

Wet deposition of mercury within the vicinity of a cement plant before and during cement plant maintenance

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ABSTRACT

Hg species (total mercury, methylmercury, reactive mercury) in precipitation were investigated in the vicinity of the Lehigh Hanson Permanent Cement Plant in the San Francisco Bay Area, CA., USA. Precipitation was collected weekly between November 29, 2007 and March 20, 2008, which included the period in February and March 2008 when cement production was minimized during annual plant maintenance. When the cement plant was operational, the volume weighted mean (VWM) and wet depositional flux for total Hg (Hg_T) were 6.7 and 5.8 times higher, respectively, compared to a control site located 3.5 km east of the cement plant. In February and March, when cement plant operations were minimized, levels were approximately equal at both sites (the ratio for both parameters was 1.1). Due to the close proximity between the two sites, meteorological conditions (e.g., precipitation levels, wind direction) were similar, and therefore higher VWM Hg_T levels and Hg_T deposition likely reflected increased Hg emissions from the cement plant. Methylmercury (MeHg) and reactive Hg ($Hg(II)$) were also measured; compared to the control site, the VWM for MeHg was lower at the cement plant (the ratio = 0.75) and the VWM for $Hg(II)$ was slightly higher (ratio = 1.2), which indicated the cement plant was not likely a significant source of these Hg species to the watershed.

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1. Introduction

Mercury (Hg) is a global pollutant, and ingestion of fish tissue is considered the primary route for human and wildlife exposure to methylmercury (MeHg), a known neurotoxin (WHO, 1990, 1991). In the USA, more than 8500 water bodies in 45 states and territories are impaired for Hg in sediments, surface water, or fish tissue (USEPA, 2009), including many water bodies where atmospheric Hg is the primary source (e.g., MPCA, 2008; NEIWPCC, 2008). Under Section 303(d) of the Clean Water Act, impaired water bodies must be addressed through the total maximum daily load (TMDL) program, which specifies the maximum pollution load a water body can assimilate and still maintain designated beneficial uses.

It is challenging for regulators to address impairments to water bodies through the TMDL program when atmospheric sources are important (USEPA, 2008). This is partially due to inter-state

boundary issues (e.g., air pollution originates out of state), and also due to regulation of air pollutants through the Clean Air Act. In California, addressing air pollutants through the TMDL program is more difficult due to a significant governmental separation between air regulation (California Air Resources Board) and water regulation (California State Water Resources Control Board). However, reducing atmospheric Hg emissions will likely result in lower fish tissue MeHg levels (Hammerschmidt and Fitzgerald, 2006; Harris et al., 2007; Hintelmann et al., 2002), as newly deposited atmospheric Hg is more rapidly converted to MeHg than native or legacy Hg (Hintelmann et al., 2002). Lowering atmospheric Hg emissions will help states meet TMDL numeric targets and restore beneficial uses, such as recreational fishing and protection of wildlife. Therefore, it is important for environmental managers to consider both atmospheric and aqueous Hg pollution inputs when developing mitigation strategies for Hg impaired water bodies.

Between 1996 and 2002, the San Francisco Bay Estuary was included on the California 303(d) List of Water-Quality Impaired Segments due to elevated Hg levels in fish tissue (USEPA, 2009). Primary Hg sources include historical gold and Hg mining, and urban and wastewater runoff (Conaway et al., 2003, 2004). In this report, Hg species (total Hg, MeHg, reactive Hg) in precipitation were characterized in the vicinity of Lehigh Hanson Permanent

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Cement, located in the San Francisco Bay Area (Fig. 1). Precipitation was collected weekly for 16 weeks at the cement plant from November 2007–March 2008, and within a shorter timeframe from two nearby control sites (Fig. 1). Data collection for precipitation coincided with annual cement plant maintenance in February and March 2008 (BAAQMD, 2009), which provided an ideal opportunity to compare Hg species in precipitation with and without inputs from the cement plant.

2. Site descriptions

2.1. Lehigh Hanson Permanente Cement Plant

Lehigh Hanson Permanente Cement Plant is located in the San Francisco Bay Area (hereafter referred to as “the cement plant”) (latitude/longitude: 37.322432/–122.079305, elevation 183 m). Beginning in May 2007, the cement plant began reliance on petroleum coke as the sole fuel used in the kiln, and was permitted to increase usage from 7.3 to 18 metric tons (t) petroleum coke h^{-1} for fuel (Brian Bateman, BAAQMD, personal communication). From December 10–13, 2007, and a few days prior (which coincided with week 2 of precipitation collection), the cement plant was allowed to incinerate up to 19.5 t h^{-1} of petroleum coke to conduct a compliance source test.

The cement plant was chosen for this investigation as it is a significant source of Hg emissions, accounting for 29% of the 2007 total estimated Hg emissions in the San Francisco Bay Area air basin (61.4 kg/214 kg, from CARB, 2009, the most recent year data were available). The cement plant is also geographically isolated from five refineries, which account for 63% of 2007 total estimated Hg emissions in the San Francisco Bay Area air basin (134 kg/214 kg) (CARB, 2009) and are located approximately 75 km north of the cement plant. Precipitation was collected near the northern property line, downwind from the cement plant (within 0.5 km of the kiln).

2.2. Control sites and wind direction

Precipitation was collected at two nearby control sites: the rooftop of the Environmental Studies building at De Anza Community College (3.5 km east of the cement plant, latitude/longitude: 37.31622/–122.04348, elevation 91 m, “De Anza College”), and in Stevens Creek County Park (2.4 km southeast of the cement plant, latitude/longitude: 37.3056/–122.0736, elevation 152 m, “SC Park”) (Fig. 1).

Wind rose plots for the sampling period were available from the La Honda climate station (~20 km east of the cement plant, elevation 229 m, data not available from the nearby Los Altos climate station) (WRCC, 2009), which indicated strongest winds originated from the west-southwest, east and east-northeast sectors.

3. Methods

3.1. Field sampling

Precipitation was collected weekly at the cement plant and De Anza College using modified Aerochem Metrics model 301 collectors (the same used for the Mercury Deposition Network; MDN, 2009). Briefly, each collector is equipped with two covered chimneys and a moisture-sensitive plate, which activates the arm controlling the cover. The left-side chimney contained an acid-washed funnel and thistle connected to a 1-L FLPE bottle, while the right-side chimney contained an acid-washed funnel connected directly to a 1-L FLPE bottle. Side by side total Hg (Hg_T) levels indicated no significant difference in Hg_T levels between the two chimneys ($p > 0.50$, $n = 7$). At SC Park, precipitation was collected on an event basis, using an acid-washed funnel and thistle connected to a 1-L FLPE bottle,

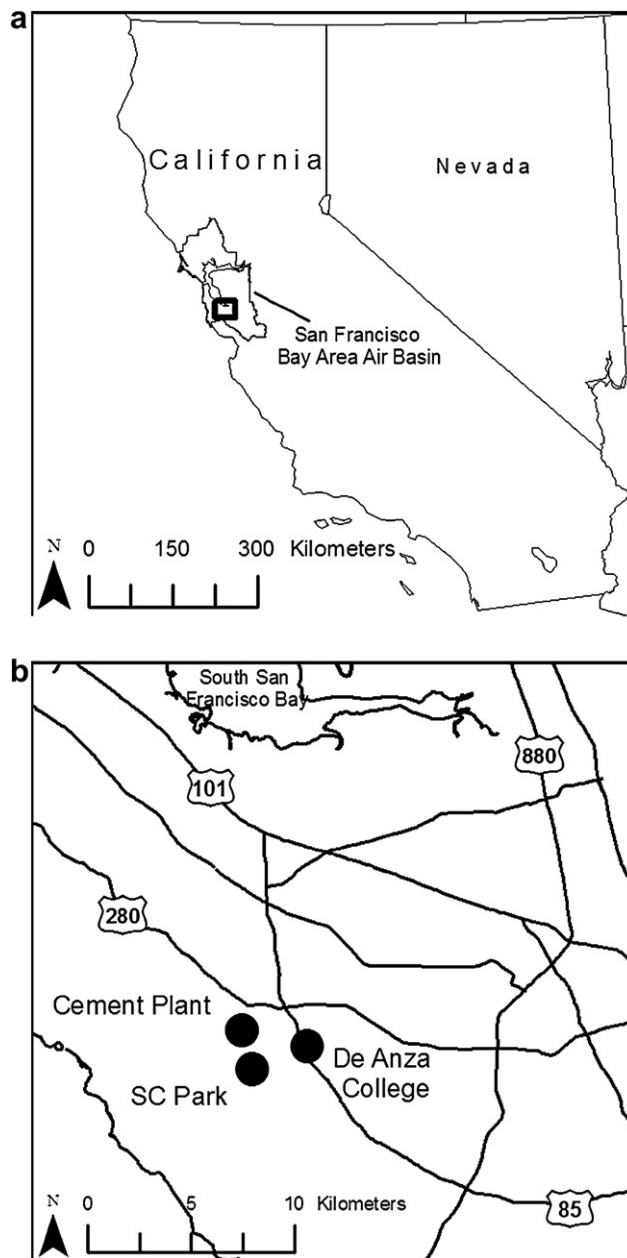


Fig. 1. Map of (a) San Francisco Bay Area Air Basin, California, USA. (b) Precipitation collection sites, including the cement plant, De Anza College and Santa Clara (SC) Park.

housed in a PVC tube. Collection bottles for all three sites were pre-filled with either 20 ml 10% HCL (for preservation of Hg species) or 20 ml of 10% HNO_3 (to preserve other metals).

Near the cement plant precipitation was collected continuously for 16 weeks, between November 29, 2007, and March 20, 2008. At De Anza College precipitation was collected for nine weeks (January 10–March 20, 2008, weeks 8–16), and at SC Park precipitation was collected during two rain events, one occurring in February (week 13) and one in March (week 16). During the four-month period, no precipitation occurred during 5 weeks (weeks 4, 7, 11, 14, 15); additionally, during week 6 precipitation was collected for one day only near the cement plant, due to equipment damage following a powerful storm. When calculating Hg_T deposition for the 4-month period (see below and Section 4.1), only one day of precipitation was included for week 6.

Hg_T deposition (ng m⁻² week⁻¹) was determined from the following equation:

$$\text{Hg}_T \text{ deposition} = [\text{Hg}_T] \times \text{precipitation} \quad (1)$$

where [Hg_T] represented the concentration of Hg_T in precipitation collected in one week (ng L⁻¹), and precipitation (mm) was measured by the network of rain gages maintained by the Santa Clara Valley Water District (SCVWD) ALERT system (Station 1522, located 1.6 km and 3.5 km, respectively, from the cement plant and De Anza College, Station 1510 located 4.8 km from SC Park; SCVWD, 2009).

At all three locations, soil samples (0–2 cm) were collected using Nalgene[®] acid-washed jars.

3.2. Laboratory methods

3.2.1. Aqueous Hg_T

For Hg_T, acidified precipitation samples were oxidized overnight with 0.5% (v/v) 0.2 N bromine monochloride (BrCl), and then pre-reduced using hydroxylamine hydrochloride. The samples were reduced further with stannous chloride (SnCl₂), converting inorganic Hg(II) to volatile Hg(0) (i.e., GEM), which was then purged from solution by argon gas. For Hg(II) (commonly referred to as reactive or labile Hg), samples were reduced with SnCl₂, leaving out the BrCl oxidation step (Hammerschmidt et al., 2007). Quantification for Hg_T and Hg(II) was by dual-stage gold amalgamation/cold vapor atomic fluorescence spectrometry (CVAFS). The oxidation–reduction steps follow established methods (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988), which are implemented in EPA Method 1631, Revision E (USEPA, 2002).

3.2.2. Solid-phase Hg_T

Following Method 1631 Appendix for cold digestion of sediments (USEPA, 2002), ~1 g wet sediment was digested in a borosilicate glass vial overnight in 10 ml of 8:2 hydrochloric acid: nitric acid. The samples were then oxidized with 0.5 ml of 0.2 N BrCl to prevent resorption of inorganic Hg(II) to organic matter, and excess oxidant was neutralized with hydroxylamine hydrochloride. After dilution, the same procedures described for reduction and quantification of aqueous Hg_T were followed.

3.2.3. MeHg

Following addition of KCl and L-cysteine, acidified samples were distilled into receiving vials under N₂ flow using an all Teflon[®] system, according to methods described by Horvat et al. (1993a,b) and codified in Method 1630 (USEPA, 2001). The pH of the distillates was then adjusted to 4.9 with 2 M acetate buffer, and ethylated using 1% sodium tetraethylborate, converting nonvolatile MeHg to gaseous methylethylmercury, which was purged onto Tenax columns, then thermally desorbed from the column and quantified by CVAFS.

3.2.4. Other metals V, Ni, Pb, Sb

A modified version of EPA 1638 (USEPA, 1996) certified by the National Environmental Laboratory Accreditation Program was employed for the determination of vanadium (V), nickel (Ni), lead (Pb) and antimony (Sb), using inductively coupled plasma mass spectrometry.

3.2.5. QAQC

Detection levels for aqueous species were as follows: Hg_T (0.15 ng L⁻¹), Hg(II) (0.15 ng L⁻¹), MeHg (0.020 ng L⁻¹), V (0.03 µg L⁻¹), Ni (0.04 µg L⁻¹), Pb (0.010 µg L⁻¹), Sb (0.003 µg L⁻¹), and the detection level for solid phase Hg_T was 0.03 ng g⁻¹. The relative percent difference (RPD) between duplicate analyses were as follows: aqueous Hg_T (1.8%, n = 13), solid phase Hg_T (5.1%, n = 4), Hg

(II) (11%, n = 6), MeHg (23%, n = 2), V (5.4%, n = 2), Ni (0%, n = 2), Pb (2.5%, n = 2), and Sb (3.1%, n = 2). Higher RPD for MeHg was due to one sample close to the detection level; when this sample was removed RPD was 3.6%. Average Hg_T levels for trip blanks were < MDL (n = 6). Average recoveries of matrix spikes and certified reference material standard were between 88% and 108% (Table 1).

All laboratory analyses were completed at Brooks Rand, LLC, located in Seattle, WA, USA.

3.3. Data for daily mass throughput at the cement plant

Data for daily mass throughput, including raw feed (tons) and petroleum coke (tons), and daily stack emissions, including SO₂ (kg) and sulfur (kg), were obtained through a Public Records request (BAAQMD, 2009). Based on throughput, the cement plant was down on the following dates: January 6–14, January 31–February 5, February 18–March 18, and March 19, which coincided partially with weeks 6, 7, 10, 12 and 16, and completely with weeks 13, 14 and 15 of this study. For correlation with Hg data, daily mass throughput and daily stack emissions were segregated by week (n = 16).

3.4. Data analysis

The volume weighted mean (VWM) is a descriptive statistic:

$$\text{VWM} = \frac{\sum_{i=1}^n (C_i V_i)}{\sum_{i=1}^n V_i} \quad (2)$$

where C_i is the concentration in precipitation (ng L⁻¹) for week i, V_i is the total volume (L) collected for week i, and n is the number of weeks sampled. In addition to comparing the VWM for Hg species between sites, two-tailed t-tests were calculated using un-weighted data to determine whether differences were due to chance (p > 0.05) or were considered significant (p < 0.05) (Sections 4.2 and 4.6). Aqueous Hg_T concentrations were transformed to normality using a log₁₀-transformation. T-tests were not used to compare Hg_T results between the cement plant and SC Park, nor between other metals (V, Ni, Pb, Sb) measured at all three sites due to insufficient data (Sections 4.2 and 4.3). Hg_T concentrations (log₁₀-transformed) measured near the cement plant were regressed on petroleum coke usage (Section 4.4) and on rain (Section 4.5). Although the sample size was small (n = 11), residuals from each regression model were investigated to verify standard assumptions were met (mean = 0 and constant variance). The statistics program, Stata, was used for data analysis.

4. Results and discussion

4.1. Hg_T at the cement plant

The VWM Hg_T concentration was highest near the cement plant compared to both control sites (cement plant: 13 ng L⁻¹; De Anza College: 3.4 ng L⁻¹; SC Park: 9.5 ng L⁻¹) (Table 2). Hg_T

Table 1

Average percent recovery ±1 standard deviation for matrix spikes and certified reference material (CRM), for Hg_T, MeHg, and other metals (V, Ni, Pb, Sb) in precipitation (aqueous phase) and sediments (solid phase).

	n	Matrix spike recovery (%)	n	CRM recovery (%)
Hg _T (aqueous)	36	108 ± 7.22		
Hg _T (solid)	20	104 ± 9.14	3	106 ± 3.79
MeHg (aqueous)	15	105 ± 11.5		
Hg(II) (aqueous)	4	106 ± 6.68		
V (aqueous)	5	85.4 ± 6.88	4	101 ± 7.77
Ni (aqueous)	9	91.2 ± 13.3	4	102 ± 3.20
Pb (aqueous)	9	101 ± 17.4	4	105 ± 5.80
Sb (aqueous)	1	88	4	100 ± 4.24

Table 2
Summary statistics for precipitation measured at the cement plant, De Anza College and SC Park, including average ± 1 standard deviation, range (in parentheses), sample size (n), and volume weighted mean (VWM), for Hg_T, MeHg, Hg(II), other metals (V, Ni, Pb, Sb) and summary statistics for sediment Hg_T levels.

	Cement plant	De Anza College	SC Park
Hg _T (ng L ⁻¹)	19 ± 19 (3.4–60) (n = 11)	4.4 ± 1.5 (2.8–6.8) (n = 6)	18 ± 13 (9.3–27) (n = 2)
Hg _T Deposition (ng m ⁻² week ⁻¹)	320 ± 340 (17–1100) (n = 11)	110 ± 85 (6.9–230) (n = 6)	390 ± 440 (82–700) (n = 2)
Hg _T VWM (ng L ⁻¹)	13 (n = 11)	3.4 (n = 6)	9.5 (n = 2)
MeHg (ng L ⁻¹)	0.22 ± 0.18 (0.018–0.44) (n = 5)	0.38 ± 0.25 (0.21–0.56) (n = 2)	NA
MeHg Deposition (ng m ⁻² week ⁻¹)	1.8 ± 1.7 (0.11–3.6) (n = 5)	2.9 ± 2.5 (1.1–4.7) (n = 2)	NA
MeHg VWM (ng L ⁻¹)	0.15 (n = 5)	0.23 (n = 2)	NA
%MeHg (of Hg _T)	2.0 ± 2.0 (0.030–4.7) (n = 5)	4.3 ± 0.67 (3.8–4.8) (n = 2)	NA
Hg(II) (ng L ⁻¹)	0.40 ± 0.16 (0.21–0.50) (n = 3)	0.37 ± 0.13 (0.22–0.45) (n = 3)	0.95 (n = 1)
Hg(II) Deposition (ng m ⁻² week ⁻¹)	16 ± 6.6 (11–23) (n = 3)	16 ± 5.0 (10–20) (n = 3)	68 (n = 1)
Hg(II) VWM (ng L ⁻¹)	0.36 (n = 3)	0.31 (n = 3)	0.95 (n = 1)
%Hg(II) (of Hg _T)	12 ± 1.8 (11–14) (n = 3)	9.0 ± 1.5 (7.9–11) (n = 3)	12 (n = 1)
V (nM)	45 ± 56 (5.4–85) (n = 2)	6.7 ± 7.1 (1.7–12) (n = 2)	60 (n = 1)
Ni (nM)	24 ± 32 (1.0–46) (n = 2)	9.8 ± 12 (1.0–19) (n = 2)	35 (n = 1)
Pb (nM)	7.0 ± 8.8 (0.74–13) (n = 2)	3.7 ± 4.2 (0.76–6.7) (n = 2)	13 (n = 1)
Sb (nM)	0.78 ± 0.89 (0.16–1.4) (n = 2)	0.43 ± 0.32 (0.21–0.66) (n = 2)	1.4 (n = 1)
Sediments(Windward) (ng g ⁻¹)	95 ± 22 (80–110) (n = 2)	130 ± 19 (120–140) (n = 2)	81 ± 5.8 (77–85) (n = 2)
Sediments(Leeward) (ng g ⁻¹)	82 ± 34 (57–110) (n = 2)	89 ± 28 (70–110) (n = 2)	97 ± 4.5 (94–100) (n = 2)

concentrations (log₁₀-transformed) were significantly higher at the cement plant ($n = 11$) compared to De Anza College ($n = 6$) ($p < 0.05$). Elevated Hg_T levels near the cement plant occurred between weeks 1 and 9 (November 29–January 31) (VWM: 18 ng L⁻¹) ($n = 7$), while lowest levels occurred between weeks 10 and 16 (February 1–March 20) when cement plant operations were minimized (VWM: 4.3 ng L⁻¹) ($n = 4$), and this difference was significant ($p < 0.05$, Hg_T log₁₀-transformed). During week 2 (December 6–13), the cement plant was permitted to increase petroleum coke usage by 15% from 17.0 to 19.5 t h⁻¹ to test compliance with emissions standards (BAAQMD, 2008); likewise, Hg_T levels in precipitation increased by 60% to their highest level (60 ng L⁻¹), despite increased volume collected (Table 3).

4.2. Hg_T comparison between the cement plant and control sites

Side-by-side data for the cement plant and De Anza College were available for weeks 8, 9, 10, 12, 13 and 16 ($n = 6$) (Fig. 2). The

cement plant was partially or completely down during the latter four weeks (weeks 10, 12, 13, 16; no rain occurred during weeks 11, 14, and 15). During weeks 8–9, and weeks 10, 12, 13, and 16, the ratio between VWM Hg_T levels at the cement plant and De Anza College was 6.7 and 1.1, respectively (Fig. 2). For the same weeks, the ratios between average Hg_T deposition were 5.8 and 1.1, respectively, and the ratios between average Hg_T concentrations were 7.4 and 1.6, respectively. Due to the close proximity between the two sites (3.5 km apart), meteorological conditions (e.g., precipitation levels, wind direction) were similar, and therefore higher Hg_T levels when the cement plant was operational likely reflected increased Hg emissions from the cement plant. Although Hg_T deposition and concentration were higher compared to De Anza College when the cement plant was operational, t -tests were not significant (both log₁₀-transformed), which was likely due to insufficient data ($n = 2$ weeks prior to plant closure) ($p > 0.10$). During plant closure, differences were also not significant ($p > 0.50$, both log₁₀-transformed).

Table 3
Weekly Hg_T concentration (ng L⁻¹) and Hg_T wet deposition rates (ng m⁻² week⁻¹), and weekly cement plant fuel use and stack emissions (data for cement plant from BAAQMD, 2009).

Date	Week	Cement plant		De Anza college		SC park		Cement plant mass throughput ^a		Cement plant stack emissions ^a	
		Hg _T (ng L ⁻¹)	Hg _T deposition (ng m ⁻² week ⁻¹)	Hg _T (ng L ⁻¹)	Hg _T deposition (ng m ⁻² week ⁻¹)	Hg _T (ng L ⁻¹)	Hg _T deposition (ng m ⁻² event ⁻¹) ^e	Raw feed (tons)	Petroleum coke (tons)	SO ₂ (kg)	Sulfur (kg)
2007–2008	#										
11/29–12/6	1	37	220					31,490	2217	2810	1405
12/6–12/13	2	60	360					42,230	2899	1874	936.7
12/13–12/20	3	8.0	210					25,040	2073	3190	1595
12/20–12/27	4 ^b							25,440	2401	2004	1002
12/27–1/3	5	13	27					27,940	2311	3176	1588
1/3–1/4	6 ^c	6.6	470					4350	339.3	427.3	213.6
1/10–1/17	7 ^b							8376	539	518.7	259.0
1/17–1/24	8	44	790	4.9 ^d	88			34,285	2196	2060	1030
1/24–1/31	9	13	1100	2.8	230			26,657	1878	3238	1618
1/31–2/7	10	3.4	77	5.3	120			3761	269.9	397.1	198.4
2/7–2/14	11 ^b							30,410	2261	1779	888.4
2/14–2/21	12	4.9	78	2.8	45			12,680	904.5	857.3	404.2
2/21–2/28	13	4.6	210	4.0	180	9.3	700	0	0	0	0
2/28–3/6	14 ^b							0	0	0	0
3/6–3/13	15 ^b							0	0	0	0
3/13–3/20	16	17	17	6.8	6.9	27	82	783.8	56.25	64.86	32.66

^a Daily mass throughput and daily stack emissions data from the Lehigh Hanson Cement Plant were obtained from the Bay Area Air Quality Management District Public Records request (BAAQMD, 2009).

^b Hg data were not available for weeks 4, 7, 11, 14 and 15 due to insufficient or no precipitation.

^c Data for week 6 are for one day only (Jan 3–Jan 4).

^d Data collection for De Anza College began during week 8 (no rain week 7).

^e For SC Park, precipitation was collected during two events, and the Hg deposition rate was calculated per rain event (not per week).

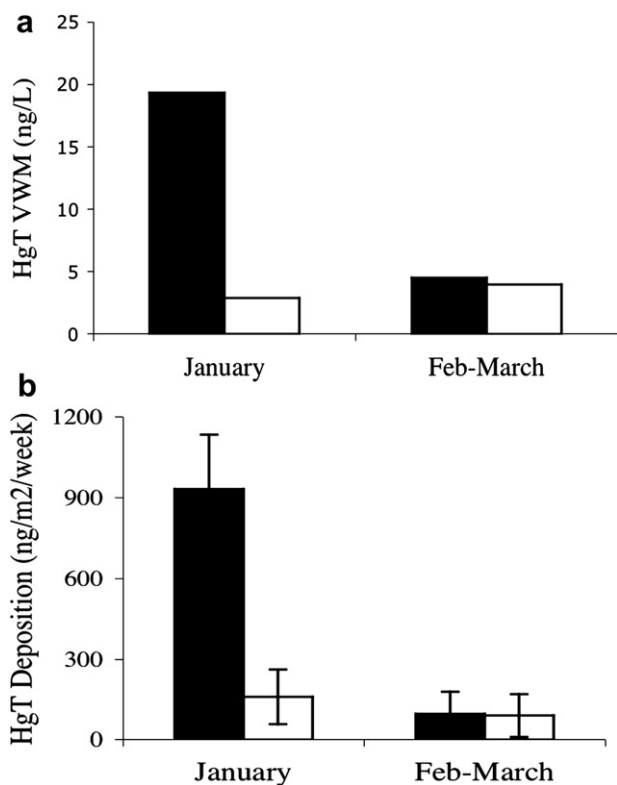


Fig. 2. Comparison between Hg_T levels at the cement plant (black bar) and the control site (De Anza College) (white bar) during January, when the cement plant was operational ($n = 2$), and during February and March ($n = 4$), when the cement plant was closed due to annual maintenance, a) Hg_T volume weighted mean (VWM) (ng L⁻¹) b) Hg_T deposition ± 1 standard deviation (ng m⁻² week⁻¹).

Precipitation was collected at SC Park during weeks 13 and 16 (during both weeks, cement plant operations were down). The ratio between VWM Hg_T levels and Hg_T deposition rates at the cement plant and SC Park was 0.52 and 0.24, respectively. At SC Park, Hg_T concentration and Hg_T deposition were higher than those at the cement plant (Table 3), which was unexpected considering SC Park was more isolated from Hg point sources. Elevated Hg_T levels may reflect increased Hg inputs in throughfall (Choi et al., 2008; St. Louis et al., 2001), as the sampling area was located near trees in a forested park. Particulates were also observed in the collection bottle, which were not filtered prior to analysis since acid was pre-dispensed before deployment. Higher precipitation levels in SC Park also contributed to elevated Hg_T deposition; precipitation was 1.6 and 3.0 times higher than precipitation measured near the cement plant during weeks 13 and 16, respectively.

4.3. Other metals (V, Ni, Pb, Si)

Other metals (V, Ni, Pb, Sb) were measured during week 13 (at the cement plant and De Anza College) and week 16 (at all three sites) (Fig. 3). Both V and Ni are associated with petroleum coke emissions (Hower et al., 2005), while Pb and Sb levels typically reflect waste incineration emissions (Dvonch et al., 2005). Results from the December 10–14, 2007 cement plant compliance test showed increased emissions for all metals (e.g., Hg, V, Ni, Pb, Sb) when the hourly mass of incinerated petroleum coke was increased by 15%; metal emissions were ranked as follows (maximum g h⁻¹): Hg (10) > Ni (0.47) > V (0.25) > Pb (0.065) > Sb (0.043) (BAAQMD,

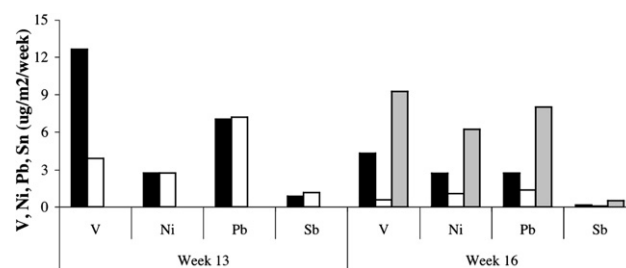


Fig. 3. Deposition of other metals (V, Ni, Pb, Sb) ($\mu\text{g m}^{-2} \text{ week}^{-1}$) during weeks 13 and 16 at the cement plant (black bar) and two control sites (De Anza College, white bar; SC Park, gray bar). No rain occurred between weeks 13 and 16, and the cement plant was closed during both weeks. SC Park was not monitored during week 13, and during week 16 higher deposition reflected more rainfall (3 times), as concentrations for all metals were similar or lower at SC Park compared to the cement plant (Table 3).

2008), which confirmed all metals were associated with incineration of petroleum coke.

Deposition rates were compared rather than concentrations (Fig. 3), since more rain fell during week 13 compared to week 16 (46 mm versus 1.0 mm at the cement plant and De Anza College; 76 mm versus 3.0 mm at SC Park, Table 3). There were insufficient data to calculate *t*-tests for metals at the three sites. Plant operations were minimized during week 12, and completely down from week 13 until the end of week 16 (the last week of the study). The final rain event occurred during week 16, just 4 days before cement plant operations resumed. Therefore Fig. 3 included data collected for metals only during cement plant closure.

During week 13, Ni, Pb and Sb deposition rates were similar between the cement plant and De Anza College, while V deposition was higher near the cement plant (Fig. 3). The latter suggested V may have a slightly longer atmospheric lifetime compared to the other metals, or V was more concentrated near the cement plant and may take longer to attenuate. V may also have a higher affinity for particulates. During week 16, after nearly 4 weeks of no plant operations and 20 days since the previous rain event, deposition for all metals decreased near the cement plant and De Anza College. However unlike week 13, deposition rates for all metals were higher at the cement plant during week 16, which may be due to more sustained particulates near the cement plant.

During week 16, other metals were also measured at SC Park, where deposition was higher compared to the cement plant and De Anza College (Fig. 3). Concentrations for all metals were lower at SC Park compared to the cement plant, but higher than those measured at the De Anza College. Precipitation was 3 times higher at SC Park compared to the other two sites (see Section 4.2), which resulted in higher deposition.

4.4. Correlation between Hg_T, fuel use, raw feed and sulfur emissions

Assuming no hazardous materials are used as fuel, the primary sources of Hg emissions from portland cement processing include combustion of fossil fuels (e.g., petroleum coke) and incineration of raw materials (e.g., limestone) at high temperatures (i.e., 350 °C) (USEPA, 1997). Raw materials and petroleum coke were highly correlated ($r^2 = 0.97$, $p < 0.001$, $n = 15$, data from BAAQMD, 2009), and both were positively associated with Hg_T concentrations in precipitation, although raw materials were more highly correlated (\log_{10} Hg_T versus raw materials: $r^2 = 0.65$; \log_{10} Hg_T versus coke: $r^2 = 0.58$, $p < 0.05$ for both). The associations between the Hg_T deposition rate (ng m⁻² week⁻¹) and raw materials and petroleum coke were weaker (\log_{10} Hg_T deposition versus raw feed: $r^2 = 0.15$; \log_{10} Hg_T deposition versus coke: $r^2 = 0.20$, $p > 0.10$ for both), indicating rain does not

effectively washout Hg near the cement plant (discussed further in Section 4.5).

Raw materials and fuel both contribute to Hg emissions; however the air quality permit is based primarily on fuel consumption. For regulatory purposes, the following regression model may provide information on the consequences of increasing petroleum coke on Hg_T levels in precipitation, when petroleum coke is the sole fuel used (see Fig. 4):

$$\log_{10} \text{Hg}_T = 0.69 + 0.29 \text{ petroleum coke} / 1000t \quad (3)$$

$$(r^2 = 0.58, p < 0.05)$$

A regression equation in which the dependent variable is log₁₀-transformed may be interpreted as follows: for a 1000 t weekly increase in petroleum coke usage, the average Hg_T concentration in precipitation (ng L⁻¹) near the cement plant is expected to increase by 95% (=100 × (10^{0.29×1.00} - 1)). In 2008, the cement plant applied for a permit to increase petroleum coke usage by 33% from 18 to 24 t h⁻¹ (=1.008 × 1000 additional t coke week⁻¹), but withdrew the request (Brian Bateman, BAAQMD, personal communication). From the regression model, this increase may lead to a 96% increase in the average Hg_T level in precipitation (=100 × (10^{0.29×1.008} - 1)). Due to the low sample size (n = 11), more observations are needed to verify this relationship.

Hg_T levels in precipitation (log₁₀-transformed) were not well correlated with sulfur levels measured in stack emissions (r² = 0.25, p > 0.05). This was possibly due to technology designed to remove sulfur but not Hg, or may reflect variability in Hg species emitted. For European cement plants, the estimated proportion of Hg species is: 80% gaseous elemental Hg (GEM), 17% reactive gaseous Hg (i.e., RGM or Hg(II)), and 3% particulate-bound (Hg_p) (Pacyna et al., 2006). GEM, RGM and Hg_p were monitored in 2007 and 2008 near the cement plant and intermittent peaks were observed (Rothenberg et al., in press). It is likely the proportion of each Hg species was not constant during the 16-week study, which increased the variability between sulfur levels and precipitation Hg_T levels.

4.5. Washout effect and the scavenging ratio

Two relationships are used to investigate the importance of scavenging of Hg_T by rainfall: the washout effect and the scavenging (or washout) ratio (Guentzel et al., 1995; Lamborg et al., 1995; Lynam and Gustin, 2008; Mason et al., 1997; Steding and Flegal, 2002). The washout effect is characterized by a negative correlation between Hg_T concentrations and rainfall, and indicates

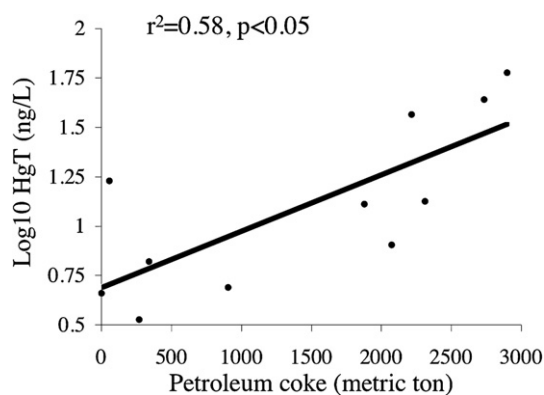


Fig. 4. Regression between log₁₀ Hg_T concentrations (ng L⁻¹) in precipitation versus petroleum coke (t) (r² = 0.58, p < 0.05). Data for daily fuel usage obtained from a Public Records request to the Bay Area Air Quality Management District (BAAQMD, 2009).

dilution and rapid washout of Hg_T. An inverse correlation was observed between Hg_T levels (log₁₀-transformed) and precipitation near the cement plant and De Anza College, although relationships at both sites were not significant (cement plant: r² = 0.15, p > 0.05; De Anza College: r² = 0.43, p > 0.05). A stronger correlation indicates proximity to a source, while a lack of correlation suggests non-local sources may be important (Steding and Flegal, 2002). Therefore, it is interesting to note an inverse correlation was stronger at De Anza College, located 3.5 km east of the cement plant. It is possible Hg_T concentrations were more sustained near the cement plant, similar to V, which was not diminished over time like other metals (see Section 4.3). For both sites, the sample size was small (cement plant: n = 11, De Anza College: n = 6), and therefore regression results were likely biased.

The scavenging ratio (S, unitless) is defined as the mass of a substance (e.g., Hg) per unit mass of rain or air (Duce et al., 1991):

$$S = \frac{\text{Hg}_{\text{rain}} \times \rho_{\text{atm}}}{\text{Hg}_p \times \rho_{\text{rain}}} \quad (4)$$

where [Hg_{rain}] = concentration of Hg_T in precipitation (ng L⁻¹), ρ_{atm} = 1.2 kg m⁻³, [Hg_p] = the concentration of particulate Hg (Hg_p) in the atmosphere (ng m⁻³) and ρ_{rain} = 1 kg L⁻¹. RGM was also water-soluble (Schroeder and Munthe, 1998), and therefore the scavenging ratio was calculated using the sum of Hg_p + RGM. Atmospheric Hg levels (including Hg_p and RGM) were monitored at the same location near the cement plant November 26–December 12, 2007 (17 days) using an automated Tekran 2537A/1130/1135 speciation unit (Landis et al., 2002) (Rothenberg et al., in press), and overlapped precipitation collection during week 1 and the first six days of week 2 (November 29–December 6, December 6–12). During the 17-day deployment, Hg_p + RGM averaged 38 pg m⁻³.

Values between 200 and 2000 for other metals are considered typical in areas where scavenging of particles is an important process (Duce et al., 1991). When the cement plant was operational the scavenging ratio was 820 ± 660, and during plant closure the ratio was 240 ± 200. When the data for all weeks were combined, the scavenging ratio was 600 ± 600 (range: 100–1900). Lower values during cement plant closure were due to reduced Hg_T concentrations in precipitation (Section 4.1). When the cement plant was operational, the values for the scavenging ratio were considered elevated compared to those measured in Wisconsin (477 ± 547 and 181 ± 129, from Lamborg et al., 1995), while the average (i.e., 820) was lower compared to the Chesapeake Bay (average = 1110, from Mason et al., 1997), and lower than those observed in Florida near the Everglades (winter: 2000–3000, summer: 3000–6000, from Guentzel et al., 1995). Lower scavenging values likely reflected higher Hg_p + RGM levels due to proximity to the cement plant (this study: 38 pg m⁻³, Chesapeake Bay: 18 pg m⁻³, from Mason et al., 1997; Florida 1.5–12.8 pg m⁻³, from Guentzel et al., 1995; Wisconsin: winter: 7 pg m⁻³, summer 26 pg m⁻³, from Lamborg et al., 1995).

4.6. Comparison with mercury deposition network dataset

In 2007, data pooled from over 85 Mercury Deposition Network (MDN) sites in the USA defined maximum Hg_T levels in precipitation as greater than 18 ng L⁻¹ (MDN, 2009). MDN sites are typically located away from point sources to capture background levels of Hg_T. Therefore, it was not surprising the average Hg_T level near the cement plant during weeks 1–9 (when the cement plant was operational) was greater than 18 ng L⁻¹ (average: 26 ng L⁻¹), while the average Hg_T level during weeks 10–16 (when the cement plant was down) was 7.4 ng L⁻¹, which corresponded to the third lowest category (6–8 ng L⁻¹ from MDN, 2009); i.e., similar to other background sites.

Between January 2000 and December 2006, the MDN network included Moffett Field (site # CA72; from MDN, 2009), located 11 km northeast of the cement plant. Total Hg_T deposition at the cement plant between November 29, 2007 and March 20, 2008 was $3.5 \mu g m^{-2}$. At Moffett Field, during the same 4-month period in previous years, total Hg_T deposition was $1.5 \mu g m^{-2}$ (2001–2002), $1.0 \mu g m^{-2}$ (2002–2003), $1.5 \mu g m^{-2}$ (2003–2004), $1.3 \mu g m^{-2}$ (2004–2005), and $2.5 \mu g m^{-2}$ (2005–2006). When the cement plant was operational (weeks 1–9), Hg_T deposition (\log_{10} -transformed) was significantly higher compared to levels measured at Moffett Field for the corresponding weeks in 2000–2001, 2002–2003, 2004–2005 ($p < 0.05$), while Hg_T concentrations (\log_{10} -transformed) were significantly higher compared to levels measured at Moffett Field during the same timeframe in 2002–2003, 2004–2005, 2005–2006 ($p < 0.05$). When the cement plant was not fully operational (weeks 10–16), Hg_T deposition and Hg_T concentration (both \log_{10} -transformed) were similar to those measured at Moffett Field for the same weeks for all six years ($p > 0.05$); i.e., the cement plant was similar to a background site.

4.7. MeHg and reactive Hg levels in precipitation

MeHg was measured in precipitation at the cement plant (weeks 2, 3, 5, 9, 10) and one control site (De Anza College) (weeks 9, 10). At the cement plant, the ratio between the MeHg VWM between weeks when the cement plant was fully operational and when the cement plant was down was 0.92, indicating no effect to MeHg levels from cement plant operations. MeHg levels at the cement plant were not significantly higher than those measured at De Anza College ($p > 0.05$). During weeks 9–10, the ratio between the MeHg VWM at both sites was 0.75, which indicated slightly higher MeHg levels at the control site. Munthe et al. (2003) measured Hg species directly in the stacks of several European power plants and waste incinerators, and reported emissions of MeHg were insignificant in all stack gases although other Hg species varied. Results from this study were in agreement, i.e., cement plant emissions were not a significant source of MeHg to the atmosphere during this sampling period.

Hg(II) was measured at the cement plant and De Anza College (weeks 9, 10, 13) and at SC Park (week 13). During this time, the cement plant was down partially during week 10 and completely down during week 13. The ratio of Hg(II) VWM between the cement plant and De Anza College for weeks 9, 10, and 13 was 1.2; when only weeks 10 and 13 were compared (when the cement plant was down), the ratio was 1.1 ($p > 0.05$). Hg(II) was measured at SC Park in precipitation collected during week 13; the Hg(II) VWM ratio between the cement plant ($n = 3$) and SC Park ($n = 1$) was 0.38. Although Hg(II) was measured in fewer samples, results suggested the portion of Hg considered more labile (i.e., more reactive) was similar between the cement plant and De Anza College.

4.8. Comparison of soil Hg_T levels between three sites

Soils (0–2 cm) were collected at two locations within all three sites, one less obstructed (windward side) and one more protected (leeward side) (Table 2). No significant differences were observed between Hg_T levels from the windward and leeward sites, nor among the three sites ($p > 0.50$). Average Hg_T soil levels from all three sites were lower than sediment Hg_T levels for a study of 26 sites throughout the San Francisco Bay (average: $96 \pm 18 \text{ ng g}^{-1}$ from this study; average: 200 ng g^{-1} , Conaway et al., 2003), and only 5/12 observations were considered contaminated (i.e., $>100 \text{ ng g}^{-1}$). Higher Hg_T levels in the San Francisco Bay reflected elevated inputs from atmospheric sources as well as historical mining and wastewater runoff (Conaway et al., 2003; Flegal et al., 2005), while soils for this study were from upland sites and Hg_T levels likely reflected atmospheric inputs. Comparable Hg_T soil

levels across all three sites suggested soils were washed into the Bay through storm water runoff, which was reported for other regions of the estuary (Conaway et al., 2007). Greater spatial sampling is needed to characterize the distribution of soil Hg levels, especially near the cement plant.

5. Conclusions

Hg emissions from the cement plant do not all enter the global circulation cycle and undergo long-range transport; Hg is also deposited within the vicinity of the cement plant through wet deposition. During cement plant closure, the VWM for Hg_T was reduced by a factor of 4.2. When the cement plant was not operational, Hg_T wet deposition rates and Hg_T concentrations in precipitation were similar to those measured at background sites, including a nearby control site (3.5 km east of the cement plant, De Anza College), other sites dispersed nationally in the MDN network, and historically at Moffett Field (11 km northeast of the cement plant), while Hg_T concentrations were significantly higher during normal operations at the cement plant ($p < 0.05$). From this study, it was not possible to determine whether fuel use or raw feed (i.e., limestone) was the predominant Hg source. However, due to the strong correlation between the two ($r^2 = 0.97$), lower fuel use would likely translate into lower use of raw materials. Although data were collected for only one rainy season, results from this study suggested a reduction in cement plant operations (i.e., lower fuel use) would lead to a corresponding decrease in Hg_T deposition to the surrounding community.

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References

- Bay Area Air Quality Management District (BAAQMD), 2008. Source Test Report 2007 Emissions Compliance Tests, Hanson Permanente Cement, Cupertino, California. In: Prepared for Hanson Permanente Cement by John S. Peterson, The Avogadro Group, LLC, 11.02.08, 78 pp.
- Bay Area Air Quality Management District (BAAQMD), 2009. Public Records request, www.baaqmd.gov/Divisions/Legal/Public-Records-Request.aspx (Cited August 2009).
- Bloom, N.S., Creclius, E.A., 1983. Determination of mercury in seawater at sub-nanogram per liter levels. *Marine Chemistry* 14, 49–59.
- Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Analytica Chimica Acta* 208, 151–161.
- California Air Resources Board (CARB), 2009. Facility Search Results. www.arb.ca.gov/app/emsinv/facinfo/facinfo.php (Cited August 2009).
- Choi, H.-D., Sharac, T.J., Holsen, T.M., 2008. Mercury deposition in the Adirondacks: a comparison between precipitation and throughfall. *Atmospheric Environment* 42, 1818–1827.
- Conaway, C.H., Squire, S., Mason, R.P., Flegal, A.R., 2003. Mercury speciation in the San Francisco estuary. *Marine Chemistry* 80, 199–225.
- Conaway, C.H., Watson, E.B., Flanders, J.R., Flegal, A.R., 2004. Mercury deposition in a tidal marsh of south San Francisco Bay downstream of the historic New Almaden mining district, California. *Marine Chemistry* 90, 175–184.
- Conaway, C.H., Ross, J.R.M., Looker, R., Mason, R.P., Flegal, A.R., 2007. Decadal mercury trends in San Francisco Estuary sediments. *Environmental Research* 105, 53–66.

- Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, J.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knapp, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5, 193–259.
- Dvonch, J.T., Keeler, G.J., Marsik, F.J., 2005. The influence of meteorological conditions on the wet deposition of mercury in southern Florida. *Journal of Applied Meteorology* 44, 1421–1435.
- Flegal, A.R., Conaway, C.H., Scelfo, G.M., Hibdon, S.A., Sanudo-Wilhelmy, S.A., 2005. A review of factors influencing measurements of decadal variations in metal contamination in San Francisco Bay, California. *Ecotoxicology* 14, 645–660.
- Guentzel, J.L., Landing, W.M., Gill, G.A., Pollman, C.D., 1995. Atmospheric deposition of mercury in Florida: the FAMS project (1992–1994). *Water Air and Soil Pollution* 80, 393–402.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury in freshwater fish linked to atmospheric mercury deposition. *Environmental Science and Technology* 40, 7764–7770.
- Hammerschmidt, C.R., Lamborg, C.H., Fitzgerald, W.F., 2007. Aqueous phase methylation as a potential source of methylmercury in wet deposition. *Atmospheric Environment* 41, 1663–1668.
- Harris, R.C., Rudd, J.W.M., Amyot, M., Babiarz, C.L., Beaty, K.G., Blanchfield, P.J., Bodaly, R.A., Branfireun, B.A., Gilmour, C.C., Graydon, J.A., Heyes, A., Hintelmann, H., Hurley, J.P., Kelly, C.A., Krabbenhoft, D.P., Lindberg, S.E., Mason, R.P., Paterson, M.J., Podemski, C.L., Robinson, A., Sandilands, K.A., Southworth, G.R., St. Louis, V.L., Tate, M.T., 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proceedings of the National Academy of Sciences* 104, 16586–16591.
- Hintelmann, H., Harris, R., Heyes, A., Hurley, J.P., Kelly, C.A., Krabbenhoft, D.P., Lindberg, S., Rudd, J.W.M., Scott, K.J., St. Louis, V.L., 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the MEAALICUS study. *Environmental Science and Technology* 36, 5034–5040.
- Horvat, M., Bloom, N.S., Liang, L., 1993a. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples, part 1, sediments. *Analytica Chimica Acta* 281, 135–152.
- Horvat, M., Bloom, N.S., Liang, L., 1993b. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples, part 2, water. *Analytica Chimica Acta* 282, 153–168.
- Hower, J.C., Thomas, G.A., Mardon, S.M., Trimble, A.S., 2005. Impact of co-combustion of petroleum coke and coal on fly ash quality: case study of a western Kentucky power plant. *Applied Geochemistry* 20, 1309–1319.
- Lamborg, C.H., Fitzgerald, W.F., Vandal, G.M., Rolfhus, K.R., 1995. Atmospheric mercury in northern Wisconsin: sources and species. *Water Air and Soil Pollution* 80, 189–198.
- Landis, M.S., Stevens, R.K., Schaedlich, F., Prestbo, E.M., 2002. Development and characterization of annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environmental Science and Technology* 36, 3000–3009.
- Lynam, S.N., Gustin, M.S., 2008. Speciation of atmospheric mercury at two sites in northern Nevada, USA. *Atmospheric Environment* 42, 927–939.
- Mason, R.P., Lawson, N.M., Sullivan, K.A., 1997. The concentration, speciation and sources of mercury in Chesapeake Bay precipitation. *Atmospheric Environment* 31, 3541–3550.
- Mercury Deposition Network (MDN), 2009. Mercury Deposition Network: a NADP Network. <http://nadp.sws.uiuc.edu/mdn/> (Cited August 2009).
- Minnesota Pollution Control Agency (MPCA), 2008. Minnesota Statewide Mercury TMDL. <http://www.pca.state.mn.us/water/tmdl/tmdl-mercuryplan.html> (Cited August 2009).
- Munthe, J., Wangberg, I., Iverfeldt, A., Lindqvist, O., Stromberg, D., Sommar, J., Gardfeldt, K., Peterson, G., Ebinghaus, R., Prestbo, E., Larjava, K., Siemens, V., 2003. Distribution of atmospheric mercury species in Northern Europe: final results from the MOE project. *Atmospheric Environment* 37, S9–S20.
- New England Interstate Water Pollution Control Commission (NEIWPCC), 2008. Northeast Regional Mercury TMDL. <http://www.neiwpcc.org/mercury/MercuryTMDL.asp> (Cited August 2009).
- Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., 2006. Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. *Science of the Total Environment* 370, 147–156.
- Rothenberg, S.E., McKee, L., Gilbreath, A., Yee, D., Conner, M., Fu, X. Evidence for short range transport of atmospheric mercury to a rural, inland site, *Atmospheric Environment*, in press. doi:10.1016/j.atmosenv.2009.12.032.
- St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Hall, B.D., Rolfhus, K.R., Scott, K.J., Lindberg, S.E., Dong, W., 2001. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environmental Science and Technology* 35, 3089–3098.
- Santa Clara Valley Water District (SCVWD), 2009. Santa Clara Valley Water District ALERT Gage System. <http://alert.scvwd.org> (Cited August 2009).
- Schroeder, W., Munthe, J., 1998. Atmospheric mercury – an overview. *Atmospheric Environment* 32, 809–822.
- Steding, D.J., Flegal, A.R., 2002. Mercury concentrations in coastal California precipitation: evidence of local and trans-Pacific fluxes of mercury to North America. *Journal of Geophysical Research* 107, 4764. doi:10.1029/2002JD002081.
- U.S. EPA. (USEPA), 1996. Method 1638, Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-mass Spectrometry. USEPA, Washington, D.C.
- U.S. EPA (USEPA), 1997. Mercury study report to Congress. EPA-452/R-97-003.
- U.S. EPA. (USEPA), 2001. Method 1630, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Spectrometry. USEPA, Washington, D.C.
- U.S. EPA. (USEPA), 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. USEPA, Washington, DC.
- U.S. E.P.A. (USEPA), 2008. Listing Waters Impaired by Atmospheric Mercury under Clean Water Act Section 303(d) Memorandum, March 27, 2008. <http://www.epa.gov/owow/tmdl/mercury5m/> (Cited August 2009).
- U.S. E.P.A. (USEPA), 2009. Impaired Waters and Total Maximum Daily Loads. <http://www.epa.gov/owow/tmdl> (Cited August 2009).
- Western Region Climate Center (WRCC), 2009. Wind Rose Plots for La Honda, CA. Obtained from. <http://www.raws.dri.edu/wraws/ccaf.html> (Cited August 2009).
- World Health Organization (WHO), 1990. Environmental Health Criteria. In: Methylmercury, vol. 101. World Health Organization, Geneva. 1990.
- World Health Organization (WHO), 1991. Environmental Health Criteria. In: Inorganic Mercury, vol. 118. World Health Organization, Geneva. 1991.