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Mercury biogeochemical cycling in the ocean and policy implications ☆

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ABSTRACT

Anthropogenic activities have enriched mercury in the biosphere by at least a factor of three, leading to increases in total mercury (Hg) in the surface ocean. However, the impacts on ocean fish and associated trends in human exposure as a result of such changes are less clear. Here we review our understanding of global mass budgets for both inorganic and methylated Hg species in ocean seawater. We consider external inputs from atmospheric deposition and rivers as well as internal production of monomethylmercury (CH_3Hg) and dimethylmercury ($(CH_3)_2Hg$). Impacts of large-scale ocean circulation and vertical transport processes on Hg distribution throughout the water column and how this influences bioaccumulation into ocean food chains are also discussed. Our analysis suggests that while atmospheric deposition is the main source of inorganic Hg to open ocean systems, most of the CH_3Hg accumulating in ocean fish is derived from *in situ* production within the upper waters (<1000 m). An analysis of the available data suggests that concentrations in the various ocean basins are changing at different rates due to differences in atmospheric loading and that the deeper waters of the oceans are responding slowly to changes in atmospheric Hg inputs. Most biological exposures occur in the upper ocean and therefore should respond over years to decades to changes in atmospheric mercury inputs achieved by regulatory control strategies. Migratory pelagic fish such as tuna and swordfish are an important component of CH_3Hg exposure for many human populations and therefore any reduction in anthropogenic releases of Hg and associated deposition to the ocean will result in a decline in human exposure and risk.

1. Introduction

Monomethylmercury (CH_3Hg) is a neurotoxin that can cause long-term developmental delays in children and has been linked to impaired cardiovascular health in adults (Axelrad et al., 2007; Choi et al., 2009; Grandjean et al., 1997: Roman et al., 2010; Karagas et al., in press; Fitzgerald and Clarkson, 1991). For most fish eating populations, marine fish are the major source of human exposure to CH_3Hg globally. For example, in the United States over 90% of the population-wide CH_3Hg intake is from marine and estuarine fish species (Carrington and Bolger, 2002; Sunderland, 2007; U.S. EPA, 2002). In an effort to reduce risks associated with human and wildlife exposures, the United Nations Environment Program (UNEP) is currently leading negotiations toward a global legally binding instrument on reducing global anthropogenic mercury (Hg) emissions and use in products (UNEP, 2010). One uncertainty in understanding the potential effectiveness of such agreements relates to how emissions reductions on a global scale will affect concentrations in marine fish. Better constraints on estimated lifetimes of different Hg forms in the ocean and biogeochemical factors driving interspecies conversions are needed to understand factors controlling accumulation in marine food webs. Here we review the sources of Hg and CH_3Hg to open ocean regions, their areal and vertical distributions and synthesize information on temporal and spatial trends of the dominant species in seawater. Additionally, we review available data on CH_3Hg concentrations in biological tissues and discuss potential impacts from anthropogenic emissions of Hg on human exposures and risks from marine fish.

The majority of Hg inputs to open ocean regions are from wet and dry atmospheric deposition (Mason et al., 1994a; Mason and Sheu, 2002; Sunderland and Mason, 2007; Soerensen et al., 2010).

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This inorganic mercury (Hg^{II}) can be transported laterally and vertically by ocean circulation and settling of suspended particulate matter, or may be reduced to dissolved gaseous elemental mercury (Hg^0) and evaded to the atmosphere. Physical and biological characteristics of ocean basins determine both the lifetime of anthropogenic inorganic Hg in upper ocean waters and its relative conversion to the more toxic and bioaccumulative CH_3Hg. Generally, model simulations have suggested that anthropogenic impacts are greatest in the surface mixed layer of the ocean (54 m annual modeled average; Soerensen et al., 2010; Strode et al., 2011; Fig. 1(A)). Note that throughout this manuscript we use the terms *surface waters/mixed layer* to refer to the top 100 m of the ocean while the term *subsurface waters* refers to those waters below the mixed layer but above the permanent thermocline, typically < 1000 m. In the subsurface waters, penetration of anthropogenic Hg is varied and complicated by the lateral and vertical movement of water masses through upwelling and deep-water formation in different ocean basins, and with differences in the intensity of vertical transport processes (Sunderland and Mason, 2007; Strode et al., 2011; Mason and Sheu, 2002). Estimates of anthropogenic Hg enrichment vary among models that have different spatial and temporal resolution and consider different transport processes and evaluation of these models is constrained by limited measurements. Overall, anthropogenic Hg enrichment of deep ocean water (> 1500 m) is smaller than surface and subsurface waters due to the long timescales for lateral and vertical transport to the deep ocean (Sunderland and Mason, 2007). Understanding the impacts of human activities on fish CH_3Hg concentrations requires combining our knowledge of the time-scales required for penetration of anthropogenic Hg in the vertical marine water column with the dominant regions where inorganic Hg is converted to CH_3Hg.

Both CH_3Hg and dimethylmercury ($(CH_3)_2Hg$) are present in the ocean at detectable concentrations (e.g., Mason and Fitzgerald, 1990). While, as discussed below, there is the potential for different pathways for the formation and degradation of the

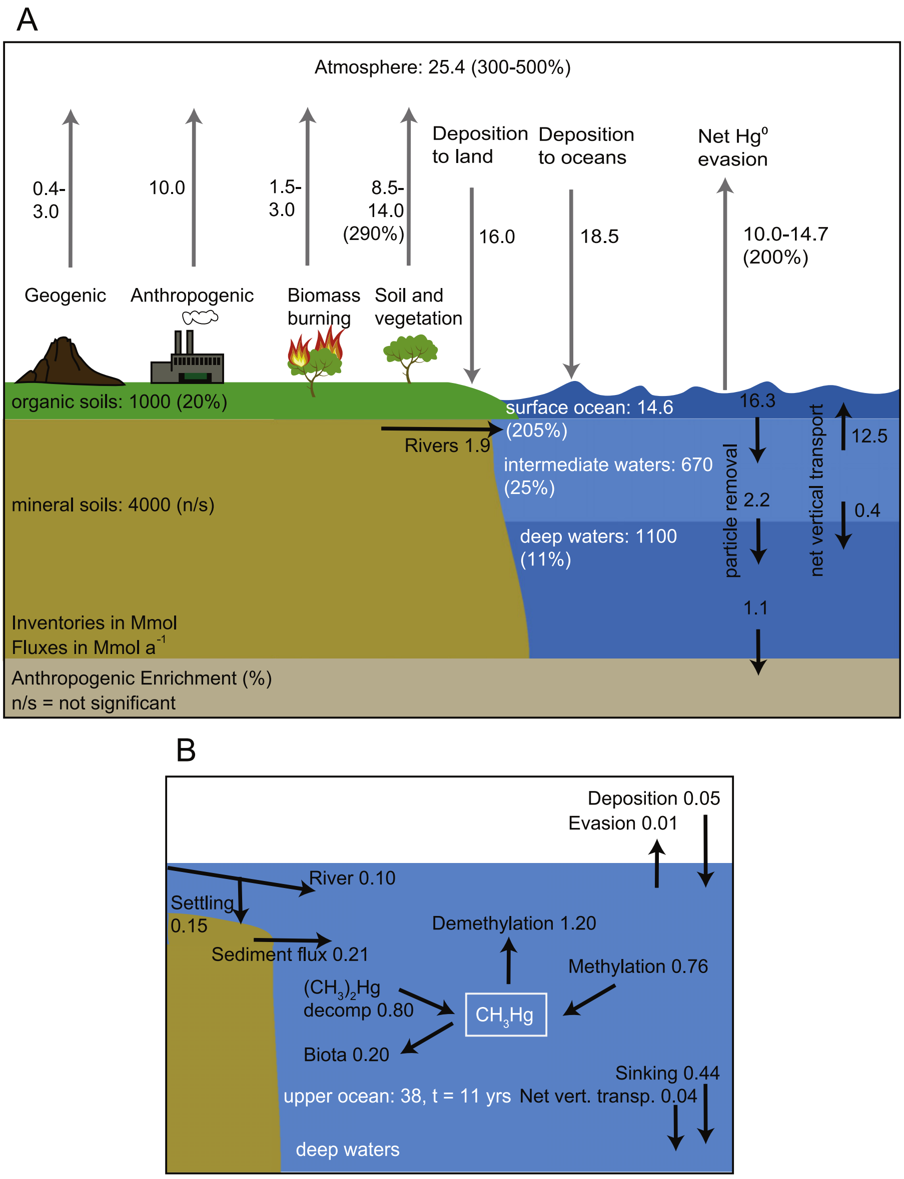

Fig. 1. (A) A recent estimate of the fluxes of mercury at the Earth's surface based on simulations using the GEOS-Chem global mercury model, and building on previous studies (Soerensen et al., 2010; Selin et al., 2008; Sunderland and Mason, 2007; Holmes et al., 2010; Smith-Downey et al., 2010). The percentage values in brackets are the estimated increases in concentration and fluxes in the last century due to anthropogenic activities. (unpublished data); (B) Overall budget for the sources of methylated mercury to the upper ocean (defined as waters above the permanent thermocline) using data and information discussed throughout the paper. In both figures fluxes are in Mmol yr^{-1} and reservoirs are given in Mmol.

methylated Hg forms, there is little concrete evidence for such differences in the literature. Additionally, analytical methods for methylated Hg species used do not always distinguish between CH_3Hg and $(CH_3)_2Hg$ (e.g., Cossa et al., 2011; Sunderland et al., 2009). Therefore, when comparing data in the literature, we compare and contrast the total methylated concentration to make use of all available data and denote the sum of these two species as ΣCH_3Hg.

Hypothesized sources of CH_3Hg for uptake into the marine food web include production in coastal and shelf sediments (Hammerschmidt and Fitzgerald, 2004, 2006a, b), hydrothermal vents and deep-sea sediments (Kraepiel et al., 2003), and *in situ* water column methylation processes (Mason and Fitzgerald, 1990; Heimburger et al., 2010; Lehnherr et al., 2011; Cossa et al., 2011; Sunderland et al., 2009). Here we review current understanding of these processes and their magnitude to identify plausible locations for the formation of CH_3Hg that is bioaccumulated into marine food webs.

Risks associated with CH_3Hg in marine fish can be managed over the short term by dietary interventions for sensitive groups, such as women of childbearing age and young children, by switching from high to low CH_3Hg fish (Carrington et al., 2004) to effectively reduce CH_3Hg exposure (Mahaffey et al., 2011; Oken et al., 2012). However, because of the health benefits of consuming fish (Oken et al., 2012), reducing the environmental Hg burden and associated accumulation in fish is the preferred long term approach for managing exposure. This review focuses on the physical and biological processes in open ocean regions that drive the timing and magnitude of changes in fish CH_3Hg levels in response to changes in atmospheric Hg loadings. We review the best available knowledge of spatial, vertical and temporal patterns of Hg and CH_3Hg in the major oceans and discuss the major gaps in process-level understanding and measurements, and their implications for ongoing regulatory efforts for Hg and CH_3Hg.

2. Global mercury and methylmercury budgets for the open ocean

2.1. Inorganic mercury sources and sinks

Sources of Hg to open ocean regions include inputs from ocean margins (rivers, estuaries), groundwater, benthic sediments, and hydrothermal vents and direct atmospheric deposition. Models and measurements suggest that direct atmospheric deposition is the dominant source of Hg with global inputs to the ocean ranging from 14 to 29 Mmol over the past decade (Dastoor and Larocque, 2004; Holmes et al., 2010, Mason and Sheu, 2002; Selin et al., 2007; 2008; Soerensen et al., 2010; Strode et al., 2007; Sunderland and Mason, 2007). The most recent global modeling efforts, which include model evaluations based on oxidation of atmospheric Hg^0 by Br atoms (Holmes et al., 2010), suggest that total wet and dry deposition to open oceans in 2008 was 18.5 Mmol (Soerensen et al., 2010; Fig. 1(A)).

Mercury contributions from other sources to open ocean regions are much smaller on a global basis. Sunderland and Mason (2007) estimated global river discharges of Hg into the oceans using long-term mean freshwater discharges and average sediment loads of the largest 927 rivers globally (Dai and Trenberth, 2002; Ludwig et al., 1996) and available dissolved and particulate Hg data. This evaluation showed that the total Hg load from rivers to estuaries is large (>14 Mmol yr^{-1}) but that only a small portion of this Hg is transported to open ocean regions ($\sim$1.9 Mmol yr^{-1}, range 1.2–2.4). Other particle-reactive metals are similarly deposited in coastal regions (Chester, 2003).

Despite relatively small fluxes from rivers on a global basis, riverine Hg inputs can be regionally important (Fisher et al., in press; Sunderland and Mason, 2007). For example, on a basin-wide scale, inputs from rivers range from 25 to 41% of the magnitude of atmospheric deposition in the South Atlantic Ocean, North Pacific Ocean, and Mediterranean Sea but comprise a negligible fraction of inputs in the North Atlantic and South Pacific/Indian Oceans (Sunderland and Mason, 2007). Most global models presently neglect rivers as a source to oceans (Lamborg et al., 2002a; Strode et al., 2007). Soerensen et al. (2010) observed that this may be one factor explaining underestimates in dissolved Hg concentrations and associated air-sea exchange of Hg^0 in near coastal regions by the GEOS-Chem global biogeochemical Hg model. Fisher et al. (in press) showed that seasonal trends in atmospheric Hg levels measured at long-term monitoring stations in the Arctic could not be explained without evoking a dominant flux of Hg from rivers to the Arctic Ocean, which is greater in magnitude than direct atmospheric deposition. These results reinforce the need to better characterize riverine Hg fluxes on a global basis.

Limited studies suggest that groundwater Hg inputs and benthic sediment fluxes are relatively small sources of Hg to the global oceans ($\sim$0.5 to 4 Mmol yr^{-1}). Global groundwater Hg fluxes are derived by assuming groundwater inputs make up $\sim$10% of surface flow (Cossa et al., 1996; Bone et al., 2007; Black et al., 2009a; Laurier et al., 2007; Ganguli et al., 2011). It should be noted that estimated inputs from groundwater could be enhanced in some locations due to local sources (e.g., sewage impacts; Bone et al., 2007; Black et al., 2009a) but generally these inputs do not rival atmospheric sources.

Inputs of Hg from hydrothermal vents are estimated to be <3 Mmol yr^{-1} (<20% of atmospheric inputs) on a global basis (Lamborg et al., 2006). Data from four vent locations representing a wide range in geologies have total Hg concentrations between $\sim$2 and $\sim$1300 pM in vent fluids (Lamborg et al., 2006). Similar variability has been observed for other metals (Bagnato et al., 2009; Crespo-Medina et al., 2009; German and Von Damm, 2004). Nearfield removal of Hg from vents also may occur due to precipitation of sulfides and/or oxides, as found for Fe, Mn and other metals that complex strongly with sulfide (German and Von Damm, 2004). Such removal is also supported by local enrichment of Hg in hydrothermal associated deposits and sediments (e.g., Dekov, 2007). If elemental Hg (Hg^0) were released from hydrothermal vents it might be transported over longer distances due to a slower rate of oxidation in cold, dark waters (Stoffers et al., 1999; Amyot et al., 2005). However, the extent of such releases is thought to be small. From our evaluation of the existing datasets and from the lack of any demonstration of elevated concentrations in the water column in the regional vicinity of such sources (e.g., Fitzgerald et al., 1998; Fitzgerald et al., 2007), we infer that the Hg inputs from hydrothermal vents are small. In addition to deep ocean point source (hydrothermal) inputs, there is the potential for the release of Hg from deep ocean sediments. This is considered negligible given the factors controlling the flux of inorganic Hg from sediments (e.g., Hollweg et al., 2010). Additionally, a number of studies suggest removal of inorganic Hg to the solid phase at the sediment–water interface (Bloom et al., 1999; Mason et al., 2006) given that Hg is likely strongly retained by binding to organic matter and other solid phases (Ravichandran, 2004), especially in oxic environments.

Gas exchange is the major sink for ocean Hg (Mason et al., 1994a; Mason et al., 2001; Fitzgerald et al., 2007; Sunderland and Mason, 2007; Soerensen et al., 2010). Gas exchange both prolongs the lifetime of the Hg in the biosphere and partially mitigates the net impact of anthropogenic Hg inputs on the ocean. Any changes in either the efficiency of net reduction in surface waters or the rate of gas exchange will impact the relative rate of change in surface concentration in concert with changes in atmospheric Hg concentration. Additionally, changes in the rate of Hg removal from the surface ocean by particle scavenging resulting from variations in productivity also could impact the extent of re-emission to the atmosphere.

Recent improvements in analytical techniques and model development have resulted in a better understanding of the factors involved in the air-sea exchange of Hg (Andersson et al., 2007, 2008, 2011; Soerensen et al., 2010;). On a global basis, most (~70%) of the Hg deposited in marine ecosystems is reemitted to the atmosphere in gaseous elemental form (Hg^0 predominantly, but some $(CH_3)_2Hg$;Soerensen et al., 2010; Mason and Sheu, 2002; Corbitt et al., 2011), increasing the lifetime of Hg cycling through the reservoirs of the surface biosphere. Net biotic and photochemical reduction of Hg^{II} (photochemical oxidation also occurs in surface waters; Monperrus et al., 2007; Whalin et al., 2007) and subsequent evasion of Hg^0 reduces the pool of potentially bioavailable Hg^{II} that may be converted to ΣCH_3Hg and bioaccumulated into marine organisms.

2.2. Methylated Hg (ΣCH_3Hg) sources and sinks

Atmospheric inputs constitute a small fraction of the total CH_3Hg supply to the marine environment. This is estimated to range from 0.07 and 0.15 Mmol yr^{-1} (average 0.1 Mmol yr^{-1}) assuming that CH_3Hg is 0.5% of total Hg in deposition (Sunderland and Mason, 2007; Mason et al., 1997; Fitzgerald et al., 1994; Sunderland et al., 2010) (Fig. 1(B)). Evasion of $(CH_3)_2Hg$ to the atmosphere is estimated at ~0.01 Mmol yr^{-1} (Mason and Benoit, 2003). There are limited measurements of methylated Hg in hydrothermal fluids (Lamborg et al., 2006; Crespo-Medina et al., 2009) and methylated Hg ranges from <1 to 100% of the total Hg. The fluids with greater CH_3Hg appear to be associated with sedimented or back arc environments, suggesting that fluid interaction with lithologies high in organic matter are important for the formation of organometallic Hg. Fluids associated with mid-ocean ridge spreading centers, where the majority of hydrothermal flow and heat dissipation occur, are much more enriched with total Hg but have the lowest %CH_3Hg. Using the East Pacific Rise as representative for the flow-weighted average composition of hydrothermal fluids (~85 pM total and 1.7 pM ΣCH_3Hg), we can estimate that hydrothermal fluids contribute <0.05 Mmol of ΣCH_3Hg annually to the ocean. These estimates are based on a water flux of 1 Sverdrup ($10^6\ m^3\ s^{-1}$) through hydrothermal systems. Thus, we predict that hydrothermal systems are a minor source of methylated Hg to the deep ocean.

There are few measurements of Hg and CH_3Hg in deep ocean sediments and porewater (e.g., Gobeil et al., 1999; Kading and Andersson, 2011; Ogrinc et al., 2007), making estimates for the flux of methylated Hg from these deposits difficult. Available data indicate very low concentrations of total Hg, and percentages of CH_3Hg that are equivalent to or less than those in sediments on the continental margin. We have estimated for deposits on the margin that less than 8% of the Hg^{II} deposited is converted to CH_3Hg and remobilized to overlying water (Fitzgerald et al., 2007). Data for shelf and slope sediments support the magnitude of these estimates (Fitzgerald et al., 2012, Hollweg et al., 2009; Hammerschmidt and Fitzgerald, 2006a), and it is used here to estimate deep sediment inputs. Overall, the various observations and estimates crudely constrain the flux of ΣCH_3Hg from deep sea sediments to <0.08 Mmol yr^{-1}.

The transport of riverine CH_3Hg inputs offshore is estimated to be 0.1 Mmol yr^{-1}, based on an estimated 5% of total Hg being CH_3Hg and assuming that ~90% of the riverine Hg input is deposited in estuaries and the coastal zone (Sunderland and Mason, 2007). Note that the net exchange of CH_3Hg across the sediment–water interface in estuaries is included this estimate. Studies of the production and demethylation of CH_3Hg in sediments of estuarine and coastal systems (Hammerschmidt and Fitzgerald, 2004, 2006a; Hammerschmidt et al., 2004, 2008; Heyes et al., 2004, 2006; Hollweg et al., 2009, 2010; Lambertsson and Nilsson, 2006; Liu et al., 2009; Marvin-DiPasquale et al., 2003; Rodríguez Martín-Doimeadios et al., 2004; Sunderland et al., 2004, 2006) have also evaluated the potential flux from the sediments to the water column (Benoit et al., 2009; Choe et al., 2004; Covelli et al., 1999; Gill et al., 1999; Hammerschmidt and Fitzgerald, 2008; Hollweg et al., 2009, 2010; Sunderland et al., 2010). However, few have examined the bidirectional exchange (i.e., particle deposition, sediment flux and resuspension). In most studies where both Hg methylation and CH_3Hg demethylation have been measured in sediment, the ratio of the methylation to demethylation rate constants is of the same order as the fraction CH_3Hg (Heyes et al., 2006; Kim et al., 2006). This suggests that *in situ* concentrations are established by a steady state between these processes and through additional losses of CH_3Hg to overlying waters.

While relatively high benthic fluxes of CH_3Hg have been estimated for estuarine environments such as Baltimore Harbor, Long Island Sound, Chesapeake Bay, San Francisco Bay, and New York Harbor (Mason et al., 2006; Choe et al., 2004; Hammerschmidt et al., 2004, 2008) and for other contaminated environments (e.g., Gulf of Trieste; Covelli et al., 1999), the more limited data suggest fluxes are lower from shelf and slope sediments (Hollweg et al., 2009, 2010; Hammerschmidt and Fitzgerald, 2006a). Recent studies on the continental shelf and slope of New England (NW Atlantic) indicate higher water column CH_3Hg in proximity to the shelf/slope (<1000 m) suggesting its production and mobilization from the sediments (Hammerschmidt et al., 2012; Hammerschmidt and Bowman, 2012; Fitzgerald et al., 2012). Many of the sediment flux estimates are based on simple diffusion and porewater concentration gradients and it is evident from studies with benthic flux chambers that these diffusive estimates are up to an order of magnitude less than those obtained from benthic chambers (Gill et al., 1999; Choe et al., 2004; Hammerschmidt and Fitzgerald, 2008).

On a global basis, estimates of sediment flux inputs of dissolved CH_3Hg from the coastal and shelf sediments to the ocean range from a low value of 0.01 Mmol yr^{-1} (diffusive flux only; Hollweg et al., 2010; Cossa et al., 1996) to 0.15 Mmol yr^{-1} (Hammerschmidt and Fitzgerald, 2006a). Alternatively, given the Fitzgerald et al. (2007) estimate that the fraction of CH_3Hg fluxing from sediments is ~8% of the total Hg sediment depositional flux and using the global Hg deposition flux to shelf/slope sediments of 2.9 Mmol yr^{-1} (Sunderland and Mason, 2007), the CH_3Hg flux is estimated at 0.21 Mmol yr^{-1}. These two approaches suggest that the overall CH_3Hg flux from sediments is ≤ 0.2 Mmol yr^{-1} (Fig. 1(B)).

The deposition of CH_3Hg to shelf and slope sediment (~0.15 Mmol yr^{-1}), estimated using the fluxes in Sunderland and Mason (2007) and 5% CH_3Hg in sedimentary material (Fig. 1(B)), is of the same order as the sediment inputs, suggesting little net input from coastal sediments to the water column. Sediment resuspension is a potential source of CH_3Hg in some locations (Kim et al., 2008) and could potentially increase the magnitude of the net sediment flux (Benoit et al., 2009; Sunderland et al., in press). However, such data are extremely limited for shelf environments.

We conclude that the magnitude of the CH_3Hg flux to overlying waters of the shelf and slope (~0.2 Mmol yr^{-1}) is similar to the overall net sedimentation that occurs in these regions (~0.15 Mmol yr^{-1}) (Fig. 1(B)). The net input from the coastal environment is likely to vary globally depending on the extent of the shelf environment and other factors, including, for example, organic matter and Hg loadings, and the extent of hydrologic exchange. The modeling and data of Sunderland et al. (2010), for example, demonstrate that while the within sediment formation and demethylation of CH_3Hg in the Bay of Fundy were large, they were essentially equivalent. These authors also concluded that the flux from sediments to overlying waters was small relative to sedimentary deposition and that most CH_3Hg was supplied from external sources (exchange with the North Atlantic Ocean and terrestrial inputs; Sunderland et al., 2010, in press). Similar results can be inferred from mass balance estimates for the inshore coastal sediments of the Gulf of Mexico (Liu et al., 2009; Harris et al., this issue), especially close to the Mississippi River delta. Similarly, sedimentary inputs to the water column were estimated at ~25% of total CH_3Hg loadings to the Hudson River estuary (Balcom et al., 2010). However, a much greater fraction of the inputs is from sediment flux in other estuaries, such as Long Island Sound and San Francisco Bay (Hammerschmidt and Fitzgerald, 2006a; Davis et al., In review).

The flux estimates discussed above (Fig. 1(B)) suggest that external sources of ΣCH_3Hg (riverine inputs and coastal sources and atmospheric deposition) are insufficient to account for the ΣCH_3Hg sinks in the ocean, which include accumulation into biota and removal by fisheries, photochemical and biological degradation into inorganic Hg, and net removal to the deep ocean and deep sea sediments. This suggests that production within the ocean system is important. The various potential *in situ* sources of ΣCH_3Hg to the ocean water column are discussed below. Both CH_3Hg and $(CH_3)_2Hg$ are broadly distributed throughout the ocean water column and the observed concentrations are difficult to explain without *in situ* production. Initial studies in the equatorial Pacific Ocean suggested sub-thermocline maxima in both CH_3Hg and $(CH_3)_2Hg$ (e.g., Kim and Fitzgerald, 1988, Mason and Fitzgerald, 1990, 1991, 1993). These results have since been confirmed in a number studies in the North and South Atlantic in the 1990s (Mason et al., 1998; Mason and Sullivan, 1999), multiple studies in the Mediterranean Sea (Cossa et al., 2009; Heimburger et al., 2010; Horvat et al., 2003), and more recent studies in the North Pacific, North Atlantic, Indian Ocean and Southern Ocean (Sunderland et al., 2009, 2011; Cossa et al., 2011; Hammerschmidt et al., 2012; Hammerschmidt and Bowman, 2012; Lamborg, 2009; Bowman et al., 2012).

This limited dataset for ΣCH_3Hg, which is illustrated with published data in Fig. 2, indicates that concentrations are relatively low in open ocean surface waters, maximal in the intermediate layers, especially in regions of low oxygen, and low and relatively constant in deeper waters (> 1000 m). These vertical distributions are most consistent with *in situ* formation of ΣCH_3Hg in association with the decomposition of organic matter (Bowman et al., 2012; Cossa et al., 2011; Hammerschmidt and Bowman, 2012; Lamborg et al., pers. comm.; Mason and Fitzgerald, 1993; Mason et al., 1998; Mason and Sullivan, 1999; Sunderland et al., 2009; Kirk et al., this

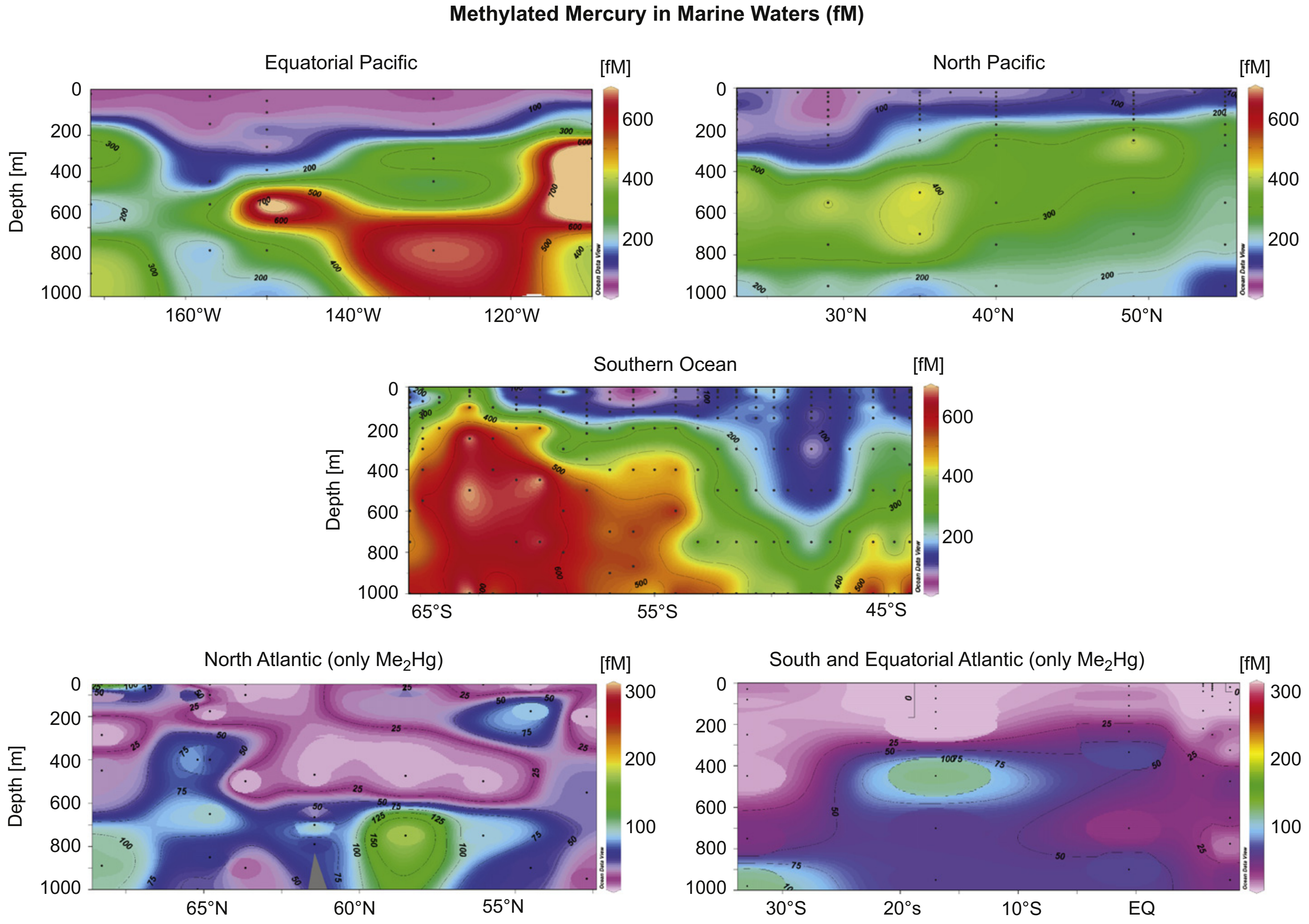

Fig. 2. Distributions of methylated mercury (methylmercury and dimethylmercury (Me_2Hg)) in various ocean basins. Data compiled from the literature: equatorial Pacific (Mason and Fitzgerald, 1993); North Pacific (Sunderland et al., 2009); Southern Ocean (Cossa et al., 2011); North Atlantic (Mason et al., 1998); South and equatorial Atlantic (Mason and Sullivan, 1999). In the plot for the Equatorial Pacific surface water concentrations were set to DL (50 fM) when measurements were below DL. Note that the scale for the bottom plots of dimethylmercury is different. All figures created using the data in the referenced manuscripts.

issue). The link to organic carbon degradations is demonstrated, for example, by the relationship between the amount of ΣCH_3Hg and the extent of organic carbon remineralization (Sunderland et al., 2009), and correlations between ΣCH_3Hg and apparent oxygen utilization, another measure of carbon degradation (Mason and Fitzgerald, 1990, 1993; Mason and Sullivan, 1999; Heimburger et al., 2010; Cossa et al., 2011).

The higher $\%CH_3Hg$ in the subsurface (Fig. 2), typically below the seasonal mixed layer, provides an indication of the relative importance of this region in CH_3Hg production. This distribution suggests that the transition regions (the base of the euphotic zone) and subsurface waters where particulate organic matter is being degraded are locations of enhanced net methylation of Hg. In addition to direct formation of CH_3Hg from Hg^{II}, there is also a source of CH_3Hg from remineralization of sinking particles and decomposition of $(CH_3)_2Hg$ (Mason and Fitzgerald, 1993; Mason and Sullivan, 1999; Lehnherr et al., 2011; Fig. 1(B)). If CH_3Hg was also produced in the mixed layer (Lehnherr et al., 2011), the observed low concentrations suggest production is balanced by demethylation (Hammerschmidt and Bowman, 2012), and to a lesser extent by bioaccumulation (Fig. 1(B)). Demethylation is the major sink for CH_3Hg in the upper ocean, based on rates of decomposition in the literature (Whalin et al., 2007; Monperrus et al., 2007; Lehnherr et al., 2011; Mason and Sullivan, 1999). Overall, the residence time of CH_3Hg is relatively short (~10 years) for the upper ocean (mixed layer and subsurface waters above the permanent thermocline), based on the fluxes in Fig. 1(B). This residence time is comparable to the horizontal mixing times of these subsurface waters, and therefore it is unlikely that CH_3Hg formed in coastal environments can be transported sufficiently offshore to be a major source for open ocean ecosystems. While advective transport of dissolved CH_3Hg from coastal systems is likely not an important source to open ocean fish, there is the potential for "bioadvection" of CH_3Hg due to either feeding of offshore fish in coastal environments, or due to migration of lower food chain biota (Fitzgerald et al., 2007). Such transport could be bidirectional through transport of CH_3Hg from the ocean to estuaries and to the upper reaches of streams from the migration and death of fish, such as salmon (Sarica et al., 2004).

Currently, there is little information and consensus on the regions of maximum production of ΣCH_3Hg although there is a general agreement that the formation is linked to the decomposition of organic matter. It is known that less than 15% of the organic matter produced in the mixed layer is exported to depths greater than 100 m and < 5% to depths greater than 1000 m (Antia et al., 2001), due to grazing and organic matter decomposition through the microbial loop. Anaerobic bacteria are the major methylating organisms in coastal and freshwater environments but it appears that they are not important in the marine water column as methylation appears to be most closely linked to organic carbon decomposition that occurs throughout the upper ocean waters (Heimburger et al., 2010; Sunderland et al., 2009; Malcolm et al., 2010).

3. Spatial trends in Hg concentrations

Concentrations of total dissolved Hg (< 0.45 μm) in ocean waters vary by location horizontally and vertically. A compilation of information on the ranges of Hg and its various forms in coastal (excluding estuaries) and open ocean environments is shown in Table 1. For offshore water masses, measurements suggest that the total dissolved Hg is typically < 3 pM. Developing an understanding of spatial variation of Hg in the ocean from available data is complicated by the wide timespan over which samples have been collected since the development of both "clean techniques" and low level detection methods (~30 years), and the lack of studies examining seasonal variability in the upper ocean (see references in Table 1). Additionally, there is evidence for changes in the amount and distribution of atmospheric loadings of Hg to the ocean over time as a result of emission controls in North America and Europe and an increase in industrialization in Asia and other developing regions (e.g., Pirrone et al., 2010; Streets et al., 2009a, b, 2011; Sunderland et al., 2009).

Table 1
Mercury concentration and speciation in open ocean waters. All data in pM for Hg, fM for methylated Hg. Values are calculated as averages for the either the entire water column of for upper water column (< 1500 m, typically) and deeper waters (> 1000 m), or for mixed layer and subsurface waters, based on the reported data in the references noted.

Location	Diss Hg^h (pM)	Tot Hg (pM)	Diss CH_3Hg (fM)	Dissolved $(CH_3)_2Hg$ (fM)	ΣCH_3Hg (fM)	$\%\Sigma CH_3Hg$	Refs
Atlantic Ocean							
North	1.0 ± 0.4^c	2.4 ± 1.6^a	< 500	80 ± 70		up to 7	1
	$0.8–1.5^a$	2.3 ± 0.8^b	20–150	< 10?			2
	$0.9–1.3^b$	1.6 ± 0.4^c					3
		2.1 ± 0.6^c					1, 10
							13, 14
							13
Eq and South		1.7 ± 0.7^c	25–200	up to 110		5–10	5
		2.9 ± 1.7^d					5
		1.7 ± 0.7^b					5
Pacific Ocean							8
North		0.6 ± 0.3^a	20–100	< 5–20	170 ± 120	15 ± 7	8
		1.2 ± 0.3^b					11
		1.1 ± 0.4					13, 15
		$0.3–1.0^a$					13
		$1.0–1.5^b$					
Eq and South		1–2	up to 500	up to 670		2–15	4, 9
Southern Ocean		0.6–2.8			20–860	up to 78%	12

Notes: Unless otherwise noted, data represent the entire water column. In some instances, data is vertically separated: (a) waters above the permanent thermocline; (b) waters below 1500 m; (c) surface waters (mixed layer); (d) subsurface waters (below mixed layer but above the permanent thermocline; (h) dissolved Hg or reactive Hg measurement.

References: 1. Mason et al. (1998); 2. Cossa et al. (1997); 3. Cossa et al. (2004); 4. Mason and Fitzgerald (1991; 1993); 5. Mason and Sullivan (1999); 6: Mason and Sullivan (1999); 7. Dalziel (1995); 8: Laurier et al. (2004); 9: Gill and Fitzgerald (1988); 10: Dalziel (1995); 11: Sunderland et al. (2009); 12: Cossa et al. (2011); 13: Lamborg et al. (2009); 14: Bowman et al. (2012); Hammerschmidt et al. (2012).

This issue is discussed in greater detail below. However, by comparing roughly contemporaneous data from different parts of the world, some trends are apparent. For example, the IOC cruises of the 1990s and early 2000s documented significant gradients in total Hg in surface and subsurface water in both the Atlantic and Pacific Oceans (Mason et al., 1998; Mason and Sullivan, 1999; Laurier et al., 2004). Sunderland et al. (2009) evaluated the differences in concentrations across surface waters of the North Pacific Ocean and found that higher concentrations corresponded to a region of enhanced atmospheric Hg^{II} deposition from Asian sources. Overall, such distributions confirm that Hg is far from uniformly distributed in the surface ocean, which is consistent with its estimated short residence time in the mixed layer (<1 yr; Soerensen et al., 2010).

Mercury concentrations can differ among intermediate and deep waters (Figs. 3 and 4). A synthesis of earlier data, discussed in Laurier et al. (2004), suggested that there were higher concentrations in the North Atlantic compared to the North Pacific deep waters. Such a scenario would occur if there was sufficient input of Hg to the deep Atlantic through sinking North Atlantic Deep Water (NADW), as has been shown for other contaminants and tracers. For example, chlorofluorcarbon (CFC) and tritium data indicate penetration of these compounds to the bottom of the North Atlantic as far south as 40° N in the late 1980s (Fine, 2010; Jenkins, 2010), and even further south for CFCs in the western boundary currents of the Atlantic (to 24° N in 1992; Schlitzer, 2010). Deep ocean penetration, even south of the equator, is also shown for “bomb-derived” ^{14}C (Schlitzer, 2010; Key, 2010), added to the atmosphere by bomb testing in the early 1960s. In contrast, there is no evidence of penetration of these tracers below 1000 m in the North Pacific. An anthropogenic signal in the upper waters is apparent for Hg, and especially in the Atlantic, as shown in Fig. 4(b) (the BATS site; 31° 40′ N, 64° 10′ W) and discussed below, but there is less indication of elevated values in the deep waters at BATS when comparing the data in Figs. 3 and 4. This suggests that the penetration of anthropogenic Hg into the deep North Atlantic has not been sufficient to result in a measurable change in concentration at the BATS site (31° 40′ N, 64° 10′ W).

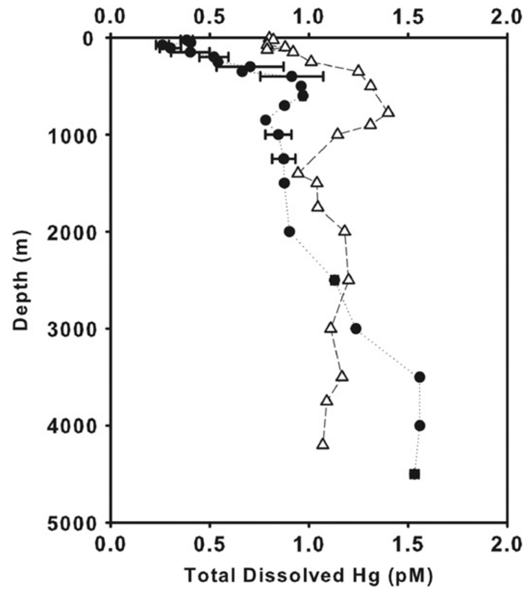

Fig. 3. Consensus Value full depth profiles for BATS in the North Atlantic (31°40′N, 64°10′W) (open triangles; UConn and WHOI data) and the SAFe site (30°N, 140°W) in the North Pacific (WSU and WHOI data). Reprinted from Lamborg et al., 2012. *Limnology and Oceanogrpahy—Methods* 10, 90–100. Copyright 2012 by the Association for the Sciences of Limnology and Oceanography, Inc.

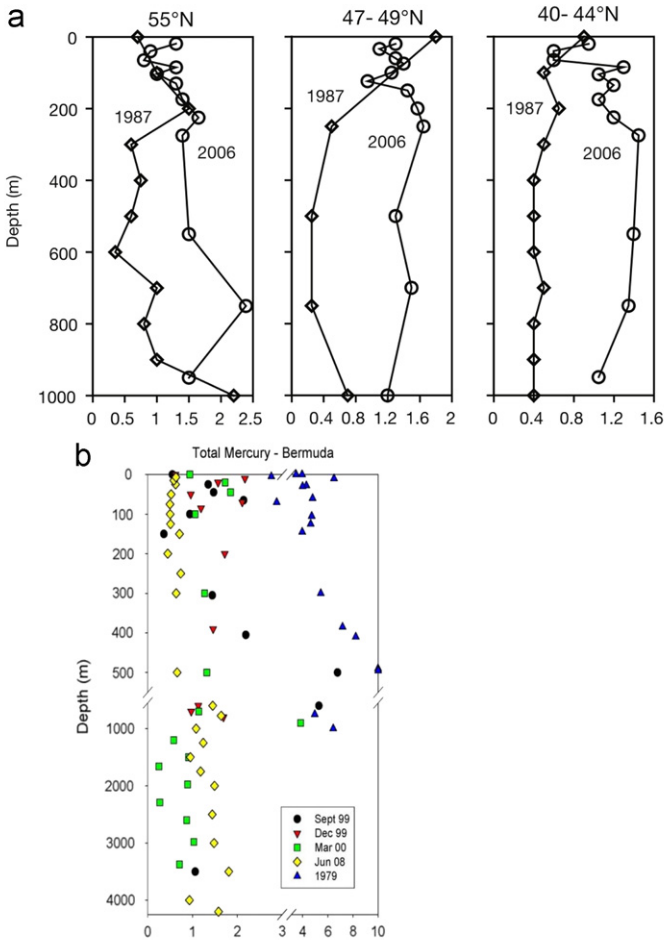

Fig. 4. Comparison of concentrations of total mercury in waters of the North Atlantic and the North Pacific. (a) data for a number of sites in the North Pacific Ocean. Figure reprinted from Sunderland et al., 2009. *Global Biogeochemical Cycles* 23, GB2010 with permission from the American Geophysical Union, copyright 2012; (b) data for a site near Bermuda (BATS) in the North Atlantic Ocean. Figure reprinted from Mason and Gill (2005) with permission from the Mineralogical Association of Canada.

Limited data from the far North Atlantic ($>50°$ N) (Mason et al., 1998) suggests somewhat higher concentrations in the sinking deep waters (1–2 pM) but the data is too limited to provide definitive evidence of a anthropogenic signal. Similarly, higher concentrations are evident in the sinking waters in the Antarctic (Antarctic Bottom Water (AABW)) which has an average concentration around 1.4 pM (Cossa et al., 2011; Sunderland et al., 2011). However, recently formed AABW would not have reached the SAFe site (30° N, 140° W) in the North Pacific (Fig. 3) and so cannot account for the higher concentrations measured at depth at this location.

The comparison of two profiles in Fig. 3, one from the Atlantic near Bermuda (the BATS site) and another from the North Pacific (the SAFe site) provides further data for understanding inter-ocean deep water differences. Through the thermohaline circulation, Hg in deep water (NADW); 2000–4000 m at BATS) moves from the North Atlantic, and mixes with AABW, before eventually being transported into the North Pacific (the “Ocean Conveyor Belt”; Broeker and Peng, 1982). Hammerschmidt and Bowman (2012) found similar NADW concentrations at another N. Atlantic station (35.4° N, 66.5° W) suggesting that these deep Atlantic water concentrations are representative. However, in the North Pacific most previous studies, as summarized in Laurier et al.

(2004), and shown in Table 1, have found lower concentrations, closer to 1 pM, than the values shown in Fig. 3.

Horizontal segregation (i.e., higher concentrations in the deep Pacific Ocean) is observed for the macronutrients (nitrate, phosphate, silicate) and some metals (Cd, Zn and Ag), but not for Fe, Al or Pb (Bruland and Lohan, 2004; Chester, 2003). For Fe, a relatively particle reactive metal, concentrations are very similar in the deep Atlantic and deep Pacific while Al has lower concentrations in the North Pacific deep waters as it is actively scavenged. In contrast, Pb has a substantial deep ocean anthropogenic signal in the North Atlantic as concentrations are five times higher than in the deep Pacific. The differences between basins results from the relative importance of deep water scavenging during the overall circulation relative to the additional inputs from the sinking and remineralization of organic matter during the roughly 1000 year long residence time of water in the deep ocean (e.g., Broeker and Peng, 1982; Chester, 2003). For the more particulate reactive metals, deep water scavenging results in the continual depletion during transit, and for metals such as Pb, anthropogenic inputs have exacerbated the amount in the Atlantic deep waters relative to the Pacific (Bruland and Lohan, 2004; Chester, 2003).

Overall, it appears from consideration of the datasets collected over the last 30 years that Hg behaves similarly to Fe and does not exhibit a strong enough anthropogenic signal in the deep North Atlantic that we can detect that North Atlantic deep water concentrations are greater than those of the North Pacific. Model simulations tend to support the notion of higher concentrations in the deep Atlantic (Strode et al., 2007; Sunderland and Mason, 2007; Soerensen et al., 2010). There has been a substantial collection of data recently through the GEOTRACES and CLIVAR programs and with other recent cruises and it is likely that the compilation of these data will lead to a more refined understanding of Hg changes during deep ocean water circulation.

Concentrations of dissolved Hg in surface water can be modestly depleted relative to deeper depths, which is indicative of surface scavenging by plankton and other particulate material (Fig. 3). This mechanism is supported by the frequently observed peak in concentration within or just above the thermocline region in the water column, in the location of major particle remineralization, and often concomitant with oxygen depletion (utilization) associated with strong net respiration driven primarily by microorganisms degrading sinking particulate matter (Volk and Hoffert, 1985). This "nutrient-type" behavior in the upper water column should be expected as Hg is known to be bioactive (as indicated by its bioaccumulation and association with soft tissue remineralization in deep waters). Below this depth, Hg concentrations often decrease to a uniform value in deep water ($>$1000 m).

However, there are multiple alternatives to this "typical" profile, including surface water enrichments (Fig. 5) and relatively uniform, "conservative-type" distributions (Fig. 4). Surface water enrichments should be expected because the principal route of Hg inputs to the ocean is atmospheric deposition. Concentrations of dissolved Hg in the mixed layer are typically $<$1 pM, while ocean precipitation often contains 50 pM or more. It should therefore be expected that Hg concentrations in surface waters range widely because (1) inputs of Hg to the ocean from the atmosphere can be sporadic, (2) the subsequent mixing of this enriched water into the surface ocean depends on local physics and can be variable, and (3) the depth of enrichment obtained from rain/ocean mixing can be anywhere from a few centimeters from the surface to many meters deep. Mixed layer samples, taken below the depth of immediate atmospheric input and as indicated by local hydrography, tend to be much less variable and are generally depleted of Hg with respect to deep waters (Cossa et al., 1997; Mason and Gill, 2005). Vertical profiles that are fairly uniform with depth tend to be observed in locations that are highly oligotrophic, such as the Sargasso Sea (Fig. 3), where scavenging rates tend to be lower.

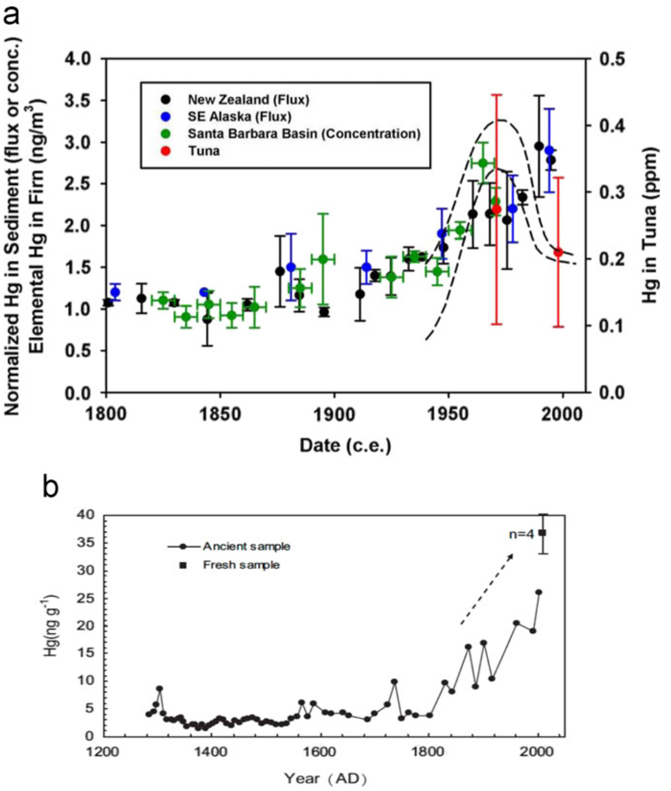

Fig. 5. (a) A compilation of data from a number of sources by Lamborg showing the historical trends in concentration for New Zealand sediment cores (Lamborg et al., 2002b); Alaskan lake sediments (Engstrom, pers. comm.); Santa Barbara basin marine sediments (Young et al., 1973); North Pacific tuna (Kraepiel et al., 2003); and elemental mercury trapped in firn (Fain et al., 2009); (b) historical trend in mercury concentration as recorded in bird eggs from the South China Sea. Figure reprinted from Xu et al., 2011. *Environmental Pollution* 159, 889–896 with permission from Elsevier.

Additionally, in some locations such the tropics of the Northern Hemisphere, there is potentially an anthropogenic signal in waters that show a mid-depth maximum because these waters were derived from the sinking of water masses from the surface in the temperate regions decades earlier (e.g., Cossa et al., 2004; Gill and Fitzgerald, 1988; Mason and Fitzgerald, 1993; Fig. 4(b)). Thus, differences in Hg concentrations between surface and deeper upper ocean waters may be related to historical enrichment of Hg in this sinking surface water, and the additional increases in concentration due to particle remineralization in subsurface waters as they are transported laterally. Such a scenario was observed in North Pacific Intermediate Water (Hammerschmidt and Bowman, 2012) and is supported by modeling studies of the equatorial and North Pacific by Mason et al. (1994b). This model suggested that the enhanced mid-depth water concentration in equatorial waters (Mason and Fitzgerald, 1993) was both a result of lateral transport and particle input. Additionally, equatorial upwelling of these waters supported the high concentrations and evasion of Hg^0 observed in this region (Mason and Fitzgerald, 1993; Mason et al., 1994b). Similarly, the mid-depth maxima in profiles from the North Atlantic (Cossa et al., 2004; Gill and Fitzgerald, 1988) reflect the transport of water masses with elevated concentrations laterally (Fig. 4(b)). Similar profiles have been observed for Pb, another metal that has a strong atmospheric signal and whose global biogeochemical cycle has also been substantially altered due to anthropogenic inputs (e.g., Wu and Boyle, 1997).

4. Temporal trends in Hg inputs and concentrations

4.1. Temporal trends in mercury inputs

Anthropogenic Hg emissions have increased atmospheric concentrations by at least a factor of three over the last century (e.g., Fitzgerald et al., 2005; Schuster et al., 2002; Lamborg et al., 2002b; Fain et al., 2009). Additionally, there is evidence of inputs of Hg into the atmosphere prior to the rapid industrialization in the last century due to the use of Hg in precious metal mining (Cooke et al., 2009; Schuster et al., 2002; Streets et al., 2011) and these sources should have further enlarged the inputs of Hg to the ocean (Hudson et al., 1995; Streets et al., 2011). Given such inputs, a concomitant increase in ocean Hg concentrations is likely, especially in surface waters that are actively exchanging Hg with the atmosphere (Fig. 1(A)). The percentage increases shown in Fig. 1(A) reflect only those of the last century and therefore underestimate the total change, especially for the sub-surface waters, due to all human-related inputs of Hg into the atmosphere, which have mostly occurred during the last 400 years (see Streets et al., 2011).

4.2. Temporal trends in seawater

Seawater Hg concentrations are regionally variable depending on proximity to anthropogenic sources and major deposition pathways. For example, within the last few decades, there has been a decrease in Hg emissions from Europe and North America due to regulatory control and an increase in emissions from Asia as a result of rapid industrialization in this region (Pirrone et al., 2010; Streets et al., 2011). These variations appear to be reflected in the decreasing Hg concentrations in upper ocean waters of some oceans while, for others, concentrations are increasing (Fig. 4), as projected by the model of Sunderland and Mason (2007). These changes track those of other pollutants added to the ocean from the atmosphere (e.g., Pb, CFCs, anthropogenic carbon and bomb-derived ^{14}C; Wu and Boyle, 1997; Doney and Bullister, 1992; Druffel, 1996; Sabine et al., 2004; Schlitzer, 2010; Fine, 2010).

Modeling of the impact of anthropogenic emissions on oceanic Hg concentrations uniformly predicts that surface ocean concentrations of Hg should have changed by a larger degree than those deeper, due primarily to the affect of dilution and the mode of addition (i.e., mostly from the atmosphere) (Streets et al., 2011; Strode et al., 2011). To date, it has been difficult to verify this increase with field data because of concerns about the validity of some early Hg measurements. Although deep ocean sediments accrue at rates too low to be useful records of recent deposition changes, there are some marine sediments that document increased loadings of Hg in an analogous way to that of lake sediments. These samples are from unusual locations and analysis of sediments from one such location, the Santa Barbara Basin (Young et al., 1973), shows a historical profile that matches lake reconstructions, suggesting that lake sediments can act as good proxies for marine loadings (Fig. 5(a)). Many of these lake sediment records show that atmospheric Hg deposition has increased by a factor of three or more during the last 100 years (Fitzgerald et al., 1998, 2005; Yang et al., 2010). There is also evidence for decreases in the last few decades for locations in the Northern Hemisphere, especially in Europe and North America, which is consistent with predicted emission trends (e.g., Engstrom and Swain, 1997; Kamman and Engstrom, 2002). Many of the sedimentary records are restricted to the last 100 years or so due to the limitations of ^{210}Pb dating and, therefore, do not provide any clear information about changes in deposition that may have occurred prior to this period (Cooke et al., 2010), which is recorded in other archives such as ice cores (e.g., Schuster et al., 2002).

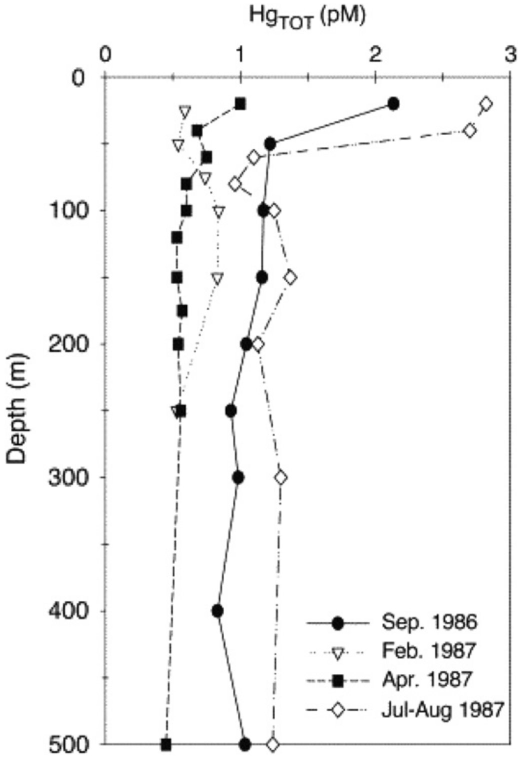

Fig. 6. Seasonal distributions of total mercury in the upper ocean of the North Pacific collected during the VERTEX Program (33°N, 139°W). Reprinted from Laurier et al., 2004. *Marine Chemistry* 90, 3–19 with permission from Elsevier.

What is more difficult to gauge is the change in concentration of Hg in seawater. It is possible to compare profile information collected at the same location and separated by significant time, keeping in mind the caveats about variability noted above. For example, as pointed out in Laurier et al. (2004) based on the data from Gill and colleagues from the VERTEX program (Fig. 6), there can be large seasonal changes in Hg water column concentrations that could be the result of deposition/mixing or perhaps more likely from changes in currents and ocean physics. With such large intra-annual variation at one site, the prospect of trying to discern relatively small changes in the mixed layer over a few decades is challenging.

With that caveat, two datasets have been compiled and compared that show changes in the Atlantic and Pacific Oceans (Fig. 4; Mason and Gill, 2005; Sunderland et al., 2009). Results suggest that Hg levels in have increased in the North Pacific Ocean between 200 and 1000 m (below the mixed layer) during the last few decades (Fig. 4(a)). Global scale models suggest that most change to the ocean as a result of anthropogenic emissions in the last 100 years should be confined to the upper ocean and the permanent thermocline in the North Pacific. These data are consistent with known circulation and ages of water masses. Results from Bermuda (Fig. 4(b)) suggest that there has been a substantial decrease in both Hg concentration and profile shape. Other historic data from the North Atlantic are similar (Cossa et al., 1992). The extent of changes for Hg and the changes in profile "shape" are consistent with data for Pb at the same location (Wu and Boyle, 1997), indicating that these changes may represent a valid trend. It could be argued that the reason for the rapid decrease of Pb is its removal from gasoline and that Hg has not similarly decreased. However, controls on emissions in North America and Europe have resulted in large declines in emissions over the past several decades (Streets et al., 2011) and concurrent decreases in Hg deposition have been observed in lakes in the mid-continental USA (e.g., Engstrom and Swain,

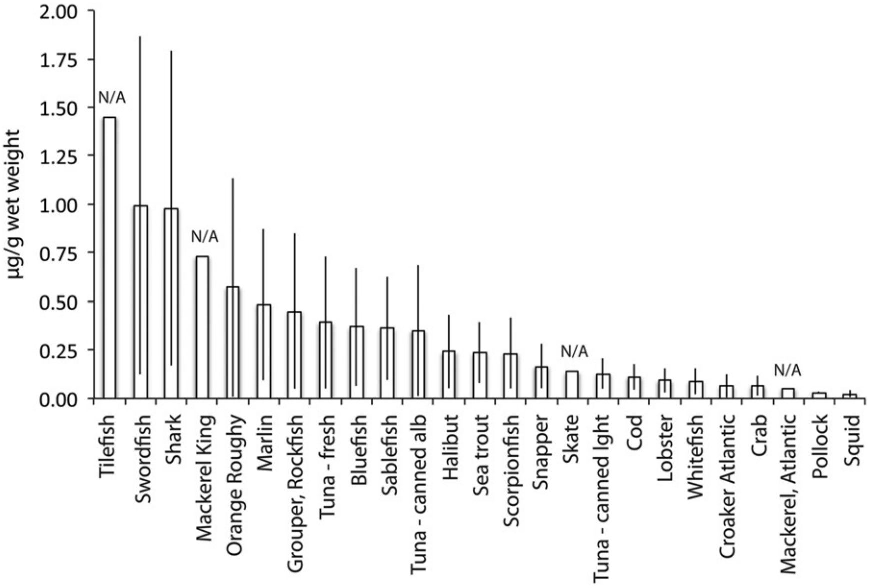

Fig. 7. Reported mercury concentrations (μg/g wet weight) in fish sold in the U.S. commercial market as available on the US FDA website, accessed in 2012. Figure drawn using the data (averages and standard deviation) from the website. N/A indicates that no standard deviation was listed.

1997). A similar reduction in Hg deposition to the North Atlantic is also possible given that the dominant path of air masses in winter is from the continental USA. While there are little data on decreases in deposition at Bermuda for Hg, this has been documented for other metals (Cd has decreased by 80%, Zn by ~55%, Cu and Ni by ~60%; Kim et al., 1999) (Fig. 7).

Data from the Mediterranean Sea also indicate a decrease in water concentration between 1990 and 2004 (Cossa et al., 1997; Coquery and Cossa, 1995). The trends in the available data are therefore consistent with the notion that the Atlantic and Mediterranean were significantly perturbed during the last 30–50 years but are now recovering as industries in North America and Europe have gradually improved emissions control technologies (e.g., Pirrone et al., 2010). Sunderland and Mason (2007) estimated that about 130 Mmol of anthropogenic Hg resides in the upper 1500 m of the ocean as a result of integrated inputs since industrialization. This amount translates into an approximate increase of about 0.24 pM if evenly distributed over depth, but given emission scenarios, concentrations in the North Atlantic are likely much more highly impacted by anthropogenic pollution than the Pacific Ocean (Sunderland and Mason, 2007). To the extent that anthropogenic Hg can be compared to anthropogenic C (e.g., Sabine et al., 2004), we would expect that about half the perturbation is confined to the upper 400 m in the Atlantic. The residence time of Hg is probably shorter than that of carbon in the mixed layer, so its distribution is likely biased slightly deeper than that for anthropogenic C. Overall, given the dominance of atmospheric inputs, we conclude that the secular changes in Hg portrayed in Fig. 4 are consistent with our understanding of Hg inputs and ocean cycling.

We also expect increases in ΣCH_3Hg in the ocean as a result of this anthropogenic enrichment because there is likely a first order relationship between the pools of available inorganic Hg and ΣCH_3Hg formed in the upper ocean. The CH_3Hg concentration in historical archives, such as marine bird feathers, increases over time, supporting this assertion. These archives show an increase of a factor of 4 for the North Atlantic during the last century (Monteiro and Furness, 1997; Monteiro et al., 1996) and a factor of 2–3 for the North Pacific (Vo et al., 2011). Evidence obtained from analysis of eggshells provides similar results (Fig. 5(b); Xu et al., 2011). These increases are somewhat greater than the estimated increases for total Hg inputs, likely reflecting other biological changes such as shifts in trophic structure and diet that may have exacerbated CH_3Hg bioaccumulation.

Overall, an increase in the relative rate of formation of ΣCH_3Hg could be linked to factors such as: (1) the increasing eutrophication of the ocean, which would result in more organic matter degradation and more methylation (Sunderland et al., 2009); (2) increases in the extent of low oxygen regions in the open ocean (Stramma et al., 2008); or (3) changes in microbial structure in the ocean water column. Because the organisms that produce ΣCH_3Hg in the ocean are not known, besides being part of the microbial loop (Heimburger et al., 2010), the importance of changes in community structure on the extent of Hg methylation cannot be evaluated. Alternatively, other factors besides changes in input may lead to a disconnect between the magnitude of Hg inputs and CH_3Hg bioaccumulation. Potential scenarios are increasing eutrophication of the ocean (a biodilution effect); changes in plankton community structure and/or changes in fish stocks due to fishing pressure (Driscoll et al., this issue).

In summary, the following hypotheses are evident from examination of all the available information: (1) surface ocean concentrations and distributions are variable and changing at different rates in response to fluctuations in atmospheric inputs; and (2) there have been greater historical inputs into some ocean basins such as the North Atlantic and Mediterranean Sea. Although the relationship between fish CH_3Hg concentration and total dissolved Hg is not the same for all waters, it is likely that fish CH_3Hg levels have changed in concert with changes in atmospheric inputs. As noted above, most modeling assessments of estimated changes in the upper ocean are based on anthropogenic emissions within the last century. Earlier releases to the atmosphere as a result of Hg extraction and use in mining and other activities (Hudson et al., 1995; Cooke et al., 2009; Schuster et al., 2002; Streets et al., 2011) will have further impacted ocean concentrations given the long residence time of Hg in deep ocean waters and its overall mixing dynamics.

5. Bioaccumulation and concentrations in marine biota

Individuals in North America are exposed to CH_3Hg primarily from the consumption of marine seafood (Mahaffey et al., 2004;

Table 2
Concentrations and bioaccumulation factors of MeHg in marine plankton[a].

Location	Water	Phytoplankton			Zooplankton		LogBAF (L/kg)	Refs
	Filt. CH_3Hg (pM)	MeHg[b] (pmol/g)	% MeHg	logBAF (L/kg)	MeHg[b] (pmol/g)	%MeHg		
Long Island Sound	0.15	0.5	9	4.2	5.5 ± 1.0		4.6	1
Jamaica Bay, NY	0.10	0.3	10	4.2	–			2
San Francisco Bay, CA	0.09	0.3–1	< 2	3.5–4.1				10
Gulf of St. Lawrence, Canada	0.58				22 ± 5	13	4.5 ± 0.2	11
Mesocosm Exp.	0.2–0.3			3.3[d]	2–6	~5	3.8–4.3	3, 4
North Sea	0.10	0.30	3	3.5				5
Bay of Fundy	0.30	0.75	6	3.4	2.4	30	3.8	6
NW Atlantic shelf	0.30	1.5		3.7				7
Tropical Pacific	(0.25)[c]				8.5 ± 5.5	28 ± 26	4.5	8
Southern Ocean	(0.3)[c]				14.0 ± 5.0	45 ± 29	4.7	8, 12
Arctic Ocean	(0.1)[c]				20 ± 15	70 ± 38	5.3	9
Mediterranean, Gulf of Lyons	0.23	0.8 ± 0.6	2	3.5	3.9 ± 2.7	12–21	4.2	13
Mediterranean, Marseille Bay	(0.25)				2.6 ± 2.0		4.0	13

References: 1: Balcom et al. (2004), 2: Balcom et al. (2008), 3: Kim et al. (2006), 4: Kim et al. (2008), 5: Baeyens et al. (2003), 6: Sunderland et al. (2010), 7: Hammerschmidt and Fitzgerald, (2006b), 8: Hirota et al. (1979), 9: Campbell et al. (2005), 10: Luengen and Flegal (2009), 11: Lavoie et al. (2010), 12: Hirota et al. (1989), 13: Daniel Cossa, personal communication, Cossa et al., in review.

[a] Wet-weight MMHg concentrations assume water content is 95% in phytoplankton and 90% in zooplankton (Knauer and Martin, 1972).

[b] All biota concentrations on a wet weight basis.

[c] Dissolved concentrations assuming averages of data in Table 1 or from Lehnherr et al. (2011).

[d] Modeled value based on mesocosm data.

U.S. EPA, 2002; Sunderland, 2007). Despite the toxicological significance of CH_3Hg in oceanic biota, there is limited understanding of factors controlling accumulation in marine food webs, especially into primary producers and consumers. Available data are collated in Table 2. Because CH_3Hg is biomagnified at every level of the food web (Mason et al., 1996; Wiener et al., 2003), levels in piscivorous wildlife are the greatest (Wiener et al., 2003). While CH_3Hg is also bioconcentrated from water by marine phytoplankton (Mason et al., 1996; Hammerschmidt and Bowman, 2012), comparatively little is known about the concentrations, dynamics, and controls on CH_3Hg bioavailability and uptake in marine environments.

Most research on Hg in marine systems has focused on quantifying levels in fish, particularly those consumed by humans (e.g., U.S. FDA, 2011; Fig. 7). As found in freshwater environments, CH_3Hg levels in marine fish appear to vary as a function of location (Rivers et al., 1972; Colaco et al., 2006), diet or trophic position and life history (Hammerschmidt and Fitzgerald, 2006b; Szczebak and Taylor, 2011), feeding depth (Choy et al., 2009; Monteiro et al., 1996), and age/size within a given species (Barber et al., 1972; Boush and Thieleke, 1983). As a result, fish with the greatest concentrations of CH_3Hg are either apex predators, old, or those that frequently feed in environs that have increased CH_3Hg levels in prey, such as king mackerel (*Scomberomorus cavalla*), shark, and swordfish (*Xiphias gladius*) and the long-lived demersal tilefish (*Lopholatilus chamaeleonticeps*) (Fig. 7).

As uptake of CH_3Hg into invertebrates from water is small, nearly all of the CH_3Hg accumulated by zooplankton (Tsui and Wang, 2004; Mason et al., 1996) and fish (Hall et al., 1997) is from diet. In contrast, Hg^{II} accumulated into phytoplankton is not readily assimilated by grazers (Mason et al., 1996; Lawson and Mason, 1998), as found for other cations (for Hg, Ag and Cd, assimilation efficiency (AE) is $<30\%$; for CH_3Hg, AE is 60–80%) (Mason et al., 1996; Reinfelder and Fisher, 1991). Similar low AE's are found for plantivorous fish, and these differences result in the increase in the %total Hg as CH_3Hg with trophic level. While the factors influencing CH_3Hg bioconcentration by primary producers in marine ecosystems are not well known, the speciation of CH_3Hg, which can vary between complexes with chloride and organic ligands in seawater, is important (Mason et al., 1996; Lawson and Mason, 1998). Passive uptake of uncharged chloride complexes is hypothesized to be an important route of both CH_3Hg and Hg^{II} accumulation in autotrophs (Mason et al., 1996). Recent studies suggest that Hg and CH_3Hg bound to thiols and other small organic complexes can be taken up into microbes by processes other than passive diffusion (Schaefer and Morel, 2009, Ndu, 2011).

Table 2 compiles the existing information on CH_3Hg in marine plankton, most of which is focused on biologically productive, near-shore ecosystems. It also shows data for zooplankton and illustrates the need for additional research while providing initial insight into the accumulation of CH_3Hg in marine food webs. From those investigations that measured CH_3Hg in both phytoplankton and filtered water, it is evident that bioaccumulation factors (BAFs, $L\,kg^{-1}$) of CH_3Hg by phytoplankton are relatively consistent among multiple near-shore ecosystems (Table 2). BAF is the wet weight concentration in organisms (mole kg^{-1}) divided by that in associated filtered water (mole L^{-1}). Investigations in freshwater and laboratory systems suggest that planktonic growth and cell size, both of which are often reduced in oligotrophic water, are related inversely to phytoplankton CH_3Hg concentrations (Mason et al., 1996; Pickhardt et al., 2002; Chen and Folt, 2005; Driscoll et al., this issue). Thus, a greater BAF for CH_3Hg in phytoplankton might be expected in oligotrophic waters. Similarly, BAF values for open water zooplankton (Table 2) are greater than those of coastal systems (Kim et al., 2006; 2008). Marine fish having CH_3Hg levels on the order of about 1 $\mu mol\,kg^{-1}$ wet weight, such as swordfish and king mackerel (U.S. FDA, 2011), have BAFs of about 10^7 given that CH_3Hg in surface waters often range from about 20 to 200 fM (Fitzgerald et al., 2007). This confirms the notion that CH_3Hg is biomagnified at all trophic levels (presumably 2–4 trophic levels), but that the initial bioconcentration of CH_3Hg by phytoplankton represents the greatest single contribution to bioaccumulation in marine food webs.

6. Future directions and research needs

Trace metal clean measurements of Hg species in the ocean span about 30 years and there is substantial variability in seawater Hg concentrations due to changes related to anthropogenic input variations over time and space during this period, as noted above. This applies to other trace metals (e.g., Pb, Ag; Wu and Boyle, 1997; Bruland and Lohan, 2004). The temporal and distributional data regarding concentration and speciation of Hg in the ocean is somewhat spotty (Mason et al., 1998; Mason and Sullivan, 1999; Mason and Fitzgerald, 1993; Cossa et al., 1992). However, this condition is rapidly changing as a result of a few recent initiatives, such as the Hg collections during the CLIVAR studies and the on-going GEOTRACES program (Sunderland et al., 2009; 2011; Hammerschmidt and Bowman, 2012; Lamborg et al., 2009; Bowman et al., 2012; Cossa et al., 2011). Fig. 8 illustrates some of the major efforts to describe horizontal and vertical distributions of Hg in the ocean. In addition to multi-station transects, the figure includes cruises where a few single stations (noted by triangles) were sampled for Hg species. The figure shows that the level of coverage of the ocean with Hg data is slowly increasing and, with some exceptions, locations of oceanographic importance have been targeted. Importantly, no recent studies have focused on locations of deep water formation, where the impact of anthropogenic inputs to the surface ocean over time may be recorded. Regions with poorer coverage include the Southern, Indian, and South Pacific Oceans, much of the Arctic Ocean and some important marginal seas such as the Gulf of Mexico, Caribbean Sea, Arabian Sea, Bay of Bengal, Sea of Okhotsk, and Sea of Japan, as discussed in other papers in this special issue.

Based on the research and modeling discussed above, the following key experimental developments, research plans and strategies are evident for the continued advancement of understanding of the behavior and fate of Hg species in the oceans. More oceanographic studies are warranted as much information and understanding can be gained from high-resolution water column sampling of dissolved and particulate phases and plankton in all the major ocean basins. The scientific community should actively seek opportunities to carry out further studies. While these studies should focus on collecting information throughout the water column, there should be a focus on regions of particular interest, such as the mixed layer, regions of low oxygen, especially those below productive surface waters such as the eastern tropical Pacific Ocean. While much of this work will be completed within the GEOTRACES program, and have been collected through other studies, such as in association with the CLIVAR program, there is a need for studies that include specific process-orientated investigations.

In addition to the open ocean, there is also a need for high-resolution water column profiles for Hg speciation on continental margins and associated upper slope stations (~500–2000 m) to examine the processes linking the biogeochemical cycling of Hg in coastal regions to the open ocean. It has been recognized that these regions are important for the exchange of many substances, including dissolved organic carbon, carbonate species, and other metals such as Fe. More studies in these regions will allow for a better estimation of the importance of coastal/ocean exchange in the global ocean Hg cycle. Finally, there are regions of special significance that require focused studies, such as the Arctic Ocean and Southern Ocean, and regions of high biological productivity, such as the upwelling zones off South America and Africa.

In concert with a call for the increased study of the ocean, there is a concomitant and much needed continued examination of the methods for the measurement of Hg and its species in ocean waters. Much progress in the comparison of sampling and analytical methods has been achieved through the GEOTRACES Intercalibration Study but there is a continued need to further intercalibrate, especially for the methods of determining methylated Hg species. Overall, $(CH_3)_2Hg$ has only been determined on board in some studies but in all cases using similar approaches (Mason and Fitzgerald, 1990, 1993; Mason et al., 1998; Mason and Sullivan, 1999; Hammerschmidt and Bowman, 2012; Lamborg et al., 2009.; Bowman et al., 2012). There are currently three main approaches for the measurement of CH_3Hg in ocean waters, which either rely on determination at sea, or back at the laboratory. The on-board methods are either direct ethylation after acid digestion of a large volume sample (Bowman and Hammerschmidt, 2011) or liquid-liquid extraction using methylene chloride, re-extraction into water and ethylation (Mason and Fitzgerald, 1993). Alternatively, samples have been frozen after stripping of $(CH_3)_2Hg$ for later analysis by the distillation/ethylation approach; or have been acidified and then analyzed by similar methods (Sunderland et al., 2009) or by hydride generation/CVAFS (Cossa et al., 2011; Heimburger et al., 2010). Because $(CH_3)_2Hg$ is not stable in acidified water (Black et al., 2009b; Mason, 1991), later analysis of acidified samples provides a value for ΣCH_3Hg if the samples have not been pre-stripped of volatile

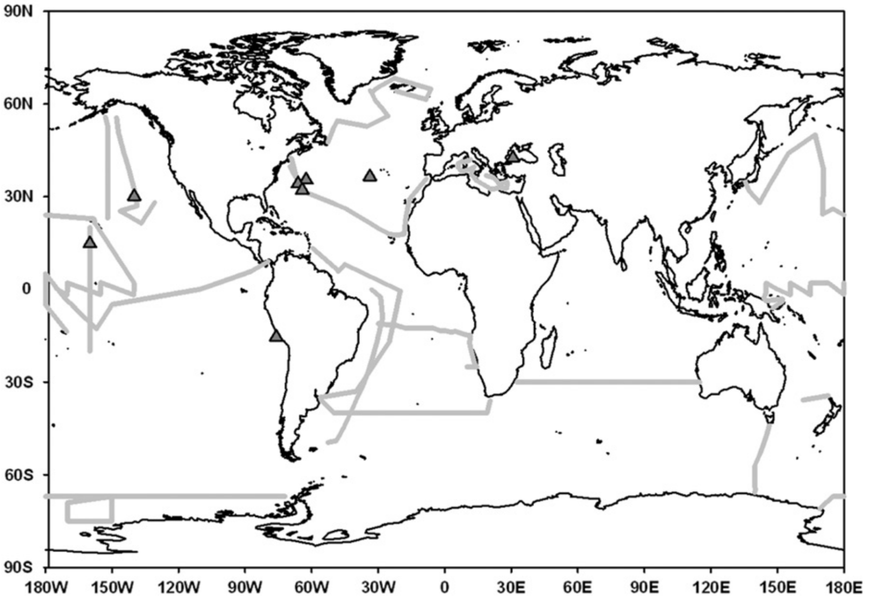

Fig. 8. Map showing tracks of the various cruises in the ocean where detailed Hg analysis (water column profiles speciation measurements) has been made. Triangles indicate cruises where measurements were restricted to only one or a few profiles.

Hg species. While further studies are required, it has been shown that the conversion of $(CH_3)_2Hg$ to CH_3Hg is quantitative upon acidification (Black et al., 2009b). Overall, as there has been minimal intercomparison of the methods for ΣCH_3Hg and because continual intecalibration is always a goal, there is a need to further compare and contrast the results obtained by the various methods, either separate analysis of CH_3Hg and $(CH_3)_2Hg$ or the determination of ΣCH_3Hg of an acidified sample.

Development of new technologies has advanced understanding by allowing the collection of semi-continuous data. For example, continuous measurement of Hg^0 at the air-seawater interface is now possible based on new techniques (Andersson et al., 2008, 2011) and these methods are amenable to on-board measurement with limited supervision and therefore should be an component to all on-going international oceanographic activities, in conjunction with the measurement of atmospheric concentrations with a Tekran analyzer, with or without the speciation unit. The speciation unit is a specialized instrument that requires much higher levels of expertise. Because of the importance of atmospheric deposition as a source of Hg to the ocean, it is also necessary to collect samples for the determination of wet and dry deposition (both gaseous and particulate) of ionic Hg whenever possible. Such studies should be coordinated and integrated with developing international programs such as the Global Mercury Observation Network (GMOS).

As noted, comprehensive and systematic investigations of CH_3Hg bioaccumulation and biomagnification in lower food chain organisms (phytoplankton and size-fractionated zooplankton) should be pursued in both near-shore and open-ocean marine systems in conjunction with the analysis of CH_3Hg and total Hg in filtered water. Where possible, analysis of multiple fish species that are both consumed by humans and occupy multiple trophic levels (i.e., planktivores to apex piscivores) should be included. To further understand trophic dynamics and sources of CH_3Hg, it would be advantageous to measure the stable isotopic composition of Hg (e.g., Senn et al., 2010; Gehrke et al., 2011), and if possible CH_3Hg, of biota at all levels of the trophic cascade. Unlike studies of freshwater lakes, there have been few systematic investigations of CH_3Hg bioaccumulation and biomagnification in either nearshore or open ocean marine systems. Ideally, prey items (small fish) should be analyzed as "whole-body" instead of fillet to better understand trophic transfer and estimate BAF (Gray, 2002), whereas muscle-only determinations can suffice for risk assessment for human consumption. In coastal ecosystems, there is an additional need to differentiate CH_3Hg accumulation through pelagic and benthic food webs. Stable isotopes of carbon and nitrogen, and if possible in conjunction with stable Hg isotope analysis (Atwell et al., 1998; Senn et al., 2010) can provide substantial information on the factors related to sources and bioaccumulation across trophic levels.

7. Summary and policy implications

Anthropogenic Hg emissions have impacted ocean ecosystems at varying levels globally. Estimates of human impacts on total Hg levels range from negligible changes in concentrations in the deep ocean waters (>1500 m) of the Pacific to an expected doubling of concentrations in the North Pacific surface and subsurface waters over the next few decades due to the growth of Asian emissions (Sunderland et al., 2009). Changes of this magnitude have been seen in the last 30 years for the upper North Atlantic Ocean (Fig. 4). Impacts of anthropogenic Hg inputs on the ocean are spatially variable due to differences in inputs globally and from ocean circulation. The anthropogenic component of these Hg inputs is also changing temporally and therefore there is a need to understand and model these trends and their impact on inputs to the ocean from the atmosphere.

While less important on a global scale, there is also a need to track and determine the degree to which Hg inputs to coastal waters are changing due to changes in watershed deposition and also through changes in point source inputs to these waters. Changes in other management practices that impact watershed runoff, and especially sediment and nutrient loadings to coastal waters (Driscoll et al., this issue) also need to be evaluated. Studies in freshwater systems and modeling suggest that CH_3Hg concentrations in higher trophic level fish of the open ocean will respond slowly to changes in anthropogenic inputs, given the global nature of Hg transport in the atmosphere and the potential importance of inputs from deeper waters, where CH_3Hg levels are higher, to the surface due to upwelling and meridional circulation. At current loading rates, it is likely that fish CH_3Hg concentrations will increase into the future for many ocean basins given the model predictions of increasing Hg levels in the future (e.g., Sunderland and Mason, 2007; Selin et al., 2010). Additionally, for many important commercial species (e.g., bluefin tuna), migration can result in fish being exposed to Hg from multiple different marine environments.

While the exact processes of conversion of inorganic Hg into methylated Hg forms are not known, it can be concluded that the sources of CH_3Hg to ocean waters are different from terrestrial water bodies and the coastal zone where methylation is thought to be tied to the microbial activity of sulfate-reducing and iron-reducing bacteria, and perhaps other microbes, dominantly in sediments (e.g., Gilmour et al., 1992; Hammerschmidt et al., 2006; Hamelin et al., 2011). The presence and high proportion of $(CH_3)_2Hg$ in the open-ocean water column provides further evidence that the main organisms or processes responsible are different. Furthermore, methylation in the open-ocean water column is more important than production in deep-sea sediments in terms of the CH_3Hg that is accumulating in ocean fish.

There is a need to convey a message that while elevated levels of CH_3Hg in marine fish are a concern there are many health benefits associated with consuming marine fish (Mahaffey et al., 2011; Oken et al., 2012). There is a need to develop outreach and information for the public that incorporates a balanced risk and benefit analysis and provides clear guidance on the best fish for consumption by different population groups. Additionally, there should be additional efforts made to inform the population on other concerns related to fish consumption, such as the potential for overfishing of certain species, especially apex predatory fish, and the impacts of marine aquiculture on the environment. Overall, the outreach needs to convey the message that it is possible to consume marine fish and other seafood to receive the maximum benefits without being adversely impacted by the elevated levels of CH_3Hg in top predator fish.

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