Marine Biogeochemical Cycling of Mercury

William F. Fitzgerald,*,† Carl H. Lamborg,‡ and Chad R. Hammerschmidt‡

Department of Marine Sciences, University of Connecticut, 1080 Shenecosett Road, Groton, Connecticut 06340, and Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

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Contents

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

† University of Connecticut.
‡ Woods Hole Oceanographic Institution.

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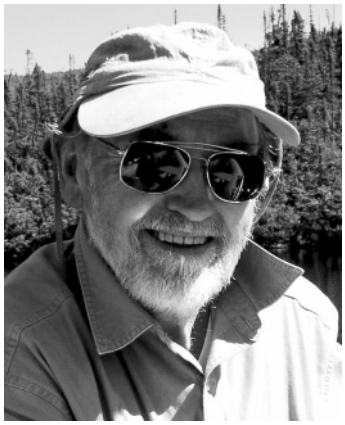

William F. Fitzgerald has been pursuing Hg in the environment for nearly forty years. He is a native Bostonian and first generation American, whose interest in chemistry began at Boston Technical High School. He was educated as a classical chemist and received a B.S. and M.S., respectively, from Boston 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

Chad R. Hammerschmidt received a B.S. (1997) and M.S. (1999) from the University of Wisconsin—La Crosse. He then began graduate studies at the University of Connecticut, where he was a U.S. Environmental Protection Agency STAR graduate fellow and received a Ph.D. in oceanography under the guidance of Professor William F. Fitzgerald in 2005. Dr. Hammerschmidt is currently a Postdoctoral Scholar in the Department of Marine Chemistry and Geochemistry at the Woods Hole Oceanographic Institution. His research interests include the biogeochemical cycling of Hg, MMHg, and other biologically active contaminants and trace metals in the environment. He has published broadly with recent papers ranging from mosquitoes as bioindicators of Hg loadings to Hg methylation and bioaccumulation in the coastal zone.

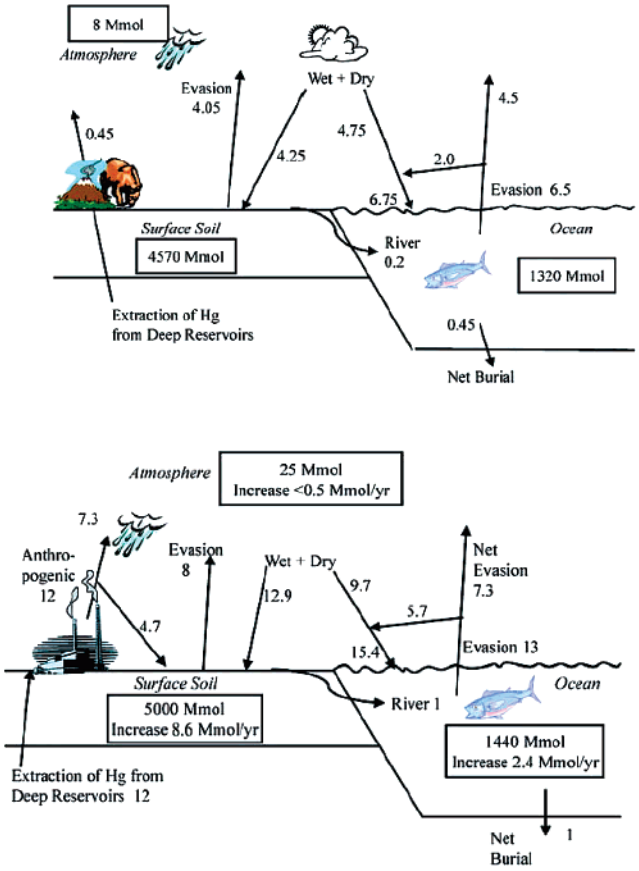

Figure 1. Global Hg cycle. The top panel represents the preindustrial cycle (ca. 200 years ago), while the bottom panel is the current status. All fluxes are in Mmol year^{-1}, while the reservoir burdens are listed as Mmole inside boxes, along with estimates of the current rate of change in each reservoir.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

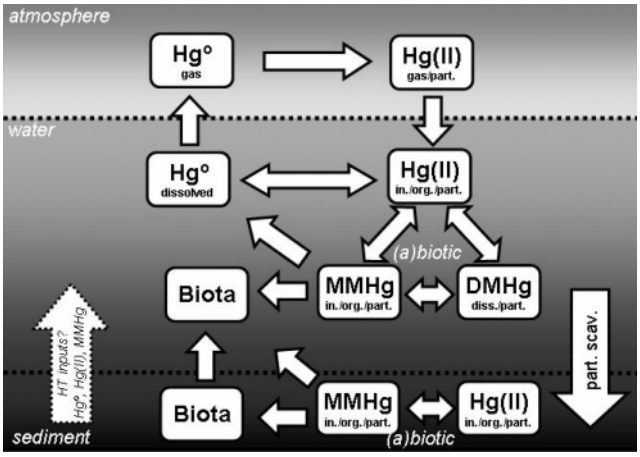

Figure 2. Biogeochemical cycling of Hg in the ocean.

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 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.

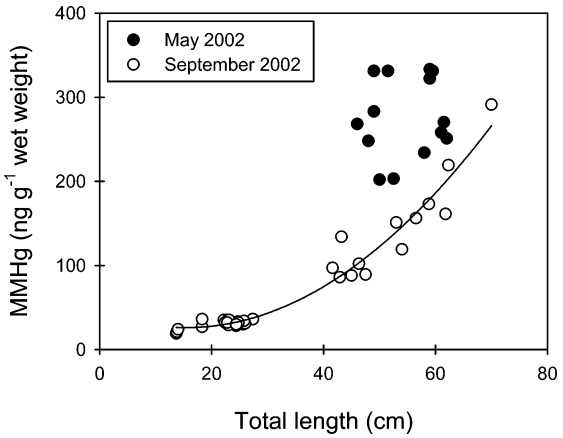

Figure 16. MMHg in axial muscle versus total length of bluefish sampled from Long Island Sound in May and September 2002. Reprinted Figure 6 from ref 119, copyright 2006, with kind permission of Springer Science and Business Media.

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

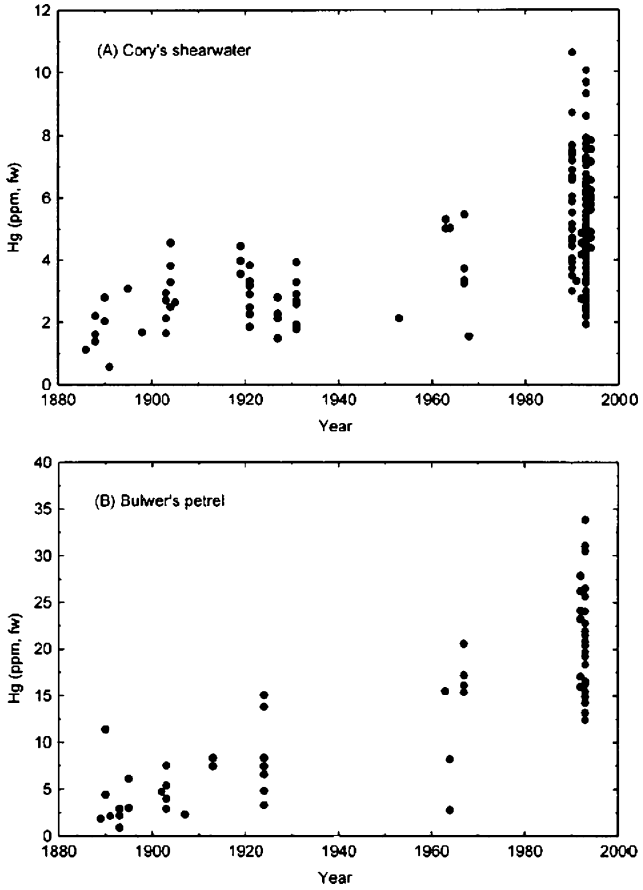

Figure 17. Historical concentrations of Hg in seabird feathers from museum and contemporaneously collected samples. Panel A shows results for Cory's shearwater, an epipelagic feeder, while the results of Panel B are for Bulwer's petrel, a mesopelagic feeder. Copyright 1997 Society of Environmental Toxicology & 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.

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