The air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans

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Abstract

Air-sea exchange is an important component of the global mercury (Hg) cycle as it mediates the rate of increase in ocean Hg, and therefore the rate of change in levels of methylmercury (MeHg), the most toxic and bioaccumulative form of Hg in seafood and the driver of human health concerns. Gas evasion of elemental Hg (Hg⁰) from the ocean is an important sink for ocean Hg with previous studies suggesting that evasion is not uniform across ocean basins. To understand further the factors controlling Hg⁰ evasion, and its relationship to atmospheric Hg deposition, we made measurements of dissolved Hg⁰ (DHg⁰) in surface waters, along with measurements of Hg in precipitation and on aerosols, and Hg⁰ in marine air, during two GEOTRACES cruises; GP16 in the equatorial South Pacific and GA03 in the North Atlantic. We contrast the concentrations and estimated evasion fluxes of Hg⁰ during these cruises, and the factors influencing this exchange. Concentrations of DHg⁰ and fluxes were lower during the GP16 cruise than during the GA03 cruise, and likely reflect the lower atmospheric deposition in the South Pacific. An examination of Hg/Al ratios for aerosols from the cruises suggests that they were anthropogenically-enriched relative to crustal material, although to a lesser degree for the South Pacific than the aerosols over the North Atlantic. Both regions appear to be net sources of Hg⁰ to the atmosphere (evasion>deposition) and the reasons for this are discussed. Overall, the studies reported here provide further clarification on the factors controlling evasion of Hg⁰ from the ocean surface, and the role of anthropogenic inputs in influencing ocean Hg concentrations.

Keywords: mercury; elemental mercury; gas evasion; aerosols; precipitation; air-sea exchange; South Pacific; North Atlantic

1. Introduction

Human activity has substantially increased the amount of mercury (Hg) in the biosphere. Air-sea exchange of Hg is a critical part of the global Hg cycle as wet and dry deposition are the dominant sources of Hg to the ocean, accounting for 70% or more of the inputs, and gas exchange is the dominant sink, being about 90% of the outputs from the ocean (Driscoll et al., 2013; Fitzgerald et al., 2007; Lamborg et al., 2014; Mason et al., 2012). The net reduction and evasion of elemental Hg (Hg^0) from the ocean surface (Soerensen et al., 2010), and a concurrent reduction and evasion from terrestrial surfaces, prolongs the overall residence time of Hg in the biosphere prior to its eventual burial in sediments and soils (Amos et al., 2015). This recycling also prolongs the response time of Hg in surface reservoirs of the biosphere to changes in anthropogenic inputs. Furthermore, the extent of air-sea exchange influences surface ocean total Hg (HgT) concentrations and indirectly impacts the rate of change of methylmercury (MeHg) concentrations in the upper ocean, where most of the fish and seafood consumed by humans reside. Therefore, a clear understanding of the factors affecting gas exchange of Hg^0 at the ocean surface is needed to accurately predict the response time of the ocean to changes in the magnitude and location of anthropogenic inputs, which will impact ocean fish MeHg concentrations, which are the primary driver of human-health concerns related to MeHg exposure (Clarkson and Magos, 2006; Mahaffey et al., 2011). Additionally, climate change will also impact ocean fish MeHg through changes in ecosystem characteristics and food web structure.

Evasion also substantially contributes to atmospheric boundary layer Hg^0 over the ocean (Soerensen et al., 2010; Strode et al., 2007), and to a lesser degree, the concentrations of Hg^0 in the terrestrial boundary layer. Models suggest that the Hg^0 evasion flux has increased dramatically (~200%) from the pre-industrial era and that the current flux is between 10-15 Mmol yr^{-1} ($75\text{-}110 \text{ pmol m}^{-2} \text{ d}^{-1}$; Mason et al., 2012). Early measurements in various ocean regions suggested that Hg^0 evasion fluxes were typically higher than this range of model estimates. Also, these studies concluded that most surface waters were supersaturated with dissolved gaseous Hg (DGHg) relative to the atmosphere (e.g. Mason, 2009), although models suggest that this is not always the situation. In some cases, the evasion fluxes based on measurements likely reflected short-term variability in surface ocean concentrations and not

yearly averages (e.g. Mason et al., 1998), while, in other instances, the dissolved concentrations of Hg^0 may have been incorrectly measured.

Estimates of gas evasion rely on the determination of the dissolved Hg^0 (DHg^0) concentration, and estimation of the flux, in most cases, using a gas exchange model, such as the Nightingale parametrization of gas exchange (Beale et al., 2013). Most studies in the open ocean have found that surface water DHg^0 generally contains <10% dimethylmercury (Mason and Fitzgerald, 1993; Mason et al., 2001; 2012; Munson et al., 2015; Soerensen et al., 2014). Based on our data (Bowman et al., 2015; Bowman et al., 2016), this was true for the North Atlantic and South Pacific Ocean regions discussed in this paper.

Recent semi-continuous high resolution measurements of DHg^0 in surface water (Andersson et al., 2008a; Andersson et al., 2008b; Kuss et al., 2011; Soerensen et al., 2014; Soerensen et al., 2013) suggest that while concentrations may vary among oceans they are relatively consistent within a geographic region. Previous high resolution studies in the North Atlantic in the vicinity of Bermuda suggested that the concentration of DHg^0 was relatively consistent over the region sampled (26-34 °N, 62-65 °W), and over 3 years of sampling (Soerensen et al., 2013). However, these concentrations, and the associated fluxes, were higher than those measured in the eastern North Atlantic (Kuss et al., 2011), suggesting intra-basin differences in DHg^0 concentration. Comparison of shelf and off-shore data indicated that Hg input was a potential driver of the differences observed in DHg^0 in the western North Atlantic. (Soerensen et al., 2013)

Observations from the Metzyme cruise in the tropical Pacific Ocean (Soerensen et al., 2014) further suggest a relationship between DHg^0 and Hg inputs. The highest concentrations of DHg^0 in surface ocean, found in the Inter-Tropical Convergence Zone (ITCZ), were likely due to elevated deposition and the proposed efficient scavenging of ionic Hg by high atmospheric moisture and rainfall (Soerensen et al., 2014; NASA, 2016). A similar pattern was observed during the North Atlantic studies by Kuss et al. (2011), who found that the location of the maximum DHg^0 concentration shifted in the vicinity of the equator as the ITCZ changed latitudes seasonally. These peaks in concentration coincident with the ITCZ were simulated by computer modeling using the GEOS-Chem atmospheric transport model linked to a global ocean model (MITgcm) (Soerensen et al., 2014; Zhang et al., 2014), although the overall magnitude of the modeled increase in concentration was less than the observations (Soerensen et al., 2014).

This discrepancy suggests that other sources of DHg^0 , or other processes, were important for DHg^0 formation in these regions.

Based on the relatively low predicted atmospheric inputs of Hg to low-latitude South Pacific regions, we hypothesized that the concentration and evasional flux of Hg^0 would also be low if driven by atmospheric Hg inputs. For the North Atlantic, we predicted that both deposition and evasion would be higher than in the South Pacific. Additionally, given the upwelling that occurs in the eastern tropical Pacific Ocean off South America, we anticipated that changes in temperature and productivity would also influence the formation of DHg^0 as biological processes could mediate the overall rate of conversion of divalent Hg (Hg^{II}) to Hg^0 , and together with sinking particles enhance the removal of Hg. As many of the recent studies have focused on the North Atlantic Ocean, we also compare and contrast our measurements in the subtropical Pacific Ocean with that of the Atlantic Ocean, and other Pacific Ocean studies. Additionally, we use our measurements of Hg in rain and aerosols, and the literature, to estimate the fluxes at the sea surface for the South Pacific and North Atlantic, and contrast these inputs with the gas evasion flux. Furthermore, we compare our measurements with the output of computer models.

2. Methods

2.1 Sampling Approach and Sample Analysis

We made high-resolution measurements of atmospheric and dissolved gaseous Hg^0 along the GEOTRACES GP16 section in the Pacific Ocean from 25 October to 20 December, 2013 aboard the R/V *Thomas G. Thompson* from Manta, Ecuador to Papeete, Tahiti, although sampling only began off Lima, Peru (Figure 1a). For DHg^0 , seawater from the ship's intake at 5-10 m depth, which is used to measure surface temperature, salinity and fluorescence, was subsampled with an automatic continuous equilibrium system (Andersson et al., 2008a; Soerensen et al., 2013) while the ship was moving, and not while sampling at the designated stations (Fig. 1a). Quantification at 10 minute resolution relied on a Tekran 2537A Hg vapor analyzer. We also measured atmospheric Hg^0 with the same temporal resolution as the water measurements. On this cruise, the same Hg analyzer was used for the quantification of surface water DGHg and atmospheric Hg^0 . A switching valve changed between the sampling lines on a regular basis. For much of the cruise, the switching was set so the water was sampled more frequently than the air (e.g., water for 3 h; air for 1 h). The instrument was calibrated daily using

the internal calibration source and had a detection limit of $<0.2 \text{ ng m}^{-3}$ for air, and $<2 \text{ fM}$ for seawater. Moisture from the equilibrator was prevented from reaching the Tekran as air passed through both an in-line Teflon filter and a soda lime trap, which were routinely changed. High-resolution ancillary measurements of wind speed, salinity, temperature, precipitation, and *in situ* fluorescence (a proxy for algal productivity) were aggregated into 2-h averages for statistical analyses. For the calculations of concentration and flux, DGHg in the sampled seawater is assumed to be entirely DHg^0 . Most studies focused on gas exchange do not speciate the DGHg, as surface waters are being sampled ($<10 \text{ m}$ deep typically), and it is assumed that measured surface water DGHg concentrations reflect concentrations of DHg^0 . This was true for the North Atlantic and South Pacific Ocean regions discussed in this paper (Bowman et al., 2015; Bowman et al., 2016).

The GEOTRACES GA03 North Atlantic cruise, which was completed during 2010 and 2011 in two legs using the R/V *Knorr* covered the subtropical and temperate Atlantic with transects from Woods Hole, MA, USA to the Cape Verde Islands, via Bermuda, and from Lisbon, Portugal to the Cape Verde islands (Fig. 1b). There was no underway continuous measurement system for either DGHg or atmospheric Hg^0 during this cruise, but samples were collected using a trace-metal clean “towed fish” pumping system (Bruland et al., 2005) and filtered through pre-rinsed capsules ($0.2 \text{ }\mu\text{m}$, Pall AcroPak-200) into acid-cleaned borosilicate glass and polycarbonate bottles (Hammerschmidt et al., 2011). Discrete measurements of DHg^0 and dimethylmercury were made within 2 h of water sampling and filtration using a 2-L sample purged with Hg -free N_2 at 0.8 L min^{-1} (Bowman et al., 2015). On GA03 and GP16, surface water samples ($\sim 2 \text{ m}$ depth) for HgT determination were also collected with the towed fish sampling device. Total Hg was measured within 48 h of sampling as described in Bowman et al. (2016).

During the North Atlantic GA03 cruise, aerosol total suspended particulate (TSP) samples were collected on quartz microfiber filters that had been baked at $480 \text{ }^\circ\text{C}$ for 12 h and stored wrapped in foil. Samples were collected using a high volume TSP sampler (model 5170-BL, Tisch Environmental) (Shelley et al., 2015). The samplers were deployed on the ship’s flying bridge as high off the water as possible (14 m above sea level). To avoid contamination from the ship’s stack exhaust, aerosol sampling was controlled with respect to wind sector and wind speed using an anemometer interfaced with a Campbell Scientific CR800 datalogger. The samplers operated only when the wind was $\pm 60^\circ$ from the bow and $>0.5 \text{ m s}^{-1}$. When the wind failed to

meet these two criteria, the motors were shut off automatically and not allowed to restart until the criteria were met for five continuous minutes (Shelley et al., 2015). The sampling approach was the same on the South Pacific GP16 cruise, however, the sector wind direction/speed control device detailed above was not operational and aerosols were collected only while the ship was on station and pointing into the wind (C. Buck, pers. comm.). During transit, winds were not favorable for aerosol sampling without contamination.

During the North Atlantic cruise, the volume of air filtered and the sampling duration averaged 1437 m³ (range, 432 m³ to 2189 m³) and 17.8 h (range, 5.3 h to 29.6 h), respectively while for the Pacific cruise, ~200 m³ of air were sampled. In both instances, subsamples of the filters for Hg were frozen and transported to Woods Hole Oceanographic Institution for analysis of HgT. Mercury in aerosols was leached from filter punches with high-purity 2 M HNO₃ for 30 min in a 60 °C sonicated water bath, and analyzed for HgT after oxidation with BrCl, SnCl₂ reduction, purging with Hg-free N₂, and dual Au-amalgamation CVAFS detection (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979). Procedural precision averaged 3 ± 2 relative percent difference (RPD; n = 3) and the method detection limit for aerosol HgT was 0.03 pmol/filter.

Rain was collected on an *ad hoc* basis on both cruises using an N-CON precipitation sampler (Model 00-120 ADS) mounted to the forward railings of the flying bridge, away from the super-structure to minimize splash contamination. Furthermore, the sampler was not operated in high wind conditions to minimize the collection of sea spray. As the sampler was not sector controlled the wind direction was monitored throughout precipitation events, and the sampler closed manually when the wind was not coming from ± 60° to the bow. The precipitation sampler was fitted with a polyethylene collection funnel (613 cm²). The funnel was attached to a 500 mL Teflon sample bottle by a Teflon collar, which was placed inside a 25-L plastic bucket to hold the sampling apparatus in place. The edge of the funnel was approximately flush with the top of the bucket. The funnel and bottle assemblage were cleaned with acid prior to deployment, and rinsed thoroughly with 0.1 M HCl and deionized water (both ultra-high purity) between each rain event. Unfiltered rainwater collected during GP16 and GA03 was analyzed for HgT (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979) and MeHg (Bowman and Hammerschmidt, 2011) immediately upon collection. Relative standard deviation of duplicate and triplicate rain sample measurements during both GA03 and GP16 ranged between 0.4 and 3% for HgT (n = 4).

Parameters needed for correlation analysis and for determination of the gas exchange parameters detailed in Section 2.2 were obtained from in situ measurements during the cruises. Data for wind speed, water temperature, salinity and fluorescence are typically collected at high resolution – every minute or more frequently – and were averaged into hourly values for plotting and for calculations of the gas exchange parameters. Correlations between parameters were tested for significance based on the correlation coefficients of the regression analyses. Tests for significance relied on the software that is part of the SigmaPlot program (version 10).

Concentrations of Al in aerosols were determined by ICP-MS using a Thermo Element 2 instrument at Florida State University (Shelley et al., 2015). Filter samples were digested using a procedure that was validated during the GEOTRACES Intercalibration study (Morton et al., 2013) prior to analysis. Three day (72 h) air mass back trajectories for the North Atlantic GA03 samples were simulated for the start and end of each aerosol sampling interval using the GDAS meteorology in the publically available NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model run in normal mode (Draxler and Rolph, 2013; Rolph, 2013). Further details can be found in Shelley et al (2015).

2.2 Flux Calculations and Modeling

Percent saturation of DHg^0 was determined as:

$$\% \text{saturation} = 100([\text{DHg}^0]_w / [\text{DHg}^0]_{\text{eq}} - 1)$$

where $[\text{DHg}^0]_w$ is the measured concentration of DHg^0 (pmol m^{-3}), and $[\text{DHg}^0]_{\text{eq}}$ is the concentration in the water at equilibrium with the atmosphere. Thus, $[\text{DHg}^0]_{\text{eq}} = [\text{Hg}^0]_a / H$ where $[\text{Hg}^0]_a$ is the air concentration (pmol m^{-3}) and H is the dimensionless Henry's law coefficient, which is temperature dependent (Andersson et al., 2008). With this formula, a %saturation of 0% represents the surface waters being equivalent to the equilibrium value. The estimation of gas exchange flux used the approach detailed in Soerensen et al. (2010) with some modification. The general method uses the following equation to determine the flux (F):

$$F (\text{pmol m}^{-2} \text{ d}^{-1}) = k_w([\text{DHg}^0]_w - [\text{Hg}^0]_a / H)$$

where k_w is the mass transfer coefficient (m d^{-1}) calculated using the Nightingale et al. (2000) formulation, derived for CO_2 , relating the exchange coefficient to the wind speed, and amended for Hg^0 using the relationship between the Schmidt numbers (Sc) for both gases:

$$k_w = (0.222u_{10}^2 + 0.333u_{10})(Sc_{\text{Hg}^0}/Sc_{\text{CO}_2})^{-0.5}$$

where u_{10} is the measured wind speed (m s^{-1}) on the ship adjusted to a 10 m height. The values of Sc for Hg^0 were calculated as: $Sc_{\text{Hg}^0} = \nu/D$, where ν is the kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) and D is the diffusivity ($\text{cm}^2 \text{s}^{-1}$) (Poissant et al., 2000). The value for D for Hg^0 was determined using the Wilke-Chang formulation which includes its temperature dependence, and is related to the viscosity of water (N) (Soerensen et al., 2010):

$$D (\text{cm}^2 \text{s}^{-1}) = 1.025 \times 10^{-7} (T/N)$$

For determining Sc_{Hg^0} :

$\nu = N/\rho = 0.017 \exp(-0.25T')$ where T' is the temperature in $^{\circ}\text{C}$ (Poissant et al., 2000). For CO_2 , Sc is determined using a temperature-dependent equation (Poissant et al., 2000). The Sc_{Hg^0} and Sc_{CO_2} are determined from these calculations, which then allows for the determination of k_w with changing temperature and wind speed.

The wet deposition flux was estimated using the concentration of Hg in rain (nmol m^{-3}) and the average annual rainfall (h ; m yr^{-1}), which was obtained from the literature (see the Supporting Information, Fig. S1):

$$\text{Flux}_{\text{wet}} = [\text{Hg}] \cdot h$$

The range in the estimate given in the Table 3 was determined by considering the variability in the measurements of concentration, and the variation in the rainfall amounts for the regions under consideration. The dry particulate deposition flux was similarly calculated using the measured aerosol concentrations and a dry deposition velocity applicable to the size of aerosols within the marine boundary layer atmosphere:

$$\text{Flux}_{\text{dry}} = v_{\text{da}} [\text{Hg}]$$

where v_{da} is the aerosol dry deposition velocity. Given the quadratic relationship between aerosol size and deposition velocity (Seinfeld and Pandis, 1998), and as the particle size distribution was not ascertained for the aerosols collected, a value ($v_{\text{da}} = 0.5 \text{ cm s}^{-1}$) was chosen as representative of the aerosol size, based on the likely aerosol size range for marine aerosols (Gichuki and Mason, 2014; Seinfeld and Pandis, 1998). Again, the ranges in the flux estimates given in Table 3 take into account the variation in concentration and in v_d with aerosol size.

A similar formula was used to estimate the dry deposition of reactive gaseous Hg (RGHg). As no atmospheric measurements of RGHg were made during the cruises, the results from other ocean expeditions were used to determine a suitable range of values (Laurier et al., 2003; Laurier

and Mason, 2007; Gichuki et al., 2014). In addition, the results of a compilation of data from these measurements, which related the maximum daily RGHg to ozone concentrations (Fig. S2), was used with literature values of ozone over the ocean regions (Fig. S3) to estimate RGHg. As the distribution of RGHg concentration with time of day has been shown to track UV, based on field data (Fig. S2; Laurier et al., 2003; Laurier and Mason, 2007), and approach zero at night, the average hourly value for a day was taken as half the peak concentration (i.e. the average hourly area based on peak triangulation). These estimated concentrations are similar to those derived from modeling these data (Holmes et al., 2009; Soerensen et al., 2010). The deposition flux was calculated in a similar manner to that for aerosols using an appropriate value for the dry deposition velocity of RGHg (v_{dg}). The values for v_{dg} were obtained from the modeling of previous data by Holmes et al. (2009), who concluded that an average value of 0.5 cm s^{-1} was representative of the subtropical region, and is similar to that used for other soluble reactive gases, such as nitric acid.

In scaling the dry deposition estimates to a yearly value it is assumed that the concentrations do not vary substantially with season. There is little measured information to support this conclusion but such an assumption is supported by model output, especially for the South Pacific region. In the discussion sections of the paper, reference is made to the Soerensen et al. (2010) global mercury gas exchange model. Details of this model are provided in the SI (Fig. S5) as well as in the description of the methods above.

3. Results and Discussion

3.1 Surface Hydrography of the Cruises

The South Pacific GP16 cruise started within the Peru upwelling region and the initial stages of the cruise sampled these waters. Based on the salinity (S), temperature (T) and water masses crossed during the cruise, the sampled region was divided into three sections (Fig. 2). The three regions were divided based on surface water characteristics, and taking into account their differences in physical chemistry and biogeochemical characteristics, as discussed in the literature (Kessler, 2006; Fielder and Talley, 2006; Johnson et al., 2002; Perez and Kessler, 2009). Region 1, east of 102°W , characterizes the core of the Peru upwelling-affected region, where T and S increased with longitude (Fig. 2a). This region reflects the core of region impacted by the Peru upwelling and the initial advection of these waters away from the continent

(Fielder and Talley, 2006; Fig. S1b). The S and T differences in this region were smaller during the cruise period (Oct-Dec) than at other times of the year when upwelling is more pronounced. Region 2, between 102° to 128°W, was defined to encompass the transition region in the eastern South Pacific where there was relatively constant T and S. This region represents the transition from the upwelling waters to the waters of the South Equatorial Current which flow north-west (Kessler, 2006). Region 3, represents the waters >128°W, where S decreased and T increased with increasing longitude. This region represents the north edge of the South Pacific gyre and the higher salinity surface waters are referred to as the Subtropical Surface Water by Friedler and Talley (2006).

The thermocline is deeper and stratification weaker in Region 3 than it is closer to the continent, and closer to the equator. Nutrient concentrations are lower in Region 3 than in the other regions, and are highest in Region 1 due to inputs from upwelling. Given the circulation in the region, the surface waters in Region 3 are younger, based on chlorofluorocarbon age dating (Fielder and Talley, 2006), reflecting the influence of meridional circulation in this region compared to the older, upwelled waters near the continent. The western most region of the cruise track overlaps with the region of higher precipitation referred to as the South Pacific Convergence Zone (SPCZ) which extends the area of higher rainfall to about 140 °W (Fig. S1; Linsley et al., 2006).

The two cruises in the North Atlantic, which were part of the GA03 expedition (Fig. 1b), covered various water masses, although the majority of the sampling took place within waters of the North Atlantic gyre (Jenkins et al., 2015). Close to the North American continent, the waters were colder due to the presence of Labrador Seawater, and further offshore the cruise crossed the Gulf Stream which was sampled between Woods Hole and Bermuda (Fig. 3a). After Bermuda, the waters sampled were mainly North Atlantic Central Water, which is divided into the western and eastern section, with the highest salinity occurring around 40 °W. Closer to the West African continent, the waters are colder due to the upwelling that occurs in this region (Fig. 3b), and these waters have higher nutrient concentrations (Jenkins et al., 2015). There is little salinity difference in this region however. Temperature and S decrease northward in the eastern North Atlantic (Fig. 3b) due to the flow southward of the Canary Current off southern Europe and North Africa. Fluorescence was high close to North America and in the vicinity of Lisbon (Fig.

3c & 3d), reflecting the importance of nutrient inputs to coastal waters and the role of upwelling in the southeastern North Atlantic.

3.2 Elemental Mercury and Gas Evasion

Concentrations of DHg^0 measured during the GEOTRACES GP16 cruise in the South Pacific are shown in Figure 4. Water column total Hg concentrations and Hg speciation results from the cruise are detailed in Bowman et al. (2016) and summarized in the Supporting Information (Table S1: surface water HgT; Table S2: average values for Hg species in top 200 m). The DHg^0 concentration (Fig. 4a), percent saturation (Fig. 4b), and Hg^0 evasional flux (Fig. 4c) vary among the three regions noted above. Concentrations of DHg^0 were low in surface water from Region 1 ($<102^\circ\text{W}$; mostly <40 fM, except for the locations closest to the continent) with an average of 33 ± 5 fM ($n = 360$; Table 1). Waters were near saturation ($25 \pm 19\%$) with a resultant low evasional flux in Region 1 (35 ± 35 $\text{pmol m}^{-2} \text{d}^{-1}$), with occasional values indicating deposition of Hg^0 to the water surface. In Region 2 ($102\text{--}128^\circ\text{W}$), surface waters were similarly saturated with DHg^0 ($25 \pm 19\%$) and concentrations were not different from those in Region 1 (31 ± 4 fM, $n = 470$). The average flux of DHg^0 from Region 2 was somewhat greater (50 ± 30 $\text{pmol m}^{-2} \text{d}^{-1}$) but not statistically different from that of Region 1 ($p > 0.05$). In Region 3 ($>128^\circ\text{W}$), DHg^0 concentrations and percent saturation tended to increase with increasing water T, resulting in an increasing flux to the atmosphere across Region 3. This region had the highest concentrations of DHg^0 (up to 70 fM; mean = 46 ± 13 fM, $n = 372$), percent saturation (30–190%) and flux (175 ± 95 $\text{pmol m}^{-2} \text{d}^{-1}$; range 65 to 385 $\text{pmol m}^{-2} \text{d}^{-1}$) (Table 1; Fig. 4) with the highest values most west, coincident with the highest T measured on the cruise.

The fraction of total Hg as DHg^0 , calculated using the nearest measured surface water HgT concentrations from Bowman et al. (2016), averaged $25 \pm 7\%$ ($n = 33$) across the entire GP16 section of the South Pacific, with the consistency among locations suggesting that input of Hg^{II} was an important factor driving the concentration of DHg^0 in this region. There was some variability in the fraction of total Hg as DHg^0 among locations as $\%\text{DHg}^0$ was lowest in colder eastern waters ($15.9 \pm 3.0\%$ for $<87^\circ\text{W}$) and highest and more variable furthest west ($26.7 \pm 5.9\%$ for $>125^\circ\text{W}$), suggesting different net rates of formation and/or evasion between these regions, which is likely driven by differences of T and associated solubility of Hg^0 .

Concentrations of DHg^0 were significantly related to those of total Hg ($r^2 = 0.13$, $p = 0.05$, $n =$

33), although it is clear that other factors must also contribute to the variability given the small r^2 value.

In the North Atlantic, water for DHg^0 analysis were only collected as discrete samples during the GA03 cruises while the ship was underway and are therefore more limited ($n=22$). Given the cruise track (Fig. 1b) and the water characteristics (Fig. 3), the locations were divided into the western ($>40^\circ\text{W}$) and the eastern ($<40^\circ\text{W}$) North Atlantic. These designations also allow for easier comparison of the data with other values in the literature. Concentrations of DHg^0 , %saturation, and gas exchange flux were higher for the western region compared to the eastern North Atlantic (Table 2) although the differences are not statistically different given the relatively high variability in the data. The % DHg^0 was very similar throughout the cruise and was overall lower than the values found in the South Pacific, even though the total Hg concentrations were generally higher in the North Atlantic. The %saturation for the North Atlantic was higher than found in the eastern regions of the South Pacific cruise but comparable to values found in Region 3. Fluxes were relatively variable but higher than found in the South Pacific.

Atmospheric input of Hg likely influences net Hg^0 production and evasion in the South Pacific. Concentrations of DHg^0 were correlated with ancillary variables including salinity ($r^2 = 0.23$, $p < 0.001$, $n = 129$), with overall higher DHg^0 at lower salinity (Fig. 5b). The correlation between DHg^0 and salinity was strongest in Region 3, where there was an increase in DHg^0 with decreasing salinity ($r^2 = 0.86$, $p < 0.001$, $n = 40$). The salinity of the surface waters in Region 3 are mostly related to wind driven circulation as these waters represent the northern region of the South Pacific gyre, as discussed above. Additionally, the annual amount of precipitation increases with westward longitude away from South America in this region (Fig. S1), and this is primarily due to the fact that the latter stages of the cruise sampled in waters that are impacted by the SPCZ. While the cruise did not encounter the core of the SPCZ, the higher precipitation in the region is related to this feature.

The correlation between DHg^0 and salinity also varies inversely in Region 1 in the South Pacific (Fig. 5b). Here, upwelling inputs of less saline, Hg-rich subsurface water (Bowman et al., 2016) are likely contributing to this trend. In Region 1, there were somewhat higher DHg^0 concentrations in the colder waters suggesting the potential importance of upwelling inputs of DHg^0 from depth, where Hg⁰ in subsurface water was >100 fM (Bowman et al., 2016). While

dimethylmercury in subsurface water, which was between 10 and 140 fM ($n = 4$) at the most coastal stations of Region 1, may also have contributed to greater DGHg in upwelled water (Bowman et al., 2016), the underway sampling was delayed until $>78^{\circ}\text{W}$ and did not sample much of the core of the upwelling region. There was no significant relationship between DHg^0 and T (Fig. 5a) except in the latter stages of the cruise (Region 3), where both DHg^0 and T increased to the west, and the two were strongly correlated ($r^2 = 0.75$; $p < 0.001$; $n = 40$). Again, it is likely that T is acting as a proxy for different water masses rather than reflecting a direct impact of T on DHg^0 formation.

Finally, the relationship between DHg^0 and fluorescence in the South Pacific was complex with little correlation overall (Fig. 5c). Surface water in Region 1 had the highest fluorescence but relatively low concentrations of DHg^0 and there was little relationship between the two variables. In contrast to Region 1, surface waters in Region 3 had low fluorescence and elevated DHg^0 . Given the more limited dataset for the North Atlantic it was not possible to tease out relationships between DHg^0 and ancillary variables to the same degree. Overall, there was little evidence in the data of any correlation with S , T or fluorescence, or any strong latitudinal or longitudinal trends in DHg^0 .

Other recent studies have measured either similar or higher concentrations of DHg^0 in the surface ocean (Table 1). The 2011 Metzyme cruise, which sampled waters between Hawaii and American Samoa, measured DHg^0 at locations ($10\text{--}16^{\circ}\text{S}$, $160\text{--}175^{\circ}\text{W}$) comparable to the values from the western end of the GP16 GEOTRACES cruise ($\sim 10^{\circ}\text{S}$, up to 148°W) and found similar concentrations ($40\text{--}70$ fM) and flux (<240 $\text{pmol m}^{-2} \text{d}^{-1}$; Table 1; Soerensen et al., 2014). In contrast, higher concentrations of DHg^0 have been measured in the western North Atlantic Ocean, and were typically >100 fM in the vicinity of Bermuda (Soerensen et al., 2013). Surface waters near Bermuda, sampled during the early and late summer in 2008-2010, were highly saturated ($>500\%$ on average) even though the fraction of total Hg as DHg^0 was lower (range = $10\text{--}20\%$) than found in the eastern South Pacific on the GP16 cruise. Similar concentrations to those determined by Soerensen et al. (2013) near Bermuda were found in the western North Atlantic during GA03 (Tables 1 & 2). The warmer T and higher HgT concentrations of the subtropical North Atlantic surface waters likely contribute to the differences in both DHg^0 concentration and percent saturation compared to the colder upwelling waters in the eastern South Pacific. Elevated concentrations of DHg^0 were observed in the ITCZ region of the Pacific

Ocean during the Metzyme cruise, when the ITCZ was north of the equator (Soerensen et al., 2014), and in the Atlantic Ocean (Kuss et al., 2011; Table 1). The results of both measurement and modeling suggest that higher dissolved concentrations and fluxes of Hg^0 within the ITCZ are driven by enhanced atmospheric deposition of Hg due to high precipitation rates.

Soerensen et al. (2013) found a positive relationship between DHg^0 and temperature for the four open-ocean and two coastal cruises discussed in their paper, although the relationships were not always positive for an individual cruise. There also was a correlation between DHg^0 and salinity for the ocean cruises but not the coastal cruises and concentrations of DHg^0 were correlated with wind speed on most cruises. Fluorescence data was limited, but correlations with DHg^0 were found for those cruises where fluorescence measurements were made (Soerensen et al., 2013).

The lack of a correlation with fluorescence in the South Pacific suggests that productivity has little influence on the net formation of DHg^0 in that region. Earlier studies have suggested that upwelling could be an important source of Hg^{II} to the equatorial Pacific Ocean and to the formation of DHg^0 in the productive upwelling zone (Mason and Fitzgerald, 1993; Mason et al., 1994). However, more recent measurements of HgT during the Metzyme cruise also do not indicate that concentrations in surface waters were substantially elevated in Hg in the equatorial upwelling region (Munson et al., 2015), but this does not mean that upwelling inputs are not important. Measured particulate sinking fluxes at the equator at 60 m during the Metzyme cruise were much higher than those at locations further north (Munson et al., 2015) but overall the upwelling flux was greater than the evasion and particulate flux suggesting that upwelling was providing Hg input that is then advected away from the equator, as had been previously suggested (Mason et al., 1994).

This may be so for the upwelling region of the South Pacific even though the HgT concentrations were relatively low in the recently upwelled waters. As noted in Bowman et al. (2016), filtered HgT concentrations in surface waters were low (<0.2 pM) except for the upwelling region where they were up to a factor of three higher (0.39 ± 0.12 pM; $n = 5$, between 80°W and the Peru margin). This suggests substantial input of Hg from upwelling in this region, given that enhanced primary productivity and particulate export should have depleted surface concentrations compared to the more oligotrophic regions covered during the cruise. Bowman et

al. (2016) estimated upwelling fluxes of HgT to decrease from high values of 2200 pmol m⁻² d⁻¹ near the coast to 70 pmol m⁻² d⁻¹ further west (around 95°W).

Wind speed was relatively constant throughout the GP16 South Pacific cruise (Fig. 2b), therefore, differences in Hg⁰ evasion were mostly driven by DHg⁰ concentration and other factors. This pattern is different than that reported for other regions of the ocean where wind speed is an important parameter influencing both concentration and flux. During the Metzyme cruise, both variations in DHg⁰ concentration and wind speed appeared to drive the flux of Hg⁰ (Soerensen et al., 2014). In the North Atlantic, wind speed differences have previously been proposed as the main driver of Hg⁰ evasion (Kuss et al., 2011; Soerensen et al., 2013).

There is somewhat of a latitudinal trend, based on the averages in Table 1, with higher fluxes in the Northern Hemisphere and within the ITCZ compared to the Southern Hemisphere for both oceans, although data are more limited south of the equator. Given the higher anthropogenic emissions north of the equator, this trend likely reflects differences in current anthropogenic inputs of Hg to the atmosphere north of the equator, and the associated higher deposition to the Northern Hemisphere as a result.

3.2 Mercury in Air, Aerosols and Precipitation

3.2.1 Mercury in Precipitation

Rain was sampled during the latter stages of the Pacific GP16 cruise (Region 3) and had an average HgT concentration of 11 ± 6 pM (n = 5; range 3-16 pM). During the North Atlantic U.S. GEOTRACES GA03 cruise, concentrations in rain ranged from 10 to 110 pM (25 ± 29 pM, n = 11), with no consistent trend east to west or north-south. The highest HgT concentration in rain during the GA03 cruise was measured north of the Cape Verde Islands and likely included a significant amount of scavenged Saharan dust.

The rain concentrations measured during GP16 are similar to those found during a 1990 cruise in the equatorial Pacific (14.4 ± 6.5 pM; Mason et al., 1992) in a similar area (rain collected between 10°N to 18°S; 150°W to 180°W), suggesting that current deposition is not significantly enhanced compared to those earlier collections. Concentrations of HgT in South Pacific rain are less than those found in precipitation to the North Atlantic during GA03 and measured at Bermuda (volume weighted mean concentration (VWM) 23.5 pM; Gichuki and Mason, 2014), and in the equatorial Atlantic (VWM 17.8 pM; Lamborg et al., 1999)

Methylmercury measured during one rain event at 39 °N, 69 °W in the eastern North Atlantic (GA03) during a tropical storm averaged 0.41 ± 0.23 pM ($n = 4$) and was 1–2% of the HgT concentrations. There are few measurements of MeHg in rainfall over the open ocean, but the concentration and %MeHg found is comparable to measurements made at a coastal site in Maryland, USA (0.36 ± 0.4 pM, $n = 70$; Mason et al., 2000) and measurements in coastal North Carolina (1.1 ± 0.1 pM, $n = 76$; Kieber et al., 2008). Long-term measurements on the coast of California have found a VWM of 0.5 pM for MeHg in rain (Conaway et al., 2010; Weiss-Penzias et al., 2015). However, other open-ocean measurements have generally found lower MeHg concentrations. Mason et al. (1992) found that MeHg concentrations were below the detection limit of 0.05 pM in the equatorial Pacific Ocean. Similarly, Lamborg et al. (1999) measured concentrations of < 0.1 pM in the equatorial Atlantic.

3.2.2 *Mercury in Aerosols*

Measured concentrations of Hg in atmospheric aerosols collected during the GP16 South Pacific cruise (Fig. 6a) were greatest in the eastern South Pacific closer to South America and low further offshore. Low concentrations were also found during an earlier equatorial Pacific Ocean cruise (2.6 ± 1.9 pg m⁻³ $n = 10$; Mason et al., 1992). Our measurements of Hg in aerosols during the North Atlantic GA03 cruise were elevated compared to the South Pacific and ranged from <1 to 13 pg m⁻³ (Fig. 6c), of similar magnitude and range to previous measurements (Lamborg et al., 1999). In the North Atlantic during GA03, aerosol Hg concentrations were greatest near continents, and in particular the eastern North Atlantic where aerosol inputs from West Africa dominate. The primary reason for these higher Hg concentrations in this region was the high aerosol mass; e.g. in the region indicated as Saharan-influenced in Fig. 6, concentrations of iron (Fe) and aluminum (Al) were >500 ng m⁻³, while they were typically <10 ng m⁻³ for the remote open ocean (Shelley et al., 2015). Thus, while Fe and Al aerosol concentrations varied by almost four orders of magnitude during the North Atlantic GA03 cruises, the Hg concentrations varied by less than two orders of magnitude, because of the relatively low Hg content in dust aerosols (Fig. 6c). Based on the metal concentrations and air mass back trajectory analysis, the samples were clustered into groups according to the likely sources regions: North America, Europe, Marine or Saharan dust (Fig. 6d; Shelley et al., 2015).

It is therefore interesting to consider the source of Hg in aerosols collected in the relatively remote environment of the eastern and central South Pacific compared to that of the North Atlantic. Given the low Hg concentrations in aerosols, it is tempting to conclude that the concentrations represent background values. However, comparison of Hg concentrations with measurements of Al (A. Aguilar-Islas, pers. comm.) in aerosols, a crustal element whose atmospheric concentration has only a minor anthropogenic component, we conclude that the Hg is not primarily of crustal origin. The mass ratio for Hg/Al in crust is $\sim 7 \times 10^{-8}$ (Rudnick and Gao, 2003) and the Hg/Al ratios in aerosols are clearly elevated above this value even for the South Pacific (Fig. 6b), where they were up to 50 times greater than the crustal value. The lowest aerosol Hg/Al ratios were close to the continent suggesting that anthropogenic inputs are impacting the central Pacific Ocean relatively more, which seems reasonable given that an important anthropogenic source is likely Asian emissions (Soerensen et al., 2010). Alternatively, higher crustal input closer to the coast could be diluting the anthropogenic signal there.

Over the North Atlantic, Hg/Al ratios in aerosols during GA03 were more than 100 times greater than the crustal ratio (Fig. 6d), indicating substantial anthropogenic influence for this ocean, as has been found for other metals. Many anthropogenic elements (e.g., Pb, As, Zn, Ag) have similarly high enrichment ratios (>100) for the North Atlantic (Chester, 2003; Shelley et al., 2015). Greater Hg/Al ratios were found in aerosols closer to North America and Europe, with the lowest ratios in the eastern North Atlantic off of West Africa (Fig. 6d; Shelley et al., 2015). The locations off of West Africa with the highest aerosol Hg concentrations had the lowest enrichment factors, supporting the notion that atmospheric inputs are likely dominated by Saharan dust particles. Indeed, there was strong evidence for a dust event (high particulate mass) in this location during the cruise

Aerosol Hg also was likely derived from different source regions in the South Pacific. The lowest Hg/Al ratios were found closer to the continent, suggesting dust input to the boundary layer air in the region occupied during the cruise. The highest Hg/Al ratios were found in aerosols further south within the trade winds and likely represent inputs from more southern countries in South America (Peru, Bolivia and Chile) in addition to emissions from Asia. The data are however insufficient to gain further insights into sources of anthropogenic particulate Hg into the atmosphere in this region.

3.2.3 *Atmospheric Mercury*

The concentration of total gaseous mercury (TGHg) in the marine boundary layer, predominantly Hg^0 (Laurier et al., 2003), increased with longitude during the Pacific GP16 cruise (Fig. 7). In Region 1, the average concentration of TGHg was $1.41 \pm 0.06 \text{ ng m}^{-3}$ and increased to $1.54 \pm 0.04 \text{ ng m}^{-3}$ in Region 2. The highest concentrations were measured in Region 3, where TGHg averaged $1.64 \pm 0.11 \text{ ng m}^{-3}$. Among all GP16 measurements, TGHg averaged $1.53 \pm 0.11 \text{ ng m}^{-3}$. Variability of TGHg concentration was highest in Region 3 (6.5% relative standard deviation, RSD) and lowest in Region 2 (RSD = 2.8%). Overall, there was a significant increasing trend in concentration with longitude ($r^2 = 0.65$; $p < 0.01$; $n = 34$).

The higher atmospheric TGHg concentrations in Region 3 likely reflect the impact of increased evasion of Hg^0 in that area. Model estimates (Soerensen et al., 2010; Strode et al., 2007) suggest that about half the Hg^0 in the boundary layer atmosphere in this region is from gas evasion. We estimated from our measurements above that the evasion in Region 3 is about 5× greater than in Region 1. The average differences in the atmospheric TGHg concentration for Regions 1 and 3 reflects a total difference in inventory of $625 \text{ pmol Hg m}^{-2}$, assuming a 500 m boundary layer thickness. Given the differences in Hg^0 evasion between these two regions, this difference in inventory could be made up in about three days by the enhanced evasion in Region 3, assuming all other sources and sinks are the same. This timescale is comparable with the timescale of the trade wind air mass movement across the region given the measured wind speeds (Fig. 2) and the distance ($\sim 20^\circ$). These calculations suggest that enhanced evasion in Region 3 is the major reason for the higher marine boundary layer Hg^0 concentrations above the ocean in this region.

The concentrations measured during the GP16 cruise were higher than those found in the South Pacific during the Metzyme cruise ($1.15 \pm 0.05 \text{ ng m}^{-3}$) and during an equatorial Pacific cruise in 1990 ($0.93 \pm 0.22 \text{ ng m}^{-3}$; Mason, 1991). Higher concentrations have been found in various studies in the North Pacific, as summarized in Laurier et al. (2007), but there are few data available for the South Pacific Ocean. Additionally, the measured concentrations are somewhat higher than modeled values (Soerensen et al., 2010). As noted above, the higher concentrations found here could reflect the fact that the region is dominated by westerly flowing trade winds and that the air mass TGHg concentration is constantly being enhanced by gas evasion inputs of Hg^0 . In regions of more variable wind direction, the impact of gas evasion on

the boundary layer concentration could be less evident. Modelling studies strongly support the notion that evasion is an important source of Hg^0 to the marine boundary layer in this region (>50%) (Soerensen et al., 2010; Strode et al., 2007). Clearly, more open-ocean air measurements are needed to better understand the sources of Hg^0 in the remote ocean, and the impacts of wind direction and mixing.

3.3 Sources and Mass Balance

3.3.1 South Pacific

In the South Pacific region of the GP16 cruise, deposition of Hg is relatively low given the low rainfall, which is about $5\times$ less than in the Pacific Ocean ITCZ, except in the region of the SPCZ. Given the rainfall depth in this region (<50-200 cm yr^{-1} ; Fig. S1), the annual wet deposition of Hg is estimated to be <20 $\text{nmol m}^{-2} \text{yr}^{-1}$ throughout the area, with deposition as high as 25 $\text{nmol m}^{-2} \text{yr}^{-1}$ in more westerly locations and a lower flux closer to South America. Wet deposition Hg flux estimates for the three regions are based on the measured concentrations in rainfall in Region 3 and the estimated annual average amount of wet deposition for each region (30, 80 and 150 cm yr^{-1} , respectively; Fig. S1; Table 3). The westward increase of wet deposition of Hg in the South Pacific mirrors the increasing DHg^0 concentrations in the surface waters during the cruise (Fig. 4a). Overall, the estimated gas exchange fluxes (up to 140 $\text{nmol Hg m}^{-2} \text{yr}^{-1}$ at the most westerly stations) are substantially greater than wet deposition, except for locations closest to South America where there was net gas deposition on some occasions (Table 3).

Estimates of dry deposition fluxes to the area of the South Pacific Ocean occupied by the U.S. GEOTRACES cruise were made based on the measured concentrations of Hg in aerosols (Fig. 6), averaged for each of the three regions, and the dry deposition velocity, as detailed in the Methods. Dry aerosol deposition fluxes were estimated at <0.5 $\text{nmol Hg m}^{-2} \text{yr}^{-1}$ (Table 3). The relative ratio of wet:dry particulate deposition in the South Pacific is similar to that found in other studies (~10%; Lamborg et al., 1999). No measurements were made of the atmospheric gaseous Hg speciation so the estimate of dry deposition of reactive gaseous mercury (RGHg) was derived based on an established relationship from a number of studies between RGHg and ozone for the marine boundary layer (Laurier and Mason, 2007; Figs. S2 & S3), as detailed in the Methods. Given the relatively high ozone concentration in this area of the Pacific Ocean in

Regions 1 and 2 (>20 ppbv; Conley et al., 2011; Fig. S3), the estimated daily average RGHg concentration is 5 pg m^{-3} . This concentration is comparable to that measured in the North Pacific Ocean when ozone concentrations were above 20 ppbv (Laurier et al., 2003; Fig. S2). For Region 3, the ozone concentration is lower, and for this region a daily average concentration of 10 pg m^{-3} was used. Thus, the total estimated average atmospheric Hg deposition is $9.6 \text{ nmol m}^{-2} \text{ yr}^{-1}$ for Region 1, $14.8 \text{ nmol m}^{-2} \text{ yr}^{-1}$ for Region 2, and $24.4 \text{ nmol m}^{-2} \text{ yr}^{-1}$ for Region 3, with the uncertainties indicated determined by the range in concentrations and the uncertainty in the deposition variables (Table 3). These inputs are a varying fraction of the estimated average gas evasion in these regions; respectively, 13, 18 and $64 \text{ nmol m}^{-2} \text{ yr}^{-1}$. Based on these estimates, deposition therefore accounts for, respectively, 74%, 82% and 38% of the evasional flux in the three regions.

3.3.2 North Atlantic

The data presented above for gas evasion and wet and dry deposition can be used to calculate net deposition to the Atlantic for three regions defined based on the Hg/Al ratios in Fig. 6d: the western Atlantic (west of 55°W), which is impacted by North American and Saharan inputs; the central Atlantic (east of 55°W and south of 25°N), which receives marine-sourced and dust inputs; and the eastern Atlantic which is impacted by European inputs (east of 30°W and north of 25°N). Based on the measurements reported here and the literature (Gichuki et al., 2014; Lamborg et al., 1999; Bowman et al., 2015; Soerensen et al., 2013), estimates for deposition and evasion for these regions were generated with the same approach as described above for the South Pacific (Table 3). Precipitation amounts were taken from Fig. S1 and dry deposition of RGHg was derived based on the observation that surface ozone concentrations in these regions are >25 ppbv on average (Boylan et al., 2015; Fig. S4). Overall, as has been suggested by others (Gichuki and Mason, 2014; Soerensen et al., 2010), the atmospheric inputs account for 66% and 78% of evasion in the western and central Atlantic, respectively, and thus these regions are a net source of Hg to the atmosphere. The eastern Atlantic region is within balance in terms of atmospheric inputs and outputs, given the uncertainties in these estimates. Various model results (Soerensen et al., 2010; 2014; Zhang et al., 2012) support these observations. The likely source of Hg supporting the enhanced evasion in the western and central basin is higher Hg concentrations in the subsurface waters (0.68 ± 0.26 for the upper 200 m, $n =$

155) compared to the eastern region (0.43 ± 0.26 for the top 200 m, $n = 14$; Bowman et al., 2015). Additionally, inputs from North American rivers and inputs with the Gulf Stream could also be contributing Hg to the western North Atlantic (Amos et al., 2014).

Gichuki and Mason (2014) made similar estimates for the North Atlantic near Bermuda and also concluded that there was net evasion of Hg^0 and that deposition accounted for roughly a third of the evasional flux from surface waters. They suggested that the net evasion was a consequence of the legacy elevated deposition of Hg to the North Atlantic due to earlier higher anthropogenic inputs from North America and Europe, reflected in elevated subsurface concentrations (above 1000 m; Mason et al., 2012). Inputs from vertical mixing of these waters would lead to enhanced evasion. The authors noted that this conclusion was consistent with the model results of such a scenario (Soerensen et al., 2012). However, the analysis by Lamborg et al. (2014) suggests that the amount of anthropogenic Hg in the North Atlantic is not sufficient to provide enough additional evasion to support the current flux.

These authors also suggest that there is not a substantial anthropogenic burden in the South Pacific. In Region 1 of the South Pacific, upwelling is likely the source of the additional Hg evaded to the atmosphere. Soerensen et al. (2010) estimated that Hg inputs to surface water from Ekman pumping is $60\text{--}70 \text{ nmol m}^{-2} \text{ yr}^{-1}$ closer to South America, decreasing to $20\text{--}60 \text{ nmol m}^{-2} \text{ yr}^{-1}$ by 80°W , with further decreased inputs from depth until in the central regions there is zero net input or even net export of Hg from surface to deeper waters (Fig. S5). The modeled estimated upwelling flux of Soerensen et al. (2010) near South America is at the low end of the range of Hg upwelling estimates based on measurements during GP16 (Bowman et al., 2016). Both estimates support the notion that upwelling is contributing Hg and DHg^0 to Region 1, but may not account for the discrepancies between evasion and deposition in the more central South Pacific (Region 3).

The Soerensen et al. (2010) model predicts a wet plus dry deposition flux of up to $50 \text{ nmol m}^{-2} \text{ yr}^{-1}$ for Region 3 (Fig. S5), and somewhat lower values for the other regions, but the model estimates are 3–5 times greater than the values estimated from oceanographic measurements. In a more recent paper (Soerensen et al., 2014), the model input for locations occupied during the Metzyme cruise in the South Pacific in October ($1\text{--}15^\circ\text{S}$, $150\text{--}175^\circ\text{W}$) was dominated by atmospheric inputs, with an even higher estimated input flux. In contrast, the modeled evasional flux is of similar magnitude in both models, and is overall comparable to the measured values

(Fig. 4b). The Soerensen et al. (2010) model predicts low saturation/undersaturation close to the continent for the South Pacific, with higher concentrations and evasion further west (Fig. S5), as observed during the cruise.

There is an obvious discrepancy between the model estimates of wet and dry deposition to the central South Pacific and those based on the measurements reported here. The rain samples were collected in the latter part of the cruise, all in Region 3, so the concentrations are representative of the region. Therefore, based on our measurements, it appears that the central subtropical South Pacific (Region 3) is a net source of Hg to the atmosphere (i.e., evasion exceeds deposition). While the Peru upwelling system produces a flow of 19 Sv, which equates to an input of around 0.6 Mmol yr⁻¹ of Hg, based on the measured concentrations during GP16 (Bowman et al., 2016), this is likely not supplying Hg for evasion at the western locations. Given the area over which upwelling occurs in this region, this equates to an input of 30-100 nmol m⁻² yr⁻¹, comparable to the more offshore fluxes estimated by Bowman et al. (2016), and likely supports upwelling in Regions 1 and 2. Similarly, Mason et al. (1994) concluded based on modeling that upwelling of water at the equator provided Hg that supported evasion of DHg⁰ in the tropical regions both north and south of the equator.

The source of Hg needed to balance evasion in Region 3 is likely supplied by regional circulation. As noted above, the waters of Region 3 are those of the South Pacific gyre, termed Subtropical Surface Waters. While these waters have higher HgT concentrations than those further east (Bowman et al., 2016), the fraction of the HgT as Hg⁰ was also higher (27% on average) in these waters compared to those of the other regions (e.g. 16% in Region 1). The deeper (>100m) and weaker thermocline in this region (Fielder and Talley, 2006) suggests that there is potentially more input of Hg from deeper waters, and the low nutrients and productivity suggest there would be less particle removal via scavenging. This suggests that as these waters are being advected through the gyre circulation, the relative concentration of Hg⁰ is increasing, and therefore the evasion rate, which could occur if the rate of evasion is overall less than the rate of formation of Hg⁰ in the mixed layer. The net average Hg^{II} reduction rate in the Soerensen et al. (2010) model is 13.4 Mmol yr⁻¹ or 37 nmol m⁻² yr⁻¹, which is higher than the evasion rates estimated for Regions 1 and 2, but lower than that of Region 3. As this region has low productivity, particle scavenging is less of a sink for mixed layer Hg than in more productive easterly regions. This suggests that the scenario of greater water column Hg^{II} reduction than Hg⁰

evasion in the source waters to Region 3 is a reasonable explanation for the higher concentrations and net evasion found in this region.

A similar conclusion of net evasion was reached for the Mediterranean Sea, where mass balance modeling also indicates that it is a net source of atmospheric Hg (Rajar et al., 2006). In the Mediterranean Sea, in addition to the anthropogenic Hg legacy, emissions into the deep ocean from geothermal sources are an important source. Regions of net deposition are less well documented. Tseng et al. (2013) estimated that there was net deposition in winter for the South China Sea, and the Sorensen et al. (2010) model indicates that for various oceanic regions there is net deposition at certain times of the year (Fig. S5) with winter being the most likely season in ice-free high latitude waters due to the colder temperatures.

3.3.3 Conclusion

Overall, results from our high resolution measurements and detailed profiling of the ocean have improved our understanding of the exchange of Hg at the air-sea interface and have highlighted the fact that different regions of the ocean may be either a net source or sink for atmospheric Hg. In the locations examined here, we proposed that the South Pacific is a net source of Hg to the atmosphere with the likely balancing Hg input in the eastern regions being the upwelling of waters off the coast of South America. In contrast, while the western North Atlantic is also a region of net evasion, in this instance it is possible that the source of Hg to balance the net evasion is the higher concentrations of Hg in the subsurface waters of the region, which are the legacy of past historical inputs of Hg to the North Atlantic from anthropogenic sources (Lamborg et al., 2014). The importance of legacy Hg inputs versus other sources however needs further examination.

While global Hg models simulate to a reasonable degree the distributions and fluxes derived from high resolution measurements, it is likely that the continual gathering of such data will lead to further refinements in model formulations and their predictability, which is essential for their usefulness in predicting further changes and trends in Hg concentrations and speciation in ocean waters, and subsequently the levels of MeHg in the marine organisms consumed by humans and wildlife, so that accurate future exposure predictions are possible.

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Figures

Figure 1: a) Cruise track of the U.S. GEOTRACES GP16 cruise in 2013 in the Southeastern tropical Pacific Ocean; and b) the cruise track for the two legs of the GEOTRACES GA03 cruise in the North Atlantic in 2010 and 2011. Figures from Bowman et al. (2016) *Marine Chemistry* 186: 156-166 and Bowman et al. (2015) *Deep Sea Research II* 116: 251-261, and used with permission of Elsevier. *Numbers on the cruise tracks represent locations where full water column profiles were collected for GEOTRACES parameters, including mercury speciation. The North Atlantic 2010 cruise covered the region from Lisbon to the Cape Verde islands, while the remainder was completed on the 2011 cruise from Woods Hole.*

a)

b)

Figure 2: Ancillary parameters measured in surface waters in conjunction with underway mercury sampling during the U.S. GEOTRACES eastern Pacific GEOTRACES GP16 cruise: a) temperature ($^{\circ}\text{C}$) and salinity; and b) wind speed (m s^{-1}) and in situ fluorescence (relative units). Dotted lines in a) depict the different regions discussed in the text.

Figure 3: Ancillary parameters measured in surface waters in conjunction with mercury sampling during the U.S. GEOTRACES North Atlantic GEOTRACES GA03 cruise: temperature ($^{\circ}\text{C}$) and salinity from a) the zonal transect from Woods Hole to West Africa as shown in Figure 1b and b) the meridional transect off Europe and West Africa; and wind speed (m s^{-1}) and in situ fluorescence (relative units) for c) the zonal transect; and d) the meridional transect.

Figure 4: Underway measurements of dissolved elemental mercury in surface waters during the Pacific U.S. GEOTRACES GP16 cruise: a) dissolved gaseous mercury concentration (fM); b) percent saturation of elemental mercury; and c) estimated gas exchange flux ($\text{pmol m}^{-2} \text{d}^{-1}$; positive values represent flux to the atmosphere). Dotted lines in a) delineate the three regions discussed in the text, while in b) the line indicates 100% saturation (equilibrium with the atmosphere) and in c) represents zero flux.

a)

b)

c)

Figure 5: Relationships between dissolved Hg^0 on the Pacific GEOTRACES GP16 cruise and a) temperature ($^{\circ}C$); b) salinity, and c) fluorescence in each of the three regions occupied during the cruise; Region 1= open circles, Region 2 =grey squares, and Region 3 = black diamonds.

Figure 6: Atmospheric aerosol concentrations of total Hg (THg) (pg m^{-3}) and relative mass ratios of Hg to aluminum (Al) for the US GEOTRACES cruises: a) concentration and b) Hg/Al for GP16; and c) concentration and d) Hg/Al for GA03. Areas highlighted in dotted ellipses in d) represent the different source regions for the aerosols to the North Atlantic as determined based on HYSPLIT back trajectory analysis of the air masses at the time of sampling. The molar ratio of Hg/Al is 7×10^{-8} on a mass basis and is equivalent to the smallest symbols in the figures b) and d).

Figure 7: Daily average concentration of total gaseous mercury in the atmosphere above the ocean (ng m^{-3}) measured during the GP16 cruise in the South Pacific. The regression line for the correlation between concentration and longitude is shown. Error bars represent standard deviations when more than two samples were collected within a day.

Table 1: Measured dissolved elemental mercury concentrations (fM) and associated fluxes (pmol m⁻² d⁻¹) for various recent studies in the lower latitude (<40°) Atlantic and Pacific Oceans

Location	Year	Lat -Long	DHg⁰ (fM)	Flux (pmol/m⁻²d⁻¹)	Ref.
N.W. Atlantic	2008	30-35°N, 60-65°W	128 ± 20	360 ± 348	Soerensen et al. (2013)
N.W. Atlantic	2009	25-35°N, 60-65°W	111 ± 14	250 ± 84	Soerensen et al. (2013)
N.W. Atlantic	2010-11	>25°N, 40-70°W	59 ± 37	147 ± 187	Bowman et al. (2015)*
N.E. Atlantic	2008	15-35°N, 10-20°W	50 ± 10	125	Kuss et al. (2011)
N.E. Atlantic	2010-11	>15°N, 9-40°W	47 ± 30	71 ± 80	Bowman et al. (2015)*
Atlantic ITCZ	2008	0-15°N, 10-20°W	140 ± 55	300	Kuss et al. (2011)
S.E. Atlantic	2008	0-15°S, 0-10°W	35 ± 15	30	Kuss et al. (2011)
S.E. Atlantic	2008	15-30°S, 0-10°E	20 ± 5	15	Kuss et al. (2011)
N.E. Pacific	2011	14-20°N, ~155°W	51 ± 4	170 ± 25	Soerensen et al. (2014)
Pacific ITCZ	2011	5-14°N, 155-160°W	105 ± 20	385 ± 265	Soerensen et al. (2014)
Eq. Pacific	2011	1°S-5°N, 155-160°W	53 ± 10	85 ± 50	Soerensen et al. (2014)
S. Pacific	2011	>1°S, >160°W	47 ± 13	95 ± 50	Soerensen et al. (2014)
S. Pacific	2013	10-13°S, >128°W	46 ± 13	175 ± 95	South Pacific, Region 3
S. Pacific	2013	10-13°S, 102-128°W	31 ± 4	50 ± 30	South Pacific, Region 2
S. Pacific	2013	10-13°S, 75-102°W	33 ± 5	35 ± 35	South Pacific, Region 1

Notes: * Fluxes were estimated as part of this study and were not calculated by Bowman et al. (2015)

Table 2: Concentrations of dissolved elemental mercury (DHg^0 , fM), fraction of the total as DHg^0 , the percent saturation and the estimated gas exchange flux for the discreet samples collected in the North Atlantic during the GEOTRACES G03 cruise. The concentration data were taken from Bowman et al. (2015) and used to calculate the additional information in the table. N=number of samples.

Location	n	DHg^0 (fM)	$\%DHg^0/Hg_T$	% Saturation	Flux ($\text{pmol m}^{-2} \text{d}^{-1}$)
Eastern North Atlantic	10	47 ± 30	18 ± 10	210 ± 130	71 ± 80
Western North Atlantic	12	59 ± 37	14 ± 10	245 ± 150	147 ± 187

Table 3: Mass balance estimates of annual air-sea exchange fluxes for various regions in the South Pacific and North Atlantic Oceans. Flux estimates are in units of $\text{nmol m}^{-2} \text{yr}^{-1}$. Values in brackets give the range in uncertainty in these estimates based on variations in the measured concentrations (one standard deviation) and the uncertainty in the values used for the flux calculations, and the range in values is reflective of the combined standard error.

Region	Gas Exchange ($\text{nmol m}^{-2} \text{yr}^{-1}$)	Wet Deposition ($\text{nmol m}^{-2} \text{yr}^{-1}$)	Particulate Deposition ($\text{nmol m}^{-2} \text{yr}^{-1}$)	RGHg Deposition ($\text{nmol m}^{-2} \text{yr}^{-1}$)
<i>South Pacific</i> 75-102°W	13 (2-20)	3.3 (1.6-5.2)	0.38 (0.2-0.6)	5.9 (3-8)
102-128°W	18 (7-29)	8.8 (4.4-13.2)	0.14 (0.05-0.3)	5.9 (3-8)
>128°W	64 (30-100)	16.5 (8.4-25)	0.09 (0.04-0.15)	7.9 (6-12)
<i>North Atlantic (<40 °N)</i> >55 °W	90 (40-150)	54 (36-81)	2.4 (1.2-4.8)	4* (2-8)
30-55 °W	46 (25-70)	30 (20-45)	2.0 (0.4-5.0)	4* (2-8)
<30 °W	40 (20-60)	30 (20-45)	3.9 (1.6-9.8)	4* (4-8)

Notes: * Values estimated by Gichuki and Mason (2014)