Shipboard measurements of gaseous elemental mercury along the coast of Central and Southern California

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[1] Gaseous elemental mercury (GEM) in the atmosphere was measured during an oceanographic cruise in coastal waters between San Diego and San Francisco, California during the CalNex 2010 campaign. The goal of the measurements was to quantify GEM in the various environments that the ship encountered, from urban outflow, the Port of Long Beach and associated shipping lanes, coastal waters affected by upwelling, the San Francisco Bay, and the Sacramento ship channel. Mean GEM for the whole cruise was 1.41 ± 0.20 ng m–3, indicating that background concentrations were predominantly observed. The ship’s position was most often in waters off the coast of Los Angeles (74% of time with latitude < 34.3°N) and mean GEM for this section was not significantly (P > 0.05) higher than the whole cruise mean. South of 34.3°N, GEM was observed to vary diurnally and as a function of wind direction, displaying significantly higher concentrations at night and in the morning associated with general transport from the land to the sea. GEM and CO concentrations were positively correlated with a slope of 0.0011 ng m–3 ppbv–1 (1.23 × 10–7 mol mol–1) during periods identified as “Los Angeles urban outflow”, which given the inventoried CO emissions for the region, suggests a larger source of GEM than is accounted for by the inventory. The timing of the diel maximum in GEM (9:00 local time) was intermediate between the maxima of CO and NO2 (6:00) and that of NO and SO2 (10:00–12:00), suggesting that a mixture of urban and industrial sources were contributing to GEM. There was no observable postsunrisedip in GEM concentrations due to reaction with atomic chlorine in the polluted coastal atmosphere. On three occasions, significantly higher GEM concentrations were observed while in the Port of Long Beach (~ 7 ng m–3), and analyses of wind directions, ratios of GEM with other copollutants, and the composition of single particles, suggest that these plumes originated from the local waste incinerator in the Port area. A plume encounter from a large cargo ship allowed for the estimation of a mass-based emission factor for GEM (0.05 ± 0.01 mg kg–1 fuel burned). GEM enhancements observed in the Carquinez Straits, were lower than expected based on the observed NOx/SO2 ratios in the plumes and emissions inventories of the nearest oil refineries. In a region north of Monterey Bay known for upwelling, GEM in the air was positively correlated with dimethyl sulfide (DMS) in seawater and in the air. Using the observed GEM/DMS(g) relationship and the calculated mean DMS ocean-atmosphere flux for the cruise, an ocean-atmosphere flux of GEM of 0.017 ± 0.009 μmol m–2 d–1 was estimated. This flux was on the upper end of previously reported GEM ocean-atmosphere fluxes and should be verified with further measurements of Hg species in seawater and air.

1. Introduction

[2] Mercury (Hg) is a ubiquitous element in the Earth’s atmosphere with both natural and anthropogenic sources. Once in the atmosphere, Hg can be wet or dry deposited to the Earth’s surface and become bioaccumulated in food webs. A potent neurotoxin, Hg poses a health risk to humans who consume predatory fish [Mergler et al., 2007; Mahaffey et al., 2004]. The majority of fish consumed by humans is of marine origin [U.S. Environmental Protection Agency (EPA), 2002a] and the dominant input of mercury to the world ocean is through atmospheric deposition [Mason et al., 1994; Fitzgerald et al., 2007]. Thus, understanding the sources of Hg to the atmosphere and its fate and transport is important for guiding policy on controlling Hg emissions [Pirrone et al., 2010].

[3] Atmospheric Hg is dominated by the gaseous elemental form (Hg0, GEM) which generally comprises >99% of total airborne Hg and is fairly uniformly distributed in the Northern Hemisphere, with a range of concentrations of 1.3–1.7 ng Hg m\(^{-3}\) air at STP [Pirrone et al., 2010]. Other forms of airborne Hg are largely operationally defined and include gaseous Hg\(^{II}\) compounds [collectively termed reactive gaseous Hg (RGM)], and particulate bound Hg (PBM). Concentrations of RGM and PBM are typically low (expressed in pg m\(^{-3}\)); however, these are the main species to measure in order to estimate flux due to their short atmospheric residence times [Lindberg et al., 2007].

[4] Modeling of atmospheric Hg has been a focus of many groups over the past three decades [e.g., Shia et al., 1999; Dastoor and Larocque, 2004; Selin et al., 2007]. In spite of recent improvements with nesting a regional model inside a global model [Zhang et al., 2012], there are still uncertainties in the emissions inventories and in the chemical oxidation mechanisms, which cause the models to have poor agreement with observations of Hg in wet deposition in places like the Ohio River Valley, for example [Zhang et al., 2012]. One limitation for the models is the lack of observational data in areas downwind of emissions sources to better quantify these sources. Another limitation is the lack of observations in key locations like along coastlines where continental air containing anthropogenic Hg emissions interacts with the halogen-rich and humid atmosphere of the coast [Mason and Sheu, 2002; Malcolm et al., 2009; Riedel et al., 2012; Beldowska et al., 2012]. In particular, GEM reacts with chlorine radicals (Cl) [Ariya et al., 2002], and these can be formed in marine air that has had interactions between urban NO\(_x\) and sea-salt aerosols [Wagner et al., 2012].

[5] Atmospheric mercury measurements in California are sparse in the literature compared to the eastern U.S., but those that exist suggest there is a detectable signature from anthropogenic and natural emissions within California. Holmes et al. [2010] looked at GEM concentrations from the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) flights over California and Nevada and saw enhancements due to point sources in the Los Angeles/Long Beach port areas, from biomass burning, and from seawater associated with enhanced atmospheric dimethyl sulfide (DMS). Snyder et al. [2008] observed morning enhancements in GEM across the Los Angeles basin and suggested these resulted from fumigation of accumulated point source emissions within the basin that mixed to the surface during the breakup of the nocturnal inversion. Thus, evidence exists of Hg emissions in the Los Angeles Basin which may have regional impacts, yet there have been no studies of the behavior of Hg in the air just offshore.

[6] The objectives of this study were to make measurements of GEM on an oceanographic cruise along the coast of southern and central California in order to assess and/or quantify (1) anthropogenic point source emissions on land and from ships, (2) the interaction of GEM with urban air masses rich in oxidants, and (3) the impact of the ocean source of GEM in a region of coastal upwelling. To achieve our goals, we took part in the CalNex 2010 sampling campaign on the Woods Hole Oceanographic Institute R/V Atlantis (T. B. Ryerson et al., The 2010 California research at the nexus of air quality and climate change (CalNex) field study, submitted to Journal of Geophysical Research, 2012), which sought to research issues at the intersection of climate and air quality including the effect of the marine boundary layer on processing urban and industrial emissions. GEM data were combined with ancillary onboard measurements including CO, CO\(_2\), oxides of nitrogen (NO\(_x\)), SO\(_2\), DMS, ozone (O\(_3\)) and oceanographic and meteorological parameters.

2. Methods

2.1. GEM Measurements

[7] Measurements of GEM and other copollutants were taken between 14 May 2010 and 8 June 2010 onboard the R/V WHOI Atlantis as it sailed from San Diego to San Francisco, California. The ship spent most of the time off the coast of Los Angeles as can be seen from locations plotted in Figure 1A. Segments of the cruise were identified when emissions of a certain type (e.g., urban outflow, ship plumes) were likely encountered based on a suite of various chemical and physical parameters measured on the Atlantis (Ryerson et al., submitted manuscript, 2012).

[8] Air was sampled through 10 m of unheated 1/4” polytetrafluoroethylene (PTFE) tubing at a rate of 1 LPM at STP, from a forward mast at 18 m above the ocean surface with a downward facing quartz fiber filter inlet shielded from precipitation. GEM was quantified using an automatic dual channel, single amalgamation cold vapor atomic fluorescence analyzer (Model 2537A, Tekran®, Inc., Toronto, Canada) with a soda-lime column and a 0.2 µm PTFE filter just upstream. With this system, GEM concentrations were made every 5 min. The soda lime was changed every 3 days during the cruise. Once-daily automatic calibrations using a Hg permeation source were performed, and these were checked against manual injections of known quantities of Hg vapor before and after the cruise. An activated charcoal canister was periodically placed at the inlet to test the zero level of the Hg sampling system. This system was designed to capture only GEM since PBM and RGM would be lost on the quartz filter at the inlet (Eric Prestbo, personal communication). The detection limit reported by Tekran® for the 2537A is 0.05 ng m\(^{-3}\) for a 5 L sample, and the reproducibility is 0.08 ng m\(^{-3}\) based on the standard deviation of two collocated instruments sampling a shared inlet. Based on reproducibility of the calibrations and comparison with injected standards during this campaign, the accuracy is estimated at 95% and the precision at ambient concentrations is estimated at 98%.
2.2. Ancillary Parameters

Detection limits were estimated by multiplying the estimated imprecision at low signal:noise by 3. SO₂ was measured with pulsed fluorescence with a detection limit of 0.3 ppbv [Bates et al., 2008]. NO and NO₂ were measured with gas-phase chemiluminescence and light emitting diode (LED) photolysis and have detection limits of 0.006 and 0.018 ppbv, respectively [Lerner et al., 2009]. CO was measured with vacuum ultraviolet resonance fluorescence spectroscopy and has a detection limit of 3 ppbv and CO₂ was measured with nondispersive infrared absorption spectroscopy and has a detection limit of 0.2 ppmv [Lerner et al., 2009]. Ozone was measured using UV absorption with a detection limit of 3 ppbv [Williams et al., 2008]. An aerosol time-of-flight mass spectrometer measured real-time single particle size and composition; data are shown with 5 min time resolution [Gard et al., 1997]. Seawater DMS was measured using sulfur chemiluminescence with a detection limit of 0.6 nM [Bates et al., 2000]. Gas phase DMS was measured with a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS) with a detection limit of 18 ppt for measurements at a 1 min time resolution [Jordan et al., 2009].

Figure 1. Cruise track of the R/V Atlantis between San Diego and San Francisco, California, 14 May to 8 June 2012 with 5 min GEM concentrations and known GEM point source emissions. (A) Entire cruise track, (B) Southern California, (C) Port of Los Angeles, and (D) San Francisco Bay and Carquinez Straits. Magenta dots in Figures 1C and 1D indicate the ship’s position during plume encounters detailed in Figures 4 and 8, respectively.
Relative wind direction data were used to flag measurements when emissions from the Atlantis may have been sampled (relative wind > 75 degrees off the bow). Mean true wind directions were determined by vector averaging. Statistical analyses were carried out using Origin 7.5. Differences between population means were determined using a two-sample t-test and were considered significant if \( P < 0.05 \).

### 2.2. California Hg Emissions

[11] Anthropogenic Hg emissions in California are a small contributor to global emissions (approximately 1 Mg in 2010 or 0.05% of global emissions) [California Air Resources Board (CARB), 2008; EPA, 2012]. However, about 40% of California’s point sources are located in the South Coast and Bay Area Air Quality Districts, which include the areas around San Francisco and Los Angeles. Oil refineries, waste incinerators, cement production and metal manufacturing facilities are the major classes of industries that emit Hg in these metropolitan areas (Table 1). Gasoline and diesel facilities are the major classes of industries that emit Hg in various industry types. Hg emission estimates from 2008 for both the South Coast and Bay Area Air Quality Districts are given in Table 1.

#### 3. Results and Discussion

### 3.1. Overview of Cruise Segments

[13] While the majority of the cruise was spent in Southern California (74% of time, latitude < 34.3\(^\circ\)N), the ship encountered many environments between San Diego and Sacramento, and was likely influenced by varying emissions sources. Segments of the cruise were identified when the ship was in a particular geographic location (e.g., Sacramento Ship Channel) and/or was likely experiencing emissions of a distinct type, such as urban outflow, port industries, and ships at sea (Ryerson et al., submitted manuscript, 2012). GEM and other chemical species’ mean and maximum concentrations for these segments are given in Table 2. In general the differences in mean GEM concentrations between cruise segments were small (< 0.2 ng m\(^{-3}\)). The segment with the highest mean GEM concentration was the Port of Los Angeles (1.49 ng m\(^{-3}\)), which was significantly higher than the mean of all data.

#### Table 1. Major Hg Emitters in San Francisco and Los Angeles Areas

<table>
<thead>
<tr>
<th>Name</th>
<th>City</th>
<th>Total Hg Emissions kg yr(^{-1})</th>
<th>Estimated % GEM of Total Hg Emitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lehigh Southwest Cement</td>
<td>Cupertino</td>
<td>81.3</td>
<td>75</td>
</tr>
<tr>
<td>Conoco Phillips Refinery (1)</td>
<td>Rodeo</td>
<td>79.5</td>
<td>80</td>
</tr>
<tr>
<td>Conoco Phillips Refinery (2)</td>
<td>Rodeo</td>
<td>35.1</td>
<td>80</td>
</tr>
<tr>
<td>Valero Refinery</td>
<td>Benicia</td>
<td>14.2</td>
<td>80</td>
</tr>
<tr>
<td>Bubbling Well Pet Memorial</td>
<td>Fairfield</td>
<td>3.0</td>
<td>20-50</td>
</tr>
<tr>
<td>Shell Refinery</td>
<td>Martinez</td>
<td>3.0</td>
<td>80</td>
</tr>
<tr>
<td>All sources</td>
<td>Bay Area Quality District</td>
<td>240.0</td>
<td></td>
</tr>
<tr>
<td>Exxon-Mobil Refinery</td>
<td>Torrance</td>
<td>73.1</td>
<td>80</td>
</tr>
<tr>
<td>SE Resources Recovery (SERRF) Incinerator</td>
<td>Long Beach</td>
<td>60.3</td>
<td>22</td>
</tr>
<tr>
<td>Quemetco Metals Processing</td>
<td>City of Industry</td>
<td>10.1</td>
<td>80</td>
</tr>
<tr>
<td>Chevron Refinery</td>
<td>El Segundo</td>
<td>7.1</td>
<td>80</td>
</tr>
<tr>
<td>BP West Coast Refinery</td>
<td>Carson</td>
<td>7.0</td>
<td>80</td>
</tr>
<tr>
<td>All sources</td>
<td>South Coast Air Quality District</td>
<td>170.0</td>
<td></td>
</tr>
</tbody>
</table>

1. 2008 California Air Resources Board Inventory.
2. Hg speciation data taken from 2002 National Emissions Inventory [US EPA, 2002b], which has fixed ratios for each emitting type.

#### Table 2. Chemical Concentrations by Cruise Segment

<table>
<thead>
<tr>
<th>Cruise Segment</th>
<th>Mean (Maximum) Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N )</td>
<td>GEM (ng m(^{-3}))</td>
</tr>
<tr>
<td>Outflow</td>
<td>570</td>
</tr>
<tr>
<td>Ships</td>
<td>146</td>
</tr>
<tr>
<td>Port</td>
<td>447</td>
</tr>
<tr>
<td>Open Ocean</td>
<td>355</td>
</tr>
<tr>
<td>Mont. Bay</td>
<td>156</td>
</tr>
<tr>
<td>SFBay/Carquinez</td>
<td>358</td>
</tr>
<tr>
<td>Sac. Ship Channel</td>
<td>129</td>
</tr>
<tr>
<td>W. Sacramento</td>
<td>458</td>
</tr>
<tr>
<td>All Southern CA</td>
<td>4608</td>
</tr>
<tr>
<td>All cruise</td>
<td>6789</td>
</tr>
</tbody>
</table>

1. Cruise segments determined by analysis of ancillary parameters such as wind direction, \( \text{CO}_2 \), and \( \text{CO} \) concentrations. Southern CA defined as all locations south of 34.3\(^\circ\)N latitude. \( N \) refers to 5 min GEM measurements.
and the means from other segments. The Port segment had the highest maximum value for GEM (7.21 ng m\(^{-3}\)) and also the highest maxima for CO, NO\(_2\), and SO\(_2\). The highest mean CO and CO\(_2\) values were during the “outflow” conditions, when mobile sources were likely more dominant, compared to the Port segment, which had higher SO\(_2\) and NO mean concentrations, and likely reflects a greater proportion of stationary source emissions in the Port area. Outflow conditions also had significantly higher mean GEM concentrations compared to the Southern California mean. Mean concentrations of CO\(_2\), CO, NO, NO\(_2\), and SO\(_2\) were significantly higher from Southern California compared to means from the entire cruise, however this was not the case for GEM, which had slightly higher concentrations (not significant) during the whole cruise relative to Southern California. This suggests that in spite of the relatively polluted conditions in Southern California, the GEM emissions in this region were relatively low and did not greatly contribute to the Hg atmospheric burden. Likewise, GEM concentrations were not greatly elevated in the San Francisco Bay and Carquinez Straits (maximum = 1.53 ng m\(^{-3}\)) where several oil refineries are located suggesting that GEM emissions in this region were relatively low as well.

\[14\] The open ocean and Monterey Bay sections of the cruise had the cleanest air quality conditions, with NO + NO\(_2\) concentrations around 0.3–1.2 ppbv (compared to ~20 ppbv at the Port). GEM was significantly lower during open ocean conditions compared to all the data, suggesting the ocean source of GEM was not a strong contributor. Inland locations at West Sacramento and in the Sacramento Ship Channel were also relatively unpolished (NO + NO\(_2\) = 1.4–2.3 ppbv), which is consistent with these locations being rural. Mean GEM concentrations were significantly higher in the West Sacramento region but not higher in the Ship Channel compared to all the data suggesting multiple sources of GEM.

### 3.2. Diel Patterns in the South Coast Region

\[15\] The sea/land breeze diel circulation within the Los Angeles Basin and adjacent waters involves a relatively strong transport of air from the ocean into the basin during the day and a weaker transport of urban air offshore during the night [Wagner et al., 2012]. Figure 2 shows wind direction frequency, and median gaseous pollutant concentrations as a function of wind direction, and Figure 3 shows the mean diel cycles for these parameters from all locations south of 34.3°N latitude. The coastline was generally to the north or northeast in this region, except in Santa Monica Bay, where east and southeasterly directions also pointed toward land. The wind observations here show a strong transport broadly consistent with a sea breeze, which occurred between 14:00–20:00 local time, most frequently from the W and SW sectors (55% of time) and was associated with the diel minima in GEM, CO\(_2\), CO, and NO\(_2\). A weaker and shorter-lived land breeze between 04:00–08:00 occurred with the diel maximum in GEM, CO\(_2\), CO, and NO\(_2\). GEM median concentrations were 1.33 ± 0.12 ng m\(^{-3}\) in the W sector compared to 1.45 ± 0.11 ng m\(^{-3}\) in the NE sector, a similar dependence on wind direction as CO\(_2\), CO, and to some extent NO\(_2\). However, the diel pattern of GEM displayed a later maximum at 09:00–11:00, compared with the early morning maxima in CO\(_2\), CO, and NO\(_2\).

\[16\] Median NO was strongly enhanced in the S, SW, and SE sectors indicating the directions of nearest combustion sources in the Port area. Median SO\(_2\) was also enhanced in the S sector along with the SE, E, and NE sectors. SO\(_2\) and NO displayed later diel maxima (10:00–14:00) compared with CO\(_2\), CO, and NO\(_2\). The GEM diel maximum occurred between the diel maxima of CO\(_2\), CO, and NO\(_2\), and the maxima of SO\(_2\) and NO. If the former group of pollutants represents more aged emissions dominated by mobile and inland sources and the latter represents fresh emissions dominated by point sources near the coast, the diel pattern of GEM suggests that both types of sources contribute.

\[17\] The diel cycle of “background” GEM (> 1.7 ng m\(^{-3}\) removed) is also shown in Figure 3. Comparing these data with the diel cycle of all GEM data reveals that background GEM was generally observed during the daytime and evening hours (12:00–22:00 local time) and most GEM enhancements occurred during land breeze or transition periods (00:00–11:00). Background GEM was most depleted relative to all GEM during the hours of 02:00 and 04:00 (difference of ~0.1 ng m\(^{-3}\)), yet by 08:00 the difference between the means was only ~0.025 ng m\(^{-3}\). This argues against significant loss of GEM via oxidation by Cl atoms, which would be identifiable by a postsunrise dip in background GEM concentrations due to the production of Cl atoms from CINO\(_2\) photodecomposition at sunrise [Wagner et al., 2012; Riedel et al., 2012].

### 3.3. Los Angeles Port Emissions

\[18\] The Los Angeles/Long Beach Port has some of the largest Hg emitting point sources in Southern California within about 10 km. The observed GEM:SO\(_2\) relationship during these periods is shown in Figure 4A and the NO:SO\(_2\) relationship is shown in Figure 4B, along with the corresponding published ratios for each Hg-emitting facility in the area. Many of the GEM concentrations during the Port segment were at or near background levels; out of four hundred forty-seven 5 min GEM data, only six observations were > 2 ng m\(^{-3}\) and 50 observations were > 1.7 ng m\(^{-3}\). Nonetheless, the few enhanced GEM observations allow for a rough estimate of emission fluxes from point sources in the area. The ratios of GEM enhancements vs. the copollutants CO, CO\(_2\), and NO\(_2\) in Plumes 1, 2, and 3 are given in Table 3, along with the 2008 emissions inventories for some of the major local point sources. Plumes 1 and 2 occurred when the ship was stationary in the upper Port area (denoted by the large magenta dot in Figure 1C) on two separate days, 5/20/10 (16:15 GMT) and 5/27/10 (16:50 GMT). The 5 min mean wind direction during these two observations was 126 and 165°, respectively. Plume 3 (smaller magenta dot in Figure 1C) occurred on 5/20/10 (18:45 GMT) in a location more to the SW, and was associated with a wind direction of 42°. From Figure 4A we noted that the reported GEM/NO\(_2\) from the Southeast Resource Recovery Facility (SERRF) facility qualitatively agrees with the observed ratios during the highest GEM enhancements; reported emissions ratios from the Exxon-Mobil facility were about a factor of 5 lower. The observed NO\(_2\)/SO\(_2\) ratios shown in Figure 4B qualitatively reveal the contributions from multiple sources in the area. There appear to be three different ratio profiles: NO\(_2\) > 10 ppbv and SO\(_2\) < 2 ppbv is most likely indicative of mobile sources, NO\(_2\) > 50 ppbv and SO\(_2\) > 10 ppbv is similar to
the emissions ratio from the SERRF facility, and when \( \text{NO}_x > 50 \text{ ppbv} \) and \( \text{SO}_2 > 10 \text{ ppbv} \), this is similar to the emissions ratio of the BP Wilmington facility (the closest refinery to the Port). Closer examination of Plume 1 provides further evidence that there was significant contribution from the SERRF incinerator facility. GEM was near background levels until 09:15 local time, when it increased to 7.2 ng m\(^{-3}\), with an associated peak in \( \text{NO}_x \), and a smaller peak in \( \text{SO}_2 \) (Figure 5A). Analysis of aerosol single particle chemistry for this time period shows several spikes during the morning of 27 May (Figure 5B), in particles with compositions characteristic of incinerator emissions, such as enhancements in Cl, Pb, and Zn (Figure 5B) [Moffet et al., 2008]. All of the spikes in incinerator-type particles occurred when the wind direction was 125–150°, putting the facility directly upwind of the ship (large magenta dot on Figure 1C). One of these spikes (though not the largest) coincided with the spike in GEM (Plume 1). Given the observed wind speed at this time of 1.6 m s\(^{-1}\) and a distance of 2 km between the ship and the incinerator, this suggests a transport time of \( \sim 20 \text{ min} \). In-plume reduction of Hg(II) compounds to GEM by \( \text{SO}_2 \) is not expected to have had a large influence in Plume 1 given the short transport time and an estimated reduction rate on the order of 3% per hour [Lohman et al., 2006].

Figure 2. Wind direction frequency and median concentrations of chemical species by 45° wind direction bins for all 5 min data from Southern California (south of 34.3°N).
obtained from the City of Long Beach, the main sources of Hg in the waste stream would have been electronic and household hazardous waste. Beginning in the spring of 2010 aggressive efforts were taken to divert these items from the waste stream and subsequent emissions of Hg from the SERRF incinerator in 2011 decreased to ~2% of the value reported in the 2008 CARB inventory. However, our results here suggest that during May 2010 when the GEM spike was observed, full Hg waste reductions had not yet occurred and emissions were closer to the 2008 levels.

3.4. Los Angeles Urban Outflow

Los Angeles urban outflow conditions typically occurred at night or the early morning when winds tended to be from the northern or eastern sectors (Figures 2 and 3). The highest GEM enhancements under these conditions were when the ship was located in the Santa Monica Bay, (Figure 1B) (max GEM = 1.70 ng m\(^{-3}\), Table 1). These time periods reveal different chemical profiles compared to what was observed in the Port segments. NO\(_x\) vs. SO\(_2\) in Figure 6B shows two distinct sources of polluted air, consistent with mobile emissions (NO\(_x\) > 10 ppbv, SO\(_2\) < 1.5 ppbv) and refinery emissions (NO\(_x\) 15 ppbv, SO\(_2\) > 1 ppbv). GEM concentrations in the suspected refinery plumes (Figure 6A) were less than those predicted based on the 2008 GEM inventory for the Chevron facility located in Santa Monica Bay at El Segundo, suggesting that refinery emissions were lower in 2010 than 2008. GEM was not correlated with SO\(_2\) in outflow conditions (\(R^2 = 0\)), but GEM and CO were positively correlated (Figure 6C) producing a slope of 0.031 ng m\(^{-3}\) ppmv\(^{-1}\), which corresponds to 3.5 \(\times\) \(10^{-9}\) mol mol\(^{-1}\). Assuming 3.85 \(\times\) \(10^{10}\) mol of CO were released annually in the South Coast Air Quality District [CARB, 2008], and using the observed GEM/CO ratio in outflow conditions, GEM emissions can be roughly estimated at 1500 kg annually. This value is a factor of 20 larger than the GEM point source emissions from the South Coast Air Quality District (Table 1). Because CO emissions in Los Angeles are dominated by mobile sources, the question arises whether these could be contributing to GEM enhancements. Previous tests on gasoline in the San Francisco Bay Area showed that the average Hg content was 0.5 ng g\(^{-1}\) [Conaway et al., 2005]. Assuming 32 \(\times\) \(10^9\) L of gasoline were consumed in Imperial, Los Angeles, Orange, Riverside, San Bernardino, and Ventura counties during 2008 [California Department of Transportation, 2012], this suggests that approximately 12 kg of Hg could be emitted annually from automobiles across these six counties, which is a minor contributor. Another contributing source could be reemission of GEM from land and vegetation surfaces from the cumulative deposition of anthropogenic Hg over time. Although data on this are sparse, models suggest that reemission is important globally, contributing three times the emissions from primary anthropogenic sources [Selin et al., 2007].

3.5. Ship Emissions

The R/V Atlantis sampled the exhaust of many large ships in and around the Port of Los Angeles, during CalNex. One such encounter, which lasted almost 50 min, was with a cargo ship, the M/V Margrethe Maersk [Lack et al., 2011], in which NO\(_x\) concentrations increased from near zero outside the plume to almost 100 ppbv within the plume. CO\(_2\) and GEM concentrations and CO\(_2\) and NO\(_x\) concentrations were positively correlated (Figure 7). The slope of the linear relationship between GEM and CO\(_2\) for this plume is 0.031 ng m\(^{-3}\) ppmv\(^{-1}\), which converts to 3.5 \(\times\) \(10^{-9}\) mol mol\(^{-1}\). Assuming 3170 g CO\(_2\) per kg of fuel burned [Williams et al., 2009], and using the observed GEM:CO\(_2\) ratio, gives a
mass-based emissions factor of 0.05 ± 0.01 mg GEM per kg fuel burned. This corresponds to roughly 14 Mg yr⁻¹ of Hg for global shipping, which is a minor contributor globally (<1% global anthropogenic sources), but may be an important source locally in ports.

[23] Limited data on marine fuels suggest that the Hg content of both distillate and residual marine fuels spans two orders of magnitude (0.001 to 0.1 mg kg⁻¹) [Lloyd’s Register Engineering Services, 1995]. Without the Hg content in the fuel that was being burned during the plume encounter, it is difficult to assess the effects of combustion and emission control on Hg content in the plume. Furthermore, significant amounts of HgII and particulate Hg could be emitted in ship exhaust and these species were not measured here. More data are needed on Hg in ship plumes to verify the large range in Hg content in fuels and to determine if there are differences in Hg emissions factors between ships burning residual vs. distillate fuels.

3.6. San Francisco Bay and Carquinez Straits Emissions

[24] Gaseous elemental mercury concentrations in the industrial and urban regions of the San Francisco Bay and the Carquinez Straits (maximum GEM = 1.53 ng m⁻³) were not nearly as high compared to GEM concentrations in the Port of Los Angeles or in Los Angeles urban outflow. Figure 1D shows the GEM concentrations measured, the locations of oil refineries, and the locations of the highest SO₂ observations (~9 ppbv). Figure 8A shows the GEM:SO₂ relationship and Figure 8B shows the NOₓ:SO₂ relationship in this region. For comparison, the mean reported total Hg:SO₂ and NOₓ:SO₂ ratios from 2008 CARB inventory for the local refineries are also shown. Similar to the Los Angeles Outflow, Figure 8B shows a cluster of points associated with high SO₂/moderate NOₓ that is captured within the range of emissions ratios reported for the local refineries. The cluster of data points with SO₂ < 1 ppbv and NOₓ > 5 ppbv are characteristic of mobile source emissions. As shown in Figure 8A, however, GEM was only slightly enhanced during high SO₂ periods, and produced an observed GEM/SO₂ ratio that matched output from the Shell and Valero facilities. Note that the highest SO₂ observations corresponded to when the ship was in a part of the Carquinez Straits that was closer to the Shell and Valero, compared to the Conoco-Phillips facilities, so these results are consistent.

![Figure 4](image)

**Figure 4.** (A) GEM and (B) NOₓ 5 min measurements plotted against 5 min SO₂ data during periods when the ship was in the Port of Los Angeles. Lines show the mean reported total Hg:SO₂ and NOₓ:SO₂ ratios from 2008 CARB inventory for the point sources listed. An offset of 1.3 ng m⁻³ GEM and 10 ppbv NOₓ was added to the inventory ratios in Figures 4A and 4B, respectively.

<table>
<thead>
<tr>
<th>Observation</th>
<th>GEM/CO</th>
<th>GEM/SO₂</th>
<th>GEM/NOₓ</th>
<th>NOₓ/SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plume 1</td>
<td>0.10</td>
<td>1.14</td>
<td>0.07</td>
<td>16.0</td>
</tr>
<tr>
<td>Plume 2</td>
<td>0.21</td>
<td>5.91</td>
<td>0.24</td>
<td>24.4</td>
</tr>
<tr>
<td>Plume 3</td>
<td>0.07</td>
<td>1.53</td>
<td>0.10</td>
<td>15.8</td>
</tr>
<tr>
<td>Plume mean ± sd</td>
<td>0.13 ± 0.06</td>
<td>2.9 ± 2.2</td>
<td>0.14 ± 0.08</td>
<td>18.7 ± 4.0</td>
</tr>
<tr>
<td>Emissions inventory</td>
<td>0.87</td>
<td>2.19</td>
<td>0.52</td>
<td>4.2</td>
</tr>
<tr>
<td>SERRF²</td>
<td>0.09</td>
<td>0.70</td>
<td>0.22</td>
<td>3.2</td>
</tr>
<tr>
<td>Chevron</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
<td>2.8</td>
</tr>
<tr>
<td>BP Carson</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>1.1</td>
</tr>
</tbody>
</table>

¹Calculated as (GEMplume − GEMbackground) / (COplume − CObackground). Background values used were GEM: 1.3 ng m⁻³, CO: 132 ppbv, SO₂: 0.1 ppbv, NOₓ: 1 ppbv.
²SERRF emissions have been combined with the Quemetco emission from Table 1 (same location).
3.7. GEM Emissions From Coastal Waters

Photolytic processes are generally the main driver of Hg$^{2+}$ reduction to Hg$^0$ in surface waters, although biotic reduction can also occur [Pirrone et al., 2010; Soerensen et al., 2010]. Hg$^0$ has generally been observed to be supersaturated with respect to atmospheric concentrations in most oceanic locations. As a result, the global oceans represent a large emission source of GEM, on par with the magnitude of the anthropogenic source [Pirrone et al., 2010], but the estimates are very uncertain. A review of measurements of the GEM ocean-air flux determined by dissolved gaseous Hg concentrations and gas exchange models shows a wide range of values, from $1 \times 10^{-4}$ to 0.01 nmol m$^{-2}$ d$^{-1}$ [Sprovieri et al., 2010b]. Coastal and inland seas typically have the highest evasional fluxes [Pirrone et al., 2010].

This cruise afforded an opportunity to assess the GEM emissions from coastal waters where upwelling could result in higher GEM evasion rates through an increased Hg (II) flux into the mixed layer. On 2 June 2010 near noon local time the ship was offshore of Pt. Ano Nuevo, an area known for strong upwelling [Ryan et al., 2010]. Here an atmospheric GEM enhancement of ~0.3 ng m$^{-3}$ was observed, that was sustained for ~5 h over ~60 km (Figure 9). During this period GEM concentrations were uncorrelated with CO ($R^2 = 0.01$), but were weakly positively correlated with wind speed ($R^2 = 0.19$), sea surface temperature ($R^2 = 0.54$), and chlorophyll ($R^2 = 0.07$). GEM was negatively correlated with salinity ($R^2 = 0.20$). GEM was also positively correlated with DMS in seawater ($R^2 = 0.28$) and DMS in the atmosphere ($R^2 = 0.16$). Because DMS is an indicator of oxidative stress and cell lysis in marine phytoplankton [Wolfe and Steinke, 1996], the correlation of GEM with DMS suggests that the GEM observed here is related to phytoplankton cell lysis. The correlations of GEM with sea surface temperature and salinity suggest that as the water moves away from the upwelled region, which is relatively cold and saline, it warms and the phytoplankton die (or get consumed). GEM and

![Figure 5](image-url) Close-up of LA Port event with the highest GEM observation. (A) GEM, NO$_x$, SO$_2$, and wind direction. (B) Aerosol time-of-flight mass spectrometer results for percent of submicron particles with compositions representative of incineration particles.

![Figure 6](image-url) Scatter plots with linear fits of (A) GEM vs. SO$_2$, (B) NO$_x$ vs. SO$_2$, and GEM vs. CO during times classified as Los Angeles outflow.
DMSP (DMS precursor) are then released to the water column creating supersaturation and a net evasion flux, which is also dependent on wind speed.

The slope of the GEM:DMS\(_0\) relationship was 0.0089/C6\(0.005\) ng m\(^{-3}\) pptv, which converts to 9.9/C2\(10^{-4}\) mol GEM mol\(^{-1}\) DMS. The calculated DMS ocean to atmosphere flux in this region, based on seawater DMS concentrations, wind speed, and sea surface temperature ranged from 8 to 39 m mol m\(^{-2}\) d\(^{-1}\) (mean 17 \(\pm\) 9.5 \(\mu\)mol m\(^{-2}\) d\(^{-1}\)). Based on the GEM:DMS\(_0\) relationship, the corresponding GEM flux for this region was 0.017/C6\(0.009\) m mol m\(^{-2}\) d\(^{-1}\). This value is on the upper end of the measurements reported in Sprovieri et al. [2010b]. To determine if Hg\(^0\) subsurface concentrations could sustain such a high evasion rate, we estimated that given an open ocean concentration of 1 pM Hg\(^0\) in the mixed layer [Mason and Sullivan, 1999], the observed flux would ventilate all of the Hg\(^0\) in a 50 m mixed layer in \(~2\) days. This would likely outstrip the inventory of Hg\(^0\) even with upwelling. Thus, for the observed flux to be plausible, there must be a fast conversion of Hg(II) to Hg\(^0\). If Hg(II) is around 2 pM in the mixed layer [Mason and Sullivan, 1999], then the reduction rate would have to be around 10% per day to sustain the observed flux. This is an order of magnitude higher than what is thought to be the Hg\(^0\) formation rate in the equatorial Pacific [Mason et al., 1994]. Thus, because not a lot is known about Hg in upwelling regions, more data are needed to constrain the concentrations of Hg species, and compare the expected flux with that observed here.

### 4. Conclusions

These data contribute to the understanding of the various anthropogenic and natural sources of GEM in the atmosphere of coastal California. Overall, most GEM concentrations were representative of background conditions. The mean GEM concentration from Southern California (< 34.3\(^\circ\)N), near most of the anthropogenic sources, was not higher than the mean concentration for the entire cruise. However, certain periods were identified when the air sampled was likely influenced by Port of Long Beach emissions, Los Angeles urban outflow, cargo ships, Carquinez Strait emissions, and natural oceanic emissions. GEM enhancements were observed during all these events and estimates of the GEM flux from these sources were made. In the Port of Long Beach, GEM was enhanced up to 7 ng m\(^{-3}\) on three occasions, and observed GEM/SO\(_2\) and NO\(_x\)/SO\(_2\) ratios were consistent with the 2008 Hg, SO\(_2\), and NO\(_x\) inventories for the incinerator facility. Furthermore, single particle composition during the largest event showed enhancements in the elements characteristic of incinerator emissions.

The Los Angeles urban outflow was observed generally at night and in the early morning, when CO, CO\(_2\), and NO\(_x\) displayed their diel maxima. GEM and CO concentrations were positively correlated with a slope of 0.0011 ng m\(^{-3}\) ppbv\(^{-1}\) (1.23 \(\times\) 10\(^{-7}\) mol mol\(^{-1}\)) during these periods, which given the inventoried CO emissions for the region, suggests a larger source of GEM than is accounted for by the inventory. Reemissions of previously deposited mercury may be contributing to this discrepancy.

The diel maximum in GEM concentrations for all data from < 34.3\(^\circ\)N occurred in the midmorning (8:00–12:00 local time), which was intermediate between the diel maxima of CO and CO\(_2\), and the diel maxima of NO and SO\(_2\). This suggests...
that there are two types of sources of GEM from the urban area, one associated with point sources in the Port (higher NO and SO₂) and another associated with sources located farther away from the coast (higher CO and CO₂). There was no observable postsunrise dip in GEM concentrations during relatively unpolluted conditions, which suggests that reaction of GEM with atomic chlorine was probably not a large sink for GEM.

A plume from a large cargo ship was observed with a positive correlation between GEM:CO₂ and GEM:NO. Using conversions for g CO₂ per kg of fuel burned, an estimate of a mass-based emissions factor of 0.05/C₆₀.01 mg GEM per kg fuel burned for this particular plume was obtained. This corresponds to roughly 14 Mg yr⁻¹ of Hg for global shipping, which is a minor contributor globally (< 1% global anthropogenic sources), but may be an important source locally in ports. These estimates are limited by lack of knowledge of the Hg content in the unburned fuel and Hg speciation in the atmosphere.

Gaseous elemental mercury concentrations in the Carquinez Straits where many large oil refineries are located were rarely significantly elevated above the background. In an area where observed NOₓ:SO₂ ratios indicated impacts from local oil refineries, the observed GEM concentrations were less than those predicted based on the 2008 emissions inventories for these facilities, indicating that GEM emission may have been reduced.

In a roughly 60 km part of the cruise track, between Monterey Bay and the Golden Gate, GEM was enhanced and positively correlated with DMS in seawater and the atmosphere. This suggests an oceanic source of GEM. The measured DMS flux in this region was 17 ± 9.5 μmol m⁻² d⁻¹, which implies a GEM flux of 0.017 ± 0.009 μmol m⁻² d⁻¹. This flux is on the high end of what has been observed in other locations and more data are needed to understand the potential for extremely high GEM fluxes in regions affected by coastal upwelling.

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