Marine Biogeochemical Cycling of Mercury

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Received August 31, 2006

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1. Introduction

In *Walden*, Thoreau[1] noted that "the largest pond is as sensitive to atmospheric changes as the globule of mercury in its tube". Here, we consider the modern understanding of the biogeochemistry, speciation, distribution, behavior, and fate of mercury in the ocean, the Earth's grandest pond. Elemental mercury (Hg^0) and surficial deposits of vermilion colored cinnabar (HgS) are readily apparent in mineralized regions (i.e., "mercury belts"[2]), and human involvement with this fascinatingly useful element predates recorded history. Today, anthropogenic interferences in the global Hg cycle are significant.[3−5] Mercury thermometers are becoming antiques, and "zero Hg" legislation is not uncommon. Societal responses and concerns are driven primarily by international worries relating to human exposure to monomethylmercury (MMHg), which is the highly toxic form of Hg that accumulates in aquatic and terrestrial organisms. MMHg is produced from inorganic forms of Hg by microorganisms, particularly sulfate-reducing bacteria (SRB),[6−8] although other functional groups also may be important (e.g., iron reducers[9]). Aquatic ecosystems appear to be the most susceptible to MMHg contamination, as they are major repositories of natural and pollution-derived Hg and host active populations of Hg methylating bacteria. Indeed, natural processes of MMHg production, bioaccumulation, and biomagnification often result in fish MMHg levels that exceed those deemed safe for human consumption by regulatory agencies (e.g., U.S. EPA[10]).

Consumption of fish is the principal route of human exposure to MMHg.[11] Moreover, most of the fish consumed by humans is of marine origin,[12] and largely from the coastal zone.[13] Given concerns related to MMHg and human health and its production and prevalence in natural waters, one might anticipate that the cycling of Hg in the oceans would be thoroughly investigated and well-known. Unfortunately, that is not the case. Indeed, the biogeochemistry of Hg in the marine environment is characterized by undersampling and understudy. As this thematic volume illustrates, genuine trace metal knowledge for the oceans is less than 40 years old.[14−17] In general, prior efforts were compromised by sampling artifacts and analytical deficiencies.[18] In fresh waters, ultraclean trace metal techniques ("clean-hands, dirty hands" protocols) and high-quality Hg measurements did not appear until the late 1980s.[19]

1.1. Overview and Uncertainties

A useful though simplified view of marine Hg cycling is depicted in Figure 1.[20] This illustration captures major features and suggests appropriately that the Hg distribution in the oceans is not yet well established. The oceanic Hg reservoir, in contrast to the atmospheric pool, is far larger than annual fluxes, and thus shows a much smaller anthropogenically related increase over the past 150 years—about 10% according to Figure 1. Mason and Sheu[20] suggest that most of this change has occurred in the deep ocean (greater than 500 m, in their model). However, this representation is contrary to the known penetration of anthropogenic CO_2, which is limited, on average, to the upper 1000 m of the ocean.[21] Anthropogenic Hg in the oceans, most of which is derived from atmospheric deposition, would be expected to show a distribution similar to that of CO_2, such as depicted in the GRIMM model.[22] In the GRIMM representation, the

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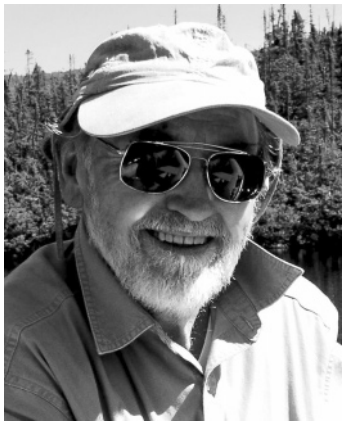
10.1021/cr050353m CCC: $65.00
Published on Web 02/14/2007



William F. Fitzgerald has been pursuing Hg in the environment for nearly forty years. He is a native Bostonian and first generation American, whose interest in chemistry began at Boston Technical High School. He was educated as a classical chemist and received a B.S. and M.S., respectively, from Boston College and the College of the Holy Cross. The lure of the oceans moved him toward marine biogeochemistry and graduate studies in the newly formed Massachusetts Institute of Technology and Woods Hole Oceanographic Institution Joint Program in Oceanography. He received his Ph.D. in 1970 as the first graduate in Chemical Oceanography. His future scientific focus was spurred and shaped, while a graduate student, when he became aware of the Minamata Bay methylHg poisoning, a major human tragedy, and the limited knowledge of Hg cycling in nature. He is currently a Board of Trustees Distinguished Professor in the Department of Marine Sciences at the University of Connecticut, where he established The Mercury Laboratory in the early 1970s. Dr. Fitzgerald, along with his students and co-workers, has been recognized nationally and internationally for pioneering and on-going efforts concerned with the complex and ultratrace cycling of Hg in the environment. In 2003, and in recognition of his "outstanding contributions to environmental chemistry", he received the Patterson Award and Medal from the Geochemical Society.

Carl Lamborg received a B.A. in Chemistry from Oberlin College in 1986, a M.S. degree in Environmental Chemistry from the University of Michigan School of Public Health in 1992, and a Ph.D. in Chemical Oceanography at the University of Connecticut in 2003. He is currently an assistant scientist in the department of Marine Chemistry and Geochemistry at the Woods Hole Oceanographic Institution. His research interests include the atmospheric and aquatic chemistry of trace metals, especially mercury. Recent research and publications have included investigations of Hg and methylHg cycling in hydrothermal vents and the Black Sea, as well as the behavior and fate of Fe, Zn, and Co in the open ocean.

Hg pool in the surface mixed layer of the ocean (0−100 m) has increased about 90% (from 29 to 54 Mmol), while the larger Hg pool in the main thermocline (100−1000 m) has risen only about 20% (from 900 to 1080 Mmol); the cold, slow-mixing abyssal ocean (1000−4000 m) has not changed appreciably. These are critical estimates because the total annual accumulation of MMHg in all ocean fish is about 0.2 Mmol.[23] Although, the Mason and Sheu and the GRIMM

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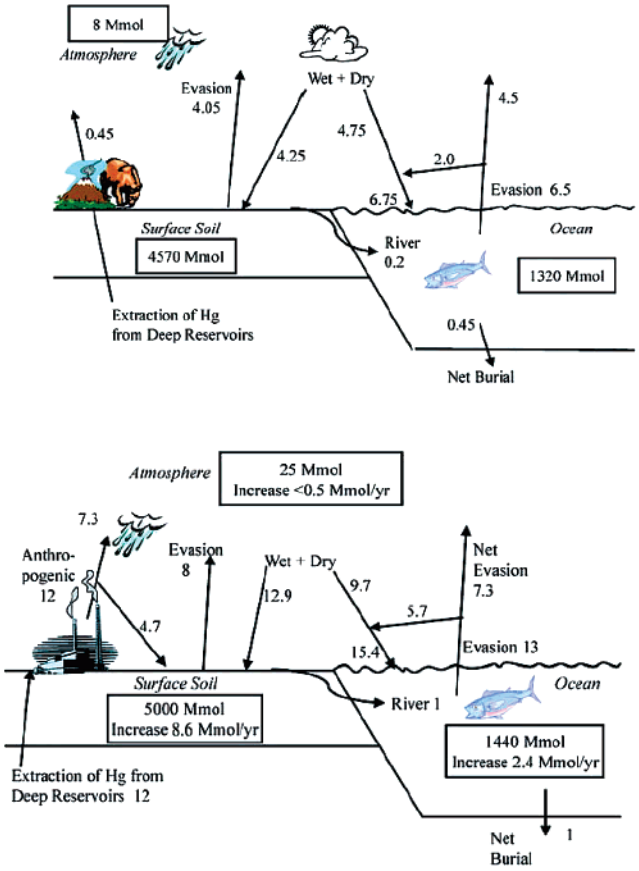

Figure 1. Global Hg cycle. The top panel represents the preindustrial cycle (ca. 200 years ago), while the bottom panel is the current status. All fluxes are in Mmol year^{-1}, while the reservoir burdens are listed as Mmole inside boxes, along with estimates of the current rate of change in each reservoir. Reproduced from ref 20, Copyright 2002, by permission of the American Geophysical Union.

models differ significantly in their representation of ocean mixing and biogeochemical cycling of Hg, both are simpli-

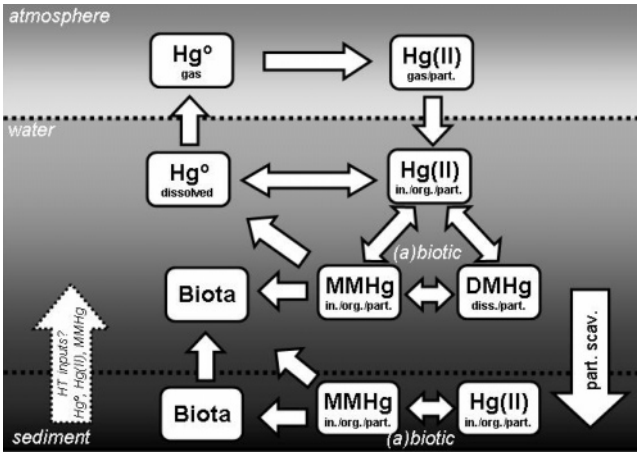

Figure 2. Biogeochemical cycling of Hg in the ocean.

fications of a very complex system. Nevertheless, they represent our current capability to integrate knowledge of marine Hg cycling, and they are therefore extremely useful. For example, these scaling exercises beg the following questions: How well are these predicted anthropogenic changes constrained? Is Hg currently increasing, as suggested, in the biogeochemically active regions of the Earth's surface? How might these changes and differences influence levels of MMHg in biota?

1.2. Mechanistic Understanding

Paradoxically, mechanistic and speciation information for Hg in the oceans is better constrained, and there is agreement on some principal aspects of the marine biogeochemistry of Hg. For example, it is well-established that atmospheric deposition is the primary source of Hg to the oceans (Figure 1).[20] Hg does not correlate with the major marine nutrient cycles (e.g., N, P, Si) and as a result does not display a nutrient-type distribution.[24] Rather, profiles of Hg show evidence of atmospheric inputs and scavenging at depth.[25] The limited oceanographic data do suggest a "scavenging" distribution with greater amounts in deep waters of the North Atlantic compared to the North Pacific Ocean.[24,26,27]

Figure 2 illustrates the potential biotic and abiotic reactions, transformations, exchanges within and among reservoirs, and biological uptake of the primary Hg species in marine systems. Hg is found typically in three chemical forms in the marine environment: elemental Hg (Hg^0), divalent ionic Hg (Hg(II)) in a variety of inorganic and organic complexes, and methylated forms that include both MMHg and dimethylmercury (DMHg). All of these species groups are linked intricately through the Hg(II) pool. For example, Hg(II) may be reduced to Hg^0 or transformed to MMHg by both biological and abiological mechanisms. Hg^0 is a major species in natural waters, and its cycling is especially important and pronounced in the marine environment.[22,28−31]

Indeed, the biotic[31−33] and abiotic production,[34,35] oxidation,[34,36,37] and sea−air exchange of Hg^0 dominate the transport and deposition of Hg on local, regional, and global scales.[22,29] Net MMHg production in coastal marine sediments[38−41] is substantial, and recent work suggests that most MMHg in marine fish might have a near-shore sedimentary origin (see section 7.4).[42] MMHg production in the water column of the open ocean has been hypothesized,[43] and both MMHg and DMHg have been found in the low-oxygen regions of upper waters in the equatorial Pacific Ocean.[44−46] Open-ocean water-column sources of MMHg are not likely to be mediated by anaerobic SRB, except possibly in low-oxygen microenvironments. Abiotic production is possible,[47−49] and other bacterial groups, as noted, might have roles. However, advection of alkylmercury species from near-shore regions is an intriguing source especially in the equatorial Pacific, which is characterized by a variety of zonal currents and countercurrents that have a near-shore origin.[50] Moreover, particulate Fe, with a potential neritic linkage, has been observed >900 km into the open North Pacific.[51]

With the exception of the upper waters in the Equatorial Pacific, and coastal regions, there is little evidence for MMHg levels in the water column that are above the current detection limit of about 0.05 pM.[24,42] DMHg has been observed during two Atlantic expeditions, and a weak correlation ($r^2 = 0.2$) with apparent oxygen utilization was found.[52] Further, the major source of DMHg at depth is unknown, but it may be production in the upper ocean and advected in recently formed sinking waters. It is also evident that the aqueous lifetimes for both MMHg and DMHg are short compared to ocean mixing time scales (500−1000 years). DMHg concentrations decrease with age of the water mass, and there is no buildup of MMHg that is detectable in deep waters of the Atlantic or Pacific.[24,26,52,53] Significant levels of MMHg have been observed recently in hydrothermal (HT) vent fluids.[54] Although results of this exploratory study suggest a substantial flux of MMHg from submarine HT systems, near-field demethylation and deposition appear to limit the significance of this source to the oceans and its biota.

This review examines the shape and status of Hg science in the oceans. We are focusing on current knowledge and understanding of its marine cycling, its biogeochemistry, and its place in the global environment, especially the critical linkages to the atmosphere, watersheds, fresh waters, and human activities. This examination also will include analytical details, oceanic patterns, mechanisms, methylation, HT and sedimentary interactions, speciation, organic complexation, bioaccumulation, and modeling.

2. Analytical Methods

In this section, we summarize some of the analytical and methodological innovations that have made accurate determination of Hg in the marine environment possible. Equally important to the highly sensitive and selective methods for Hg analysis has been appreciation of the need for, and implementation of, "ultraclean" sample preparation, collection, and handling techniques. The late Clair Patterson, provocateur of environmental Pb research, is often credited with bringing this critically important issue to the attention of other environmental trace-metal scientists.[15] While clean techniques had been in use in studies of some metals, Patterson's warnings about sample cleanliness were widely influential and especially important for Pb (where contamination was large and widespread) and Hg (where environmental levels are so low that even minor contamination is ruinous[19]).

2.1. Hg Detection

The technique used most frequently for Hg determination in environmental samples employs cold vapor atomic

fluorescence detection (CVAFS).[55] This method makes use of Hg autofluorescence: the narrow band emission of ultraviolet (UV) radiation by Hg^0 atoms during relaxation to ground state following absorption of radiation of nearly identical wavelength (253.7 nm). Thus, analyte Hg atoms may be excited with radiation from a Hg vapor lamp, and their fluorescence may be observed with little filtering. This results in extraordinary selectivity and sensitivity, with typical detection limits in the tens of femtomoles range. Hg determinations in seawater also have been made by atomic absorption spectrometry,[56] neutron activation,[57,58] inductively coupled plasma atomic emission spectrometry,[59] and inductively coupled plasma mass spectrometry (ICPMS)[60].

In a 1979 paper, Fitzgerald and Gill[61] introduced the Au amalgamation preconcentration step that has made possible measurement of Hg in the atmosphere and natural waters. This work benefited from earlier analytical efforts to measure Hg in air.[62−64] In this approach Hg^0 is first collected on a Au surface, which is frequently in the form of either gold-coated quartz sand or beads packed into a quartz "trap" tube. This can be used for sampling Hg^0 in air, by drawing gases through the trap, or for other media after extraction of Hg(II) (typically, by acid "digestion"), reduction of Hg(II) to Hg^0 with a reducing agent (e.g., Sn(II)), and then sparging Hg^0 from solution and onto the trap. Following the Au-surface preconcentration, the Au is heated and liberated Hg^0 is delivered via a carrier gas (Ar or He) to a detector. When a sample is "digested" with a strong oxidizing agent (e.g., UV light, MnO_4^-, BrCl), the determination is referred to as "total Hg".[18]

2.2. Speciation Analysis

Certain species of Hg in seawater can be quantified by modifying the "total Hg" approach in the following ways. Dissolved volatile Hg species (Hg^0 and DMHg) may be sparged from a water sample directly, without addition of a reducing agent, and separated with Tenax (DMHg only) and Au traps in series. MMHg is less volatile and determined after chromatographic separation from Hg(II). To promote volatilization and chromatographic separation, aqueous Hg species often are derivatized with $Na(C_2H_5)_4BO_4$, to form methylethylmercury (MEHg, the MMHg derivative) and diethylmercury (DEHg) from Hg(II). Derivatization is difficult for bulk seawater, and thus the analytical process is preceded by isolation of MMHg from seawater salts and solids, by either solvent extraction[42] or distillation.[65] Once MEHg is synthesized, it is sparged from solution and preconcentrated on Carbotrap or Tenax. The sorbed Hg species (MEHg and any residual DMHg and DEHg) are then desorbed by heating the Tenax, separated with a gas chromatographic column (generally OV-3 on Chromosorb), pyrolytically reduced to Hg^0, and determined by CVAFS.[55,66]

These same analytical techniques are applicable to the determination of Hg associated with marine sediments, particles, and biota. Prior to analysis, analyte Hg species must be extracted from the solid phase. For total Hg, this is accomplished traditionally with a strong acid digestion, often in conjunction with wet-chemical oxidation. Extraction of MMHg from sediments and biological tissues is not much more complicated, as MMHg is relatively resistant to thermal and chemical demethylation. MMHg extractions typically involve either aqueous-phase distillation with weak acid[67] or digestion with alkaline[66] or dilute acid solutions.[68,69]

An operationally defined "reactive Hg" species[11,70] also is assayed commonly in marine waters. In this technique, Hg is sparged from solution after addition of a reducing agent but without prior chemical digestion or oxidation. This "easily reducible" Hg(II) subset, which is thought to include complexes with inorganics and low-molecular weight organics, has been argued to be a proxy for Hg that is available to participate in various biogeochemical reactions including reduction and methylation. While this assay has met some success in aiding understanding of Hg cycling, further examination has illustrated its highly operational nature[71] and its inappropriateness as a universal proxy.[72]

2.3. Analytical Innovations

Recent analytical innovations have come in two general classes: (1) on-line or automated analyzers and 2) exploitation of the large family of Hg stable isotopes by ICPMS. Automated and on-line systems include continuous air monitors (some with speciation capability), flow injection systems for dissolved Hg^0 and MMHg analysis, and direct-pyrolysis total Hg analyzers for solid matrixes.[73−79] While analysis of the Hg isotope fraction, now made possible with the latest generation of multicollector ICPMS systems, is still in its infancy,[80−83] deliberate stable isotope additions in bench- and watershed-scale process studies are in frequent use.[84,85] In particular, and as an extension of earlier applications using radioactive ^{203}Hg,[86,87] stable isotope additions are being applied widely for assays of Hg methylation and MMHg demethylation in sediments.[39,40,42,88−92] For transformation experiments with sediments, enriched stable isotopes of Hg (as Hg(II) and CH_3Hg) typically are injected at tracer levels into intact cores (often at 1−10% of ambient Hg levels), incubated under in situ conditions, and subsequently extracted for analysis. Although gross rates of Hg methylation and demethylation determined from these tests presumably overestimate the natural rate of transformation, they have provided valuable information regarding environmental factors affecting the processes. Applications of these techniques are discussed in sections 7.2 and 7.3.

3. Oceanographic Mercury Distributions

Marine biogeochemistry/chemical oceanography can be defined broadly as the science that studies the reactions and interactions (e.g., biological, chemical, geological, physical) of substances in the oceans and the effects of mixing processes on their distributions. If the biogeochemical activities of an element, for example, occur at very slow rates or involve rapid recycling, or if the water-column/sedimentary processing is of limited magnitude, then the distribution of the element in the oceans will be governed by simple mixing. Elements such as Na and Cl show conservative patterns in the marine environment. Nonconservative distributions are displayed by biologically active constituents such as nutrients (NO_3^-, HPO_4^{2-}, and $Si(OH)_4$), gases (O_2 and CO_2), trace metals (Fe, Zn, and Cu), and tectonically or diagenetically generated species such as ^3He and Rn. There is no question that Hg is both biologically, chemically, and geologically active, so a nonconservative distribution should be expected. What is found?

3.1. Total, Reactive, and Dissolved Hg

Laurier et al.[27] and Mason and Gill[24] have summarized and interpreted Hg data from the principal open-ocean investigations that have taken place since 1979. North Pacific results are presented in Figure 3. In 1987, and as shown for the VERTEX V7 T7 station, Gill and Bruland[25] reported

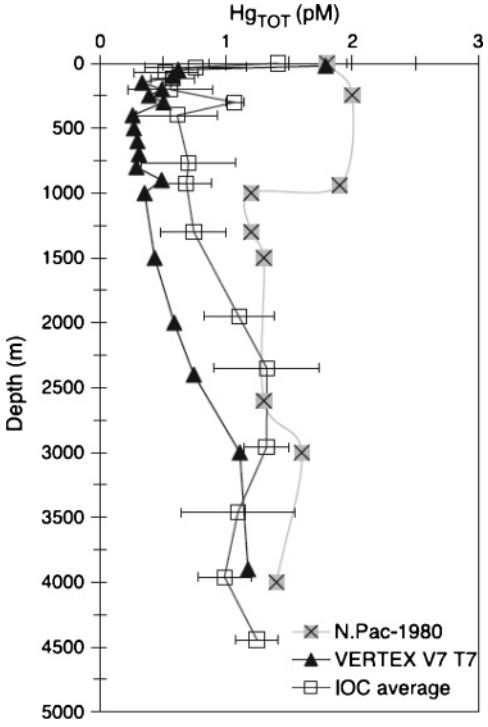

Figure 3. Vertical profiles of total dissolved Hg from the North Pacific Ocean. Reprinted from ref 27, Copyright 2004, with permission from Elsevier.

what can be described as "a classic vertical distributional profile for mercury in the northeast Pacific Ocean".[93] This distribution for Hg shows a transient-type, atmospherically enhanced level of 1.8 pM at the surface and a minimum of 0.3 pM in the upper ocean, which is a sign of apparent scavenging by particulates. There are increasing concentrations of Hg at depth (to ca. 1.2 pM near 4000 m), suggestive of regeneration/remineralization processes. A station sampled in the central subtropical North Pacific in 1980 (N.Pac-1980; Figure 3) showed similar deep water values (1.4 ± 0.4 pM) but greater concentrations over the upper 940 m (1.9 ± 0.7 pM) and no scavenging minimum or thermocline maximum.[94] Also presented in Figure 3 is the average Hg distribution from the 2002 IOC (Intergovernmental Oceanographic Commission) cruise, which includes data from three deep stations and six others (sampled to about 1500 m), distributed over a large portion of the North Pacific between Japan and Hawaii. Considering the spatial and temporal variability, and analytical uncertainties associated with these investigations, the Hg levels between 1000 and 3000 m are probably not statistically different and regeneration at depth appears likely.

Laurier et al.[27] also presented an interocean comparison of results from the 1996 IOC expedition to the South and equatorial Atlantic with those of the 2002 IOC cruise in the North Pacific. Given the caveats related to undersampling, natural variability, and analytical uncertainly, this comparison, which is shown in Figure 4, suggests that Hg scavenging is occurring in the water column and there may be a decline in average Hg concentrations between the deep waters of the South Atlantic and the North Pacific. The authors note that this "inter-ocean fractionation and distribution agrees quite well with the estimated oceanic residence time for Hg at ca. 350 yrs." This conclusion is quite tenuous, however, given the degree of variation associated with Hg concentrations in deep water of the Atlantic (Figure 4).

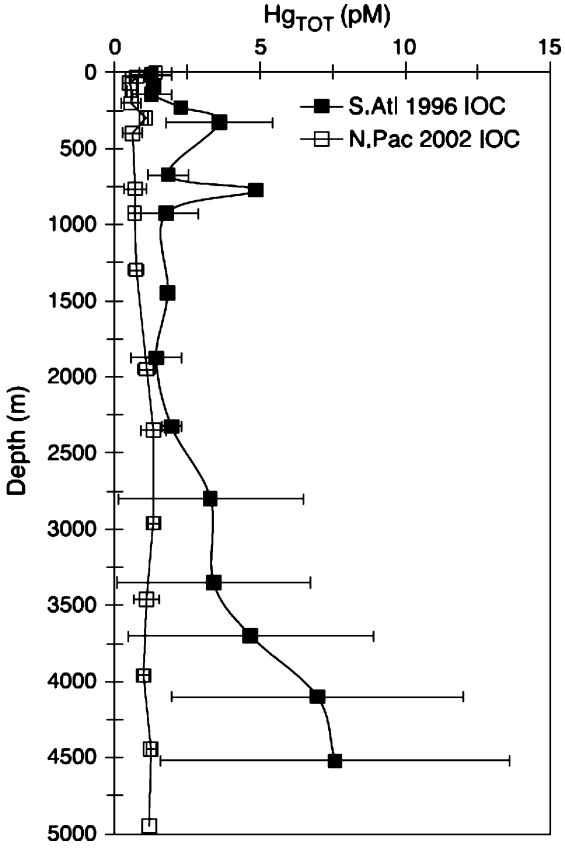

Figure 4. Vertical profiles of total dissolved Hg from the South Atlantic and North Pacific Ocean basins. Reprinted from ref 27, Copyright 2004, with permission from Elsevier.

Evidence of temporal changes for Hg in the upper ocean that occur over seasonal to decadal time scales is presented, respectively, by Laurier et al.[27] and Mason and Gill.[24] Total dissolved Hg, as illustrated in Figure 5 for the upper 500 m of the water column in the North Pacific (33 °N, 139 °W), shows well-defined seasonal variations that differ by a factor of 2−3 over a 12-month period. In contrast, a decrease of Hg in the upper reaches of the water column of the western North Atlantic Ocean near Bermuda has reportedly occurred between 1979[94] and 1999/2000.[95] These data are illustrated in Figure 6.[24] The latter phenomenon has been attributed to a likely decline in anthropogenic Hg inputs to the North Atlantic. This pattern is similar to that reported for Pb in seawater from the same region.[96] A 20-year decrease of Hg in the North Atlantic is less certain, however, as the difference in Hg levels between 1979 and 1999 near Bermuda is within the variation observed over an annual cycle in the North Pacific (Figure 5). Moreover, there is evidence to suggest that levels of Hg^0 in the oceanic atmosphere have not changed during the same time period.[97]

3.2. Monomethylmercury (MMHg)

The detection limit for MMHg in seawater is currently about 0.05 pM.[98] It must be lowered to explore the oceanic cycling of this toxicologically important species. Indeed, and with the exception of the coastal zone and peripheral seas, the only unequivocal evidence for oceanic levels of MMHg greater than the detection limit is that reported for the Equatorial Pacific Ocean.[44−46] MMHg is distributed throughout the water column of the Black and Mediterranean Seas.[98,99] Mason et al.[26] reported finding MMHg at depth in

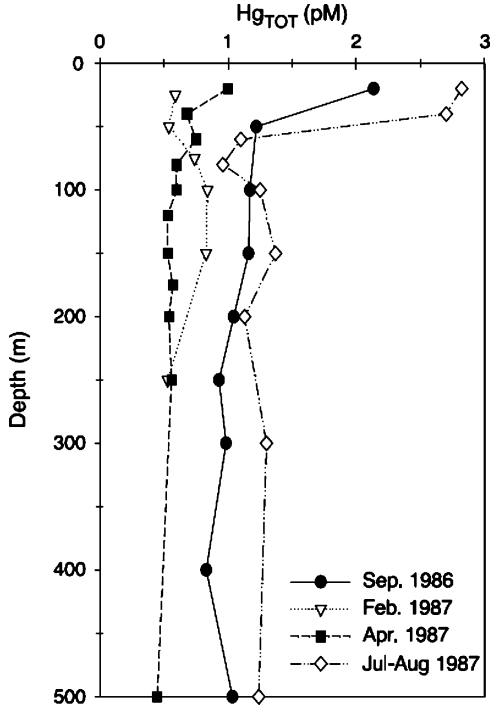

Figure 5. Seasonal variations in total dissolved Hg measured during VERTEX in the NE Pacific Ocean. Reprinted from ref 27, Copyright 2004, with permission from Elsevier.

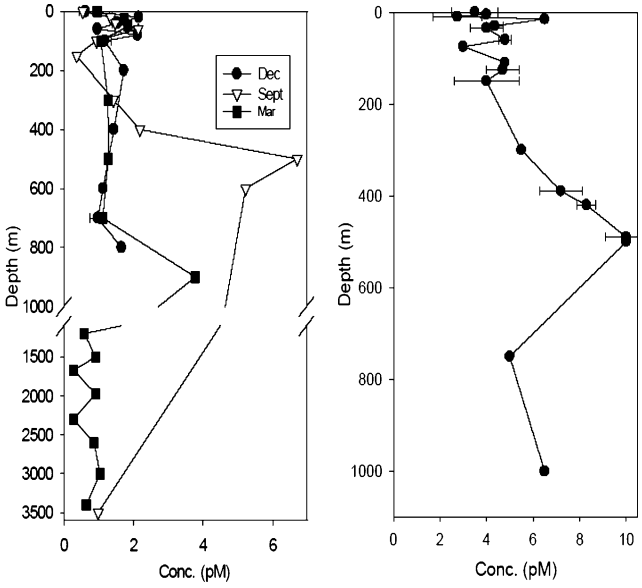

Figure 6. Total dissolved Hg from the NW Atlantic Ocean near Bermuda. The left panel shows measurements made in 1999/2000, while the right panel displays results from a 1979 campaign. Reprinted from ref 24, Copyright 2005, by permission from the Mineralogical Association of Canada.

the North Atlantic Ocean. However, the authors question the reliability of these measurements given the high detection limit (0.5 pM) and likely problems with the analyses.[24] Moreover, subsequent investigations with better sensitivity (i.e., 0.05 pM) have not detected MMHg in the open Atlantic.[52] MMHg was not detected during the 2002 IOC cruise in the North Pacific Ocean.[24] MMHg cycling in hydrothermal environs (section 4), hypoxic/anoxic systems (e.g., Black Sea; section 5), and marine sediments (section 7) are considered separately.

3.3. Dimethylmercury (DMHg)

DMHg has been found at depth in the open ocean and peripheral seas.[44,46,52,99,100] However, it has not been detected in the mixed layer where evasional losses may occur and decomposition via photolysis and thermal instability are likely. Mason and Fitzgerald[46] have suggested that DMHg might be a source of MMHg in the water column (Figure 2). Unfortunately, this mechanism cannot be evaluated until MMHg can be measured at levels below the current limit of detection in seawater.

During the 1996 IOC campaign in the South Atlantic Ocean, DMHg levels were greatest in recently formed intermediate and deep waters.[52] These water masses are respectively the Antarctic Intermediate Water (AIW) and Antarctic Bottom Water (ABW). Mason and Sullivan[52] also noted a weak correlation between DMHg and apparent oxygen utilization in the upper 1500 m of the water column ($r^2 = 0.2$). They suggested that the primary origin of DMHg at depth is biologically mediated synthesis in surface waters, which sink as part of the thermohaline circulation. Moreover, and with reference to the 1993 IOC study in the North Atlantic, Mason et al.[26] suggested that some heterotrophically driven production of DMHg may be occurring at depth. The latter hypothesis is consistent with results from the Equatorial Pacific,[44,46] where DMHg and MMHg were enriched in low-oxygen waters below the thermocline and not present in the mixed layer. Given the relatively short lifetime of DMHg (0.3−30 years)[46] relative to the millennial scale ventilation rate of deep waters, it seems likely that some production must occur at depth. When results from the 1993 and 1996 IOC cruises are compared, there is a significant decrease in DMHg associated with the core region (2000−3000 m) of North Atlantic Deep Water (NADW) during its southward journey through the Atlantic Ocean. The mean values of 0.16 ± 0.08 pM obtained in the North Atlantic study are much greater than the 0.021 ± 0.011 pM found in the South and Equatorial Atlantic.[52] While this pattern may suggest net decomposition of DMHg as the water mass ages, it is more likely that levels reflect region-specific differences of in situ production.

3.4. Elemental Hg

As the species that forges a sea−air link in the cycle, a comprehensive understanding of aqueous Hg^0 cycling and its temporal and spatial patterns is critical in improving predictive models for the aquatic and atmospheric biogeochemistry of Hg and MMHg in natural waters. With an aqueous solubility that is comparable to that of oxygen, Hg^0 is a ubiquitous component of natural waters. Analytically, it is measured as dissolved gaseous Hg (DGM) and is corrected, as necessary, for DMHg.[44−46] Hg^0 is controlled biologically and photochemically on relatively short time scales, and therefore automated measurements are playing a greater role in field studies.[74,76,101,102] Hg^0 is found at all depths in the oceans and is usually supersaturated, especially in surface waters. Indeed, and on occasion, Hg^0 is nearly 50% of the total Hg in the mixed layer.[53] It can be produced by direct reduction of labile reactive Hg species, and this reaction can involve bacterial and/or photochemical processes.[34,35,103,104] As illustrated in Figure 2, demethylation of MMHg also may yield small quantities of Hg^0.[26,46] Fitzgerald and Lamborg[93] summarized Hg^0 levels as well as the concentrations of other Hg species in natural waters. The marine portion of this

Table 1. Concentrations of Hg Species in Marine Waters[a]

location	dissolved total Hg	particulate total Hg	dissolved reactive Hg	dissolved MMHg	particulate MMHg	dissolved DMHg	dissolved Hg^0
			Estuaries/Coastal				
San Francisco Bay[105]	0.4−174	0.3−439	n/a	0−1.6	0−1.92	n/a	0.043−9.8
Long Island Sound[106,108]	1.6−13.1	<0.1−24.1	<0.1−7.6	0−3.3	<0.01−2.91	n/a	0.037−0.89
North Sea and Scheldt Estuary[111,113]	0.5−14	0.1−6[c]	n/a	0.05−1.37	0.0009−0.0435[c]	n/a	0.06−0.8
Siberian Estuaries[258]	0.7−17	0.15−9.4	n/a	n/a	n/a	n/a	n/a
Loire and Seine Estuaries[110]	1−6	0.42−13.3[c]	<0.4−2.1	n/a	<0.0015−0.0296[c]	n/a	<0.05−0.454
Chesapeake Bay[116]	∼3−40[b]	n/a	n/a	∼0.05−0.8[b]	n/a	n/a	∼0.1
Pettaquamscutt River[132]	∼1−25	∼0−18	0.4−8[b]	<0.05−4	<0.05−6.88	n/a	<0.025−0.4
Brazilian Lagoons[275]	18.5−55.2	18−230	0.18−0.43	n/a	n/a	n/a	n/a
			Open Ocean				
Mediterranean Sea[98,109]	0.8−6.4[b]	n/a	<0.2−0.97[b]	<0.15[b]	n/a	<0.13−0.29	<0.02−0.39
Black Sea[99]	1.8−11.8	n/a	n/a	<0.03−1.04	n/a	<0.004−0.04	0.21−1.16
Equatorial Pacific Ocean[46]	n/a	0.11−5.87	0.4−6.9[b]	<0.05−0.58[b]	n/a	<0.005−0.67	0.015−0.69
North Pacific Ocean[27]	0.15−1.94	n/a	n/a	n/a	n/a	n/a	n/a
North Atlantic Ocean[26]	2.4 ± 1.6	0.035 ± 0.02	0.8 ± 0.44	1.04 ± 1.08	n/a	0.08 ± 0.07	0.48 ± 0.31
South Atlantic Ocean[52]	2.9 ± 1.7[b]	0.1 ± 0.05	1.7 ± 1.2[b]	<0.05−0.15	n/a	<0.01−0.1	1.2 ± 0.8

[a] All values are in pM, except where noted. [b] These samples were unfiltered. n/a = not available. [c] Units of nmol of Hg per gram of suspended material, dry weight.

compilation is reproduced in Table 1 along with recent additions. Notice that although coastal waters such as San Francisco Bay[105] and Long Island Sound[106−108] are likely to have greater concentrations of Hg^0, open-ocean levels often are comparable (e.g., South Atlantic[52]). Sea−air gas-exchange of Hg^0 has been the primary focus of these oceanographic efforts to date. No studies have attempted to assess the marine Hg^0 cycle in an oceanic context. However, there have been a variety of mechanistic investigations, and these are outlined in section 6.1.

3.5. Total Hg and MMHg in the Coastal Zone

The cycling of Hg in coastal marine systems is comparable to that in the open ocean, although levels of Hg species are enhanced. In general, Hg(II) is delivered via either rivers and/or direct atmospheric deposition and is either reduced to Hg^0, with potential evasion to the atmosphere, or scavenged and buried in sediments. A small portion is converted to methylated species, which is primarily MMHg. With the exception of the Black Sea[99] and the deep waters in the Mediterranean,[98,100,109] DMHg has not been detected in the water column of peripheral seas or the coastal zone. This suggests either that the lifetime of DMHg in coastal systems is too short for measurable concentrations to prevail or that MMHg is the primary product of methylation under such conditions.

Levels of total Hg in filtered estuarine and coastal waters, containing both dissolved and colloidal species, are enhanced relative to those in the surface ocean and typically range from about 1 to 10 pM, with most waters containing between 1 and 5 pM.[88,105,106,110−115] Levels of total Hg in unfiltered near-shore waters are considerably greater and more variable (2−600 pM),[88,105,106,114,116] which can be attributed to variable suspended particle loads. Hg species have a high affinity for suspended particles and associated organic ligands. Distribution coefficients (K_D, L kg^{-1}) for total Hg most often range from 10^5 to 10^6 in estuarine and coastal waters.[105,110,111,113,115,117,118] Accordingly, suspended particulate matter often is a proxy of total Hg levels in unfiltered waters for a given system.[105,110,111]

There is considerably less information on the distribution and cycling of MMHg in near-shore waters, but in the systems examined to date, MMHg is a minor fraction (1−10%) of total Hg. Levels of MMHg in oxic surface waters range typically from 0.05 to 0.4 pM,[42,88,98,105,111,113,114,116,119] and with the exception of highly turbid estuarine waters, much of the MMHg is in dissolved or colloidal phases.[42,88,114] K_D values for MMHg in oxic surface waters are less than those of total Hg and range from 10^4 to 10^5.[42,113,119] Sources of MMHg to estuarine and coastal waters include, largely, rivers, water pollution control facilities, and in situ production, mostly in sediments (section 7.2).

4. Hydrothermal Interactions

Hg is found in abundance in metalliferous deposits associated with subaerial and submarine volcanism.[82,120−125] Its chalcophilic (sulfur-loving) nature results in accumulation of Hg (as cinnabar and metacinnabar) in chalcopyrite, sphalerite, and other sulfide minerals in oceanic hydrothermal systems. Additionally, Hg has been observed in nascent elemental form as liquid metal droplets at locations of active hydrothermal venting.[124] A recent study has found significant concentrations of Hg in submarine hydrothermal fluids, ranging from 4 to 16 pM, and reported that this Hg was present almost entirely as MMHg.[54] Scaling these results to the entire ocean suggests a potential flux of total Hg of 0.1−0.4 Mmol $year^{-1}$. Interestingly, hydrothermal vent organisms do not always have particularly elevated concentrations of Hg or deleterious effects from high Hg exposures.[126−130] This suggests that either the Hg does not travel far beyond the point of its introduction to ambient seawater, it is not particularly bioavailable (i.e., demethylated), or these organisms have evolved effective means to alleviate the accumulation of Hg in their tissues. Clearly, further study of Hg in hydrothermal systems is warranted.

5. Hypoxic and Anoxic Marine Systems

Low-oxygen marine waters are notably understudied with regard to Hg cycling but are particularly worthy of examination. Indeed, Hg speciation, and, by extension, mechanistic and reaction details, are more likely to be apparent in the aqueous phase of these regimes, as the transition zone from oxygenated to anoxic/sulfidic conditions can take place over

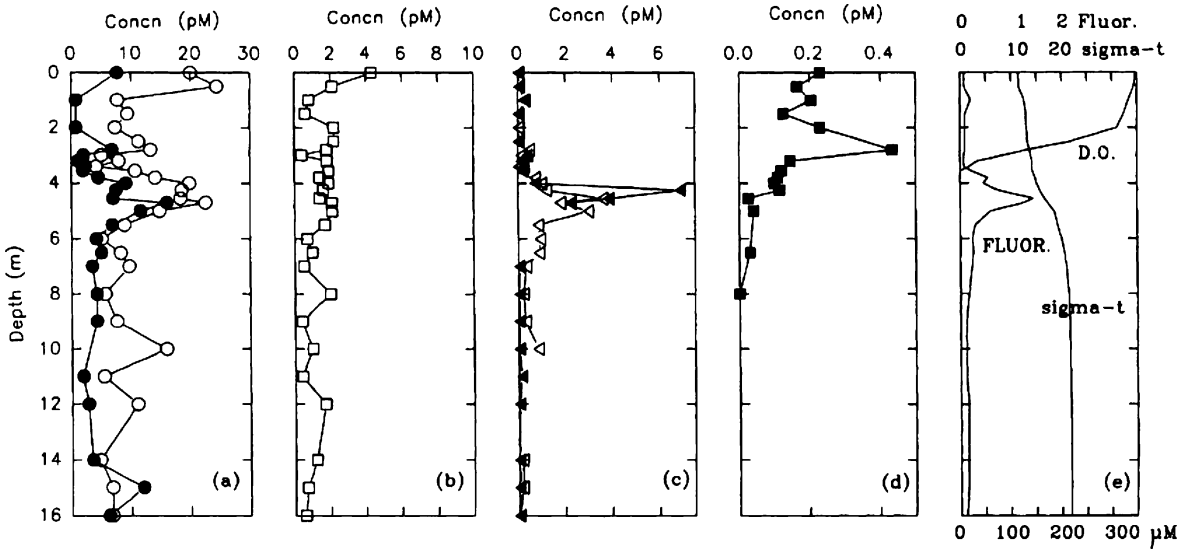

Figure 7. Hg species profiles from the permanently stratified Pettaquamscutt River estuary, Rhode Island. This set of profiles is from August. Symbols are total Hg = open circles; particulate Hg = filled circles; reactive Hg = open squares; dissolved MMHg = open triangles; particulate MMHg = filled triangles; and elemental Hg = filled squares. Reprinted with permission from ref 132. Copyright 1991 by the American Society of Limnology and Oceanography, Inc.

a range of meters, as compared to millimeters in sediments (section 7.2). The permanently stratified Black Sea, which possesses anoxic deep waters, is a model system for such investigations.[99] Profiles of Hg species in the Black Sea showed that the greatest levels of MMHg occurred at the top of the suboxic zone, where dissolved oxygen and sulfide were low. This supports the hypothesis that the bioavailability of Hg, as controlled by sulfide speciation, may have a major influence on MMHg production.[131] Several additional chemical and readily resolved features were evident, including significant levels of DMHg, peaks of Hg^0 at the oxic/anoxic transition, and a highly correlated relationship between dissolved Hg and sulfide that suggests cinnabar solubility may control Hg distributions in the anoxic zone. Results from the Black Sea are comparable to the speciation and distribution of Hg in the permanently stratified Pettaquamscutt River estuary, Rhode Island,[132] where maxima of dissolved Hg^0 and MMHg were found at redox boundaries, although DMHg was not detected (Figure 7). The greatest concentrations of particle-associated Hg were observed in the redox transition zone of the Pettaquamscutt Estuary, likely due to coprecipitation with Fe and Mn oxides, as has been observed elsewhere (Black Sea[99,133] and Framvaren Fjord[134]).

Another important reason for studying Hg cycling under low-oxygen conditions is their potential to facilitate the dispersion of MMHg into ecosystems. Under hypoxic/anoxic conditions, the zone of optimized Hg methylation, which is commonly in the sediments, may migrate into the water column, as evidenced by the anoxic systems described above. This might result in decreased methylation of Hg (i.e., less Hg(II) substrate) but greater MMHg bioaccumulation than under oxic conditions, where MMHg availability is limited by mobilization from sediments. Coastal hypoxia events are a widespread and increasingly common phenomenon, often connected to human-related loadings of nutrients to watersheds, especially in populated environs. Moreover, large areas of some near-shore environments undergo seasonal and/or semipersistent hypoxia/anoxic resulting in biological "dead zones". The aggravating influence of these events on Hg bioaccumulation has yet to be investigated.

6. Biogeochemical Cycling, Inorganic Speciation, and Organic Complexation of Mercury

6.1. Elemental Hg Cycling

As noted in section 3.4, one of the most influential biogeochemical transformations in the Hg cycle is the reduction of Hg(II) to Hg^0, which can result in evasion of the volatile elemental form from the ocean. Unfortunately, there is paucity of knowledge of the specific mechanisms that lead to the reduction reaction. This is due, at least partially, to the challenges associated with experimentally examining the transformation of a chemical present at femtomolar concentrations in natural waters and linked to a variety of complex photochemical and biological processes that rapidly produce and oxidize Hg^0. However, a growing number of studies making use of innovative analytical systems, both in laboratory and field applications, are revealing some general trends.

Hg(II) can be reduced photochemically.[31,34,35,101,103,135−138] The radiation responsible for this reduction appears to be relatively broad spectrum, with UV wavelengths being more effective but certainly not the exclusive source of reduction energy. Because visible light absorption results in Hg reduction, it appears that chromophoric dissolved organic matter (CDOM) also is involved in the reduction reaction. Indeed, the impact of humic materials on Hg(II) reduction has been noted,[135,139,140] but the exact mechanism of CDOM involvement is not yet fully understood. Hg complexed with dissolved organic carbon (DOC) may be reduced directly. Alternatively, indirect reduction may result from the photochemical generation of reduction equivalents via CDOM that is not complexed with Hg. As discussed in section 6.2, a large percentage of Hg in natural waters is complexed with DOC, and thus the discrimination between possible mechanisms is an important aspect of Hg biogeochemistry to be explored. In the case of Fe cycling, photoreduction of Fe(III) to Fe(II) requires complexation by DOC,[141] and we might expect Hg to behave similarly.

The redox cycling of Hg(II) is made more complex by competing oxidation reactions that convert Hg^0 to

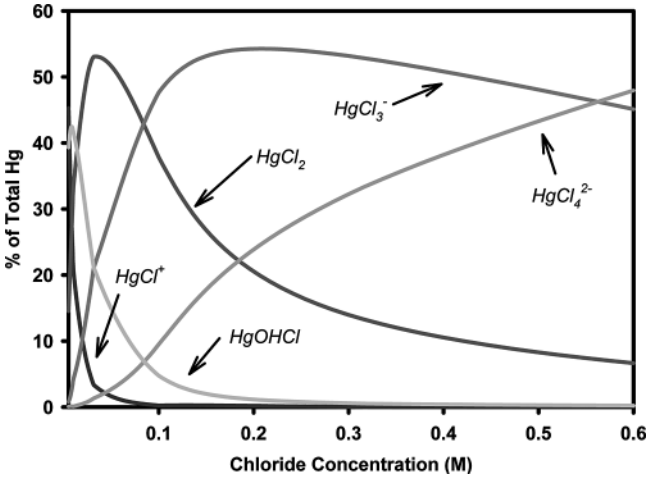

Figure 8. Progression of Hg−Cl complexes over the range of estuarine and marine salinities.

Hg(II).[34,37,142] Some of these reactions also appear to be driven photochemically and mediated by DOC, as with the reduction reactions noted above. The balance between reduction and oxidation reactions, with varying dependencies on light and DOC, results in diel variations in Hg^0 production which, in turn, result in variations of Hg^0 in sunlit waters when air−water exchange remains relatively constant.[74,79,101,140,143] Such a diurnal trend may be expected under quiescent conditions at sea but is not yet observed.

Microbes also have been implicated in Hg(II) reduction.[31,33,144] Relatively high concentrations of Hg(II) may induce transcription of a suite of bacterial genes encoded on the *mer* operon,[144−146] resulting in enzymatic uptake and reduction of Hg. Reduction of Hg(II) has been correlated with plankton cell density at ambient concentrations as well,[33] but it is unclear whether this is the result of mercuric reductase, an alternative mechanism of cell-mediated reduction, or reduction facilitated by cellular exudates.

6.2. Inorganic and Organic Complexation of Hg(II) and MMHg

The speciation of Hg(II) is hypothesized to exert the primary control on bioavailability of Hg to methylating microorganisms in fresh and salt waters.[131] Furthermore, there is growing evidence that speciation is significant in the reduction of Hg(II) to Hg^0.[31,135,140,147,148] Thus, knowledge of the speciation of Hg(II) complexes is of central importance to understanding its broader biogeochemical cycling.

The inorganic speciation of Hg(II) in natural waters is dominated by chloride. Recent research has revealed that under no typical conditions are hydroxide complexes a significant contributor to Hg speciation.[72] Instead, under low-chloride and oxic conditions, organic complexes are dominant. In oxic estuarine and seawater conditions, and as illustrated in Figure 8, a progression of chloride complexes is expected in the absence of organic complexing agents.

Complexation of Hg by organic molecules has long been suspected to be important in natural waters, but only recently have analytical approaches to resolving this phenomenon been developed adequately.[72,131,149−156] In oxic estuarine and coastal marine systems, there appears to be more than an adequate amount of Hg-complexing equivalents (i.e., low nM) present in the DOC pool, and with sufficient affinity ($K' = 10^{21}-10^{30}$), to completely "out-compete" chloride for Hg^{2+} (Figure 9).[72,151,152]

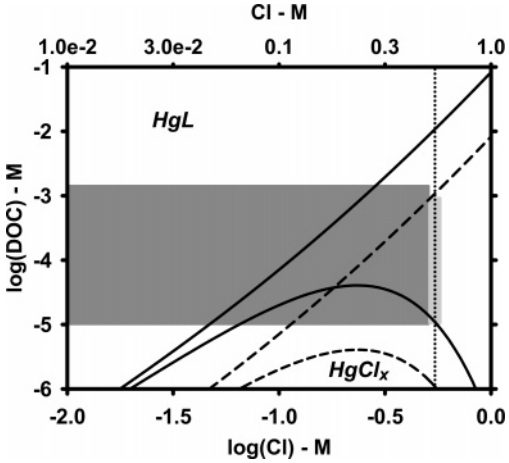

Figure 9. Divalent Hg speciation in oxic natural waters using a Hg−Cl-organic ligand (L) complexation model. The two sets of curved lines represent combinations of ligand abundance and strength. The solid lines represent conditions where the L/DOC molar ratio is 5×10^{-6}, while the dashed lines are for L/DOC = 50×10^{-6}. The pair of lines that curve slightly upward represents the speciation expected if organic ligand strength is constant at log $K' = 22$, while the pair of lines that curve strongly downward represents the case where log K' of the organic ligand complex varies linearly with salinity between 22 and 25. Above the lines, speciation is dominated by organic complexes (HgL), while below the line speciation is as one of the Cl complexes (as in Figure 8). The dark gray box represents typical fresh and estuarine waters, while the light gray region represents oceanic conditions. Reprinted from ref 158, Copyright 2004, with permission from Elsevier.

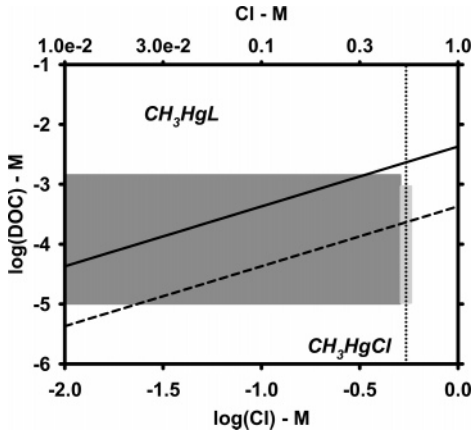

Figure 10. Speciation of MMHg using a MMHg-Cl-L model.[84,154,158] Solid and dashed line conditions and boxes are the same as in Figure 9. Only one affinity condition is considered for the organic ligand complex, log $K' = 13$.

The speciation for MMHg exhibits many of the same patterns as Hg(II). Formation constants for MMHg organic ligand complexes are quite high, being estimated to range between $10^{12.6}$ and $10^{13.6}$ for isolated freshwater humic and fulvic acids, and ligand abundances are presumed similar to those for Hg^{2+}.[155] To date, no measurements of organic ligand abundance or affinity for MMHg have been made in bulk seawater. As with Hg(II), chloride is an important inorganic ligand for MMHg.[154] Figure 10 shows that, under typical seawater conditions, MMHg is likely to be found as the chloro complex, although this hypothesis awaits confirmation.

The site of Hg binding in macromolecular DOM appears to be reduced sulfur functional groups.[157] Dyrssen and Wedborg[154] have noted that the natural ligand affinities of DOM for Hg^{2+} were of the same order as those of model

simple thiols. Ligand to DOC ratios range from <1 to ~60 ppm (i.e., <1−60 out of 10^6 organic carbon atoms is associated with a Hg binding equivalent).[84,158] The abundance of Hg binding ligands is substantially less than the amount of reduced sulfur within the DOC pool. In soil organic matter, this appears to be due, at least partially, to the bidentate nature of the Hg−L bond, which would require that two available thiolic functional groups be located near one another.[157,159] Such a steric requirement would imply that Hg binding sites are a small fraction of the total thiol pool. Additionally, the Hg binding sites examined in DOC, thus far, are by definition the highest affinity examples in what is undoubtedly a continuum of abundances and strengths.[160]

There is growing interest in the source and fate of such organic molecules in the ocean because they strongly complex other metals in addition to Hg.[161,162] However, not much is known currently. A recent report[163] has documented the release of thiolic ligands from phytoplankton in response to increased exposure to trace metals (Cu, Zn, and Cd), and therefore, the presence of Hg binding equivalents in the ocean could be at least partially a result of organisms conditioning the water to alleviate the accumulation of Hg (and other metals).

6.3. Sulfide Competition

The complexation of Hg^{2+} and MMHg is different under anoxic conditions. Dissolved sulfide has a strong affinity for both Hg species as well as other trace metals (e.g., Fe, Cu), although the affinity of most metals for sulfide is less than that with Hg^{2+}.[164] Indeed, and excluding kinetic limitations and competition by other metals, complexation by sulfide should dominate the speciation of Hg^{2+} and MMHg,[131,154] even when a stability constant of 10^{30} is assumed for associations of Hg with organic ligands.[151] Thermodynamically, Hg−sulfide complexes also should dominate the speciation of Hg in oxic waters, where low (pM to nM) concentrations of sulfide are maintained by in situ production. There are reasons to believe that the sulfide sequestered in Fe and Cu complexes is not labile, however, and thus organic ligands would dominate under these conditions.[164] In anoxic waters, such as those in permanently stratified marine basins (section 5) and in sediment pore fluids (section 7.2), chloride and organics are not expected to out-compete sulfide for Hg species.

7. Sedimentary Hg Accumulation and Processing

7.1. Sediment Geochemistry

Scavenging by organic-rich particles is a major sink for Hg(II) in coastal marine[107,116] and open-ocean systems,[22] resulting in deposition to sediments. The affinity of Hg(II) for natural organic matter, as outlined above (section 6.2), is well established[72,150,165] and is further evidenced by exceedingly high partitioning coefficients (K_D, L kg^{-1}) for Hg(II) and organic-rich suspended particles in estuarine and coastal waters (see section 3.5; $K_D = 10^5-10^6$ L kg^{-1}).[105,110,111,113,115,117,118] While little is known about Hg in deep-ocean sediments, the strong predepositional associations of Hg(II) with organic matter are maintained in many coastal deposits. Selective leaching experiments suggest that most Hg(II) is associated with organic material in the solid phase,[39,166] although formation of solid Hg−sulfide phases (i.e., cinnabar) can be significant in highly sulfidic deposits.[167,168] Moreover, solid-phase total Hg often is correlated with the level of organic material among surface deposits within a given coastal marine system.[40−42,90,92,105,111,169−172] There are exceptions to this generalization, however, particularly in anthropogenically impacted coastal embayments,[173,174] where differences in Hg and organic matter sources, coupled with abbreviated water-column residence times, may result in considerable variability of Hg/organic matter ratios in sediments.

Concentrations of total Hg in marine sediments vary 1000-fold within and among locations (Table 2), often depending on the proximity to, and relative source strength of, natural and anthropogenic loadings. Levels of total Hg in marine deposits are lowest in regions that are remote from fluvial and anthropogenic point sources (e.g., continental shelves, peripheral seas), where direct atmospheric Hg deposition is presumed to be a principal source. The influence of watershed and anthropogenic sources on total Hg in sediments increases with proximity to major rivers and urbanized/industrialized regions. Mean concentrations of total Hg in sediments of the Scheldt River Estuary, Boston Harbor, and Chesapeake Bay, for example, are 5−10 times greater than those in remote continental shelf regions (Table 2). Moreover, solid-phase total Hg often decreases with distance from rivers and highly populated regions within coastal embayments.[172,175,176] The greatest levels of Hg in near-shore marine deposits are associated with direct industrial inputs (e.g., Minamata Bay) and effluent from Hg mining activities (i.e., Gulf of Trieste; Table 2). At a particular location, there often is little variation of total Hg within the upper 10 cm of marine sediment,[39,89,171,175,177,178] likely a result of bioturbation and sediment mixing associated with tidal/fluvial currents.

Not unexpectedly, organomercury species are present in marine sediments. It appears that MMHg is the principal and ubiquitous organomercurial in coastal deposits, although there is limited evidence suggesting that forms such as DMHg, ethylmercury, and phenylmercury may exist in trace amounts.[156,179−181] MMHg in the solid phase of sediment also varies by 1000-fold (comparable to total Hg) within and among locations (Table 2), and organic matter appears to be a major control on distributions in surface deposits. MMHg is related strongly to the concentration of organic material within a given coastal marine or estuarine system.[40−42,90,92,111,170,178] Moreover, MMHg often is correlated with total Hg, as might be expected given the covariation of both Hg species with organic matter. This has been observed both within[42,90,111,170,174,182] and among systems.[42] Although levels of both MMHg and total Hg can vary considerably within a particular system, Table 2 shows that the percentage of total Hg as MMHg in surface sediments, estimated from the mean level of each constituent, is constrained to a relatively narrow range among coastal marine systems having considerable differences in climatology, geography, and Hg contamination (range, 0.1−0.75%; mean = 0.47%). It has been hypothesized that the relatively consistent fraction of total Hg as MMHg among such disparate systems may be related to proportional sediment−water partitioning and solid-phase retention of MMHg and Hg(II) and that organic matter largely controls the partitioning.[42,90]

Scavenging by metal oxyhydroxides may influence the sediment−water partitioning of Hg species.[39,166,177,182−184] However, recent studies have shown that distribution coefficients of both Hg(II) and MMHg are correlated positively with the concentration of organic matter in sediments.[39,41,42,182] This is consistent with results that suggest Hg species are associated primarily with organic material in the solid

Table 2. Hg Speciation in Surface Deposits of Marine Systems (with Ranges in Parentheses)

location	total Hg (nmol g^{-1} dry wt)	MMHg (pmol g^{-1} dry wt)	mean MMHg/total Hg (%)
Southern New England shelf[42]	0.10 (0.04−0.16)	0.74 (0.36−1.13)	0.74
Bering Sea[276]	0.15 (<0.05−1.15)		
Bay of Fundy, Canada/U.S.[41]	0.21 (0.05−0.70)	1.55 (0.25−7.38)	0.74
Caspian Sea[277]	0.25 (<0.05−2.25)		
South China Sea[278]	0.30 (0.10−0.64)	0.19 (0.05−0.27)	0.06
Arctic Ocean[279]	0.36 (0.17−0.58)		
Greenland shelf[280]	0.36 (0.03−1.40)		
Bering Sea[278]	0.44 (0.39−0.56)	1.04 (0.28−3.10)	0.24
Baltic Sea[278]	0.46 (0.19−1.56)	3.45 (0.18−10.0)	0.75
Lagoon of Bizerte, Tunisia[281]	0.52 (0.04−3.22)	2.32 (<0.4−14.6)	0.45
Patuxent River estuary, Maryland[170]	0.61 (0.29−0.80)	2.08 (0.60−3.90)	0.34
Laurentian Trough[184]	0.65 (0.30−0.90)		
Bay of Haifa, Israel[282]	0.65 (0.05−2.85)		
Long Island Sound, NY/CT[175]	0.70 (0.1−3.0)		
Bay of Biscay, France[262]	0.8 (0.1−2.3)	0.6 (<0.5−1.2)	0.1
Long Island Sound, NY/CT[90]	0.96 (0.20−1.73)	7.14 (1.00−16.0)	0.74
Chesapeake Bay, Maryland[40]	0.99 (0.04−8.6)	4.45 (0.20−16.7)	0.45
San Francisco Bay, California[105]	1.1 (0.1−3.5)	2.5 (<0.1−17)	0.2
Izmir Bay, Turkey[172]	1.32 (0.20−3.14)		
Bay of Naples/Tyrrhenian Sea[283]	1.59 (0.40−8.75)		
Southern Baltic Sea, Poland[168]	1.78 (0.41−4.22)		
Lavaca Bay, Texas[182]	1.79 (0.03−3.92)	12.5 (0.14−51.7)	0.70
Yatsushiro Sea[176]	2.21 (0.43−11.7)		
Chesapeake Bay, Maryland[173]	2.25 (0.05−6.15)	14 (0.5−50)	0.62
Seine River Estuary, France[171]	2.3 (1.5−5.0)	12 (0.5−30)	0.5
Scheldt River Estuary, Belgium[284]	2.31 (0.76−4.73)	13.9 (7.00−24.6)	0.60
Tyrrhenian Sea[285]	3.08 (0.20−6.60)		
Boston Harbor, Massachusetts[286]	4.10 (1.55−10.0)		
Venice Lagoon, Italy[287]	6.5 (0.5−17)		
Kastela Bay, Adriatic Sea[288]	11.0 (2.50−30.7)	48 (15−100)	0.44
Minamata Bay, Japan[289]	16.2 (1.70−24.1)		
Gulf of Trieste, Adriatic Sea[290]	26.2 (0.05−117)	84.5 (1.00−301)	0.32

phase.[39,166] In most coastal marine deposits, where total organic content typically comprises 1−10% of dry mass (about 0.4−4% total organic carbon), K_D values for Hg(II) (range $10^{3.0}$−$10^{5.0}$) are consistently about $10^{1.5}$−10^2 greater than those for MMHg, which range from $10^{1.5}$ to $10^{3.5}$.[41,42,90,178,182] K_D values for Hg(II) and MMHg in sediments are 10−10^2 less than those in oxic overlying water, which may be attributed, in part, to a greater abundance of dissolved sulfide and organic ligands relative to solid-phase complexation sites on particles.[131,158] Laboratory studies suggest that the partitioning of Hg species between solid and pore water phases is rapid.[90,185] Resulting concentrations of Hg species in filtered pore fluids often range from 5 to 50 pM for Hg(II) and from 1 to 30 pM for MMHg.[39,42,88,89,166,177,178,182,184,186] The fraction of total Hg as MMHg in coastal marine pore fluids typically ranges from 5% to 50%, with most values between 10% and 30%,[39,42,166,178,182] a fraction that is considerably greater than that in the solid phase (i.e., <1%, Table 2).

7.2. MMHg Production and Cycling

Most MMHg in marine systems is derived from natural processes that methylate Hg(II). In situ sedimentary production is a primary source of MMHg in many near-shore systems,[42,107,116] where it is apparent that biological methylation of Hg(II) is more important than abiotic mechanisms.[187] Potential abiotic methylating agents for Hg(II) in marine environments include acetate,[188−191] organic acids with a methyl group in the α-position,[192] other methylated metals,[47,48] and humic substances.[49,193,194] While a variety of aerobic and anaerobic microorganisms have been shown to produce MMHg in pure culture,[146] including iron-reducing bacteria,[9] it is presumed that sulfate-reducing bacteria (SRB) are the primary functional group of microorganisms mediating the transformation of Hg(II) to MMHg in marine sediments,[7] although the biochemical mechanism is not known.[195] The activity of SRB is extraordinarily large in coastal marine deposits, where they are responsible for most (50−90%) of the organic carbon mineralization.[196] The net production of MMHg in coastal marine sediments can be influenced by a variety of factors that affect either the activity of methylating and demethylating bacteria or the availability of Hg species for transformation. These factors can include loadings of Hg(II), partitioning of Hg species with solid-phase organic material, the effect of sulfide on speciation of Hg complexes, the availability of labile organic substrates, temperature, and sediment disturbance (e.g., bioturbation).

MMHg production is optimal near oxic−anoxic transition zones (i.e., redox transition zones) that are commonly found close to sediment−water interfaces in many marine systems. Solid-phase MMHg concentrations often are greatest at, or just below, the sediment−water interface and decrease with depth.[39,42,89,166,171,174,178,182,186,197] Solid-phase MMHg is the net result of concomitant methylation/demethylation reactions, adsorption/desorption mechanisms, and diffusional/advective processes. Localized mixing of sediment by infauna can homogenize profiles of metals associated strongly with the solid phase over time scales of months to years (i.e., total Hg). Accordingly, in situ production and sequestration of MMHg must occur more rapidly to establish such vertical structure in the sedimentary column. This is supported by sediment profiles of Hg methylation potentials, assayed by incubation with added Hg(II), which often show good agreement with solid-phase MMHg over the vertical.[39,42,89,198]

The vertical structure of Hg methylation and associated MMHg concentration profiles can be attributed to the effect that sulfide, the metabolic product of SRB, has on

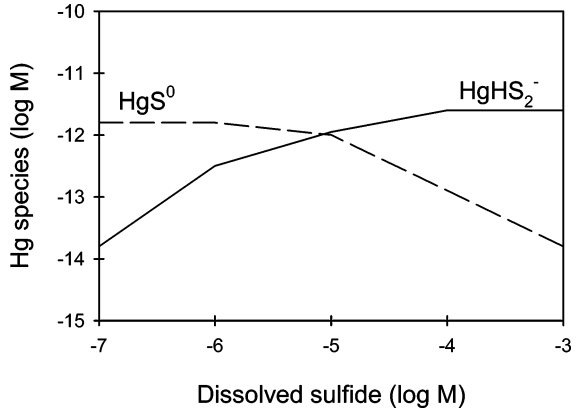

Figure 11. Changes in concentration of HgS^0 and $HgHS_2^-$, the dominant Hg−S complexes in sediment pore fluids, as a function of sulfide estimated using the solid-phase Hg speciation model of Benoit et al.[131] The log K values for formation of $HgSR^+$ and $Hg(SR)_2$ were set at 38 and 43, respectively.

the speciation and subsequent bioavailability of dissolved Hg(II) complexes to methylating bacteria. Recent research suggests that Hg(II) must be dissolved to enter a bacterial cell and be methylated, and that Hg(II) mostly likely enters by passive diffusion through the cellular membrane as a dissolved, neutrally charged complex.[199−201] As noted in section 6.3, sulfide exerts a dominant control on the speciation of dissolved Hg(II) in sediment pore fluids (e.g., $HgHS_2^-$, $HgSH^+$, HgS^0, $Hg(S_x)_2^{2-}$),[131,202] and HgS^0 is presumed to be the Hg−S complex most available to bacteria in pore water.[200,201] Figure 11 shows results of the solid-phase chemical speciation model of Benoit and co-workers.[131] The model predicts that HgS^0 is the major dissolved species when S^{2-} is less than about 10^{-5} M while the charged $HgHS_2^-$ complex is dominant at greater levels. Maximum rates of Hg methylation often are found in surface deposits and sedimentary horizons where SRB activity is significant and accumulation of sulfide is minimized (e.g., redox transition zone), thereby favoring speciation of dissolved Hg−S complexes as HgS^0. The activity of SRB, which can be enhanced near oxic−anoxic boundaries, also may influence rates of Hg methylation.[197,203]

Levels of dissolved sulfide generally are low (<10 μM) in surface deposits (uppermost 2−4 cm) of many coastal marine systems, particularly those distant from allochthonous sources of labile organic material and/or nutrients that enhance planktonic productivity and subsequent benthic respiration. Low concentrations of dissolved sulfide in the presence of active sulfate reduction are likely maintained by pore-water bioirrigation/chemical oxidation, by sulfide-oxidizing bacteria, and by titration of free sulfide with iron.[204−206] Hence, and for a range of S^{2-} that is less than 10 μM but equal to or greater than dissolved Hg(II) (typically 5−50 pM), HgS^0 is predicted to be the dominant Hg(II) complex in many coastal marine sediments. As emphasized in section 6.3, dissolved organic ligands in marine sediment pore fluids, having a measured abundance (20 nN) and Hg binding strength ($\log K_f = 25.0\ N^{-1}$),[158] cannot compete with sulfide for Hg^{2+}.[39]

The prediction of HgS^0 as the primary Hg(II) species in pore fluids of surface sediments has important implications for the production of MMHg. Indeed, it suggests that a major fraction of the Hg(II) in pore water is available biologically for uptake and transformation. Accordingly, and if the availability of Hg(II) limits the gross rate of MMHg production, then one might expect a positive correlation between potential Hg methylation rates and the concentration of Hg(II) in filtered pore waters of low-sulfide sediments. Recent field investigations have found that gross potential rates of Hg methylation in marine deposits, assayed by incubation with tracer-quantity additions of a stable isotope of Hg, are related positively to the ambient concentration of Hg(II) in filtered pore fluids.[42,90] Although Hg methylation varies seasonally as a function of temperature and inferred bacterial activity,[88,90,92,178] these relationships suggest that there is excess Hg methylating potential in coastal marine sediments, and MMHg production is limited largely by the availability of dissolved Hg(II) (i.e., HgS^0) to methylating bacteria. This implies that environmental factors that affect the level of HgS^0 in sediment pore fluid will influence the gross rate of MMHg production. These factors can include loadings of Hg(II), the level of dissolved sulfide (controlling the speciation of dissolved Hg−S complexes), and sediment organic content, which, as noted, largely influences the sediment−water partitioning of Hg species. Thus, and in sediments of two contrasting marine systems, potential gross rates of Hg methylation are correlated inversely with the K_D of Hg(II).[42,90] Therefore, deposits with less organic matter have proportionately more Hg(II) in the dissolved phase (i.e., lower K_D) and the potential for Hg methylation is enhanced. These results suggest that the availability of dissolved Hg(II) to methylating bacteria is a primary control on the gross production of MMHg in coastal marine sediments.

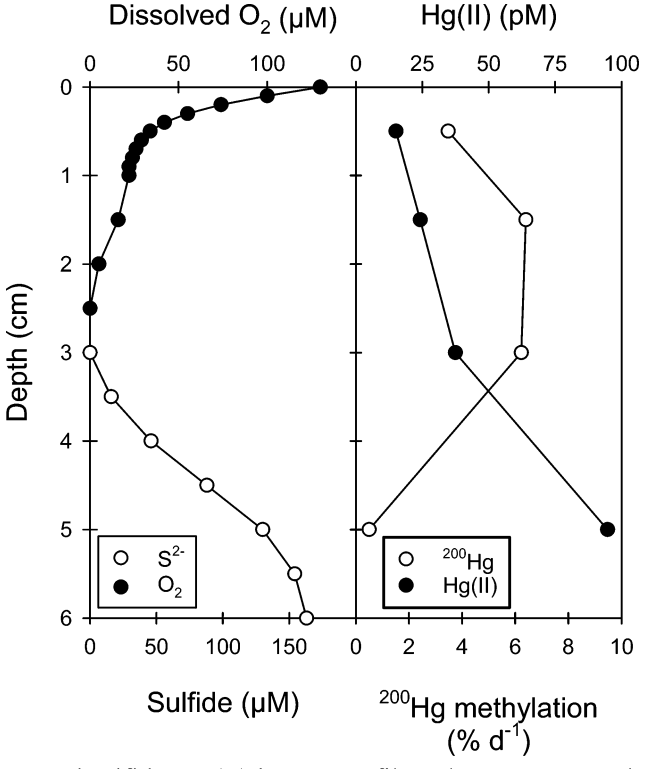

Figure 12. Profiles of dissolved oxygen and sulfide, Hg(II) in 0.2-μm filtered pore water, and potential methylation rates of added ^{200}Hg isotope in sediment at station JB1 in Jamaica Bay, New York/New Jersey Harbor, February 2003. Adapted from ref 207 with permission.

Dissolved sulfide is enhanced in some near-shore deposits, and although it increases the solubility of Hg species, it inhibits MMHg production. Figure 12 shows vertical profiles of dissolved oxygen and sulfide, Hg(II) in filtered pore water, and potential gross rates of Hg methylation, assayed by

addition of an enriched stable isotope of Hg ($^{200}Hg^{2+}$), in a sulfide-replete deposit of New York/New Jersey Harbor. These results show prominently the effect of sulfide on both the solubility and speciation/bioavailability of Hg(II) for methylation. Dissolved sulfide is low (<10 μM) in the upper few centimeters of sediment and increases with depth between about 3 and 6 cm at this location (Figure 12). Although the solid-phase concentration of Hg(II) does not vary in the upper 6 cm of sediment at this site,[207] Hg(II) in pore water increases with depth and dissolved sulfide. This can be attributed to competition of dissolved S^{2-} with solid-phase organic matter for Hg(II) and is consistent with Hg−S complexes being the major dissolved Hg(II) and MMHg species in pore fluids (section 6.3).[131,154] Greater pore-water Hg(II) at depth in this profile, however, does not relate to a greater potential rate of Hg methylation. Indeed, the potential rate of Hg methylation is greatest in the redox transition zone and almost zero at 5 cm depth, the horizon of greatest dissolved sulfide and Hg(II) in pore water (Figure 12). A low rate of Hg methylation in the presence of high pore-water Hg(II) can be attributed to the effect of dissolved sulfide on the chemical speciation and subsequent bioavailability of Hg(II) in pore fluids. The chemical speciation model of Benoit et al.[131] (Figure 11) predicts that bioavailable HgS^0 is the major Hg(II) complex in the upper 3 cm of sediment at JB1, which is the zone that has the greatest Hg methylation potential. Hg methylation is inhibited in deeper, more sulfidic sediments at JB1 because $HgHS_2^-$ is the likely major Hg−S complex in pore water, and it is much less bioavailable to methylating bacteria than HgS^0.[199,200] Comparable vertical variations of Hg methylation potential and dissolved sulfide have been observed in salt marsh deposits.[186]

While the availability of Hg(II) appears to be a primary control on MMHg production in coastal marine deposits, other biogeochemical factors can affect the rate of Hg methylation by influencing the activity of methylating bacteria. These can include the availability of labile organic substrates,[7,203] temperature,[88,90,92,178,197] and sediment disturbance/bioturbation.[39,42,89,174] It is unlikely that the availability of SO_4^{2-}, which is 28 mM in seawater, limits microbial sulfate reduction and Hg methylation in either estuarine or coastal marine deposits.[8]

The solid-phase concentration of MMHg or the percentage of total Hg as MMHg (%MMHg) often is used as a proxy of net MMHg production in coastal marine deposits. This approach is supported by the generally good agreement between sediment profiles of MMHg concentration and potential gross rates of Hg methylation assayed with isotopic tracers.[39,42,89,198] Moreover, it has been found that potential rates of Hg methylation are correlated frequently with either %MMHg or MMHg concentration among locations within some,[40,88,89] but not all,[42,90] coastal marine systems. While such relationships may imply that the gross rate of Hg methylation is linked directly to net MMHg production/accumulation in sediments, substantial losses of MMHg are expected via demethylation and mobilization to overlying water. In Long Island Sound, for example, the flux of MMHg to overlying water is 10-fold greater than the amount accumulated in sediments.[90]

7.3. Demethylation of Organomercurials

Compared to Hg methylation, there is a paucity of information on demethylation of organomercurials and associated environmental controls, particularly in marine systems. Both MMHg and DMHg are stable thermodynamically in water and in the presence of oxygen, but they are susceptible to photolysis.[208] Studies in freshwater systems have shown that MMHg is demethylated both photochemically[209−211,222] and microbiologically in the water column.[212,213] It is most likely that comparable reactions occur in seawater. Microbial processes are presumed to be the dominate mechanisms for MMHg demethylation in sediments, where multiple genera of aerobic and anaerobic bacteria can demethylate MMHg.[214,215] Demethylation of organomercurials is known to occur by two general pathways designated by the oxidation state of the carbon product evolved from the methyl group:[216,217] (1) a "reductive" pathway, where CH_4 is synthesized from the methyl group, and (2) an "oxidative" pathway that produces CO_2. Reductive demethylation is the major pathway in Hg-polluted sediments,[218] where it is suspected that an inducible system of enzymes related to the *mer* operon,[144−146] notably organomercury lyase and mercuric reductase, catalyzes the demethylation and reduction (i.e., detoxification) of Hg compounds. Oxidative demethylation, which may be analogous to the metabolism of other C_1 compounds (e.g., CH_3Br) by heterotrophic bacteria, appears to be the dominant pathway in sediments with low Hg contamination and where methanogenic and sulfate-reducing bacteria are mediating organisms.[218,219]

Experimental additions of either MMHg with isotopically enriched Hg or high-specific-activity $^{14}CH_3Hg$ have permitted tracer-level assays of demethylation rates in estuarine and marine deposits.[40,88,91,92,220] Results from these studies suggest that rate constants of MMHg demethylation are 10−1000 times greater than those of Hg methylation and that the turnover of MMHg in marine sediments is on the order of days. Moreover, potential rates of MMHg demethylation as well as methylation/demethylation rate constant ratios vary considerably within and among systems. Future and ongoing research is examining environmental controls on MMHg demethylation and how differences in methylation/demethylation rates influence solid-phase concentrations and sediment−water fluxes of MMHg.

Table 3. Mean Measured or Estimated Diffusional Sediment−Water Fluxes of MMHg from Coastal Marine Deposits

location	sediment−water flux (pmol m^{-2} d^{-1})
continental shelf (NW Atlantic)[42]	9
San Francisco Bay, CA[178]	30
New York/New Jersey Harbor[207]	44
Long Island Sound, CT/NY[39]	47
Lavaca Bay, TX[221]	210
Gulf of Trieste, Adriatic Sea[177]	2300

7.4. Benthic MMHg Mobilization

Mobilization from sediments is an important source of MMHg to coastal marine systems and, potentially, the open ocean and its biota. Effluxes of MMHg from coastal marine sediments have been measured with in situ flux chambers[177,178,221] and estimated from gradients of MMHg in filtered pore water.[39,42,207,221] Table 3 shows mean measured and estimated diffusional sediment−water fluxes of MMHg, which can be interpreted as net benthic production, among a variety of coastal marine systems. While the production and mobilization of MMHg from sediments varies spatially and seasonally within a particular system[39,178] it is apparent

from Table 3 that the average benthic MMHg effluxes also differ widely among systems.

The significance of sedimentary MMHg production and mobilization can be readily illustrated. In Long Island Sound, for example, the flux of MMHg from sediments[39] (about 55 mol year^{-1}) accounts for nearly 70% of all MMHg loadings[107] and is comparable to the amount accumulated by primary producers in the Sound (about 50 mol year^{-1}).[119] Second, and although the source of MMHg in marine fish is largely unknown, an annual flux of about 0.2 Mmol of MMHg to the ocean is required to sustain the average concentration in marine fish ($\sim$0.2 μg g^{-1} wet weight[23]). If sediments of the coastal zone, which is about 8% of the area of the global ocean, were the primary source of MMHg, an estimated flux of about 20 pmol m^{-2} day^{-1} is required to sustain this bioaccumulative uptake. The average diffusional efflux of MMHg from sediments at remote locations on the continental shelf of the northwestern Atlantic Ocean (9 pmol m^{-2} day^{-1}; Table 3) is within about a factor of 2 of that needed to sustain the estimated annual bioaccumulative uptake by marine fish (i.e., 20 pmol m^{-2} day^{-1}). Moreover, the benthic efflux of MMHg may be enhanced considerably by mobilization from deposits that are impacted more severely by anthropogenic Hg. For example, and as shown in Table 3, benthic fluxes of MMHg in San Francisco Bay, New York/New Jersey Harbor, Long Island Sound, and the Gulf of Trieste are much greater than those estimated for the continental shelf sediments. Third, coastal marine deposits are a substantial reservoir of Hg(II) for the production of MMHg. It is estimated conservatively that about 130 Mmol of Hg(II) is present in the upper 1 cm of sediment in the coastal zone (roughly 3×10^{13} m^2), given a mean sediment Hg(II) concentration of 0.3 nmol g^{-1} dry weight among the four continental margin locations in Table 2 (New England shelf and South China, Bering, and Baltic Seas) and an average bulk density of 1.5 g cm^{-3}. This burden is about three times greater than that in the mixed layer of the open ocean (54 Mmol[22]) and is nearly 500-fold greater than the amount of Hg accumulated annually by marine fish (i.e., 0.2 Mmol year^{-1}).[23]

As summarized in section 7.2, results from gross Hg methylation experiments suggest that MMHg production is limited mostly by the availability of Hg(II) to methylating bacteria in coastal marine deposits. This implies, as suggested, that environmental factors that affect the availability of Hg(II), hypothesized as HgS^0, to methylating bacteria in sediments will influence the gross, and potentially net (i.e., sediment−water efflux), rate of MMHg synthesis. An important factor in this regard may be loadings of Hg(II) to the sediments. This can be examined by comparing benthic MMHg mobilization and Hg(II) burial fluxes among systems. Although the number of coastal marine systems having estimates for both fluxes is limited, Figure 13 shows a log−log plot of mean sediment−water MMHg mobilization versus Hg(II) burial for sediments on the continental shelf of southern New England, Long Island Sound, and the Gulf of Trieste (Table 3). Hg loading to the benthos of Long Island Sound (210 nmol m^{-2} year^{-1}) is from a well-constrained mass balance,[107] and that for the Gulf of Trieste (11000 nmol m^{-2} year^{-1}) is based on measured sediment Hg concentration and mass accumulation rates.[177] The burial flux of Hg(II) at the continental shelf sites (48 $\pm$ 41 nmol m^{-2} year^{-1}) is estimated from the mean level of Hg(II) in surface deposits[42] (0.10 $\pm$ 0.06 nmol g^{-1} of dry weight) and the average rate of sediment accumulation near these locations (480 $\pm$ 290 g m^{-2} year^{-1}).[223] This estimate is in good agreement with the atmospheric Hg flux (wet + dry deposition) measured at four sites in coastal Connecticut[107] (40 $\pm$ 10 nmol m^{-2} year^{-1}), and suggests much of the Hg(II) on the continental shelf may be derived from direct atmospheric deposition.[25] The relationship in Figure 13, which spans a 10^2 range of sediment−water efflux and Hg(II) burial, suggests a direct connection between loadings of Hg(II) and the net production of MMHg in coastal marine deposits. For each of these systems, and on average, the flux of MMHg from sediments is about 8% of Hg(II) loadings to the sediments.

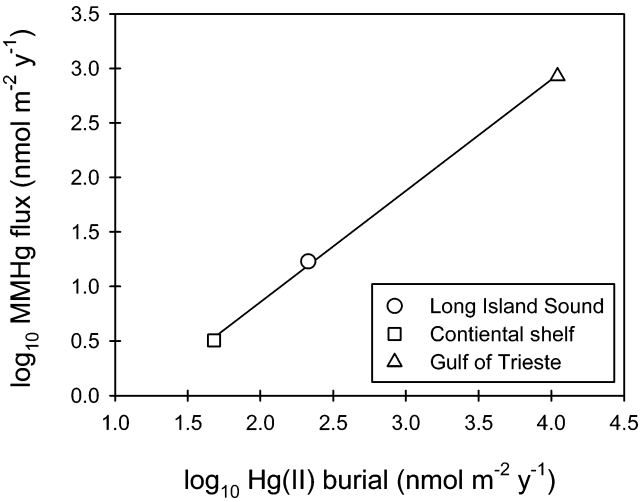

Figure 13. Annual sediment−water flux of MMHg versus burial of Hg(II) in sediments of Long Island Sound, the continental shelf of southern New England, and the Gulf of Trieste.

8. MMHg in Marine Food Webs

Toxicologically, accumulation of MMHg in biota is the most important feature of the marine Hg cycle. Humans are exposed to Hg principally by the consumption of fish and fish products,[11] and nearly all of this Hg is as MMHg.[119,224−230] Most of the fish consumed by humans is of marine origin,[12] and some marine fish MMHg levels may pose a threat to public health. Transfer of MMHg from a maternal seafood diet to prenatal life stages can inhibit the neurological and cardiovascular development of children.[231−234] Additionally, MMHg may affect adversely the cardiovascular health of adults who eat fish.[235]

Most studies and measurements of Hg in biota of the ocean have been motivated by such human health concerns. Local, federal, and international agencies have conducted and sponsored numerous investigations of Hg levels in fish often consumed by humans. Federal agencies in the United States, for example, have surveyed Hg levels in more than 4500 marine fin- and shellfish, representing >50 species, to make recommendations concerning which fish species have the greatest and lowest average concentrations (Table 4).[236] Such research has led to the U.S. Environmental Protection Agency warning against consumption of tilefish, shark, swordfish, and king mackerel as a result of high Hg levels (Table 4).[10] While this and comparable data sets are valuable for making informed decisions regarding dietary choices, they provide little additional information regarding either the temporal and spatial variability of Hg levels in biota or underlying processes and mechanisms influencing Hg bioaccumulation and biomagnification in marine systems.

Table 4. Levels of Total Hg (μg g^{-1} Wet Weight), Most of Which Is MMHg, in Seafood[236,291]

fish species	mean (range)[a]	n[b]
tilefish	1.45 (0.65−3.73)	60
shark	0.99 (ND−4.54)	351
swordfish	0.98 (ND−3.22)	618
king mackerel	0.73 (0.23−1.67)	213
orange roughy	0.55 (0.30−0.86)	49
halibut	0.25 (ND−1.52)	46
cod	0.10 (ND−0.42)	39
scallop	0.05 (ND−0.22)	66
tuna (canned, light)	0.12 (ND−0.85)	347
tuna (canned, albacore)	0.35 (ND−0.85)	399
tuna (fresh/frozen, yellowfin)	0.33 (ND−1.08)	87

[a] ND denotes "not detected." [b] Number of samples analyzed.

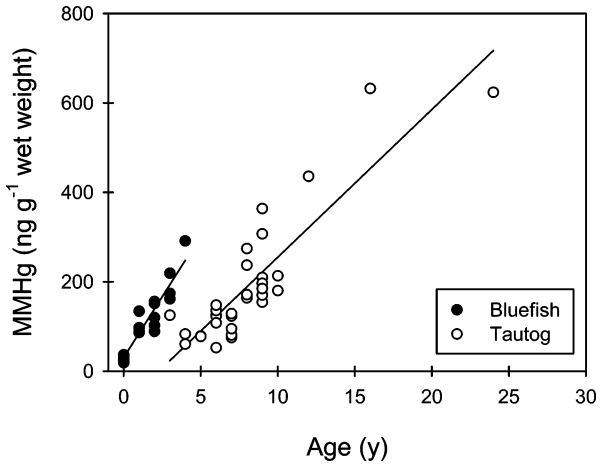

Figure 14. Relationship between MMHg in axial muscle and age of bluefish (*Pomatomus saltatrix*) and tautog (*Tautoga onitis*) sampled from Long Island Sound.[119]

Only a limited number of studies have investigated the bioaccumulation and biomagnification of MMHg in marine food webs, and most focused on the coastal zone. Marine biota obtain MMHg from water, sediment, and food. MMHg and Hg(II) are concentrated from water by unicellular organisms,[237] whereas diet is the primary source of MMHg in multicellular heterotrophs.[238,239] Slow rates of elimination, relative to the rate of uptake, result in the bioaccumulation of MMHg.[240] That is, MMHg concentrations typically increase with the age/size of an organism,[119,224−227,229,241−250] as shown in Figure 14 for bluefish and tautog sampled from Long Island Sound. Relatively slow rates of MMHg depuration also result in its biomagnification during trophic transfers; MMHg increases in concentration with progressively greater trophic levels in a food web.

Table 5 shows the biomagnification of MMHg in three coastal marine/estuarine food webs. Princess Royal Harbour is a marine embayment in western Australia that is contaminated with inorganic Hg from a fertilizer plant.[251] Long Island Sound (northeastern U.S.[107]) and the North Sea[113] (western Europe) are coastal systems impacted less severely by atmospheric deposition and fluvial sources of Hg. As noted in section 3.5, levels of MMHg in filtered coastal waters range typically from 0.05 to 0.4 pM, or about 0.00001−0.00008 ng g^{-1}, which encompasses concentrations determined for Long Island Sound and the North Sea (Table 5). Microseston (i.e., phyto- and bacterioplankton) bioconcentrate Hg species from surface water. The increase of MMHg between water and microseston is $10^{4.2}$ in Long Island Sound and $10^{4.8}$ in the North Sea, which is comparable to the $10^{3.7}$ increase between water and microseston on the continental shelf of southern New England[42] and freshwater systems ($10^{3.8}$−$10^{5.2}$).[252,253] This is the greatest biomagnification step for MMHg in the food webs of Long Island Sound, the North Sea, and, by extension, other comparable marine ecosystems. MMHg accumulated by microseston is transferred successively to grazing zooplankton, prey fishes, and piscivorous fish, ultimately resulting in a 10^6−10^7 magnification of MMHg between water and muscle of predatory fish species (Table 5). Moreover, the percentage of total Hg as MMHg (i.e., %MMHg) increases concomitantly with the concentration of MMHg among trophic levels (Table 5). While forms of Hg(II) are bioconcentrated from water at the base of the food web, Hg(II) is not bioaccumulated or transferred as efficiently as MMHg between higher trophic levels. Indeed, and even in highly polluted Princess Royal Harbour,[251] MMHg is greater than 90% of total Hg in the muscle of piscivorous and prey fishes (Table 5). It has been hypothesized that much, if not most, of the MMHg in biota of coastal marine systems is derived from in situ sedimentary production.[39,119]

Patterns of MMHg accumulation in food webs of the open ocean are largely unknown because there has been no systematic examination of concentrations in surface water, microseston, zooplankton, and, for the most part, fishes. As noted above, there are only a limited number of investigations of MMHg bioaccumulation in marine fish, and most of these studies have focused on piscivorous species in narrowly defined coastal regions and peripheral seas that often are impacted by point sources of Hg contamination. It is expected that levels of MMHg in microseston of the open ocean are about 10^4 greater than those in surface water, as they are in the coastal zone and freshwater lakes, but definitive determinations of either parameter are absent for the open ocean. Moreover, future investigations must consider "bioadvection" of MMHg among coastal systems and between the coastal zone and the open ocean. Many species of marine fish are migratory and, thereby, transport MMHg about the oceans. A striking example of marine fish migration has been observed for Atlantic bluefin tuna, some of which migrate seasonally across the Atlantic (Figure 15).[254] Such behavior suggests that MMHg produced in Chesapeake Bay, for

Table 5. MMHg Biomagnification in Three Coastal Marine Food Webs

	Princess Royal Harbour[225]		Long Island Sound[119]		North Sea[292]	
food-web component	MMHg (ng g^{-1} wet wt)	%MMHg[a]	MMHg (ng g^{-1} wet wt)	%MMHg	MMHg (ng g^{-1} wet wt)	%MMHg
piscivorous fish	2300	>95	140	98	150	94
prey fish	460	93	24	92	100	96
benthic invertebrates	140	45			51	63
zooplankton			1.1			
microseston	2	10	0.5	9	1.2	3
filtered surface water			0.00003	3	0.00002	5

[a] Percentage of total Hg present as MMHg

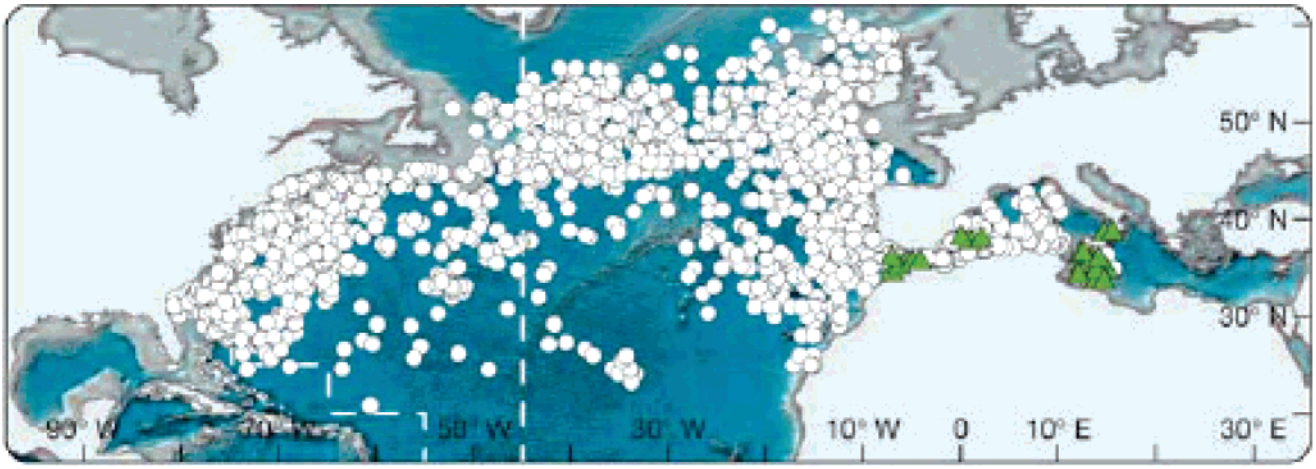

Figure 15. Multiannual record of geopositions for three bluefin tuna (*Thunnus thynnus*) implanted with satellite-transmitting tags (white circles) and locations where 26 tuna implanted with archival tags were captured (green triangles). All fish were tagged in coastal waters near either North Carolina or Massachusetts. Reprinted by permission from Macmillan Publishers Ltd: *Nature* (http://www.nature.com) (ref 254), copyright 2005.

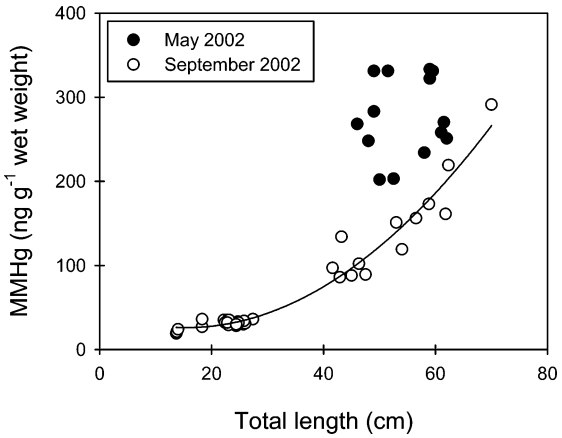

Figure 16. MMHg in axial muscle versus total length of bluefish sampled from Long Island Sound in May and September 2002. Reprinted Figure 6 from ref 119, copyright 2006, with kind permission of Springer Science and Business Media.

example, may be accumulated by migratory prey fish that transport MMHg to shelf waters, where they may be eaten by bluefin tuna that later are captured in the Mediterranean Sea. Such transport of MMHg with migratory fish has been observed recently for bluefish, a coastal piscivore that moves seasonally between temperate and subtropical waters. The mean MMHg content of bluefish migrating northward and into Long Island Sound in May 2002 was 2-fold greater than that of comparably sized bluefish migrating southward 4 months later (Figure 16).[119]

9. Models of Hg Cycling in the Ocean

Several conceptual and mathematical models of Hg cycling in the ocean have been formulated to aid in hypothesis development and testing. They can be separated into three general categories: (1) local scale, dealing primarily with a single small body of water; (2) regional scale, dealing with larger bodies or segments of basins; and (3) global scale, incorporating the whole ocean into models dealing with atmospheric cycling as well. Some of the first attempts at constructing fully constrained models of Hg cycling in a water body were made for lakes,[70,255] although models for Framvaren Fjord, the Equatorial Pacific Ocean, and the Pettaquamscutt River Estuary[46,132,134] were developed contemporaneously. While several models preceded these, most were based on data of questionable quality. The first fully-constrained global scale model was that of Mason et al.,[29] which has since been revised in significant ways.[20,22,23,256,257] More recently, marine Hg research and associated models have focused on the coastal zone and, in particular, on impacted embayments such as Minamata Bay, San Francisco Bay (SFB), Chesapeake Bay (CB), Long Island Sound (LIS), Narragansett Bay, New York/New Jersey Harbor (NYH), French macrotidal estuaries, and the Gulf of Trieste.[3,20,107,115,116,258−264] This discussion will focus on several coastal examples and the salient features of the global models.

9.1. Long Island Sound (LIS), Chesapeake Bay (CB), San Francisco Bay (SFB), and New York/New Jersey Harbor (NYH)

LIS and CB are examples of coastal marine systems expected to be quite common and useful analogues with respect to their Hg cycling. These are regionally important commercial and recreational resources, and their watersheds are home to large human populations. Both systems contain substantial urbanized areas and receive nearly identical total Hg loadings normalized by water body area (ca. 300 nmol m^{-2} $year^{-1}$).[107,116] NYH is comparable in many respects, but the area of the Harbor (500 km^2) is small relative to the size of the watershed (42000 km^2), which is similar to that of LIS (41000 km^2). Accordingly, and while atmospheric deposition to the watershed is a primary source of Hg in each system, loadings from the watershed are focused into a much smaller area in NYH and SFB as compared to LIS and CB. Table 6 summarizes the mass balance studies for these systems. It should be noted that changes in anthropogenic activity within the systems and their watersheds suggest that mass balance and steady state are not required to currently exist. The degree of temporal change in these systems, however, is small relative to the uncertainty of measurements used to construct the mass balances. In these cases, therefore, mass balances provide a test for the consistency of measurements and process estimates, an important gauge of our biogeochemical understanding and a tool for comparing Hg cycling among systems.

There are some common findings among the mass balances for the coastal marine systems studied that include the

Table 6. Mass Balance Models for Three Coastal Embayments in the United States[a]

	New York/New Jersey Harbor[207,264] (area = 500 km^2)		San Francisco Bay[263] (area = 1236 km^2)		Long Island Sound[39,107] (area = 3250 km^2)		Chesapeake Bay[116] (area = 12000 km^2)	
term	Hg flux	MMHg flux	Hg flux	MMHg flux	Hg flux	MMHg flux	Hg flux	MMHg flux
				Sources				
atmospheric dep.	27 (54)	0.5 (1)	20 (16.2)	0	130 (40)	3.5 (1.1)	1300 (108)	6.5 (0.54)
river/watershed	2270 (4540)	21 (42)	1208 (977)	1 (0.8)	970 (298)	22.5 (6.9)	2125 (177)	27.6 (2.3)
water treatment facilities	140 (280)	3 (6)	19 (15.4)	0	60 (18.5)	1.5 (0.5)	n/a	n/a
net methylation	n/a	8 (16)	n/a	2 (1.6)	n/a	55 (17.2)	n/a	63.2 (5.3)
				Sinks				
bioaccumulation	n/a	12.5 (25)	n/a	n/a	n/a	50 (15.6)	50 (4.2)	50 (4.2)
evasion	60 (120)	0	3 (2.4)	0	400 (123)	0	580 (48)	0
net ocean export	1560 (3120)	14 (28)	513 (415)	2 (1.6)	80 (25)	1.5 (0.5)	1085 (90)	37.8 (3.2)
burial	820 (1640)	4 (8)	732 (592)	1 (0.8)	680 (209)	5.2 (1.6)	1890 (158)	9.5 (0.8)
photodecomposition	n/a	2 (4)	n/a	n/a	n/a	27 (8.3)	n/a	n/a
				Total Sources/Sinks				
total	2440 (4880)	32.5 (65)	1247 (1009)	3 (2.4)	1160 (357)	84.5 (26)	3605 (300)	97.3 (8.1)

[a] Fluxes are mol year^{-1}; values in parentheses are area normalized, nmol m^{-2} year^{-1}. n/a = not available or not considered.

following: (1) Total Hg loadings to all marine systems are generally dominated by direct and/or indirect (i.e., riverine) atmospheric inputs (e.g., LIS and CB; Table 6). (2) With a few notable exceptions (e.g., Minamata Bay), internal production is an important source of MMHg. (3) Mass balances for total Hg generally result in good closure, indicating that the major features of Hg cycling have been identified and appropriately described (Table 6). (4) The number of these mass balance studies is relatively small, and they do not currently include coastal or estuarine systems that are relatively pristine.

Budgets for NYH and SFB are shown in Table 6 to represent exceptions to these common themes. In these systems, the nearly 100-fold difference in watershed/estuary area results in a much lower direct atmospheric input of Hg than for CB and LIS. Furthermore, and relative to all of the Hg entering the system, SFB and NYH appear to methylate a smaller proportion of their load. Dividing the net methylation term by the total input of Hg reveals that LIS, CB, SFB, and NYH internally methylate about 5, 2, 0.2, and 0.3% of Hg loadings to each system. While the net methylation flux for CB was not measured and is therefore highly uncertain (i.e., closing term in the budget), the methylation/Hg loading ratio for CB is within the same order of magnitude as that for LIS, where all fluxes were determined. The striking difference between SFB and NYH and the other two systems is likely the result of reduced bioavailability of Hg delivered from the watershed.[105,207,265] In the case of NYH, allochthonous organic material (terrestrial and/or sewage) appears to inhibit the sediment−water partitioning and subsequent bioavailability of Hg(II) for methylation in NYH relative to LIS and other coastal systems where most benthic organic matter is derived from planktonic sources.[207] In SFB, a large percentage of the total Hg load arrives in the form of mineral particles that are likely insoluble and unavailable.[266] It also is interesting to contrast the Hg "scrubbing" properties of the three systems, namely the fraction of their total load that is exported to the ocean. These values are 7, 30, 41, and 64% for LIS, CB, SFB, and NYH, respectively. The Hg withholding feature of coastal embayment/estuaries may represent a "good news/bad news" situation where Hg retention within coastal systems yields less export but results in its accumulation in biologically active regions of the ocean important for human health. The impact of these competing effects can be examined by normalizing Hg export to freshwater input on the watershed scale and then scaling to the total freshwater input to the ocean (10^6 m^3 s^{-1}). In the case of LIS, where the total freshwater input during the study was 618 m^3 s^{-1} and the total Hg and MMHg export fluxes were 80 and 1.5 mol year^{-1}, respectively,[107] fluxes of 0.13 and 0.002 Mmol year^{-1} are estimated for the global ocean. This first-order estimation is supported by more rigorous estimations of the continental input of Hg to the ocean[109] and suggests these fluxes are quite small compared to other inputs to the global ocean (see below). Thus, from a human health perspective, Hg retention within coastal systems could be less desirable than export offshore into regions of generally lower productivity if this results in less bioaccumulation and human exposure. Without information concerning Hg cycling on continental shelves, however, this is currently impossible to assess.

9.2. Global and Oceanic Hg Models

The study of lakes and coastal systems, while complex, is constrained by growing sets of concentration and flux data for various Hg species. Modeling the global cycle of Hg, however, has and continues to be hampered by the lack of available data. Furthermore, sources of Hg to the ocean and atmosphere are not well constrained, and many of the important processes (e.g., evasion) have not been or cannot easily be determined. Remarkably, however, a great deal of progress has been made in the arena of understanding the processes associated with the global Hg cycle. For example, the mass balance and secular change model of Mason, Fitzgerald, and Morel, the "MFM" model,[29] was able to reconcile all fluxes and budgets to within a factor of 2 based on concentration, speciation, and emissions data that were available at the time. MFM identified some important features of the global Hg cycle that more recent investigations have confirmed: (1) Atmospheric deposition is the dominant input term to the world ocean. (2) Riverine fluxes, while important at the margins, are a small part of the global budget. (3) Evasion is a major process whereby Hg leaves the ocean. (4) Deep sea burial is a relatively small term, which requires that most Hg is removed from participation in the global cycle on century time scales through sequestration on land. (5) Human activity has likely perturbed the cycle by increasing emissions to the atmosphere (and therefore the rest of the surface environment) by approximately a factor of 3.

These major features, as noted previously and illustrated in Figure 1, are described by the model of Mason and Sheu,[20] a recent revision to the MFM model. This model, as well as the GRIMM simulation,[22] suggests that the net evasion to the atmosphere is less than predicted by MFM but that it remains a very important sink for Hg in the ocean as a whole. The diminished evasion flux in the Mason and Sheu model is the result of oxidation of Hg^0 within the marine boundary layer, likely driven by reactive halogen species. Oxidation in the marine boundary layer results in rapid recycling of Hg between Hg^0 in surface water and gas-phase ionic Hg in the air above the ocean. In both of these MFM revisions, the ocean is a net sink for Hg, at 2.4 Mmol $year^{-1}$ in the Mason and Sheu projection and 4 Mmol $year^{-1}$ in the GRIMM model.[22] In both cases, the majority of this Hg is transferred below the euphotic zone (>500 m;[20] >100 m[22]) as a result of particle scavenging. As noted in the Introduction, however, and as simulated by the GRIMM model, most of the pollutant Hg inputs over the past 150 years have likely remained, on average, at depths $\leq$ 1000 m.

Both of these MFM revisions draw heavily on the long-term increase of Hg deposition garnered from analysis of lake sediments from various locations in both hemispheres.[22,267−270] These archives indicate that the flux of Hg into the atmosphere has increased by approximately a factor of 3 since the Industrial Revolution. This places a fairly firm constraint on the relative strength of natural and anthropogenic sources to the atmosphere. Unfortunately, no comparably reliable archive for the long-term change of Hg concentrations or fluxes in the ocean has yet been developed. A record of temporal change from such an archive would be enormously useful in understanding the way in which the atmosphere and ocean interact to control Hg cycling and would be helpful to distinguish between different modeled views of the system.

One potential set of archives are fish and seabird tissues to be found in many museum collections worldwide.[271] Theoretically, both archives should be useful and provide complimentary results. In practical terms, however, there are reasons to be skeptical of the veracity of these data. Museum specimens are not typically collected or stored under conditions that would preserve their integrity with respect to Hg concentrations. This can be expected to be especially true for fish flesh, which usually is stored in a preservative such as formalin. Furthermore, the Hg content of fish flesh is related to the fish's age and cumulative exposure (e.g., Figure 14), which requires information regarding the fish age and/or length as well as sampling location to interpret. Bird feathers appear to be more stable with regard to Hg and may be cleaned to remove surficial contamination prior to analysis. Furthermore, Hg is deposited in feathers in proportion to the bird's instantaneous exposure and is somewhat easier to interpret. Figure 17 shows results from feather Hg analysis of two seabird species breeding in the Azores.[271] Results for both species, though feeding on differing prey items, suggest substantial changes in the MMHg content of their feathers during the past 150 years (approximately 2−3×) and are in general agreement with the results for the surface ocean compartment in the GRIMM model.[22]

There are some Hg concentration data for fish, water, and air that stretch back to advent of the use of clean techniques (1970s, early 1980s). In recent work, some of these data have been compiled but show no clear temporal change in Hg levels.[27,97,257] It must be noted that the seabird archive extends

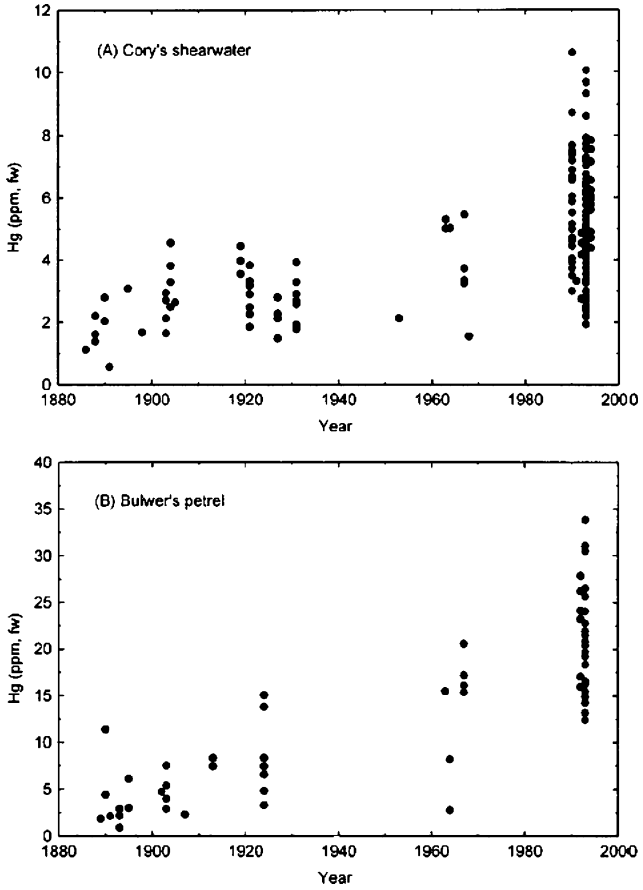

Figure 17. Historical concentrations of Hg in seabird feathers from museum and contemporaneously collected samples. Panel A shows results for Cory's shearwater, an epipelagic feeder, while the results of Panel B are for Bulwer's petrel, a mesopelagic feeder. Copyright 1997 Society of Environmental Toxicology & Chemistry. From *Environmental Toxicology & Chemistry*, by L. R. Monteiro and R. W. Furness (ref 271). Reprinted by permission of Allaince Communications Group, a division of Allen Press, Inc.

to the late 1800s, which is a comparable time over which predictions made by MFM and similar models should be compared. Looking for small changes, on the order of 1% change in the Hg content of the ocean per year using the sparse datasets covering the shorter term (e.g., fish and water samples) is a daunting task. Furthermore, while the present situation could be one where the system has been significantly perturbed since the Industrial Revolution, the current trend in change could be flat or even decreasing.

There is an urgent need for marine monitoring programs as well as the development of additional archives to fully understand the past and present dynamics of Hg in the marine environment. For example, numerical simulations of air/sea interactions and their impact on the global Hg cycle[272−274] are out-pacing the development of required datasets, especially regarding marine Hg distributions and speciation. Thus, the oceans are currently understudied and undersampled with regard to Hg.

10. Acknowledgments

We are most appreciative of the current and past efforts of our colleagues and peers in their quest to understand the marine biogeochemical cycling of Hg and its wider environmental and human health implications. Indeed, the importance of the oceans in the Hg cycle and the critical

need for more information were formally recognized by the Hg community at the ***Eighth International Conference on Mercury as a Global Pollutant*** (August 2006, Madison, WI). In the preparation of this review, W.F.F. received partial support from grants from the NSF-Office of Polar Program and the Hudson River Foundation, C.H.L. from the Woods Hole Oceanographic Institution, and C.R.H. from the Postdoctoral Scholar Program at WHOI, with funding from the Doherty Foundation

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CR050353M