Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16)

Katlin L. Bowman^{a*†}, Chad R. Hammerschmidt^a, Carl H. Lamborg^{b†}, Gretchen J. Swarr^b, Alison M. Agather^a

^aDepartment of Earth & Environmental Sciences, Wright State University, Dayton, OH, 45435, United States

^bMarine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, 02543, United States

*Corresponding author

E: klbowman@ucsc.edu

T: 330-261-1039

[†]Present address:

A415 Earth & Marine Sciences

University of California

1156 High Street

Santa Cruz, CA 95064

Email: chad.hammerschmidt@wright.edu (C.R. Hammerschmidt), clamborg@ucsc.edu (C.H. Lamborg), gswarr@whoi.edu (G.J. Swarr), agather.2@wright.edu (A.M. Agather)

Abstract

Monomethylmercury is a neurotoxin formed in the ocean that accumulates in fish. To better understand the chemical cycling of mercury (Hg) in the ocean, multiple Hg species were measured during the 2013 U.S. GEOTRACES section in the eastern tropical South Pacific Ocean (GP16) from Peru to Tahiti. Total Hg (HgT), elemental Hg (Hg⁰), monomethyl-Hg (MMHg), and dimethyl-Hg (DMHg) were measured in high resolution across the section, which included productive surface waters in the Peru upwelling region, a suboxic oxygen minimum zone (OMZ), and an expansive hydrothermal vent plume from the East Pacific Rise (EPR). Filtered HgT accumulated in upwelled waters near the coast of Peru where oxygen concentrations were the lowest, and MMHg represented 10–20% of the total Hg upwelling flux. The buoyant hydrothermal plume was not enriched with Hg; however, water below 2500 m had anomalously high concentrations of filtered HgT beneath the plume and in warmer bottom waters in the eastern part of the section. Elemental Hg represented <10% of HgT in the water column and concentrations were greatest near the Peru margin. Concentrations of MMHg and DMHg were greatest in low-oxygen thermocline waters, and in the upwelling region, vertical maxima of MMHg were found at the top, core, and bottom of the suboxic OMZ. The MMHg:DMHg molar ratio was variable throughout the upper water column, however, DMHg was the dominant form of methylated Hg in deep water masses. This section is the first examination of Hg speciation and distributions near the Peru coast, a region that supports a highly productive fishery and a potential source of MMHg to consumers of seafood.

1. Introduction

Biogeochemical cycling of mercury (Hg) in the ocean is controlled by abiotic and biotic processes that occur in the water column. Mercury can be either reduced to elemental Hg (Hg^0 ; Amyot et al., 1997; Costa and Liss, 1999; Mason et al., 1995), or methylated to dimethyl-Hg ($(\text{CH}_3)_2\text{Hg}$, hereafter DMHg) and monomethyl-Hg (CH_3Hg^+ , hereafter MMHg; Lehnherr et al., 2011; Monperrus et al., 2007; Whalin et al., 2007), the latter of which bioaccumulates and biomagnifies in marine food webs (Choy et al., 2009; Hammerschmidt et al., 2013).

The distribution and biogeochemical cycling of Hg in the ocean has important implications for human health. Humans are exposed to Hg primarily as MMHg, through the consumption of marine fish (Sunderland, 2007; Višnjevec et al., 2014). Fish is an important source of omega-3 fatty acids that support brain development and protect against cardiovascular disease; however, frequent consumption of fish containing elevated concentrations of MMHg has been linked to neurological and cardiovascular impairments in adults (Auger et al., 2005; Mergler et al., 2007; Stern, 2005; Yokoo et al., 2003; Zahir et al., 2005). Mercury exposure to children in utero is of particular concern as studies have linked elevated levels of MMHg in maternal cord blood to decreased neurological development and cognitive performance later in life (Bose-O'Reilly et al., 2010; Karagas et al., 2012; Oken et al., 2008).

Methylation of inorganic Hg has been linked to low-oxygen regions of the water column in multiple ocean basins (Bowman et al., 2015; Hammerschmidt and Bowman, 2012; Kirk et al., 2008; Lehnherr et al., 2011; Mason et al., 2012; Munson et al., 2015), however, the mechanistic underpinnings of this association are not well understood. The Peru upwelling region is home to persistent and very low oxygen conditions ($2\text{--}10\ \mu\text{M O}_2$; Codispoti et al., 2005) but has not been previously studied for MMHg and DMHg. Low-oxygen regions, such as those found near the

Peru coast, are increasing in size and intensity as ocean surface temperatures rise (Capone and Hutchins, 2013). Therefore, it is necessary to examine the behavior of MMHg and DMHg in the Peru upwelling region to understand how mercury biogeochemistry will change in a warming climate.

To better understand the distribution and cycling of Hg in the Pacific Ocean, we measured concentrations of total Hg (HgT) and MMHg in suspended particles and filtered seawater, and dissolved gaseous Hg⁰ and DMHg in high resolution vertical profiles at 35 stations during October–December 2013 as part of the U.S. GEOTRACES section of the eastern South Pacific (GP16, Fig. 1). The cruise traversed ~8000 km from Peru to Tahiti and included sampling of water from the Peru continental margin and oxygen minimum zone (OMZ; Fig. 2), and a large buoyant hydrothermal plume spreading west from the East Pacific Rise (EPR).

2. Methods

2.1. Sample collection

Filtered water and suspended particles were collected and analyzed with vetted trace-metal clean techniques (Bishop et al., 2012; Hammerschmidt et al., 2011; Lamborg et al., 2012), similar to those described previously for the U.S. GEOTRACES North Atlantic sections (Bowman et al., 2015). Surface water samples (~2 m depth) were collected using a trace-metal clean “towed fish” pumping system described by Bruland and colleagues (2005). Seawater was sampled at 18 full-depth stations (36 water depths at each station), four stations on the South American margin (6–23 depths per station), and 13 upper water column stations (12 depths <1000 m) with 12-L Teflon-coated Go-Flo bottles deployed from a trace-metal clean rosette (Cutter and Bruland, 2012). Go-Flo bottles containing seawater were transferred from the rosette

to a clean laboratory van where seawater was filtered through pre-rinsed capsules (0.2 µm, Pall AcroPak-200) and silicone tubing into 2-L Teflon bottles for determination of Hg⁰, DMHg, and MMHg, and 0.25-L borosilicate glass bottles for measurement of HgT. All sample bottles were cleaned rigorously with acid prior to use (Hammerschmidt et al., 2011). Filtered seawater was transferred from Go-Flo bottles to the bottom of sample bottles with tubing so as to not degas volatile Hg species (Bowman and Hammerschmidt, 2011).

McLane *in situ* pumps (Bishop et al., 2012) were used to sample suspended particles (1–51 µm) onto quartz fiber filters from the 18 full-depth stations (16 pumping depths each) and four stations on the continental margin (5–8 depths). Quartz fiber filters were subsampled into 25-mm diameter punches (representing 25–100 L of seawater each) that were frozen and transported to Wright State University for analysis of particulate MMHg and HgT. Aerosols were collected using a high-volume aerosol sampler and 47 mm diameter Whatman 41 filter discs as described by Shelley and colleagues (2015). Whatman filter subsamples representing ~200 m³ of air were frozen and transported to Woods Hole Oceanographic Institution for analysis of HgT.

Air-sea exchange of Hg was determined from measurements of total gaseous Hg (TGM) in ambient air and dissolved gaseous Hg (DGM) in surface water (Andersson et al., 2008a). Total Hg in air was measured using a Tekran 2537 automated ambient air analyzer with a sampling inlet placed on the bridge of the ship, approximately 20 m above sea level. Dissolved gaseous Hg in surface water was determined using a continuous equilibrium system; incoming surface water from the ship's bow inlet source was equilibrated with a stream of argon gas, Hg was measured by a Tekran 2537, and DGM calculated as:

$$DGM = Hg_{eq}/k_H$$

where Hg_{eq} is the Hg concentration in the out-going gas stream and k_H is the dimensionless Henry's law constant for elemental Hg at a given temperature and salinity (Andersson et al., 2008b). The air-sea flux of Hg was determined as:

$$Hg_{flux} = k \times (DGM - TGM / k_H)$$

where k is the gas-transfer velocity described in Andersson et al., 2008.

2.2. Mercury analysis

Mercury species in filtered seawater were analyzed on board the research vessel in a dedicated laboratory van under clean conditions. Gaseous Hg^0 and DMHg were determined within 2 h of sampling from 2-L water samples with a purge-and-trap method (Bowman and Hammerschmidt, 2011). Samples were purged with Hg-free N_2 (30 L total at 0.4 L min^{-1}), and effluent gas from the bottle was first passed through reagent-grade soda lime to help remove water vapor and aerosols. Dimethylmercury was concentrated on Bond Elut resin (Agilent; Baya et al., 2013) and Hg^0 on a Au-trap downstream of the Bond Elut (Lamborg et al., 2012; Tseng et al., 2004a). Dimethylmercury was quantified by gas-chromatographic cold vapor atomic fluorescence spectrometry (GC-CVAFS; Bowman and Hammerschmidt, 2011; Tseng et al., 2004b) and Hg^0 by dual Au-amalgamation CVAFS (Bloom and Fitzgerald, 1988) following thermal desorption from the traps. Each Au-trap was calibrated at every station after loading with a known amount of Hg^0 . Procedural precision of Hg^0 determinations averaged 20 ± 15 relative percent difference (RPD; $n = 27$ pairs). Bond Elut traps for DMHg analysis were calibrated every 2–3 stations with known additions of methylethylmercury, a volatile derivative of MMHg. Procedural precision of DMHg analyses averaged 27 ± 20 RPD ($n = 17$). Method detection limits were 0.01 pM for Hg^0 and 0.002 pM for DMHg. Bond Elut traps were replaced frequently (after 12–24 uses) when deterioration of the resin became visually apparent. Continued use of

deteriorating Bond Elut results in poor trapping efficiency and the generation of a vapor residue that can coat the fluorescence cuvette, reducing analytical sensitivity. Bond Elut was not a good alternative to Tenax for MMHg determination in seawater. Organic compounds derivatized from seawater by NaTEB with a similar volatility to methylethylmercury were collected on Bond Elut and interfered with the MMHg chromatographic peak.

Seawater purged of DMHg and Hg^0 was transferred to a 2-L polycarbonate bottle for MMHg analysis. Samples were acidified to 1% with trace-metal grade H_2SO_4 for 12–24 h, then neutralized with 12 M KOH, adjusted to pH 5 with 4 M acetate buffer, amended with ascorbic acid (to 0.3 mM), and derivatized with sodium tetraethylborate (NaTEB; Bowman and Hammerschmidt, 2011; Munson et al., 2014). Derivatized samples were purged with Hg-free air (30 L total at 0.8 L min^{-1}) to transfer volatile methylethylmercury from solution onto Tenax resin after the effluent gas stream passed through reagent-grade soda lime. Monomethylmercury (as methylethylmercury) was quantified by GC-CVAFS (Bowman and Hammerschmidt, 2011; Tseng et al., 2004b). Individual Tenax traps were calibrated every 2–3 stations with aliquots of an aqueous CH_3HgCl standard (prepared in reagent-grade water) that was calibrated versus TORT-2 reference material (lobster hepatopancreas, National Research Council of Canada). Recovery of known additions of MMHg from seawater averaged $84 \pm 12\%$ ($n = 3$) and procedural precision averaged 35 ± 22 RPD ($n = 6$). Method detection limit for MMHg was 0.02 pM.

Total Hg was measured in 0.25-L seawater samples within 48 h of sampling after oxidation with BrCl , SnCl_2 reduction, purging with Hg-free N_2 , and dual Au-amalgamation CVAFS detection, similar to U.S. EPA method 1631E (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979). Total Hg in seawater was calibrated against aqueous Hg(II) standards traceable

to the U.S. National Institute of Standards and Technology. Procedural precision averaged 7 ± 9 RPD ($n = 29$) and the method detection limit for HgT was 0.03 pM.

Mercury in suspended particles was leached from filter punches with high-purity 2 M HNO_3 for 4 h in a 60 °C water bath (Bowman et al., 2015; Hammerschmidt and Fitzgerald, 2006). MMHg in the digestate was quantified by flow-injection GC-CVAFS (Tseng et al., 2004b) and analyses were calibrated with procedural standards. The method detection limit for particle-associated MMHg in seawater was 0.002 pM. Recovery of known additions of MMHg from filter punches averaged $98 \pm 20\%$ ($n = 7$) and procedural precision averaged 16 ± 11 RPD ($n = 16$). Separate aliquots of the same digestates were oxidized with BrCl and analyzed for HgT by dual Au-amalgamation CVAFS (Hammerschmidt and Fitzgerald, 2006). Procedural precision averaged 8 ± 8 RPD ($n = 10$) and the method detection limit for particulate HgT was 0.03 pM. Mercury in aerosols was leached from filter punches with high-purity 2 M HNO_3 for 30 min in a 60 °C sonicated water bath (Morton et al., 2013), and analyzed for HgT similar to suspended particles. Procedural precision averaged 3 ± 2 RPD ($n = 3$) and the method detection limit for aerosol HgT was 0.03 pmol/filter.

3. Results

3.1. Physical oceanography of the section

The section covered a large portion of the eastern tropical South Pacific Ocean and included sampling of multiple water masses. Deep and bottom water masses sampled were Lower Circumpolar Deep Water (LCDW), Pacific Deep Water (PDW), and modified PDW (mPDW; Fig. 2). Deep water masses from the Indian, Pacific, and Atlantic Oceans shoal and mix in the Antarctic Circumpolar Current (ACC). This mixture of deep water masses, referred to as

Circumpolar Deep Water (CDW), is ventilated and downwelled during convergence between the ACC and the Subantarctic Front, and spreads north into the Pacific Ocean (Kawabe and Fujio, 2010; Rintoul et al., 1999; Talley et al., 2011). Density stratification divides CDW into two layers: 1) a deeper layer of LCDW that has greater dissolved oxygen due to entrainment of North Atlantic Deep Water (NADW), and 2) an upper layer (Upper Circumpolar Deep Water; UCDW) composed of Indian Deep Water and PDW (Talley et al., 2011). LCDW was at depths >4000 m at stations west of the East Pacific Rise. UCDW flows into the Pacific basin and becomes PDW through internal upwelling and diffusion. PDW was the dominant water mass at most stations between 2000 and 4000 m depth. In the North Pacific, deep upwelling of LCDW mixes it with North Pacific Deep Water (NPDW) to form mPDW that flows south through the basin and along the coast of South America (Kawabe and Fujio, 2010). Modified PDW ($[\text{Si}] = 150 \mu\text{mol kg}^{-1}$) was between 2000–4000 m near South America, and at depths greater than 3500 m between 99–110° W (Fig.2). A tongue of high silicate ($>145 \mu\text{mol kg}^{-1}$) deep water, indicative of mPDW, has been previously reported between 99–110° W in the South Pacific (WOCE transect P18; Talley et al., 2007). Concentrations of silicate and dissolved oxygen suggest that LCDW is the youngest deep water mass followed in increasing age by PDW and mPDW (DeVries and Primeau, 2011; Gebbie and Huybers, 2012; Kawabe and Fujio, 2010).

Antarctic Intermediate Water (AAIW) forms north of the Subantarctic Front in the southeast Pacific and was identified between 700 and 1000 m depth across the section (Rintoul et al., 1999). Water between 1000–2000 m was too saline to be AAIW and too dilute to be classified as PDW and is here considered a mixture of the two water masses (AAIW/PDW; Fig. 2a). Surface waters included South Pacific Subtropical Mode Water overlying Subantarctic Mode Water (Talley et al., 2011). El Niño Southern Oscillation conditions were neutral during the

sampling period (NOAA, 2014), and normal wind-driven coastal upwelling was encountered. Oxygen concentrations approached zero in the thermocline underlying productive surface water between 100° W and the Peru margin (St.1–13; Fig. 2).

3.2. Total Hg

Filtered HgT had a nutrient-like vertical distribution due to scavenging at the surface, remineralization in low-oxygen thermocline waters, and accumulation in deep water (Fig. 3a). At all stations and depths, filtered HgT concentrations averaged 0.78 ± 0.41 pM ($n = 754$) excluding elevated concentrations at Station 5 near the Peru margin (3.0–4.1 pM, $n = 3$), and suspended particulate HgT averaged 0.075 ± 0.094 pM ($n = 337$; Supplementary Information). The range of filtered HgT concentrations measured across this entire section (0.070–2.9 pM) agree well with measurements in the North and Central Pacific Ocean (Hammerschmidt and Bowman, 2012; Laurier et al., 2004; Munson et al., 2015; Sunderland et al., 2009).

Wind-driven upwelling near Peru resulted in increased concentrations of HgT in surface and thermocline waters. Filtered HgT in surface water (2 m) was < 0.2 pM across most of the section; however, concentrations were up to $3\times$ greater and averaged 0.39 ± 0.12 pM ($n = 5$) between 80° W (Station 6) and the Peru margin, despite greater biological productivity and scavenging near Peru. Concentrations of HgT in surface water of the upwelling region are modest compared to surface waters that receive inputs from localized sources (4.4 pM in Japanese coastal waters; Laurier et al., 2004) and Saharan dust (2–4.5 pM, 0–23° N, eastern Atlantic; Pohl et al., 2011). Mercury scavenged at the surface is released from sinking particles during organic matter remineralization, and there was a strong inverse correlation between concentrations of dissolved oxygen and filtered HgT in the upper 20–1000 m among all stations ($r = -0.60$, $p < 0.0001$).

Upwelling fluxes of HgT to the mixed layer were calculated for stations from the Peru margin to Station 11 based on concentrations near the bottom of the mixed layer (5–56 m depth) and an upwelling rate derived from ^7Be inventories ($w_H = 2.39 \text{ m d}^{-1}$; Kadko, Unpublished results). Upwelling fluxes of HgT decreased moving away from the coast and ranged from 70 to $2,200 \text{ pmol m}^{-2} \text{ d}^{-1}$. These fluxes are comparable to equatorial upwelling fluxes measured in the central Pacific ($400\text{--}820 \text{ pmol HgT m}^{-2} \text{ d}^{-1}$; Mason and Fitzgerald, 1993; Munson et al., 2015), and about an order of magnitude greater than that in the Mauritanian upwelling region of the northeastern Atlantic ($24\text{--}27 \text{ pmol HgT m}^{-2} \text{ d}^{-1}$; Bowman et al., 2015; Kadko and Johns, 2011). Depositional fluxes of HgT from the atmosphere to the mixed layer were minimal compared to upwelling. Dry deposition to the upwelling region is estimated to be $0.45\text{--}4.6 \text{ pmol HgT m}^{-2} \text{ d}^{-1}$, based on aerosol Hg measurements made there and assuming a depositional rate of 1.1 cm s^{-1} (Arimoto et al., 1997). Precipitation volumes in the arid upwelling region were insufficient for Hg analysis; however, we estimate that wet deposition of Hg was only about $11 \text{ pmol HgT m}^{-2} \text{ d}^{-1}$ based on a mean measured concentration of $11 \pm 6 \text{ pM}$ ($n = 5$) in rain sampled near Marquesas Islands and assuming an average precipitation rate of 1 mm d^{-1} (RSS, 2016) in the region.

Mercury is removed from the upwelling region by evasion to the atmosphere, bioaccumulation, and sinking particles. Surface waters in the upwelling region were supersaturated with DGM and the evasional flux of Hg to the atmosphere was $77\text{--}108 \text{ pmol HgT m}^{-2} \text{ d}^{-1}$. Removal of Hg (as MMHg) by bioaccumulation ranged from $0.021\text{--}0.15 \text{ pmol MMHg m}^{-2} \text{ d}^{-1}$ based on a bioaccumulation factor for mesotrophic water ($10^{3.5} \text{ L kg}^{-1}$; Driscoll et al., 2012) and net primary production value of $250 \text{ mg C m}^{-2} \text{ d}^{-1}$ (Ocean Productivity, 2015). Total Hg in sinking particles was not measured; however, Munson and colleagues (2015) found an

average export flux of 157 ± 58 pmol HgT m⁻² d⁻¹ from the equatorial upwelling region of the central Pacific Ocean. Estimated inputs of Hg to the mixed layer are greater than removal fluxes, suggesting that Hg is exported from the upwelling region by horizontal advection, equatorward via the Peru-Chile Current and Peru Coastal Current, and poleward via the Peru-Chile Countercurrent and Poleward Undercurrent (Talley et al., 2011).

Eddies propagating from the coast of South America may influence concentrations of filtered HgT in the open-ocean. Long-lived (>3 months) mesoscale eddies form near the coast of South America in the Peru Chile Current System and migrate west towards warmer, more saline water (Chaigneau and Pizarro, 2005). Vertical exchange of tracers such as nutrients, carbon, and heat are typically observed in the mixed layer of eddies but can extend down to 2000 m in the eastern South Pacific (Klein and Lapeyre, 2009). Satellite altimetry data of sea surface height (CCAR, 2016; Supplementary Information) indicated a negative anomaly at Station 9 (12° S, 89° W) suggestive of a cyclonic eddy, and a positive anomaly at Station 13 (14° S, 99° W) suggestive of an anticyclonic eddy (Chaigneau and Pizarro, 2005). Across the entire section, the average concentration of filtered HgT was 0.70 ± 0.33 pM ($n = 255$) in the thermocline (150–1000 m) and 0.75 ± 0.28 pM ($n = 108$) in intermediate waters (1000–2000 m). At Station 13, where there was an anticyclonic eddy, filtered HgT was similar to average thermocline concentrations (0.52 ± 0.10 pM, $n = 12$; $p = 0.057$), but significantly lower in intermediate waters (0.41 ± 0.052 pM, $n = 6$; $p < 0.001$, Kruskal-Wallis One Way ANOVA). Downwelling within the anticyclonic eddy may vertically transport Hg-depleted surface water deeper into the water column.

At Station 9 where there was a cyclonic eddy, filtered HgT was significantly greater in both thermocline (1.3 ± 0.18 pM, $n = 13$) and intermediate waters (1.2 ± 0.10 pM, $n = 5$, $p < 0.001$, Kruskal-Wallis One Way ANOVA) compared to the rest of the section, and greater in

surface water (0.37 pM at 2 m) compared to adjacent stations (0.10 pM at Station 8, 0.12 pM at Station 10). Sanial and colleagues (Unpublished results) observed a ^{228}Ra anomaly at 1000 m at Station 9, indicative of recent (<10 y) contact with sediment. Localized upwelling within the cyclonic eddy may have transported Hg derived from the Peru margin to the open ocean, but interestingly, concentrations of Hg^0 , MMHg, and DMHg were not increased in either thermocline or intermediate waters at Station 9 compared to adjacent stations (Fig.3b-d). Inorganic Hg transported from the margin may have been bound as a complex that inhibited either reduction or methylation. Peru margin sediments are characterized as anoxic and highly sulfidic (Böning et al., 2004), conditions that favor the formation of nanoparticle HgS that, when not stabilized by sufficient dissolved organic matter, can aggregate and become less available for microbial uptake and transformation (Deonarine and Hsu-Kim, 2009; Graham et al., 2012). Concentrations of filtered HgT also were increased near the seafloor at Station 9 (2 pM at 4100 m depth). Disturbance of bottom water from the eddy at Station 9, however, likely did not increase concentrations of filtered HgT . Deep current anomalies below 2500 m have not been reported (Adams et al., 2011; Zhang et al., 2014) and there were no associated increases in either turbidity or particulate HgT in the deepest water samples.

In waters deeper than 2000 m, filtered HgT averaged 1.09 ± 0.29 pM ($n = 228$) and the greatest concentrations were observed in mPDW from the North Pacific (1.25 ± 0.23 pM, $n = 55$). Among deep water masses, LCDW contained the lowest concentrations of filtered HgT (0.96 ± 0.15 pM, $n = 11$), which agrees well with measurements of HgT in CDW sampled in the Southern Ocean (1.19 ± 0.27 pM; Cossa et al., 2011). Average concentrations of HgT in older deep water from the North Pacific range from 1.1 ± 0.3 to 1.7 ± 0.2 pM (Laurier et al., 2004; Hammerschmidt and Bowman, 2011; Munson et al., 2015) and are greater than values for

relatively younger deep water in the South Pacific (0.98 ± 0.14 pM, Munson et al., 2015; 1.09 ± 0.29 pM, this study). Increasing HgT with age in deep water is consistent with the release and accumulation of Hg as biological material sinks and decomposes. This trend is reversed in the Atlantic Ocean where average deep water concentrations are $2\times$ greater in younger water from the North Atlantic (1.1 ± 0.2 pM) compared to older water in the South Atlantic (0.47 ± 0.08 pM), most likely from anthropogenic inputs of Hg to source regions of NADW formation (Lamborg et al., 2014).

Filtered HgT concentrations were not enriched within the buoyant submarine hydrothermal vent plume extending west from the EPR (Stations 18–36; 0.99 ± 0.25 pM, $n = 137$). In contrast to Hg, concentrations of filtered Al, Fe, and Mn were increased in the plume between 2000 and 3000 m depth (Resing et al., 2015). The absence of a Hg enrichment in the EPR plume is both different than a hydrothermal plume in the North Atlantic near the Mid Atlantic Ridge, where filtered HgT was $10\times$ greater than NADW immediately above a vent field (Bowman et al., 2015) and surprising because HgT concentrations up to 11,000 pM have been measured in vent fluids at the EPR in the North Pacific (Crespo-Medina et al., 2009). Total Hg in suspended particles was significantly greater at EPR plume Stations 18 and 20 at depths >2350 m (0.070 ± 0.035 pmol Hg μg^{-1} , $n = 14$), compared to concentrations in deep water at other stations (0.017 ± 0.014 pmol Hg μg^{-1} , $n = 120$; $p < 0.001$, Mann-Whitney Rank Sum Test). Partitioning coefficients for HgT also were greater in deep water at Stations 18 and 20 ($\log K_d = 8 \pm 0.3$, $n = 14$) compared to other locations ($\log K_d = 7 \pm 0.3$, $n = 104$; $p < 0.001$, Mann-Whitney Rank Sum), suggesting that Hg is scavenged from hydrothermal fluids at this particular vent site. It is possible that in some vent fluids, particularly those high in sulfur, HgS precipitates

before ascending into the plume. More measurements of Hg in vents and plumes are needed to determine the significance of hydrothermal activity as a source of Hg to the deep ocean.

3.3. Excess Hg in Pacific deep and bottom waters

Deep water below 2500 m contained greater concentrations of filtered HgT than expected from remineralization alone (Fig. 4a). Lamborg and colleagues (2014) observed a ratio of filtered HgT to remineralized phosphate (P_{remin}) of 1 pmol/ μmol in deep ocean waters unaffected by anthropogenic Hg inputs as a result of Hg and P remineralization from the decomposition of sinking biological material. Models based on radiocarbon measurements estimate that deep water in the southeastern Pacific Ocean is 800–900 y old (DeVries and Primeau, 2011; Gebbie and Huybers, 2012; Khatiwala et al., 2012), therefore, most of the Hg in deep water should be from natural rather than anthropogenic sources, and the Hg: P_{remin} ratio should be ~ 1 pmol/ μmol (Lamborg et al., 2014). Benthic input of Hg in the open-ocean has not been observed previously and it is unlikely that efflux from sediment affects a layer of deep water this thick (1000 m).

At the EPR ridge crest (Station 18), where hydrothermal emissions were not a source of excess Hg (Section 3.2.), the Hg: P_{remin} ratio was 0.95 ± 0.13 pmol/ μmol ($n = 10$) in water > 2500 m and consistent with prior observations of PDW. Similarly, the Hg: P_{remin} ratio was also ~ 1 in the Bauer Basin east of the ERP (Station 15; Fig. 4a). However, Hg: P_{remin} was > 1 pmol/ μmol west of the EPR at depths below the plume (Stations 20–32), suggesting the existence of a source of Hg in addition to organic matter remineralization (Fig. 4a). Dissolution of Hg from larger sinking particles ($> 51 \mu\text{m}$) that were not measured in this study may be a source of Hg below the plume at these stations. Dissolved Fe and Al are modestly elevated below 3000 m in the absence of excess ^3He (Resing et al., 2015); resuspension of hydrothermally enriched sediment from

previous emissions in addition to sinking particles may be a source of metals to deep water beneath the plume.

In the eastern part of the section (Stations 1–17), concentrations of filtered HgT up to 2.5 pM were measured in relatively warm deep water (1.5–1.6 °C) and Hg:P_{remin} ratios were >1 pmol/μmol, with the exception of Station 15 (Fig. 4a-b). East of the EPR in the Peru Basin, bottom water flows north from the South Pacific Basin through the Chile Rise (41° S) and the Peru-Chile Trench, and across the Sala-y-Gomez and Nazca Ridges (25° S; Lonsdale, 1976). Water interaction with these sills intensifies deep vertical mixing in the Peru Basin and transfers heat to bottom water (Lonsdale, 1976). The source of excess Hg relative to P_{remin} in these waters could be from either sediment disturbed during deep vertical mixing or interaction with seamounts located along the Sala-y-Gomez and Nazca Ridges (Lonsdale, 1976; Mikhailik et al., 2012). Filtered Al also was slightly elevated at Stations 1–13 (Resing et al., 2015); however, there are no known active vent sites east of the EPR in the South Pacific (German and Von Damm, 2006).

3.4. Elemental Hg

Elemental Hg accounted for $7 \pm 9\%$ ($n = 727$) of filtered HgT and concentrations averaged 0.045 ± 0.061 pM ($n = 734$). The greatest concentrations of Hg⁰ were near the Peru margin (0.14 ± 0.11 pM, $n = 56$ at Stations 1 & 5) and within the upwelling region (Fig. 3b). Subsurface concentration maxima were observed in the OMZ where microbial processes may reduce Hg during organic matter remineralization (Lehnherr et al., 2011; Monperrus et al., 2007; Whalin et al., 2007). Concentrations of Hg⁰ in the thermocline (150–1000 m) were variable, but on average were 2.5× greater in the eastern suboxic thermocline (0.065 ± 0.075 pM, $n = 116$).

than in the more oxygenated thermocline to the west (Stations 14–36; 0.026 ± 0.036 pM, $n = 146$).

Upwelling fluxes of dissolved gaseous Hg (DGM; $\text{Hg}^0 + \text{DMHg}$) ranged from $0.05\text{--}380$ $\text{pmol m}^{-2} \text{ d}^{-1}$; DGM was not measured at the bottom of the mixed layer at Stations 2 and 3 on the shelf (~ 5 m), therefore upwelling fluxes for these stations are not included. The shallowest depth where both Hg^0 and DMHg were measured on the shelf was at 20 m, where, interestingly, DMHg was 20–50% of DGM. At the base of the mixed layer, DMHg accounted for 11% of DGM on the slope and $\leq 3\%$ in the rest of the upwelling region. Surface waters were supersaturated with DGM in the upwelling region (Mason et al., Unpublished results), indicating evasion of gaseous Hg to the atmosphere: our results suggest that DMHg may be a part of this flux. Upwelling and evasion of DMHg over the shelf may have important implications for the Peruvian coast. In northern California, for example, upwelled DMHg may be transported to the surrounding coastland by fog and decomposed to MMHg by atmospheric oxidants, creating an atmospheric source of MMHg to the local ecosystem (Conaway et al., 2009; Weiss-Penzias et al., 2016).

Negative N^* values suggest there was active denitrification ($\text{N}^* = [\text{NO}_3^-] - 16[\text{PO}_4^{3-}] + 2.95$; Gruber and Sarmiento, 1997) in the suboxic upwelling region where the fraction of HgT as Hg^0 was greatest. Reduction of inorganic Hg by denitrifying bacteria has been observed in culture (Kritee et al., 2008; Schaefer et al., 2002), and Munson and colleagues (2015) found a correlation between denitrification and Hg^0 at a station in the central tropical Pacific Ocean. There was a significant, but weak, negative correlation between N^* and Hg^0 in the upper 1000 m of the water column ($r^2 = 0.27$, $p < 0.001$; Supplementary Information). At some stations vertical maxima of Hg^0 and minima of N^* were found at the same depth; however, coincidence of N^*

and Hg^0 variations was inconsistent among all stations; Munson and colleagues (2015) also found inconsistencies between stations. Coinciding maxima of Hg^0 and nitrite were more commonly found at the secondary nitrite maximum in suboxic water as opposed to the primary nitrite maximum at the top of the OMZ, where the source of nitrite can be both ammonia oxidation and nitrate reduction (Buchwald and Casciotti, 2013).

Concentrations of Hg^0 were low in deep water (0.05 ± 0.06 pM, $n = 271$) and represented $5 \pm 6\%$ of total Hg ($n = 265$). There are few measurements of Hg^0 in the deep ocean; Munson and colleagues (2015) measured higher concentrations in the central South Pacific (0.14 ± 0.04 pM) and we observed concentrations that were an order of magnitude greater in the North Atlantic (0.36 ± 0.16 pM; Bowman et al., 2015). The concentration difference between young deep water in the Atlantic and old deep water in the Pacific could reflect either oxidation of Hg^0 over time or different rates of Hg reduction between the two basins. Indeed, we observed that Hg^0 concentrations differed considerably between relatively younger (0.42 ± 0.09 pM, $42 \pm 8\%$ of total Hg) and older NADW (0.26 ± 0.10 pM, $30 \pm 15\%$ of total Hg) in the western and eastern basins, respectively, of the North Atlantic Ocean (Bowman et al., 2015).

3.5. MMHg and DMHg

Among all stations and depths, the mean concentration of filtered MMHg was 0.07 ± 0.06 pM ($n = 469$) and DMHg averaged 0.07 ± 0.07 pM ($n = 655$); the sum of the two species, total methylated Hg (MeHg_T), represented $19 \pm 16\%$ of Hg_T ($n = 420$), similar to $\%\text{MeHg}_T$ in the Central Pacific and upper water column of the North Pacific (Munson et al., 2015; Sunderland et al., 2009). Concentrations of MMHg in suspended particles averaged 0.71 ± 0.99 fM ($n = 335$; Supplementary Information). Vertical maxima of filtered MMHg and DMHg

concentrations were observed in the OMZ across the entire section. At Stations 14–36, outside of the suboxic zone, vertical profiles had maxima of MMHg and DMHg both within the OMZ and one additional maximum of MMHg near the subsurface chlorophyll maximum (Fig.5). Vertical maxima of MMHg in the euphotic zone have been observed previously in the North Atlantic Ocean (Bowman et al., 2015) and in the Mediterranean Sea (as MeHg_T; Heimbürger et al., 2010). At Stations 1–13, filtered MMHg had a complex vertical distribution with 1 to 3 distinct vertical maxima organized around the suboxic zone: 1) at the top where oxygen concentrations rapidly decreased, 2) within the core where oxygen concentrations approached zero, and 3) at the bottom where vertical mixing with deeper water increased oxygen concentrations (Fig. 5). If these maxima are driven by *in situ* microbial methylation, a broad range of microorganisms may be capable of MMHg production in this region of the ocean. Vertical maxima of DMHg were found at depths similar to those of filtered MMHg at Stations 1–13, and the greatest concentrations were within the core of suboxic waters. At some stations, DMHg maxima were observed to be slightly deeper than that of MMHg near the top of the suboxic zone (Stations 5–8, Fig.5); deeper maxima of DMHg may have resulted from evasion to the atmosphere from shallower waters, or a different methylation pathway (i.e. methylation of MMHg).

Upwelling fluxes of filtered MMHg ranged from 30 to 400 pmol MMHg m⁻² d⁻¹, representing 10–20% of the Hg_T upwelling flux. Similar to Hg_T, MMHg upwelling fluxes were greater than those measured in the Mauritanian upwelling region (5 pmol MMHg m⁻² d⁻¹, $w_H = 0.3 \text{ m d}^{-1}$; Kadko and Johns, 2011) and comparable to the equatorial Pacific (34 pmol MMHg m⁻² d⁻¹, Munson et al., 2015). The suboxic layer resulting from high productivity in the upwelling region (Stations 1–13) was 75–600 m thick and spanned depths in both the upper water column (<150 m) and thermocline (150–1000 m). Average concentrations of MMHg and

DMHg were significantly greater in both the upper water column ($p < 0.001$) and thermocline ($p < 0.001$, Mann-Whitney Rank Sum Test) at stations within the suboxic zone compared to stations further west (Stations 14–36; Table 1). Concentrations of MMHg and DMHg in the upper water column and thermocline at Stations 14–36 compare well with measurements from the Central and North Pacific (Hammerschmidt and Bowman, 2012; Munson et al., 2015).

In thermocline waters elsewhere, such as the central and North Pacific Ocean, Southern Ocean, and Mediterranean Sea, concentrations of MeHg_T are positively correlated with apparent oxygen utilization (AOU), highlighting the importance of heterotrophic microbial activity on Hg methylation (Cossa et al., 2009; Cossa et al., 2011; Munson et al., 2015; Sunderland et al., 2009). The strength of this correlation, however, appears to decrease in ocean basins with less productive surface waters. The strongest correlations between MeHg_T and AOU have been observed in the thermocline beneath productive waters of the Mediterranean Sea ($r^2 = 0.81$, $p < 0.01$; Cossa et al., 2009) and Southern Ocean ($r^2 = 0.72$, $p < 0.001$; Cossa et al., 2011). In the eastern tropical Pacific (this section), the correlation was statistically significant, but weak ($r^2 = 0.23$, $p < 0.001$, 150–1000 m) and similar to that for the central Pacific ($r^2 = 0.49$, $p < 0.001$; Munson et al., 2015). In studies that traversed an oligotrophic gyre, the relationship between MeHg_T and AOU was nonlinear in the North Pacific (Sunderland et al., 2009) and insignificant in the North Atlantic Ocean ($p = 0.075$; Bowman et al., 2015). Either nutrient limitations or different biological communities in less productive regions of the ocean may weaken the correlation between MeHg_T and AOU.

Inorganic Hg can be methylated by some strains of Fe-reducing bacteria (Fleming et al., 2006; Kerin et al., 2006); however, there was no correlation between methylated Hg and either filtered total Fe or Fe(II) (Pete Sedwick and Jim Moffett, personal communication). Mercury

methylation by sulfate-reducing bacteria that methylate Hg via the acetyl-CoA pathway can be inhibited under cobalt-limited conditions (Ekstrom and Morel, 2008). Concentrations of methylated Hg were unrelated to those of either total or labile cobalt (Nick Hawco, personal communication); however, concentrations of Co in this section may not have been limiting where MMHg and DMHg maxima were observed.

On the South America continental margin, MMHg in suspended particles increased near the sediment-water interface (Station 2 and 4), and uniquely, DMHg concentrations were $1.5\text{--}2\times$ greater than those of filtered MMHg (Stations 2–4; Fig. 6). This is different than the continental shelf and slope in the North Atlantic where concentrations of filtered MMHg were greater than those of DMHg near the seafloor (Fitzgerald et al., Unpublished results). Higher concentrations of organic matter in sediment underlying the productive upwelling region may have scavenged MMHg from pore fluids and attenuated its flux to overlying water (Hammerschmidt et al., 2004), while gaseous DMHg would not be affected similarly. On the slope (Station 4), oxygenated bottom water contained concentrations of filtered MMHg and DMHg that were twice as high as bottom water on the shelf. Increased flux from surface sediments due to bioturbation is not likely because concentrations of filtered HgT at the same station on the slope did not increase with proximity to the sediment-water interface. High sulfide concentrations in anoxic sediments inhibit the bioavailability and subsequent methylation of inorganic Hg (Hammerschmidt et al., 2008). Accordingly, sulfide may have resulted in a lower flux of methylated Hg from the suboxic shelf compared to the more oxic slope.

Deep water at Stations 14–36 contained $4\times$ less MeHg_T (0.13 ± 0.097 pM, $n = 77$) than CDW and AABW in the Southern Ocean (Cossa et al., 2011), and $2\times$ less than NADW in the North Atlantic (Bowman et al., 2015); concentrations of MMHg and DMHg were in the same

range as the Central Pacific (Munson et al., 2015) and higher than the North Pacific (Hammerschmidt and Bowman, 2012). Decreasing concentrations of MMHg and DMHg with water mass age may suggest decomposition of methylated Hg with time during thermohaline circulation. However, older deep water at Stations 1–13 in the eastern part of the section contained significantly more MMHg and DMHg compared to younger deep water at Stations 14–36 (Table 1, $p < 0.001$, Mann-Whitney Rank Sum Test) which is inconsistent with this trend. The fraction of HgT as MMHg and DMHg also was greater in the eastern part of the section ($p < 0.001$ for MMHg and DMHg, Mann-Whitney Rank Sum Test), which may be a characteristic of Hg enriched waters associated with warmer deep water (Section 3.3). Greater concentrations of MMHg and DMHg in the entire water column at Stations 1–13 may also be related to increased particle mass from productive surface waters. The mass of suspended particles (1–51 μm size fraction) was 5–10 $\times$ greater in the eastern part of the section (Stations 1–13; Phoebe Lam, personal communication), and laboratory experiments have observed Hg methylation in particle aggregates (8–300 μm) that is thought to be facilitated by anaerobic microbes in low-oxygen regions of the particles (Ortiz et al., 2015).

The MMHg:DMHg molar ratio was variable across the section with a median value of 1.65 in the upper water column (<150 m), 0.91 in the thermocline (150–1000 m), and 1.52 in intermediate waters (1000–2000 m). Concentrations of MMHg were significantly greater than DMHg in the upper water column ($p < 0.001$), but similar in thermocline ($p = 0.84$) and intermediate waters ($p = 0.061$, Mann-Whitney Rank Sum Test). In deep water (>2000 m) the MMHg:DMHg molar ratio was also variable, however, the median ratio was 0.64 and there was a significant difference between MMHg and DMHg concentrations ($p < 0.001$, Mann-Whitney

Rank Sum Test), suggesting that DMHg was the dominant form of methylated Hg in deep water across this section.

4. Conclusions

Mercury speciation and distribution was examined across a large section of the South Pacific Ocean including the Peru upwelling region, a suboxic OMZ, and an expansive submarine hydrothermal vent plume. Total Hg was not enriched in the hydrothermal vent plume, however, excess Hg was found in deep water underlying the plume and in relatively warm bottom water in the eastern part of the transect. In deep water, total Hg accumulated with age and DMHg was the dominant methylated species. Maximum concentrations of Hg⁰, MMHg, and DMHg were found in the suboxic OMZ underlying productive surface waters in the upwelling region. While concentrations of MMHg and DMHg were greatest in the OMZ there was not a strong correlation with apparent oxygen utilization. Regardless, the expansive area of low oxygen water associated with the Peru upwelling region generated input fluxes of filtered HgT that exceeded export fluxes, and up to 20% of the upwelling HgT flux was as MMHg. The growing size and intensity of upwelling regions predicted for this coming century (Capone and Hutchins, 2013) will likely increase the flux of HgT and MMHg near the coast of Peru, a region that supports one of the largest fisheries in the world (FAO, 2015).

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Figure 1. U.S. GEOTRACES GP16 water sampling stations in the eastern tropical South Pacific Ocean. Stations with identification numbers were sampled with full depth profiles, unlabeled stations were demi-stations (upper 1000 m) or shelf stations.

Figure 2. Oxygen concentrations are overlain with silicate contours ($\mu\text{mol kg}^{-1}$) to outline the following water masses: Antarctic Intermediate Water (AAIW), Pacific Deep Water (PDW), modified PDW (mPDW), and Lower Circumpolar Deep Water (LCDW). The OMZ in the Peru upwelling region was suboxic ($2\text{--}10 \mu\text{mol kg}^{-1} \text{O}_2$) at Stations 1–13.

Figure 3. Distributions of filtered HgT (A), Hg^0 (B), MMHg (C), and DMHg (D). Sampling points are black dots and stations with full-depth profiling are identified numerically in the gray bathymetric section.

Figure 4. Average ($\pm$ SD) concentrations of filtered HgT versus remineralized phosphate in water >2500 m depth (A). The dashed line is the expected $\text{Hg:P}_{\text{remin}}$ ratio ($1 \text{ pmol}/\mu\text{mol}$) for deep water unaffected by anthropogenic Hg inputs (Lamborg et al., 2014). Potential temperature at depths >2500 m is plotted in panel B.

Figure 5. Filtered MMHg (grey triangles), DMHg (white circles), and oxygen (blue line) at Stations 5, 6, and 8 in the upwelling region, and Station 18 outside of the upwelling region.

Figure 6. Filtered and particulate MMHg, and DMHg in the water column on the continental shelf (Stations 2–3) and slope (Station 4) of Peru.

Figure 1

Figure 2

Figure 3

Figure 4

A

B

Figure 5

Figure 6

Table 1. Average concentrations of DMHg and filtered MMHg at Stations 1–13 (suboxic thermocline) and Stations 14–36 (no suboxic conditions).

Depth (m)	Filtered MMHg (pM)		DMHg (pM)	
	Stations 1–13	Stations 14–36	Stations 1–13	Stations 14–36
<150	0.073 ± 0.062 ($n = 63$)	0.040 ± 0.047 ($n = 36$)	0.033 ± 0.050 ($n = 68$)	0.001 ± 0.003 ($n = 64$)
150–1000	0.097 ± 0.063 ($n = 110$)	0.043 ± 0.043 ($n = 72$)	0.11 ± 0.078 ($n = 110$)	0.054 ± 0.065 ($n = 117$)
>2000	0.083 ± 0.049 ($n = 64$)	0.050 ± 0.060 ($n = 95$)	0.11 ± 0.065 ($n = 69$)	0.078 ± 0.071 ($n = 179$)