Mercury speciation in Pacific coastal rainwater, Monterey Bay, California

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ABSTRACT

We measured mercury speciation in coastal rainwater samples from Monterey Bay, California in 2007–2008 to investigate the source of monomethylmercury (MMHg) in rainwater and determine the relative importance of wet atmospheric deposition of MMHg to coastal waters compared to other sources on the central Pacific coast. Total mercury (HgT) ranged from 10 to 88 pM, with a sample mean ± standard deviation of 33 ± 22 pM (volume-weighted average 29 pM). MMHg concentrations ranged from 0.12 to 2.3 pM with a sample mean of 0.7 ± 0.5 pM (volume-weighted average 0.68 pM). Reactive mercury (HgR) concentrations ranged from 0.87 to 47 pM, sample mean 7.8 ± 8.3 pM (volume-weighted average 6.1 pM). Acetate concentration in rainwater, measured in a subset of samples, ranged from 0.34 to 3.1 μM, and averaged 1.6 ± 0.9 μM (volume-weighted average 1.3 μM). Dimethylmercury (DMHg) concentrations were below the limit of detection in air (<0.01 ng m^{-3}) and rainwater (<0.05 pM). Despite previous suggestions that DMHg in upwelled ocean waters is a potential source of MMHg in coastal rainwater, MMHg in rain was not related to coastal upwelling seasons or surface water DMHg concentrations. Instead, a multiple linear regression analysis demonstrated that MMHg concentrations were positively and significantly correlated ($p = 0.002$, adjusted $R^2 = 0.88$) with those of acetate and HgR. These data appear to support previous suggestions that the aqueous phase methylation of Hg(II) by acetate may be the source of MMHg in rainwater, but imply that acetate concentrations in rainwater play a more important role relative to HgR than previously hypothesized. However, the calculated chemical speciation of Hg(II) in rainwater and the minimal predicted complexation of Hg(II) by acetate suggest that the aqueous phase methylation of Hg(II) by acetate is unlikely to account for the MMHg found in precipitation, or that the mechanism of this reaction in the atmosphere differs from that previously reported (Gardfeldt et al., 2003).

1. Introduction

Atmospheric deposition represents an important source of mercury to many aquatic systems (Fitzgerald et al., 1998; Rice et al., 2009), and knowledge regarding the speciation of the mercury deposited is important in determining its availability to biological systems. Monomethylmercury (MMHg) is the form of mercury of greatest interest in the environment because it is biomagnified in food chains to toxic levels in higher trophic level organisms, including humans (Fitzgerald et al., 2007). Although the principal source of MMHg in aquatic systems is generally considered to be mercury methylation by sulfate-reducing and iron-reducing

bacteria in sediment (Benoit et al., 2003; Kerin et al., 2006), MMHg constitutes up to about 5% of the mercury in rainwater (Bloom and Watras, 1989; Downs et al., 1998; Hall et al., 2005; Hultberg et al., 1995; Munthe et al., 1995), and thus up to 5% of wet atmospheric deposition of mercury. In addition, atmospherically deposited mercury may be more available to methylation than mercury already within a system, which can be rendered less available by complexation or sorption (Harris et al., 2007; Mason et al., 2000; Rolfhus et al., 2003). Thus, atmospheric deposition of mercury may represent an important MMHg source and substrate of MMHg production in aquatic environments.

Current hypotheses for the source of MMHg in rainwater center on abiotic methylation of mercury in rain by carboxylic acids, particularly acetate (Gardfeldt et al., 2003; Hammerschmidt et al., 2007). It has been suggested that acetate is present in rainwater in excess of "methylatable mercury", and thus methylatable mercury is proposed to be the limiting reactant in the aqueous

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phase formation of MMHg in rain (Hammerschmidt et al., 2007). Reactive mercury (HgR), which is the fraction of mercury easily reducible with tin chloride at low pH, is often used as a proxy for methylatable mercury (Mason and Fitzgerald, 1990). It has been reported that there is a linear relationship between mean concentrations of MMHg and HgR in rainwater when data from North America are pooled across large geographic areas (Hammerschmidt et al., 2007).

Another hypothesis for the presence of MMHg in rainwater is the decomposition of dimethylmercury (DMHg) that has been released to the atmosphere by evasion from upwelling oceanic water (Black et al., 2009; Bloom et al., 1996; Mason et al., 1998; Prestbo et al., 1996). Although atmospheric DMHg has been discredited as a source of MMHg in continental precipitation (Hammerschmidt et al., 2007), the importance of this source bears further examination for coastal and oceanic precipitation, especially in areas where coastal upwelling occurs and where DMHg is known to be seasonally present in marine surface water (Conaway et al., 2009). The relatively low MMHg concentrations observed in oceanic rainwater have been cited to argue against the importance of DMHg as a source of MMHg in marine rain (Hammerschmidt et al., 2007). However relatively high concentrations of MMHg have been observed in rainwater in areas of coastal upwelling (Bloom and Watras, 1989), suggesting that the evasion of DMHg from the ocean and its subsequent degradation in the atmosphere may be a source of MMHg in precipitation in some areas.

Monterey Bay, California has a Mediterranean climate with a rainy season that typically lasts from November to April. Precipitation events differ in their source over this period, generally arriving from two distinct directions. The regional climate conditions are dominated by the position of the North Pacific high pressure system (a subtropical anticyclone), which shifts north in the summer and south in the winter (Halliwell and Allen, 1987). The summer position of this high pressure system typically deflects storm systems to the north of California, resulting in a dry summer climate. As the pressure system shifts south and decreases in strength in the winter, storms originating from the Gulf of Alaska low pressure system reach the California coast. These storms arrive in California from the west or northwest, sometimes travelling along the west coast, to reach Monterey Bay (Dorman et al., 1995). Although many or most of the storms that arrive at the California coast are from the west or northwest, the greatest rainfall in the area, which falls between December and March, is delivered by storms originating from the Central Pacific, arriving at the coast from the southeast and southwest ("Pineapple Express" events). These northward moving systems and associated fronts have relatively warmer and moister air compared to their Gulf of Alaska originating counterparts, and meet the southern facing slopes of the Santa Cruz Mountains to create short periods of high intensity rainfall (Nuss, 1996), with over 5 cm of precipitation per day.

The changes in the direction and strength of prevailing winds associated with the movement of the North Pacific high pressure system also cause seasonal coastal upwelling along the Pacific coast of North America. Upwelling conditions predominate in Monterey Bay between March and June (Breaker, 2005; Collins et al., 2003; Pennington and Chavez, 2000) such that the rainy season can overlap the onset of spring coastal upwelling. Upwelling in Monterey Bay has been demonstrated to transport subsurface DMHg to surface waters (Conaway et al., 2009), which, as described above, is a potential source of methylated mercury to the atmosphere, and therefore coastal rainwater.

Monterey Bay provides a unique location to study the sources and speciation of mercury in rainwater because: (1) it is influenced by storms originating in two distinct regions (i.e., the Gulf of Alaska and the Central Pacific), and (2) it experiences pronounced coastal upwelling that is a seasonal source of DMHg to surface waters (Conaway et al., 2009). Consequently, this study was designed to investigate the importance of storm origin and storm track on concentrations of various mercury species in local rainwater.

2. Methods

Coastal rainwater samples ($n = 40$) were collected over several storm events in the 2007–2008 rainy season at locations in Santa Cruz County (37°N 122°W), in central California, at locations within a few km of Monterey Bay coastline. Sampling was manually conducted with acid-cleaned borosilicate glass funnels (taken from an Aerochem Metrics sampler wet/dry sampler) connected with a Teflon collar to acid-cleaned PFA Teflon receiving bottles. Rather than bulk collection of precipitation from entire length of rainy periods (which lasted from hours to weeks), we collected discrete and sequential samples over multi-hour periods during storm events. Sample collectors were deployed at the onset of rainfall events, and retrieved at the end of substantial rainfall for the event or interim periods of very light rainfall intensity. The median collection time represented by individual sample bottles was about 3 h (maximum 15 h). At the end of collection time, sample bottles were immediately preserved or analyzed as detailed below. Collectors were deployed on a stand 1 m above the ground surface. Care was taken to place sampling bottles/funnels in open areas away from the influence of trees or buildings to prevent collecting any throughfall, and samples were visually inspected to assure they were free of leaves or other debris. Precipitation depth was measured by sample volume collected in bottles when used to calculate volume-weighted concentrations, or from a personal weather station in the Santa Cruz area (PWS KCAFELTO5, MADIS ID C3046) when used to calculate regional wet mercury deposition. A time series of average daily precipitation and sample collection during the study period is shown on Fig. 1. Water collected in this study represents a total of about 20 cm of precipitation, which is roughly 25–35% of the total precipitation depth for September 2007 to May 2008 in the Santa Cruz area (51–67 cm). The 40 samples were collected over 21 days, which is 33% of the days experiencing measurable precipitation depth during the study period.

Rainwater samples collected for MMHg analysis were either stored in the dark at 4 °C and analyzed within 2–3 days of collection, or frozen immediately after collection and analyzed within 3 months, both of which are consistent with accepted methods of preservation and storage outlined by Parker and Bloom (2005). MMHg analysis on aliquots of 20–100 mL of sample (depending on available volume) was performed by direct aqueous phase ethylation (Holz et al., 1999), trapping on Tenax, and detection by isothermal GC-CVAFS (Horvat et al., 1993). The MMHg detection limit was about 0.06 pM, calculated as either $3\times$ the standard deviation of bubbler blanks, or when bubbler blanks had no quantifiable MMHg peak, $3\times$ the standard deviation of multiple analyses of a low concentration MMHg standard converted to a volume-based detection limit. Average analytical precision based on relative percent difference of replicate analyses of samples ($n = 4$) was 3%. The relative percent difference of field replicates ($n = 3$) averaged 13%. Direct ethylation resulted in quantitative analysis of MMHg in rainwater, as average recovery of MMHg spikes ($n = 9$) added just before analysis was 95%. Funnel blanks, measured by rinsing funnels both before and after sample collection with ultrapure (18 MΩ cm) water (Milli-Q) water, showed no detectable MMHg (<0.06 pM).

Analysis of HgR was performed within 5 days of collection on unpreserved samples stored in the dark at 4 °C, consistent with the preferred method of preservation and storage from Parker and
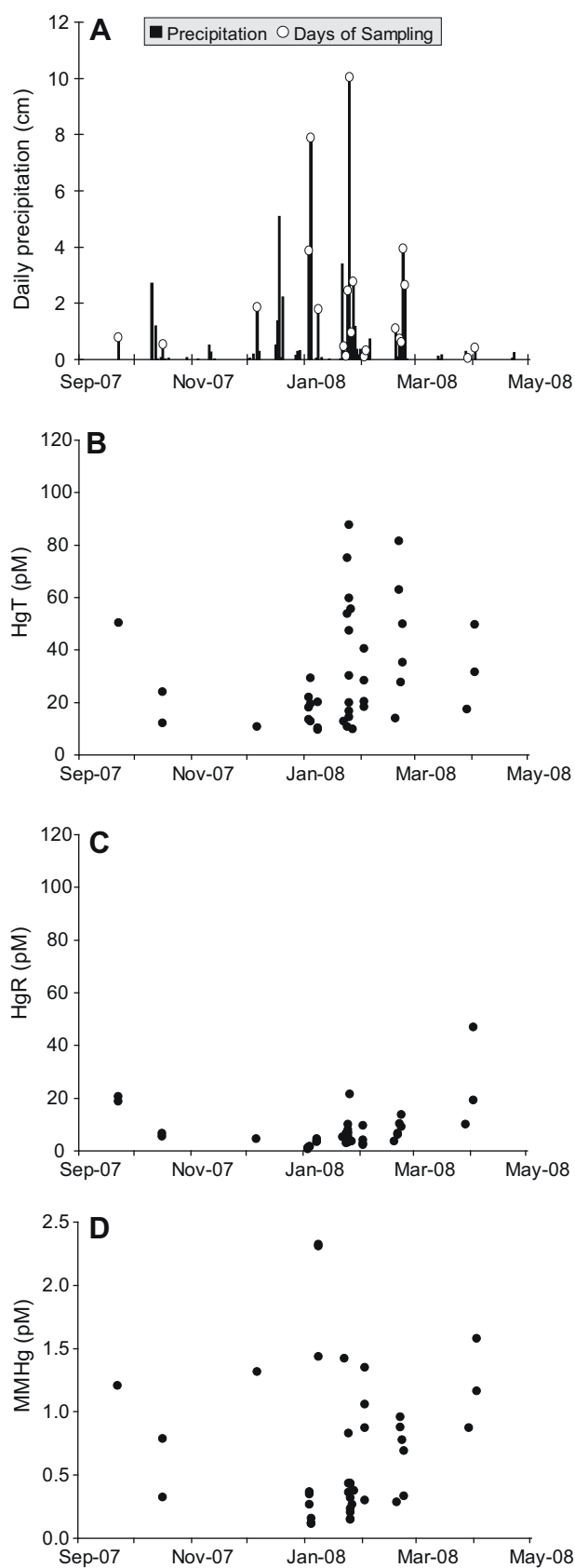
Fig. 1. Daily precipitation depth and mercury speciation in Santa Cruz, California rainwater, rainy season 2007–2008: (A) Daily precipitation depth (measured at PWS KCAFELTO5, MADIS ID C3046) with circles denoting days when samples were collected (note that multiple samples were taken on some days); (B) Concentrations of total mercury, HgT; (C) reactive mercury, HgR; and (D) monomethylmercury, MMHg.

Bloom (2005). Samples volumes of 10–50 mL were placed in a gas purging vessel and brought to a total volume of 150 mL with Milli-Q water, then 0.5 mL of 20% (w/w) $SnCl_2$ in 1.2 M HCl was added. The Hg^0 produced was purged onto gold-coated sand traps for 20 min at 200 mL min^{-1} with low-mercury nitrogen gas. The average HgR detection limit, based on $3\times$ the standard deviation of blanks, was 0.2 pM. Funnel blanks, measured by rinsing funnels pre- and post-deployment with Milli-Q water, were less than 15% of the lowest sample concentration for individual sampling events. Average analytical precision based on relative percent difference of duplicate analyses of samples ($n = 12$) was 9%. The average relative percent difference of replicate field samples ($n = 4$) was 16%.

Analysis of HgT was performed after subsamples were removed for HgR analysis and the remaining sample amended to 0.5% (v/v) BrCl in the original collection bottle. Analysis was performed by $SnCl_2$ reduction, gold amalgamation trapping and quantification by CVAFS (Gill and Fitzgerald, 1987). The average HgT detection limit, based on $3\times$ standard deviation of method blanks, was 1 pM. Analyses of certified reference material ORMS-3 (Elevated Mercury in River Water, National Research Council Canada) gave a value of 70 pM, and was therefore similar to the certified value 63 ± 6 pM. Average analytical precision of HgT, based on relative percent difference of duplicate analyses of samples ($n = 5$) was 3%. The average relative percent difference in HgT concentrations for field duplicates ($n = 4$) was 57%.

The relatively high (57%) difference in HgT field duplicates is troubling, but may represent variation in wind-suspended particles contributing to HgT, as wind speed during the time our field replicates were collected was very high (>15 m s^{-1}). Although analytical error due to sub-sampling is a possibility (Landing et al., 1998; Parker and Bloom, 2005), we assume that the variability we measured and reported between field replicates for HgT was real, and was not an analytical artifact and does not reflect analytical imprecision. We realize the high natural variability we measured between field replicates collected during extreme storm events is greater than has been reported by others for field replicated collected under calmer precipitation events (e.g., Landing et al., 1998). This may be due to differential washout and particle entrainment in rainwater, but the field replicates were sampled under conditions which precluded dry atmospheric deposition from being sampled, and any particles collected in the rainwater are representative of those precipitation events. In addition, our field replicates had relatively low HgT concentrations (17 ± 7 pM), which could also contribute to the large relative differences measured.

Atmospheric DMHg was measured using an apparatus constructed based in part upon recommendations in Bloom et al. (2005). A vacuum pump was used to draw air (300 mL min^{-1} for 2–3 h) through a trap (ice-cooled Teflon gas impinger) to condense water vapor, a 0.45 μm Teflon filter to remove particulates, a trap (15% OV-3 on Chromasorb) to remove other semi-volatile organic matter, and finally a Carbotrap to quantitatively capture DMHg. Carbotraps were analyzed by isothermal GC-CVAFS. The sampling device was tested by measuring volatile ethylmethylmercury generated by reacting aliquots of a MMHgCl standard solution with sodium tetraethylborate and then purging onto Carbotrap, which demonstrated quantitative recovery of volatile organomercury. There were no procedural DMHg blanks, so based on the detection limit of the instrument (0.5 pg) and the average air sampling volume (0.04 m^3), we estimate a DMHg detection limit of 0.01 ng m^{-3}. Measurements of DMHg in air were made at Long Marine Laboratory and on the UC-Santa Cruz campus on September 24 and December 14 in 2007, and March 25 and May 25 in 2008.

In the latter half of the 2008 rainy season (mid-February to April), samples were analyzed for acetate based on standard methods (Avery et al., 2001; Dionex, 2005). Sub-sampling (10 mL)

was done immediately after rainwater collection into clean 35 mL glass vials and preserved by amendment to 0.4% (v/v) HPLC-grade chloroform and stored at 4 °C until analysis. Acetate concentration was measured by ion chromatography using a Dionex ICS-2000 with an AS18 4-mm analytical column and detection using suppressed conductivity. We used an injection loop of 25 μL, and 23 mM KOH eluent at 1 mL min^{-1} flow rate at 30 °C. All samples were analyzed within two weeks, and samples reanalyzed after 1 month showed no change in concentration.

Three-day atmospheric back trajectories were calculated for every 3 h spanning the duration of the precipitation events using NOAA's HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1997). An ensemble of trajectory starting locations around the Santa Cruz sampling site consisted of nine points equally spaced in a $0.5° \times 0.5°$ grid (with the site in the center) and five vertical levels (500–2500 m above modeled ground level). Based on an inspection of upper air radiosonde data taken in twice-daily in Oakland, CA, these altitudes are assumed to span the vertical extent of the mixed layer during times of precipitation (i.e. frontal passages). Thus, a total of 360 trajectories or 25,920 hourly intervals (termed "trajectory points") were calculated for each 24-h period. Meteorological fields were used from the National Center for Environmental Prediction Eta Data Assimilation System (EDAS) (http://www.nco.ncep.noaa.gov/pmb/products/) that has 40 km horizontal resolution and 26 vertical levels. The EDAS spatial domain includes most of North America, but ends in the Pacific Ocean between 135 and 150° W longitude depending on the latitude. A semi-quantitative trajectory analysis method called gridded frequency distribution (GFD) was used to determine the likely transport pathways impacting the site (cf. Weiss-Penzias et al., 2009). A GFD effectively shows the amount of time that air has spent in a given $1° \times 1°$ region, by averaging the intersection of trajectory points in each grid cell along the paths of an ensemble of trajectories. The GFD is presented in terms of "location probability", which is defined as the number of trajectory points in a given cell as a fraction of the number of trajectory points in the most populous cell. HYSPLIT also calculates boundary layer height and precipitation along each trajectory and these parameters are presented to discern differences in transport conditions among subsets of the data.

3. Results and discussion

3.1. Chemical concentration and speciation in rainwater

Concentrations of HgT and MMHg measured in coastal rainwater in this study (Fig. 1, Table 1) are consistent with HgT concentrations previously reported in rainwater on the central California coast (Steding and Flegal, 2002) and with HgT and MMHg concentrations measured in precipitation elsewhere on the Pacific Coast (Bloom and Watras, 1989) and North America (Downs et al., 1998; Hall et al., 2005; Miller et al., 2008; Rolfhus et al., 2003). As expected, the observed HgT concentrations are somewhat lower than concentrations measured in precipitation at sites on the US Atlantic coast that are impacted by local and regional industrial pollution (Kieber et al., 2008; Mason et al., 2000; Miller et al.,

2008). Concentrations of MMHg in rainwater were higher than those measured in the open ocean precipitation, e.g., <0.05 pM in the equatorial Pacific (Mason et al., 1992), which agrees with the idea that atmospheric conditions in terrestrial or coastal areas are more favorable for the net formation of MMHg in rainwater than those over the open ocean (Hammerschmidt et al., 2007). Volume-weighted averages of mercury concentration (calculated using precipitation depth measured via bottle catch) are also given on Table 1 to account for effects of size of individual samples collected when calculating the yearly concentration.

The fraction of HgT represented by MMHg (or %MMHg) in rainwater samples was 0.3–22% of HgT, with an average of 3.7% and a median of 1.9%. The reason for the observed higher values (>8%) is not clear, but most occurred during the same rain event (January 8, 2008) and all involved below average HgT and above average MMHg. The median %MMHg here is consistent with those measured in rainwater from predominantly marine sources at a coastal site in North Carolina (Kieber et al., 2008), and other continental locations (Lamborg et al., 1995), but somewhat higher than those measured by Mason et al. (2000, 1997) in Chesapeake Bay ($\sim$0.5%). Downs et al. (1998) suggest that a relatively low % MMHg (<1%) is typical for more polluted regions, such as urban areas and industrially (coal burning) impacted areas as a result of higher HgT concentrations. Consequently our observed average % MMHg of 3.7% is consistent with coastal sites in relatively clean HgT areas.

The molar ratio of MMHg to HgR ranged from 0.01 to 0.63, with a median value of 0.078. This ratio is notably different from that presented in Hammerschmidt et al. (2007) for both the value of 0.025 ± 0.006 when averaging rainwater samples analyzed across North American sites, as well as their predicted steady-state MMHg:Hg(II) ratio of 0.025 ± 0.002. Hammerschmidt et al. (2007) used the data of Bloom and Watras (1989) to calculate a MMHg:HgR ratio for rain in Washington state along the Pacific coast (arguably the most comparable published data to our study) of 0.034. However, this value is based on the mean MMHg and mean HgR calculated separately for the entire data set, rather than the mean of MMHg:HgR ratios for individual samples, which would be more appropriate. We estimated the MMHg:HgR ratio based on the data for individual samples from Sequim WA (rain and light rain) presented on Fig. 2 and Table 2 in Bloom and Watras (1989), excluding samples without data for both MMHg and HgR, and calculated an approximate mean MMHg:HgR ratio of 0.051 ± 0.024 (range 0.03–0.1). The same data, using a weighted mean to account for composite MMHg sample values, were used to estimate a mean MMHg concentration in that study of 0.7 ± 0.4 pM and a mean HgR concentration of 14 ± 13 pM. These recalculated values of mercury concentrations and molar ratios for Pacific coastal rain in Washington State are more similar to our data for rainwater along the central California Pacific coast.

3.2. Diurnal variation of mercury speciation

There were no clear diurnal trends in concentrations of HgT, HgR, or MMHg in our study, based on three different statistical analyses. In the first approach samples were divided into "day"

Table 1
Summary of concentrations of mercury species and acetate measured in coastal Pacific rainwater and gas-phase dimethylmercury measured at Santa Cruz, California.

	HgT (pM)	MMHg (pM)	%MMHg	HgR (pM)	Acetate (μM)	DMHg (ng m^{-3})
Samples collected	$n = 41$	$n = 40$		$n = 41$	$n = 9$	$n = 4$
Range	10–88	0.11–2.3	0.3–22	0.65–47	0.34–3.1	<0.01
Mean $\pm$ standard deviation	32 ± 21	0.71 ± 0.57	3.7	7.4 ± 8.1	1.6 ± 0.9	
Median	23	0.43	1.9	5.8	1.9	
Volume-weighted average	29	0.70		5.9	1.3	

$y = 0.052x + 0.35$
$R^2 = 0.076$ $p = 0.11$
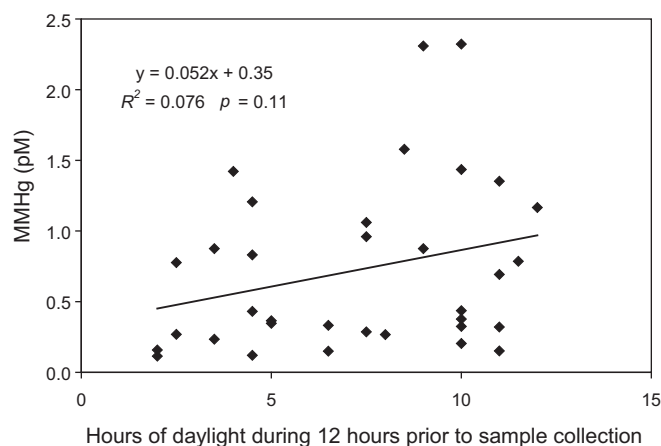
Fig. 2. Plot and result of a simple linear regression between monomethylmercury (MMHg) and number of hours of sunlight during the 12 h prior to samples' collection in Santa Cruz, California rainwater, rainy season 2007–2008.

(06:00 to 18:00 h) or "night" (18:00 to 06:00 h) sample collection times, and samples with collection times that overlapped day/night time classifications were removed. There was no statistically significant ($p \leq 0.05$) difference in group means for HgR or HgT ($p = 0.29, 0.78$; Student's t-test), but MMHg was 70% higher by a significant difference in the "day" ($p = 0.037$, Student's t-test). In the second approach days were divided into four time periods (24:00 to 06:00, 06:00 to 12:00, 12:00 to 18:00, and 18:00 to 24:00 h), similar to the periods used by Kieber et al. (2008). There were no significant differences between HgR or HgT group means ($p = 0.74, 0.57$; ANOVA), but there was, again, a significant difference in MMHg ($p = 0.038$), revealing a 12:00 to 18:00 h peak in rainwater MMHg concentration. However, an examination of the data revealed that the statistical significance of diurnal trends in MMHg concentration in the first two approaches were dependent on two samples with high MMHg concentrations that were determined to be statistical outliers (Q test). With those outliers removed (2 outliers from 16 "day" samples in the t-test, 2 outliers from 12 samples in the 12:00 to 18:00 h group in the ANOVA), there was no significant statistical difference in MMHg concentration in day/night ($p = 0.11$, Student's t-test) or in the four time periods ($p = 0.18$, ANOVA). Although we have no reason to question the validity of the two outliers, their relative influence makes it difficult to conclude that there is indeed a diurnal trend in MMHg concentrations. In the final approach to identify potential diurnal trends we specifically tested for the influence of sunlight on

concentrations of MMHg in rainwater. We found no significant relationship ($p = 0.11$, linear regression) between MMHg concentration and the number of sunlight hours during the 12 h period prior to sample collection (Fig. 2).

The lack of statistically significant diurnal trends in our study contrasts with the weak diurnal trend (with a mid-afternoon peak) observed for total dissolved mercury and MMHg concentration in North Carolina rainwater (Kieber et al., 2008), and with the mid-afternoon peak in HgT in samples collected from tropical storm Ernesto (Miller et al., 2008). Photochemical processes have been shown to be important for gas-phase reactive mercury on a diurnal scale (Laurier and Mason, 2007), and photochemical decomposition is an important degradation pathway for MMHg from surface waters of both freshwater (Sellers et al., 1996) and marine systems (Monperrus et al., 2007). Nevertheless, our results suggest that diurnal and photochemical processes are not the dominant control of the concentration of MMHg (nor HgT or HgR) in coastal rainwater.
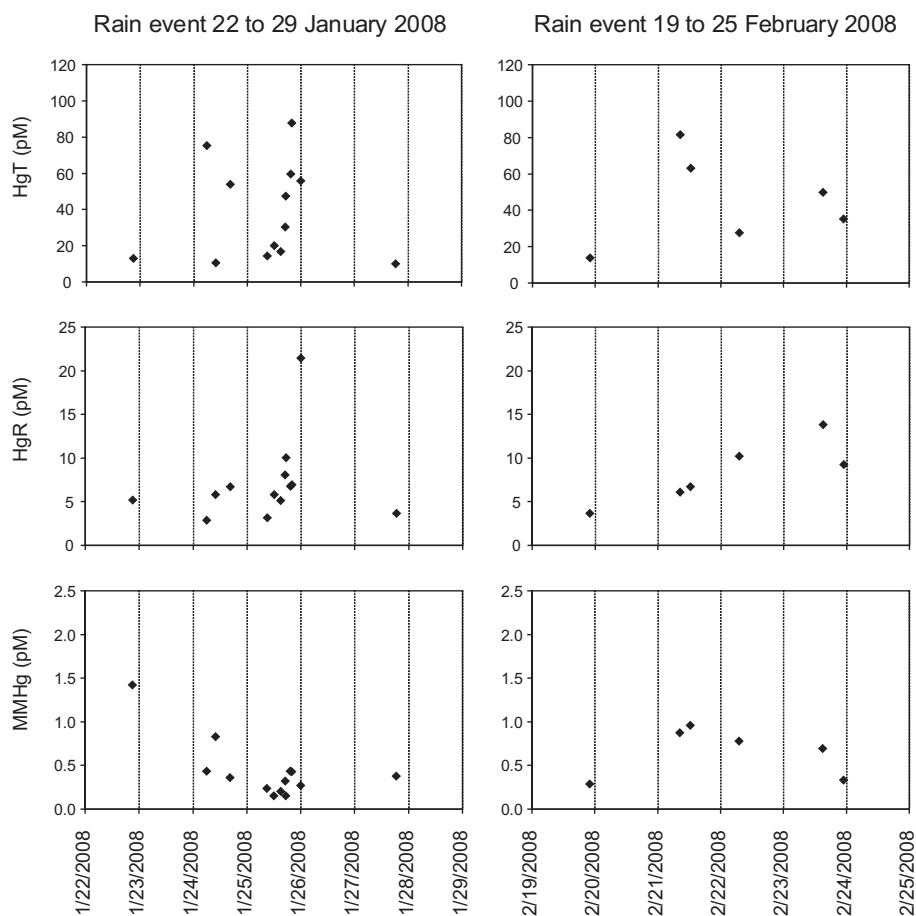
3.3. Correlation between physical processes and chemical parameters in sequential samples during single rain events

In order to investigate washout effects and evidence of atmospheric production of MMHg, we analyzed changes in chemical parameters during four rainy periods (early and late January, early and mid/late February) when sequential rainwater samples ($n > 3$) were collected over a rain event. Temporal changes were investigated using simple linear regression analysis with sampling time as the independent variable and concentration as the dependent variable, and with a significant ($p \leq 0.05$) slope indicating a change over time. Two of these rainy periods are illustrated on Fig. 3.

A decrease with time of the concentration of a chemical species during a rain event can indicate that the chemical is predominantly in particulate or water-soluble gas phases, and therefore washed out of the atmosphere during large precipitation events. A washout effect has been observed for HgT in continental (Mason et al., 1997), coastal (Bloom and Watras, 1989; Kieber et al., 2008), and oceanic rain (Lamborg et al., 1999), demonstrating that rainwater can effectively remove oxidized and particulate mercury from the atmosphere (Downs et al., 1998). Concentrations of HgT in our study show no trend with time in sequential samples taken during the same event, which is consistent with other observations of HgT in central California coast rainwater by Steding and Flegal (2002), who concluded that HgT in rainwater in this area is not dominated by the particles washed out of the atmosphere, and that variations in mercury concentration were associated with non-local processes.

Concentrations of HgR increased ($p = 0.03$) during the mid/late February event (19–25 February 2008), but showed no significant change in the other three rainy periods investigated. The reason for this increase is unknown, but preliminary atmospheric back trajectory modeling (not shown) suggests a change from relatively slower to faster-moving storm systems, and thus a potential increase in long-range transport over the period observed. However, more data (i.e., events showing changes in HgR concentrations) are needed to test this hypothesis.

Concentrations of MMHg decrease ($p = 0.009$) during the late January rainy period (22–29 January 2008), but show no significant change in the other three rainy periods examined. However, the statistical significance of the trend in MMHg concentration during the late January rainy period was dependent on a single outlier (Q test), and that there was no significant change ($p = 0.3$) with the outlier removed. Thus, the lack of a strong, consistent decrease of MMHg through the course of these individual rain events is consistent with the results of other studies of coastal rainwater that

Table 2
Summary of wet atmospheric deposition of mercury species from coastal Pacific rainwater, Santa Cruz, California. Wet deposition based on average annual precipitation depth (73 cm), average wet month precipitation depth (110 cm), or observed 2007–2008 daily maximum (10 cm). Total deposition to Monterey Bay is based on annual Santa Cruz deposition rate (73 cm) and estimated surface area of Monterey Bay (500 km^2). Annual and wet season wet deposition calculations use yearly volume-weighted mean mercury concentrations from this study, daily maximum calculation uses volume-weighted mean concentrations for samples collected that day.

	Deposition rate		
	HgT	MMHg	HgR
Average annualized deposition (pmol m^{-2} day^{-1})	57	1.4	12
Deposition to Monterey Bay (mol yr^{-1})	11	0.3	2.2
Average wet season deposition November–April (pmol m^{-2} day^{-1})	100	2.4	21
Daily maximum based on 10 cm day^{-1} (this study) (pmol m^{-2})	3100	24	620

Fig. 3. Time series of total mercury (HgT), reactive mercury (HgR), and monomethylmercury (MMHg), in sequential samples collected during two periods of rain. The concentration of HgR shows a statistically significant ($p = 0.03$, linear regression) increasing trend during the 19 to 25 February 2008 event. The concentration of MMHg shows a statistically significant ($p = 0.009$) decrease during the 22 to 29 January 2008 event, but has no significant trend ($p = 0.3$) if the initial 1.4 pM outlier (Q test) is excluded. Other panels show no significant trend ($p > 0.5$, linear regression).

show the absence of a washout effect for MMHg (Bloom and Watras, 1989; Kieber et al., 2008), which may reflect the production of MMHg in the rain itself via abiotic methylation (Kieber et al., 2008), and is discussed further below.

3.4. Correlation between physical processes and chemical parameters on MMHg levels in coastal rainwater

Despite previous suggestions that DMHg in upwelled ocean waters is a potential source for MMHg in coastal or oceanic rainwater (Bloom et al., 1996; Conaway et al., 2009; Mason et al., 1998), concentrations of MMHg in rain do not appear related to atmospheric DMHg concentrations, or to seasonal upwelling of DMHg in coastal waters. Concentrations of DMHg in surface waters of Monterey Bay were low (<0.03 pM) in September and December of 2007, but relatively high (0.06—0.29 pM) in March and May of 2008 as a result of coastal upwelling (Conaway et al., 2009). The end of the rainy season coincides with the onset of the spring upwelling season, but provides only a relatively narrow time window for potential influence of upwelling on the speciation of mercury in rainwater. Despite this, MMHg concentrations in three rainwater samples collected during one storm event in late March — early April 2008 were only 0.87—1.58 pM (Fig. 1D). Although these MMHg concentrations are higher than the mean concentration of 0.7 ± 0.5 pM across the entire sampling period, they are not markedly so given the dramatic increase of DMHg in surface water

of Monterey Bay. In addition, the concentration of DMHg in air was less than the limit of detection (0.01 ng m^{-3}) when measured both in autumn/winter and during the active spring upwelling season. Taken together, these data suggest that upwelling and evasion of DMHg from the ocean to the atmosphere is not the predominant source of MMHg in coastal rainwater.

Rather than being related to air—sea exchange of methylated mercury species, the occurrence of MMHg in coastal rainwater was more consistent with the abiotic methylation of divalent mercury in the atmosphere, as proposed previously (Gardfeldt et al., 2003; Hammerschmidt et al., 2007). A multiple linear regression analysis was used to identify correlations between MMHg concentrations in rainwater and other variables, namely precipitation depth and concentrations of HgT, HgR, and acetate. A comparison of statistically significant ($p < 0.05$) models using AIG scores identified the best fit being the model including acetate and HgR ($p = 0.002$, adjusted $R^2 = 0.84$, multiple linear regression) as independent variables. Both acetate and HgR were positively correlated with MMHg, but in the multiple linear regression model acetate accounted for 79% of the variance in the MMHg concentration data, while HgR only 5% (results of simple linear regressions are shown in Fig. 4). Acetate concentrations measured in our rainwater samples ranged from 0.34 to 3.1 μM, with a sample mean of 1.6 ± 0.9 μM and a volume-weighted average of 1.3 μM. These concentrations are relatively low compared to volume-weighted concentrations of acetate in urban (8—15 μM) areas, but
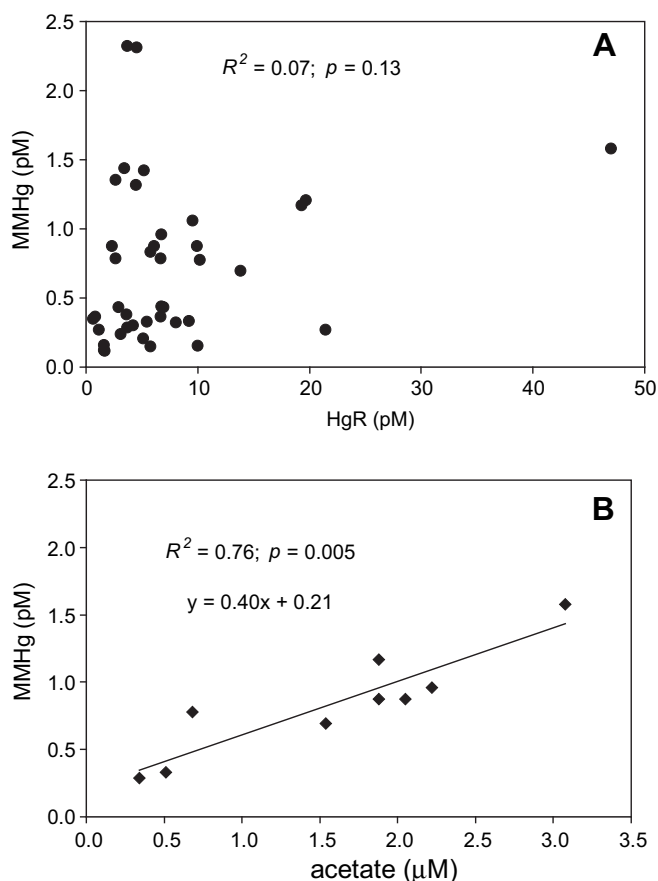
Fig. 4. Plots and results of a simple linear regressions between (A) monomethylmercury, MMHg, and reactive mercury, HgR, in Santa Cruz, California rainwater, rainy season 2007–2008; and (B) monomethylmercury and acetate mid-February–April 2008. Results of a multiple linear regression analysis are presented in the text.

consistent with concentrations measured in rural (0.6–9 μM) and coastal marine (1–6 μM) rainwater elsewhere (Avery et al., 2001; Khare et al., 1997). Although the number of samples for which we analyzed both acetate and MMHg was relatively small ($n = 9$), and this positive relationship should be confirmed with more extensive sampling, these data support the hypothesis that MMHg in rainwater is derived from the aqueous phase methylation of Hg(II) by acetate in the atmosphere. If one assumes the relationships between MMHg concentrations and those of acetate and HgR in rainwater to be causal, then these data also suggest that acetate, not HgR, is the dominant control on the aqueous phase methylation of MMHg in precipitation.

Gardfeldt et al. (2003) reported that the methylation of Hg(II) by acetate proceeded via a Hg(II)-acetate complex (most likely Hg$(CHCOO)_3^-$), and that the rate of MMHg production was largely independent of the concentration of acetate as long as the dominant Hg(II) species was Hg$(CHCOO)_3^-$. Although acetate is far in excess of Hg(II) in rainwater, the speciation of Hg(II) is unlikely to be dominated by acetate in rainwater. Using the thermodynamic stability constants employed by Gardfeldt et al. (2003) and references therein, we calculate that under typical rainwater conditions (pH $= 4.5$–6, [acetate] $= 5$ μM, $[Cl^-] = 10$ μM, and [Hg(II)] $= 50$ pM) Hg(II) speciation will be dominated by hydroxide and chloride species. Acetate would not be predicted to account for more than 1% of the Hg(II) complexation in rainwater under environmentally relevant conditions at acetate levels even as great as 200 μM, which is substantially higher than acetate levels reported for precipitation

(Avery et al., 2001; Khare et al., 1997). Thus, if the abiotic methylation of Hg(II) in rainwater by acetate proceeds via an Hg–acetate complex, then any increase in acetate concentration in natural rainwater under environmentally relevant conditions will result in an increase in Hg–acetate complexes, and therefore an increase in the rate of MMHg production via this pathway. The positive correlation between acetate and MMHg concentrations in our rainwater samples (Fig. 4) is consistent with this idea, although it should be noted that a small increase in acetate concentration will result in an increase in Hg–acetate complexes, but not a substantial shift in the overall Hg(II) speciation or complexation. Using the range of mercury and acetate concentrations observed in our study, we estimate that acetate will complex less than 0.01% of the Hg(II) pool. Given the first order rate constant for the methylation of Hg(II) by acetate described by Gardfeldt et al. (2003) and our calculated concentrations of Hg–acetate complexes, this methylation pathway would be insufficient to account for the MMHg concentrations measured in Monterey Bay precipitation. This does not preclude acetate from being involved in the production of MMHg in precipitation, but would suggest that Hg–acetate complexes are not the only species involved, and that the reaction mechanism for the methylation of Hg(II) or Hg^0 in the atmosphere is different than that described by Gardfeldt et al. (2003).

Another reason to question the idea that the relationship between acetate and MMHg in rain is a casual one is that MMHg concentrations in continental rain are not particularly elevated compared to those observed in coastal rain. Higher acetate concentrations are observed in urban and continental precipitation (up to 15 μM; (Avery et al., 2001)) compared to acetate measured in coastal precipitation both in our study (up to 3 μM) and elsewhere (1–6 μM; Avery et al., 2001; Khare et al., 1997). However, as mentioned above, the average MMHg concentrations in Monterey Bay rainwater are comparable to those measured at other coastal areas and North American continental locations. This lack of elevated MMHg concentrations in continental rain where acetate concentrations are elevated compared to coastal marine precipitation suggests either that 1) Hg(II) speciation or acetate speciation is different in continental versus coastal and marine precipitation, 2) rates of MMHg production are in fact greater over continents but concentrations of MMHg are not higher because of higher rates of MMHg degradation in these same areas, or 3) the MMHg–acetate correlation is associative rather than causal, and another means of atmospheric mercury methylation has yet to be identified.

3.5. Methylmercury concentration in rainwater as a function of storm track

To investigate the potential effect of storm track on MMHg concentration in rain, ensembles of back trajectories were calculated during precipitation events and gridded frequency distributions (GFDs) created for the highest and lowest quartile volume-weighted daily mean MMHg concentrations (Weiss-Penzias et al., 2009). Three types of GFDs are shown on Fig. 5, representing 1) all altitudes, 2) only those locations where greater than 75% of the trajectory points were above the modeled boundary layer, and 3) total precipitation in each grid cell. Panel (a) reveals that high MMHg samples are associated with air masses that spend more time at locations nearest to Santa Cruz. This indicates a possible upwelling and/or local natural or anthropogenic emission component. However, because there are more cells visible in panel (b), this suggests a free tropospheric component with possible impacts from trans-Pacific emissions. High MMHg samples are also associated with less precipitation near to Santa Cruz, and this suggests that there is less of a washout effect, leading to higher MMHg concentrations. The low MMHg samples have only one grid
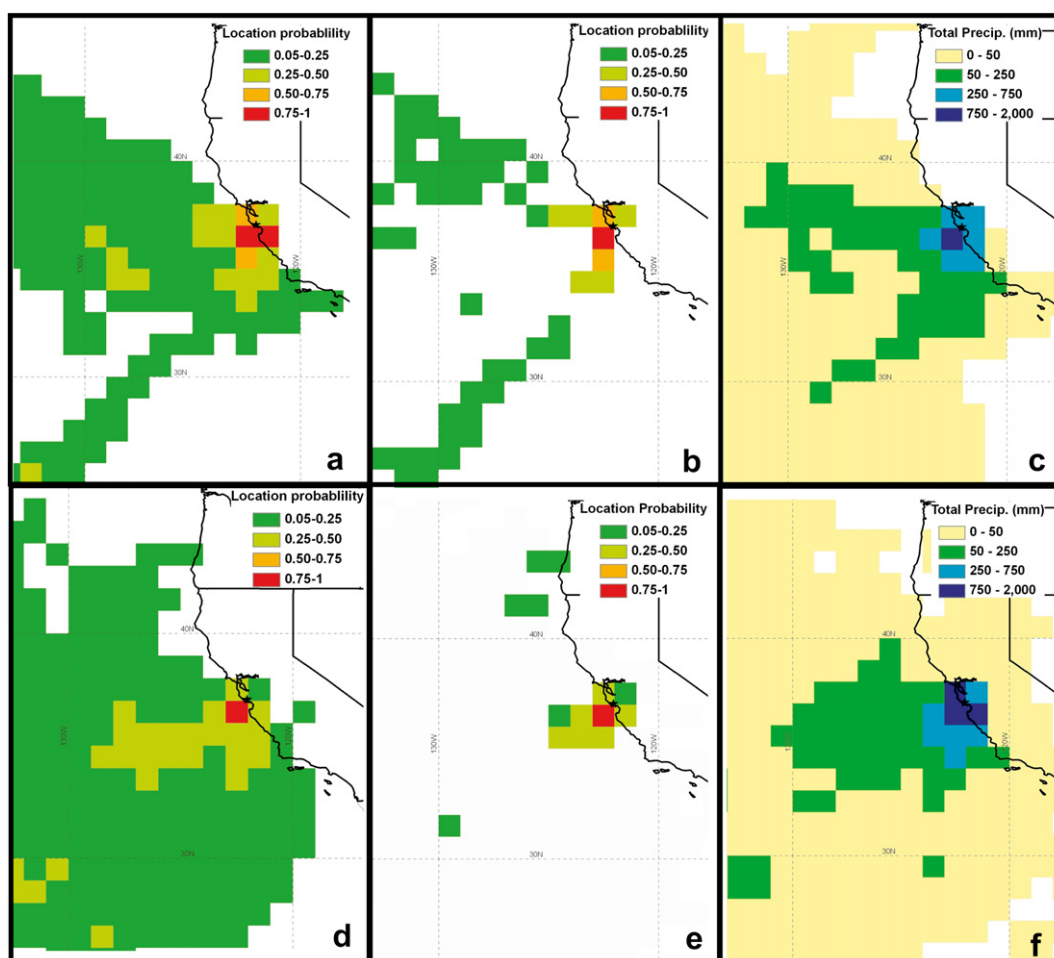
Fig. 5. Gridded frequency distributions of 72-h back trajectories for the upper (a–c) and lower (d–f) quartile events at Santa Cruz, CA during 2007–2008. Panels a/d show the distribution of trajectory points at all altitudes, b/e show only those grid cells that have > 75% of trajectory points above the modeled boundary layer, and c/f show the modeled precipitations amounts.

cell with >0.50 location probability, suggesting faster-moving storms as they arrive at Santa Cruz. Panel (e) suggests that these storms contain very little contribution from the free troposphere.

Previously observed low concentrations (<0.1 pM) of MMHg observed in oceanic precipitation (Lamborg et al., 1999; Mason et al., 1992) compared to MMHg concentrations (mean ∼0.7 pM) measured at coastal Pacific sites (Bloom and Watras, 1989; this paper) suggests that some change in atmospheric chemistry occurs at coastal margins that affects the production of MMHg in the atmosphere. This difference could be a result of enhanced decomposition of MMHg over the ocean via reactive halogens (Hammerschmidt et al., 2007; Sheu and Mason, 2004). Alternatively, the difference could be related to greater sources of carboxylic acids (i.e., acetate as a methylating agent) to the atmosphere in the coastal zone. Anthropogenic emissions of acetate, including biomass combustion (wood, forest fire, agriculture) and motor vehicle exhaust (the predominant source in urban areas) represent a large source of acetate to the atmosphere, as do biogenic emissions of acetate from vegetation and soil (Chebbi and Carlier, 1996). The complexity of atmospheric chemistry requires more complete data on the chemical composition of rainwater than has been collected to date in a single study in order to understand both the thermodynamics and kinetics of reactions related to the production and decomposition of MMHg in the atmosphere. As a result, further investigations of atmospheric mercury chemistry are needed that combine detailed measurements of mercury speciation, major anions and cations, and organic acids and organic matter in atmospheric aerosols, particles, and cloud droplets. Such studies will allow for a better understand of the aqueous phase, solid phase, and heterogeneous reactions involved in the atmospheric cycling of MMHg.

3.6. Atmospheric deposition of mercury to Monterey Bay

As a result of local topography, average annual precipitation depth around Monterey Bay ranges from 48 cm in the city of Monterey to over 150 cm in the Santa Cruz Mountains, with an average in Santa Cruz of about 73 cm. Wet atmospheric deposition rates of mercury species based on volume-weighted average mercury concentrations and precipitation depth measured at Santa Cruz are presented on Table 2. On an annual basis the flux of MMHg to Monterey Bay through rainfall (1.4 pmol m^{-2} d^{-1}) is relatively small compared to estimated diffusive fluxes of MMHg from coastal marine sediments elsewhere, which range from 9 to 2300 pmol m^2 d^{-1} (Fitzgerald et al., 2007). Although annualized deposition rates may be appropriate for mass balance calculations, given the regional Mediterranean climate a more ecologically relevant approach might be to consider the rate of MMHg deposition over the length of the wet season or individual rain events to describe pulses of bioavailable mercury to local ecosystems. For example,

the average wet season deposition of MMHg is 2.4 pmol m^{-2} d^{-1}, which by comparison is about 25% of the mean estimated diffusive flux of MMHg from sediment (9 pmol m^2 d^{-1}) on the continental shelf of New England (Hammerschmidt and Fitzgerald, 2006). As another example, using the 2007–2008 maximum daily precipitation (10 cm) and the volume-weighted MMHg concentration for samples collected on that day (0.24 pM), atmospheric deposition of MMHg on the rainiest day of the year was 24 pmol m^{-2}. Thus, on a yearly basis the atmospheric deposition of MMHg appears to be at most a relatively small direct source of MMHg in coastal marine systems, but its relative importance increases if one considers shorter time-scales, which may be more relevant from an ecological perspective. In addition, this pulse of MMHg to the marine environment via precipitation is to surface waters, and may be more readily taken up at the base of the epipelagic food web than benthic fluxes.

Acknowledgements

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