9.04

Geochemistry of Mercury in the Environment

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9.04.1 INTRODUCTION

Mercurial, the metaphor for volatile unpredictable behavior, aptly reflects the complexities of one of the most insidiously interesting and scientifically challenging biogeochemical cycles at the Earth's surface. Elemental mercury is readily recognized as a silvery liquid at room temperature. Its gas phase is important geochemically, since mercury and some of its compounds have relatively high vapor pressures. Mercury (Hg, from the Latin *hydrargyrum* or "watery silver") is sulfur loving (i.e., chalcophilic) and extremely active biologically. It is mobilized tectonically, and significant deposits are found in mineralized regions characterized by subduction zones and deep-focus earthquakes (Schlüter, 2000). Many of the major deposits are shown in Figure 1 (Kesler, 1994).

The remarkable and useful qualities of mercury and its major mineralized form (cinnabar, HgS) have been well known for thousands of years. The Almadén mine in Spain, for example, the "richest known single source of cinnabar and quicksilver," has been active for more than 2,500 years (Goldwater, 1972). Mercury products (e.g., thermostats, batteries, switches, and fluorescent lighting) and applications (e.g., chlor-alkali production, dentistry, pharmaceuticals, and catalysis) have been a practical part of modern life, while the wastes have been quite detrimental. Today, mercury emissions associated with fossil fuel burning, especially coal, and high-temperature combustion processes (e.g., municipal waste incineration) represent the primary sources of pollutant mercury to the environment on a global scale. As a result, mercury emissions since the mid-nineteenth century appear to have been in step with increases in emissions of CO_2 (Lamborg *et al.*, 2002b). During the past decade, emissions, discharges, and nonpoint source inputs of mercury appear to have peaked and may be diminishing in many developed countries. Unfortunately, and on a global scale, declines are countered by increases in anthropogenic mercury releases from developing nations, particularly in Asia (Pacyna and Pacyna, 2002). Additionally, environmental gains through pollution controls, remediation, and regulations are tempered by the large reservoir of historic mercury, the pollution "legacy," residing in watersheds and sediments of many terrestrial, freshwater, and marine environments.

Although mercury has been used in "spring tonics," as a "cure" for syphilis, and a panacea for other afflictions, it is now recognized as a highly toxic trace metal that concentrates in aquatic food webs. According to Clarkson (1997), the principal human exposure to inorganic mercury species is from elemental mercury vapor, which is derived principally from industries such as gold and silver mining and chlor-alkali plants, and from dental amalgams. Deleterious health effects (e.g., "mad hatters disease") have been known since ancient times, and as Clarkson states, "severe exposure results in a triad of symptoms, erethism, tremor, and gingivitis." Today, however, the principal mercury-related human health concern is associated with exposure to the highly neurotoxic organomercury species, monomethylmercury (MMHg). This exposure is due almost entirely to consumption of fish and fish products (Fitzgerald and Clarkson, 1991; National Research Council, 2000). Inorganic mercury, whether natural or pollution derived, can be readily methylated in aquatic systems. Mercury methylation appears to be predominately biotic, although some abiotic production is likely in natural waters (Benoit *et al.*, 2003; Gårdfeldt *et al.*, 2003). *In situ* methylation of "reactive" or bioavailable mercury by sulfate-reducing bacteria (SRB) (and possibly others) has been documented to result in the accumulation of MMHg in freshwater food webs and fish (e.g., Westöö, 1966; Wood *et al.*, 1968; Jensen and Jernelöv, 1969; Wiener *et al.*, 1990a; Gilmour and Henry, 1991; Watras and Bloom, 1994; Watras *et al.*, 1994; Hall *et al.*, 1998; Fleming *et al.*, 2006). This linkage is quite evident in the elevated MMHg in fish from reservoirs created by dam construction and subsequent flooding of landscapes (e.g., Cox *et al.*, 1979; Bodaly *et al.*, 1984; Tremblay *et al.*, 1998). A similar process is thought to occur in the marine water column, possibly first through the formation of dimethylHg (DMHg) followed by decomposition to MMHg (Mason and Fitzgerald, 1993; Mason *et al.*, 1998; Mason and Sullivan, 1999a, b). Microbially mediated methylation continues to amplify the insidiousness of current and historic mercury pollution and health risks to wildlife and humans. Indeed, toxicologically, methylation of inorganic mercury is the most important transformation affecting the behavior and fate of mercury in aquatic systems. Its accumulation in freshwater and marine fish can reach levels that not only pose a threat to human health (Grandjean *et al.*, 1997; Davidson *et al.*, 2000), but can also reduce the reproductive success of piscivorous wildlife (e.g., Scheuhammer, 1991; special section of *Environmental Toxicology and Chemistry*, 1998, 17(2): 137–227, 12 papers, M. W. Meyer, ed.) and the fish themselves (Wiener *et al.*, 1990b; Wiener and Spry, 1996; Hammerschmidt *et al.*, 2002). Wiener *et al.* (2002) presented an up-to-date review of

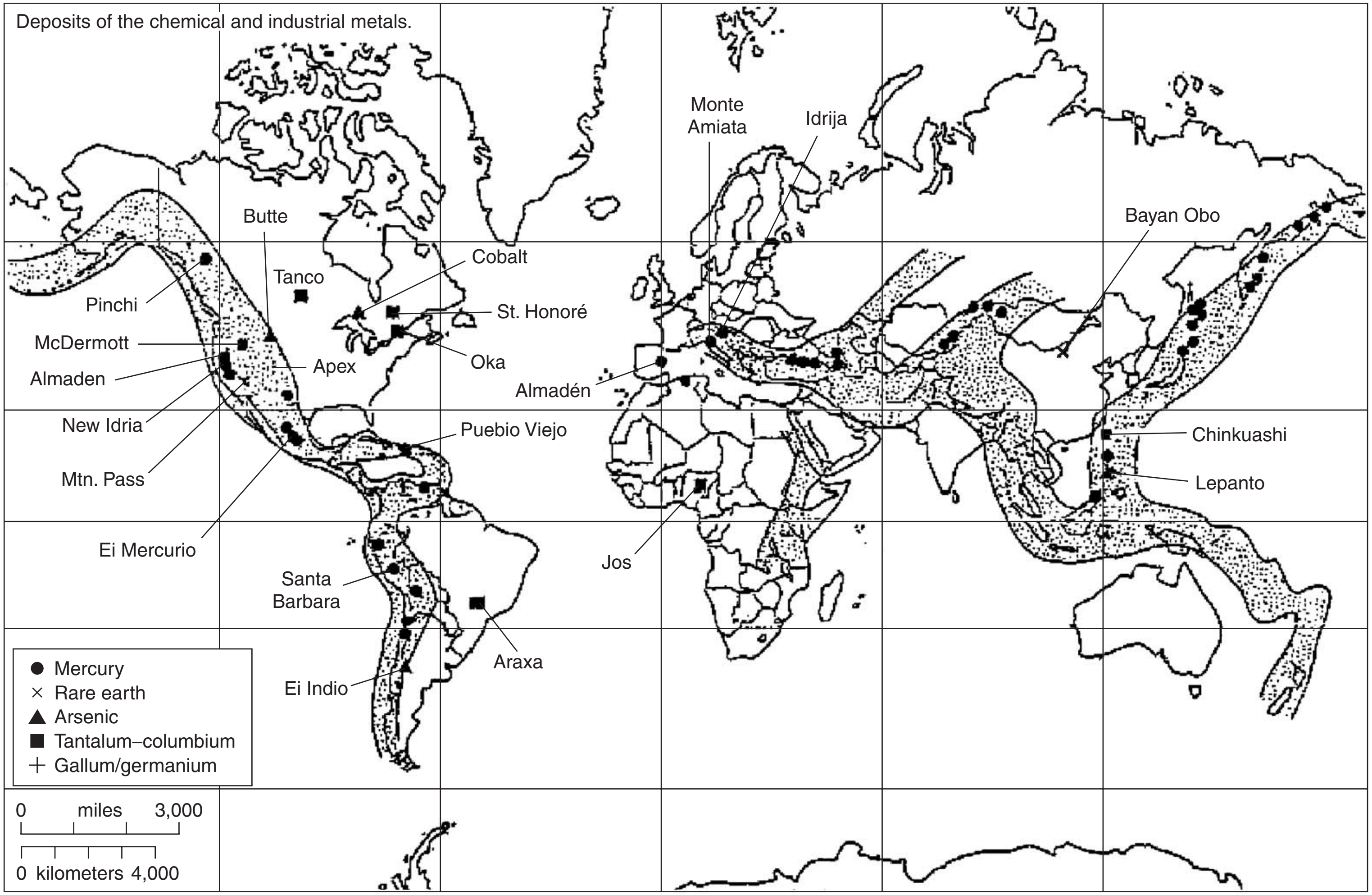


Figure 1 The global Hg belt. Source: Kesler (1994).

mercury toxicology in a number of different animal species.

MMHg poisoning is known as "Minamata disease." Unfortunately, between 1950 and 1975, major industrially related mass poisonings, severe debilitation, and many deaths occurred in Minamata and Niigata (Japan) and in Iraq. The Japanese poisonings resulted from consumption of locally caught fish and seafood that had been contaminated principally by MMHg discharged with wastewater from factories making acetaldehyde (Chisso Co. Ltd and Showa Denko Co. Ltd). The MMHg was synthesized abiotically as a by-product during the production of acetaldehyde (inorganic mercury was used as a catalyst). In the Iraqi tragedy, the source was contaminated bread, which had been made with flour, unknowingly milled from wheat treated with MMHg as a fungicide (Bakir *et al.*, 1973). There is an extensive scientific, medical, and general literature as well as news accounts of these tragedies. The following works on the Japanese poisonings provide an overview and useful starting point for a more in-depth examination: Smith (1975), Japan Public Health Association (2001), The Social Scientific Study Group on Minamata Disease (2001) and George (2001). There are other examples of severely mercury contaminated sites and the interested reader is directed to the volume entitled *Mercury Contaminated Sites—Characterization, Risk Assessment and Remediation*, edited by Ebinghaus *et al.* (1998), which also contains descriptions of the Minamata situation.

In the mid-twentieth century, Goldschmidt (1954) cryptically summarized knowledge of the environmental cycling of mercury as, "not much information is available concerning the geochemistry of mercury." Moreover, and as he emphasized for that period, "most of the modern analytical data are due to A. Stock and co-workers," which were derived from their pre-World War II studies (e.g., Stock and Cucuel, 1934). In contrast, at the beginning of the twenty-first century, dozens of environmentally related mercury publications appear yearly. There is an abundance of distributional data, an enhanced knowledge of the biogeochemical cycling of mercury and the impact of anthropogenic activities, a fuller appreciation of the utility, dangers, and complexities characterizing the mobilization, interactions, and fate of this biologically active element, and an awareness of daunting challenges inherent in studying a metal that includes a gas phase as a major feature of its biogeochemistry at the Earth's surface. The potential risks of human exposure to MMHg, especially prenatally, and the potential deleterious ecological consequences from localized to global-scale mercury pollution have given much impetus to mercury studies and regulatory activities internationally. As of the summer of 2006, there have been seven international conferences on "Mercury as a Global Pollutant," since 1990. The city of Minamata, the venue for the sixth conference in 2001, provided conferees with poignant evidence of the tragic legacy of mercury contamination. The abstracts and publications from these broadly based meetings, which include basic biogeochemistry, environmental and pollution-related studies, ecological and human toxicology, and analytical developments, chronicle the rapid worldwide expansion of mercury research and knowledge.

This chapter focuses principally on the low-temperature environmental biogeochemistry of mercury. We present the current understanding of mercury cycling at the Earth's surface (soils, sediments, natural waters, and the atmosphere). Our coverage, as appropriate, will include the anthropogenic interferences (i.e., mercury pollution) and biological mediation, which affect significantly the speciation, behavior, and fate of mercury in the environment. Complementary information on mercury geochemical cycling in and among the various earthly reservoirs is presented in other chapters of this treatise.

9.04.1.1 The Global Mercury Cycle

Major features of the global mercury cycle have been illustrated using the relatively simple three-reservoir mass balance developed by Mason, Fitzgerald, and Morel in 1994 ("MFM"). Refinements are considered in Section 9.04.7. The MFM model provides estimates of natural and anthropogenic fluxes and an assessment of impact from human-related mercury emissions on the natural cycle for 1990 (Figure 2a). The pre-industrial situation is shown in Figure 2b. It is evident that the atmosphere and oceans play important roles in the distribution and redistribution of mercury at the Earth's surface. Indeed, atmospheric mercury deposition to the oceans greatly exceeds riverine inputs. The MFM model also suggests that the natural cycle of mercury has been severely perturbed. Human-related mercury emissions dominate the cycle such that most of the mercury in the atmosphere and surface oceans is anthropogenic. Moreover, the integrated estimate for total loadings from globally dispersed, anthropogenic mercury emissions between 1890 and 1990 is 1,000 Mmol (200 kt). The MFM simulation predicts that ~95% of this mercury

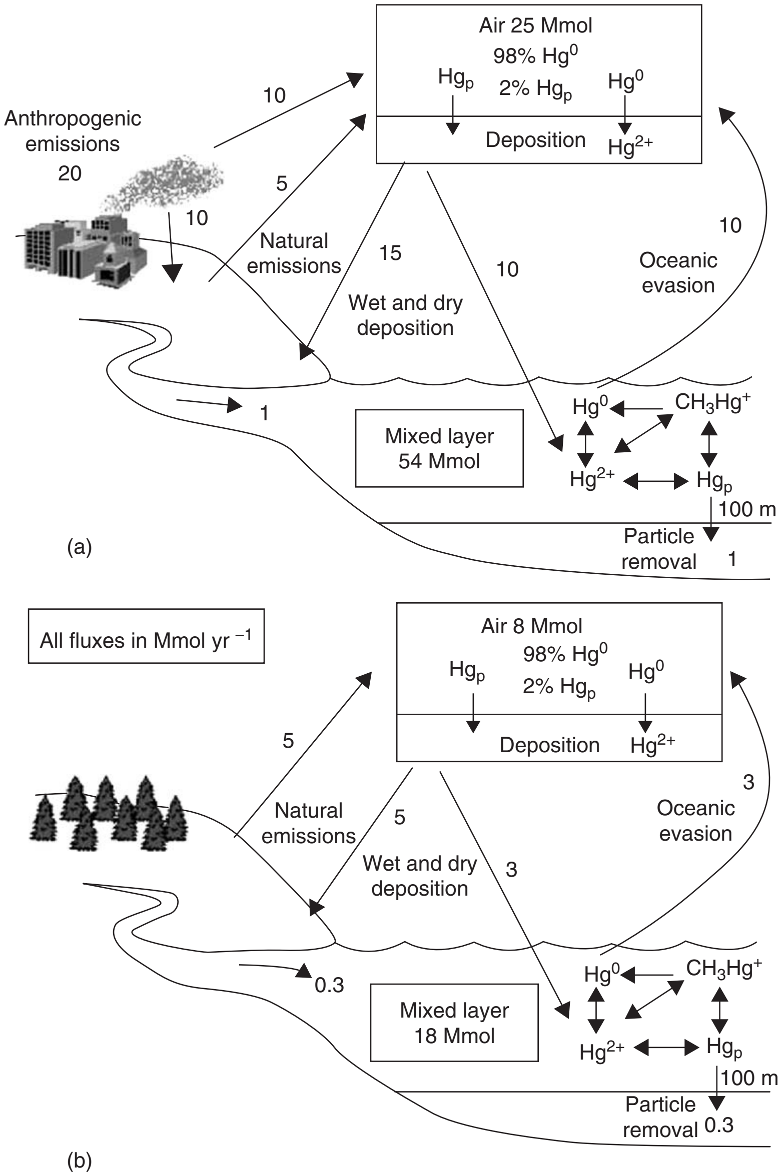


Figure 2 Fluxes of Hg on a global scale. (a) The current condition and (b) the preindustrial condition. All fluxes in megamoles of Hg per year. Note the balance of deposition to and evasion from the ocean, making soils the primary sink on decade/century timescales. One result of human activity has been a tripling of Hg in the atmosphere and surface ocean. After Mason *et al.* (1994).

is sequestered in terrestrial systems, with the remainder in the oceans and atmosphere. The MFM analysis suggested that about half of the modern pollution-related emissions (20 Mmol yr^{-1}) enter the global cycle while the other half is deposited near sources. The MFM estimate for the globally dispersed anthropogenic contribution is similar to the most recent estimate of 9.6 Mmol yr^{-1} (for 1995) reported by Pacyna and Pacyna (2002).

Elemental mercury, a monatomic gas, is the dominant atmospheric form and has a long residence time in the troposphere (>1 year; Fitzgerald *et al.*, 1981; Slemr *et al.*, 1981; Lindqvist *et al.*, 1991; Lamborg *et al.*, 2000, 2002b). Such longevity allows emissions of mercury into the atmosphere from natural and anthropogenic sources to be dispersed widely across the Earth's surface. The redox couple of Hg^0 with the stable mercuric ion (Hg^0/Hg^{2+}; $E^\circ = 0.85$ V) is similar to that of the Fe(II)/Fe(III) couple, thereby providing the potential for dynamic oxidation and reduction cycling in the range of common environmental redox (i.e., pe) conditions. A unique and important example of this is the biologically and abiotically mediated reduction of Hg^{2+} resulting in widespread supersaturation of Hg^0 in freshwater and saltwater and subsequent evasion (Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993; Amyot *et al.*, 1997; Rolfhus, 1998). Field and laboratory observations in aqueous systems have documented the important influence of photochemical and bacterial reactions on the *in situ* reduction of Hg^{2+} (Mason and Fitzgerald, 1993; Amyot *et al.*, 1997; Rolfhus, 1998; Rolfhus and Fitzgerald, 2001), and therefore link Hg^0 production and evasion from the ocean to the complex biogeochemical cycles of carbon, nitrogen, phosphorus, and sulfur. Through evasion, the ocean prolongs the residence of mercury at the Earth's surface and exacerbates the human perturbation of the global mercury cycle. The MFM analysis shows such oceanic emission of Hg^0 to be substantial (10 Mmol) and comparable to the atmospheric input of mercury to the oceans.

Although the marine biogeochemical cycling of mercury is greatly simplified in the MFM simulation, the importance of the ocean as both a sink for atmospheric deposition as well as a substantial source of mercury into the atmosphere (Kim and Fitzgerald, 1986; Nriagu, 1989; Lindqvist *et al.*, 1991; Mason *et al.*, 1994) is consistent with models that use more realistic physical and biogeochemical oceanic dynamics (Hudson *et al.*, 1995; Mason *et al.*, 2001; Lamborg *et al.*, 2002b).

The oceans actively and significantly participate in the transport and transformation of this toxic metal. Thus, there is an obvious need to increase knowledge and understanding concerning the biogeochemical cycling of mercury and MMHg and the impact of anthropogenically related inputs in the marine environment. A cursory examination of papers presented at the international mercury conferences is sufficient to show that there has been much interest in and support for studies examining linkages between the cycling of mercury in the atmosphere, anthropogenic emissions/discharges, deposition to terrestrial systems, and the bioaccumulation of MMHg in freshwaters (e.g., Mercury in Temperate Lakes Program—Watras *et al.*, 1994; METAALICUS Project; USEPA, 1997 Mercury Study Report to Congress; Ebinghaus and Krüger, 1996; Petersen *et al.*, 1995; The Nordic Network—Lindqvist *et al.*, 1991; Iverfeldt, 1991a). In contrast, mercury cycling in the oceans has received scant attention. This is unfortunate as there is evidence, for example, that the mercury content in fish has been increasing over the past several decades in the North Atlantic (e.g., Monteiro and Furness, 1997). Moreover, in 2001, growing recognition of human exposure to MMHg from marine fish and fish products prompted the US Food and Drug Administration (USFDA) to place four pelagic marine fish (tilefish, king mackerel, swordfish, and shark) on their consumer advisory list (USFDA Consumer Advisory, 2001). The advisory emphasizes the need for women of childbearing age to limit their consumption of marine fish to 12 oz per week.

A more stringent fish consumption advisory reference dose (Schober *et al.*, 2003) was issued by the US Environmental Protection Agency (USEPA) in 2001. Women of childbearing age were cautioned to limit their MMHg intake to 0.1 μg kg^{-1} of body weight per day. It is illuminating to translate this recommendation into fish consumption. A summary of the MMHg content in some major marine fish and shellfish is presented in Table 1. Using fresh tuna with an average MMHg concentration of 0.32 μg g^{-1} wet weight (Table 1) as an example, the recommended weekly consumption for a 50–70 kg woman of childbearing age would be 35–49 μg or the equivalent of ~110–155 g (~4–5.5 oz, half a typical can) of fresh tuna. This is much smaller than the USFDA recommendation, which is equivalent to 0.5 μg kg^{-1} of body weight per day (however, a maximum of 12 oz of fish per week is recommended). The current provisional advisory from the Joint Food and Agricultural Organization/World Health Organization Expert Committee on Food Additives (JECFA, 2000) is 0.5 μg kg^{-1} of body weight per day. For further information regarding MMHg and fish consumption, the reader should refer to the useful and informative publication from the US National Academy of Sciences entitled *Toxicological Effects of Methylmercury* (NAS, 2000). The examining committee from the

Table 1 Levels of total mercury (μg g^{-1} wet weight) in seafood (USFDA, 2001). Most (>95%) of the total mercury in edible fish tissue is MMHg.

Fish species	*Mean (range)*	n^a
Tilefish	1.45 (0.65–3.73)	60
Swordfish	1.00 (0.10–3.22)	598
King Mackerel	0.73 (0.30–1.67)	213
Shark	0.96 (0.05–4.54)	324
Tuna (fresh or frozen)	0.32 (ND–1.30)	191
Tuna (canned)	0.17 (ND–0.75)	248
Atlantic cod	0.19 (ND–0.33)	11
Pollock	0.20 (ND–0.78)	107
Mahi mahi	0.19 (0.12–0.25)	15
American lobster	0.31 (0.05–1.31)	88

Sources: Grieb *et al.* (1990), Bloom (1992), and Hammerchmidt *et al.* (1999).
[a] Number of samples analyzed.
ND denotes that the mercury level was not detectable.

National Research Council of the NAS reached the following consensus: "the value of EPA's current reference dose for MeHg, 0.1 μg kg^{-1} per day is scientifically justifiable for the protection of public health."

In summary, mercury entering the marine environment may continue to actively participate in aquatic chemistry, while much of the mercury deposited from the atmosphere to terrestrial systems is sequestered. Given the importance of the oceans as a whole in global mercury cycling, and international concerns and issues regarding human exposure to MMHg through marine fish and seafood consumption, the current situation is one of insufficient study and undersampling. Indeed, there have been relatively few open-ocean cruises to examine mercury biogeochemistry (e.g., Kim and Fitzgerald, 1986; Gill and Bruland, 1987; Gill and Fitzgerald, 1988; Mason and Fitzgerald, 1993; Dalziel and Yeats, 1985; Dalziel, 1992; Cossa *et al.*, 1997; Mason *et al.*, 1998; Mason and Sullivan, 1999a, b; Lamborg *et al.*, 1999; Leermakers *et al.*, 2001), and almost no longer-term, seasonally oriented mid-ocean studies. Even in the more accessible near-shore zones, the biogeochemistry of mercury is understudied. In this regard, estuaries and adjacent coastal waters, as regions of high biological productivity, MMHg production, and fishery activity, are of special interest. They are major repositories for natural and pollutant mercury (see Section 9.04.6).

9.04.2 FUNDAMENTAL GEOCHEMISTRY

In this section, we consider aspects of the fundamental geochemistry and biogeochemistry of mercury used later in the chapter. These topics include (1) solid Earth abundance and distribution, (2) isotopic composition and recent advances in mercury cosmochemistry, (3) the formation and distribution of minable mercury deposits, and (4) mercury in fossil fuels.

9.04.2.1 Solid Earth Abundance and Distribution

A summary of mercury data from the report of Turekian and Wedepohl (1961) is shown in Table 2. Owing to the chalcophilic nature of its associations, mercury is found in higher abundances in intrusive magmatic rocks and locations of subaerial and submarine volcanism. Peak concentrations in these rocks may be as high as several percent in ore-grade minerals (e.g., 35% mercury in sphalerite; Ozerova, 1996). Also as a result of this association, the distribution of highest mercury concentrations in rocks at the surface and near-surface mirrors regions of current and past tectonic activity and has been described as the "global mercury belt" (e.g., Gustin *et al.*, 2000). As noted in greater detail in Section 9.04.3, mercury concentrations in soils weathered from this material can be very high as well (e.g., Steamboat Springs, NV, USA: 1.2–14.6 ppm; Gustin *et al.*, 2000) and represent a potentially significant source of mercury to the atmosphere at a variety of spatial scales through low-temperature volatilization. These rocks and their weathered products are rich in other metals as well, and emission of mercury from soils and rock has been used as a tool for large-scale ore and petroleum exploration as well as an indicator of tectonic activity (e.g., McCarthy, 1968; Varekamp and Buseck, 1983; Klusman and Jaacks, 1987). These general characterizations are significant then, as we later consider the cause for concentrations of mercury in soils removed from the mercury belt that are also elevated above the crustal abundances.

Table 2 Mercury content of selected rocks and sediments.

Rock type	*Hg content* (ppm)
Ultrabasic igneous	0.0X[a]
Basaltic rocks	0.09
High- and low-Ca granites	0.08
Syenites	0.0X
Shales	0.4
Sandstones	0.03
Carbonates	0.04
Deep-sea carbonate	0.0X
Sediment	
Deep-sea clays	0.X

Source: Turekian and Wedephol (1961).
[a] The X notation indicates order of magnitude estimate.

Also indicated in Turekian and Wedepohl's compilation is a relatively high concentration of mercury in sedimentary material rich in organic carbon, such as shales. Mercury associations with organic matter are considered in later sections (Sections 9.04.5 and 9.04.8). Here, we stress that such associations can lead not only to higher concentrations of mercury in these types of rock units but also to the transport of mercury away from sites of sediment accumulation as a result of petroleum movement (White, 1967; Fein and Williams-Jones, 1997). The mercury content of major rock types has not been systematically revisited since Turekian and Wedepohl's report, and there is evidence that some of their values may be overestimates. As an example, the recent recovery and analysis of glacial till in Glacier Bay National Park by Engstrom and Swain (1997) indicated much lower concentrations of mercury (<10 ppb). It is reasonable to assume, however, that mercury concentration trends across rock types suggested by Turekian and Wedepohl and the geochemistry they suggest are valid.

9.04.2.2 Isotopic Distributions

Mercury has a relatively even distribution of its seven stable isotopes (196, 0.15%; 198, 10.0%; 199, 16.7%; 200, 23.2%; 201, 13.2%; 202, 29.8%; 204, 6.8%; Friedlander *et al.*, 1981; Lauretta *et al.*, 2001). This pattern presented cosmochemists with a formidable task when mercury-isotopic distributions in meteorites were examined (e.g., Jovanovic and Reed, 1976; Thakur and Goel, 1989). Analytical difficulties apparently resulted in inaccurate determinations of the bulk abundance and isotopic composition of some meteorites, leading to the so-called mercury problem; examined meteorites did not show the same bulk abundance and isotopic distribution as terrestrial material (Grevesse, 1970; Lauretta *et al.*, 1999). Subsequent advances in mass spectrometry, and especially the development of multicollectors, have shown that the isotopic distributions of mercury in terrestrial and extraterrestrial material are very similar (e.g., Allende meteorite: 0.03–0.3 ppm; Lauretta *et al.*, 2001).

With so many isotopes from which to choose, one might expect examination of mercury-isotopic fractionation in natural media to be a profitable area of research as it has been, for example, with lead, light metals, nonmetals, and an increasing number of transition metals (e.g., Alleman *et al.*, 2001; Richter *et al.*, 1992; Hoefs, 2004; Anbar, 2004; Rouxel *et al.*, 2004). To date, this has not been widely explored, but there is some indication of geogenic fractionation leading to isotopic signatures of particular ores (Klaue *et al.*, 2000; Evans *et al.*, 2001; Hintelmann and Lu, 2003; Smith *et al.*, 2005). As of this writing, published reports of biological fractionation have not been verified. The wide range of stable isotopes is being used in deliberate addition experiments ranging from bench scale to whole-watershed-scale (e.g., Hintelmann and Evans, 1997; Hintelmann *et al.*, 2002). These advances will be highlighted in Section 9.04.8.

The radioisotope ^{203}Hg has played an important role in laboratory investigations of mercury biogeochemistry (e.g., Gilmour and Riedel, 1995; Stordal and Gill, 1995; Costa and Liss, 1999). Continued production of ^{203}Hg-enriched material has been curtailed recently, and thus future mechanistic studies will instead feature the use of stable isotopes.

9.04.2.3 Minable Deposits

As mentioned, higher mercury concentrations in rock and soil are associated with the global mercury belt. However, the occurrence of minable deposits is not continuous along this belt. In addition to Almadén (Spain), the most productive mercury mines included Idrija (Slovenia), New Almaden (CA, USA), and Huancavelica (Peru). Very high concentrations of mercury have been reported to be associated with oceanic hydrothermal sulfide chimneys and their weathered remains (e.g., Koski *et al.*, 1994; Ozerova, 1996; Stoffers *et al.*, 1999). In all of these cases, mercury occurs almost exclusively as cinnabar (red HgS), with smaller amounts of metacinnabar (black HgS) and elemental mercury (often as inclusion with HgS in minerals such as sphalerite and chalcopyrite). HgS is extremely insoluble (log K_{so} (cinnabar) $= -36.8$; Martell *et al.*, 1998) under typical surface water conditions, and thus transport of mercury from these mineral-rich environments at the Earth's surface generally involves sediment transport (e.g., Ganguli *et al.*, 2000). The fate of cinnabar in anoxic sediments is addressed in Section 9.04.5. Transport of mercury to and from ore bodies invariably involves hydrothermal systems in the subsurface, with HgS solubility strongly controlled by fluid pH, temperature, chloride, sulfide, and organic carbon contents (White, 1967; Varekamp and Buseck, 1984).

9.04.2.4 Occurrence of Mercury in Fossil Fuels

Even with the stated stability of cinnabar, mercury is mobile in the surface environment. This is indicated by the relatively high concentration of mercury in organic-rich deposits, such as fossil fuels and shales. As we will explore later, mercury has high affinities for organic carbon as well as sulfide. Interest in fossil fuel recovery and burning as a source of mercury to the environment has led to a few published studies in this area and we summarize some of these data in Table 3. With notable exceptions, concentrations in coal appear higher than those in oil, suggesting preferential burial of mercury in terrestrial and coastal systems rather than in pelagic marine environments. Although mercury concentrations are not as high in various refined

Table 3 Mercury content of fossil fuels.

Sample type	*Total Hg* (ng g^{-1})
Coal	
China[a]	220
Std. ref. mat.[b]	77.4–433.2
Global estimate[c]	20–1,000
Unrefined petroleum[d]	
Crude oil	<d.l. to >7,000
Condensate	<d.l. to >12,000
Refined petroleum[d]	
Light distillates	1 ± 3
Utility fuel oil	1 ± 1
Asphalt	0.3 ± 0.3
Gasoline	0.2–3
Diesel	0.4–3
Kerosene	0.04
Heating oil	0.59
Naphtha	3–60
Petroleum coke	0–250

[a] Wang *et al.* (2000). [b] Long and Kelly (2002). [c] Pacyna and Pacyna (2002). [d] Wilhelm (2001) and the references therein.

petroleum materials as in coal, the oil and gas recovery process often liberates large amounts of mercury leading to localized contamination of marine sediments (e.g., Grieb *et al.*, 2001). The concentration of mercury is sufficiently high in some crude petroleum materials to also pose a corrosion hazard to the drilling and transportation apparatus and represents a significant engineering problem (e.g., Wilhelm, 1999; Bloom, 2000).

9.04.3 SOURCES OF MERCURY TO THE ENVIRONMENT

There have been few well-designed studies to constrain mercury emission estimates from natural sources and allow global extrapolations. Indeed, some work has been extraordinarily misleading. For example, in flawed studies based on the accumulation of mercury and other metals in glacial ice, Jaworowski *et al.* (1981) estimated the annual mercury flow into the atmosphere at 1,000 Mmol with an anthropogenic contribution at 50 Mmol! Low- and high-temperature volatilization processes were offered by Jaworowski *et al.* as a potential explanation for the huge natural fluxes of mercury. Such inaccuracies as well as the paucity of reliable investigations begs the question "What is the appropriate flux range for global mercury emissions from sources such as volcanism, biomass burning, and low-temperature volatilization from natural waters and soils?" The MFM simulation (Mason *et al.*, 1994) of the global mercury cycle estimates natural terrestrial emissions at 5 Mmol annually. Such emissions would include inputs from subaerial volcanism under erupting and nonerupting conditions, and the preindustrial mercury fluxes from mineralized regions, forest fires, biological activities, and natural waters. Today, volcanism and volatilization from mineralized regions may be the only purely natural sources of mercury, because, and as illustrated in Figure 2, anthropogenic mercury contamination is present throughout the atmosphere, biosphere, the terrestrial realm, and the hydrosphere. Thus, a portion of the emissions from these secondary reservoirs represents recycled pollutant mercury; this component has often been overlooked when the source strengths from "natural sources" have been compared and assessed relative to modern anthropogenic mercury inputs.

9.04.3.1 Volcanic Mercury Emissions

The determination of global volcanic mercury fluxes from direct measurements is at best a hazardous, expensive, labor-intensive, and, perhaps, impossible task. Reasonably well-constrained global estimates, however, can be achieved through the use of elemental ratios and a geochemical indexing approach. Sulfur provides an appropriate index, since it is a major component of volcanic emanations, and there is agreement on its global flux to the atmosphere. An example of this approach is the work of Patterson and Settle (1987), who combined Pb/S, Tl/S, and Bi/S ratios measured in volcanic gases collected under eruptive and quiescent (fumarolic) conditions with the global volcanic sulfur flux to "approximate global volcanic emissions of these three metals to the atmosphere." One of the present authors (Fitzgerald) measured mercury during the Patterson and Settle study. Results from this research were presented at two conferences (Fitzgerald, 1981, 1996), and Fitzgerald's estimate of 40 t yr^{-1} appears in the paper by Patterson and Settle (1987). Given the potential importance of volcanic mercury inputs, and the lack of investigations, a detailed description of the mercury study is included here.

Patterson, Settle, Buat-Menard (University of Bordeaux), Fitzgerald, and colleagues (see "Acknowledgments" section) evaluated volcanic metal fluxes using an experimental design based on the hypothesis that metal volatilization would be dependent on temperature, sulfur and halogen composition of magma, and mobilization by volcanic gases. Therefore, volcanoes and fumaroles were selected to provide a range of temperatures and S/Cl ratios. The characteristics of the volcanic gas samples are tabulated in Table 4. The four volcanoes examined were Kilauea (Hawaii, USA), Mt. Etna (Sicily, Italy), Vulcano (Aeolian Islands, Italy), and White Island (New Zealand).

Plumes were sampled for mercury using a simple gas train consisting of a preblanked (pyrolyzed) glass fiber prefilter stage for particulate phases, followed by two gold traps arranged in tandem to collect gaseous mercury (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988). The fumarolic collections were made with a gas-sampling train designed by Clair Patterson and modified for mercury (Patterson and Settle, 1987; shown here in Figure 3). Any mercury associated with aerosols or the gas phase that escaped the two cold traps was collected by a gas-sampling train analogous to the plume samplers. The gas was pumped through this system at ~1 l min^{-1}.

In general, and as illustrated for the 1977 study of 100 °C fumarole at Kilauea, essentially all of the mercury and the other metals are trapped in the 0 °C condensate (Table 5). Thus, fumarolic gas collectors for metal studies can be simplified. The observed Hg/S weight ratio in the Kilauea condensate was 0.9×10^{-6}. The Hg/S ratios from the other investigations are summarized in Table 4. Values range from 0.7 to 14×10^{-6} with a suggestion that Hg/S may increase as the S/Cl decreases. Dedeurwaerder *et al.* (1982) were part of the Mt. Etna study and their results for the Bocca Nuevo plume are included in the summary. Their plume-sampling apparatus was based on the Fitzgerald technique and similar to that described above. The sulfur-flux weighted mean volcanic Hg/S from all locations is 5×10^{-6}.

Estimates of global volcanic sulfur emissions are summarized in Table 6. We have chosen a value of 9×10^6 t of S per year as representative of the recent estimates. Therefore, by applying the determined Hg/S ratio, a global mercury flux from subaerial volcanism is estimated to be ~45 t yr^{-1}, or 0.23 Mmol annually. These average emissions are only 5% of the natural flux of 5 Mmol yr^{-1} estimated by Mason *et al.* (1994). Thus, and under long-term mean conditions, other types of terrestrial volatilization processes for mercury would dominate. Given this conclusion, it is important to place additional constraints on the validity of the 45 t yr^{-1} estimate for subaerial volcanic mercury emissions.

First, Varekamp and Buseck (1986) reported an average Hg/S weight ratio of 7.4×10^{-6} for emissions under nonerupting conditions from Mts. Hood, Shasta, and St. Helens in the United States, and from Mt. Etna. In 1981, these investigators reported a very high Hg/S weight ratio of $6{,}000 \times 10^{-6}$ for Mt. St. Helens

Table 4 Volcano sampling locations and gas characteristics.

Volcano	*Date*	*Type of gas*	*Temp.* (°C)	*S (wet gas)* (mg S m^3)	*S/Cl* (weight)	*Cl/F* (weight)	*Hg/S* (weight)	*Hg/Bi* (weight)
Kilauea Caldera	6/23/77	Fumarole	100	22,800	40	2	0.9	
Kilauea Pu'u O'o	5/12/84	Eruptive plume	1,140	110	9		0.7	0.0019
Mt. Etna Bocca Nuova[a]	6/7/80	Eruptive plume	1,100	4.3	0.7	8	11–14	
Mt. Etna SE Crater	6/8/80	Eruptive plume	1,100	2.5	0.7	4	<13	
Vulcano Site A	6/11/80	Fumarole	280	5,500	0.3	90	0.9	
White Island Site A	7/22/83	Fumarole	180	33,000	45	30	0.9	
White Island Site B	7/22/83	Fumarole	590	54,000			~0.44	0.024
White Island Site C	7/22/83	Fumarole[b]	650			180		0.0015

After Patterson and Settle (1987).
[a] Dedeurwaerder *et al.* (1982). [b] Collected using plume filter device.

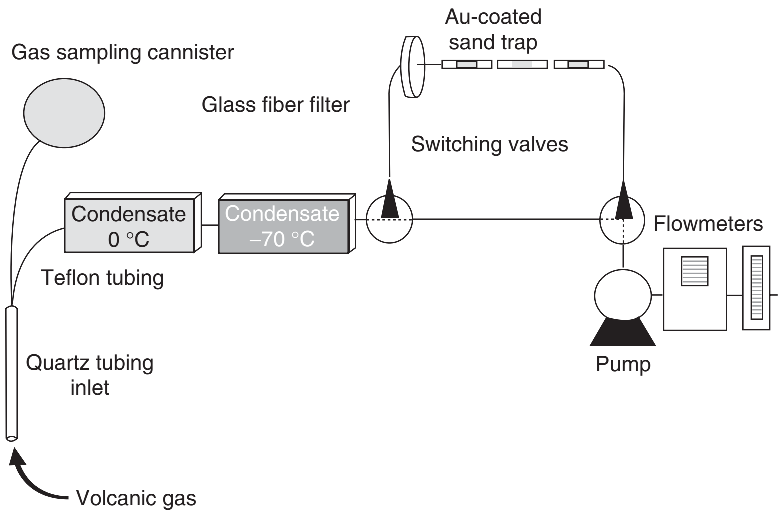


Figure 3 Hg sampling apparatus used to collect fumarole gas samples. After Patterson and Settle (1987).

Table 5 Mercury and sulfur concentrations in volcanic gas at sulfur fumarole site, Kilauea caldera.

Collection	*Hg concentration*	*Total Hg* (ng)	*Total S* (g)	*Hg/S ratio* (weight)
0 °C condensate	120 ng g^{-1}	59,200	4.0	14.8×10^{-6}
270 °C condensate	10 ng g^{-1}	150	0.1	1.5×10^{-6}
Volcanic gas free of water	0.88 ng g^{-1}	230	60	3.9×10^{-9}
Total		59,600	64	9.3×10^{-7}
Ambient air	10.2 ng m^{-3}			

Table 6 Estimates of the global annual sulfur flux from volcanic activity.

Method	*S flux* (10^6 t yr^{-1})	*Reference*
Rate of S loss per volcano	5.0	Stoiber and Jepsen (1973)
	3.8	Cadle (1975)
	4–5	Friend and Rusool (1973)
S measurements from selected volcanoes	9.4	Stoiber *et al.* (1987)
	Nonexplosive (4.5)	
	Explosive (4.9)	
Literature review	9	Spiro *et al.* (1992)
Satellite survey of SO_2 emissions	6.5	Bluth *et al.* (1993)
	Nonexplosive (4.5; Stoiber *et al.*, 1987)	
	Explosive (2.0)	
Satellite and modeling	7.5–10.5	Halmer *et al.* (2002)

under erupting conditions (Varekamp and Buseck, 1981). However, the mercury and sulfur measurements were not measured simultaneously and, according to Varekamp (personal communication), should not be used for a global-scale analysis of this kind. Thus, we suggest that a mean Hg/S ratio of 5×10^{-6} and the annual emission estimate of 45 t is of the appropriate magnitude. Nriagu and Becker (2003), using the same Hg/S ratio and a more detailed volcanic SO_2 emissions inventory, derived much the same conclusion (~95 t yr^{-1}; 60% eruptive, 40% degassing).

Second, the scale of volcanic mercury fluxes can be approximated indirectly. For example, using the Hg/Bi ratios listed in Table 4 as well as the Lambert *et al.* (1988) estimate for annual global bismuth emissions of 1,500 t, we obtain a range for the global volcanic mercury flux of 2–36 t yr^{-1}. Hinkley *et al.* (1999) suggest that the Lambert *et al.* values are a factor of 3 or 4 too high.

A comparable value of 18 t annually is obtained using Olafsson's (1975) estimate of mercury emissions (7×10^5 g Hg/6×10^{14} g ejecta) for the volcanic eruption at Heimay, Iceland,

and an estimate of 6 km^3 (~15 × 10^{15} g) for annual, subaerial lava production (~20% of total annual lava production being subaerial; Crisp, 1984; Varekamp, personal communication).

Thus, annual global volcanic mercury emissions estimated or measured in several ways are <0.5 Mmol (100 t), and our work yielded an average value of 0.23 Mmol (45 t). This scaling serves two purposes: (1) it provides a framework for further, needed studies of mercury cycling associated with volcanism, and (2) it provides a reasonably well-constrained estimate for global emissions for modeling and assessment of human perturbations of the natural mercury cycle. It is clear that average volcanic mercury inputs are small relative to estimates for modern anthropogenic mercury fluxes (~9.6 Mmol; Pacyna and Pacyna, 2002) to the global mercury cycle. Indeed, and using an atmospheric residence time of 1.25 years (Lamborg *et al.*, 2002b), the average yearly terrestrial deposition of mercury from volcanism would be ~0.07 μg m^{-2}. Since volcanic eruptions vary in time and space, large-scale eruptions might be apparent in natural archives such as lake sediments (Chapter 9.03), and ice cores. Carefully collected and dated lake sediments, however, do not reveal unusually high accumulations in strata coincident with large explosive aperiodic volcanic eruptions (e.g., Pinatubo in 1991, Krakatau in 1883, or Tambora in 1815). In contrast, and according to Schuster *et al.* (2002), volcanic mercury depositional signals may be evident in a recent study of the Fremont Glacier in Wyoming, USA. For example, their results suggest an average global mercury depositional peak increase of 16 μg m^{-2} yr^{-1} from the 1883 Krakatau eruption, which released ~21 km^3 of volcanic material (Rampino and Self, 1984). As the pre-eruption mercury deposition was ~2 μg m^{-2} yr^{-1}, the Krakatau event is extraordinarily prominent at ~8× the background. In contrast, a mercury signal associated with the June 1991 Mount Pinatubo eruption in the Philippines, which released ~5 km^3 ash and pumice and ~50 × 10^{12} g SO_2 or 25 × 10^{12} g S (USGS Fact Sheet 113-97), is not evident in the Fremont Glacier ice core. If Mt. Pinatubo were assumed to be analogous to Krakatau according to the Fremont ice core, then the predicted mercury deposition would be ~4× less or ~4 μg m^{-2} yr^{-1}. The anthropogenically enhanced background mercury deposition for 1991 in the ice core was considerably larger at ~11 μg m^{-2} yr^{-1}. Thus, given the large pollution-derived mercury deposition, the uncertainty inherent in reconstructed fluxes, and the assumptions, the lack of a mercury signal from Mt. Pinatubo could reasonably be expected.

We suggest that the work of Schuster *et al.* (2002), while somewhat speculative and not well constrained, is provocative and stimulating. Moreover, there is reasonable coherence with the Hg/S for volcanic emissions shown in Table 4. For example, the Hg/S of 5 × 10^{-6} when combined with the 25 × 10^{12} g sulfur emission estimates for the Mt. Pinatubo eruption yields a mercury input of 125 × 10^6 g mercury or ~0.6 Mmol. This is just 6% of the 10 Mmol anthropogenic mercury emissions estimated by the MFM simulation for the global contribution in 1990. Therefore, the measured Hg/S ratio suggests that the Mt. Pinatubo eruption would not be detectable as well. The Krakatau eruption would be predicted to be ~2.4 Mmol, which would result in an average enhancement of global mercury deposition of only 1 μg m^{-2} yr^{-1}. It must be noted, however, that work from long peat cores has suggested that large aperiodic volcanic eruptions may have left detectable signals in that archiving medium as well (e.g., Martínez-Cortizas *et al.*, 1999; Roos-Barraclough *et al.*, 2002). The lack of identifiable volcanic signals in lacustrine sediments is likely due to the "smoothing" effect that a several-year residence time of mercury within a lake and its watershed would exert on such short-duration signals.

In summary, it has been demonstrated that Hg/S ratios measured for a variety of volcanic plumes and fumaroles, when indexed to estimates of global sulfur emissions from volcanism, yield a mean volcanic mercury flux of 0.23 Mmol (45 t), which is consistent with other estimates and observations. Accordingly, average yearly mercury emission from volcanoes is small relative to natural terrestrial fluxes to the atmosphere (5 Mmol) and modern pollution mercury entering the global cycle (9.6 Mmol). Over the 100 years time period used in the MFM simulation, anthropogenic mercury inputs to the global atmosphere were 1,000 Mmol, while average mercury emissions from volcanoes would be 23 Mmol. Periodic large eruptions, such as Tambora, Krakatau, Mt. St. Helens, and Mt. Pinatubo, would add significantly to this flux but for very short periods.

9.04.3.2 Mercury Input to the Oceans via Submarine Volcanism

The few attempts to determine mercury concentrations in oceanic hydrothermal fluids have not been successful. As a consequence, we must estimate the fluxes of mercury associated with submarine volcanic activity indirectly. First, we assume that the Hg/S of 5×10^{-6} established for subaerial volcanism (Table 4) can be applied to the hydrothermal inputs associated with submarine tectonic activity, and second, that oceanic lava production is $\sim 5\times$ as large as the amounts formed subaerially (e.g., Crisp, 1984). Accordingly, the submarine inputs would be ~1.3 Mmol annually. An upper estimate of 1.8 Mmol yr^{-1} was proposed by Fitzgerald *et al.* (1998), who used oceanic mercury profiles and an estimate for the rate of vertical mixing in the water column. The agreement for these estimates negates the extraordinarily large fluxes (20–40×) suggested by heat flow calculations (e.g., Rasmussen, 1994), and provides additional support for an average Hg/S ratio for volcanic emissions of $\sim 5\times10^{-6}$. An input of 1–2 Mmol yr^{-1} is significant and comparable with worldwide river input as estimated by MFM (1994). It is probable, however, that only a small fraction of the tectonically associated marine mercury inputs mixes with bulk ocean water. It is likely that mercury will be removed from the hydrothermal fluids through coprecipitation of metal sulfides and scavenging by precipitating hydrous oxides of manganese and iron as hydrothermal fluids mix with the oxygenated seawater near their entry points. Moreover, elevated levels of mercury are present in the hydrothermally derived metal-rich deposits found on the East Pacific Rise (Bostrom and Fisher, 1969) and the Gorda Ridge (Koski *et al.*, 1994). Stoffers *et al.* (1999) observed some nascent elemental mercury around the sulfide chimneys of the White Island (New Zealand) complex, but given the scaling arguments above it would appear that submarine volcanism does not represent a significant source of mercury to the global ocean.

9.04.3.3 Low-Temperature Volatilization

As noted in the previous section, direct low-temperature weathering inputs from mineralized mercury deposits to aquatic environments occur primarily through sediment transport of cinnabar-containing material. Volatilization is an additional form of low-temperature weathering in which mercury is unparalleled by other metals. The volatility of elemental mercury is well documented, and to the extent that mercury-containing materials possess some fraction of their burden in the elemental form, weathering by volatilization will occur. Other mercury species are somewhat volatile as well (Table 7), but most are less so by orders of magnitude than elemental mercury.

Table 7 Henry's law constants for selected mercury species (at STP).

Equilibrium	*H* (M atm^{-1})
$Hg^0_{(g)} \leftrightarrow Hg^0_{(aq)}$	0.11
$Hg(OH)_2(g) \leftrightarrow Hg(OH)_2(aq)$	1.2×10^4
$HgCl_{2(g)} \leftrightarrow HgCl_{2(aq)}$	1.4×10^6
$(CH_3)_2Hg_{(g)} \leftrightarrow (CH_3)_2Hg_{(aq)}$	0.13
$CH_3HgCl_{(g)} \leftrightarrow CH_3HgCl_{(aq)}$	2.2×10^3

Sources: Sanemasa (1975), Iverfeldt and Lindqvist (1982), and Lindqvist and Rodhe (1985).

Volatilization of mercury from soils and rock to the atmosphere has only recently received significant attention. Unlike air–water gas exchange, air–soil/rock gas exchange has not been described in theoretical terms; thus, all that is known of mercury volatilization is from direct flux measurements and the results of soil manipulation experiments. Several others (e.g., Poissant and Casimir, 1998, and references therein) have noted from measured fluxes and their temperature dependence the similarity of estimated and theoretical activation energies of vaporization (~60 and 85 kJ mol^{-1}, respectively). Measurements using flux chambers and micrometeorological techniques are the most numerous (see special section of *J. Geophys. Res.* 104(D17), 1999). As noted in Section 9.04.2, Klusman and colleagues (e.g., Klusman and Jaacks, 1987) attempted to develop a tracer approach based on measurements of $^{222}Rn/He/Hg$ to estimate the flux of mercury from soils indexed to the fluxes of the other gases. Their work, however, has not been extended beyond small-scale applications. Finally, isotope addition experiments, including those of Schlüter (2000) using radioactive ^{203}Hg additions and those of Lindberg and colleagues using stable isotopes in the METAALICUS program (see Section 9.04.8), are proving very insightful.

The results from some volatilization measurements over a number of substrates are shown in Table 8, and vary widely. In general terms, the various studies indicate that higher concentrations of mercury in the soil/rock substrates lead to higher evasional fluxes. Other factors are strongly influential as well. These include temperature, light, wind speed, and soil moisture (e.g., Gustin *et al.*, 1999). It is clear that evasion of mercury from mineralized areas can be significant; however, the results from other substrates are currently limited by the large uncertainties and variability inherent in making such difficult measurements. Gustin and colleagues have made efforts to scale up their measurements, made primarily from Nevada, to the western United States and Mexico (10 Mg yr^{-1}; Gustin *et al.*, 2000). Thus,

Table 8 Some examples of measured fluxes over natural soils.

Location	*Method(s)*	*Soil conc.* (ng g^{-1})	*Evasional flux* (ng $m^{-2}h^{-1}$)	*Reference*
Sweden	FC	NA	−2 to 2	Xiao *et al.* (1991)
Tennessee, USA	FC	61–469	−1.81 to 54.94	Carpi and Lindberg (1998)
Quebec, Canada	FC	NA	0.62–8.29	Poissant and Casimir (1998)
Nevada, USA	FC and MM	1,200–14,600	50–600	Gustin *et al.* (1999)
Nova Scotia, Canada	FC	NA	−1.4 to 4.3	Boudala *et al.* (2000)

FC, flux chamber; MM, micrometeorology (Bowen ratio).

this important area of research is still developing and should be active in the future.

In his review of soil volatilization experiments, Schlüter (2000) also highlighted the importance of the dissolved organic carbon concentration in the soil fluids, with higher concentrations of fulvic acids, for instance, leading to an enhancement of mercury reduction and evasion by generating Hg(I) and then aiding the disproportionation reaction of (2Hg(I) = Hg(0) + Hg(II)) through sequestration of Hg(II). The source of the reducing equivalents in soils appears to be species generated indirectly through photoreduction of some kind (e.g., organic carbon and Fe(II); Schlüter, 2000). The flux from nonenriched soils, though, is substantially lower than that from the mineralized areas and may average around 0.2 $\mu g\,m^{-2}\,yr^{-1}$ (Schlüter, 2000).

Combining estimates for volcanic and low-temperature inputs of mercury from mineralized areas and nonenriched soils to the atmosphere allows an estimate of the total amount of natural terrestrial emissions to be made. The volcano work benefits from the existence of tracing species such as sulfur that make tractable the scaling of individual measurements to the global scale. In the case of low-temperature volatilization, however, no such index has yet been developed. Therefore, translating values such as those of Table 8 into global fluxes is difficult.

Using the data from Nevada (Gustin *et al.*, 2000; 0.011 Mmol yr^{-1}; $1.8 \times 10^{11}\,m^2$ area), an emission rate of $\sim 10\,\mu g\,m^{-2}\,yr^{-1}$ for the global mercury belt areas can be estimated. Further assuming that these enriched areas represent no more than ~15% of the continental area suggests a maximum contribution for volatilization from these areas of ~5.6 Mmol yr^{-1}. The addition of the small volcanic contribution suggests that natural emissions of mercury to the atmosphere are <5.8 Mmol yr^{-1} and that subaerial and submarine emissions combined are <7.1 Mmol yr^{-1}.

The volatilization estimates are crude extrapolations, as they are based on assumptions of soil concentration distributions and understanding of driving forces behind volatilization. They do suggest, that the emissions measured and estimated in some of the work cited are consistent in the first order with Mason *et al.* (1994) and that natural land-based sources of mercury to the atmosphere are consistent and likely to be ~5 Mmol yr^{-1}. It has also been noted that a flux 5 Mmol yr^{-1} for natural sources is consistent with the rate of atmospheric deposition in the preindustrial past indicated by analysis of lake sediments (e.g., Lamborg *et al.*, 2002a). Finally, it must be noted that emissions from soils removed from natural enrichments likely contain a significant fraction of mercury initially mobilized by anthropogenic activities that was subsequently deposited to soils (see Section 9.04.3.6).

9.04.3.4 Anthropogenic Sources

The human-related sources of mercury to the environment are numerous and widespread. Most direct inputs of mercury from point sources to aquatic systems have largely been contained in most developed countries. Inputs of mercury into the environment via the atmosphere are of the greatest concern. These emissions, coupled with long-distance transport of elemental mercury, have resulted in elevated concentrations of mercury in fish from locations that are removed from anthropogenic sources (e.g., open-ocean, and semi-remote regions in the United States, Canada, Scandinavia; Wiener *et al.*, 2002). A summary of the fluxes from major sources (for 1995) is shown in Table 9 (total of 9.6 Mmol yr^{-1}). High-temperature processes, principally coal and municipal waste burning, dominate anthropogenic inputs of mercury to the atmosphere. The emission of anthropogenic mercury is higher in the Northern Hemisphere (NH), as a result of greater industrial activity and population density. Between 1990 and 1995,

Table 9 Major classes of anthropogenic missions of mercury to the atmosphere in 1995.

Source type[a]	*1995 flux* (Mmol yr^{-1})
Stationary combustion	7.4
Nonferrous metal production	0.8
Cement production	0.7
Waste disposal	0.6
Pig iron and steel production	0.1
Total	9.6

After Pacyna and Pacyna (2002).

[a] Stationary combustion includes fossil fuel burning power plants while waste disposal includes municipal waste combustion.

the emissions from developed economies in North America and Europe have declined substantially. Unfortunately, they have almost been completely replaced by emissions from countries, especially in Asia, that have rapidly developing economies that are coal driven. Accordingly, Asian sources of mercury currently constitute 56% of all anthropogenic emissions. Based on the Pacyna and Pacyna inventory and the natural source strength suggested by Mason *et al.* (1994), human activity contributes ~2/3 of the mercury emitted from land-based sources each year. Similarly, these estimates suggest that the emission and deposition fluxes of mercury are currently 3× what they were in the prehuman environment. Such estimates are now widely supported by the reconstruction of mercury deposition from remote lakes worldwide (more below; e.g., Fitzgerald *et al*., 1998). Reconstruction of deposition in the recent past (ca. 30 years) is less certain. Many of the lake sediment archives examined thus far either accumulate too slowly or possess enough inherent variability that recent changes are difficult to definitively reconstruct. Furthermore, lake watersheds act to buffer rapid changes. As a result, there is evidence from a variety of archiving media for increases, decreases, and relatively less change in Hg deposition in the last few decades (e.g., Fitzgerald, 1995; Bindler *et al*., 2001; Roos-Barraclough *et al*., 2002; Kraepiel *et al*., 2003; Shotyk *et al*., 2003; Fitzgerald *et al*., 2005). Some of these observations are quite clear, but perhaps regionally confined (e.g., Iverfeldt *et al*., 1995; Kamman and Engstrom, 2002).

9.04.3.5 Mining

Mining has been a long-standing and continuing source of environmental mercury contamination. Indeed, a partial analog the alchemist's quest to transmute base metals into gold is contained in the *patio* process in which naturally occurring but trace amounts of gold and silver are amalgamated (concentrated) using large amounts of liquid mercury. The dense amalgam can be separated from the crushed, parent rock or from placer and alluvial deposits, often with much loss of mercury to air and aquatic systems. The gold or silver is recovered by heating the amalgam and vaporizing the mercury. This technology has been employed broadly and often crudely since its introduction by Bartolome de Medina in 1557 (Nriagu, 1979). Historically, uses of mercury in gold and silver mining were especially significant in the Americas from the mid-1500s to the turn of the twentieth century. This unhealthy and ecologically damaging practice continues today, and on a large scale in many countries (e.g., China, Brazil, Philippines, Kenya, and Tanzania). In their review of current gold mining, Lacerda and Salomons (1998) found that environmental losses of mercury are large, 1–1.7 kg per kilogram of gold recovered. Much of the pollutant mercury accumulates in the surrounding lands, watersheds, waterways, and mine tailings, and the associated environmental and human-health concerns are primarily local and regional. However, there are global worries as well, because a portion of the mercury is emitted into the atmosphere (Porcella *et al*., 1997).

Mercury losses occur not only with the processing and recovery of gold and silver, but in the mining and production of mercury. For example, the nineteenth century "gold rush" in the western United States was fueled by mercury mining in California. Egleston (1887) reports that between 1850 and 1889, the mercury yield from California mines, especially from the New Almaden operation (85%), was 1,518,380 flasks (~34.5 kg per flask). This was comparable with the combined output of the two other major mines, the Almadén (Spain) and Idrija, Austria (now in Slovenia), which produced 1,291,636 and 347,586 flasks, respectively, over the same time period. Moreover, and as Egleston emphasizes, "according to the best California authorities, the loss in the best constructed furnaces as near as can be approximated is not less than 15–20%, and in many of the works the losses will probably amount to double that." Mercury mining activities continue today in Spain, though with a higher sensitivity to prevent mercury releases to the environment. Despite this, mercury mines remain significant sources of mercury to watersheds and coastal marine systems, including inoperative sites such as Idrija and Clear Lake, California, that supply mercury from abandoned tailings.

9.04.3.6 Biomass Burning, Soil, and Oceanic Evasion—Mixed Sources

There are three prominent processes that release mercury of mixed natural and anthropogenic origin into the atmosphere. These three include biomass burning (deliberate and natural) and the evasion of mercury from soils and the ocean. The general factors controlling emission of mercury from soils have been discussed in Section 9.04.3.3. The mercury released from soils that are not naturally enriched (unlike some of the mineralized substrates described) is mercury derived principally from atmospheric deposition and is released from the upper horizon pool (Schlüter, 2000, and references therein). As the mercury that is deposited from the atmosphere is of mixed origin, so is the mercury emitted into the atmosphere from these soils. Therefore, though mercury may be released from completely natural and undisturbed soils as regulated by ambient biogeochemical processes, the current flux is not entirely natural. In the case of nonenriched soils, this is not very significant as these materials are net sinks of atmospheric mercury deposition (see Section 9.04.6). In the case of biomass burning and especially oceanic evasion, however, the fluxes to the atmosphere may be very important in the global mercury cycle. As with soils, these processes mobilize both natural and anthropogenic mercury and represent sources of mixed origin. In this way, these media act to recycle mercury in the environment, extending the residence time of mercury at the Earth's surface.

Recent measurements of mercury in biomass burning plumes from research aircraft suggest that this process releases substantial amounts of mercury. Brunke *et al.* (2001) and Friedli *et al.* (2001) used CO and CO_2 as indexing species to establish fluxes of mercury of $\sim$1–5 $\mathrm{Mmol\,yr^{-1}}$. A first-order estimate, based on the relative strengths of truly anthropogenic emissions and truly natural emissions, suggests that some two-thirds of the mercury released by biomass burning was initially released by human activities (i.e., 0.67–3.4 $\mathrm{Mmol\,yr^{-1}}$ anthropogenic; 0.33–1.6 $\mathrm{Mmol\,yr^{-1}}$ natural).

Oceanic evasion is a major component of the mercury cycle. As described in greater detail in Section 9.04.5, there are a number of processes that may lead to evasion of elemental mercury from the ocean. Mason *et al.* (1994) found that evasion from the ocean had tripled in magnitude in concert with the increase in anthropogenic activities. Therefore, as with biomass burning, nearly two-thirds of the mercury currently evading from the ocean is anthropogenic.

9.04.3.7 Watersheds and Legacy Mercury

Watersheds are sources of mercury to the aquatic environment. However, similar to biomass burning and evasion, the mercury released from watersheds is of mixed origin. Because the residence time of mercury within watersheds is fairly long (see Section 9.04.6), the potential for the buildup of "legacy" mercury exists. This feature is relevant when considering how rapidly a system might respond to decreased mercury loadings. Therefore, though decreases in mercury deposition to a watershed may occur, the watershed will contribute more mercury to its receiving waters than enters it each year. Legacy mercury, however, was released into the environment as a result of human activity and should be viewed as an anthropogenic source term.

9.04.4 ATMOSPHERIC CYCLING AND CHEMISTRY OF MERCURY

Mercury is found in the atmosphere in both gas and particle phases. Greater than 95% of mercury exists as gas-phase elemental mercury (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988; Iverfeldt, 1991a). There is growing evidence to suggest that some chemical form of Hg^{2+} also exists in the gas phase (the so-called reactive gaseous mercury (RGM); Stratton and Lindberg, 1995; Sheu and Mason, 2001; Landis *et al.*, 2002). Concentrations of total gaseous mercury (TGM; including elemental, ionic, and gaseous alkylated forms such as DMHg) in remote areas are typically in the range 1–2 ng (as mercury) $\mathrm{m^{-3}}$. Concentrations below 1 $\mathrm{ng\,m^{-3}}$ are to be found under certain conditions (more below) and higher values are often observed in urban/suburban locations. Some selected concentration and deposition data are shown in Table 10. Particle-phase atmospheric mercury appears to be largely Hg^{2+} and comprises a few percent of total atmospheric mercury in the troposphere (Iverfeldt, 1991a; Fitzgerald *et al.*, 1991). There is only one published report of mercury in the stratosphere to our knowledge and no measurements in other regions of the upper atmosphere (Murphy *et al.*, 1998). Not surprisingly, the authors found the concentration of particulate mercury increased above the tropopause as a result of enhanced oxidation of elemental mercury by ozone and the condensation of the less-volatile Hg^{2+} onto ambient particles.

The vertical profile of mercury in the troposphere has been determined in a few cases

Table 10 Atmospheric deposition concentration data.

Location	*TGM* (ng m^{-3})	*Hg$_T$ in precipitation* (ng l^{-1})	*Deposition* (mg m^{-2} yr^{-1})	*Calculated lifetime* (years)	*References*
Florida, USA	1.4–3.1	13–23	15–28	0.3–0.7	Guentzel *et al.* (1995) and Gill *et al.* (1995)
Tennessee, USA	5.8 ± 3.6	3	30	1.2	Lindberg *et al.* (1992)
Michigan, USA	2.0	10	9 ± 3	1.4	Hoyer *et al.* (1995)
S. Atlantic Ocean	1.4	4	6	1.5	Lamborg *et al.* (1999)
Wisconsin, USA	1.6 ± 0.4	6	7	1.5	Lamborg *et al.* (1995)
Alert, CAN	1.2	~15	5	1.5	Schroeder *et al.* (1998) and Schroeder (personal communication)
Global average	1.6	NA	5.6	1.8	Lamborg *et al.* (2002b)
Eq. Pacific	1.3	3	4	2	Mason and Fitzgerald (1993)
Sweden	2.9 ± 0.7	10	13 ± 12	2 ± 1	Lindqvist *et al.* (1991)

After Lamborg *et al.* (2001).

(Banic *et al.*, 2003; Landis and Stevens, 2001). In most situations, it appears that there is little change in the mercury-mixing ratio with altitude, indicating thorough vertical mixing and an atmospheric residence time that is long enough to make this possible. There have been some suggestions that elemental mercury decreases with altitude, while reactive gaseous mercury increases, creating a gradient for atmospheric deposition on large scales of the more soluble and surface-active Hg^{2+}. For example, Landis and Stevens (2001) have suggested that the vertical RGM gradient is of the order of 400 pg m^{-3} over the troposphere (6,340 m, isobaric). This is a rather large gradient, representing ~25% of the total atmospheric mercury. Applying a vertical eddy diffusivity of 1 m^2 s^{-1} (Seinfeld, 1986) to this gradient provides an estimate of the potential rate of removal of RGM on a large scale of 2 μg m^{-2} yr^{-1} (or ~10–30% of the observed flux at most locations). It must be noted that these data sets are only now being developed and therefore the flux estimate made above is highly speculative.

The situation of horizontal profiling is better developed. Figure 4 illustrates data from a number of sampling locations worldwide, show a small but discernible interhemispheric gradient in TGM. Values for TGM in the NH (~1.7 ng m^{-3}) are larger than in the south (~1.2 ng m^{-3}) as a result of the NH representing a greater proportion of land-based natural and anthropogenic emissions. Horizontal gradients on smaller scales (i.e., plumes) have also been observed including continental scale, urban plumes, and single industries (see Fitzgerald, 1995 and the references therein; Lamborg *et al.*, 2002b).

Assuming little vertical variation in the mixing ratio of total mercury in the troposphere and using the available horizontal surface-based measurements, Mason *et al.* (1994) estimated the total atmospheric burden of mercury to be 25 Mmol (5 kt; Figure 2a). Accordingly, the average tropospheric air column mercury burden is ~10 μg m^{-2}. If the emissions of mercury as outlined in Section 9.04.3 is equal to 20 Mmol yr^{-1}, then the average residence time of mercury in the atmosphere is ~1.25 years. Such a residence time is relatively long on atmospheric timescales (e.g., the mixing time for the hemispheres is ~1.3 years; Geller *et al.*, 1997), and thus we should expect to find mercury reasonably well mixed vertically and horizontally as we do. This global-scale value is within the range of similar estimates made from various specific locations (Table 10).

It was quickly realized that the mercury species to be found in greatest abundance in precipitation was ionic mercury (e.g., Fogg and Fitzgerald, 1979). Some typical values of total mercury in precipitation are shown in Table 10. Extensive databases of precipitation mercury concentrations are available from monitoring networks in the United States, Canada, and Nordic countries (e.g., US Mercury Deposition Network, 2006). The discrepancy between the dominant gas- and precipitation-phase species implied a process of oxidation of elemental mercury in the atmosphere and its subsequent scavenging as being a major component of the mercury cycle. Since the initial work, and partially in response to increased governmental interest in long-range atmospheric transport of pollutant mercury, there has been an extraordinary increase in research on the atmospheric chemistry of mercury. Many mechanisms for

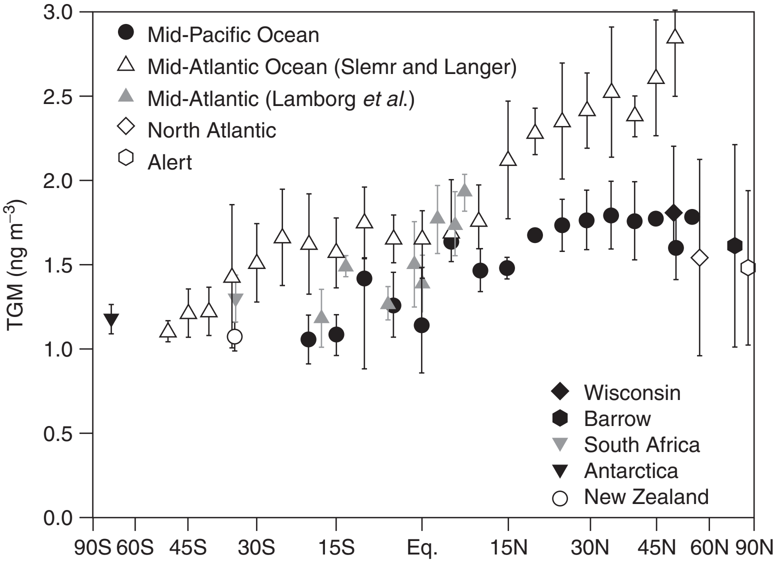


Figure 4 Total gaseous Hg in the atmosphere at several locations. Notice the discernible interhemispheric gradient, resulting from greater emissions of Hg to the atmosphere in the more industrialized NH (data from Fitzgerald (1995)—mid-Pacific (filled circles); Slemr and Langer (1992)—mid-Atlantic (open triangles); Lamborg *et al.* (1999)—mid-Atlantic (shaded triangles); Mason *et al.* (1998)—North Atlantic (open diamonds); Schroeder *et al.* (1998)—Alert, NWT (open hexagons); Lamborg *et al.* (1995)—rural Wisconsin, USA (filled diamonds); Lindberg *et al.* (2002)—Point Barrow, Alaska, USA (filled hexagons); Ebinghaus *et al.* (2002)—Cape Town, RSA (shaded inverted triangles) and Antarctica (filled inverted triangles); Fitzgerald (1989)—Ninety Mile Beach, NZ (open circles). Figure from Lamborg *et al.* (2002b).

elemental mercury oxidation in the atmosphere have been proposed and a few have been studied in detail through laboratory experiments (e.g., Munthe, 1992; Hall *et al.*, 1995; Tokos *et al.*, 1998; Lin and Pehkonen, 1999; Sommar *et al.*, 2001; Ariya and Ryzhkov, 2003; Raofie and Ariya, 2003, 2004; Pal and Ariya, 2004a, b). These include homogeneous gas- and heterogeneous-phase reactions occurring in cloud-water/precipitation and aerosols. The principal constraint on gas-phase oxidation is that the overall reaction rate must be similar to the residence time of mercury. The rate constants for oxidation by ozone and hydroxyl radical are consistent with this constraint. In heterogeneous-phase reactions, oxidation may be partially balanced by reduction, leading to complex cycling of mercury species within cloud-water or aerosols that includes influences by sorbent surfaces such as soot (Pleijel and Munthe, 1995). Some of the proposed mechanisms are shown in Figure 5. The ongoing challenge for those studying atmospheric mercury is to identify which of these mechanisms is actually influential in the atmosphere and under what conditions. Lamborg *et al.* (2002b), based on strong rainwater correlations between Hg and ^{210}Pb, have suggested that a mechanism including gas-phase oxidation followed by particle and precipitation scavenging is the dominant overall process for the removal of mercury from the global atmosphere. The atmospheric chemistry embedded in the transport and deposition model of Shia *et al.* (1999), which included many of these reactions, estimated the atmospheric residence of mercury to be ~1.7 years. Their simulation highlighted the importance of aqueous-phase reduction reactions in controlling the atmospheric residence time of mercury. In more urbanized environments and close to sources, dry deposition of particulate mercury emitted from sources or forming shortly after emission is likely to be the dominant removal mechanism (e.g., Keeler *et al.*, 1995; Chiaradia and Cupelin, 2000).

There are, however, new findings from the Arctic and from mid-ocean that suggest this is not the entire story. One of the more dramatic observations in mercury biogeochemistry in recent years is the so-called spring-time depletion of mercury in high latitudes. Schroeder *et al.* (1998) were the first to observed this phenomenon at Alert on the northern tip of Ellesmere Island (Canada). Total gaseous mercury at this location shows a fairly steady value of 1.5 ng m^{-3}, typical of stations representative of the global pool in the NH. However, at the advent of polar sunrise and lasting for several weeks, the concentration begins to fluctuate between the baseline value and near-zero, with the depletion episodes lasting hours to days. There is also a high correlation between

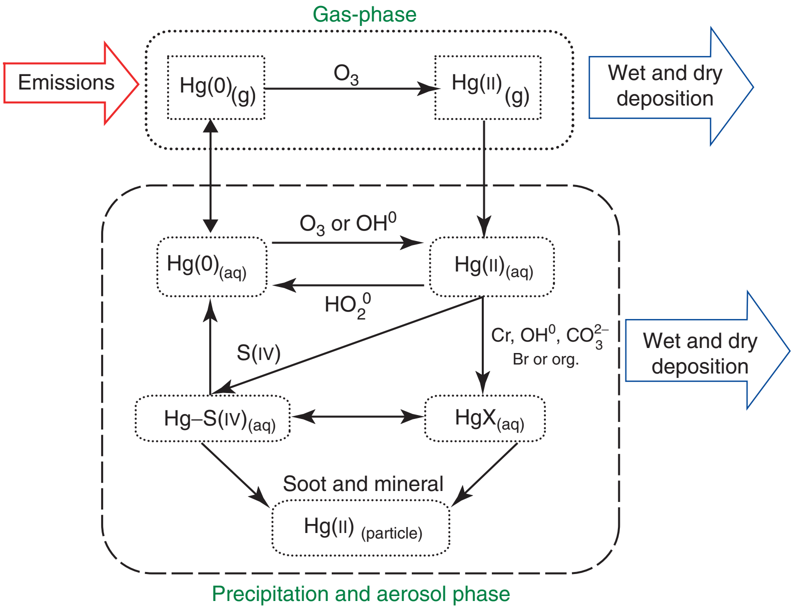


Figure 5 Summary of some of the important physical and chemical transformations of mercury in the atmosphere. Figure style adapted from Shia *et al.* (1999); reactions from Shia *et al.* (1999), and Lin and Pehkonen (1999) and the references therein.

depletion of mercury and ozone, thus forging a connection between mercury and the chemistry and physics of Arctic haze formation and breakdown (Figure 6; Barrie and Hoff, 1985; MacDonald *et al.*, 2000). Further work by Bill Schroeder and his colleagues as well as others in the Arctic (e.g., Lu *et al.*, 2001; Munthe and Berg, 2001 and references therein; Lindberg *et al.*, 2002) and Antarctic (Ebinghaus *et al.*, 2002) confirms this phenomenon as recurrent, seasonal, and occurring in both polar regions (though perhaps more dramatically in the Arctic). Working at mid-ocean, Mason *et al.* (2001) have observed a rapid oxidation of mercury near the air–sea interface resulting from reactions with sea-spray halogens. As Lindberg *et al.* (2002) and others have observed, the reaction in the Arctic is also coincident with a buildup of reactive bromine compounds in the polar atmosphere, pointing to a possible mechanistic similarity between the Arctic and mid-ocean phenomena (e.g., Ariya and Ryzhkov, 2003; Raofie and Ariya, 2003). In both cases, the generation of significant concentrations of oxidized mercury in the gas phase may lead to significant dry depositional fluxes in addition to fluxes associated with precipitation. The assessment made by Schroeder *et al.* (1998) when describing the depletion events initially was that perhaps 0.5 Mmol of mercury was deposited to the Arctic as a result of this phenomenon (a boundary layer of 500 m over 2×10^5 km^2 containing 1.84 ng m^{-3} emptied of its mercury five times: 4.6 μg m^{-2} yr^{-1}). This is significant but not an enormous unanticipated sink for mercury on a global scale. However, the flux could still be quite significant for delicate Arctic ecosystems and their human inhabitants. This bears further scrutiny. The polar and mid-ocean works also imply that such a mechanism should be looked for in other atmospheric environments and may be of broad significance.

Research on pathways of mercury dry deposition in addition to particle phase and RGM suggests that plants (especially trees) may take up elemental mercury from the atmosphere into their leaves above a certain "compensation point" concentration (Hanson *et al.*, 1995; Benesch *et al.*, 2001; Rea *et al.*, 2002). Elemental mercury absorbed in this way could then be deposited onto soils in the form of litterfall (e.g., Johnson and Lindberg, 1995; Grigal *et al.*, 2000; Lee *et al.*, 2000; St. Louis *et al.*, 2001). Forest foliage may also act as a particle interceptor, effectively increasing the dry deposition velocity of particles (throughfall; Iverfeldt, 1991b). Throughfall and litterfall studies suggest that the removal of mercury from the atmosphere in forests might be as much as 3× more than "open-field" deposition.

Long-term monitoring of data sets of mercury in the troposphere have now been developed at several locations. A recent compilation of results from sites in the NH show little change in total gaseous mercury (TGM)

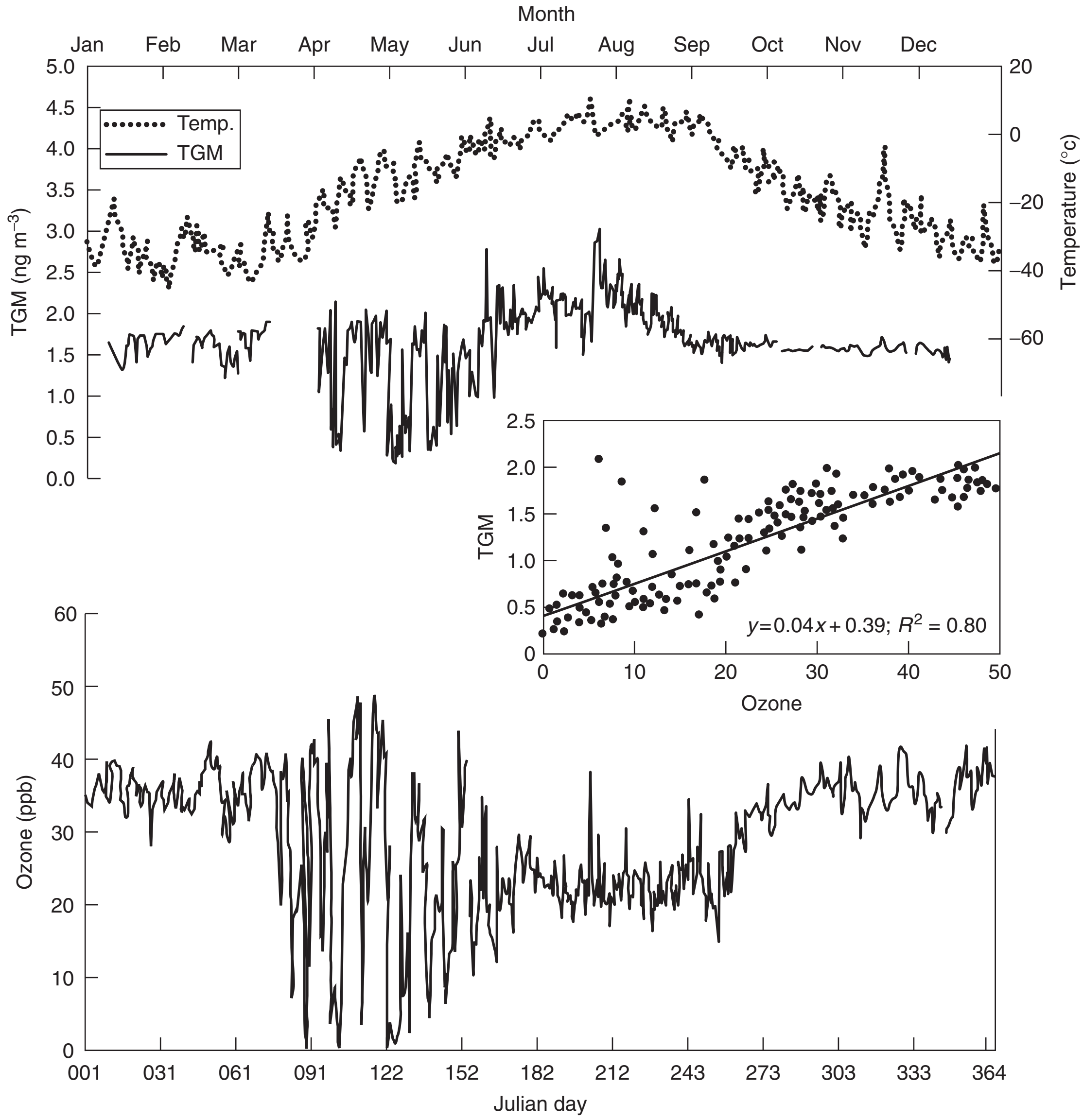


Figure 6 Depletion of Hg^0 in the atmosphere during Arctic spring as observed by Schroeder *et al.* (1998) at Alert. The traces, from top to bottom, are surface air temperature, total gaseous mercury, and ozone. The inset illustrates the correlation between mercury and ozone during the spring depletion period. Source: Schroeder *et al.* (1998).

concentrations over the last decade (Slemr *et al.*, 2003). Such research efforts are being performed in a social context of decreased mercury emissions from a number of countries (see Section 9.04.3). It is therefore difficult to predict the future direction of secular change of mercury in the atmosphere. However, as suggested, it may be that the reduced emissions from developed countries and relatively uncontrolled sources in Eastern Europe, for example, will be offset by increased emissions associated with developing economies such as China.

However, assuming for the moment that the atmosphere is near a steady state between emissions and deposition (Mason *et al.*, 1994), the emissions estimates of Section 9.04.3 can be used to gauge the magnitude of the depositional flux (20 Mmol yr^{-1}). This flux is not uniform, with low latitudes receiving more mercury per unit area than high latitudes and continental regions more than oceanic areas. These general trends are the result of several factors. If wet deposition tends to be more important in the removal of mercury than dry processes, wetter regions such as the tropics can be expected to have higher overall fluxes of mercury. This trend is evident even on regional scales, as for instance the flux of mercury to lakes on the wet side of New Zealand's South Island are much higher than on the dry side (Lamborg *et al.*, 2002a). The difference between mid-continent and mid-ocean fluxes of mercury from the atmosphere appears to be one driven principally by transport from the continents, where sources to the atmosphere are strong, a process recently traced using ^{222}Rn (Lamborg *et al.*, 1999).

There remains an intriguing inconsistency between experiments related to the mechanisms for mercury removal. Many laboratory, field, and model efforts indicate that the lifetime of mercury in the atmosphere must be 1–2 years, but there exist a number of plausible removal mechanisms (such as foliar mercury uptake followed by litterfall) that suggest the flux from the atmosphere is more consistent with lifetimes that are <1 year. The likely resolution of this problem lies in the observation that majority of the Earth's surface is covered by areas that are not temperate or boreal forests, including the open-ocean and tropical regions. The deposition to the ocean is consistent with an atmospheric residence time in excess of 1 year, while the mercury cycling within tropical forests is understudied.

9.04.5 AQUATIC BIOGEOCHEMISTRY OF MERCURY

A brief overview of the marine biogeochemical cycle of mercury was presented in the introduction. Here, a broader picture of the reactions and species-specific interactions involving mercury in natural waters appears in Figure 7. This mechanistic scheme, taken from Fitzgerald and Mason (1997), is derived in part from the simulation of the biogeochemistry of mercury in temperate lakes (Hudson *et al.*, 1994). Hudson and colleagues (1994) as part of the successful and scientifically influential Mercury in Temperate Lakes Program (MTL) conducted in northern Wisconsin, USA, developed a mercury cycling model (MCM). Comparable models have been developed for other freshwater environments such as the Florida Everglades (Beals *et al.*, 2002) and Onondaga Lake, a highly mercury-contaminated and USEPA-designated "superfund" site (Gbondo-Tugbawa and Driscoll, 1998). We anticipate that, as information increases, analog biogeochemical MCMs will be developed and applied for marine systems. Accordingly, we have chosen to illustrate major features of the aquatic

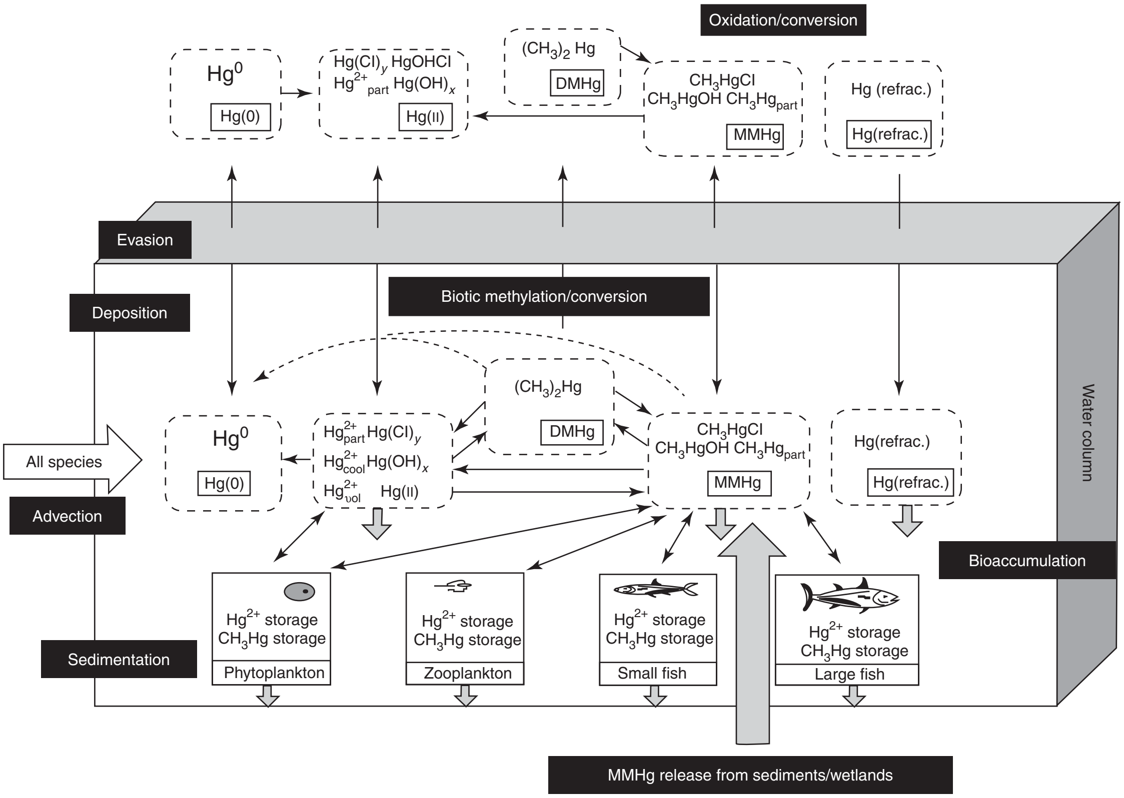


Figure 7 Generalized view of mercury biogeochemistry in the aquatic environment. Prominent processes are labeled (Hudson *et al.*, 1994).

cycling of mercury using the near-shore environment as a generalized working analog for aquatic systems.

Although organic and inorganic ligands and organisms differ in fresh and salty environments, much of the biogeochemical processing and movement of mercury are expected to be similar. Representative distribution and speciation data for mercury in natural waters are presented in Table 11. MMHg was first determined in freshwaters by Bloom (Bloom, 1989; Watras *et al.*, 1994), and is now well documented (e.g., Verta and Matilainen, 1995; Mason and Sullivan, 1997). In 1990, Mason and Fitzgerald reported finding methylated mercury species, including DMHg, in the open-ocean waters of the equatorial Pacific Ocean (Mason and Fitzgerald, 1990, 1993). Their presence has been confirmed for the Atlantic Ocean, Mediterranean Sea, and estuaries (Cossa *et al.*, 1994; Mason *et al.*, 1998; Mason and Sullivan, 1999a, b). Likewise, the production and supersaturation of Hg^0 is well documented in fresh- and saltwaters since the initial papers were published by Vandal *et al.* (1991) for lakes and Kim and Fitzgerald (1986) for the equatorial Pacific Ocean. As Figure 7 shows, the cycling of Hg^0 and MMHg is intimately linked by their competing and critical roles in the aquatic biogeochemistry of mercury (substrate hypothesis). Notice that, in general, the speciation, transformation pathways, reactions, and processes can be connected to reactive mercury. This reactant or "substrate" should be viewed broadly to encompass labile inorganic and organically associated mercury species. Sources include atmospheric deposition/exchange, watersheds, riverine inputs, sewage, and other human-related discharges.

Using Table 11 as background and Figure 7 as a guide, important features associated with mercury cycling in all natural waters but especially seawater are re-emphasized and highlighted in the following summary:

1. The principal source of the toxic species, MMHg, in marine and many freshwater aquatic systems is *in situ* biologically mediated conversion of labile reactive mercury. As discussed, SRB have been implicated as the primary synthesizers (Compeau and Bartha, 1985; Winfrey and Rudd, 1990; Gilmour and Henry, 1991). The bioamplification of MMHg in the aquatic food chain yields concentrations in fish that are often more than a million times greater than its levels in water. Many freshwater systems also receive significant inputs of MMHg from their watersheds, particularly wetlands (e.g., Hultberg *et al.*, 1994; Hurley *et al.*, 1995; St. Louis *et al.*, 1996). Salt marshes can also be prolific generators of MMHg, but do not appear to be larger sources than coastal sediments (Langer *et al.*, 2001). They are, however, important nurseries for many aquatic organisms and could represent locations of significant MMHg accumulation in the early life stages of some fish species.
2. Hg^0 is an important species in air and water, and *in situ* direct reduction of labile reactive mercury by biotic (i.e., bacterial) and abiotic (i.e., photochemical) means is a principal pathway for its aqueous production (Amyot *et al.*, 1994, 1997; Rolfhus, 1998; Costa and Liss, 1999); biological demethylation mechanisms (see Figure 7) yield small amounts of Hg^0 (Mason *et al.*, 1993). The mechanisms of reduction are unclear and are the focus of current study. The reverse reaction, oxidation of Hg^0, also occurs (e.g., Amyot *et al.*, 1997; Lalonde *et al.*, 2001). Thus, ambient Hg^0 concentrations can be expected to vary in space and time in response to changes in the forces that drive the reduction and oxidation reactions (e.g., bacterial activity, light, temperature, dissolved organic carbon (DOC), and total mercury). Examples of diel and seasonal variations in Hg^0, consistent with this view, are becoming more common in the literature (e.g., Lindberg *et al.*, 2000; Rolfhus and Fitzgerald, 2001; Amyot *et al.*, 2001; O'Driscol *et al.*, 2003; Tseng *et al.*, 2003, 2004; Balcom *et al.*, 2004).
3. Reiterating, *in situ* Hg^0 production (natural waters are generally supersaturated) and emissions to the atmosphere are major processes; they exert a first-order (primary) control on the overall biogeochemistry and bioavailability of mercury in aqueous systems, and the water–air fluxes must be considered in global/regional atmospheric and aquatic biogeochemical models of the mercury cycle; the reduction reactions (leading to aqueous emissions of Hg^0) are recycling mercury derived from both natural and anthropogenic sources of mercury, and, thereby, extending the lifetime of pollutant and natural mercury in active reservoirs.
4. The aqueous production of Hg^0 competes for reactant (i.e., labile reactive mercury) with the *in situ* biological synthesis of MMHg; thus, water bodies with a large production of Hg^0 will have less bioavailable mercury, smaller amounts of MMHg in biota, and reduced mercury accumulation in the sediment (Wiener *et al.*, 1990b; Rada and Powell, 1993; Fitzgerald *et al.*, 1991).

Table 11 Mercury species concentrations in a variety of natural waters. All data in picomolar, except where noted.

Location	*Dissolved total Hg*	*Particulate total Hg*	*Dissolved reactive Hg*	*Dissolved MMHg*	*Particulate MMHg*	*Dissolved DMHg*	*Dissolved Hg^0*	*References*
Freshwaters								
Lake Michigan, USA	1.6	0.58	NA	0.025–0.05	0.01–0.015	NA	0.140 ± 0.085	Mason and Sullivan (1997)
Lake Superior, USA/ Canada	ca. 0.5–5[a]	0.04–0.43[b]	0.08–0.57	0.008–0.064	0.00005–3.9[b]	NA	0.03–0.17	Rolfhus *et al.* (2003)
Lake Hoare, Antarctica[a]	2.7–6.8	NA	0.4–1.2	< 0.4–1.2	NA	NA	NA	Vandal *et al.* (1998)
Everglades	5–10[a]	NA	0.15–0.5[a]	0.25–2.5[a]	NA	NA	0.025–0.225	Hurley *et al.* (1998)
Wisconsin lakes, USA	3–6	1–2	NA	0.1–0.9	0.15–0.35	< 0.003	0.035–0.355	Watras *et al.* (1994) and Fitzgerald *et al.* (1991)
Estuaries/coastal								
San Francisco Bay, USA	0.4–174	0.3–439	NA	0–1.6	0–1.92	NA	0.043–9.8	Conaway *et al.* (2003)
Long Island Sound, USA	1.6–13.1	< 0.1–24.1	< 0.1–7.6	0–3.3	< 0.01–2.91	NA	0.037–0.89	Vandal *et al.* (2002) and Rolfhus and Fitzgerald (2001)
North Sea and Scheldt estuary	0.5–14	0.1–6[b]	NA	0.05–1.37	0.0009–0.0435[b]	NA	0.06–0.8	Baeyans and Leermakers (1998) and Leermakers *et al.* (2001)
Siberian estuaries	0.7–17	0.15–9.4	NA	NA	NA	NA	NA	Coquery *et al.* (1995)
Loire and Seine estuaries	1–6	0.42–13.3[b]	< 0.4–2.1	NA	< 0.0015–0.0296[b]	NA	< 0.05–0.454	Coquery *et al.* (1997)
Chesapeake Bay, USA[a]	~ 3–40	NA	NA	~ 0.05–0.8	NA	NA	~ 0.1	Mason *et al.* (1999)
Pettaquamscutt R., USA	~ 1–25	~ 0–18	0.4–8[a]	< 0.05–4	< 0.05–6.88	NA	< 0.025–0.4	Mason *et al.* (1993)
Brazilian lagoons	18.5–55.2	18–230	0.18–0.43	NA	NA	NA	NA	Lacerda and Gonçalves (2001)
Open ocean								
Mediterranean Sea	0.8–6.4[a]	NA	< 0.2–0.97[a]	< 0.15[a]	NA	< 0.13–0.29	< 0.02–0.39	Cossa *et al.* (1997)
Black Sea	1.6–11.8	NA	NA	< 0.025–1.04	NA	< 0.002–0.041	0.21–1.16	Cossa and Coquery (in press) and Yigiterhan *et al.* (2006)
North Pacific	0.1–2	NA	NA	NA	NA	NA	NA	Laurier *et al.*, 2004
Eq. Pacific Ocean[a]	NA	0.11–5.87	0.4–6.9	< 0.05–0.58	NA	< 0.005–0.67	0.015–0.69	Mason and Fitzgerald (1993)
North Atlantic	2.4 ± 1.6	0.035 ± 0.02	0.8 ± 0.44	1.04 ± 1.08[c]	NA	0.08 ± 0.07	0.48 ± 0.31	Mason *et al.* (1998)
South Atlantic	2.9 ± 1.7[a]	0.1 ± 0.05	1.7 ± 1.2[a]	< 0.05–0.15	NA	< 0.01–0.1	1.2 ± 0.8	Mason and Sullivan (1999a, b)

[a] These samples were unfiltered. [b] Units of nmol Hg gm^{-1} of suspended material, dry weight. [c] Likely includes anomalously high results.
NA, not available.

5. Given the affinity of Hg^{2+} for sulfur (i.e., sulfydryl groups) and its ability to form very stable organomercury chelates, organic complexation will exert an important control on the bioavailability of mercury.
6. Inorganic complexation with sulfur is a primary reaction in reducing environments. This reaction may occur in oxygenated waters where, for example, microenvironments develop such that oxygen is depleted and sulfate reduction takes place. This is one possible explanation for the presence of MMHg in ocean surface waters. There is a triad of competing ligands for free mercury in most aqueous systems. Organic ligands compete with chloride in saltwater and with hydroxide in freshwater, while sulfur becomes especially competitive as oxygen levels decline, and SRB activity increases.

As a point of analytical and environmental interest, Hg^0 is more readily measured in natural waters than MMHg. Since the *in situ* production of MMHg and Hg^0 is proportional to the supply of reactive mercury, a comprehensive understanding of the aqueous Hg^0 cycle and its temporal and spatial patterns may provide a means to constrain and improve predictive models for the aquatic and atmospheric biogeochemistry of mercury and MMHg in natural waters. For a sense of the potential geochemical benefits from automated Hg^0 measurements, readers should refer to some recent field studies of Hg^0 (e.g., Lindberg *et al.*, 2000; Amyot *et al.*, 2001; Balcom *et al.*, 2000).

9.04.5.1 Environmental Mercury Methylation

Given the importance of *in situ* synthesis of MMHg through conversion of less-toxic mercury species and its prominent role in the aquatic cycling of mercury (Figure 7), aqueous mercury methylation merits added consideration. As outlined, bacterial mediation enhances the rates at which mercury, a "soft acid," can form alkylated species in aquatic environments. This extraordinary interaction and its potential consequences have provided the rationale for much environmentally related mercury research over the past three decades. Indeed, the biologically mediated synthesis of alkylated mercury species can readily account for most of the MMHg accumulating in biota, especially large fish, in most marine and freshwaters (Wiener *et al.*, 1990a; Fitzgerald and Watras, 1989; Watras *et al.*, 1994; Rolfhus and Fitzgerald, 1995; Benoit *et al.*, 2003; Hammerschmidt *et al.*, 2004).

9.04.5.1.1 Near-shore regions

The near-shore environment provides a useful biogeochemical framework for outlining current knowledge regarding mercury methylation in aqueous systems. Mechanistically, recent work in freshwaters and near-shore sediments has not only pointed to SRB as methylating agents, but transition regions between oxygenated and anoxic conditions (e.g., low oxygen/hypoxic) as the principal sites of MMHg production (e.g., Gilmour and Henry, 1991; Watras *et al.*, 1994; Langer *et al.*, 2001; Hammerschmidt and Fitzgerald, 2004; Hammerschmidt *et al.*, 2004). While mercury methylation does occur in the water column and is especially important throughout most of the oceans (i.e., pelagic regions, e.g., Topping and Davies, 1981), the major sites for production are associated with particles and depositional environments such as lake and coastal/estuarine sediments, wetlands, and marshes (Watras *et al.*, 1994; Gilmour *et al.*, 1998; Langer *et al.*, 2001; Hammerschmidt *et al.*, in preparation). Microbial production of MMHg in sediment is influenced by a number of environmental factors that affect either the activity of methylating organisms (i.e., SRB) or the availability of inorganic mercury for methylation. For example, recent studies of MMHg levels in bulk surface sediment (e.g., Benoit *et al.*, 1998a; Gilmour *et al.*, 1998; Krabbenhoft *et al.*, 1999; Mason and Lawrence, 1999; Hammerschmidt and Fitzgerald, 2004; Sunderland *et al.*, in press) have shown dependencies on inorganic mercury, organic matter, and sulfide. In marine and estuarine sediments, where seawater provides ample sulfate, rates of sulfate reduction are influenced mostly by availability of organic matter and temperature (Skyring, 1987). King *et al.* (1999, 2000, 2001) have demonstrated that the rate of mercury methylation is closely related to that of sulfate reduction.

Estuarine/marine systems that are highly productive or receive autochthonous inputs of organic matter are prime locales for enhanced rates of mercury methylation and ecosystem exposure to MMHg. However, recent studies have illustrated that although significant mercury methylation occurs in such environs, production of MMHg is attenuated by accumulation of sulfide, the metabolic by-product of sulfate reduction (Figure 8; Gilmour and Henry, 1991). In estuarine and marine sediments, where activity of SRB is high and largely independent of sulfate, sulfide inhibition of mercury methylation is clearly demonstrated by the inverse relationship with sulfate. In contrast, mercury methylation in freshwater systems is directly related to sulfate,

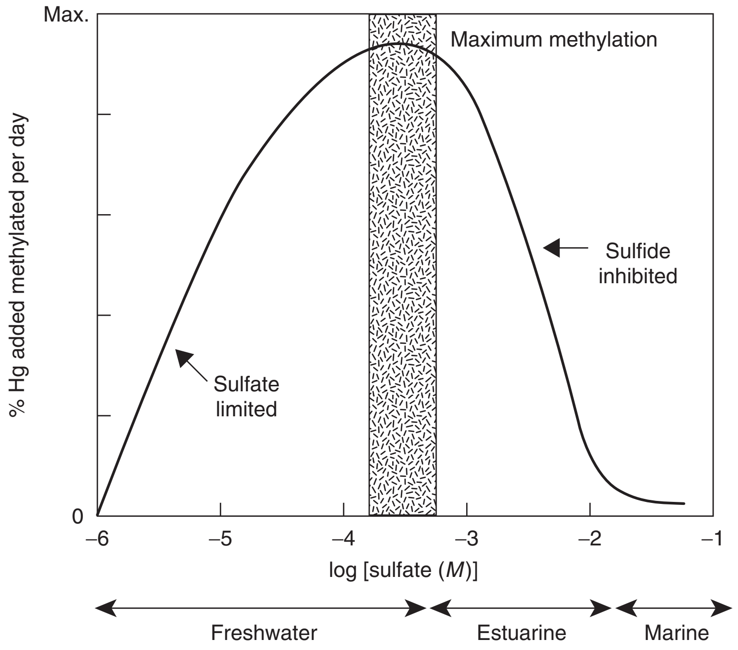


Figure 8 Sulfate/sulfide controls on mercury methylation in aquatic environments—the "Gilmour curve." At relatively low sulfate concentrations (most freshwaters), methylation of mercury is limited by the rate of sulfate reduction. At higher sulfate concentrations (saltwaters), sulfide buildup from relatively high rates of sulfate reduction results in decreased bioavailability of mercury. Reproduced with kind permission of Springer Science and Business Media from Langer *et al.* (2001); after Gilmour and Henry (1991).

which limits SRB metabolism. Hence, maximum mercury methylation occurs in sediments where organic matter and sulfate are sufficiently high as to stimulate SRB metabolism, but not so high as to cause accumulation of sulfide that inhibits the availability of mercury for methylation (Gilmour and Henry, 1991, figure 8, the "Gilmour curve").

A mechanism by which sulfide affects methylation of mercury was recently proposed by Benoit *et al.* (1999a, b, 2001a, b). Sulfide affects the chemistry of inorganic mercury in sediments by precipitating it as solid mercuric sulfide and forming dissolved mercury–sulfide complexes, including HgS^0, HgS_2^{2-}, and $HgHS_2^-$. HgS^0 is a major dissolved mercury–sulfide complex when sulfide is $<10^{-5}$ M, and charged complexes, mainly as $HgHS_2^-$, are dominant at greater levels (Figure 9; Benoit *et al.*, 1999a). The mechanism for uptake of inorganic mercury by methylating bacteria is not known, though the research of Benoit *et al.* points to diffusion of neutrally charged HgS^0 through the cellular membrane as the key factor. As a result, maximum rates of mercury methylation occur in sediments where SRB activity is significant but the accumulation of sulfide is minimized, thereby favoring speciation of dissolved Hg–S complexes as HgS^0.

Sulfide oxidation occurs both microbially and abiotically. In coastal sediments that are not subject to water column anoxia, burrowing animals mix the upper few centimeters of sediment (i.e., bioturbation), homogenizing the sedimentary solid-phase and pore water constituents (e.g., Gerino *et al.*, 1998). In doing so, underlying anoxic (i.e., sulfidic) sediments are mixed with overlying oxic sediments, thereby minimizing accumulation of sulfide via dilution and abiotic and microbially mediated oxidation reactions. Sulfide-oxidizing bacteria (SOB) are chemolithotrophs that use sulfide as a source of energy and reducing power. Bioturbation also can stimulate SRB activity by translocating organic matter from surface sediments to depth (Hines and Jones, 1985; Skyring, 1987; Gerino *et al.*, 1998). Hence, bioturbation of estuarine sediments likely stimulates mercury methylation by both enhancing SRB activity and minimizing accumulation of sulfide. Biologically mediated reworking of coastal/estuarine sediments, in general, keeps some portion of the historic (buried) inventory of anthropogenic mercury ("mercury pollution legacy") active. Given that legacy mercury can be methylated and mobilized in the coastal zone (unlike in lakes), a significant delay is likely between reductions in modern loadings and expected declines in MMHg in the fish stock. This unfortunate expectation for marine systems must be emphasized when considering the expected and observable benefits from "zero

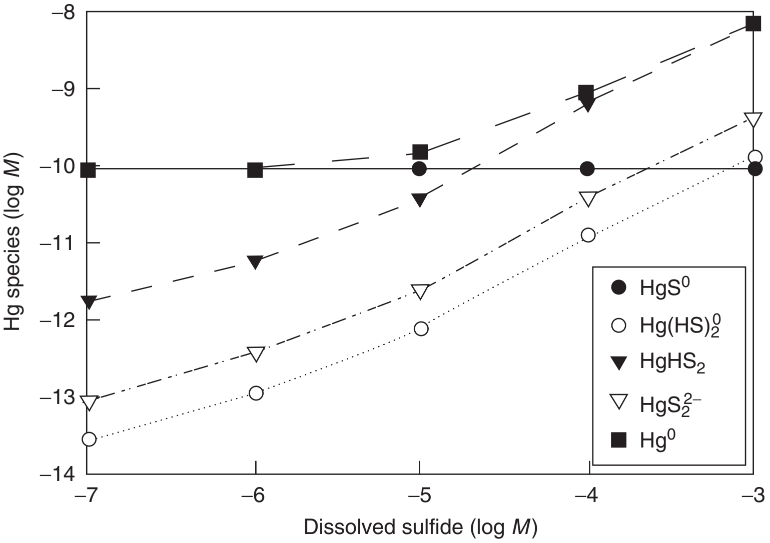


Figure 9 Dissolved-mercury speciation in sediment pore waters as a function of sulfide concentration. Note that the most bioavailable form, HgS^0, is the dominant chemical form at log $S < \sim(-4.7)$. Source: Benoit *et al.* (1999a).

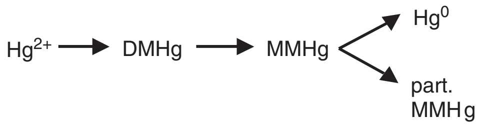
mercury use" environmental legislation and remediation efforts.

In sediments that are less bioturbated, SOB promote mercury methylation by minimizing accumulation of sulfide. These bacteria proliferate in redox transition zones overlying SRB. By consuming sulfide, SOB minimize its accumulation, promoting speciation of mercury–sulfide complexes as HgS^0 and facilitating uptake of inorganic mercury by proximal SRB. The well-defined relationships between redox transition zones, rates of mercury methylation, and MMHg distributions in salt marsh sediments are illustrated in Figure 10 (Langer *et al.*, 2001). These results are consistent with those predicted by the hypotheses of Benoit *et al.* (1999a, b). Clearly, the diverse chemistry and microbiology of the redox transition zone makes it an important location for MMHg synthesis in sediments. Although SRB appear to the principal methylators, there is also evidence for mercury methylation by iron-reducing bacteria (Gilmour, personal communication).

Demethylation in the water column and sediments is receiving increasing attention. Both abiotic (e.g., Sellers *et al.*, 1996, 2001) and biotic (e.g., Pak and Bartha, 1998; Marvin-Dipasquale and Oremland, 1998; Marvin-Dipasquale *et al.*, 2000; Hintelmann *et al.*, 2000) processes are implicated. The result is that MMHg accumulation in aquatic systems represents a balance between methylation, bioaccumulation, and the demethylation processes. In sediments, MMHg decomposition is particularly important, and it is possible that some sediments represent net sinks, rather than net sources, for MMHg in the water column.

9.04.5.1.2 Open-ocean mercury cycling

In contrast to the near-shore, mercury methylation in the water column is thought to be the primary source of MMHg in the open ocean, though lateral inputs from continental shelves are also potentially important sources (Hammerschmidt and Fitzgerald, 2006). As shown in Table 11, DMHg is found in seawater, but has not been observed in common freshwaters (Mason *et al.*, 1993; Mason and Fitzgerald, 1993; Mason and Sullivan, 1999a, b). Indeed, MMHg is the predominant alkylated species in temperate lakes, while DMHg and (to a lesser extent) MMHg are common constituents of the dissolved mercury pool in ocean waters. The unique presence of DMHg in seawater prompted Mason and Fitzgerald (1993, 1996) to propose the following reaction sequence:



where DMHg would be the principal product from the methylation of inorganic mercury with MMHg and Hg^0 derived from the decomposition reactions. The primary source of Hg^0 in aqueous systems, however, remains the *in situ* direct reduction of labile reactive mercury by

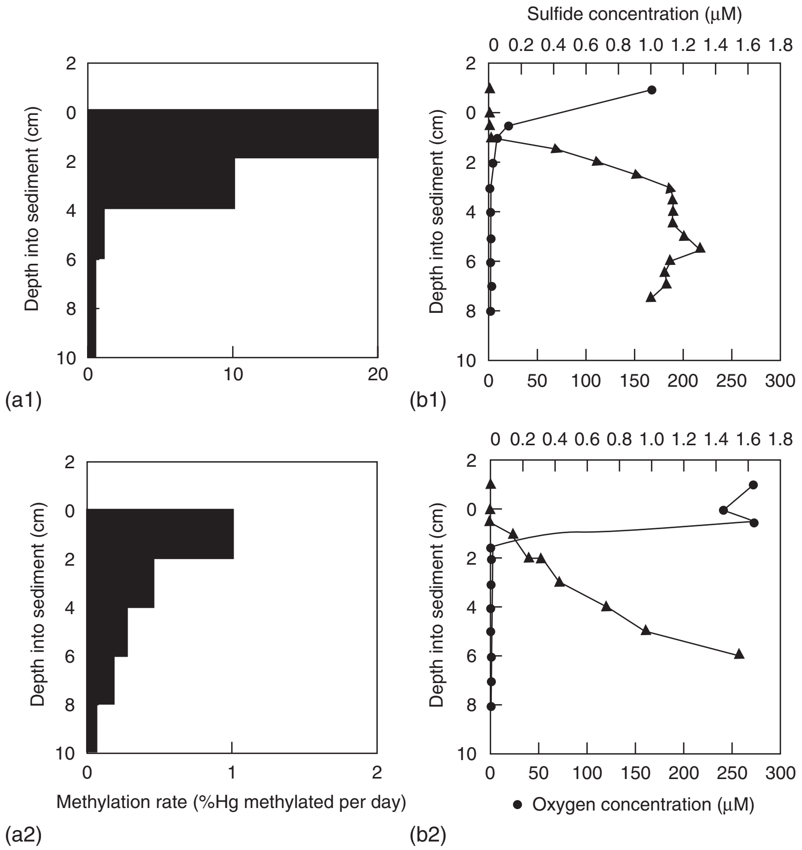


Figure 10 Vertical profiles of methylation rates (a1, a2) and sulfide/oxygen concentrations (b1, b2) in the sediments of sandy (1) and muddy (2) sites in a salt marsh (Barn Island, CT, USA). Maximum methylation occurs in the top 2 cm of these sediments and is coincident with the redox transition zone. Note also that the rates are an order of magnitude faster in the sandy sediments. Reproduced with kind permission of Springer Science and Business Media from Langer *et al.* (2001).

biotic (i.e., bacterial) and abiotic (i.e., photochemical) processes (Figure 7). Decomposition is the principal loss term for DMHg, while particulate scavenging and decomposition are important sinks for dissolved MMHg. This view of mercury cycling in the ocean is very speculative. DGM formation has been little studied, and the organisms responsible for methylation in the open ocean are not known (nor have the pathways been elucidated).

9.04.5.1.3 Open-ocean mercury profiles

An appreciation of the challenges of ultratrace metal investigations can be gained from a consideration of mercury speciation and distributional information for open ocean. A classic vertical distributional profile for mercury in the northeast Pacific Ocean is shown in Figure 11 (Gill and Bruland, 1987). As expected with a biogeochemically active element, mercury shows a nonconservative distribution, one that is not governed by simple mixing of ocean waters. Total mercury concentrations range from 1.8 pM at the surface to 0.3 pM in the upper ocean minimum. The atmospheric mercury enrichment in the near-surface waters was captured due to recent rains and short-term stratification. The minimum is indicative of mercury removal via particulate scavenging processes that are biologically mediated. The gradual increase in mercury at depth may reflect regeneration processes. Today, and given the analytical improvements since the Gill and Bruland report, a more comprehensive suite of mercury species can be determined, along more insightful biogeochemical reaction-based explanations for the distributional patterns in space and time. A summary of such extensive mercury measurements appears in Table 11.

An example of recent data comes from the Third IOC Baseline Trace Metal Cruise, which took place during May–June of 1996 in the equatorial and South Atlantic (Mason and Sullivan, 1999a, b). We selected vertical profiles for mercury species for one station (#8 at 17° S, 25° W) from among six others examined as part

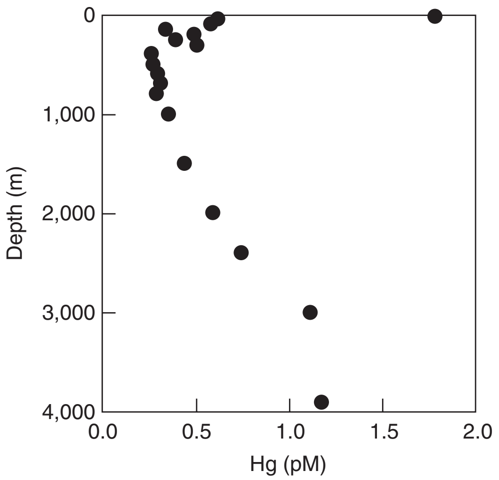


Figure 11 Vertical profile of total dissolved mercury in the northeast Pacific Ocean. After Gill and Bruland (1987).

of the Mason and Sullivan Program. These data are presented in Figure 12. DMHg, Hg^0 (total dissolved gaseous mercury—the small contribution of DMHg), and total mercury are plotted versus depth. In addition, and as a reference, the distributions of dissolved silicon and salinity are shown. First, the results confirm the presence of methylated mercury species, especially DMHg, and Hg^0 in oxygenated ocean waters. Here, however, and in contrast to the North Atlantic (Table 11), MMHg levels were at the detection level (0.05 pM). Mason and colleagues (1998) noted, given the uncertainty and the high detection limit (0.5 pM) in their study, that the values reported for MMHg in the North Atlantic may be too high. If these values were greater than for the South Atlantic, this trend would suggest that MMHg is either decomposing or scavenged more rapidly than it is formed. The prominence of Hg^0 ($>50\%$) relative to the total mercury present (average of 2.4 ± 1.4 pM) is a most striking feature. Its abundant presence at depth is consistent with the hypothesis outlined above where MMHg, which is produced as DMHg decomposes. A portion of the MMHg is scavenged by particulate matter and Hg^0 produced as the relatively stable product (under dark conditions) of the decomposition of the MMHg.

Most DMHg is produced in the near-surface waters, but, as illustrated in Figure 12, little is found in the euphotic zone because DMHg is readily decomposed photochemically. DMHg accumulates in the intermediate depths (see profile) above 1,500 m. Below 1,500 m, small but significant concentrations (0.02–0.03 pM) occur, but they are considerably smaller than values (0.16 ± 0.8 pM) in the source region of the North Atlantic Deep Water (NADW; Mason *et al.*, 1998). While the DMHg decline in the modestly advecting NADW (southward travel time ~100 years to reach the study regions of South Atlantic and equatorial Atlantic) is significant, decomposition rate estimates for DMHg in advecting deep ocean waters imply that sufficient production must be occurring to yield measurable concentrations (Mason and Sullivan, 1999a, b). This production is presumably fueled by the very small transport of carbon from the surface regions to below 1,500 m.

In summary, mercury speciation studies in oceanic systems are revealing the complex interactions of this biologically active and reactive element. However, as emphasized, the spatial and temporal coverage is sparse and many of the biogeochemical insights and hypotheses attempting to explain the behavior and fate of in-marine systems are speculative. Indeed, the challenging and complicated marine biogeochemistry of mercury beckons the curious and innovative. There is much to discover.

9.04.6 REMOVAL OF MERCURY FROM THE SURFICIAL CYCLE

The work summarized in Section 9.04.3 notwithstanding, most studies indicate that soils and terrestrial sediments act as net sinks of mercury on timescales of centuries. Such a statement is supported by a review of the mercury content of soils from around the world and supporting data that allow determinations of mercury inventories in various soil horizons (Table 12). For comparison, we have estimated the "excess mercury" inventories resulting from anthropogenic activities using the integrated human emission inventory over the last 100 years estimated by Mason *et al.* (1994; 947 Mmol total, 447 Mmol globally uniform, 500 Mmol near source). As the continental area of the globe is $\sim1.5\times10^8\ \text{km}^2$ and assuming uniform distribution and no soil loss, we expect to find from $0.6\ \text{mg m}^{-2}$ in remote areas to $2.6\ \text{mg m}^{-2}$ in "nonremote" areas (taken to be one-third of the continental area). Most of the lake sediment data cited fit this range reasonably well. The soil data also display agreement depending on the assumed depth of penetration of the modern mercury signal. Matilainen *et al.* (2001) found that additions of radioactive ^{203}Hg were quantitatively retained in the organic humus layer of their test soils (O horizon), and thus we might expect little vertical penetration of the modern signal. This leads to the conclusion that most of the mercury that has been deposited to soils in the last

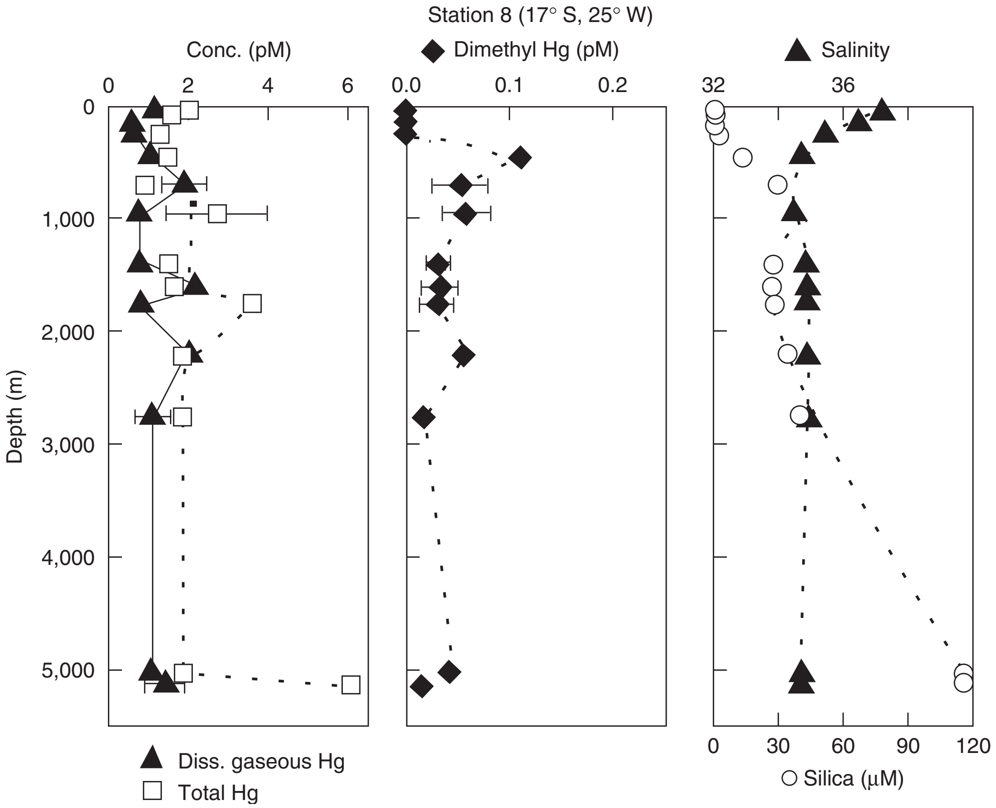


Figure 12 Vertical profiles of total dissolved mercury and mercury species in the South Atlantic, from station 8 of the IOC Baseline South Atlantic Cruise. Monomethyl Hg was below detection at all depths, while measurable dimethyl Hg was found within and below the thermocline. Dissolved gaseous mercury, dominated by Hg^0, represents the majority of mercury at many depths at this location. Source: Mason and Sullivan (1999a, b).

~100 years is still present in active biogeochemical zones in these systems.

These estimates suggest that human-related contributions to soil loadings of mercury (the excess mercury) are a significant if not always dominant contributor to the total soil column mercury inventory. The natural weathering inputs of mercury to soils may be examined if we assume that the residence time of mercury within soils is similar to that of organic carbon, citing the strong associations between mercury and humic materials already mentioned. Estimates of organic carbon residence within soils is wide ranging and dependent on ecological setting, but may average ~100 years. This approach is supported by the observation that agricultural fields, which experience net losses of organic carbon as a result of human use, show lower mercury inventories than undisturbed soils (Grigal *et al.*, 1994). As 100 years is the approximate timescale over which major human perturbation has taken place, we may subtract the estimated excess mercury loading from the total inventory to arrive at an estimate of the weathering input (Table 12). In most instances, the natural and excess loadings are comparable as was the ratio of natural to human-related emissions inventories during that period. Thus, it appears that on millennial timescales, soils are not net sinks for mercury, and release their burden to natural waters through runoff and erosion and to the atmosphere by volatilization and from fires.

Such bulk, integrative studies are supported by short-term studies of mercury loadings to watersheds and subsequent runoff in surface streams. A number of studies have indicated that 70–95% of the mercury deposited under these conditions is retained within the soils of the watersheds. Retention estimates made in this way could be biased low due to the slow release of "legacy mercury" deposited over the previous decades that increases in magnitude as the total watershed inventory increases (e.g., Mierle, 1990; Aastrup *et al.*, 1991; Swain *et al.*, 1992; Krabbenhoft *et al.*, 1995; Scherbatskoy *et al.*, 1998; Lawson and Mason, 2001; Kamman and Engstrom, 2002; Lamborg *et al.*, 2002a).

The flux of mercury from the continents to the ocean in river runoff has been estimated to

Table 12 Concentrations of mercury in soils and terrestrial sediments and estimates of the anthropogenic mercury inventory (xsHg).

Location(s)	*Soil/sed. Hg conc.* (ng g^{-1})	*Soil/sed. Hg inventory* (mg m^{-2})	*References*
Soils			
Cedar Creek, MN, USA	140 ± 30	0.3 ± 0.2	Grigal *et al.* (1994)
Organic layer			
0–10 cm	36 ± 7	3.4 ± 0.5	
10–50 cm	11 ± 4	7 ± 4	
Fr. Guiana (rain forest)	122–318		Roulet and Lucotte (1995)
0–30 cm			
Sweden O Horizon	320 ± 10	~1.5	Alriksson (2001)
B Horizon	43 ± 3		
C Horizon	13 ± 1		
Nevada, USA	100–15,000		Gustin *et al.* (1999)
Lake sediments			
Northern Quebec, Canada	25–450		Lucotte *et al.* (1995)
NS and NZ lakes	10–300	0.32–0.95[a]	Lamborg *et al.* (2002b)
Ice cores			
Fremont Glacier, USA	0.002–0.035	~1[a]	Schuster *et al.* (2002)
Model estimate			
Est. avg. anthrop. signal		0.6–2.6[a]	This work; Mason *et al.* (1994)
Coastal sediments			
Long Island Sound, USA	< 30 to > 600	~30–170[a]	Varekamp *et al.* (2000)
Northern Adriatic Sea	20–230	~13[a]	Fabbri *et al.* (2001)
Chesapeake Bay, USA	60 to > 1,000	NA	Mason *et al.* (1999)
Gulf of Cadiz, Spain	~50–250	~75[a]	Cossa *et al.* (2001)
Gulf of Trieste, Adriatic Sea	100–23,300	~12,000[a]	Covelli *et al.* (2001)
Florida Bay, USA	~10–236	~1.6[a]	Kang *et al.* (2000)
San Francisco Bay, USA	20–700 (MMHg: 0–3.5)	NA	Conaway *et al.* (2003)
S. Baltic Sea	2–340	1.2[a]	Pempkowiak *et al.* (1998)
S. China Sea, Malaysia	20–127	NA	Kannan and Falandysz (1998)
Anadyr est., Bering Sea, Russia	77–2,100	NA	Kannan and Falandysz (1998)
Mouth of St. Lawrence est., Canada	~50–100	~4.5[a]	Gobeil and Cossa (1993)
Greenland	~6–275	NA	Asmund and Nielsen (2000)
Santa Barbara Basin, USA	60–160	NA	Young *et al.* (1973)
Pelagic sediments			
Arctic Ocean	10–116	NA	Gobeil *et al.* (1999)
Kara Sea	75–2,045	NA	Seigel *et al.* (2001)
W. Mediterranean	~80	NA	Cossa *et al.* (1997)
Laptev Sea	25–140	NA	Cossa *et al.* (1996)

[a] Includes just the anthropogenic or excess Hg.

be ~1–5 Mmol yr^{-1} (Mason *et al.*, 1994; Cossa *et al.*, 1996). While some of this material is volatilized as outlined in Section 9.04.5, most is buried in coastal sediments (e.g., Fitzgerald *et al.*, 2000). Deeper coastal sediments or remote, surface lacustrine sediments are of the order of 10–50 ng g^{-1} dry weight. Typical surface sediments, even from systems not receiving direct inputs from industrial activities, can be 10× the background value. Extreme examples, such as the near-shore sediments of the Gulf of Trieste (NE Adriatic Sea), which receives the river discharge from the mercury mining and mineralized area of Idrija, are also to be found (Table 12). This enrichment of surface coastal sediments is not likely to be due to sediment diagenesis, as the flux of mass and mercury to the sediment overwhelms upward diffusion (Gobeil and Cossa, 1993). Thus, the excess mercury associated with the enrichments may be used to gauge the impact of human activity on the coastal zone, as shown in Table 12. Many of the values estimated here are larger than that expected from release of mercury from watersheds following atmospheric deposition. This estimate was made by assuming ~25% of the continental deposition (250 Mmol) was delivered to 10% of the ocean area ($3.6 \times 10^7\,\mathrm{km}^2$) giving $4\,\mathrm{mg\,m}^{-2}$. This difference is the result of periods when significant non-atmospheric point- and area-source inputs to coastal systems and their watersheds were in effect. Such a condition exists currently, for example, in the case of relatively unrestricted gold mining in Amazonia resulting in large documented accumulations of mercury in the river sediments and presumably in the coastal sediments of the western equatorial Atlantic (e.g., Lechler *et al.*, 2000). The residence time of mercury in this pool is difficult to estimate given our relatively sparse data, but is likely to be similar to the residence time of the sedimentary material. For example, Herut *et al.* (1996) found that mercury contamination of the sediments of Haifa Bay, Israel, was disappearing in a manner consistent with sediment remobilization, and could have a half-life in excess of 100 years. These sediments then represent a significant sink for mercury on the global scale. This pool should also be viewed as an environmental and public health concern for the future because this material is concentrated in a relatively small area of the ocean and one that is biologically productive and commercially important (see Section 9.04.5).

Finally, open-ocean sediments receive a portion of the mercury deposited to the ocean. Here, the data are particularly sparse and only a handful of studies are available to guide our discussion. Concentrations of mercury in these materials can be found in Table 12. Given the slow rate of accumulation and rapid recycling of material in the upper ocean, it is to be expected that little of this mercury is of anthropogenic origin, though one study claims to observe surface enrichments consistent with pollution inputs in a relatively near-shore and heavily impacted region (Seigel *et al.*, 2001). Gobeil *et al.* (1999) found evidence for diagenetic remobilization of mercury along with Fe/Mn and Mercone *et al.* (1999) have proposed coupled Hg/Se diagenesis and mineral formation under the slow sediment accumulation conditions present in the open ocean. They argued that this remobilization could result in surface enrichments not associated with anthropogenic inputs. We estimate the total amount of mercury associated with marine sediments to be 6×10^7 Mmol (~10 ng Hg g^{-1} of sediments, 1% organic carbon content and 12×10^{15} t organic carbon total; Lalli and Parsons, 1993). With inputs of mercury to open-ocean sediments on the order of 1 Mmol yr^{-1} (Mason *et al.*, 1994), the sedimentary pool should be expected to represent the primary sink for mercury on million year timescales.

9.04.7 MODELS OF THE GLOBAL CYCLE

Secular change in the global mercury cycle as a result of human activity is one of the major themes in this chapter and a focus of research currently. One of the most insightful research activities in pursuit of this theme has been the development of historical archives of mercury change. As of early 2000, this development effort has focused on three archives: peat bogs, lake sediments, and ice cores. All are used to reconstruct historical changes in the flux of mercury from the atmosphere.

Peat cores are generally collected from bogs dominated by *Sphagnum* moss species and from systems that are ombrotrophic ("rain fed"). Under these conditions, it is assumed that the moss is only able to receive mercury from the atmosphere, as these systems are isolated from groundwater and geologic inputs other than dust. Mercury delivered to the moss is incorporated in the live material at the surface and remains associated even as the moss continues to grow vertically. Therefore, collection and sectioning of a peat core, followed by dating and mercury analysis, should reveal any changes in the rate of incorporation of mercury into the moss. As discussed by Benoit *et al.* (1998b), the source of the mercury archived could include mercury associated with rain and dust as well as elemental mercury taken up from the gas phase by the moss. A number of studies have made successful use of the peat archive (e.g., Jensen and Jensen, 1990; Norton *et al.*, 1997; Benoit *et al.*, 1998b; Martinez-Cortizas *et al.*, 1999). There are, however, other reports of variable element mobilities, including the dating isotope ^{210}Pb (e.g., Damman, 1978; Urban *et al.*, 1990; Norton *et al.*, 1997). In our recent work in Nova Scotia, we found evidence for mobility of lead but not mercury (Lamborg *et al.*, 2002b). We therefore submit that peat archives, or sections of archives, that are dated with ^{210}Pb may yield inaccurate estimates of mercury deposition, while other dating techniques may result in reliable data. For example, in Nova Scotia, we dated surface peat using a co-occurring moss species *Polytrichum* that develops annual markings on the male gametophytes. The results of that analysis when compared to lake sediments and rain measurements indicated that dry deposition of dust or uptake of elemental mercury and/or RGM by the *Sphagnum* may contribute some of the mercury archived in peat, but that the contribution was likely small.

Sediments collected from remote lakes have been the most profitable of the archives studied to date. In most cases, lake sediments are free of diagenetic mobility that plagues the use of peat, allowing reliable dating and more precise reconstructions (see Chapter 9.03). The lake approach does have drawbacks, however, as suitable lakes (small watersheds, simple morphology, little in-/outflow) are often difficult to find in a location of interest. In the higher latitudes of the NH, where extensive glaciation was in effect, small seepage lakes tend to be more common, and thus much of this reconstruction work has been performed in Scandinavia, Canada, and the northern US (e.g. Swain *et al.*, 1992; Lockhart *et al.*, 1998; Bindler *et al.*, 2001; Fitzgerald *et al.*, 2005). Suitable lakes are being investigated currently in additional locations such as in the tropics, temperate, and subpolar Southern Hemisphere. Extension of lake sediment studies to these new regions should bolster the conclusions from the northern studies. The general picture emerging from the use of lake sediments (and peat) is one of widespread, global-scale 2–4 times increase in the amount of mercury delivered from the atmosphere since the advent of the industrial revolution. As noted in Section 9.04.3.4, many of the lake systems studied thus far have had slow sediment accumulation rates and watersheds that act as low-pass filters, rendering accurate reconstructions of secular change in Hg deposition in the last few decades very difficult. However, the similarity in timing and scale of the increased mercury deposition across these varied systems leaves little doubt that the signal is real and the result of the substantial impact that human activity has had on the global mercury cycle. Application of this information to modeling efforts (see below) represents an important step forward in our understanding of how the mercury cycle operates.

Ice core archives are receiving increasing attention. In general, these archives are not as useful as sediments due to the relatively low rate of accumulation (usable ice cores are generally to be found in dry high latitudes and accumulate at slow rates). Furthermore, recent work by Marc Amyot and colleagues (Lalonde *et al.*, 2002) has suggested that mercury deposited in snow is photoactive and may be lost from the media following reduction to elemental mercury. However, as described in Section 9.04.3, Schuster *et al.* (2002) analyzed ice core samples from the relatively rapidly accumulating ($\sim 70\,\mathrm{cm\,yr^{-1}}$) Fremont Glacier (WY, USA) to reconstruct deposition over the last 270 years. As indicated in Table 12, their results are consistent with predictions made for the inventory of anthropogenic mercury made here based on the model of Mason *et al.* (1994). Therefore, mountain glaciers may represent an important archive for future development. We noted that this glacial core also apparently preserved signals associated with volcanic eruptions that have not been found in lake sediment archives, but that these signals are difficult to interpret, as they appear not to be self-consistent. In a more conventional location for ice core studies, Boutron *et al.* (1998) used snow blocks to estimate changes in mercury deposition to Greenland over the last 40 years. Their work illustrates other fundamental difficulties associated with studying Hg in ice cores (small sample sizes and exceptionally low levels, $< 1\,\mathrm{pg\,g^{-1}}$). Stretching even further back, Vandal *et al.* (1993) used core material from Dome C in Antarctica to reconstruct mercury accumulation at that location to before the last glacial maximum ($\sim$34 kyr BP). This unique study found evidence that increased deposition of mercury to Antarctica during that last glacial maximum was attributable to increased evasion from the ocean and suggests that mercury in ice cores may be a useful paleoproductivity proxy.

Seabird feathers may provide a proxy for oceanic mercury secular change (Monteiro and Furness, 1997). This unique data set includes feathers retrieved from museum specimens of exclusively pelagic, piscivorous seabirds such as shearwaters and petrels. While there is scatter associated with the values, as should be expected from such a natural archive, an increase of $\sim 3\times$ between 1885 and 1994 can be seen in the mercury concentration of the feathers. Furness, Monteiro, and coworkers have extended their work to include studies on the movement of mercury within living birds and the relationship between prey concentrations of mercury and those observed in the bird's feathers (Monteiro *et al.*, 1998; Monteiro and Furness, 2001), which aid in the interpretation of the feather record. This approach has so far been applied to the NE Atlantic (Azores), and should be extended to other ocean regions.

A number of mathematical models have been developed to test the consistency of a variety of environmental mercury data sets as well as aid in generating testable hypotheses concerning those aspects of the global mercury cycle that are difficult to observe directly (Lantzy and MacKenzie, 1979; Millward, 1982; Mason *et al.*, 1994; Hudson *et al.*, 1995; Shia *et al.*, 1999; Bergan *et al.*, 1999; Bergan and Rodhe, 2001; Lamborg *et al.*, 2002b; Seigneur *et al.*, 2003).

The earliest efforts were limited by the general lack of high-quality data available at the time. Mason *et al.* (1994; MFM) therefore can be said to be the first global mercury model capable of providing meaningful insight into the whole cycle. The findings of MFM, including their reconstruction of the cycle in its preindustrial and modern forms, have been illustrated (Figure 2) and discussed in Section 9.04.1. As demonstrated, the atmospheric deposition predictions from MFM can be compared with anthropogenic mercury inventories in soils and sediments and appear to accurately predict the flux of mercury from the atmosphere to these archives. Additional insights from MFM include an atmosphere/ocean system that is nearly balanced, indicating the influential role of oceanic evasion in redistributing and sustaining the lifetime of mercury at the Earth's surface. Furthermore, MFM found that anthropogenic activities should have tripled the current atmospheric deposition of mercury, resulting in a tripling of the amount of mercury entering terrestrial and marine ecosystems. As indicated by the lake sediment archives, this is what is found. Finally, the MFM model estimated that only 50% of the mercury emitted to the atmosphere as a result of human activities is able to participate in the global cycle, and that the remaining mercury is removed from the atmosphere close to the source. Thus, the MFM treatment describes the current condition of the mercury cycle as one significantly perturbed by human activity on local, regional, and global scales.

As with any modeling effort, MFM was partially supported by a number of assumptions based on, in some cases, scant information. Since MFM, several other modeling efforts have sought to address particular hypotheses concerning some of these assumptions. For example, Hudson *et al.* (1995) included additional reservoirs to their simulated ocean than were used in MFM in an effort to gauge the importance of ocean mixing in modulating mercury increases in the environment. They also introduced a more complex emissions source function indexed to CO_2 that released less mercury overall than in MFM, and did so in a nonlinear fashion. The conclusions from this work were quite similar to MFM but did indicate that ocean mixing should be considered an important process in the global-scale biogeochemistry of mercury. Perhaps most importantly, ocean mixing increases the size of the oceanic pool and as a result increases the predicted residence time of mercury in the ocean. An increased oceanic residence time could result in an increased overall rate of mercury methylation, particularly as much of this time would be spent in the lower oxygen/microbially active region of the permanent oceanic thermocline. Additional consideration of the oceanic biogeochemistry of mercury by Mason and Fitzgerald (1996) supports this model view, particularly as an explanation for local imbalances in the air–sea exchange of mercury in certain regions such as the equatorial Pacific. Hudson *et al.* (1995) were also the first authors to directly compare their results with those provided by the lake sediments and noted, among other findings, that emissions from gold and silver mining prior to 1900 predicted to be significant were not to be found in the archives.

Three other recent global models (Shia *et al.*, 1999; Bergan *et al.*, 1999; Bergan and Rodhe, 2001) focused on the atmospheric aspects of the global cycle and have been able to place important constraints on which of the several chemical mechanisms proposed for elemental mercury oxidation are likely to be important at this scale. Particularly noteworthy are the efforts by Bergan and colleagues, who have exploited the data on interhemispheric concentrations of elemental mercury in the air. Exchange between the two hemispheres is relatively slow (~1.3 years) due to physical forcings, but yet the north/south gradient of elemental mercury is relatively weak (Slemr and Langer, 1992; Fitzgerald, 1995; Lamborg *et al.*, 1999). As the emissions of mercury in the NH are estimated to be larger than in the south, Bergan and colleagues used gradient and mixing time information to place constraints on the atmospheric lifetime of mercury. More recently, we have extended this approach through inverse box modeling (Lamborg *et al.*, 2002b), which used the gradient and lake sediment data explicitly to constrain both the atmospheric lifetime as well as aspects of the oceanic cycle including evasion, particle scavenging, and burial. This particular model (the global/regional interhemispheric mercury model, or GRIMM) suggests that evasion from the ocean is less than that estimated in MFM and that the ocean is a net sink.

Our inverse, or data assimilation, model underscores the importance of developing new data sets to improve our understanding of mercury biogeochemistry. As mentioned here, models such as Hudson *et al.*, Bergan *et al.*, and Lamborg *et al.* are principally driven by atmospheric and atmospherically related data. As these efforts are using essentially the same data, it is not surprising that the conclusions from these efforts are fairly similar. A more rigorous test of the current view of the global mercury cycle will require wholly new information, particularly from the ocean.

9.04.8 DEVELOPMENTS IN STUDYING MERCURY IN THE ENVIRONMENT ON A VARIETY OF SCALES

9.04.8.1 Acid Rain and Mercury Synergy in Lakes

As noted, sulfate reduction is thought to be the driving biogeochemical process behind mercury methylation in many ecosystems. In freshwaters that are relatively low in sulfate, recent increases in sulfate deposition associated with the acid rain phenomenon are hypothesized to result in increased rates of sulfate reduction and subsequently in mercury methylation (e.g., Gilmour and Henry, 1991; see Chapter 9.10, for details on acid rain geochemistry). Thus, not only are lakes receiving more total mercury than in the preindustrial past, they may be methylating a greater proportion of this load. Swain and Helwig (1989), for example, have noted that the concentration of mercury in Minnesota fish (usually dominated by MMHg), has increased by 10× 2, while deposition of mercury has increased by only 3× 3. Recent work by Branfireun *et al.* (1999, 2001) has recreated this phenomenon through sulfate additions to microcosms in the Experimental Lakes Area of Ontario, and there are ongoing efforts to expand this research to watershed/whole-lake scales (D. R. Engstrom, personal communication).

9.04.8.2 METAALICUS

METAALICUS is a project titled *Mercury Experiment to Assess Atmospheric Loading in Canada and the United States*. As described in this chapter, the atmosphere is the principal avenue for the mobilization of mercury in the environment, and anthropogenic mercury emissions to the atmosphere, especially from coal combustion, have contaminated all the major reservoirs. We noted the strong interest and support for studies examining linkages between the cycling of mercury in the atmosphere, anthropogenic emissions, deposition to terrestrial systems, and the bioaccumulation of MMHg in freshwaters. We have suggested that there has been much emphasis on freshwater fish contamination at the expense of marine studies, given that the major exposure of humans to MMHg is through the consumption of marine fish and seafood products. Given our concerns as a caveat, we note that many scientists and "stakeholders" think that an unequivocal connection between direct atmospheric mercury deposition and the levels of MMHg in fish in freshwater or marine systems has not been established. In other words, if mercury deposition is reduced, through, for example, controls on mercury emissions from coal-burning power plants, would MMHg concentrations in fish decline? The METAALICUS team of scientists from the United States and Canada is now attempting empirically to address questions of linkages between mercury deposition and the bioaccumulation of MMHg in fish. They are conducting a whole ecosystem experiment in which stable isotopes of mercury are added to a lake, its upland watershed and adjoining wetland, and mercury in fish as well as the food chain are examined. The project, which began in 1999 and is funded through 2004, is being conducted in the Experimental Lakes region.

The objectives of METAALICUS are as follows (taken from the METAALICUS 2006, web page):

1. to determine the relationship between the rate of atmospheric loading of mercury to lakes and the rate of mercury accumulation in fish;
2. to determine the response time of mercury levels in fish to changes in atmospheric loading of mercury;
3. to determine the relative importance of different sources of mercury to fish (the upland watersheds, adjacent wetlands, and the lake surface) by the addition of three different stable isotopes of mercury; and
4. to calibrate and parametrize a mechanistic model that will be used to predict reductions in fish mercury concentrations following controls on mercury emissions.

The use of stable isotopes of mercury to track pathways of inputs and uptake is innovative. The additions will be increased over time to levels comparable with the current mercury deposition in the northeastern United States. The work is ongoing and, to date, a few papers have been published (Hintelmann *et al.*, 2002; Babiarz *et al.*, 2003; Kelly *et al.*, 2003; Lalonde *et al.*, 2003; Amyot *et al.*, 2004; St. Louis *et al.*, 2004; Branfireun *et al.*, 2005). We wish to re-emphasize that in productive near-shore regions of marine ecosystems, the legacy of pollution-derived mercury in the surficial sediments is likely to predominate over "new mercury" as a substrate for methylation. The intense bioturbation in coastal marine sediments can keep much historical mercury active, relative to the more quiescent sediments of lakes. Unfortunately, the mechanistic predictions for declines in fish mercury levels following controls on mercury emissions, derived from the anticipated successful METAALICUS program, will not be applicable to the marine environment.

The detailed mechanistic studies represented in METAALICUS, designed to illustrate the connections between atmospheric deposition and Hg accumulation in fish, have recently been supported in a broad-scale way (Hammerschmidt and Fitzgerald, 2005). This study noted a highly significant correlation between the Hg content of mosquitoes (which are aquatic predators during their larval life stages) and local atmospheric Hg deposition.

9.04.8.3 Ambient Isotopic Studies of Mercury—Biological Fractionation of Mercury Isotopes

With improvements in inductively coupled plasma mass spectrometry (ICP-MS) detectors, there is great interest in the possibility that there may be biologically induced fractionation of the stable isotopes of mercury. As noted, there have only recently been meaningful measurements of the isotopic composition of mercury in media other than rocks and meteorites. This is largely due to the difficulty in measuring isotopic ratios with suitable accuracy for such a heavy element. However, the range of isotopic masses presented by the mercury system (196–204) at the extreme offers a 4% difference in mass which approaches that of elements whose isotopic composition are routinely used to study cycling in the environment (e.g., ^{14}N–^{15}N: 7%). It is theoretically possible that biological and physical processes could fractionate mercury by mass.

If fractionation of mercury isotopes does occur, then their possible uses are obviously extraordinary. Isotopic variations would provide biogeochemical tracers for the mercury cycle. For example, the mercury incorporated into MMHg should be isotopically lighter than the bulk mercury of sediment pore waters. Watersheds/rivers may have a unique isotopic pattern, while wastewater effluents another. Coals from different regions may show variations that would characterize the mercury emissions, as has been documented for lead. Perhaps, preindustrial atmospheric deposition will show a mercury isotopic signature distinct from the modern distribution. The possibilities are many, but evidence for biologically induced fractionation is lacking. Interest was spurred by a recent controversial report (Jackson, 2001a, b; Hintelmann *et al*., 2001) indicating substantial fractionation of mercury isotopes in a lacustrine food chain. There is ongoing research in several laboratories (e.g., Amouroux *et al*., 2003; Krupp *et al*., 2003), and two recent reports suggest that isotopic signatures are to be found in particular sulfide deposits that are likely geogenic in origin (Hintelmann and Lu, 2003; Smith *et al*., 2005). There is, as of this writing, no published report of convincing evidence for biological fractionation of Hg isotopes, but the search continues.

9.04.8.4 Tracing Atmospheric Mercury with ^{210}Pb and Br

As noted in Section 9.04.4, an ongoing effort among researchers studying the atmospheric chemistry of mercury is the determination of which reaction mechanisms are most influential in the field. Tracers are exceptionally powerful tools in this regard, as they greatly simplify the process of scaling up individual measurements to a wide range of scales. They are often integrative as well, so that discrete measurements of mercury and tracers in a particular medium at a particular time can be easily generalized to a whole year or area. Two tracers have recently shown some promise in understanding the large-scale behavior of mercury in the atmosphere and in complementary ways: ^{210}Pb and Br.

Lamborg *et al*. (1999, 2000) have demonstrated a strong correlation between Hg and ^{210}Pb in precipitation from samples collected in remote continental (Wisconsin) and mid-ocean (tropical South Atlantic) locations. The relationship from these collections was very similar and indicates that ^{210}Pb may be a useful tracer of mercury in precipitation. The geochemistry of ^{210}Pb is well described and this tracer has been useful for atmospheric studies of numerous kinds. The correlation between these two species implicates, by analogy, a homogeneous gas-phase oxidation of mercury that is first order as ^{210}Pb is generated from the homogeneous-phase first-order radioactive decay of ^{222}Rn. As the flux of ^{222}Rn to the atmosphere is known and constant, the current flux of mercury to and from the atmosphere can be estimated from Hg/^{210}Pb ratios, and the universality of the ratio used to examine regionality of mercury deposition.

Two recent findings suggest that bromine may also be an important tracer and clue in the atmospheric chemistry of mercury. Lindberg *et al*. (2002) have noted that the advent of mercury depletion events in the Arctic is coincident with the buildup of reactive bromine compounds (such as BrO) in the polar atmosphere. Halogen compounds are potent oxidizers of mercury, stabilizing the Hg(II) created by forming halogen complexes. For example, BrCl is routinely used to oxidize solutions for mercury analysis in the laboratory. It has also been noted that such reactive compounds can be created *in situ* from sea salt in aerosols in the marine boundary layer (e.g., Disselkamp *et al.*, 1999), supporting the hypothesis contained in Mason *et al.* (2001) of a rapid oxidation of elemental mercury over the ocean. Roos-Barraclough *et al.* (2002) recently presented findings from long peat cores that showed a strong correlation between higher deposition of mercury coincident with higher deposition of bromine over relatively long timescales (centuries). The cause of this correlation is still unknown and may have as much to do with sources of mercury to the atmosphere as well as the atmospheric chemistry of mercury.

9.04.8.5 Mercury and Organic Matter Interactions

Mercury, the quintessential soft metal, forms exceptionally strong associations with natural organic matter (e.g., Mantoura *et al.*, 1978). This behavior has been recognized as influential in a number of aspects of mercury biogeochemistry. For example, lakes have often been shown to have higher mercury in higher DOC waters (e.g., Vaidya *et al.*, 2000). This indicates that watersheds (the principal supply of the DOC in lakes) can contribute significant amounts of mercury as well, and that the DOC mobilization from uplands mobilizes mercury and MMHg. In addition, higher concentrations of DOC provide enhanced complexation capacity for mercury in the water column of lakes, enhancing mercury solubility and increasing mercury residence within the lake (e.g., Ravichandran *et al.*, 1999). There are also competing effects of DOC on the reduction of mercury within natural waters. Recently, Amyot *et al.* (1997), Rolfhus (1998), and Costa and Liss (1999) have indicated that DOC may act to both enhance and inhibit mercury reduction (and therefore mercury evasion) in both fresh- and saltwater depending on the concentration of organic carbon in the water. The mechanisms for these intricate redox processes are not well known, but DOC is clearly an important master variable.

The magnitude of mercury–organic interactions (strength of the complexes and the abundance of the complexing agents) has been studied through partitioning experiments of various kinds. Mantoura *et al.* (1978), a frequently cited report, made use of a form of size-exclusion chromatography to separate free mercury from organically complexed mercury. Other important work includes that of Hintelmann *et al.* (1997), who employed dialysis membranes to estimate MMHg partitioning between organic and inorganic complexes, and the recent work of Benoit *et al.* (2001c), who used calibrated octanol–water partitioning behavior of mercury species to study mercury-binding ligands in sediment pore waters from the Everglades. For other trace metals, electrochemical techniques have often been used, and one such study has been published for mercury (Wu *et al.*, 1997). Watson *et al.* (1999) have suggested recently that the gold-stripping electrodes used for this determination do not quantitatively release mercury, making this approach somewhat suspect. Lamborg *et al.* (2003), who developed a wet chemical analog to the electrochemical approach, found affinity results similar to those of Benoit *et al.* and the high end of Mantoura *et al.* from bulk water samples (most of the other studies have been performed on isolated DOC fractions). The general assumption has been that it is the reduced sulfur moieties (thiols) in the macromolecules of natural water DOC that are the sites for binding, and recent spectroscopic evidence supports this (Xia *et al.*, 1999; Hesterberg *et al.*, 2001). However, Lamborg *et al.* (2003) have found ligand concentrations, when normalized to DOC, which suggest mercury-binding functional group abundances on the order of parts per million. This is well below the abundance of reduced sulfur, which is generally found to be in the parts per thousand range. It therefore appears that the locations for mercury binding are rare in the DOC pool but still present in 10–1,000× excess of mercury.

In saltwater, organic matter complexation of mercury may not compete with the more abundant chloride ion (see Section 9.04.5). In estuaries, ligand exchange was observed by Rolfhus and Fitzgerald (2001) and by Tseng *et al.* (2001). One result of the exchange of mercury from organic to inorganic complex forms is a general increase in the reactivity of mercury within estuaries. The change in complexation can result in dramatic changes in the reactivity of the mercury as a result (e.g., enhanced Hg^0 production, Rolfhus and Fitzgerald, 2001).

9.04.8.6 Bioreporters—A New Technique for Ultra-Trace Determinations of Mercury

Modern biotechnology offers the potential for the development of highly sensitive reagents and methods to determine mercury species such as bioreactive or bioavailable mercury and

MMHg. In one of the earliest studies on the subject, Barkay and colleagues (Selifonova *et al.*, 1993) suggested that mercury-specific luminescent reagents could be bioengineered (i.e., biologically synthesized and amplified with molecular techniques), for use in environmental studies. They reported the successful development of three "biosensors" for Hg(II). These were created by combining or fusing the "the well-understood Tn21 mercury resistance operon (*mer*) with promoterless *luxCDABE* from the marine bacterium, *Vibrio fischer.*" Light production via *luxCDABE* is controlled by the *mer* regulatory gene and promoter, which is in turn activated by reactive mercury species. These combined reagents are commonly referred to as "bioreporters," where the light can be detected photonically and quantified. Aspects of the techniques are patented (e.g., Rosson, 1996, patent states "the lux operon complex comprises *luxC*, *luxD*, *luxA*, *luxB*, and *luxE* genes but is free of (1) a promoter for the complex and (2) an inducible regulatory gene for the complex"). The Sanseverino *et al.* (2002) US patent application indicates that "an exemplary bioreporter is an *E. coli* that has been modified to respond to Hg(II) as a result of incorporation of a *merRop/lux* gene cassette into its genome."

The first applications were encouraging. However, the mercury "bioreporters" were semiquantitative and not sensitive at environmentally useful levels (i.e., picomolar to femtomolar). Progress in lowering detection limits has been swift. For example, in 1993, Selifonova and coworkers could work in the 1 nM range, and Tescione and Belfort (1993) at 10 nM. Virta *et al.* (1995) reported a laboratory detection limit of 0.1 fM for mercury using "firefly luciferase gene as a reporter, the mer promoter from transposon Tn21, and *Escherichia coli* (*E. coli*) MC1061 as the host organism." Today, the methods, in general, are quite advanced and the sensitivity appears suitable for studies even in pristine ecosystems such as the open ocean and remote lakes (see recent reports by Kelly *et al.*, 2001; Scott *et al.*, 2001; Barrocas *et al.*, 2001).

Quantification, the operational nature of "bioavailability" and the need to add a suspension of nonstandardized genetically engineered bacteria as an integral part of the analysis are limitations to broad application of the "bioreporter" techniques to environmental studies of mercury in aqueous systems. However, variations on this bacterial recombinant DNA technological approach are promising. That is, mercury-activated organic molecules can be bioengineered, isolated, and purified to provide reagents for mercury investigations. Wylie *et al.* (1991, 1992) produced monoclonal antibodies specific for ionic mercury and applied the immunoassay to water. Their experiments were conducted in the nanomolar range, concentrations too high for investigating mercury in most natural aquatic environments. However, it is likely that the detection limits can be lowered significantly, and the mercury-specific antibody reagent technique optimized for natural waters.

9.04.9 SUMMARY

In this chapter, we have summarized some of the gains made in understanding the environmental biogeochemistry of mercury since Goldschmidt's groundbreaking work. Much of this advancement has come since the early 1970s, and the growth in mercury research continues at breakneck pace. This is fortunate as there is a need for urgency, we believe, in these endeavors. While human activity has perturbed the mercury cycle by a smaller degree than, for example, lead, the implications for continued perturbation on human and ecological health are enormous.

The way forward will be a fascinating and challenging one. As we have summarized, this is because the biogeochemistry of mercury operates at a variety of time- and space scales and in many environmental media. Owing to the complexity of the processes and the minute quantities of material often encountered in the environment, future research will also require new hypotheses and new instrumentation. Similarly, and as with so many environmental research efforts, new collaborations among scientific disciplines will be required.

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REFERENCES

Aastrup M., Johnson J., Bringmark E., Bringmark L., and Iverfeldt A. (1991) Occurrence and transport of mercury within a small catchments area. *Water Air Soil Pollut.* **56**, 155–168.

Alleman L. Y., Church T. M., Veron A. J., Kim G., Hamelin B., and Flegal A. R. (2001) Isotopic evidence of contaminant lead in the South Atlantic troposphere and surface waters. *Deep-Sea Res. II* **48**(13), 2811–2827.

Alriksson A. (2001) Regional variability of Cd, Hg, Pb and C concentrations in different horizons of Swedish forest soils. *Water Air Soil Pollut. Focus* **1**, 325–341.

Amouroux D., Donard O. F., Krupp E., Pecheyran C., Besson T., and Fitzgerald W. F. (2003) Isotopic fractionation of mercury species in top predators fishes (tuna and whale) from world ocean: preliminary results. In *Abstracts of ASLO Aquatic Sciences Meeting,* Salt Lake City, UT, USA, Feb. 8–14.

Amyot M., AuClair J. C., and Poissant L. (2001) *In situ* high temporal resolution analysis of elemental mercury in natural waters. *Anal. Chim. Acta* **447**, 153–159.

Amyot M., Gill G. A., and Morel F. M. M. (1997) Production and loss of dissolved gaseous mercury in coastal seawater. *Environ. Sci. Technol.* **31**, 3606–3611.

Amyot M., Mierle G., Lean D. R. S., and McQueen D. J. (1994) Sunlight-induced formation of dissolved gaseous mercury in lake waters. *Environ. Sci. Technol.* **28**(13), 2366–2371.

Amyot M., Southworth G., Lindberg S. E., Hintelmann H., Lalonde J. D., Ogrinc N., Poulain A. J., and Sandilands K. A. (2004) Formation and evasion of dissolved gaseous mercury in large enclosures amended with (HgCl$_2$)-Hg-200. *Atmos. Environ.* **38**(26), 4279–4289.

Anbar A. D. (2004) Iron stable isotopes: beyond biosignatures. *Earth Planet Sci. Lett.* **217**, 223–236.

Ariya P. A. and Ryzhkov A. (2003) Atmospheric transformation of elemental mercury upon reactions with halogens. *J. Phys. IV* **107**, 57–59.

Asmund G. and Nielsen S. P. (2000) Mercury in dated Greenland marine sediments. *Sci. Total Environ.* **245**, 61–72.

Babiarz C. L., Hurley J. P., Krabbenhoft D. P., Trinko T. R., Tate M., Chadwick S. P., and Armstrong D. E. (2003) A hypolimnetic mass balance of mercury from a dimictic lake: results from the METAALICUS project. *J. Phys. IV* **107**, 83–86.

Baeyans W. and Leermakers M. (1998) Elemental mercury concentrations and formation rates in the Scheldt estuary and the North Sea. *Mar. Chem.* **60**, 257–266.

Bakir F., Damluji S. F., Amin-Zaki L., Murtadha M., Khalidi A., al-Rawi N. Y., Tikriti S., Dahahir H. I., Clarkson T. W., Smith J. C., and Doherty R. A. (1973) Methylmercury poisoning in Iraq. *Science* **181**(96), 230–241.

Balcom P. H., Fitzgerald W. F., Lamborg C. H., Rolfhus K. R., Vandal G. M., Langer C. S., and Tseng C.-M. (2000) Mercury cycling in and emissions from Long Island Sound. Presented at 11th International Conference on Heavy Metals in the Environment, Ann Arbor, MI, USA, Aug.

Balcom P. H., Fitzgerald W. F., Vandal G. M., Lamborg C. H., Rolflus K. R., Langer C. S., and Hammerschmidt C. R. (2004) Mercury sources and cycling in the Connecticut River and Long Island Sound. *Mar. Chem.* **90**(1–4), 53–74.

Banic C. M., Beauchamp S. T., Tordon R. J., Schroeder W. H., Steffen A., Anlauf K. A., and Wong H. K. T. (2003) Vertical distribution of gaseous elemental mercury in Canada. *J. Geophys. Res.* **108**(D9), Art. no. 4264.

Barrie L. A. and Hoff R. M. (1985) Five years of air chemistry observations in the Canadian Arctic. *Atmos. Environ.* **19**, 1995–2010.

Barrocas P. R. G., Landing W. M., and Procter L. M. (2001) A bacterial biosensor for aquatic mercury(II) speciation and bioavailability. In *Abstracts of the 6th International Conference on Mercury as a Global Pollutant*. Minamata, Japan, 130pp.

Beals D. I., Harris R. C., and Pollman C. (2002) Predicting fish mercury concentrations in Everglades marshes: handling uncertainty in the Everglades mercury cycling model (E-MCM) with a Monte Carlo approach. Abstracts of Papers of the American Chemical Society 223: 200–ENVR, Part 1 APR 7 2002.

Benesch J. A., Gustin M. S., Schorran D. E., Coleman J., Johnson D. A., and Lindberg S. E. (2001) Determining the role of plants in the biogeochemical cycling of mercury on an ecosystem level. Presented at the 6th International Conference on Mercury as a Global Pollutant, Oct. Minamata, Japan.

Benoit J. M., Fitzgerald W. F., and Damman A. W. (1998a) The biogeochemistry of an ombrotrophic bog: evaluation of use as an archive of atmosphere mercury deposition. *Environ. Res.* **78**(2), 118–133.

Benoit J. M., Gilmour C. C., Heyes A., Mason R. P., and Miller C. L. (2003) Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In *Biogeochemistry of Environmentally Important Trace Elements* (eds. Y. Chai and O. C. Braids). ACS Symposium Series #835 262–297. American Chemical Society, Washington, DC.

Benoit J. M., Gilmour C. C., and Mason R. P. (2001a) Aspects of bioavailability of mercury for methylation in pure cultures of *Desulfobulbus propionicus* (1pr3). *Appl. Environ. Microbiol.* **67**, 51–58.

Benoit J. M., Gilmour C. C., and Mason R. P. (2001b) The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). *Environ. Sci. Technol.* **35**, 127–132.

Benoit J. M., Gilmour C. C., Mason R. P., and Heyes A. (1999a) Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **33**, 951–957.

Benoit J. M., Gilmour C. C., Mason R. P., Riedel G. S., and Riedel G. F. (1998b) Behavior of mercury in the Patuxent River estuary. *Biogeochemistry* **40**, 249–265.

Benoit J. M., Mason R. P., and Gilmour C. C. (1999b) Estimation of mercury–sulfide speciation in sediment pore waters using octanol–water partitioning and implications for availability to methylating bacteria. *Environ. Toxicol. Chem.* **18**, 2138–2141.

Benoit J. M., Mason R. P., Gilmour C. C., and Aiken G. R. (2001c) Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. *Geochim. Cosmochim. Acta* **65**(24), 4445–4451.

Bergan T., Gallardo L., and Rodhe H. (1999) Mercury in the global troposphere: a three-dimensional model study. *Atmos. Environ.* **33**, 1575–1585.

Bergan T. and Rodhe H. (2001) Oxidation of elemental mercury in the atmosphere: constraints imposed by global scale modeling. *J. Atmos. Chem.* **40**, 191–212.

Bindler R., Renberg I., Appleby P. G., Anderson N. J., and Rose N. L. (2001) Mercury accumulation rates and spatial patterns in lake sediments from West Greenland: a coast to ice margin transect. *Environ. Sci. Technol.* **35**(9), 1736–1741.

Bloom N. (1989) Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* **46**(7), 1131–1140.

Bloom N. S. (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* **49**, 1010–1017.

Bloom N. S. (2000) Analysis and stability of mercury speciation in petroleum hydrocarbons. *Fres. J. Anal. Chem.* **366**, 438–443.

Bloom N. S. and Fitzgerald W. F. (1988) Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Anal. Chim. Acta* **208**, 151–161.

Bluth G. J. S., Schnetzler C. C., Krueger A. J., and Walter L. S. (1993) The contribution of explosive volcanism to global atmospheric sulfur dioxide concentrations. *Nature* **366**, 327–329.

Bodaly R. A., Hecky R. E., and Fudge R. J. P. (1984) Increases in fish mercury levels in lakes flooded by the Churchill River Diversion, northern Manitoba. *Can. J. Fish. Aquat. Sci.* **41**, 682–691.

Bostrom K. and Fisher D. E. (1969) Distribution of mercury in East Pacific sediments. *Geochim. Cosmochim. Acta* **33**(6), 743–745.

Boudala F. S., Folkins I., Beauchamp S., Tordon R., Neima J., and Johnson B. (2000) Mercury flux measurements over air and water in Kejimkujik National Park, Nova Scotia. *Water Air Soil Pollut.* **122**, 183–202.

Boutron C. F., Vandal G. M., Fitzgerald W. F., and Ferrari C. P. (1998) A forty year record of mercury in central Greenland snow. *Geophys. Res. Lett.* **25**(17), 3315–3318.

Branfireun B. A., Bishop K., Roulet N. T., Granberg G., and Nilsson M. (2001) Mercury cycling in boreal ecosystems: the long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. *Geophys. Res. Lett.* **28**(7), 1227–1230.

Branfireun B. A., Krabbenhoft D. P., Hintelmann H., Hunt R. J., Hurley J. P., and Rudd J. W. M. (2005) Speciation and transport of newly deposited mercury in a boreal forest wetland: a stable mercury isotope approach. *Water Resour. Res.* **41**(6), Art. no. W06016.

Branfireun B. A., Roulet N. T., Kelly C. A., and Rudd J. W. M. (1999) *In situ* sulphate stimulation of mercury methylation in a boreal peatland: toward a link between acid rain and methylmercury contamination in remote environments. *Global Biogeochem. Cycles* **13**(3), 743–750.

Brunke E. G., Labuschagne C., and Slemr F. (2001) Gaseous mercury emissions from a fire in the Cape Peninsula, South Africa, during January 2000. *Geophys. Res. Lett.* **28**(8), 1483–1486.

Cadle R. D. (1975) Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere. *J. Geophys. Res.* **80**(2), 1650–1652.

Carpi A. and Lindberg S. E. (1998) Application of a Teflon dynamic flux chamber for quantifying soil mercury flux: test and results over background soil. *Atmos. Environ.* **32**(5), 873–882.

Chiaradia M. and Cupelin F. (2000) Gas-to-particle conversion of mercury, arsenic and selenium through reactions with traffic-related compounds (Geneva)? Indications from lead isotopes. *Atmos. Environ.* **34**(2), 327–332.

Clarkson T. W. (1997) The toxicology of mercury. *Crit. Rev. Clin. Lab. Sci.* **34**(4), 369–403.

Compeau G. C. and Bartha R. (1985) Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* **50**(2), 498–502.

Conaway C. H., Squire S., Mason R. P., and Flegal A. R. (2003) Mercury speciation in the San Francisco Bay estuary. *Mar. Chem.* **80**, 199–225.

Coquery M., Cossa D., and Martin J.-M. (1995) The distribution of dissolved and particulate mercury in 3 Siberian estuaries and adjacent arctic coastal waters. *Water Air Soil Pollut.* **80**(1–4), 653–664.

Coquery M., Cossa D., and Sanjuan J. (1997) Speciation and sorption of mercury in two macro-tidal estuaries. *Mar. Chem.* **58**, 213–227.

Cossa D. and Coquery M. (in press) The Mediterranean mercury anomaly, a geochemical or a biological issue. *Handbook of Environmental Chemistry, Review Series in Chemistry* (ed. A. Saliot). Part 5: The Mediterranean Sea. Springer, Berlin.

Cossa D., Coquery M., Gobeil C., and Martin J.-M. (1996) Mercury fluxes at the ocean margins. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (eds. W. Baeyens, R. Ebinghaus, and O. Vasiliev). NATO ASI: Series 2. Environment. Kluwer, Boston, vol. 21, pp. 229–248.

Cossa D., Elbaz-Poulichet F., and Nieto J. M. (2001) Mercury in the Tinto–Odiel estuarine system (Gulf of Cádiz, Spain): sources and dispersion. *Aquat. Geochem.* **7**, 1–12.

Cossa D., Martin J.-M., Takayanagi K., and Sanjuan J. (1997) The distribution and cycling of mercury species in the western Mediterranean. *Deep-Sea Res. II* **44**(3–4), 721–740.

Cossa D., Sanjuan J., and Noel J. (1994) Mercury transport in waters of the Strait of Dover. *Mar. Pollut. Bull.* **28**(6), 385–388.

Costa M. and Liss P. S. (1999) Photoreduction of mercury in sea water and its possible implications for Hg-0 air–sea fluxes. *Mar. Chem.* **68**(1–2), 87–95.

Covelli S., Faganeli J., Horvat M., and Brambati A. (2001) Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea). *Appl. Geochem.* **16**, 541–558.

Cox J. A., Carnahan J., Dinunzio J., McCoy J., and Meister J. (1979) Source of mercury in new impoundments. *Bull. Environ. Contamin. Toxicol.* **23**, 779.

Crisp J. A. (1984) Rates of magma emplacement and volcanic output. *J. Volcanol. Geotherm. Res.* **20**, 177–211.

Dalziel J. A. (1992) Reactive mercury on the Scotian Shelf and in the adjacent Northwest Atlantic Ocean. *Mar. Chem.* **37**(3–4), 171–178.

Dalziel J. A. and Yeats P. A. (1985) Reactive mercury in the central North Atlantic Ocean. *Mar. Chem.* **15**(4), 357–361.

Damman A. W. H. (1978) Distribution and movement of elements in ombrotrophic peat bogs. *Oikos* **30**, 480–495.

Davidson P. W., Palumbo D., Myers G. J., Cox C., Shamlaye C. F., Sloane-Reeves J., Cernichiari E., Wilding G. E., and Clarkson T. W. (2000) Neurodevelopmental outcomes of Seychellois children from the pilot cohort at 108 months following prenatal exposure to methylmercury from a maternal fish diet. *Environ. Res.* **84**(1), 1–11.

Dedeurwaerder H., Decadt G., and Baeyens W. (1982) Estimations of mercury fluxes emitted by Mount Etna volcano. *Bull. Volcanol.* **45**(3), 191–196.

Disselkamp R. S., Chapman E. G., Barchet W. R., Colson S. D., and Howd C. D. (1999) BrCl production in NaBr/NaCl/HNO_3/O^3 solutions representative of sea-salt aerosols in the marine boundary layer. *Geophys. Res. Lett.* **26**(4), 2183–2186.

Ebinghaus R., Kock H. H., Temme C., Einax J. W., Lowe A. G., Richter A., Burrows J. P., and Schroeder W. H. (2002) Antarctic springtime depletion of atmospheric mercury. *Environ. Sci. Technol.* **36**(6), 1238–1244.

Ebinghaus R. and Krüger O. (1996) Emission and local deposition estimates of anthropogenic mercury in North Western and Central Europe. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (eds. W. Baeyens, R. Ebinghaus, and O. Vasiliev). NATO ASI: Series 2. Environment. Kluwer, Boston, vol. 21, pp. 135–159.

Ebinghaus R., Turner R. R., Lacerda L. D., Vasiliev B. O., and Salomons W. (1998) *Mercury Contaminated Sites—Characterization, Risk Assessment and Remediation.* Springer, Regensburg, Germany, 548pp.

Egleston T. (1887) *The Metallurgy of Silver, Gold, and Mercury in the United States*. Wiley, New York.

Engstrom D. R. and Swain E. B. (1997) Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* **31**(4), 960–967.

Evans R. D., Hintelmann H., and Dillon P. J. (2001) Natural variation in mercury isotope ratios of coals and cinnabars. *Proceedings of the 6th International Conference on Mercury as a Global Pollutant*. Minimata, Japan, October 15–19.

Fabbri D., Gabbianelli G., Locatelli C., Lubrano D., Trombini C., and Vassura I. (2001) Distribution of mercury and other heavy metals in core sediments of the northern Adriatic Sea. *Water Air Soil Pollut.* **129**, 143–153.

Fein J. B. and Williams-Jones A. E. (1997) The role of mercury–organic interactions in the hydrothermal transport of mercury. *Econ. Geo.* **92**, 20–28.

Fitzgerald W. F. (1981) Volcanic mercury emissions and the global mercury cycle. *Programs and Abstracts, Symposium on the Role of the Ocean in Atmospheric Chemistry*. IAMAP 3rd Scientific Assembly, Aug 17–28. Hamburg, Germany, 134pp.

Fitzgerald W. F. (1995) Is mercury increasing in the atmosphere—the need for an atmospheric mercury network (AMNET). *Water Air Soil Pollut.* **80**(1–4), 245–254.

Fitzgerald W. F. (1996) Mercury emissions from volcanos. In *Abstracts of the 4th International Conference on Mercury as a Global Pollutant*, Aug. Hamburg, Germany.

Fitzgerald W. F. and Clarkson T. W. (1991) Mercury and monomethylmercury: present and future concerns. *Environ. Health Perspect.* **96**, 159–166.

Fitzgerald W. F., Engstrom D. R., Lamborg C. H., Tseng C. M., Balcom P. H., and Hammerschmidt C. R. (2005) Modern and historic atmospheric mercury fluxes in northern Alaska: global sources and Arctic depletion. *Environ. Sci. Technol.* **39**, 557–568.

Fitzgerald W. F., Engstrom D. R., Mason R., and Nater E. A. (1998) The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **32**(1), 1–7.

Fitzgerald W. F. and Gill G. A. (1979) Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis. *Anal. Chem.* **51**, 1714–1720.

Fitzgerald W. F., Gill G. A., and Hewitt A. D. (1981) Mercury a trace atmospheric gas. Presented at the *Symposium on the Role of the Ocean in Atmospheric Chemistry*. IAMAP 3rd Scientific Assembly, Aug 17–28. Hamburg, Germany.

Fitzgerald W. F. and Mason R. P. (1997) Biogeochemical cycling of mercury in the marine environment. *Metal Ions Biol. Sys.* **34**, 53–111.

Fitzgerald W. F., Mason R. P., and Vandal G. M. (1991) Atmospheric cycling and air–water exchange of mercury over mid-continental lacustrine regions. *Water Air Soil Pollut.* **56**, 745–767.

Fitzgerald W. F., Vandal G. M., Rolfhus K. R., Lamborg C. H., and Langer C. S. (2000) Mercury emissions and cycling in the coastal zone. *J. Environ. Sci.* **12**, 92–101.

Fitzgerald W. F. and Watras C. J. (1989) Mercury in surficial waters of rural Wisconsin lakes. *Sci. Total Environ.* **87**(88), 223–232.

Fleming E. J., Mack E. E., Green P. G., and Nelson D. C. (2006) Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. *Appl. Environ. Microb.* **72**(1), 457–464.

Fogg T. R. and Fitzgerald W. F. (1979) Mercury in southern New England rains. *J. Geophys. Res.* **84**, 6987–6988.

Friedlander G., Kennedy J. W., Macias E. S., and Miller J. M. (1981) *Nuclear and Radiochemistry*, 3rd edn. Wiley, New York.

Friedli H. R., Radke L. R., and Lu J. Y. (2001) Mercury in smoke from biomass fires. *Geophys. Res. Lett.* **28**(17), 3223–3226.

Friend J. P. and Rusool S. I. (1973) *Chemistry of the Lower Atmosphere Global Sulfur Cycle*. Plenum, New York, pp. 177–201.

Ganguli P. M., Mason R. P., Abu-Saba K. E., Anderson R. S., and Flegal A. R. (2000) Mercury speciation in drainage from the New Idrija mercury mine, California. *Environ. Sci. Technol.* **34**(22), 4773–4779.

Gårdfeldt K., Munthe J., Strömberg D., and Lindqvist O. (2003) A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase. *Sci. Total Environ.* **304**, 127–136.

Gbondo-Tugbawa S. and Driscoll C. T. (1998) Application of the regional mercury cycling model to predict the fate and remediation of mercury in Onondaga Lake, New York. *Water Air Soil Pollut.* **105**, 417–426.

Geller L. S., Elkins J. W., Lobert J. M., Clarke A. D., Hurst D. F., Butler J. H., and Myers R. C. (1997) Tropospheric SF6: observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time. *Geophys. Res. Lett.* **24**(6), 675–678.

George T. S. (2001) *Minamata: Pollution and the Struggle for Democracy in Postwar Japan* (Harvard East Asian Monographs, No. 194). Harvard University Press, Cambridge, MA, 385pp.

Gerino M., Aller R. C., Lee C., Cochran J. K., Aller J. Y., Green M. A., and Hirschberg D. (1998) Comparison of different tracers and methods used to quantify bioturbation during a spring bloom: 234-thorium, luminophores, and chlorophyll *a*. *Estuar. Coast. Shelf Sci.* **46**, 531–547.

Gill G. A. and Bruland K. W. (1987) Mercury in the northeast Pacific. *EOS* **68**, 1763.

Gill G. A. and Fitzgerald W. F. (1988) Vertical mercury distributions in the oceans. *Geochim. Cosmochim. Acta* **52**, 1719–1728.

Gill G. A., Guentzel J. L., Landing W. M., and Pollman C. D. (1995) Total gaseous mercury measurements in Florida: the FAMS project (1992–1994). *Water Air Soil Pollut.* **80**, 235–244.

Gilmour C. C. and Henry E. A. (1991) Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* **71**(2–4), 131–169.

Gilmour C. C. and Riedel G. S. (1995) Measurement of Hg methylation in sediments using high specific-activity ^{203}Hg and ambient incubation. *Water Air Soil Pollut.* **80**, 747–756.

Gilmour C. C., Riedel G. S., Ederington M. C., Bell J. T., Benoit J. M., Gill G. A., and Stordal M. C. (1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* **40**, 326–346.

Gobeil C. and Cossa D. (1993) Mercury in sediments and sediment pore water in the Laurentian Trough. *Can. J. Fish. Aquat. Sci.* **50**, 1794–1800.

Gobeil C., MacDonald R. W., and Smith J. N. (1999) Mercury profiles in sediments of the Arctic Ocean basins. *Environ. Sci. Technol.* **33**, 4194–4198.

Goldschmidt V. M. (1954) *Geochemistry*. Oxford University Press, Oxford.

Goldwater L. J. (1972) *A History of Quicksilver*. York Press, Baltimore, 318pp.

Grandjean P., Weihe P., White R. F., Debes F., Araki S., Yokoyama K., Murata K., Sorensen N., Dahl R., and Jorgensen P. J. (1997) Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. *Neurotoxicol. Teratol.* **19**(6), 417–428.

Grevesse N. (1970) Solar and meteoritic abundances of mercury. *Geochim. Cosmochim. Acta* **34**, 1129–1130.

Grieb T. M., Driscoll C. T., Gloss S. P., Schofield C. L., Bowie G. L., and Porcella D. B. (1990) Factors affecting mercury accumulation in fish in the Upper Michigan peninsula. *Environ. Toxicol. Chem.* **9**, 919–930.

Grieb T. M., Petcharuttana Y., Roy S., Bloom N., and Brown K. (2001) Mercury studies in the central Gulf of Thailand. *Proceedings of the 6th International Conference on Mercury as a Global Pollutant*, Oct 15–19. Minimata, Japan.

Grigal D. F., Kolka R. K., Fleck J. A., and Nater E. A. (2000) Mercury budget of an upland-peatland watershed. *Biogeochemistry* **50**(1), 95–109.

Grigal D. F., Nater E. A., and Homann P. S. (1994) Spatial distribution patterns of mercury in an east-central Minnesota landscape. In *Mercury Pollution: Integration and Synthesis* (eds. C. Watras and J. Huckabee). Lewis Publishers, Ann Arbor, MI, chapt. III.2, pp. 305–312.

Guentzel J. L., Landing W. M., Gill G. A., and Pollman C. D. (1995) Atmospheric deposition of mercury in Florida: the FAMS project (1992–1994). *Water Air Soil Pollut.* **80**, 393–402.

Gustin M. S., Lindberg S. E., Austin K., Coolbaugh M., Vette A., and Zhang H. (2000) Assessing the contribution of natural sources to regional atmospheric mercury budgets. *Sci. Total Environ.* **259**, 61–71.

Gustin M. S., Lindberg S., Marsik F., Casimir A., Ebinghaus R., Edwards G., Hubble-Fitzgerald C., Kemp R., Kock H., Leonard T., London J., Majewski M., Montecinos C., Owens J., Pilote M., Poissant L., Rasmussen P., Schaedlich F., Schneeberger D., Schroeder W., Sommar J., Turner R., Vette A., Wallschlaeger D., Xiao Z., and Zhang H. (1999) Nevada STORMS project: measurement of mercury emissions from naturally enriched surfaces. *J. Geophys. Res* **104**(D17), 21831–21844.

Hall B., Schager P., and Ljungstrom E. (1995) An experimental-study on the rate of reaction between mercury-vapor and gaseous nitrogen-dioxide. *Water Air Soil Pollut.* **81**(1–2), 121–134.

Hall B. D., Rosenberg D. M., and Wiens A. P. (1998) Methyl mercury in aquatic insects from an experimental reservoir. *Can. J. Fish. Aquat. Sci.* **55**, 2036–2047.

Halmer M. M., Schmincke H. U., and Graf H. F. (2002) The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years. *J. Volcanol. Geotherm. Res.* **115**(3–4), 511–528.

Hammerschmidt C. R. and Fitzgerald W. F. (2004) Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* **38**(5), 1487–1495.

Hammerschmidt C. R. and Fitzgerald W. F. (2005) Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. *Environ. Sci. Technol.* **39**(9), 3034–3039.

Hammerschmidt C. R. and Fitzgerald W. F. (2006) Methylmercury cycling in sediments on the continental shelf of southern New England. *Geochim. Cosmochim. Acta* **70**(4), 918–930.

Hammerschmidt C. R., Fitzgerald W. F., Lamborg C. H., Balcom P. H., and Visscher P. T. (2004) Biogeochemistry of methylmercury in sediments of Long Island Sound. *Mar. Chem.* **90**(1–4), 31–52.

Hammerschmidt C. R., Sandheinrich M. B., Wiener J. G., and Rada R. G. (2002) Effects of dietary methylmercury on reproduction of fathead minnows. *Environ. Sci. Technol.* **36**(5), 877–883.

Hanson P. J., Lindberg S. E., Tabberer T., Owens J. G., and Kim K.-H. (1995) Foliar exchange of mercury vapor: evidence for a compensation point. *Water Air Soil Pollut.* **80**, 373–382.

Herut B., Hornung H., Kress N., and Cohen Y. (1996) Environmental relaxation in response to reduced contaminant input: the case of mercury pollution in Haifa Bay, Israel. *Mar. Pollut. Bull.* **32**(4), 366–373.

Hesterberg D., Chou J. W., Hutchison K. J., and Sayers D. E. (2001) Bonding of Hg(II) to reduced organic sulfur in humic acid as affected by S/Hg ratio. *Environ. Sci. Technol.* **35**(13), 2741–2745.

Hines M. E. and Jones G. E. (1985) Microbial biogeochemistry in the sediments of Great Bay, New Hampshire. *Estuar. Coast. Shelf Sci.* **20**, 729–742.

Hinkley T. K., Lamothe P. J., Wilson S. A., Finnegan D. L., and Gerlach T. M. (1999) Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. *Earth Planet. Sci. Lett.* **170**(3), 315–325.

Hintelmann H., Dillon P., Evans R. D., Rudd J. W. M., and Bodaly R. A. (2001) Comment: variations in the isotope composition of mercury in a freshwater sediment sequence and food web. *Can. J. Fish. Aquat. Sci.* **58**(11), 2309–2311.

Hintelmann H. and Evans R. D. (1997) Application of stable isotopes in environmental tracer studies—measurement of monomethylmercury (CH_3Hg^+) by isotope dilution ICP-MS and detection of species transformation. *Fres. J. Anal. Chem.* **358**, 378–385.

Hintelmann H., Harris R., Heyes A., Hurley J. P., Kelly C. A., Krabbenhoft D. P., Lindberg S., Rudd J. W. M., Scott K. J., and St. Louis V. L. (2002) Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environ. Sci. Technol.* **36**(23), 5034–5040.

Hintelmann H., Keppel-Jones K., and Evans R. D. (2000) Constants of mercury methylation and demethylation rates in sediments and comparison of tracer and ambient mercury availability. *Environ. Tox. Chem.* **19**(9), 2204–2211.

Hintelmann H. and Lu S. Y. (2003) High precision isotope ratio measurements of mercury isotopes in cinnabar ores using multi-collector inductively coupled plasma mass spectrometry. *Analyst* **128**(6), 635–639.

Hintelmann H., Welbourn P. M., and Evans R. D. (1997) Measurement of complexation of methylmercury(II) compounds by freshwater humic substances using equilibrium dialysis. *Environ. Sci. Technol.* **31**(2), 489–495.

Hoefs J. (2004) *Stable Isotope Geochemistry*, 5th edn. Springer, Heidelberg.

Hoyer M., Burke J., and Keeler G. (1995) Atmospheric sources, transport and deposition of mercury in Michigan: two years of event precipitation. *Water Air Soil Pollut.* **80**, 192–208.

Hudson R. J. M., Gherini S. A., Fitzgerald W. F., and Porcella D. B. (1995) Perturbation of the global mercury cycle: a model-based analysis. *Water Air Soil Pollut.* **80**, 192–208.

Hudson R. J. M., Gherini S. A., Watras C. J., and Porcella D. B. (1994) Modeling the biogeochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes. In *Mercury Pollution: Integration and Synthesis* (eds. C. Watras and J. Huckabee). Lewis Publishers, Ann Arbor, MI, chapt. V.1, pp. 473–526.

Hultberg H., Iverfeldt A., and Lee Y.-H. (1994) Methylmercury input/output and accumulation in forested catchments and critical loads for lakes in southwestern Sweden. In *Mercury Pollution: Integration and Synthesis* (eds. C. Watras and J. Huckabee). Lewis Publishers, Ann Arbor, MI, chapt. III.3, pp. 313–322.

Hurley J. P., Benoit J. M., Babiarz C. L., Shafer M. M., Andren A. W., Sullivan J. R., Hammond R., and Webb D. A. (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ. Sci. Technol.* **29**(7), 1867–1875.

Hurley J. P., Krabbenhoft D. P., Cleckner L. B., Olson M. L., Aiken G. R., and Rawlik P. S., Jr. (1998) System controls on the aqueous distribution of mercury in the northern Florida Everglades. *Biogeochemistry* **40**, 293–310.

Iverfeldt A. (1991a) Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water Air Soil Pollut.* **56**, 251–265.

Iverfeldt A. (1991b) Mercury in forest canopy throughfall water and its relation to atmospheric deposition. *Water Air Soil Pollut.* **56**, 553–564.

Iverfeldt A. and Lindqvist O. (1982) Distribution equilibrium of methyl mercury chloride between water and air. *Atmos. Environ.* **16**, 2917–2925.

Iverfeldt A., Munthe J., Brosset C., and Pacyna J. (1995) Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia. *Water Air Soil Pollut.* **80**(1–4), 227–233.

Jackson T. A. (2001a) Variations in the isotope composition of mercury in a freshwater sediment sequence and food web. *Can. J. Fish. Aquat. Sci.* **58**(1), 185–196.

Jackson T. A. (2001b) Reply: variations in the isotope composition of mercury in a freshwater sediment sequence and food web. *Can. J. Fish. Aquat. Sci.* **58**(11), 2312–2316.

Japan Public Health Association (2001) In *Methylmercury Poisoning in Minamata and Niigata, Japan* (eds. Y. Takizawa and M. Osame). Japan Public Health Association, Tokyo, 154pp.

Jaworowski Z., Bysiek M., and Kownacka L. (1981) Flow of metals into the global atmosphere. *Geochim. Cosmochim. Acta* **45**(11), 2185–2199.

JECFA (2000) *Safety Evaluation of Certain Food Additives and Contaminants WHO Food Additives Series: 44; Methylmercury*. Prep. by 53rd Joint FAO/WHO Expert Committee on Food Additives (JECFA), World Health Organization, Geneva, Switzerland. Available at http://www.inchem.org/documents/jecfa/jecmono/v44jec13.htm (accessed July 19, 2006).

Jensen A. and Jensen A. (1990) Historical deposition rates of mercury in Scandinavia estimated by dating and measurement of mercury in cores of peat bogs. *Water Air Soil Pollut.* **56**, 769–777.

Jensen S. and Jernelöv A. (1969) Biological methylation of mercury in aquatic organisms. *Nature* **223**, 753–754.

Johnson D. W. and Lindberg S. E. (1995) The biogeochemical cycling of Hg in forests—alternative methods for quantifying total deposition and soil emission. *Water Air Soil Pollut.* **80**(1–4), 1069–1077.

Jovanovic S. and Reed G. W., Jr. (1976) Interrelations among isotopically anomalous mercury fractions from meteorites and possible cosmological inferences. *Science* **193**, 888–891.

Kamman N. C. and Engstrom D. R. (2002) Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ^{210}Pb dated sediment cores. *Atmos. Environ.* **36**, 1599–1609.

Kang W. J., Trefry J. H., Nelsen T. A., and Wanless H. R. (2000) Direct atmospheric inputs versus runoff fluxes of mercury to the lower Everglades and Florida Bay. *Environ Sci. Technol.* **34**(19), 4058–4063.

Kannan K. and Falandysz J. (1998) Speciation and concentrations of mercury in certain coastal marine sediments. *Water Air Soil Pollut.* **103**, 129–136.

Keeler G., Glinsorn G., and Pirrone N. (1995) Particulate mercury in the atmosphere—its significance, transport, transformation and sources. *Water Air Soil Pollut.* **80**(1–4), 159–168.

Kelly C. A., Rudd J. W. M., Golding G., Scott K., Holoka M., Barkay T., and Bloom N. (2001) The use of genetically-engineered bioreporters to study mercury availability at trace concentrations. In *Abstracts of the 6th International Conference on Mercury as a Global Pollutant*. Minamata, Japan, 129pp.

Kelly C. A., Rudd J. W. M., and Holoka M. H. (2003) Effect of pH on mercury uptake by an aquatic bacterium: implications for Hg cycling. *Environ. Sci. Technol.* **37**(13), 2941–2946.

Kesler S. E. (1994) *Mineral Resources, Economics and the Environment*. Macmillan, New York.

Kim J. P. and Fitzgerald W. F. (1986) Sea-air partitioning of mercury over the equatorial Pacific Ocean. *Science* **231**, 1131–1133.

King J. K., Kostka J. E., Frischer M. E., and Saunders F. M. (2000) Sulfate-reducing bacteria methylate mercury at variable rates in pure culture and in marine sediments. *Appl. Environ. Microbiol.* **66**, 2430–2437.

King J. K., Kostka J. E., Frischer M. E., Saunders F. M., and Jahnke R. A. (2001) A quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on the community composition and activity of sulfate-reducing bacteria. *Environ. Sci. Technol.* **35**, 2491–2496.

King J. K., Saunders F. M., Lee R. F., and Jahnke R. A. (1999) Coupling mercury methylation rates to sulfate reduction rates in marine sediments. *Environ. Toxicol. Chem.* **18**, 1362–1369.

Klaue B., Kesler S. E., and Blum J. D. (2000) Investigation of natural fractionation of stable mercury isotopes by inductively coupled plasma mass spectrometry. In *Proceedings of the International Conference on Heavy Metals Environment*, Aug. 6–10. Ann Arbor, MI.

Klusman R. W. and Jaacks J. A. (1987) Environmental influences upon mercury, radon and helium concentrations in soil gases at a site near Denver, Colorado. *J. Geochem. Explor.* **27**, 259–280.

Koski R. A., Benninger L. M., Zierenberg R. A., and Jonasson I. R. (1994) Composition and growth history of hydrothermal deposits in Escanaba Trough, southern Gorda Ridge. In *Geologic, Hydrothermal, and Biologic Studies at Escanaba Trough, Gorda Ridge, Offshore Northern California* (eds. J. L. Morton, R. A. Zierenberg, and C. A. Reiss). US Geological Survey Bulletin 2022, pp. 293–324.

Krabbenhoft D. P., Benoit J. M., Babiarz C. L., Hurley J. P., and Andren A. W. (1995) Mercury cycling in the Allequash Creek watershed, northern Wisconsin. *Water Air Soil Pollut.* **80**, 425–433.

Krabbenhoft D. P., Wiener J. G., Brumbaugh W. G., Olson M. L., DeWild J. F., and Sabin T. J. (1999) A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients. In *US Geological Survey Toxic Substances Hydrology Program*, *Proceedings of the Technical Meeting*, Vol. 2 (eds. D.W. Morganwalp and H.T. Buxton). Contamination of Hydrologic Systems and Related Ecosystems: USGS, Water-Resources Investigations Report 99–4018B. United States Geological Survey, Reston, VA, pp. 147–160.

Kraepiel A. M. L., Keller K., Chin H. B., Malcolm E. G., and Morel F. M. M. (2003) Sources and variations of mercury in tuna. *Environ. Sci. Technol.* **37**(24), 5551–5558.

Krupp E.M., Pecheyran C., and Donard O.F.X. (2003) Investigation on the mercury isotope distribution of mercury species (MMHg and Hg^{2+}) in different fish tissue samples. In *Abstracts of the 2003 European Winter Conference on Plasma Spectrochemistry,* Garmisch–Partenkirchen, Germany, January 12–17.

Lacerda L. D. and Gonçalves G. O. (2001) Mercury distribution and speciation in waters of the coastal lagoons of Rio de Janeiro, SE Brazil. *Mar. Chem.* **76**, 47–58.

Lacerda L. D. and Salomons W. (1998) *Mercury from Gold and Silver Mining: A Chemical Time Bomb?* Springer, New York, 146pp.

Lalli C. M. and Parsons T. R. (1993) *Biological Oceanography: An Introduction*. Heinemann, Oxford, UK, 147pp.

Lalonde J. D., Amyot M., Doyon M. R., and Auclair J. C. (2003) Photo-induced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area

(Ontario, Canada). *J.Geophys. Res.-Atmos.* **108**(D6) doi:10.1029/2001JD001534.

Lalonde J. D., Amyot M., Kraepiel A. M. L., and Morel F. M. M. (2001) Photooxidation of Hg(0) in artificial and natural waters. *Environ. Sci. Technol.* **35**, 1367–1372.

Lalonde J. D., Poulain A. J., and Amyot M. (2002) The role of mercury redox reactions in snow on snow-to-air mercury transfer. *Environ. Sci. Technol.* **36**(2), 174–178.

Lambert G., Le Cloaree M.-F., and Pennisi M. (1988) Volcanic output of SO_2 and trace metals: a new approach. *Geochim. Cosmochim. Acta* **52**(1), 39–42.

Lamborg C. H., Fitzgerald W. F., Damman A. W. H., Benoit J. M., Balcom P. H., and Engstrom D. R. (2002a) Modern and historic atmospheric mercury fluxes in both hemispheres: global and regional mercury cycling implications. *Glob. Biogeochem. Cycles.* **16**(4), 1104, doi: 10.1029/2001GB001847.

Lamborg C. H., Fitzgerald W. F., Graustein W. C., and Turekian K. K. (2000) An examination of the atmospheric chemistry of mercury using ^{210}Pb and ^{7}Be. *J. Atmos. Chem.* **36**, 325–338.

Lamborg C. H., Fitzgerald W. F., O'Donnell J., and Torgersen T. (2002b) A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients. *Geochim. Cosmochim. Acta* **66**(7), 1105–1118.

Lamborg C. H., Fitzgerald W. F., Vandal G. M., and Rolfhus K. R. (1995) Atmospheric mercury in northern Wisconsin: Sources and species. *Water Air Soil Pollut.* **80**, 198–206.

Lamborg C. H., Rolfhus K. R., Fitzgerald W. F., and Kim G. (1999) The atmospheric cycling and air-sea exchange of mercury species in the south and equatorial Atlantic Ocean. *Deep-Sea Res. II* **46**(5), 957–977.

Lamborg C. H., Tseng C.-M., Fitzgerald W. F., Balcom P. H., and Hammerschmidt C. R. (2003) Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with "reducible Hg" titrations. *Environ. Sci. Technol.* **37**, 3316–3322.

Landis M. S. and Stevens R. K. (2001) Preliminary results from the USEPA mercury speciation network and aircraft measurements campaigns. Presented at the *6th International Conference on Mercury as a Global Pollutant*. Oct. Minamata, Japan.

Landis M. S., Stevens R. K., Schaedlich F., and Prestbo E. (2002) Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **36**(13), 3000–3009.

Langer C. S., Fitzgerald W. F., Vandal G. M., and Visscher P. T. (2001) Biogeochemical cycling of methylmercury at Barn Island Salt Marsh, Stonington, CT, USA. *Wetlands Ecol. Manage.* **9**, 295–310.

Lantzy R. J. and MacKenzie F. T. (1979) Atmospheric trace metals: global cycles and assessment of man's impact. *Geochim. Cosmochim. Acta* **43**, 511–525.

Lauretta D. S., Devouard B., and Buseck P. R. (1999) The cosmochemical behavior of mercury. *Earth Planet. Sci. Lett.* **171**, 35–47.

Lauretta D. S., Klaue B., Blum J. D., and Buseck P. R. (2001) Mercury abundances and isotopic compositions in the Murchison (CM) and Allende (CV) carbonaceous chondrites. *Geochim. Cosmochim. Acta* **65**(16), 2807–2818.

Laurier F. J. G., Mason R. P., Gill G. A., and Whalin L. (2004) Mercury distributions in the North Pacific Ocean—20 years of observations. *Mar. Chem.* **90**, 3–19.

Lawson N. M. and Mason R. P. (2001) Concentration of mercury, methylmercury, cadmium, lead, arsenic, and selenium in the rain and stream water of two contrasting watersheds in western Maryland. *Water Res.* **35**(17), 4039–4052.

Lechler P. J., Miller J. R., Lacerda L. D., Vinsond D., Bonzongo J.-C., Lyons W. B., and Warwick J. J. (2000) Elevated mercury concentrations in soils, sediments, water, and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments? *Sci. Total Environ.* **260**, 87–96.

Lee Y. H., Bishop K. H., and Munthe J. (2000) Do concepts about catchment cycling of methylmercury and mercury in boreal catchments stand the test of time? Six years of atmospheric inputs and runoff export at Svartberget, northern Sweden. *Sci. Total Environ.* **260** (1–3), 11–20.

Leermakers M., Galletti S., De Galan S., Brion N., and Baeyens W. (2001) Mercury in the southern North Sea and Scheldt estuary. *Mar. Chem.* **75**(3), 229–248.

Lin C. J. and Pehkonen S. O. (1999) Aqueous phase reactions of mercury with free radicals and chlorine: implications for atmospheric mercury chemistry. *Chemosphere* **38**(6), 1253–1263.

Lindberg S. E., Brooks S., Lin C. J., Scott K. J., Landis M. S., Stevens R. K., Goodsite M., and Richter A. (2002) Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **36**(6), 1245–1256.

Lindberg S. E., Meyers T. P., Taylor G. E., Jr., Turner R. R., and Schroeder W. H. (1992) Atmospheric surface exchange of mercury in a forest: results of modeling and gradient approaches. *J. Geol. Res.* **97**(2), 2519–2528.

Lindberg S. E., Vette A. F., Miles C., and Schaedlich F. (2000) Mercury speciation in natural waters: measurement of dissolved gaseous mercury with a field analyzer. *Biogeochemistry* **48**, 237–259.

Lindqvist O., Johansson K., Aastrup M., Andersson A., Bringmark L., Hovsenius G., Haakanson L., Iverfeldt A., Meili M., and Timm B. (1991) Mercury in the Swedish environment—recent research on causes, consequences and corrective methods. *Water Air Soil Pollut.* **55**(1–2), 1–261.

Lindqvist O. and Rodhe H. (1985) Atmospheric mercury—a review. *Tellus* **27B**, 136–159.

Lockhart W. L., Wilkinson P., Billeck B. N., Danell R. A., Hunt R. V., Brunskill G. J., Delaronde J., and St. Louis V. (1998) Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* **40**(2–3), 163–173.

Long S. E. and Kelly W. R. (2002) Determination of mercury in coal by isotope dilution cold-vapor generation inductively coupled plasma mass spectrometry. *Anal. Chem.* **74**, 1477–1483.

Lu J. Y., Schroeder W. H., Barrie L. A., Steffen A., Welch H. E., Martin K., Lockhart L., Hunt R. V., Boila G., and Richter A. (2001) Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **28**(17), 3219–3222.

Lucotte M., Mucci A., Hillaire-Marcel C., Pichet P., and Grondin A. (1995) Anthropogenic mercury enrichment in remote lakes of northern Quebec (Canada). *WASP* **80**, 467–476.

MacDonald R. W., Barrie L. A., Bidleman T. F., Diamond M. L., Gregor D. J., Semkin R. G., Strachan W. M. J., Li Y. F., Wania F., Alaee M., Alexeeva L. B., Backus S. M., Bailey R., Bewers J. M., Gobeil C., Halsall C. J., Harner T., Hoff J. T., Jantunen L. M. M., Lockhart W. L., Mackay D., Muir D. C. G., Pudykiewicz J., Reimer K. J., Smith J. N., Stern G. A., Schroeder W. H., Wagemann R., and Yunker M. B. (2000) Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* **254**, 93–234.

Mantoura R. F. C., Dickson A., and Riley J. P. (1978) The complexation of metals with humic materials in natural waters. *Estuar. Coast. Mar. Sci.* **6**, 387–408.

Martell A. E., Smith R. M., and Motekaitis R. J. (1998) *NIST Critically Selected Stability Constants of Metal Complexes Data Base.* NIST Stand. Ref. Database no. 46, US Department of Commerce, Gaithersburg, MD.

Martínez-Cortizas A., Potevedra-Pombal X., García-Rodeja E., Nóvoa Muñoz J. C., and Shotyk W. (1999) Mercury in a Spanish peat bog: archive of climate change and atmospheric metal deposition. *Science* **284**, 939–942.

Marvin-Dipasquale M., Agee J., McGowan C., Oremland R. S., Thomas M., Krabbenhoft D., and Gilmour C. C. (2000) Methyl-mercury degradation pathways: a comparison among three mercury impacted ecosystems. *Environ. Sci. Technol.* **34**, 4908–4916.

Marvin-Dipasquale M. and Oremland R. S. (1998) Bacterial methylmercury degradation in Florida Everglades peat sediment. *Environ. Sci. Technol.* **32**, 2556–2563.

Mason R. P. and Fitzgerald W. F. (1990) Alkylmercury species in the equatorial Pacific. *Nature* **347**, 457–459.

Mason R. P. and Fitzgerald W. F. (1993) The distribution and biogeochemical cycling of mercury in the equatorial Pacific Ocean. *Deep-Sea Res.* **40**, 1897–1924.

Mason R. P. and Fitzgerald W. F. (1996) Sources, sinks and biogeochemical cycling of mercury in the ocean. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (eds. W. Baeyens, R. Ebinghaus, and O. Vasiliev). NATO ASI: Series 2. Environment. Kluwer, Boston, vol. 21, pp. 249–272.

Mason R. P., Fitzgerald W. F., Hurley J. P., Hanson A. K., Jr., Donaghay P. L., and Sieburth J. M. (1993) Mercury biogeochemical cycling in a stratified estuary. *Limnol. Oceanogr.* **38**, 1227–1241.

Mason R. P., Fitzgerald W. F., and Morel F. M. M. (1994) The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* **58**, 3191–3198.

Mason R. P. and Lawrence A. L. (1999) Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* **18**, 2438–2447.

Mason R. P., Lawson N. M., Lawrence A. L., Leaner J. J., Lee J. G., and Sheu G.-R. (1999) Mercury in Chesapeake Bay. *Mar. Chem.* **65**, 77–96.

Mason R. P., Lawson N. M., and Sheu G. R. (2001) Mercury in the Atlantic Ocean: factors controlling air–sea exchange of mercury and its distribution in the upper waters. *Deep-Sea Res. II* **48**(13), 2829–2853.

Mason R. P., Rolfhus K. R., and Fitzgerald W. F. (1998) Mercury in the North Atlantic. *Mar. Chem.* **61**, 37–53.

Mason R. P. and Sullivan K. A. (1999a) Mercury in Lake Michigan. *Environ. Sci. Technol.* **31**, 942–947.

Mason R. P. and Sullivan K. A. (1999b) The distribution and speciation of mercury in the south and equatorial Atlantic. *Deep-Sea Res. II* **46**, 937–956.

Matilainen T., Verta M., Korhonen H., Uusi-Rauva A., and Niemi M. (2001) Behavior of mercury in soil profiles: impact of increased precipitation, acidity, and fertilization on mercury methylation. *Water Air Soil Pollut.* **125**, 105–119.

McCarthy J. H. (1968) Experiments with mercury in soil gas and air applied to mineral exploration. *Min. Eng.* **20**, 46.

Mercone D., Thomson J., Croudace I. W., and Troelstra S. R. (1999) A coupled natural immobilization mechanism for mercury and selenium in deep-sea sediments. *Geochim. Cosmochim. Acta* **63**(10), 1481–1488.

METAALICUS. http://www.umanitoba.ca/institutes/fisheries/METAALICUS1.html (accessed Jul 20, 2006).

Mierle G. (1990) Aqueous inputs of mercury to Precambrian shield lakes in Ontario. *Environ. Toxicol. Chem.* **9**, 843–851.

Millward G. E. (1982) Nonsteady state simulations of the global mercury cycle. *J. Geol. Res.* **87**, 8891–8897.

Monteiro L. R. and Furness R. W. (1997) Accelerated increase in mercury contamination in North Atlantic mesopelagic food chains as indicated by time series of seabird feathers. *Environ. Toxicol. Chem.* **16**(12), 2489–2493.

Monteiro L. R. and Furness R. W. (2001) Kinetics, dose-response, and excretion of methylmercury in free-living adult Cory's shearwaters. *Environ. Sci. Technol.* **35**(4), 739–746.

Monteiro L. R., Granadeiro J. P., and Furness R. W. (1998) Relationship between mercury levels and diet in Azores seabirds. *Mar. Ecol. Prog. Ser.* **166**, 259–265.

Munthe J. (1992) The aqueous oxidation of elemental mercury by ozone. *Atmos. Environ.* **26A**(8), 1461–1468.

Munthe J. and Berg T. (2001) Reply to comment on "Atmospheric mercury species in the European Arctic: measurement and modeling" by Berg *et al. Atmos. Environ.* **35**(31), 5379–5380.

Murphy D. M., Thomson D. S., and Mahoney M. J. (1998) *In situ* measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers. *Science* **282**, 1664–1669.

National Academy of Sciences (NAS) (2000) *Toxicological Effects of Methylmercury*. Committee on the toxicological effects of methylmercury. National Academy Press, Washington, DC.

National Research Council Committee on the Toxicological Effects of Methylmercury (2000) *Toxicological Effects of Methylmercury*. National Academy Press, Washington, DC.

Norton S. A., Evans G. C., and Kahl J. S. (1997) Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sargent Mt. Pond, Maine, USA. *Water Air Soil Pollut.* **100**, 271–286.

Nriagu J. O. (1979) Production and uses of mercury. In *The Biogeochemistry of Mercury in the Environment* (ed. J. O. Nriagu). Elsevier/North-Holland Biomedical Press, Amsterdam, pp. 23–40.

Nriagu J. O. (1989) A global assessment of natural sources of atmospheric trace metals. *Nature* **338**, 47–49.

Nriagu J. O. and Becker C. (2003) Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Sci. Total Environ.* **304**, 3–12.

O'Driscol N. J., Siciliano S. D., and Lean D. R. S. (2003) Continuous analysis of dissolved gaseous mercury in freshwater lakes. *Sci. Total Environ.* **304**, 285–294.

Olafsson J. (1975) Volcanic influence on sea water at Heimaey. *Nature* **255**, 138–141.

Ozerova N. A. (1996) Mercury in geological systems. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (eds. W. Baeyens, R. Ebinghaus, and O.Vasiliev). NATO ASI: Series 2. Environment Kluwer, Boston, vol. 21, pp. 463–474.

Pacyna E. G. and Pacyna J. M. (2002) Global emission of mercury from anthropogenic sources in 1995. *Water Air Soil Pollut.* **137**, 149–165.

Pak K.-R. and Bartha R. (1998) Mercury methylation and demethylation in anoxic lake sediments and by strictly anaerobic bacteria. *Appl. Environ. Microbiol.* **64**(3), 1013–1017.

Pal B. and Ariya P. A. (2004a) Gas-phase HO center dot-initiated reactions of elemental mercury: kinetics, product studies, and atmospheric implications. *Environ. Sci. Technol.* **38**(21), 5555–5566.

Pal B. and Ariya P. A. (2004b) Studies of ozone initiated reactions of gaseous mercury: kinetics, product studies, and atmospheric implications. *Phys. Chem. Chem. Phys.* **6**(3), 572–579.

Patterson C. C. and Settle D. M. (1987) Magnitude of lead flux to the atmosphere from volcanoes. *Geochim. Cosmochim. Acta* **51**(3), 675–681.

Pempkowiak J., Cossa D., Sikora A., and Sanjuan J. (1998) Mercury in water and sediments of the southern Baltic Sea. *Sci. Total Environ.* **213**, 185–192.

Petersen G., Iverfeldt A., and Munthe J. (1995) Atmospheric mercury species over central and northern Europe: model calculations and comparison with the observations from the Nordic air and precipitation network for 1987 and 1988. *Atmos. Environ.* **29**(1), 47–67.

Pleijel K. and Munthe J. (1995) Modeling the atmospheric mercury cycle-chemistry in fog droplets. *Atmos. Environ.* **29**(12), 1441–1457.

Poissant L. and Casimir A. (1998) Water–air and soil–air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* **32**(5), 883–983.

Porcella D. B., Ramel C., and Jernelov A. (1997) Global mercury pollution and the role of gold mining: an overview. *Water Air Soil Pollut.* **97**(3–4), 205–207.

Rada R. G. and Powell D. E. (1993) Whole-lake burdens and spatial distribution of mercury in surficial sediments in Wisconsin seepage lakes. *Can. J. Fish. Aquat. Sci.* **50**(4), 865–873.

Rampino M. R. and Self S. (1984) Sulfur-rich volcanic eruptions and stratospheric aerosols. *Nature* **310**, 677–679.

Raofie F. and Ariya P. A. (2003) Kinetics and products study of the reaction of BrO radicals with gaseous mercury. *J. Phys. IV* **107**, 1119–1121.

Raofie F. and Ariya P. A. (2004) Product study of the gas-phase BrO-initiated oxidation of Hg-0: evidence for stable Hg^{1+} compounds. *Environ. Sci. Technol.* **38**(16), 4319–4326.

Rasmussen P. (1994) Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* **28**(13), 2233–2241.

Ravichandran M., Aiken G. R., Ryan J. N., and Reddy M. M. (1999) Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. *Environ. Sci. Technol.* **33**, 1418–1423.

Rea A. W., Lindberg S. E., Scherbatskoy T., and Keeler G. J. (2002) Mercury accumulation in foliage over time in two northern mixed-hardwood forests. *Water Air Soil Pollut.* **133**(1–4), 49–67.

Richter F. M., Rowley D. B., and DePaolo D. J. (1992) Sr isotope evolution of seawater: the role of tectonics. *Earth Planet. Sci. Lett.* **109**, 11–23.

Rolfhus K. R. (1998) The production and distribution of elemental Hg in a coastal marine environment. PhD Dissertation, University of Connecticut.

Rolfhus K. R. and Fitzgerald W. F. (1995) Linkages between atmospheric mercury deposition and the methylmercury content of marine fish. *Water Air Soil Pollut.* **80**, 291–297.

Rolfhus K. R. and Fitzgerald W. F. (2001) The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT–NY. *Geochim. Cosmochim. Acta* **65**(3), 407–418.

Rolfhus K. R., Sakamoto H. E., Cleckner L. B., Stoor R. W., Babiarz C. L., Back R. C., Manolopoulos H., and Hurley J. P. (2003) Distribution and fluxes of total and methylmercury in Lake Superior. *Environ. Sci. Technol.* **37**(5), 865–872.

Roos-Barraclough F., Martinez-Cortizas A., Garcia-Rodeja E., and Shotyk W. (2002) A 14, 500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. *Earth Planet. Sci. Lett.* **202**(2), 435–451.

Rosson R. (1996) Luciferase operon-containing plasmid engineered for detecting mercury in water. US Patent Application #5571722.

Roulet M. and Lucotte M. (1995) Geochemistry of mercury in pristine and flooded ferralitic soils of a tropical rain forest in French Guiana, South America. *WASP* **80**, 1079–1088.

Rouxel O., Fouquet Y., and Ludden J. N. (2004) Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: evidence from sulfur, selenium, and iron isotopes. *Geochim. Cosmochim. Acta* **68**(10), 2295–2311.

Sanemasa I. (1975) The solubility of elemental mercury vapor in water. *Bull. Chem. Soc. Jpn.* **48**, 1975–1978.

Sanseverino J., Sayler G. S., and Ripp S. A. (2002) Bioluminescent methods for direct visual detection of environmental compounds (US Patent # 0214551). *PCT Int. Appl.*, 51pp.

Scherbatskoy T., Shanley J. B., and Keeler G. J. (1998) Factors controlling mercury transport in an upland forested catchment. *Water Air Soil Pollut.* **105**, 427–438.

Scheuhammer A. M. (1991) Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. *Environ. Pollut.* **71**, 329–375.

Schlüter K. (2000) Review: evaporation of mercury from soils. An integration and synthesis of current knowledge. *Environ. Geol.* **39**(3–4), 249–271.

Schober S. E., Sinks T. H., Jones R. L., Bolger P. M., McDowell M., Osterloh J., Garrett E. S., Canady R. A., Dillon C. F., Sun Y., Joseph C. B., and Mahaffey K. R. (2003) Blood mercury levels in US children and women of childbearing age, 1999–2000. *J. Am. Med. Assoc.* **289**, 1667–1674.

Schroeder W. H., Anlauf K. G., Barrie L. A., Lu J. Y., Steffen A., Schneeberger D. R., and Berg T. (1998) Arctic springtime depletion of mercury. *Nature* **394**, 331–332.

Schuster P. F., Krabbenhoft D. P., Naftz D. L., Cecil D., Olson M. L., DeWild J. F., Susong D. D., Green J. R., and Abbott M. L. (2002) Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **36**, 2303–2310.

Scott K. J., Hudson R. J. M., Kelly C. A., Rudd J. W. M., and Barkay T. (2001) Effects of chemical speciation on the bioavailability of Hg(II) in defined media and natural water as measured with a *mer-lux* bioreporter. In *Abstracts of the 6th International Conference on Mercury as a Global Pollutant*. Minamata, Japan, 130pp.

Seigel F. R., Kravitz J. H., and Galasso J. J. (2001) Arsenic and mercury contamination in 31 cores taken in 1965, St. Anna Trough, Kara Sea, Arctic Ocean. *Environ. Geol.* **40**(4–5), 528–542.

Seigneur C., Karamchandani P., Vijayaraghavan K., Lohman K., Shia R. L., and Levin L. (2003) On the effect of spatial resolution on atmospheric mercury modeling. *Sci. Total Environ.* **304**(1–3), 73–81.

Seinfeld J. H. (1986) *Atmospheric Chemistry and Physics of Air Pollution*. Wiley-Interscience, New York, pp. 594–597.

Selifonova O., Burlage R., and Barkay T. (1993) Bioluminescent sensors for detection of bioavailable Hg(ii) in the environment. *Appl. Environ. Microbiol.* **59**(9), 3083–3090.

Sellers P., Kelly C. A., and Rudd J. W. M. (2001) Fluxes of methylmercury to the water column of a drainage lake: the relative importance of internal and external sources. *Limnol. Oceanogr.* **46**(3), 623–631.

Sellers P., Kelly C. A., Rudd J. W. M., and MacHutchon A. R. (1996) Photodegradation of methymercury in lakes. *Nature* **380**, 694–697.

Sheu G.-R. and Mason R. P. (2001) An examination of methods for the measurements of reactive gaseous mercury in the atmosphere. *Environ. Sci. Technol.* **35**, 1209–1216.

Shia R.-L., Seigneur C., Pai P., Ko M., and Sze N. D. (1999) Global simulation of atmospheric mercury concentrations and deposition fluxes. *J. Geol. Res.* **104**(D19), 23747–23760.

Shotyk W., Goodsite M. E., Roos-Barraclough F., Frei R., Heinemeier J., Asmund G., Lohse C., and Hansen T. S. (2003) Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve." *Geochim. Cosmochim. Acta* **67**(21), 3991–4011.

Skyring G. W. (1987) Sulfate reduction in coastal ecosystems. *Geomicrobiol. J.* **5**, 295–373.

Slemr F., Brunke E. G., Ebinghaus R., Temme C., Munthe J., Wangberg I., Schroeder W., Steffen A., and Berg T. (2003) Worldwide trend of atmospheric mercury since 1977. *Geophys. Res. Lett.* **30**(10), doi:10.1029/2003GL016954.

Slemr F. and Langer E. (1992) Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature* **355**, 434–437.

Slemr F., Seiler W., and Schuster G. (1981) Latitudinal distribution of mercury over the Atlantic Ocean. *J. Geol. Res.* **80**, 1159.

Smith C. N., Kesler S. E., Klaue B., and Blum J. D. (2005) Mercury isotope fractionation in fossil hydrothermal systems. *Geology* **33**(10), 825–828.

Smith W. E. (1975) *Minamata*. Henry Holt and Company, New York.

Sommar J., Gårdfeldt K., Stromberg D., and Feng X.-B. (2001) A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. *Atmos. Environ.* **35**(17), 3049–3054.

Spiro P. A., Jacob D. J., and Logan J. A. (1992) Global inventory of sulfur emissions with $1^\circ \times 1^\circ$ resolution. *J. Geophys. Res.* **97/D5**, 6023–6036.

St. Louis V. L., Rudd J. W. M., Kelly C. A., Beaty K. G., Flett R. J., and Roulet N. T. (1996) Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Technol.* **30**(9), 2719–2729.

St. Louis V. L., Rudd J. W. M., Kelly C. A., Bodaly R. A., Paterson M. J., Beaty K. G., Hesslein R. H., Heyes A., and Majewski A. R. (2004) The rise and fall of mercury methylation in an experimental reservoir. *Environ. Sci. Technol.* **38**(5), 1348–1358.

St. Louis V. L., Rudd J. W. M., Kelly C. A., Hall B. D., Rolfhus K. R., Scott K. J., Lindberg S. E., and Dong W. (2001) Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* **35**(15), 3089–3098.

Stock A. and Cucuel F. (1934) The quantitative determination of microamounts of mercury. *Naturwissenchaften* **22**, 390.

Stoffers P., Hannington M., Wright I., Herzig P., and de Ronde C. (1999) Elemental mercury at submarine hydrothermal vents in the Bay of Plenty, Taupo volcanic zone, New Zealand. *Geology* **27**(10), 931–934.

Stoiber R. E. and Jepsen A. (1973) Sulfur dioxide contributions to the atmosphere by volcanoes. *Science* **182**, 577–578.

Stoiber R. E., Williams S. N., and Huebert B. (1987) Annual contribution of sulfur dioxide to the atmosphere by volcanoes. *J. Volcanol. Geotherm. Res.* **33**(1–3), 1–8.

Stordal M. C. and Gill G. A. (1995) Determination of mercury methylation rates using a 203-Hg radiotracer technique. *Water Air Soil Pollut.* **80**, 725–734.

Stratton W. J. and Lindberg S. E. (1995) Use of a refluxing mist chamber for measurement of gas-phase mercury(II) species in the atmosphere. *Water Air Soil Pollut.* **80**, 1269–1278.

Sunderland E. M., Gobas F. A. P. C., Branfireun B. A., and Heyes A. (in press) Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.*

Swain E. B., Engstrom D. R., Brigham M. E., Henning T. A., and Brezonik P. L. (1992) Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **257**, 784–787.

Swain E. B. and Helwig D. D. (1989) Mercury in fish from northeastern Minnesota lakes: historical trends, environmental correlates, and potential sources. *J. Minn. Acad. Sci.* **55**, 103–109.

Tescione L. and Belfort G. (1993) Construction and evaluation of a metal ion biosensor. *Biotechnol. Bioeng.* **42**(8), 945–952.

Thakur A. N. and Goel P. S. (1989) Huge variations in the isotopic ratio ^{196}Hg/^{202}Hg in some acid-insoluble resides of Sikhote Alin and other iron meteorites. *Earth Planet. Sci. Lett.* **96**, 235–246.

The Social Scientific Study Group on Minamata Disease (2001) *In the Hope of Avoiding Repetition of a Tragedy of Minamata Disease (What We Have Learned from the Experience)*. National Institute for Minamata Disease, Minamata, Japan, 140pp.

Tokos J. J. S., Hall B., Calhoun J. A., and Prestbo E. (1998) Homogeneous gas-phase reactions of Hg° with H_2O_2, O_3, CH_3I and $(CH_3)_2S$: implications for atmospheric Hg cycling. *Atmos. Environ.* **32**(5), 823–828.

Topping G. and Davies I. M. (1981) Methylmercury production in the marine water column. *Nature* **290**, 243–244.

Tremblay A., Lucotte M., and Schetagne R. (1998) Total mercury and methylmercury accumulation in zooplankton of hydroelectric reservoirs in northern Quebec (Canada). *Sci. Total Environ.* **213**(1–3), 307–315.

Tseng C. M., Amouroux D., Abril G., Tessier E., Etcheber H., and Donard O. F. X. (2001) Speciation of mercury in a fluid mud profile of a highly turbid macrotidal estuary (Gironde, France). *Environ. Sci. Technol.* **35**(13), 2627–2633.

Tseng C.-M., Balcom P. H., Lamborg C. H., and Fitzgerald W. F. (2003) Dissolved elemental mercury investigations in Long Island Sound using on-line Au amalgamation-flow injection analysis. *Environ. Sci. Technol.* **37**, 1183–1188.

Tseng C.-M., Lamborg C. H., Fitzgerald W. F., and Engstrom D. R. (2004) Cycling of dissolved elemental mercury in arctic Alaskan lakes. *Geochim. Cosmochim. Acta* **68**(6), 1173–1184.

Turekian K. K. and Wedepohl K. H. (1961) Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.* **72**, 175–192.

Urban N. R., Eisenreich S. J., Grigal D. F., and Schurr K. T. (1990) Mobility and diagenesis of Pb and ^{210}Pb in peat. *Geochim. Cosmochim. Acta* **54**, 3329–3346.

US Environmental Protection Agency (USEPA) (1997) Mercury Study Report to Congress. EPA 452/R–97–003. Available at http://www.epa.gov/oar/mercury.html (accessed Jul 19, 2006).

US Mercury Deposition Network. http://nadp.sws.uiuc.edu/mdn (accessed Jul 20, 2006).

USFAD Consumer Advisory (2001) Mercury levels in seafood species. Center for Food Safety and Applied Nutrition, Office of Seafood.

USFDA (2001) Mercury levels in seafood species. Center for Food Safety and Applied Nutrition, Office of Seafood.

Vaidya O. C., Howell G. D., and Leger D. A. (2000) Evaluation of the distribution of mercury in lakes in Nova Scotia and Newfoundland (Canada). *Water Air Soil Pollut.* **117**(1–4), 353–369.

Vandal G. M., Fitzgerald W. F., Boutron C. F., and Candelone J. P. (1993) Variations in mercury deposition to the Antarctic over the last 34,000 years. *Nature* **362**, 621–623.

Vandal G. M., Fitzgerald W. F., and Mason R. P. (1991) Cycling of volatile mercury in temperate lakes. *Water Air Soil Pollut.* **56**, 791–803.

Vandal G. M., Fitzgerald W. F., Rolfhus K. R., Lamborg C. H., Langer C. S., and Balcom P. H. (2002) *Sources and Cycling of Mercury and Methylmercury in Long Island Sound.* Final Report to CTDEP, 105pp.

Vandal G. M., Mason R. P., McKnight D., and Fitzgerald W. (1998) Mercury speciation and distribution in a polar desert lake (Lake Hoare, Antarctica) and two glacial meltwater streams. *Sci. Total Environ.* **213**, 229–237.

Varekamp J. C., Buchholdtz ten Brink M. R., Mecray E. L., and Kreulen B. (2000) Mercury in Long Island Sound sediments. *J. Coast. Res.* **16**(3), 613–626.

Varekamp J. C. and Buseck P. R. (1981) Mercury emissions from Mount St. Helens during September 1980. *Nature* **293**, 555–556.

Varekamp J. C. and Buseck P. R. (1983) Mercury anomalies in soils: a geochemical exploration method for geothermal areas. *Geothermics* **12**(1), 29–47.

Varekamp J. C. and Buseck P. R. (1984) The speciation of mercury in hydrothermal systems, with applications to ore deposition. *Geochim. Cosmochim. Acta* **48**(1), 177–185.

Varekamp J. C. and Buseck P. R. (1986) Global mercury flux from volcanic and geothermal sources. *Appl. Geochem.* **1**(1), 65–73.

Verta M. and Matilainen T. (1995) Methylmercury distribution and partitioning in stratified Finnish forest lakes. *Water Air Soil Pollut.* **80**(1–4), 585–588.

Virta M., Lampinen J., and Karp M. (1995) A luminescence-based mercury biosensor. *Anal. Chem.* **67**, 667–669.

Wang Q., Shen W., and Ma Z. (2000) Estimation of mercury emission from coal combustion in China. *Environ. Sci. Technol.* **34**, 2711–2713.

Watras C. J. and Bloom N. S. (1994) The vertical distribution of mercury species in Wisconsin lakes: accumulation in plankton layers. In *Mercury Pollution: Integration and Synthesis* (eds. C. Watras and J. Huckabee). Lewis Publishers, Ann Arbor, MI, pp. 137–152.

Watras C. J., Bloom N. S., Hudson R. J. M., Gherini S., Munson R., Claas S. A., Morrison K. A., Hurley J., Wiener J. G., Fitzgerald W. F., Mason R., Vandal G., Powell D., Rada R., Rislov L., Winfrey M., Elder J., Krabbenhoft D., Andren A. W., Babiarz C., Porcella D. B., and Huckabee J. W. (1994) Sources and fates of mercury and methylmercury in Wisconsin lakes. Watras, C. Huckabee, J. In *Mercury Pollution: Integration and Synthesis* (eds. C. Watras and J. Huckabee). Lewis Publishers, Ann Arbor, MI, chapt. I.12, pp. 153–177.

Watson C. M., Dwyer D. J., Andle J. C., Bruce A. E., and Bruce M. R. M. (1999) Stripping analyses of mercury using gold electrodes: irreversible adsorption of mercury. *Anal. Chem.* **71**, 3181–3186.

Westöö G. (1966) Determination of methylmercury compounds in foodstuffs: I. Methylmercury compounds in fish, identification and determination. *Acta Chem. Scand.* **20**(8), 2131–2137.

White D. E. (1967) Mercury and base-metal deposits with associated thermal and mineral waters. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. Barnes). Holt, Rinehart and Winston, New York, chapt. 13, pp. 575–631.

Wiener J. G., Fitzgerald W. F., Watras C. J., and Rada R. G. (1990a) Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. *Environ. Toxicol. Chem.* **9**(7), 909–918.

Wiener J. G., Krabbenhoft D. P., Heinz G. H., and Scheuhammer A. M. (2002) Ecotoxicology of Mercury. In *Handbook of Ecotoxicology* (eds. D. J. Hoffman and B. A. Rattner). Lewis Publishers, Boca Raton, FL.

Wiener J. G., Martini R. E., Sheffy T. B., and Glass G. E. (1990b) Factors influencing mercury concentrations in walleyes in northern Wisconsin lakes. *Trans. Am. Fisher. Soc.* **119**, 862–870.

Wiener J. G. and Spry D. J. (1996) Toxicological significance of mercury in freshwater fish. In *Environmental Contamination of Wildlife* (eds. W. N. Beyer, G. H. Heinz, and A. W. Redmon-Norwood). Lewis Publishers, Boca Raton, FL, pp. 297–339.

Wilhelm S. M. (1999) Design mercury removal systems for liquid hydrocarbons. *Hydrocarb. Process.* **78**(4), 61.

Wilhelm S. M. (2001) Estimate of mercury emissions to the atmosphere from petroleum. *Environ. Sci. Technol.* **35**(24), 4704–4710.

Winfrey M. R. and Rudd J. W. M. (1990) Environmental factors affecting the formation of methylmercury in low pH lakes. *Environ. Toxicol. Chem.* **9**(7), 853–869.

Wood J. M., Kennedy F. S., and Rosen C. G. (1968) Synthesis of methyl-mercury compounds by extracts of a methanogenic bacterium. *Nature* **220**, 173–174.

Wu Q., Apte S. C., Batley G. E., and Bowles K. C. (1997) Determination of the mercury complexation capacity of natural waters by anodic stripping voltammetry. *Anal. Chim. Acta* **350**, 129–134.

Wylie D. E., Carlson L. D., Carlson R., Wagner F. W., and Schuster S. M. (1991) Detection of mercuric ions in water by ELISA with a mercury-specific antibody. *Anal. Biochem.* **194**, 381–387.

Wylie D. E., Lu D., Carlson L. D., Carlson R., Babacan K. F., Schuster S. M., and Wagner F. W. (1992) Monoclonal antibodies specific for mercuric ions. *Proc. Natl. Acad. Sci. USA* **89**, 4104–4108.

Xia K., Skyllberg U. L., Bleam W. F., Bloom P. R., Nater E. A., and Helmke P. A. (1999) X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances. *Environ. Sci. Technol.* **33**, 257–261.

Xiao Z. F., Munthe J., Schroeder W. H., and Lindqvist O. (1991) Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden. *Tellus* **43B**, 267–279.

Yigiterhan O., Lamborg C. H., Fitzgerald W. F., Balcom P. H., Hammerschmidt C. R., and Murray J. (2006) *Vertical Profiles of Mercury Species at Two Sites in the Western Black Sea (OS46A-10).* Abstracts from Ocean Sciences Meeting, Honolulu.

Young D. R., Johnson J. N., Soutar A., and Isaacs J. D. (1973) Mercury concentrations in dated varved marine sediments collected off southern California. *Nature* **244**, 273–275.

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