05$ ; 2008:  $r^2 = 0.002$ ,  $p > 0.05$ ). Unlike the cement plant and the urban site, RGM and  $\text{O}_3$  were positively correlated at the rural site, indicating RGM formation was not due to simultaneous  $\text{O}_3$  depletion (2005:  $r^2 = 0.58$ ,  $p < 0.0001$ ; 2008:  $r^2 = 0.27$ ,  $p < 0.0001$ , after  $\log_{10}$ -transformation of RGM). In urban environments, RGM and  $\text{O}_3$  are often correlated due to the proximity between Hg-emitting industries and  $\text{O}_3$  precursors; however, this is not the case at the rural site. Lastly, the actual net increase in RGM at the rural site occurred faster than predicted from theoretical rate calculations, which was similar to findings from Poissant et al. (2005) (the authors assumed RGM partitioned to particulates quickly and reported theoretical production rates

for  $\text{Hg}_p$ ). Predicted rates for this study were calculated using reaction rates between GEM,  $\text{O}_3$  and OH ( $K_{\text{Hg}+\text{O}_3} = 7.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , from Pal and Ariya, 2004a;  $K_{\text{Hg}+\text{OH}} = 9.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , from Pal and Ariya, 2004b), and assuming  $[\text{OH}] = 10^6 \text{ molecules cm}^{-3}$ . Reaction rates chosen were faster than those reported by Hall (1995) and Bauer et al. (2003), as slower reaction rates would require more time to generate RGM. No precipitation was recorded during monitoring and therefore aqueous phase reactions were unnecessary for this exercise. At the rural site, the three observed highest net RGM gains ( $75.9 \text{ pg m}^{-3}$ ,  $99.0 \text{ pg m}^{-3}$ ,  $149 \text{ pg m}^{-3}$ ) occurred within 3.0–5.3 h, while the theoretical time required was from 14 to 23 h (Table 5).

Together, these findings suggested elevated RGM at the rural site was not primarily due to photo-oxidation of GEM.

## 5.3. Diurnal cycling at the urban and rural sites

The importance of boundary layer effects and short-range transport of Hg species were investigated at the urban and rural sites by considering the diurnal cycling in 2008 of Hg species (GEM, RGM and  $\text{Hg}_p$ ),  $\text{O}_3$  and its precursors ( $\text{NO}$  and  $\text{NO}_x$ ), cement emissions (e.g.,  $\text{SO}_2$ ), and relevant meteorological data (e.g., wind speed) (Table 6, Figs. 6 and 7). Diurnal cycling was not obvious near the cement plant (see Figs. S3–S4).

At the urban site diurnal trends for RGM and  $\text{Hg}_p$  were not observed, although diurnal cycling of  $\text{O}_3$ ,  $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{NO}$  was apparent (Fig. 6).  $\text{NO}_x$  and  $\text{NO}$  levels both increased  $\sim 6$  am when traffic increased.  $\text{O}_3$  increased beginning  $\sim 8$  am (following formation of  $\text{NO}_x$ ), then peaked around 12 noon and decreased to near 0 ppb by midnight. GEM and  $\text{SO}_2$  levels at the urban site were both somewhat higher between 3 am and noon. Other studies reported higher nighttime total gaseous Hg (TGM = GEM + RGM) levels due to shallow nocturnal layers that trap TGM, while thermal mixing during the day increased the boundary layer leading to a dilution in TGM levels (Feng et al., 2004; Kim and Kim, 2001). Since both  $\text{SO}_2$  and GEM were elevated at night, higher nighttime concentrations possibly reflected increased nighttime emissions from the cement plant.

Diurnal trends at the rural site differed from those observed at the urban site. Diurnal GEM trends were not observed, while trends for RGM,  $\text{Hg}_p$ ,  $\text{O}_3$ ,  $\text{NO}_x$  and  $\text{SO}_2$  were similar to one another (i.e., not significantly lagged) (Fig. 7). For these five parameters, concentrations increased beginning  $\sim 10$  am, peaked between 3

**Table 6**

Summary statistics (average  $\pm 1$  sd, and range within parentheses) for criteria pollutants ( $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{NO}_x$  and  $\text{SO}_2$ ) measured alongside Hg species in 2005, 2007, and 2008.

Site	Year	$\text{O}_3$ (ppb)	$\text{NO}_2$ (ppb)	$\text{NO}$ (ppb)	$\text{NO}_x$ (ppb)	$\text{SO}_2$ (ppb)
Cement Plant	2007	22 $\pm$ 12 (2.0–46)	11 $\pm$ 9.1 (0.10–100)	9.2 $\pm$ 14 (0.10–220)	18 $\pm$ 19 (0.10–250)	1.6 $\pm$ 0.54 (0.10–13)
	2008	23 $\pm$ 16 (0.40–92)	10 $\pm$ 9.2 (0.10–77)	7.0 $\pm$ 16 (0.10–270)	16 $\pm$ 21 (0.10–310)	1.3 $\pm$ 0.71 (0.10–9.3)
Urban	2005	24 $\pm$ 10 (0.10–49)	8.5 $\pm$ 6.9 (0.20–61)	9.6 $\pm$ 9.4 (0.30–153)	18 $\pm$ 14 (5.7–140)	1.4 $\pm$ 0.43 (0.90–5.4)
	2008	20 $\pm$ 13 (1.0–60)	10 $\pm$ 6.6 (0.10–26)	7.7 $\pm$ 14 (0.10–110)	19 $\pm$ 20 (0.10–140)	1.1 $\pm$ 0.23 (0.20–2.2)
Rural	2005	25 $\pm$ 13 (0.50–67)	9.2 $\pm$ 6.6 (1.0–46)	6.2 $\pm$ 3.0 (0.70–65)	15 $\pm$ 8.5 (0.30–68)	1.8 $\pm$ 0.32 (1.1–5.3)
	2008	33 $\pm$ 16 (0.20–78)	11 $\pm$ 8.6 (0.10–44)	2.6 $\pm$ 3.3 (0.10–28)	14 $\pm$ 10 (0.10–56)	0.78 $\pm$ 0.53 (0.10–3.4)

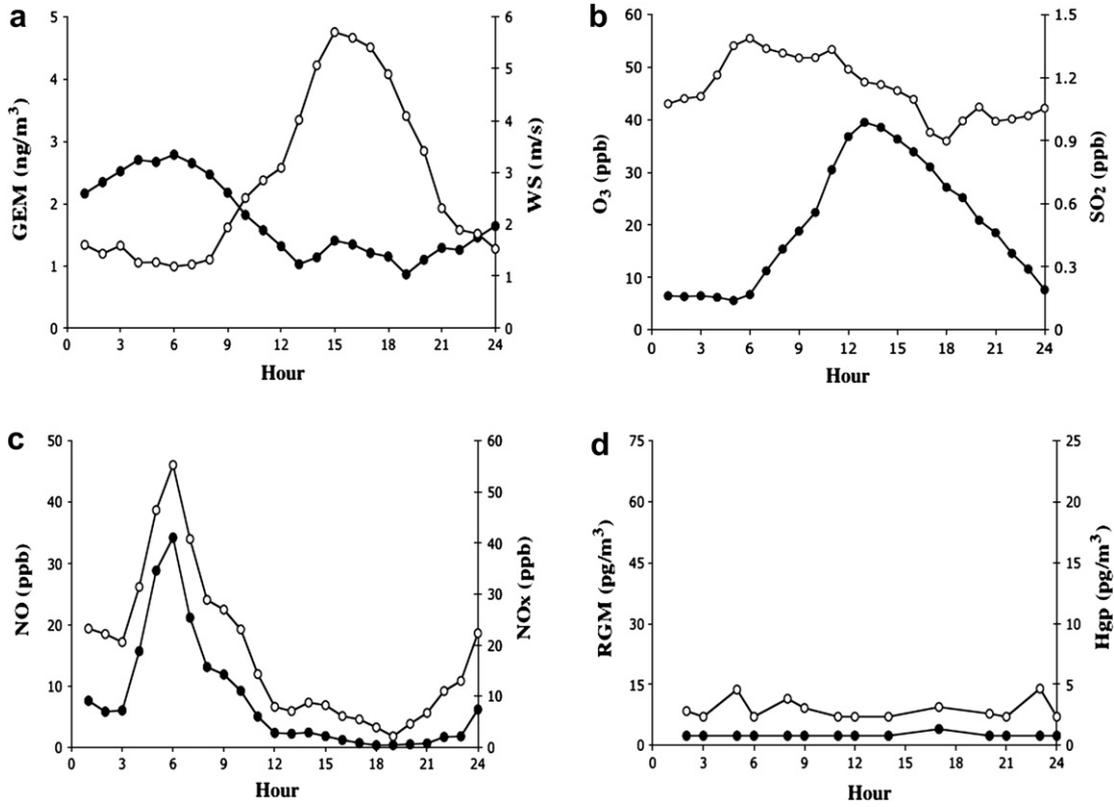


Fig. 6. Diurnal trends measured in 2008 at the urban site. Closed circles correspond to the left y-axis, and open circles correspond to the right y-axis; a) GEM (ng m<sup>-3</sup>) (averaged over 2 h) and wind speed (WS) (m s<sup>-1</sup>), b) O<sub>3</sub> (ppb) and SO<sub>2</sub> (ppb), c) NO (ppb) and NO<sub>x</sub> (ppb), d) RGM (pg m<sup>-3</sup>) and Hg<sub>p</sub> (pg m<sup>-3</sup>).

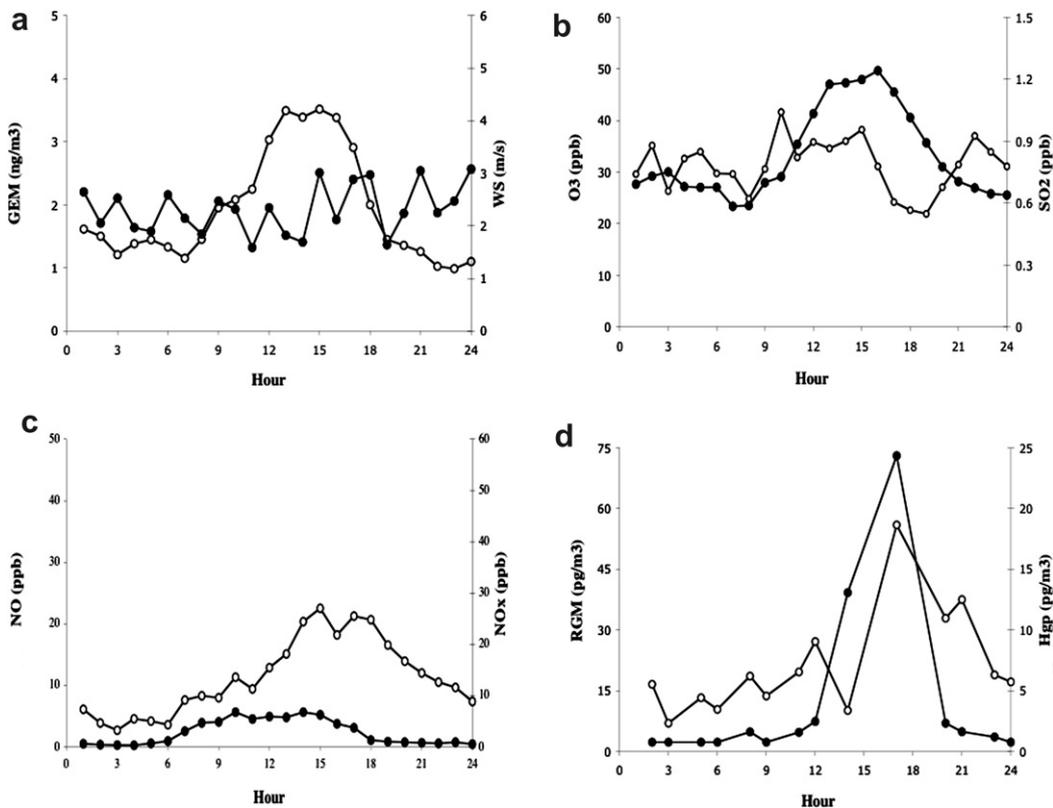


Fig. 7. Diurnal trends measured in 2008 at the rural site. Closed circles correspond to the left y-axis, and open circles correspond to the right y-axis; a) GEM (ng m<sup>-3</sup>) (averaged over 2 h) and wind speed (WS) (m s<sup>-1</sup>), b) O<sub>3</sub> (ppb) and SO<sub>2</sub> (ppb), c) NO (ppb) and NO<sub>x</sub> (ppb), d) RGM (pg m<sup>-3</sup>) and Hg<sub>p</sub> (pg m<sup>-3</sup>).

and 6 pm, and then decreased by 10 pm. Diurnal cycling for NO was also observed with maximum levels observed earlier in the day (around 9 am); however, average NO levels were higher at the urban site due to heavier traffic (2005: 1.5 times higher, 2008: 3.0 times higher).

At the rural site, a lack of diurnal cycling for GEM and a peak in RGM, Hg<sub>p</sub>, O<sub>3</sub>, NO<sub>x</sub> and SO<sub>2</sub> levels in the late afternoon suggested short-range transport of RGM from an urban center may contribute to elevated RGM levels. First, SO<sub>2</sub> is a byproduct of combustion and a primary pollutant, whereas O<sub>3</sub> is a secondary pollutant produced through the reaction between NO<sub>x</sub>, VOCs and sunlight (Finlayson-Pitts and Pitts, 1986, 1993, 1997, 2000). Although diurnal SO<sub>2</sub> trends were weaker than O<sub>3</sub> trends, the correspondence between SO<sub>2</sub> and O<sub>3</sub> indicated transport of pollutants (including RGM) within the O<sub>3</sub> plume. Second, peak concentrations for O<sub>3</sub> (and other constituents) were recorded later in the afternoon (3–6 pm at the rural site versus 12 noon at the urban site); delayed peak times suggested transport from an urban area. The third reason is related to moisture content in the air. Munthe et al. (2003) reported under dry weather conditions, RGM may persist in the troposphere long enough to undergo long-range transport (i.e., regional or hemispheric). The rural site was located more inland compared to the urban site (40 km versus 5 km from the San Francisco Bay), where average humidity levels were lower (2005: 13% lower; 2008: 32% lower, from Table 2). In addition, the mean water vapor mixing ratio was lower at the rural site (rural: 5.6 ± 1.4 g kg<sup>-1</sup>, urban: 9.0 ± 1.1 g kg<sup>-1</sup>, from Table 2). Using data from a high altitude site in the western USA, Weiss-Penzias et al. (2006) reported Asian air pollution was associated with “drier” air (mixing ratio < 2.3 g kg<sup>-1</sup>), since drier air was not likely mixed with clean “wetter” air from the marine boundary layer. Likewise, for modeled RGM levels in the southeastern USA, Sillman et al. (2007) reported highest RGM occurred in cloud free air masses, since RGM may be scavenged by cloud droplets. At the urban site, it is possible enhanced mixing of marine air diluted the urban pollution levels, unlike pollutants transported inland to the rural site.

Together, these findings suggested short-range transport of O<sub>3</sub> from an urban area (most likely originating from the west-southwest sector) contributed to higher RGM levels at the rural site, while drier conditions sustained elevated RGM levels.

#### 5.4. Dry depositional RGM flux

Dry depositional RGM flux was compared between the three sites using methodology outlined by Laurier et al. (2003) and Laurier and Mason (2007), which was based on the expected value of the gaseous mass transfer coefficient when normalized to wind speed (measured at 10 m height) (Shahin et al., 2002). The dry deposition velocity ( $k_A$ , cm s<sup>-1</sup>) was calculated using

$$k_A = D_A^{0.5} [(0.98 \pm 0.1) \mu_{10} + (1.26 \pm 0.3)] \quad (1)$$

where,  $D_A$  was the air-side diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $\mu_{10}$  was the wind speed measured at 10 m (m s<sup>-1</sup>), and the slope ± 95% confidence interval (CI) was 0.98 ± 0.1 and the estimate of the intercept (±95% CI) was 1.26 ± 0.3.  $D_A$  was calculated assuming RGM was mainly HgCl<sub>2</sub> (Laurier et al., 2003), and the air-side diffusion coefficient was estimated using the liquid molar volume  $V_m$  (Schwarzenbach et al., 1993):

$$D_A = 2.35/(V_m)^{0.73} \quad (2)$$

It was assumed the molecular mass of HgCl<sub>2</sub> was 271.52 g mol<sup>-1</sup> and the density was 5.4 g cm<sup>-3</sup> (ATSDR, 1999).  $D_A$  may also be estimated using the molecular mass,  $m$ ,

**Table 7**

Summary statistics (average ± 1 sd) for dry depositional RGM flux (ng m<sup>-2</sup> d<sup>-1</sup>), including depositional velocity ( $V_d$ ) (cm s<sup>-1</sup>), daily flux (i.e., the 24-h average), daytime flux (7 am–7 pm), nighttime flux (7 pm–7 am), and the ratio between daytime and nighttime flux (unitless).

	$V_d$ (cm s <sup>-1</sup> )	Daily flux (ng m <sup>-2</sup> d <sup>-1</sup> )	Daytime flux (ng m <sup>-2</sup> d <sup>-1</sup> )	Nighttime flux (ng m <sup>-2</sup> d <sup>-1</sup> )	Day/night (unitless)
2007 Cement	1.0 ± 0.24	15 ± 44	14 ± 49	15 ± 40	0.91
2005 Urban	1.2 ± 0.62	1.8 ± 2.3	2.4 ± 2.8	0.90 ± 1.4	2.6
2005 Rural	1.0 ± 0.30	6.7 ± 9.9	11 ± 12	2.1 ± 3.7	5.0
2008 Cement	0.88 ± 0.21	21 ± 42	17 ± 23	24 ± 52	0.71
2008 Urban	1.1 ± 0.41	2.6 ± 2.3	3.6 ± 3.3	1.8 ± 0.5	2.0
2008 Rural	0.89 ± 0.26	14 ± 29	29 ± 40	2.3 ± 1.6	12

$$D_A = 1.55/(m)^{0.65} \quad (3)$$

and both values for  $D_A$  were averaged for the calculation of  $k_A$ . The dry deposition flux,  $F$ , was then calculated using

$$F(\text{ng m}^{-2} \text{d}^{-1}) = k_A \times [\text{RGM}] \quad (4)$$

Dry deposition velocities for the cement plant and the rural site were similar, but about 20% higher at the urban site (Table 7), which was likely due to close proximity to an air field landing strip and higher average wind speed (Table 2). Average velocities for this study (0.88–1.2 cm s<sup>-1</sup>) were within the range typically reported (0.4–5.9 cm s<sup>-1</sup>, from Lindberg and Stratton, 1998), and were similar to those estimated for a semirural coastal site (0.9 ± 0.9 cm s<sup>-1</sup>, from Laurier and Mason, 2007).

Highest average RGM flux occurred at the cement plant (2007: 15 ng m<sup>-2</sup> d<sup>-1</sup>, 2008: 21 ng m<sup>-2</sup> d<sup>-1</sup>); however, daytime (i.e., 7 am–7 pm) average flux at the rural site in 2008 exceeded average flux at the cement plant (rural: 29 ng m<sup>-2</sup> d<sup>-1</sup>). It is possible lower RGM flux at the cement plant was due to fast transfer of RGM to Hg<sub>p</sub>. The ratio between average day and nighttime flux (i.e., 7 pm–7 am) at the cement plant was <1, reflecting higher nighttime emissions (ratio in 2007: 0.91, ratio in 2008: 0.71). At the urban and rural sites, the ratio was >1 (2005: rural 5.0, urban 2.6; 2008: rural 12.0, urban 2.0). For both sites, especially the rural site, higher values during the day reflected transport of RGM in the O<sub>3</sub> plume and dispersal at night.

Although the rural site was more removed from Hg sources, dry deposition flux was comparable to measurements at the cement plant. These results suggested proximity to a Hg source may not be the most important factor when considering the reach of Hg emissions. However, more sampling between coastal and inland sites is needed to verify these results.

## 6. Conclusions

Atmospheric species (GEM, RGM and Hg<sub>p</sub>) were monitored at a cement plant, an urban site and a rural site. RGM and Hg<sub>p</sub> at the cement plant were elevated compared to the other two sites; however, average GEM and daytime dry depositional RGM flux were highest at the rural site in 2008, when all three sites were monitored. Although RGM and O<sub>3</sub> peaked in the late afternoon, production of RGM through photo-oxidation was considered too slow to explain the dramatic increases in RGM at the rural site. Instead, elevated RGM was likely due to transport within the O<sub>3</sub> air plume, which was dispersed at night. Drier conditions at the rural site helped sustain RGM levels in the late afternoon. These results suggested Hg emissions from urban point sources may lead to elevated RGM levels at more remote sites, and should be further investigated.

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## Appendix. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2009.12.032.

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