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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_p), 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 ± 1.39 ng m^{-3}, RGM: 25.2 ± 52.8 pg m^{-3}, Hg_p 80.8 ± 283 pg m^{-3}), 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 ± 1.26 ng m^{-3}, daytime RGM flux: 29 ± 40 ng m^{-2} day^{-1}). Photochemical conversion of GEM was not the primary RGM source, as highest net RGM gains (75.9 pg m^{-3}, 99.0 pg m^{-3}, 149 m^{-3}) occurred within 3.0–5.3 h, while the theoretical time required was 14–23 h. Instead, simultaneous peaks in RGM, Hg_p, ozone (O_3), 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 ± 1.4 g kg^{-1}, urban: 9.0 ± 1.1 g kg^{-1}, cement plant: 8.3 ± 2.2 g kg^{-1}). Together, these findings suggested short-range transport of O_3 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.

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_p) (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_p 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_3) (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_3 is a photochemical oxidant, produced through the reaction between nitrogen oxides (NO_x = NO + NO_2), 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_3 and/or OH; however, these processes may differ between urban centers and downwind rural locations (i.e., NO_x-limited environments). O_3 concentrations tend to be higher in rural areas due to transport of the O_3 air mass

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downwind from the urban center, when the time for O_3 formation and accumulation is lengthened, while destruction of O_3 by urban pollutants may be evaded (Finlayson-Pitts and Pitts, 2000). Transport of Hg species in the O_3 air mass may also lead to the production and relocation of RGM to more remote regions, although oxidation of GEM to RGM by O_3 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_p) 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.

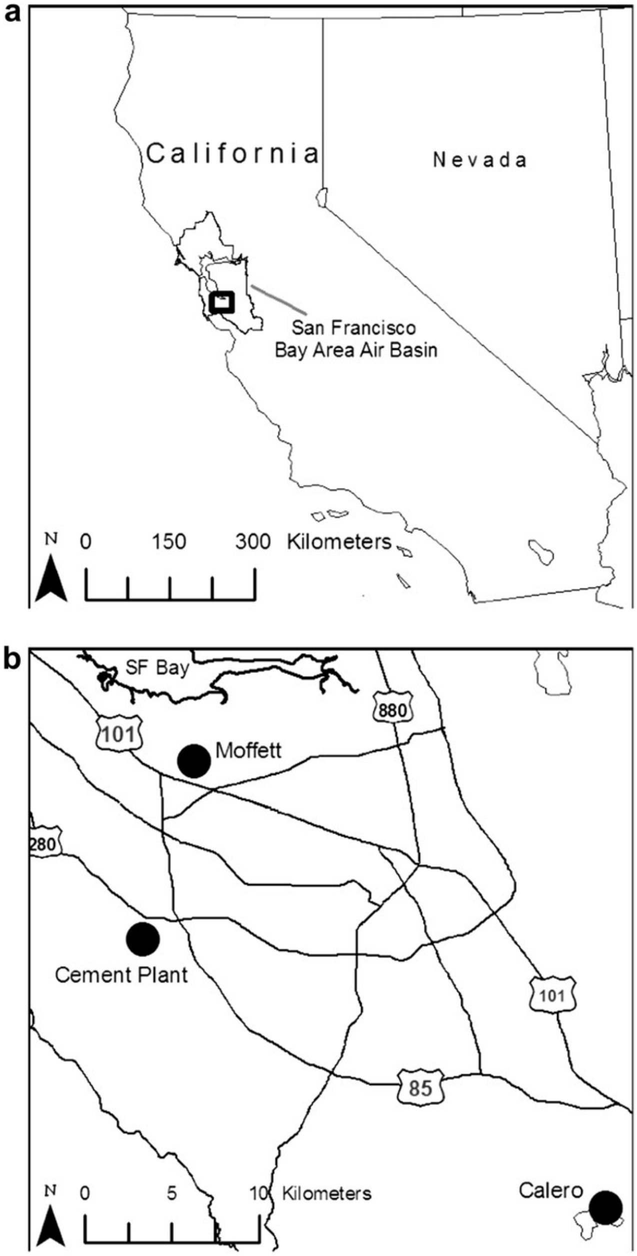

Fig. 1. Map of (a) San Francisco Bay Area air basin (b) sampling sites, including Lehigh Hanson Permanente Cement (the cement plant), Moffett Field (the urban site), and Calero Reservoir (the rural site).

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_3, NO_x, sulfur dioxide (SO_2)) 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 1.451×10^6 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^{-1} (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_p) 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_p

Atmospheric Hg species (GEM, RGM, and Hg_p) 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_p on a quartz filter assembly, and GEM on gold

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