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Total and monomethyl mercury in fog water from the central California coast

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1. Introduction

[1] Total mercury (HgT) and monomethyl mercury (MMHg) concentrations in fog collected from 4 locations in and around Monterey Bay, California during June-August of 2011 were 10.7 ± 6.8 and 3.4 ± 3.8 ng L−1 respectively. In contrast, mean HgT and MMHg concentrations in rain water from March-June, 2011 were 1.8 ± 0.9 and 0.1 ± 0.04 ng L−1 respectively. Using estimates of fog water deposition from 6 sites in the region using a standard fog water collector (SFC), depositions of HgT and MMHg via fog were found to range from 42–4600 and 14–1500 ng m−2 y−1, which accounted for 7–42% of HgT and 61–99% of MMHg in total atmospheric deposition (fog, rain, and dry deposition), estimated for the coastal area. These initial measurements suggest that fog precipitation may constitute an important but previously overlooked input of MMHg to coastal environments. Preliminary comparisons of these data with associated chemical, meteorological and oceanic data suggest that biotically formed MMHg from coastal upwelling may contribute to the MMHg in fog water. Citation: Weiss-Penzias, P. S., C. Ortiz Jr., R. P. Acosta, W. Heim, J. P. Ryan, D. Fernandez, J. L. Collett Jr., and A. R. Flegal (2012), Total and monomethyl mercury in fog water from the central California coast, Geophys. Res. Lett., 39, L03804, doi:10.1029/2011GL050324.

[2] Mercury (Hg) is a heavy-metal neurotoxin that bio-accumulates and bio-concentrates, primarily as monomethyl mercury (MMHg), in aquatic food webs to levels that are unsafe for human consumption [Fitzgerald et al., 2007]. The sources (natural and industrial) of MMHg in aquatic organisms is a matter of considerable debate, but atmospheric deposition has been implicated as a pathway of available Hg to the water and sediments where bacteria convert it MMHg [Lindberg et al., 2007]. Presumably, this includes all forms of atmospheric Hg deposition: wet (rain, snow, fog/cloud) and dry (direct reaction of airborne Hg with the surface).

[3] The complex speciation of Hg further complicates understanding its atmospheric inputs to aquatic ecosystems. MMHg is present in wet deposition, although measurements in rainwater indicate that MMHg only accounts for ~5% of the HgT in rain [Bloom and Watras, 1989; Munthe et al., 2001; Conaway et al., 2010]. However, there have only been a few measurements of HgT in fog or cloud water [Malcolm et al., 2003; Ritchie et al., 2006] – and those studies did not report measurements of MMHg. Consequently, the contribution of fog deposition to Hg fluxes is essentially unknown in coastal areas where fog water inputs are relatively substantial, such as much of coastal California.

[4] The source of MMHg in atmospheric water has been the subject of considerable debate. One hypothesis suggests that dimethyl mercury (DMHg) formed in ocean sediments is brought to the surface and overlying atmosphere due to upwelling where it photodecomposes into MMHg [Black et al., 2009; Fitzgerald et al., 2007; Hammerschmidt et al., 2007; St. Louis et al., 2007]. DMHg has been observed in surface waters of the Arctic Ocean [St. Louis et al., 2007] and the Monterey Bay during times of upwelling [Conaway et al., 2009]. However, rainwater samples from the Pacific coast during time of upwelling [Conaway et al., 2010] and from the equatorial Pacific [Mason et al., 1992] were not enhanced in MMHg. Coastal fog would presumably have more connection with surface waters compared to rain, but there have been no measurements of MMHg in fog to date.

[5] The second hypothesis of MMHg formation in atmospheric water is an abiotic mechanism involving reactions between Hg(II) compounds and the acetate ion [Gardfeldt et al., 2003; Hammerschmidt et al., 2007]. However, recent work has called this mechanism into question [Bittrich et al., 2011b] as being too slow to compete with photo-demethylation in rain water.

[6] In this work HgT, MMHg, and ion concentrations were measured in fog water and those data were compared with meteorological and other indicators of oceanic upwelling in order to provide the first estimate of wet deposition flux of HgT and MMHg through fog precipitation to coastal California and a discussion of possible sources.

2. Methods

[7] Twenty-five fog water samples were collected between 13-June-11 and 28-August-11 using a single fog collector that was moved between four different locations near Santa Cruz, California (37°N, 122°W) (Table 1): (1) on the roof of a building at the University of California, Santa Cruz (UCSC), at 230 m above sea level near the top of the redwood forest canopy and 6 km inland; (2) on a bluff at UCSC’s Long Marine Laboratory (LML), at 10 m above sea
level in open chaparral and grassland; (3) on a research boat (Moss Landing Marine Laboratory’s RV John H. Martin), at 5 m above sea level in the harbor at Moss Landing; and (4) in transit to and in the vicinity of the Monterey Bay Aquarium Research Institute (MBARI) mooring M1 in Monterey Bay, at 5 m above sea level and approx. 20 km offshore (Figure 1). Five rain water samples were also collected at UCSC in an open location between 17-March-2011 and 4-June-2011.  

[8] The fog was collected using a Caltech Active Strand Cloudwater Collector version 2 (CASCC2) [Demoz et al., 1996], which was connected with 1/4″ Teflon tubing and fittings to an acid-cleaned 250 mL borosilicate glass jar (IChem corp.) with a Teflon-lined lid. The CASCC2 was operated using an automatic timer between the local times of 22:00 to 09:00 and secured to a base 1 m off the ground. The exception was when the sampler was deployed on the boat, where it ran continuously and was approximately 5 m above the sea surface.  

[9] Fog sample volumes ranged from 1 mL to 160 mL and samples with volumes <10 mL were not considered. Samples were refrigerated immediately after collection, and then acidified to 0.4% HCl (Trace Metal Grade, Fisher Sci.) within 48 hours. They were subsequently analyzed for HgT within 2 weeks and for MMHg within 60 days of sample collection, in line with accepted storage times [Parker and Bloom, 2005]. Due to low sample volumes and replicate HgT analyses, only a subset (n = 8) of the total number of fog samples (n = 25) could be analyzed for MMHg concentrations.  

[10] Rain water was collected with an open glass funnel into an acid-cleaned Teflon bottle, as described by Conaway et al. [2010]. The funnels were protected from dry deposition of Hg by keeping them covered during dry periods. These samples were also acidified and stored in the refrigerator. They were then analyzed for HgT within 45 days and for MMHg within 180 days.  

[11] HgT and MMHg were determined using EPA methods 1631 and 1630, respectively, described in detail by Conaway et al. [2010] and references therein. Fog water method blanks were obtained by spraying the collection strands with at least 500 mL of high purity (18.2 MΩ cm) water (Milli-Q) from a standard polyethylene wash bottle, and letting this water drain out. Then a sample jar was connected and ~200 mL of blank sample was obtained by spraying with more Milli-Q. Fog water method blanks were collected within 8 hours of sample collection, usually in the evening before nighttime fog collection. The mean HgT and

Table 1. Mean, Standard Deviation and Range of Blank Corrected HgT and MMHg Measurements in Fog and Rain Water

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Sample Type</th>
<th>Sample Dates 2011</th>
<th>Samples (HgT, MMHg)</th>
<th>Mean HgT (ng L⁻¹)</th>
<th>Range HgT (ng L⁻¹)</th>
<th>Mean MMHg (ng L⁻¹)</th>
<th>Range MMHg (ng L⁻¹)</th>
<th>% MMHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLML Fog</td>
<td>6/13</td>
<td>1, 0</td>
<td>7.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Transit to mooring M1 Fog</td>
<td>6/14, 6/22</td>
<td>2, 0</td>
<td>13.3 ± 3.2</td>
<td>11.1–15.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UCSC Fog</td>
<td>6/26–8/8</td>
<td>13, 3</td>
<td>11.5 ± 7.9</td>
<td>2.6–28.7</td>
<td>6.9 ± 4.7</td>
<td>1.4–9.8</td>
<td>24–100</td>
<td></td>
</tr>
<tr>
<td>LML Fog</td>
<td>8/18–8/28</td>
<td>9, 5</td>
<td>8.7 ± 5.4</td>
<td>3.6–19.0</td>
<td>1.3 ± 0.6</td>
<td>0.4–1.9</td>
<td>7–27</td>
<td></td>
</tr>
<tr>
<td>All Locations</td>
<td>Fog</td>
<td>6/13–8/28</td>
<td>25, 8</td>
<td>10.7 ± 6.8</td>
<td>2.6–28.7</td>
<td>3.4 ± 3.8</td>
<td>0.4–9.8</td>
<td>7–100</td>
</tr>
<tr>
<td>UCSC Rain</td>
<td>3/17–6/4</td>
<td>5, 2</td>
<td>1.8 ± 0.9</td>
<td>1.1–3.3</td>
<td>0.1 ± 0.04</td>
<td>0.07–0.13</td>
<td>2–10</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Map of study location in California near the Monterey Bay. Samples for HgT, MMHg and anion analysis were collected at the Fog Chemistry sites, fog water collection was done at the Standard Fog Collector sites, and Hg dry deposition was done at Elkhorn Slough.
MMHg concentrations in fog water method blanks were 0.7 ± 0.4 (n = 33) and 0.2 ± 0.1 ng L⁻¹ (n = 2), respectively, which represented on average 7% and 6% of the HgT and MMHg concentrations in fog samples. Rain water method blanks were determined as described previously [Conaway et al., 2010]. Compared to the rain water method blanks for HgT and MMHg, the fog water blanks were considerably larger, which could be due to non-glass and non-Teflon components and the large amount of surface area associated with the CASCC2. Reported values for HgT, MMHg and anion concentrations were blank corrected by subtracting from each sample the mean blank value, which contributes ∼15% to the inaccuracy in quantifying HgT and MMHg.

Figure 2. HgT and MMHg concentrations and method blanks, from fog and rain water samples taken at 4 locations near Santa Cruz, California.

MMHg concentrations in fog water method blanks were 0.7 ± 0.4 (n = 33) and 0.2 ± 0.1 ng L⁻¹ (n = 2), respectively, which represented on average 7% and 6% of the HgT and MMHg concentrations in fog samples. Rain water method blanks were determined as described previously [Conaway et al., 2010]. Compared to the rain water method blanks for HgT and MMHg, the fog water blanks were considerably larger, which could be due to non-glass and non-Teflon components and the large amount of surface area associated with the CASCC2. Reported values for HgT, MMHg and anion concentrations were blank corrected by subtracting from each sample the mean blank value, which contributes ∼15% to the inaccuracy in quantifying HgT and MMHg.

3. Results

Concentrations of HgT and MMHg in fog and rain water samples are shown in Figure 2. Mean (not volume-weighted) HgT and MMHg concentrations of the fog samples from all locations were 10.7 ± 6.8 and 3.4 ± 3.8 ng L⁻¹, respectively; and mean HgT and MMHg concentrations for all rain samples were 1.8 ± 0.9 and 0.1 ± 0.04 ng L⁻¹, respectively (Table 1). Six samples were simultaneously measured for MMHg and the acetate and nitrate ions (auxiliary material). There were variations in fog water HgT concentrations between the UCSC and LML sampling locations, however the differences were not significant (p > 0.05; t-test). In contrast, two fog samples at the inland (6 km) station at UCSC had much higher MMHg concentrations (9.4 and 9.8 ng L⁻¹), than the third fog sample from UCSC (1.4 ng L⁻¹) and all five samples taken at the sea bluff site LML (mean = 1.3 ± 0.6 ng L⁻¹). The two fog samples with the highest MMHg concentrations exceeded their corresponding HgT concentrations by up to 27%, which we presume is due to uncertainties associated with method blank corrections.

3.1. Comparison With Previous Measurements

Previous studies have shown that mean HgT in fog water at several coastal locations in New Brunswick, Canada was 25 ng L⁻¹ and ranged from 2–450 ng L⁻¹ [Ritchie et al., 2006], while HgT in cloud water from Mt. Mansfield, Vermont had a mean concentration of 25 ng L⁻¹ and ranged from 8–72 ng L⁻¹ [Malcolm et al., 2003]. A single sample from Fresno, California during a wintertime tule fog event revealed an HgT concentration of 11 ng L⁻¹ [Bittrich et al., 2011a].

Previously reported volume-weighted mean (and range) of HgT concentrations in rain water from Santa Cruz were 6 (2–18) ng L⁻¹ [Conaway et al., 2010] and 6 (1–17) ng L⁻¹ [Steding and Flegal, 2002], which are higher than what we report here (2 (1–3) ng L⁻¹). This disparity may be an artifact of the small number of samples analyzed or different sample or event sizes.

MMHg concentrations in rain water from this work (0.1 ± 0.04 ng L⁻¹) were virtually identical to those previously measured in rain water in Santa Cruz (0.1 ± 0.1 ng L⁻¹) [Conaway et al., 2010]. In contrast, the average MMHg concentration of our fog water samples is approximately 5-fold greater than the previously reported highest MMHg values in rain water [Munthe et al., 2001; Kieber et al., 2008; Conaway et al., 2010]. Furthermore, since there are no reported MMHg measurements in fog water in the literature, the elevated MMHg concentrations reported here suggest that fog deposition could be a source of MMHg to coastal environments where it readily bioaccumulates.

3.2. Fog Water Deposition of HgT and MMHg

While the quantity of precipitation in rain water can be easily determined, this is not the case for the precipitation of fog water, which must be intercepted by vegetation or a surrogate surface in order to be quantified. A range of values for fog precipitation in coastal California have been reported in the literature, from 0.4–1.2 L m⁻² d⁻¹ [Fischer et al., 2009; Dawson, 1998]. Fog water collections using a standard 1.0 m² fog collector (SFC) in the Monterey Bay region revealed an even wider variation in fluxes depending on location (4–432 L during a 90-d campaign during June-August, 2010) (auxiliary material). While the actual deposition flux at any given location will vary according to vegetation characteristics, we assume that the range of fluxes measured by the SFCs was similar to that received per square meter of vegetated surface in an equivalent summertime period of 2011 when the fog chemistry was determined. Note that this equates to an average daily fog water flux range of 0.044 to 4.8 L m⁻² d⁻¹, overlapping the literature values for California fog precipitation cited above.
Table 2. Deposition Estimates Via Fog, Rain, and Dry for HgT and MMHg Based on Measurements Taken in the Monterey Bay Region

<table>
<thead>
<tr>
<th>Deposition Type, Time Period</th>
<th>Hg Species</th>
<th>Deposition ng Hg m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fog, June-August</td>
<td>HgT</td>
<td>42–4600</td>
</tr>
<tr>
<td>Rain, November-April</td>
<td>HgT</td>
<td>3610 ± 2400</td>
</tr>
<tr>
<td>Dry, Annual</td>
<td>HgT</td>
<td>2700 ± 1400</td>
</tr>
<tr>
<td>Fog, June-August</td>
<td>MMHg</td>
<td>14–1500</td>
</tr>
<tr>
<td>Rain, November-April</td>
<td>MMHg</td>
<td>9 ± 7</td>
</tr>
</tbody>
</table>

*The deposition via rain was obtained from Conaway et al. [2010]. Dry deposition was measured at site CA48 (Elkhorn Slough).

We then can calculate rough estimates of HgT and MMHg deposited to the Monterey Bay coastal area during the summer of 2011: 42–4600 and 14–1500 ng m⁻², respectively.

[20] Putting the Hg flux from fog water values into context (Table 2), HgT and MMHg deposition via rain water in Santa Cruz were recently estimated at 3610 and 9 ng m⁻² over the rainy season of 2007–2008 (November–April) [Conaway et al., 2010]. Mean Hg flux from dry deposition was also estimated from measurements at Elkhorn Slough at 2700 ng m⁻² y⁻¹ (auxiliary material). Thus, the relative contribution of fog water deposition of HgT and MMHg to total atmospheric deposition is estimated here to be 7–42% and 61–99%, respectively. These ratios suggest that fog water may constitute a large fraction of MMHg in that deposition. It is also important to emphasize the importance of this process to Hg loadings during the dry season, when fog is the main source of moisture and many coastal plant communities that have been observed to utilize fog water over ground water for metabolism [Dawson, 1998].

3.3. Upwelling as a Potential Source of MMHg in Coastal Fog

[21] To explore the hypothesis that high MMHg concentrations in fog could be a result of evasion of DMHg from coastal ocean upwelling, we compare the MMHg measurements with oceanic and meteorological conditions at ocean mooring M1, which is located in the mean path of upwelling filaments that flow into the Monterey Bay. The plots in Figures 3a–3d show that the anomalously high MMHg values at UCSC coincided with M1 ocean surface conditions that were relatively saline yet warm and atmospheric conditions marked by a relatively high sea-air temperature difference and relatively high relative humidity. With recent upwelling, conditions at the surface are typically saline and cold, so saline and warm conditions indicate recent upwelling followed by the warming that occurs during wind relaxations and/or reversals. By examining wind directions and speeds during the entire sampling period (July 1–Aug. 31) (Figure 3e), we note that the times of lower MMHg fog concentrations (7/17, 8/18, 8/23–25, 8/28) coincided with periods of steady upwelling favorable winds (as indicated by relatively strong northwesterly winds), whereas the highest MMHg concentrations followed a sequence of strong upwelling/strong relaxation of upwelling. These data suggest that the typical cycles of upwelling and relaxation may act as an Hg pump. From the starting hypothesis that upwelling brings DMHg-bearing sediments in contact with the oceanic mixed layer and overlying atmosphere, our data suggest that 1) the presence of recently upwelled waters (high salinity) is required and 2) the transfer of Hg into fog and subsequent transport to land may be enhanced at a specific period in upwelling/relaxation cycles, when the surface ocean has warmed, the sea-air temperature gradient is enhanced, and atmospheric humidity is elevated. Measurements of DMHg in seawater and the overlying atmosphere in association with a knowledge of upwelling and relaxation cycles would be needed to verify this hypothesis.

4. Summary

[22] Twenty-five fog water and five rain water samples were collected during the spring and summer of 2011 at several locations in the Monterey Bay area. Mean HgT and

**Figure 3.** Relationships between MMHg in fog samples at UCSC (solid circles) and LML (open squares), and mean values of (a) absolute salinity ($S_A$), (b) sea surface temperature, (c) the sea-air temperature difference, and (d) relative humidity at mooring M1 from the 24-h preceding the end of the fog sampling time. The first number on each plot is the correlation coefficient using all the data and the second number using LML samples only. (e) Stick plot showing 4-h mean wind direction and wind speed at mooring M1 over the duration of fog samples (shaded bars) analyzed for MMHg. Stick length indicates wind speed and the direction the stick is pointing indicates the direction the wind is blowing towards. Upwelling favorable winds are directed southeastward (alongshore/equatorward).
MMHg concentrations of fog water samples were 10.7 ± 6.8 and 3.4 ± 3.8 ng L\(^{-1}\) respectively. MMHg as a percentage of HgT ranged from 7 to 100%. In contrast, mean HgT and MMHg concentrations in rain water were 1.8 ± 0.9 and 0.1 ± 0.04 ng L\(^{-1}\), or 2–10% MMHg. The MMHg concentrations in fog water were about a factor of five higher than those seen previously in rain water and appear to constitute an important, and previously unrecognized, source of MMHg to coastal ecosystems.

[23] Based on a range of regional fog water fluxes estimated using standard fog water collectors and our measured HgT and MMHg concentrations, it is estimated that fog deposition accounts for 42–4600 ng m\(^{-2}\) for HgT and 14–1500 ng m\(^{-2}\) for MMHg along the central California coastline during its foggy season. Those fog water fluxes would, therefore, account for 7–42% of HgT and 61–99% of MMHg in the total atmospheric deposition (rain, fog and dry) in that region.

[24] A source of MMHg in fog is thought to be degassing of DMHg from oceanic upwelling with subsequent conversion to MMHg and uptake by cloud droplets. The data presented here suggest that the highest MMHg concentrations in fog water coincide with upwelling followed by relaxation cycles, when the surface ocean had warmed, the sea-air temperature gradient was enhanced, and atmospheric humidity was elevated. However, the small sample size in this study and the potentially far reaching consequences of the results underscore the need to continue to collect fog water in various coastal environments to determine the spatio-temporal variations in HgT and MMHg concentrations along with more detailed measurements of fog water deposition fluxes to regional ecosystems.

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References


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