Mercury in the North Atlantic Ocean: The U.S. GEOTRACES zonal and meridional sections

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Abstract

Mercury (Hg) in the ocean undergoes many chemical transformations, including *in situ* production of monomethylmercury (MMHg), the form that biomagnifies in marine food webs. Because the ocean is a primary and dynamic reservoir of Hg cycling at earth's surface and the principal source of human MMHg exposures through seafood, it is important to understand the distribution of Hg and its chemical species in marine environments. We examined total Hg, elemental Hg (Hg⁰), MMHg, and dimethylmercury (DMHg) with fully resolved high-resolution profiles during the U.S. GEOTRACES zonal and meridional sections of the North Atlantic Ocean (GEOTRACES GA03). Total Hg in filtered water had both scavenged- and nutrient-type vertical distributions, whereas concentrations of DMHg, Hg⁰, and filtered MMHg were increased in the oxygen deficient zone of the permanent thermocline across the basin, relative to water above and often below. Total Hg and MMHg on suspended particles accounted for less than 10% of total concentrations. The TAG hydrothermal vent on the Mid-Atlantic Ridge (MAR) was a

source of total Hg and MMHg to nearby waters with apparent scavenging and Hg transformation occurring in the buoyant plume. Uniquely, we observed significant horizontal segregation of filtered total Hg and MMHg, DMHg, and Hg^0 in North Atlantic Deep Water (NADW) between younger water on the western and older water on the eastern side of the MAR. Relative to eastern NADW, Hg concentrations in western NADW were greater, on average, by 1.14× for filtered total Hg, 1.6× for Hg^0 , 2.5× for filtered MMHg, and 2.6× for DMHg. Total Hg enrichment in deep water of the western basin may have resulted from downwelling of anthropogenic Hg during NADW formation. Enrichment of MMHg, DMHg, and Hg^0 in western basin NADW may be explained by either greater Hg substrate availability or greater methylation and reduction potentials in younger deep waters.

Keywords: methylmercury, hydrothermal, deep water, scavenging

1. Introduction

Mercury (Hg) is a ubiquitous environmental contaminant that originates from natural and anthropogenic sources (Fitzgerald et al., 2007). Direct atmospheric deposition is the primary source of Hg to the ocean whereas riverine discharge, mobilization from sediments, groundwater, and submarine hydrothermal inputs contribute lesser amounts (Mason et al., 2012). The majority of atmospheric Hg emissions are anthropogenic (Fitzgerald et al., 1998; Amos et al., 2013) and emissions are hypothesized to increase during the next century (Hammerschmidt, 2011; Kocman et al., 2013; Pirrone et al., 2010; Streets et al., 2009). Because the ocean is a primary and dynamic reservoir of Hg cycling at earth's surface and the principal source of human Hg exposures through seafood (Mason et al., 2012), it is important to understand the distribution of Hg and its chemical species in marine environments.

Mercury exists as four primary chemical species in seawater: mercuric ion (Hg(II)) and monomethylmercury (MMHg , CH_3Hg^+) in complexes with inorganic and organic ligands as well as elemental Hg (Hg^0) and dimethylmercury (DMHg , $(\text{CH}_3)_2\text{Hg}$), which are dissolved gases. Each of these species are hypothesized to be linked through the Hg(II) pool (Fitzgerald et al., 2007). For example, Hg(II) may be either reduced to Hg^0 or transformed to MMHg and DMHg by biological and abiotic mechanisms (Monperrus et al., 2007; Whalin et al., 2007; Lehnher et al., 2011). Hg(II) reduction occurs to such an extent that Hg^0 in estuarine and marine surface waters are usually supersaturated with respect to the atmosphere, leading to evasion (Andersson et al., 2011). Moreover, *in situ* methylation of Hg(II) is an important source of MMHg and DMHg in many marine ecosystems (Balcom et al., 2004; Hammerschmidt and Fitzgerald, 2006a; Sunderland et al., 2009; Hollweg et al., 2010; Cossa et al., 2011). MMHg is the bioaccumulative species of Hg that is present throughout the marine water column (Hammerschmidt and Bowman, 2012; Heimbürger et al., 2010; Mason et al., 2012). Harmful to humans and piscivorous wildlife, MMHg can

interfere with neurological, cardiovascular, and endocrine systems (Bose-O'Reilly et al., 2010; Scheuhammer et al., 2007; Zahir et al., 2005). In the United States and Europe, consumption of marine fish is the primary route of human exposure to MMHg (Sunderland, 2007; Višnjevec et al., 2014).

We investigated the speciation and distribution of Hg in the North Atlantic Ocean during the U.S. GEOTRACES zonal and meridional sections in Fall 2010 and Fall 2011 (GEOTRACES GA03; Figure 1). These cruise tracks included multiple oceanographic features that may influence the biogeochemical cycling of Hg species: 1) a broad continental shelf on the western margin, 2) oligotrophic surface waters in the Sargasso Sea, 3) the Mid-Atlantic Ridge with active hydrothermal venting, 4) relatively productive surface waters along the eastern margin as a result of upwelling and Saharan dust inputs, 5) multiple deep and intermediate water masses (Figure 2), and 6) age differences of North Atlantic Deep Water (NADW) between the western and eastern sides of the Mid-Atlantic Ridge. We measured high-resolution vertical profiles of Hg^0 , DMHg, MMHg, and total Hg in filtered water at 32 stations across the North Atlantic as well as particulate total Hg and MMHg at 22 stations to assemble the most comprehensive and resolved distribution of Hg species in any ocean basin. Here, we provide the first descriptive presentation of our speciation results.

2. Materials and Methods

2.1. Sample collection

Seawater was sampled with 12-L Teflon-coated Go-Flo bottles attached to a dedicated trace-metal clean rosette that was deployed with a plastic-coated hydrowire (Cutter and Bruland, 2012). Twenty full-depth stations (24–36 depths) and 12 “demi” stations (12 depths each in

upper 1000 m) were sampled and analyzed for Hg species in filtered water. Go-Flo bottles were promptly transferred to a clean laboratory van where seawater was filtered without agitation through pre-rinsed capsules (0.2 μm Pall AcroPak-200) into 2-L Teflon bottles for determination of DMHg, Hg^0 , and MMHg. An additional 0.2-L aliquot of filtered seawater was collected into 0.25-L borosilicate glass bottles for measurement of total Hg. Each sample bottle, which was cleaned rigorously with vetted methods (Hammerschmidt et al., 2011), was rinsed 3 $\times$ with sample water (about 10% bottle volume) before filling.

Suspended particles (1–51 μm) were sampled from 16 depths at 22 stations onto quartz fiber filters (Whatman QMA) with McLane *in situ* pumps (Bishop et al., 2012). Filters were subsampled in a clean laboratory into 25-mm diameter punches and stored frozen until Hg analysis at Wright State University. The volume of seawater passed through each 25-mm filter subsample ranged from about 25 to 100 L.

2.2. Mercury analysis

Hg species in filtered seawater were extracted and quantified on board the research vessel inside a clean laboratory van, which was separate from other GEOTRACES laboratories to prevent potential sample contamination from Hg^0 released to the air from mercury electrodes used by other researchers. Within 2 h of water sampling and filtration, gaseous Hg^0 and DMHg were extracted from 2-L samples by purging with Hg-free N_2 (30 L total at 0.8 L min^{-1} ; Bowman and Hammerschmidt, 2011). The sample bottles were fitted with multi-port caps (Omnifit Q-series; Danbury, CT) that allowed influent N_2 to flow through fritted glass impingers while effluent gas exited through a series of three collection traps connected by Teflon fittings. The first trap contained reagent-grade soda lime to help remove water vapor/aerosols generated from

purging, the second contained Tenax TA to concentrate DMHg, and the third contained Au-coated glass beads to collect Hg^0 (Lamborg et al., 2012). This extraction and trapping approach allows for DMHg and Hg^0 to be determined independently as opposed to trapping both species on Au as generic dissolved gaseous mercury (DGM). It also allows for species-specific differentiation of DMHg and MMHg, which are more commonly determined as total methylated mercury ($\Sigma\text{CH}_3\text{Hg}$) after sample acidification (Mason et al., 2012). DMHg was quantified after thermal desorption from Tenax by gas chromatographic cold vapor atomic fluorescence spectrometry (GC-CVAFS, Bloom, 1989; Bowman and Hammerschmidt, 2011) and Hg^0 by dual Au-amalgamation CVAFS (Bloom and Fitzgerald, 1988). Each Au-trap for analysis of Hg^0 was calibrated at every other station after direct loading with a known quantity of Hg^0 vapor. Procedural precision of Hg^0 determinations averaged 10 ± 6 relative percent difference (RPD; $n = 5$ pairs) between duplicate samples. Tenax traps for DMHg analysis were calibrated frequently between stations with known additions of methylethylmercury, a volatile derivative of MMHg. Procedural precision of DMHg analyses averaged 16 ± 18 RPD between 16 pairs of samples. The number of duplicate samples for DMHg, Hg^0 , and MMHg analysis was low relative to the total number of samples because water budgets for the Go-Flo bottles were extremely limited, particularly for an extra 2 L of water. Method detection limits were 0.01 pM for Hg^0 and 0.002 pM for DMHg.

After quantitatively stripping Hg^0 and DMHg from solution, water samples were transferred to 2-L polycarbonate bottles and acidified to 1% with trace-metal grade H_2SO_4 for MMHg determination (Bowman and Hammerschmidt, 2011). After 12–24 h, sample acidity was neutralized with 12 M KOH, pH adjusted to 5 with 4 M acetate buffer, and ethylated with sodium tetraethylborate (NaTEB). Low-Hg acetate buffer was prepared from acetic acid and

KOH, as opposed to acetic acid and sodium acetate because the sodium salt can contain significant amounts of total Hg and MMHg. Sample bottles were fitted with multi-port caps and purged with air (30 L total at 0.8 L min^{-1}) that was cleaned of Hg by passing over Au and Carbotrap. Effluent gas from the bottles passed through soda lime before methylethylmercury was concentrated on Tenax. MMHg was quantified by GC-CVAFS (Bloom, 1989; Bowman and Hammerschmidt, 2011). Recovery of known additions of MMHg from seawater averaged $105 \pm 6\%$ ($n = 3$) and procedural precision averaged 13 ± 13 RPD between 14 pairs of duplicate samples. Individual Tenax traps were calibrated frequently between stations with aliquots of an aqueous MMHgCl standard; the standard was calibrated versus digested TORT-2 reference material (lobster hepatopancreas, National Research Council of Canada) every two weeks.

Total Hg in filtered seawater was measured within 48 h of sampling from 0.2-L aliquots separate from those used for Hg^0 and organo-Hg species. Water was oxidized with BrCl solution (0.1% by volume) for >12 h and pre-reduced with NH_2OH immediately prior to analysis. Oxidized Hg species were reduced to Hg^0 with SnCl_2 , purged from solution with custom-made UConn Bubblers (Lamborg et al., 2012), and quantified by dual Au-amalgamation CVAFS (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979), after calibration with aqueous Hg(II) standards that were traceable to the U.S. National Institute of Standards and Technology (NIST). The method detection limit for total Hg in filtered seawater was 0.02 pM. Recovery of known additions of aqueous Hg(II) averaged $99 \pm 5\%$ ($n = 12$) and near-weekly measurements of total Hg in BCR-579 (Total Mercury in Coastal Seawater, European Commission) averaged 10.3 ± 0.6 pmol/kg ($n = 5$), which was within the certified range of 9.5 ± 2.5 pmol/kg. Procedural precision of total Hg measurements in filtered seawater averaged 5 ± 5 RPD between 18 pairs of samples.

Filter punches containing suspended particulate matter were stored frozen ($\leq -20^{\circ}\text{C}$) until analysis at Wright State University within two to three months of sampling. Mercury was leached from filters with high-purity 2 N HNO_3 for 4 h in a 60°C water bath (Hammerschmidt and Fitzgerald, 2006b). Aliquots of digestate were analyzed for MMHg by flow-injection GC-CVAFS (Tseng et al., 2004) after calibration with procedural MMHg standards digested similarly in 2 N HNO_3 . MMHg standards for analysis of particulate MMHg were calibrated against aqueous Hg(II) solutions traceable to the U.S. NIST. Particulate total Hg was determined from the same digestates used for MMHg analysis. Aliquots of digestates were oxidized with BrCl , pre-reduced with NH_2OH , reduced with SnCl_2 , and analyzed by dual Au-amalgamation CVAFS (Hammerschmidt and Fitzgerald, 2006b). The method detection limit for particulate MMHg was 0.002 pM and that for total Hg was 0.03 pM. Due to low analyte concentrations and limited sample volumes, analytical precision of particulate Hg determinations was assessed only during analysis of total Hg: precision of analytical replicates averaged 3 ± 3 RPD ($n = 18$).

Trace-metal clean procedures were followed throughout sample collection and processing. Collection and filtration methods, sample bottle materials and cleaning techniques, and analytical methods were evaluated rigorously during the U.S. GEOTRACES Intercalibration cruises in the Atlantic and Pacific Oceans, prior to the North Atlantic sections (Bowman and Hammerschmidt, 2011; Hammerschmidt et al., 2011; Bishop et al., 2012; Lamborg et al., 2012; Cutter and Bruland, 2012).

3. Results and Discussion

3.1. *Physical oceanography of the basin*

The zonal and meridional sections traversed multiple water masses in the North Atlantic Ocean (Figure 2). The largest water mass in the North Atlantic is NADW, which occupies the water column from about 1500 to 4000 m depth. The dominant flow of newly formed NADW is from the Labrador and Norwegian Seas into the western basin of the North Atlantic. Not until the Romanche Fracture Zone, south of the equator, does some NADW return northward and ventilate the abyss on the eastern side of the Mid-Atlantic Ridge. This path of deep water flow results in NADW of the western basin (~90 y old near Bermuda) having a radiocarbon age about 150 y younger than the eastern basin (~240 y old; Broecker et al., 1991). These age differences of NADW between the eastern and western basin are related to the speciation and concentration of Hg in NADW, as discussed below and elsewhere (Lamborg et al., accepted).

3.2. *Total Hg*

Among all stations and depths in the North Atlantic, total Hg in filtered water ranged from 0.09 to 1.9 pM (Table 1), excluding waters sampled from the TAG hydrothermal plume on the Mid-Atlantic Ridge (Station 16), which is discussed in section 3.6. The mean concentration of filtered total Hg in our study (0.89 ± 0.30 pM) is less than half of that determined from other locations in the North (Mason et al., 1998) and equatorial and South Atlantic (Mason and Sullivan, 1999) about two decades earlier. Lower concentrations in the current study may be attributed to decreased atmospheric inputs of Hg to the North Atlantic during the past 20 years (Ebinghaus et al., 2011). Alternatively, the difference may reflect on-going improvements in clean techniques for sampling and analysis of Hg in seawater, particularly as a result of testing

and development during the U.S. GEOTRACES Intercalibration (Hammerschmidt et al., 2011; Lamborg et al., 2012).

Total Hg in filtered water had both scavenged- and nutrient-type vertical distributions in the North Atlantic (Figure 3a). The concentration of filtered total Hg in the upper 100 m of the water column averaged 0.65 ± 0.32 pM ($n = 103$) among all stations during both meridional and zonal sections and were much less than concentrations in deeper water. Relative to surface water, concentrations of filtered total Hg were increased in the oxygen deficient zone (ODZ), extending from east to west across the North Atlantic (Figure 3a), consistent with release of Hg from sinking particles during remineralization. Strong scavenging of total Hg from surface waters was evident in the eastern Atlantic, where dust deposition and upwelling promote biological productivity and either bioaccumulation or scavenging of Hg from solution.

Horizontal segregation of filtered total Hg was evident in NADW, excluding the hydrothermal plume on the Mid-Atlantic Ridge that had concentrations of filtered total Hg up to 13 pM. We have hypothesized that Hg slowly accumulates in deep waters of the ocean as a result of soft-tissue remineralization at depth, resulting in older deep waters (e.g., North Pacific) having greater concentrations than younger deep water (e.g., North Atlantic; Hammerschmidt and Bowman, 2012; Lamborg et al., accepted). In contrast, younger NADW in the western North Atlantic (Stations 1–15, zonal transect) has a mean concentration of filtered total Hg (1.04 ± 0.17 pM, $n = 65$) that is about 15% greater than that in approximately 150-y older NADW in the eastern basin (mean = 0.91 ± 0.23 pM, $n = 68$; Mann-Whitney rank sum, $p < 0.001$), disregarding the TAG hydrothermal station on the Mid-Atlantic Ridge (Station 16). Greater concentrations of filtered total Hg in younger NADW of the western basin compared to the eastern North Atlantic have been attributed to younger NADW having downwelled anthropogenic Hg during deep

water formation (Lamborg et al., accepted). Such a source would be in addition to the natural and anthropogenic Hg that is added to deep waters on both sides of the Mid-Atlantic Ridge as a result of particle scavenging and remineralization. In water deeper than 4000 m, which is a combination of NADW and Antarctic Bottom Water (AABW; Jenkins et al., in review), concentrations of filtered total Hg (1.3 ± 0.1 pM) were greater than those in NADW and comparable to concentrations in AABW in the Southern Ocean (1.4 ± 0.4 pM; Cossa et al., 2011). The similarity of concentrations between the deepest waters of the North Atlantic and those in young AABW suggests that Hg is not effectively scavenged from deep waters on time scales of less than 300 years. Ineffective scavenging may result from either an attenuated particle flux at depth (Antia et al., 2001) or Hg existing predominantly as either complexes (e.g., Hg-organic ligands; Fitzgerald et al., 2007) or redox species (Hg^0 , described below) that are less relative to particles. With the exception of zonal Stations 2, 3, and 6 on the northwest continental margin, filtered total Hg was not more concentrated in water overlying the sediment interface, suggesting that diffusion and advection of dissolved and colloidal Hg from deep-sea sediments is not an important source to the ocean.

Total Hg in suspended particles accounted for less than 10% of Hg in the water column of the North Atlantic, with much greater concentrations in surface waters than at depth (Figure 3b). The vertical distribution of particulate total Hg is consistent with that of particulate organic matter in the North Atlantic (Antia et al., 2001). The mean concentration of particulate total Hg along the U.S. GEOTRACES sections (Table 1; 0.038 ± 0.039 pM) is similar to that determined by Mason and colleagues (1998) in surface waters of the North Atlantic between 50 and 70 °N (0.035 ± 0.02 pM). Similar concentrations of particulate total Hg between this study and that of Mason and co-workers (1998) further suggest that concentrations of filtered total Hg determined

in the previous study may be artificially high, unless there has been a significant change in particle-water partitioning of Hg in the North Atlantic during the past 20 years. Elevated concentrations of total Hg on suspended particles (but not in filtered water) were observed in benthic nephroid layers at meridional Station 9 in the eastern Atlantic and zonal Stations 4, 8, and 10 in the western Atlantic (Figure 3b). Particles enriched with metal-oxides apparently scavenge Hg in the TAG hydrothermal plume, which is discussed in section 3.6.

3.3. Elemental Hg

Elemental Hg has a complex vertical and horizontal distribution across the North Atlantic (Figure 4). Elemental Hg is the product of both photochemical and biological mechanisms that reduce Hg(II) substrates (Costa and Liss, 1999; Rolffhus and Fitzgerald, 2004; Poulain et al., 2007) as well as biological and photochemical demethylation of methylated Hg (Mason and Fitzgerald, 1993; Lehnher et al., 2011), with both biological reduction and demethylation potentially mediated by the *mer*-operon, including at sub-picomolar Hg concentrations (Barkay et al., 2003). Concentrations of Hg^0 varied nearly 100-fold within the North Atlantic (Table 1), with levels in thermocline and deep waters typically exceeding those in the upper 100 m of the water column (mean = 0.15 ± 0.12 pM, $n = 109$). Levels of Hg^0 in the mixed layer of the North Atlantic at our sampling locations between 17 and 40 °N are much less than those measured between 50 and 70 °N (0.65 ± 0.39 pM; Mason et al., 1998). Elemental Hg at the sea surface, sampled underway at 2 m depth with a towed fish, averaged 0.05 ± 0.03 pM ($n = 24$).

Vertical profiles of Hg^0 had a distinct nutrient-type distribution that closely followed that of total filtered Hg and nitrate in the western North Atlantic (zonal Stations 1–12 and 14), as shown for Station 12 (Figure 5a). This distribution was unexpected because nutrient-type profiles

of Hg^0 had not been documented previously. Moreover, photochemical and microbial reduction of Hg(II) in surface waters can lead to supersaturation of Hg^0 with respect to the atmosphere (Andersson et al., 2011), suggesting that maximum rather than minimum concentrations might be observed at the surface. In the western basin, Hg^0 concentrations increased with depth from the surface, were greatest in the ODZ, and relatively homogenous at greater depths. In contrast, at stations in the eastern North Atlantic (zonal Stations 16–24, and meridional Stations 11–12), Hg^0 was maximum in the ODZ with much lower concentrations in sub-thermocline waters (Figure 5b). Both Hg^0 concentrations and the fraction of filtered total Hg as Hg^0 in NADW differed significantly between the western and eastern North Atlantic (Mann-Whitney rank sum, p -values < 0.001). The mean concentration of Hg^0 in western NADW (0.42 ± 0.09 pM, $n = 66$) was nearly twice that of eastern NADW (0.26 ± 0.10 pM, $n = 72$). Likewise, the fraction of filtered total Hg as Hg^0 in NADW also was greater in the western ($42 \pm 8\%$, $n = 63$) than eastern basin ($30 \pm 15\%$ $n = 59$).

One potential explanation for the horizontal segregation of Hg^0 in NADW is that Hg^0 is downwelled during NADW formation in the Labrador and Norwegian Seas and slowly oxidized as the water ages. A study of Hg in the sub-polar North Atlantic near locations of NADW formation found that Hg^0 was produced in the mixed layer and conserved as the water mass was formed and sank to depth (Mason et al., 1998). Concentrations of Hg^0 in NADW in the western North Atlantic (0.42 ± 0.09 pM) are not different from those in surface waters of the Norwegian Sea (0.35 ± 0.18 pM; Mason et al., 1998) and support this hypothesis. However, a more recent study found concentrations of DGM ($> 90\%$ as Hg^0 in surface water; Mason et al., 1998) were 0.1 pM or less in surface waters of the Labrador Sea (Andersson et al., 2008), which is a source region for NADW formation and contradicts this hypothesis. Measurements of Hg^0 in NADW

along a meridional section of the western North Atlantic, ideally between the equator and Labrador and Norwegian Seas, would help validate whether Hg^0 is conserved during the first century of deep water flow.

Alternatively, Hg^0 concentrations in deep water may represent a balance between *in situ* reduction and oxidation reactions. While photochemical processes are thought to be the primary mechanism of Hg reduction in the surface ocean (Rolffhus and Fitzgerald, 2004), the concentration maximum of Hg^0 that extends across the Atlantic in the ODZ is indicative of a dark reaction leading to its formation at depth, likely coincident with organic matter remineralization. By extension, it is reasonable to speculate that Hg^0 in deep water masses also is formed by either an abiotic or microbial reduction process. The difference of Hg^0 concentrations in NADW between the western and eastern basins of the North Atlantic may be due to differences in either Hg reactivity or activity of reductants, including microbes, in the water. Biological reduction of Hg can be mediated by microbes containing *mer*-operon encoded proteins (Barkay et al., 2003). While the evolutionary time frame of the *mer*-operon has not been identified, it is plausible that increasing Hg in the environment during the past 150 years has exerted selective pressure on the *mer* operon (Boyd and Barkay, 2012). Accordingly, older NADW may contain less Hg^0 due to lower efficiency of microbial Hg reduction, compared to younger NADW generated during the last 100 years when anthropogenic Hg emissions were increasing. In contrast, the *mer* operon may have a much slower evolutionary time scale and the difference in Hg^0 between older eastern and younger western NADW may result from a decrease of reducible forms of Hg after >100 y. Based on the distribution and relatively low concentrations of MMHg and DMHg across the transect, reductive demethylation cannot explain the difference in Hg^0 concentrations between basins.

3.4. Monomethylmercury

Monomethylmercury in filtered water ranged from <0.002 (detection limit) to 0.60 pM in the North Atlantic Ocean (Table 1). The typical vertical distribution of filtered MMHg at most stations in the North Atlantic was relatively low concentrations in the upper 100 m (0.06 ± 0.05 pM, $n = 70$), a subsurface maximum in the ODZ, and lower concentrations in water below the thermocline (Figure 6a), which is consistent with vertical distributions observed in other ocean basins (Mason and Fitzgerald, 1993; Mason and Sullivan, 1999; Sunderland et al., 2009; Cossa et al., 2009, 2011; Hammerschmidt and Bowman, 2012). Although Hg is methylated in the mixed layer (Lehnher et al., 2011), relatively low concentrations of MMHg there can be attributed to bioaccumulation and photochemical and microbial decomposition (Monperrus et al., 2007; Lehnher et al., 2011; Black et al., 2012; Hammerschmidt and Bowman, 2012). As observed for filtered total Hg and Hg^0 , filtered MMHg concentrations in NADW were significantly greater in the western (0.15 ± 0.12 pM, $n = 31$) than eastern basin (0.06 ± 0.06 pM, $n = 64$; Mann-Whitney rank sum, $p < 0.001$), although there was more intra-basin variability of MMHg concentrations than for the other two Hg species. This comparison of MMHg concentrations in NADW neglects results from Station 16 on the Mid-Atlantic Ridge that has hydrothermal inputs. Some of the variability and greater mean concentration of filtered MMHg in NADW of the western North Atlantic can be attributed to increased concentrations near the slopes of North America and Bermuda, which may result from benthic production and mobilization to overlying water (Hollweg et al., 2010). Aside from these locations, deep ocean sediments do not appear to be an important source of MMHg to the water column of the North Atlantic, as also hypothesized for other ocean basins (Heimbürger et al., 2010; Cossa et al., 2011; Hammerschmidt and Bowman,

2012). Similar to filtered total Hg, filtered MMHg in AABW (0.18 ± 0.08 pM) was increased relative to NADW.

The primary influence on MMHg cycling in the eastern North Atlantic is strong particle scavenging (Figure 6). Scavenging in the eastern Atlantic is evident from both the very low concentrations of filtered MMHg and relatively high levels of particulate MMHg in the mixed layer and permanent thermocline (Figure 6b). Increased particulate MMHg concentrations near the African coast, which are unlike those in the rest of the North Atlantic, are the result of high dust deposition and coastal upwelling that fuel primary production. Given that suspended material had exceedingly low concentrations of MMHg (mean = 0.0007 ± 0.001 pM) and that sinking particles have similar, if not lower, concentrations of MMHg than suspended particles (Lamborg et al, 2009), we would expect release of surface-formed MMHg from sinking particles during remineralization to have little influence on levels of filtered MMHg in the thermocline. Such is the case in the far eastern North Atlantic, where there is no connection between particulate and filtered MMHg. On average, suspended particles contained less than 1% of total MMHg in the water column.

Subsurface maxima of filtered MMHg were observed in the ODZ across the North Atlantic. Maxima of methylated Hg in ODZs, or oxygen minimum zones, have been widely attributed to *in situ* production fueled by microbial remineralization of organic matter (Cossa et al., 1994, 2009; Mason & Fitzgerald, 1993; Mason and Sullivan, 1999; Sunderland et al., 2009; Heimbürger et al., 2010; Hammerschmidt and Bowman, 2012). Multiple sectional oceanographic studies have observed positive associations between concentrations of methylated Hg and either apparent oxygen utilization (AOU; Mason and Sullivan, 1999; Cossa et al., 1994, 2009, 2011; Kirk et al., 2008; Heimbürger et al., 2010; Lehnher et al., 2011) or organic carbon

remineralization rate (Sunderland et al., 2009), which could be interpreted to suggest that production of methylated Hg in the marine water column is limited by microbial methylation potential more than it is by Hg(II) availability. However, we observed no correlation between filtered MMHg concentration and either the concentration of dissolved O₂ ($p = 0.15$) or AOU ($p = 0.42$) across these far ranging sections of the North Atlantic. The range of AOU along these sections of the North Atlantic (0–227 $\mu\text{mol kg}^{-1}$) is comparable to that of other studies where relationships with MMHg were observed (Mason and Sullivan, 1999; Cossa et al., 2009, 2011; Heimbürger et al., 2010; Sunderland et al., 2009). The absence of a correlation between MMHg and either dissolved O₂ or AOU suggests that lower oxygen concentrations and the microbial community, potentially including anaerobes, in the ODZ are not unique in their ability to produce MMHg, which is consistent with results from process studies. Incubation tests with waters from the eastern equatorial Pacific Ocean and Arabian Sea imply that Hg(II) methylation is not particularly active in oxygen minimum zones and anaerobic microorganisms are not important methylators of Hg in the marine water column (Malcolm et al., 2010). Moreover, rates of Hg methylation were similar between the oxic mixed layer, near the subsurface chlorophyll maximum, and oxygen minimum zone at multiple locations in the Canadian Arctic Archipelago (Lehnherr et al., 2011). Thus, an alternative hypothesis for the maxima of MMHg in the ODZ is that MMHg may be produced throughout the marine water column and is less susceptible to decomposition and scavenging in the ODZ than it is at other depths. While the functional identities of microorganisms that demethylate MMHg are largely unknown, a slower rate of decomposition in the ODZ is consistent with the inhibitory effect of low O₂ concentrations on rates of aerobic metabolism as well as the rarity of *mer* genes in anaerobic microbes (Barkay et al., 2010).

Secondary maxima of filtered MMHg also were observed at depths shallower than the ODZ and near the chlorophyll and oxygen maxima at zonal Stations 16–22 in the eastern North Atlantic Ocean (Figure 7). Maxima of filtered MMHg (~ 0.2 – 0.6 pM) were observed between 100–200 m at these stations and within about 80 m depth of the in situ fluorescence and associated O_2 maxima. Increased MMHg concentrations immediately below the euphotic zone can be interpreted to indicate production in surface waters and may result from enhanced microbial respiration of organic carbon (Heimbürger et al., 2010).

3.5. Dimethylmercury

The distribution of DMHg in the North Atlantic is similar to that of MMHg and Hg^0 (Figure 8). Like MMHg, concentrations of DMHg in the upper 100 m were extremely low, increased in the ODZ, and were relatively homogeneous with depth. Low concentrations of DMHg in the mixed layer are a result of its evasion to the atmosphere (Black et al., 2009). Also similar to MMHg, concentrations of DMHg in NADW were considerably greater in the western North Atlantic (mean = 0.18 ± 0.12 pM, $n = 48$) than on the east side of the Mid-Atlantic Ridge (mean = 0.07 ± 0.04 pM, $n = 23$; Mann-Whitney rank sum, $p < 0.001$), excluding results from Station 16 above the ridge. Water deeper than 4000 m, a combination of AABW and NADW, contained 0.18 ± 0.12 pM of DMHg ($n = 16$), a mean concentration similar to that in western NADW. The average concentration of ΣCH_3Hg , calculated as the sum of MMHg and DMHg, in AABW was 0.37 ± 0.08 pM at stations between 20 and 30 °N, and comparable to, if not slightly less than, ΣCH_3Hg levels measured in AABW in the Southern Ocean (0.52 ± 0.11 pM; Cossa et al., 2011).

Dimethylmercury can be the dominant form of methylated Hg in the open ocean (Mason and Fitzgerald, 1993; Mason et al., 1995; Mason and Sullivan, 1999). For surface waters in which DMHg was detectable, the filtered MMHg:DMHg molar ratio was large and highly variable in the upper 100 m of the water column (18 ± 25). In contrast, MMHg:DMHg averaged 1.6 ± 1.8 in North Atlantic water deeper than 1000 m. The filtered MMHg:DMHg ratio for sub-thermocline waters in the North Atlantic is similar to that in North Pacific Deep and Bottom Waters (> 1500 m), which averaged 1.9 ± 0.4 (Hammerschmidt and Bowman, 2012), and suggests that MMHg is the dominant form of methylated Hg in deep waters. DMHg has been posited to be the immediate product of microbial methylation, with MMHg resulting from its decomposition (Mason and Fitzgerald, 1993; Mason et al., 1995; Mason and Sullivan, 1999). However, results from a recent process study suggest that the rate of MMHg formation from Hg(II) is about three orders of magnitude greater than production of DMHg from Hg(II) in seawater (Lehnherr et al., 2011), implying that DMHg may be formed primarily by methylation of MMHg.

Unlike Hg^0 in NADW, which may have been downwelled during deep water formation, DMHg in the water mass was likely formed *in situ* during thermohaline flow. DMHg concentrations in the mixed layer of the Labrador and Norwegian Seas were either undetectable or less than 0.02 pM (Mason et al., 1998). On the basis of oceanographic measurements and modeling, Mason and Fitzgerald (1993) hypothesized that DMHg accumulates slowly in seawater because its rate of formation and decomposition are of the same order of magnitude. They later observed that DMHg in recently formed NADW increased with age and depth of the water, from about 0.03 pM in the upper water column to 0.13 ± 0.08 pM at depth at stations between 50 and 60 °N (Mason et al., 1998). Our results for DMHg in NADW in the western

Atlantic (0.18 ± 0.12 pM) are consistent with this hypothesis and suggest that concentrations may have increased during southward transit between 50 and 60 °N to between 25 and 40 °N in the current study. However, the lower concentrations of DMHg in NADW of the eastern compared to the western basin are inconsistent with the hypothesis. Indeed, levels of both DMHg and filtered MMHg were significantly lower in older eastern than younger western NADW. The mean concentration of DMHg in western NADW was 2.6-fold greater than that in the eastern basin and the average level of MMHg in the west was 2.5-fold greater than in eastern NADW. The similarity of these enrichment factors indicates that concentrations of filtered MMHg and DMHg are proportional in NADW on both sides of the Mid-Atlantic Ridge. However, the difference between these enrichment factors and that of filtered total Hg in NADW (1.14-fold greater in the west), suggests that older NADW has less of a methylation potential for Hg than younger deep water in the west. This is supported by the mean fraction of total Hg as MMHg in filtered water being significantly greater in western NADW ($14 \pm 11\%$) than in eastern NADW ($7 \pm 8\%$; Mann-Whitney rank sum, $p < 0.01$). A difference in the average percentage of filtered total Hg as $\Sigma\text{CH}_3\text{Hg}$ in NADW also existed between the western ($33 \pm 16\%$) and eastern ($23 \pm 14\%$) North Atlantic but the difference was not significant at $\alpha = 0.05$ (t -test, $p = 0.08$).

3.6. TAG hydrothermal vent plume

Seawater and suspended particles were sampled from a plume at the TAG submarine hydrothermal vent mound located on the east wall of the Mid-Atlantic Ridge (Station 16, 26.14 °N, 44.83 °W; Rona et al., 1986). The buoyant plume was located between 3200 and 3400 m depth and identified during sampling with a transmissometer. Previous studies of vent systems in the Pacific Ocean have found a wide range of total Hg concentrations in hydrothermal vent fluids

(4–11,000 pM; Lamborg et al., 2006; Crespo-Medina et al., 2009) although little is known about Hg in vent systems of the Atlantic Ocean (Demina et al., 2012).

Mercury is emitted from the TAG hydrothermal vent and Hg species are scavenged and transformed in the plume (Figures 3 and 9). The maximum concentration of filtered total Hg in the plume was 13 pM at 3400 m depth, more than 10× greater than levels in surrounding NADW (Figure 9a). The speciation of Hg at the filtered total Hg maximum (3400 m depth) was 8% as Hg^0 , 3% as filtered MMHg, and less than 0.2% as DMHg, with particulate Hg comprising less than 2% of the total Hg. This speciation is in contrast to vent fluids sampled at the Gorda Ridge in the Pacific Ocean where nearly all Hg was present as MMHg (Lamborg et al., 2006). At shallower depths in the TAG plume (3200–3330 m), filtered total Hg decreased to 0.90 ± 0.04 pM, concentrations less than those in NADW above the plume (1.15 pM), and Hg^0 decreased to 0.13 ± 0.06 pM and as low as 0.05 pM at 3250 m (Figure 9a), a concentration 8-fold less than in NADW above the plume and 20-fold less than at 3400 m. The decline of filtered total Hg between the bottom and interior of the plume can be attributed to scavenging. Metal oxides are formed within the plume and concentrations of particulate total Hg follow those of particulate Fe oxides, with 27% of the total Hg at 3300 m depth being associated with particles (Figure 9b). Because Hg^0 is not particle reactive, its loss from the core of the hydrothermal plume may result from oxidation reactions.

The TAG hydrothermal vent also was a localized source of MMHg, but not DMHg, to the deep North Atlantic (Figure 9). MMHg was enriched in the hydrothermal plume relative to waters above and below. In contrast to total Hg that was reactive to particle scavenging, more than 99.5% of MMHg in the plume was in the filtered phase, resulting in MMHg accounting for $42 \pm 24\%$ of filtered total Hg in the plume at depths other than the filtered total Hg maximum at

3400 m. Particle-water partitioning coefficients of MMHg are typically an order of magnitude less than those of Hg(II) in oxic seawater (Balcom et al., 2008). The apparent absence of any DMHg enrichment in the hydrothermal plume is consistent with DMHg being less stable at higher temperatures (Mason and Sullivan, 1999) and lower pH (Wood et al., 1968; Beijer and Jernelöv, 1979) than would expected in the vent. While the source of MMHg in submarine hydrothermal fluids is unknown and may be either biological or abiotic (Lamborg et al., 2006), the two gene clusters associated with bacterial Hg methylation (Parks et al., 2013) have been identified in at least one species of hydrothermal vent bacteria, *Deferrisoma camini* (Slobodkina et al., 2012).

4. Summary

The U.S. GEOTRACES zonal and meridional sections of the North Atlantic Ocean have allowed for the first fully resolved high-resolution examination of Hg speciation within this basin. We found that filtered total Hg, MMHg, Hg⁰, and DMHg in water of the North Atlantic are vertically segregated as a function of bioaccumulation, scavenging, remineralization, and transformation reactions in the water column. A hydrothermal vent on the Mid-Atlantic Ridge was confirmed to be a source of total Hg and MMHg to deep water, as suggested by previous studies of vent fluids elsewhere. Our most significant and unexpected discovery was the horizontal segregation of Hg and its chemical species in NADW between the western and eastern North Atlantic. While greater concentrations of filtered total Hg in younger NADW of the western basin compared to the eastern North Atlantic may be attributed to younger NADW having downwelled anthropogenic Hg during deep water formation (Lamborg et al., accepted),

the reason for horizontal enrichment of Hg^0 , MMHg, and DMHg in western NADW is unknown. We speculate that younger NADW has a greater methylation and reduction potential than older waters in the mass. Both a meridional section of the western North Atlantic as well as process-based investigations are needed to better understand the enrichment of Hg^0 , MMHg, and DMHg in western NADW.

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Table 1. Summary of Hg species concentrations including results from all stations and depths.

For suspended particulate MMHg, the percentage of total Hg is referenced to only the suspended particulate phase.

Hg species	Mean $\pm$ SD (pM)	Range (pM)	% of total Hg	<i>n</i>
Filtered total Hg ^a	0.89 $\pm$ 0.30	0.09–1.89	--	605
Hg ⁰	0.31 $\pm$ 0.16	0.01–0.84	35 $\pm$ 16	600
DMHg	0.095 $\pm$ 0.10	<DL – 0.65	10 $\pm$ 11	427
Filtered MMHg	0.095 $\pm$ 0.098	<DL – 0.60	11 $\pm$ 11	432
Particulate total Hg	0.038 $\pm$ 0.039	<DL – 0.38	--	322
Particulate MMHg	0.00069 $\pm$ 0.0013	<DL – 0.010	3 $\pm$ 6	255

^aResults from the TAG hydrothermal vent plume at Station 16 are not included in the summary for filtered total Hg.

Figure captions

Figure 1. GEOTRACES GA03 water sampling stations during the meridional (red) and zonal (yellow) sections of the North Atlantic Ocean. Stations occupied in 2010 are indicated by diamonds, and stations occupied in 2011 are indicated by circles.

Figure 2. Water masses in the North Atlantic along the GEOTRACES GA03 transect, superimposed on the salinity distribution. Surface waters are mainly North Atlantic Central Water (NACW) with Atlantic Equatorial Water (AEW) at the southernmost extent of the cruise near the Cape Verde Islands. Intermediate waters include Irminger Sea Water (ISW) in the west, Antarctic Intermediate Water (AAIW) near the Cape Verde Islands, and Mediterranean Overflow Water (MOW) in the east. North Atlantic Deep Water (NADW) is between 1500 and ~4000 m. Water deeper than 4000 m is a mixture of NADW and Antarctic Bottom Water (AABW) with the fraction as AABW increasing below 5000 m (Jenkins et al., in review). Sampling points are shown as black dots and station numbers are listed intermittently throughout the grey bathymetric section.

Figure 3. Distribution of total Hg concentrations (pM) in filtered water (panel A) and suspended particles (panel B) along GEOTRACES GA03 in the North Atlantic Ocean. Isobars of dissolved oxygen have concentration units of $\mu\text{mol/kg}$. Sampling points are shown as black dots and station numbers are listed intermittently throughout the grey bathymetric sections.

Figure 4. Distribution of Hg^0 (pM) along GEOTRACES GA03 in the North Atlantic Ocean.

Isobars of dissolved oxygen have concentration units of $\mu\text{mol/kg}$. Sampling points are shown as black dots and station numbers are listed intermittently throughout the grey bathymetric section.

Figure 5. Vertical profiles of elemental Hg (grey circles), filtered total Hg (black circles), nitrate (open triangles), and dissolved oxygen (dashed line) at zonal Stations 12 (panel A) and 20 (panel B) of GEOTRACES GA03 in the North Atlantic Ocean. Error bars are covered by figure symbols; relative percent difference was 4 ± 4 ($n = 5$) for filtered total Hg, and 0.3 ± 0.7 ($n = 72$) for nitrate.

Figure 6. Distribution of MMHg concentrations (pM) in filtered water (panel A) and suspended particles (panel B) along GEOTRACES GA03 in the North Atlantic Ocean. Isobars of dissolved oxygen have concentration units of $\mu\text{mol/kg}$. Sampling points are shown as black dots and station numbers are listed intermittently throughout the grey bathymetric sections.

Figure 7. Profiles of filtered MMHg (closed circles), CTD fluorescence (solid line), and dissolved O_2 (dashed line) at zonal Stations 16–18 near the center of the North Atlantic Ocean. The grey area highlights MMHg maxima in oxic water between 100 and 200 m depth.

Figure 8. Distribution of DMHg concentrations (pM) along GEOTRACES GA03 in the North Atlantic Ocean. Isobars of dissolved oxygen have concentration units of $\mu\text{mol/kg}$. Sampling points are shown as black dots and station numbers are listed intermittently throughout the grey bathymetric section.

Figure 9. Filtered total Hg and Hg⁰ (panel A), particulate Hg and iron (panel B), and filtered MMHg and DMHg in the TAG hydrothermal vent plume (zonal Station 16). The grey area highlights the layer of the hydrothermal plume between 3200 and 3400 m depth.

Figure 1

Figure 2

Figure 3

A

B

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9