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Mercury in the Aquatic Environment: A Review of Factors Affecting Methylation

Susanne M. Ullrich,[a] Trevor W. Tanton,[a] and Svetlana A. Abdrashitova[b]*

[a]Dept. of Civil and Environmental Engineering, University of Southampton, U.K.;
[b]Institute of Microbiology and Virology, Almaty, Kazakhstan

ABSTRACT: Mercury is one of the most hazardous contaminants that may be present in the aquatic environment, but its ecological and toxicological effects are strongly dependent on the chemical species present. Species distribution and transformation processes in natural aquatic systems are controlled by various physical, chemical, and biological factors. Depending on the prevailing environmental conditions, inorganic mercury species may be converted to many times more toxic methylated forms such as methylmercury, a potent neurotoxin that is readily accumulated by aquatic biota. Despite a considerable amount of literature on the subject, the behavior of mercury and many of the transformation and distribution mechanisms operating in the natural aquatic environment are still poorly understood. This review examines the current state of knowledge on the physicochemical behavior of mercury in the aquatic environment, and in particular the environmental factors influencing its transformation into highly toxic methylated forms.

KEY WORDS: methylmercury, speciation, environmental transformation, bioaccumulation.

I. INTRODUCTION

Mercury (Hg), a toxic element, is widely distributed in the environment and is naturally present in aquatic systems in very low concentrations. The extensive past industrial use of the metal and its compounds together with widespread agricultural application of organomercurials frequently has resulted in serious contamination of surface waters and sediments (e.g., Hosokawa;[147] Wilken and Wallschläger;[334] Heaven et al.[140]). Long-range atmospheric transport of Hg from fossil fuel combustion and other sources has led to increased concentrations in freshwater systems and biota even in remote areas that are free from direct anthropogenic influences (Rada et al.,[265]; Lindqvist[200]).

The chemistry of Hg is complex, making it difficult to predict the behavior of mercuric pollutants in the natural environment. Sediments act both as sinks and potential sources of Hg (Covelli et al.[81]) and once contaminated may pose a risk

* Corresponding author.

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to aquatic life for many years (Kudo[187]). Depending on the prevailing physical, chemical and biological conditions, Hg compounds in aquatic systems can be interconverted and can be released from sediments to the water phase, taken up by aquatic biota, be lost to the atmosphere, or be transported with sediment particulate matter to new, previously uncontaminated locations.

The ecological and toxicological effects of Hg are strongly dependent on the chemical form (species) present (Clarkson[63]). Inorganic Hg forms may be transformed to organic, methylated species that are many times more toxic to aquatic organisms (WHO;[332,333] Boening[46]). The formation of methylmercury (MMHg), a potent neurotoxin, is of particular importance. Owing to its lipophilic and protein-binding properties, MMHg is readily accumulated by aquatic biota and may thus also pose a threat to humans and other fish-eating animals. Notorious incidents of mercury poisoning occurred in the 1950s and 1960s at Minamata Bay and on the Agano River in Japan (Takizawa[310]).

Many of the chemical and biological processes that control Hg methylation and bioaccumulation are still insufficiently understood, but if Hg pollution is to be effectively managed, we need to have a better understanding of the behavior of mercuric contaminants in the natural environment. This review discusses the behavior of Hg in aquatic systems and the factors that are thought to play a role in environmental MMHg formation. It also identifies areas in need of further research.

II. MERCURY IN THE AQUATIC ENVIRONMENT

A. Mercury Species in Aquatic Systems

Mercury occurs in three valence states (0, +1, and +2) and may be present in various physical and chemical forms in the natural aquatic environment. The nature and reactions of these species determine the solubility, mobility, and toxicity of Hg in aquatic ecosystems, as well as the potential for methylation. The main dissolved Hg species are elemental mercury (Hg^0), complexes of Hg(II) with various inorganic and organic ligands, and organic Hg forms, mainly methylmercury (MMHg) and dimethylmercury (DMHg). Between 10 to 30% of the dissolved Hg in the ocean is present as Hg^0 (Kim and Fitzgerald;[176] Mason and Fitzgerald[212]), and similar concentrations have been found for freshwaters (Vandal et al.;[313] Xiao et al.[341]). Hg^0 in surface waters occurs mainly from the reduction of Hg(II) compounds by aquatic microorganisms (Furukawa et al.;[111] Nelson et al.;[250] Mason et al.[216]) as well as from abiotic reduction by humic substances (Alberts et al.;[3] Miller;[237] Allard and Arsenie[4]), decomposition of organic Hg forms (Mason and Fitzgerald;[212] Mason and Sullivan[223]), and from anthropogenic discharges, a typical source being the chloralkali industry. Recent studies have shown that photoreduction of divalent Hg is another important mechanism of Hg^0 production in a wide

range of aquatic systems (Xiao et al.;[341,342] Schroeder et al.;[288] Amyot et al.;[5-9] Krabbenhoft et al.[181]), and that this process is mediated by humic material (Costa and Liss[79,80]). Hg^0 is relatively unreactive and is stable under mildly oxidizing or reducing conditions, but can be oxidized to Hg(II), particularly in the presence of chloride ions (Demagalhaes and Tubino;[89] Yamamoto[347]). Amyot et al.[5,6] have demonstrated the oxidation of Hg^0 in lake water and coastal seawater.

Most surface waters are supersaturated in Hg^0 relative to the atmosphere, especially in summer (Vandal et al.;[313] Fitzgerald et al.[104]). Due to its relatively high volatility, elemental Hg is readily lost from the aquatic environment at normal temperatures. The evasion of Hg^0 from water surfaces plays an important part in the global Hg cycle (Mason et al.;[214] Fitzgerald and Mason[105]). It has also been suggested that Hg^0 production is an important mechanism in aquatic systems for reducing the Hg(II) substrate used in the microbiological synthesis of MMHg (Fitzgerald et al.;[103,104] Mason et al.[215]).

Hg(I) is only stable as a dimer (Hg_2^{2+}) in aqueous solution and readily disproportionates into Hg^0 and Hg^{2+}, the most stable form in water. Until very recently, it was generally considered that the Hg^{2+} ion is the main species that is methylated in a bacterially mediated process (cf. Section III). Recent research, however, has shown that uncharged Hg complexes are much more likely to be taken up by bacteria (cf. Section III.B.1). Therefore, Hg speciation is a primary factor governing the methylation potential of a system.

The chemical form of Hg in aquatic systems is strongly influenced by redox (E_h) and pH conditions as well as by the concentrations of inorganic and organic complexing agents. Both the Hg^{2+} ion and the methylmercuric (CH_3Hg^+) cation have a high tendency to form complexes, in particular with soft ligands such as sulfur. Lindqvist[200] gives a list of potentially important inorganic and methylmercury complexes for fresh and sea water, and predominance diagrams showing the relative regions of stability of various soluble Hg species can be found in the literature (Hem;[90] Gavis and Fergusson;[118] Lockwood and Chen;[201] Beneš and Havlík;[24] Hudson et al.;[148] Stumm and Morgan[304]). In the absence of sulfide, the speciation of inorganic Hg in freshwaters is dominated by three uncharged complexes, $Hg(OH)_2$, HgOHCl, and $HgCl_2$ (cf. Figure 1). In the presence of increasing chloride ion concentrations, Hg^{2+} forms $HgCl^+$, $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ complexes, and in full-strength seawater (3.5% salinity), containing an average concentration of 0.56 *M* of Cl^-, it exists primarily as $HgCl_4^{2-}$ and $HgCl_3^-$ (Lockwood and Chen;[201] Hahne and Kroontje;[134] Stotzky and Babich[303]). Methylmercuric hydroxide, CH_3HgOH, is the most stable methylmercury species in the freshwater environment, whereas in seawater MMHg is present mainly as the chloride, CH_3HgCl (Craig;[82] Stumm and Morgan[304]). Equilibrium constants for MMHg and some of its complexes have been published, for example, by Stumm and Morgan.[304]

Predominance diagrams do not usually consider organic complexation due to a paucity of thermodynamic data on Hg and especially MMHg binding with polyfunctional natural ligands such as humic and fulvic acids. Hg speciation in

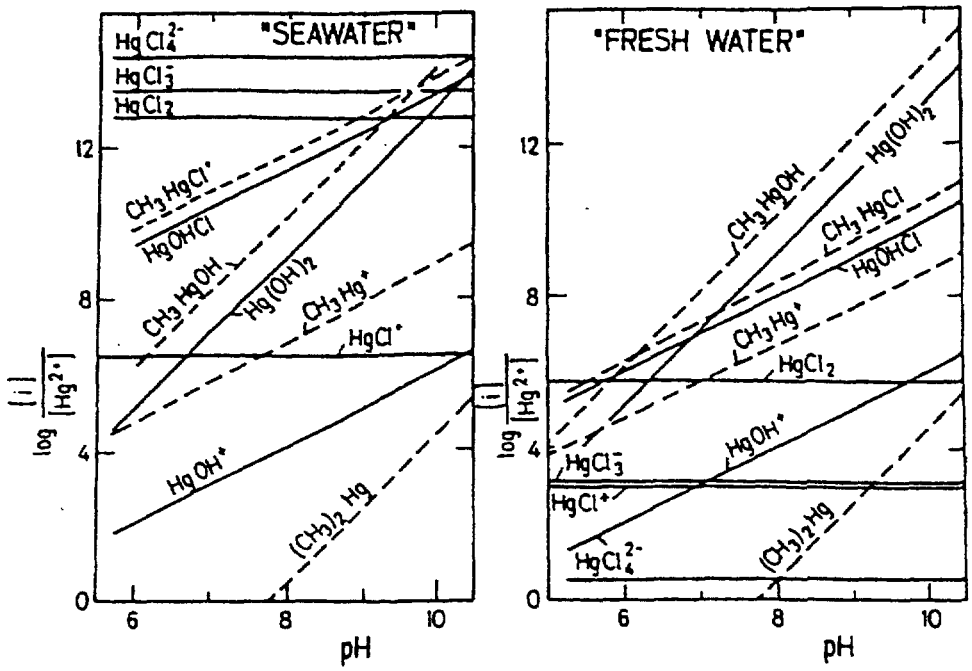

FIGURE 1. Concentration ratio diagrams illustrating the relative thermodynamic stability of mercury species in fresh water and sea water. Conditions: sea water [Cl⁻] = 0.6 *M*, $[CH_{4(aq)}] = 10^{-4}$ *M*: fresh water [Cl⁻] = 2×10^{-4} *M* $[CH_{4(aq)}] = 10^{-4}$ *M*. (Source: Stumm and Morgan.[304] Reprinted by permission of John Wiley & Sons, Inc.)

natural waters is largely dominated by organic rather than chloride or hydroxide complexes, however (Lövgren and Sjöberg;[202] Coquery et al.[71]). Particularly strong associations are formed with humic matter, where the Hg atom is most likely bound to thiol (-RSH) groups (Gavis and Fergusson;[118] Reimers et al.;[275] Beneš and Havlík;[24] Lindqvist[200]). Organic colloids comprise a substantial proportion of the traditionally defined dissolved Hg fraction (<0.45 μm) in freshwater, estuarine and marine environments (Mason et al.;[213] Watras et al.;[326] Leermakers et al.;[195] Stordal et al.;[302] Guentzel et al.[129]). In freshwaters more than 90% of Hg is complexed by organic matter (Mantoura et al.;[208] Meili[233]). Most MMHg (>70%) is probably also associated with dissolved organic carbon (DOC) in lake water (Lindqvist;[200] Hudson et al.[148]). Hudson et al.[148] have modeled the cycling of Hg in Wisconsin lakes and have calculated that 94 to 99+% of Hg(II) and 72 to 97% of MMHg in lakewaters is complexed by dissolved humic matter. In seawater, however, the proportion of Hg^{2+} bound to humics is decreased due to chloride ion competition (Lindberg and Harriss;[198] Mantoura et al.;[208] Leermakers et al.[195]). Hg complexation with humic matter also varies greatly depending on redox and pH conditions (cf. Section II.C), and the presence of sulfide ligands. Hudson et al.[148] calculated that in oxic waters sulfide may outcompete humic acid for Hg(II) and MMHg at a concentration of 10 μ*M*.

Although organic complexation is likely to dominate in oxic fresh water, under anoxic conditions the chemistry of Hg is mainly controlled by sulfide. In sediments Hg is mainly bound to sulfur as well as organic matter and inorganic particles (Morel et al.;[242] Lindberg and Harriss;[198] Dyrssen and Wedborg;[95] Fabbri et al.;[97] Mason and Lawrence[225]). Mercuric sulfide (HgS) is the main insoluble (L_{HgS} = 10^{-53} mol^2 l^{-2}) inorganic Hg compound in aquatic systems. Mercuric oxide (HgO), which is sparingly soluble (10^{-4} mol l^{-1}) is also commonly encountered in contaminated environments (Sakamoto et al.[283]). Hg compounds in the mud of Minamata Bay, for example, were mainly sulfides and oxides (Fujiki and Tajima[110]). HgS formation is generally favored at low pH and low sulfide concentrations. Under low E_h and high pH conditions, or if an excess of sulfide ions is present, HgS can be converted to soluble Hg-S complexes such as HgS_2^{2-}. Organic matter also enhances the solubility of HgS and may lead to a significant release of Hg into solution (Ravichandran et al.[270]), but other complexing agents do not appear to enhance HgS dissolution (Frimmel;[109] Ravichandran et al.[270]). Early work suggested that mercury in the HgS form is not available for bacterial methylation under anaerobic conditions, which was believed to be the reason for the generally lower MMHg concentrations encountered in sulfidic sediments, but recent research suggests that dissolved HgS^0 can in fact be methylated (Benoit et al.[26]), and that the mechanism of sulfide inhibition of Hg methylation is more complex (cf. Section III.B.6).

At high sulfide concentrations, for example, in sulfidic marine waters and interstitial waters of bottom sediments, Hg forms soluble bi- and polysulfide complexes such as $HgSH^+$, $Hg(SH)_2$, $Hg(SH)S^-$, HgS_2^{2-}, $Hg(S_x)_2^{2-}$, or $Hg(S_x)OH^-$, depending on pH and E_h conditions and S^0/S^{2-} concentrations (Gardner;[117] Dyrssen and Wedborg;[95] Paquette and Helz;[257] Jay et al.[163]). Methylmercury also forms highly stable complexes with sulfur ligands (Zepp et al.[348]), but in contrast to Hg^{2+}, the chloride complex dominates at low concentrations (0.1 n*M*) of H_2S and thiols (Dyrssen and Wedborg[95]). The most important sulfide complex of methylmercury is CH_3HgS^-.

Organomercurials may be present in surface waters due to natural processes such as biomethylation of inorganic Hg or human activities. Many of these compounds have in the past been widely used, for example, as fungicides, slimicides, or industrial catalysts, but with most of these uses now banned in many parts of the world, transformation of inorganic Hg is the predominant source of methylated Hg compounds in aquatic systems (Craig[82]). Atmospheric deposition is the main source of inorganic Hg to oceanic waters (Mason et al.;[215] Mason and Fitzgerald[220]) and many lakes (Watras et al.[328]), but it is not a significant source of MMHg (Mason and Fitzgerald[210,211]). Precipitation and surface run-off can be important sources of MMHg to freshwaters besides internal methylation (Rudd[280]).

Only methyl- and dimethylmercury are thought to occur naturally in waters, where they can be formed from divalent inorganic Hg by various mechanisms (cf. Section III). MMHg is the most ubiquitous organomercury compound in freshwa-

ter and estuarine systems, while DMHg is not normally detected. MMHg is kinetically inert toward decomposition, which accounts for its remarkable stability in natural waters (Stumm and Morgan[304]). It is efficiently degraded by microbial action, however, and can also be decomposed photochemically (cf. Section III.A.4). Organomercury compounds other than MMHg decompose rapidly in the environment (Jensen and Jernelöv;[166] Craig[82]), with typical breakdown products being organic compounds such as ethane and inorganic Hg (Hg^0 and Hg^{2+}). Compounds such as dimethyl and diphenyl Hg are volatile, nonpolar, and very poorly soluble in water. Unlike MMHg, DMHg is readily lost from aquatic systems by evaporation (Talmi and Mesmer[311]) and is not considered to be available for accumulation by aquatic organisms (Morel et al.[243]).

In contrast to freshwater systems, DMHg is the dominant methylated species in deep ocean waters (Mason and Fitzgerald;[210,211] Cossa et al.;[75] Mason et al.;[218]), where it appears to be produced from labile inorganic Hg complexes predominantly, although not exclusively, in the low-oxygen region (Mason and Fitzgerald;[210,211,220] Cossa et al.;[77] Mason et al.[221]). Little or no methylated Hg species are found in oceanic surface waters (Mason and Fitzgerald[210,211]; Cossa et al.[75]; Mason et al.[218,221]; Mason and Sullivan[223]), with enhanced demethylation, evaporation, and/or photodegradation of DMHg, and particulate scavenging of MMHg from surface waters being suggested as potential loss mechanisms (Mason and Fitzgerald;[212] Mason et al.[218,221]).

B. Mercury Concentrations in the Aquatic Environment

1. Water

Mercury is naturally present in waters at very low levels. It should be noted that accepted background levels have fallen steadily in recent years following significant improvements in both sampling and analytical techniques (Horvat[146]), while previously reported high results are now believed to have resulted from sample contamination. Recently established Hg levels in aquatic systems in Antarctica have been suggested as global baseline values. Total Hg in surface waters of antarctic lakes and glacial streams ranged from 2.2 to 9.5 p*M*, dissolved Hg from 0.5 to 2.2 p*M* and MMHg from <0.4 to 2.1 p*M* (Vandal et al.;[314] Lyons et al.[206]). Uncontaminated freshwaters generally contain <5 ng l^{-1} (≡ 25 p*M*) total Hg (Bloom;[37] Craig[82]), although up to 10 or 20 ng l^{-1} can be found in humic lakes or rivers rich in particulate Hg (Meili[233]). Total Hg concentrations in the marine environment are much lower and were found to range between 0.5 and 4 p*M* in the Mediterranean and North Atlantic (Cossa et al.;[77] Mason et al.[221]). Mercury concentrations in contaminated waters can be in the μg l^{-1} range. Dissolved Hg concentrations in the River Nura in Central Kazakhstan were typically between 0.2 and 0.5 μg l^{-1}, for example, depending on season and suspended solids content

(Heaven et al.[140]). Considerably less data are available on organic Hg compounds in natural waters. Recommended water-quality criteria in the Netherlands give target values of 0.05 μg l^{-1} for total dissolved Hg and 0.005 μg l^{-1} for organic Hg (Stumm and Morgan[304] after Behra et al., 1993).

The proportion of MMHg to total Hg is usually higher in the water column than in sediments, and is higher in freshwater than in estuarine environments. In estuarine and marine waters, MMHg is typically less than 5% of total Hg content (Coquery et al.;[71] Mason and Sullivan[223]), whereas up to about 30% of total Hg can be found as MMHg in freshwater lakes and rivers (Kudo et al.;[186] Meili;[233] Leermakers et al.[196]). Elevated concentrations of both total Hg and MMHg are frequently found in anoxic waters. Bloom[37] reported MMHg concentrations in natural surface waters are typically in the range of 0.02 to 0.1 ng l^{-1} (0.1 to 0.5 p*M*), but found up to 4 ng l^{-1} (37% of total Hg) in the anoxic bottom waters of a stratified pristine lake. DMHg has not been detected in temperate freshwater lakes (e.g., Vandal et al.;[313] Cossa et al.[74]) but is the most common methylated species in the marine environment. Up to 280 f*M* MMHg and 670 f*M* DMHg were found below the thermocline in the equatorial Pacific (Mason and Fitzgerald[210]), and up to 0.29 p*M* DMHg were detected in the Western Mediterranean (Cossa et al.[75]); average DMHg concentrations in the North Atlantic were 0.08 p*M* (Mason et al.[221]).

2. Sediments

Sediments constitute the main reservoir of Hg in freshwater systems. Background levels of Hg in uncontaminated sediments are comparable to levels in unpolluted surface soils, with average concentrations in ocean sediments in the order of 0.02 to 0.1 μg g^{-1} (Lindqvist et al.[199]). Craig[82] reported concentration ranges of 0.2 to 0.4 μg g^{-1} total Hg for uncontaminated sediments, whereas sediments in urban, industrial, or mineralized areas can contain up to 100 μg g^{-1} total Hg and up to 100 ng g^{-1} MMHg. Methylmercury concentrations in sediments are typically only about 1 to 1.5% of total Hg content and tend to be lower (typically <0.5%) in estuarine and marine environments (Olson and Cooper;[251] Bartlett and Craig;[21] Craig and Moreton;[85] Craig;[82] Bubb et al.;[53] Gobeil and Cossa;[126] Gagnon et al.;[114] Benoit et al.[25]). Total Hg concentrations in sediment porewaters are usually much higher than in the overlying watercolumn, however (e.g., Gobeil and Cossa;[126] Cossa and Gobeil[78]), and the proportion of MMHg can reach between 30 and 85% (Gagnon et al.;[114] Covelli et al.;[81] Hines et al.[141]).

Contaminated sediments may exhibit extremely high total Hg concentrations. Mud from Minamata Bay contained up to 908 μg g^{-1} (d.w.) Hg (Fujiki and Tajima[110]). MMHg was mostly less than 0.005 μg g^{-1} (d.w.) with a maximum of 0.03 μg g^{-1} (Hosokawa[147]), however, possibly due to the high sulfide content of the sediment, or the inhibition of microbial activity at high Hg levels (Chen et al.[59]). The River Nura has average sediment concentrations between 150 and 240 μg g^{-1}

(d.w.) total Hg in the most polluted section (Heaven et al.[140]), and River Elbe sediments were found to contain 12 μg g^{-1} (d.w.) total Hg and 35 ng g^{-1} (d.w.) MMHg (Hintelmann and Wilken[142]). DMHg has rarely been detected to date, but Quevauviller et al.[263] reported 211 to 233 ng g^{-1} DMHg (d.w.) in subsurface mangrove sediments.

Sediment quality criteria for Hg have been set in some countries, but due to the uncertainties regarding the bioavailability of Hg, it has been suggested that these should be applied with caution and in concert with other site-specific data (Chapman et al.[58]). It is also important to note that there has been considerable controversy in recent years regarding the 'true' methylmercury content of environmental samples, in particular sediments, after it was found that MMHg may be artificially formed during the sample preparation process. Although methods have been devised since to overcome this problem (e.g., Hintelmann et al.[144]), MMHg values cited in the literature should be interpreted with caution, and it is now generally accepted that values in excess of ca. 1% of total Hg content are probably unrealistic.

3. Biota

Freshwater biota can accumulate detectable quantities of Hg even from natural sources, and most fish nowadays have analyzable levels in their tissues. Maximum background levels for Hg in uncontaminated freshwater fish are about 0.2 μg g^{-1}, although considerably more can be found in large predators and in fish from waters near geological sources. Craig[82] reported concentration ranges of 0.01 to 1.5 μg Hg g^{-1} and 0.14 to 0.75 μg Hg g^{-1} for unpolluted marine fish and shellfish, respectively, and 0.2 to 1 μg g^{-1} for uncontaminated freshwater fish. For comparison, fish and shellfish from the highly polluted Minamata Bay contained up to 15 μg Hg g^{-1} (w.w.) and 178 μg Hg g^{-1} (d.w.), respectively (Fujiki and Tajima[110]). Human exposure to mercury occurs mainly from the ingestion of contaminated fish and seafood (Myers et al.[245]), and quality criteria have been set by various regulatory bodies. EEC quality objectives state a limit value of 0.3 μg Hg g^{-1} (w.w.) in fish (Craig[82]), whereas WHO[332] and the U.S. Food and Drug Administration (FDA[101]) have suggested maximum permissible concentrations of 0.5 and 1 μg Hg g^{-1}, respectively.

C. Mercury Transport and Distribution in Surface Waters

Mercury has a high tendency to be sorbed on surfaces. Therefore, in natural waters it is mostly bound to sediments, and a large proportion of Hg in the water phase is attached to suspended particles (Andren and Harriss;[11] Craig;[82] Mason et al.;[213] Cossa et al.[76]). MMHg is also strongly sorbed (Craig;[82] Baeyens et al.;[14] Rytuba[282]), although usually to a lesser extent than inorganic Hg (e.g., Suchanek

et al.[305]) Thus, suspended matter plays an important role in the transport of Hg and MMHg in aquatic systems (Kudo et al.;[183,185] Baeyens and Leermakers;[13] Coquery et al.;[71] Mason and Sullivan;[222,223] Maurice-Bourgoin et al.;[230] Lawson et al.[191]). Particulate transport is more important in particle-rich fresh and coastal waters than in the open sea (Coquery and Cossa;[69] Coquery et al.;[71] Fitzgerald and Mason[106]). Particulate Hg consists of Hg bound to inorganic particles and particulate organic matter, as well as biogenic particles such as bacteria, algae, and phytoplankton. Inorganic Hg tends to bind more strongly to mineral particles and detrital organic matter, whereas MMHg is more strongly associated with biogenic particles (Hurley et al.;[150] Meili[233]). In freshwater lakes, the distribution of Hg and MMHg is largely controlled by particulate scavenging in surface waters and particulate dissolution at the redox boundary (Hurley et al.[149]). Settling of particulate matter is considered a major Hg delivery mechanism to the sediment/water interface, the main site for methylation, whereas (redox-driven) upward diffusion from sediment porewater is probably less important (Hurley et al.;[149,151] Watras et al.[323]). Similarly, vertical transport of particulate matter in the ocean is the main supplier of Hg to low-oxygen waters and thus is a major factor controlling Hg methylation (Mason and Fitzgerald;[212,220] Mason and Sullivan[223]).

Oxyhydoxides and organic matter are the main vectors controlling the mobility and transport of Hg in aquatic systems. Due to the high stability of Hg-humic complexes, a high percentage of Hg in natural waters is present in organically complexed form (cf. Section II.A), and Hg concentrations in lake water or in the interstitial waters of sediments are often significantly correlated with dissolved organic matter (Lindberg and Harriss;[198] Meili et al.;[232] Watras et al.[325,326]). Hg concentrations in sediments or suspended particles are also often closely related to organic content (Lindberg and Harriss;[198] Coquery et al.;[70] Benoit et al.;[25] Mason and Lawrence;[225] Harland et al.;[139] Lawson et al.[191]). Hg appears to be more strongly sorbed by humic substances than MMHg (Hudson et al.;[148] Sjöblom et al.[291]), which may be the reason why it is less easily mobilized from sediments than MMHg (Bloom et al.;[42] Gill et al.[119]). In watersheds, MMHg is also considered more mobile than inorganic Hg (Bishop and Lee;[33] Mason and Sullivan;[222] Hurley et al.;[152] Lawson et al.[191]). The strong association of Hg with humic matter has important implications for the watershed transport of Hg (Bishop and Lee[33]). Transport of terrestrial organic matter with surface runoff can be a major source of Hg and MMHg to lakes and rivers (Mierle and Ingram;[236] Verta et al.;[317] Hurley et al.;[152] Lee et al.[194]) and may even constitute the main source of MMHg in drainage lakes receiving high amounts of runoff (Lee and Hultberg[193]). In seepage lakes, on the other hand, the relative importance of atmospheric MMHg deposition and in-lake MMHg production is increased (Verta et al.[317]). Watershed characteristics such as catchment type, land use, and soil organic content play an important role in Hg and MMHg fate and transport (Bringmark[52]). Wetlands and peatlands are sites of active MMHg production and have been recognized as important sources of MMHg for freshwaters (St. Louis et al.;[301] Hurley et al.;[152] Branfireun

et al.;[49-51] Waldron et al.[330]). Soil erosion and increased mobilization of Hg by runoff is an important source of Hg to tropical aquatic ecosystems, especially during the rainy season (Roulet et al.;[278] Maurice-Bourgoin et al.[230]), and in arid regions storm-driven runoff following forest fires may lead to elevated sediment Hg levels while simultaneously providing a carbon source for microbial methylation processes (Caldwell et al.[54]).

Iron and manganese oxides play a particularly important role in the cycling and transport of Hg in aquatic systems. This is due to their large surface areas and high capacity to adsorb and co-precipitate Hg, and to rerelease it after their dissolution (Fagerström and Jernelöv[99]). Many workers have found the distribution and concentration of dissolved and particulate Hg species to be influenced, among other factors, by the redox cycling of Fe, and less frequently Mn (e.g., Mason et al.;[213] Hurley et al.;[151] Bonzongo et al.;[47] Gagnon et al.;[115] Regnell et al.;[274] Quemerais et al.;[262] Gobeil et al.;[127] Bloom et al.[41]). Bloom et al.[41] reported, for example, that the mobility of MMHg in estuarine surface sediments was linked to the Fe redox cycle, while the mobility of Hg(II) was controlled by the formation of soluble polysulfide or organic complexes. The formation and dissolution of Fe and Mn oxides is strongly controlled by the redox state and oxygen content of waters and sediments. In anoxic conditions, oxyhydroxides dissolve and release any associated Hg (Gobeil and Cossa;[126] Gagnon et al.;[115] Cossa and Gobeil[78]), which is thought to be one reason for the frequently observed Hg and MMHg enrichment in (seasonally) anoxic waters (Hurley et al.;[149] Cossa et al.;[74] Watras et al.[327]). Seasonal and diurnal trends in MMHg concentrations in sediment porewaters (Covelli et al.;[81] Gill et al.[119]) may also be linked with redox effects. Meili[233] noted that oxyhydroxides form labile complexes with organic matter and clay minerals, which may further increase their metal scavenging capacity. The formation and dissolution of oxyhydroxides and organic complexes may influence methylation by controlling the availability of inorganic Hg.

Sediments can act both as sinks and as secondary sources of Hg. Covelli et al.[81] estimated that in the Gulf of Trieste up to 25% of Hg may be released annually from sediments and recycled at the sediment/water interface, and Stein et al.[300] have reviewed the chemical and physical processes governing the distribution of Hg between environmental media. Partition coefficients describe the equilibrium partitioning of Hg between the solid and dissolved phases. Sediment-water partition coefficients (K_d = mg sorbed Hg per kg sediment/mg dissolved Hg per liter) vary widely both within and between systems but are broadly in the order of 10^4 to 10^6 for Hg and 10^3 to 10^5 for MMHg (Hurley et al.;[150] Watras et al.;[326] Stordal et al.;[302] Coquery et al.;[71] Lyon et al.;[205] Mason and Sullivan;[222] Bloom et al.;[41] Lawson et al.[191]). Sorption/desorption phenomena and precipitation reactions are also likely to affect Hg bioavailability (King et al.[177]) and need to be taken into account when estimating rates of MMHg production in the natural environment (Bisogni[35]).

D. Influence of Environmental Factors on Hg Partitioning

The cycling and distribution of Hg between the sediment and water phases may be physically, chemically, or biologically mediated, and hence may be affected by parameters such as pH, temperature, redox changes, availability of nutrients and complexing agents. This should be considered when evaluating the effect of environmental factors on Hg methylation. The degree of binding of MMHg by sediments, for instance, depends on sediment properties as well as pH and dissolved oxygen concentrations (Reimers et al.;[275] Kudo et al.;[182] Gambrell et al.[116]). Although the proportion of Hg in dissolved form may sometimes decrease under anoxic conditions due to the formation of reduced species such as HgS (Baeyens and Leermakers[13]), oxic conditions generally favor sediment uptake of Hg and MMHg, whereas anoxic conditions favor Hg release (Wang et al.;[320] Regnell and Tunlid;[272] Regnell et al.[273]). The observed effects are most likely linked to the precipitation and dissolution of Fe and Mn oxides and oxyhydroxides. The solubility of Hg and MMHg under anoxic conditions may also be increased due to the formation of soluble sulfide complexes (Regnell et al.;[273] Benoit et al.[25]). Apart from redox effects, seasonal variations in the partitioning of Hg and MMHg may also be related to changes in biotic particulate matter (Hurley et al.;[149] Watras et al.;[323] Coquery et al.[70]).

Methylmercury release from sediments also increases with increasing temperature and nutrient addition (Wright and Hamilton[339]) and decreasing pH. Miller and Akagi[238] reported that a change in pH from 7.0 to 5.0 doubles the release of MMHg from sediments, and Hintelmann et al.[143] found that the binding of MMHg to humic and fulvic acids decreases with decreasing pH. The observed pH-dependent changes in the partitioning of MMHg between the sediment and water phases may be partly responsible for the often noted increased Hg concentrations in fish from low-pH lakes (e.g., Lindqvist et al.[199]).

The presence of organic or inorganic complexing agents also affects the partitioning of Hg. The formation of soluble humic complexes may significantly increase the solubility and mobility of Hg in aquatic systems (Miller;[237] Reimers et al.;[275] Miskimmin;[239] Melamed et al.;[234,235] Ravichandran et al.[270,271]), especially above pH 5, while $HgCl_2$ is effectively sorbed at lower pH values (Stein et al.[300] after Bodek et al. 1988). The situation in sediments may be comparable to that in soils, where adsorption of Hg to humus predominates in acidic conditions, and Hg is preferentially sorbed to mineral particles (Fe oxides and clay minerals) in the neutral to alkaline pH range, due to formation of the more particle reactive $HgOH^+$ species (Bringmark[52]). High chloride concentrations appear to reduce the amount of Hg associated with suspended particulate matter and organic colloids, most likely due to competition of Cl^- for binding sites. Increased mobilization of Hg with increasing salinity was observed both in model experiments (Reimers et al.[275]) and in estuarine and marine environments (Cossa and Noel;[72] Cossa and Martin;[73] Leermakers et al.;[195] Guentzel et al.[129]).

E. Accumulation in Aquatic Biota

Mercury, and in particular methylmercury, is effectively taken up by aquatic biota, and bioconcentration factors in the order of 10^4 to 10^7 have been reported (WHO;[332] Stein et al.[300]). Accumulation in the aquatic food chain therefore can be high even at the generally very low environmental MMHg concentrations. While MMHg typically constitutes between 10 and 30% of total Hg in the water phase, more than 85 to 90% of Hg in fish is present in the MMHg form (Grieb et al.;[128] Bloom;[39] Southworth et al.[292]). Other organomercurials are also sometimes detected. Fish caught downstream of a source of phenylmercury effluent contained both methyl and ethylmercury (Ashby and Craig[12] after Frieberg 1971), and methylmercury methanethiol (CH_3HgSCH_3) has been found in shellfish (Ashby and Craig[12] after Kitamura 1963 and Lofroth 1969). The Hg content of aquatic organisms and the percentage present as MMHg usually increases with increasing size and increasing level in the food chain (Boudou and Ribeyre;[48] Meili;[233] Watras et al.;[329] Mason et al.[226]). Hg concentrations in fish often remain high for many years after Hg inputs have ceased or contaminated sediments have been dredged (Rada and Findley;[264] Kudo;[187] Francesconi et al.;[108] Southworth et al.[293]).

The precise factors controlling the accumulation of Hg in aquatic biota are poorly understood. The high tendency of MMHg for bioaccumulation is usually explained by its high stability and lipid solubility, and by its high tendency to bind to -SH groups associated with proteins. However, this alone cannot account for the predominance of MMHg in fish muscle tissue (Mason et al.;[217] Boudou and Ribeyre[48]). MMHg is taken up by fish mainly through their diet, while direct uptake from the water is of minor importance (Bodaly et al.;[45] Boudou and Ribeyre;[48] Meili[233]). Hg concentrations in fish thus are primarily determined by the accumulation of MMHg at the base of the food chain, that is, in phyto- and bacterioplankton (Mason et al.[217,219]; Watras et al.[329]). The predominance of MMHg in fish appears to be the result of its greater trophic transfer efficiency compared with inorganic Hg (Watras and Bloom;[322] Mason et al.[219]). Uptake into biota is influenced by the physicochemical form in which Hg exists in the water. Uncharged lipophilic chloride complexes ($HgCl_2$ and CH_3HgCl) appear to be most bioavailable (Mason et al.[217,219]; Laporte et al.[190]), whereas DMHg and Hg^0 are not bioaccumulated (Morel et al.[243]). A number of other factors such as temperature, DOC, alkalinity, and in particular pH may also influence Hg bioaccumulation as well as methylation (Watras and Bloom;[322] Boudou and Ribeyre;[48] Meili;[233] Watras et al.[329]). The accumulation of Hg in the aquatic food chain has been reviewed recently (Bodaly et al.;[45] Boudou and Ribeyre[48]).

III. METHYLATION OF MERCURY IN THE AQUATIC ENVIRONMENT

A. General Aspects

The methylation of inorganic Hg in waters and sediments constitutes a key step in the cycling of Hg in aquatic systems (Fitzgerald and Mason[106]) and takes place

in both remote and impacted environments (Cossa et al.[74]). It is important to note that since both methylation and demethylation processes occur, environmental MMHg concentrations reflect *net* methylation rather than actual rates of MMHg synthesis. It appears that the combined effect of MMHg production and degradation leads to a state of equilibrium with a near constant level of MMHg in sediments (Beijer and Jernelöv;[23] Pak and Bartha[256]) that rarely exceeds 1 to 1.5% of total Hg concentration (cf. Section II.B.2), whereas the proportion of MMHg in fish and other aquatic biota may be much higher (cf. Section II.E). On the basis of mass balance studies, estimated rates for MMHg production in temperate freshwater lakes currently range from 0.5 to 5 g MMHg per km^2 per year (Watras et al.[328]).

Methylation occurs predominantly in sediments and to a lesser extent in the water column (Olson and Cooper;[251] Robinson and Tuovinen;[277] Callister and Winfrey;[55] Korthals and Winfrey;[180] Xun et al.[343]), but it should be borne in mind that water column methylation is potentially more important, because the volume of water is typically much larger than the volume of surficial sediments. Maximum methylation rates usually occur at the redox boundary, which may vary seasonally and frequently coincides with the sediment-water interface, and decrease with increasing sediment depth (Rudd et al.;[279] Korthals and Winfrey;[180] Matilainen[227]). In tropical systems, the root zones of floating aquatic macrophytes are further important sites of methylation (Mauro et al.;[231] Guimarães et al.[130]).

The effects of environmental factors on MMHg formation and decomposition were studied in the past mainly by relating MMHg concentrations in sediments, water, and aquatic biota to changes in environmental conditions. In recent years the use of radiotracers and stable isotopes has made it possible to distinguish between the two opposing processes of MMHg formation and decomposition, but it must be borne in mind that rates measured after Hg additions may differ considerably from *in situ* rates. Gilmour and Henry[122] give an overview of the techniques that are typically employed for measuring MMHg concentrations and methylation/demethylation rates in aquatic systems, and their limitations.

The methylation of Hg requires the presence of a suitable methyl donor molecule. In the natural aquatic environment, a large variety of potential donor molecules are present, most of which are biologically synthesized. Whereas it had first been assumed that Hg methylation requires the presence of bacteria, both microbially mediated and abiotic methylation mechanisms are now known, although the latter is thought to be of only minor importance.

1. Biomethylation

Biological methylation of inorganic Hg was first observed in sediments from aquaria and lakes and in coastal waters in Sweden (Jernelöv;[167] Jensen and Jernelöv[165]) and has been studied since by many other workers. Hg methylation by organisms may be enzymatic or nonenzymatic. Enzymatic methylation requires the presence of actively metabolizing organisms, while nonenzymatic methylation

requires only the methylated products of active metabolism. Detailed mechanisms for Hg methylation were first proposed by Wood et al.[336] and Landner.[188] Wood et al.[336] suspected that methylcobalamin, a vitamin B_{12} derivative (methylcorrinoid) produced by many organisms, is involved in microbial Hg methylation and suggested that the process involves nonenzymatic transfer of the methyl group of methylcobalamin to the mercuric ion. DeSimone et al.[91] have shown that methyl transfer to Hg^{2+} is a carbanion (CH_3^-) process. Although there are many potential methyl donor molecules in the aquatic environment, methylcobalamin is thought to be the only natural methylating agent capable of transferring methyl groups as carbanions (Ridley et al.[276]). This together with its prevalence in anaerobic ecosystems and living organisms makes it the most likely methyl source for environmental Hg methylation.

Metabolically produced methylcobalamin can spontaneously methylate Hg^{2+} in aqueous solution (Bertilsson and Neujahr;[31] Imura et al.[154]), but little is known about the biochemistry of MMHg formation in the natural environment. Organisms capable of Hg methylation have been found among anaerobes, facultative anaerobes, and aerobes, but the potential for microbial methylation is generally thought to be higher under anaerobic conditions, and sulfate-reducing bacteria have been identified as the principal methylators of inorganic Hg in anaerobic sediments (Compeau and Bartha[66]). Methylation of Hg is generally thought to occur inside bacteria by transfer of a methyl group from a methylcorrinoid donor molecule, although Parkman et al.[258] suggested that methylation is an extracellular process that is enhanced by the activity of bacterial exoenzymes that also catalyze the microbial decompositon of organic matter. Choi and Bartha[60] demonstrated that methylcobalamin is the methyl group donor when divalent Hg is methylated by the LS strain of *Desulfovibrio desulfuricans*. Within the cell, Hg methylation appears to be an enzyme-catalyzed process rather than a spontaneous chemical reaction, with the rate of methylation at pH 7 being 600-fold higher than transmethylation by free methylcobalamin (Choi et al.[62]). The process is oxygen sensitive, with optimal methylation conditions at 35°C and pH 6.5. The enzyme responsible for transferring methyl groups from methylcorrinoid protein to Hg^{2+} has yet to be identified. As biological Hg methylation takes place within microorganisms, cellular uptake of Hg plays a key role in the methylation process. This is discussed in detail in Section III.B.1.

2. Abiotic Methylation

Purely chemical methylation of Hg is also possible if suitable methyl donors are present. DeSimone[90] showed that water-soluble methylsilicon compounds react with Hg^{2+} to form MMHg. Organosiloxanes and other silicone-related substances have also been considered as possible methylating agents (Nagase et al.[248,249]; Watanabe et al.[321]). Akagi et al.[1] demonstrated the photochemically induced alky-

lation of mercuric chloride with methanol, ethanol, acetic acid, and propionic acid. Sewage effluent and industrial wastewater have also been reported as methyl sources in the photochemical methylation of Hg. Hamasaki et al.[136] have summarized some of the available data on photochemical methylation.

Wood[337] suggested Hg methylation can also occur as a result of transmethylation reactions between Hg and lead and tin alkyls used as gasoline additives. Jewett et al.[171] demonstrated that both trimethyl lead chloride and trimethyltin chloride are able to transfer methyl groups to Hg^{2+}. Trimethyl lead was found to be a particularly effective methylator for Hg, and high MMHg concentrations in sediments of the St. Clair River were attributed to transmethylation reactions caused by alkyllead emissions (Beijer and Jernelöv[23] after Jernelöv et al., 1972). More recent investigations of Hg methylation by organolead, organotin, and organoarsenic compounds have been carried out, for example, by Ebinghaus et al.[96]

Humic matter may be another significant environmental methylating agent (Weber[331]). Abiological formation of MMHg by humic compounds has been demonstrated, for example, by Nagase et al.[246,247] The capacity for MMHg formation generally increased with increasing temperature and Hg concentration, but was low at naturally occurring temperatures and pH values. Falter and Wilken[100] have shown that small amounts of MMHg can be formed abiotically at environmentally relevant temperatures and pH values, however. More than 400 pg MMHg, corresponding to ca. 0.05% of the added $^{200}Hg^{2+}$ spike, were produced in the acetone extract of a river sediment within 2 h at 40°C between pH 3 and 7. At 35°C, up to 160 pg could still be formed. In the river sediment itself, however, methylation was only detected at 40°C, with between 50 and 100 pg MMHg (0.005 to 0.01% of added $^{200}Hg^{2+}$) being formed.

Thus, mercury methylation may be biotic or abiotic, or may involve a mixture of biotic and abiotic processes, such as the bacterial methylation of tin (IV) species followed by abiotic methyl transfer to Hg. The relative importance of abiotic vs. biotic methylation mechanisms in the natural aquatic environment has not yet been established, but it is generally believed that Hg methylation is predominantly a microbially mediated process, and Berman and Bartha[30] demonstrated that in anoxic sediments MMHg levels resulting from chemical methylation were approximately one order of magnitude lower than those formed by biochemical Hg methylation. Ebinghaus et al.[96] reported that organo Pb, Sn, and As compounds are more effective methylators than biogenic methyl donors such as methylcobalamin, but this is probably not material in the natural environment, because *in vivo* Hg methylation is enzymatically catalyzed and is much faster than transmethylation by free methylcobalamin (Choi et al.[62]).

3. Methylation Products

MMHg may be formed from ionic Hg and many divalent Hg compounds (Yamada and Tonomura[344]), as well as from organic Hg compounds and metallic

Hg (Jernelöv;[168] Jacobs and Keeney[162]), possibly via formation of Hg^{2+}. DMHg can be synthesized from both methyl- and ionic Hg (Craig and Moreton;[85,86] Baldi et al.;[18] Filipelli and Baldi[102]). There is still considerable uncertainty, however, regarding the pathways of MMHg and DMHg formation. Filipelli and Baldi[102] have demonstrated that the initial product of the reaction between methylcobalamin and Hg^{2+} is MMHg, which is then further transformed into DMHg. The reaction is pH and temperature dependent and MMHg and DMHg formation rates are of similar magnitude at 20°C. Low pH values appear to favor the production of MMHg, while DMHg formation is favored under neutral and basic (pH>7) conditions (Jensen and Jernelöv;[165] Beijer and Jernelöv;[23] Fagerström and Jernelöv[99]). Below pH 5, DMHg is thermodynamically unstable and decomposes to form MMHg (Fagerström and Jernelöv;[99] Fitzgerald and Mason[106]), which may be one reason why DMHg has not been detected in freshwaters, where the pH is typically lower compared with estuarine and marine systems. Mason et al.[218] suggested that DMHg forms directly from Hg(II), but is rapidly decomposed to MMHg in freshwaters and hence does not accumulate to detectable levels. In deep ocean waters, on the other hand, the stability of DMHg might be enhanced by low-light, low-temperature, and high pH conditions (Fitzgerald and Mason;[106] Mason et al.[221]). Pongratz and Heumann[259,260] have also suggested that DMHg may be the primary biogenic methylation product in the ocean, and it appears that MMHg in the deep ocean is formed by decomposition of DMHg (Mason and Fitzgerald;[210,212] Fitzgerald and Mason;[105,106] Mason et al.;[221] Mason and Sullivan[223]). DMHg decomposition is thought to be primarily abiotic (Fitzgerald and Mason[106]), whereas MMHg decomposition is predominantly biologically mediated (see below). Because DMHg formation in the ocean also occurs in oxygenated environments (Mason et al.;[218,221] Cossa et al.[75]), it has been suggested that it may be formed by a different mechanism than in freshwaters (Mason et al.;[220,221] Fitzgerald and Mason[106]).

4. Demethylation

The biological and abiological decomposition of methylated Hg species is an important process regulating the organic Hg content of sediments and waters. MMHg degradation is thought to be predominantly microbially mediated (Robinson and Tuovinen[277]). Numerous bacterial strains capable of demethylating MMHg are known (Spangler et al.;[294,295] Billen et al.;[32] Robinson and Tuovinen;[277] Oremland et al.;[254] Matilainen and Verta[228]), including both aerobic and anaerobic species, but demethylation appears to be predominantly accomplished by aerobic organisms (cf. Section III.B.5). Bacterial demethylation has been demonstrated both in sediments (e.g., Billen et al.;[32] Oremland et al.[254]) and in the water column of freshwater lakes (Xun et al.;[343] Winfrey and Rudd;[335] Matilainen[227]). Degradation of methyl and phenyl mercury by fresh water algae has also been described (Beneš and Havlík[24] after Havlík *et al.*, 1979a,b).

Mercury demethylation by bacteria appears to be a predominantly reductive process (Furukawa et al.;[111] Spangler et al.;[294,295] Nelson et al.[250]). The commonly accepted mechanism of microbial MMHg decomposition involves cleavage of the carbon-mercury bond by the organomercurial lyase enzyme, yielding methane and Hg^{2+}, followed by the reduction of Hg^{2+} to Hg^0 by the mercuric reductase enzyme (Robinson and Tuovinen;[277] Summers;[309] Walsh et al.[319]). Synthesis of these enzymes is encoded by the *merB* and *merA* genes in bacteria possessing broad-spectrum Hg resistance. More recent work indicates that *mer* detoxification is not the only microbial degradation pathway, however. Oremland et al.[254] found that while methane was the sole product of MMHg degradation in aerobic estuarine sediments, aerobic demethylation in freshwater sediments and anaerobic demethylation in both freshwater and estuarine sediments produced primarily carbon dioxide, indicating the presence of an oxidative pathway. Oremland et al.[255] and Hines et al.[141] have since shown that oxidative demethylation is significant in both contaminated and uncontaminated river sediments and is most pronounced at sediment surfaces. Inhibitor studies suggest that both sulfate reducers and methanogens, and possibly other anaerobes, are involved in oxidative demethylation (Oremland et al.;[254,255] Marvin-Dipasquale and Oremland[209]). Marvin-Dipasquale and Oremland[209] recently have proposed specific mechanisms for the oxidative demethylation of Hg by sulfate-reducing bacteria and methanogens and have suggested that methanogens dominate MMHg degradation at *in situ* concentrations. Either process produces Hg^{2+}, but it is unclear whether the Hg^{2+} produced in oxidative demethylation is subsequently reduced to Hg^0 as has been demonstrated for the *mer*-mediated pathway (Robinson and Tuovinen[277]). Alternatively, it may be remethylated, bound by sulfur species, or volatilized as DMHg (Baldi et al.[16]). At present, it is also not known which of the abovementioned degradation pathways (i.e., organomercurial-lyase, or oxidative demethylation by sulfate reducers and/or methanogens) dominate under specific environmental conditions. The relative importance of these pathways has major implications for the fate of Hg in natural systems, however, and thus may ultimately determine its residence time in sediments.

Photolytic decomposition appears to be the only significant *abiotic* decomposition mechanism. DMHg in the atmosphere is photolytically decomposed to Hg^0 and hydrocarbons (Craig[82]). Phenylmercury and sulfur-bonded MMHg species (e.g., CH_3HgS^-) can undergo quite rapid photolytic decay, but photodegradation was thought to be insignificant for methylmercuric ion and methylmercuric hydroxide due to their low sunlight absorption rates (Baughman et al.[22]). Suda et al.[307] have shown that methyl- and ethylmercury are photodegraded by singlet oxgen in seawater, however, and recent work by Sellers et al.[289] demonstrates that MMHg is photolytically decomposed in surface waters, and that this process is potentially an important step in the aquatic Hg cycle. Mass-balance calculations show that microbial demethylation may not be the dominant removal mechanism for MMHg in epilimnetic freshwaters. Model simulations by Branfireun et al.[50] have since

confirmed the findings of Sellers et al.[289] The overall impact of photodegradation on the aquatic Hg cycle is still unclear, however, because the end products of MMHg photodegradation in natural waters have not yet been identified. Furthermore, although photolytic decay contributes to Hg demethylation in the water phase, it is unlikely to be significant in deeper sediments, where bacterial demethylation is more important (Xun et al.;[343] Ramlal et al.[268]).

The ability of microorganisms to degrade Hg can be employed in the treatment of sewage (Hansen et al.[138]) and Hg-contaminated liquid wastes (Baldi et al.[16,17]). Hansen et al.[138] reported that >98% of Hg present at a concentration of 70 mg l^{-1} can be removed from municipal sewage water by bacterial treatment. However, it should be noted that sewage treatment plants themselves can be sources of MMHg (Gilmour and Bloom;[124] Carpi et al.[57]). In the bioremediation field, efforts have been made to devise methods for reducing the amount of MMHg in contaminated aquatic ecosystems by stimulating the bacterial conversion of MMHg and Hg^{2+} to less harmful elemental Hg (Saouter et al.[284]). Very recently, transgenic plants have been specifically engineered to express bacterial *mer* genes (Rugh et al.;[281] Bizily et al.[36]). Such plants show a high resistance to inorganic Hg and organomercurials and may in the future be used to degrade MMHg at polluted sites and to accumulate Hg for later safe disposal.

B. Factors Affecting Methylation

The synthesis of MMHg in aquatic systems is influenced by a wide variety of environmental factors. The efficiency of microbial Hg methylation generally depends on factors such as microbial activity and the concentration of bioavailable Hg (rather than the total Hg pool), which in turn are influenced by parameters such as temperature, pH, redox potential, and the presence of inorganic and organic complexing agents. Total Hg concentrations generally are not useful in predicting MMHg concentrations (Kelly et al.[174]). While there is no simple relationship, it appears that enhanced rates of MMHg production are linked in particular with low pH, low salinity, and the presence of decomposable organic matter in reducing environments. The main factors known to affect methylation are discussed below; it should be borne in mind, however, that they cannot be viewed independently from each other, as they often interact, forming a complex system of synergistic and antagonistic effects.

1. Microbiology

Microorganisms play a pivotal role in aquatic Hg cycling and catalyze many of the inter-conversions between different forms of Hg, such as the conversion of Hg^{2+} to methyl and dimethyl Hg and the reduction of Hg^{2+} to Hg^0 (Summers and

Silver;[308] Robinson and Tuovinen;[277] Silver[290]). Mercury compounds are acutely toxic to freshwater microorganisms, but many bacteria are known to have developed resistance mechanims (Baldi;[19] Hobman and Brown[145]), and positive correlations are often found in sediments between the distribution of Hg compounds and Hg-resistant microorganisms (Timoney et al.;[312] Bubb et al.[53]). Bacterial Hg resistance is inducible and is regulated by the *mer* operon (Baldi[19]). Hg volatilization is regarded as a detoxification mechanism, whereas Hg methylation appears to be an accidental process and not a detoxification mechanism as previously suggested.

A large number of organisms, including strict and facultative anaerobes as well as aerobes, have been shown to methylate Hg *in vitro* (Wood et al.;[336] Kitamura et al.;[179] Yamada and Tonamura;[344-346] Vonk and Sijpesteijn;[318] Robinson and Tuovinen[277]), but it is not certain whether these bacteria are responsible for Hg methylation in the natural aquatic environment. Several more recent studies have indicated that anaerobic sulfate-reducing bacteria (SRB) are the principal methylators of inorganic Hg in both freshwater and estuarine sediments (Compeau and Bartha;[66,67] Berman and Bartha;[29] Gilmour and Henry;[122] Gilmour et al.[123]). Contrary to earlier assumptions (e.g., Wood et al.[336]), methanogenic bacteria seem to play only a minor role in MMHg production. Interestingly, the same bacteria that are primarily responsible for MMHg production also appear to mediate MMHg degradation (Robinson and Tuovinen[277]). Both sulfate reducers and methanogens are important demethylators in estuarine and freshwater sediments (e.g., Oremland et al.;[254,255] cf. Section III.A.4). In pure culture, the formation of DMHg from MMHg is also mediated by SRB (Baldi et al.[16,18]). DMHg formation in the ocean is thought to be microbial (Pongratz and Heumann;[259,260] Mason and Sullivan[223]), but is is not known whether SRB or other organisms are the primary methylators (Mason et al.;[220,221] Fitzgerald and Mason[106]).

Hg methylation activity in sediments is often significantly correlated with sulfate-reduction rates (Choi and Bartha;[61] King et al.[177,178]) or with the distribution of SRB populations (Devereux et al.;[92] Macalady et al.[207]), but not all SRB are capable of Hg methylation. Many studies have focussed on *Desulfovibrio* populations (e.g., Baldi et al.;[16] Choi and Bartha;[60] Choi et al.[62]) but recently King et al.[178] have noted that SRB capable of acetate utilization (i.e., members of the family *Desulfobacteriaceae*) appear to methylate Hg more effectively than members of the *Desulfovibrio* group. Macalady et al.[207] also found that *Desulfobacter* populations are important methylators in lake sediments and that they were more abundant than *Desulfovibrio*.

The efficiency of microbial MMHg production appears to depend chiefly on the activity and structure of the bacterial community (Macalady et al.[207]), Hg availability, the availability of nutrients, and the abundance of electron acceptors such as sulfate (Choi and Bartha[61]). At low concentrations, sulfate stimulates both sulfate reduction and methylation (Compeau and Bartha;[66] Gilmour et al.[123]). The *in situ* addition of small amounts of sulfate thus may lead to increased MMHg production in freshwater environments when sulfate is limiting (Gilmour et al.;[123]

Branfireun et al.[51]). Although a sulfate concentration of <10 mg l^{-1} (0.1 m*M*) generally starts to become limiting for the activities of SRB (Ingvorsen et al.;[155] Lovley and Klug[203]), they can remain active even at the very low sulfate concentrations (ca. 3 mg l^{-1}, 0.03 m*M*) typically encountered in freshwater systems by successfully competing with methanogens for common substrates, that is, hydrogen and acetate (Lovley and Klug;[203] Matilainen[227]). Compeau and Bartha[66] reported that the methylating potential of SRB is highest when sulfate is limiting and other organic substrates are available that can be utilized in place of sulfate, which may be due to the inhibitory effect of sulfide on Hg methylation. At high sulfate concentrations, the accumulation of sulfide generated by sulfate respiration interferes with Hg methylation, thereby limiting MMHg production (e.g., Baker et al.;[15] Compeau and Bartha;[66,67] Winfrey and Rudd[335]). Sulfide inhibition was previously ascribed to HgS precipitation, but is now thought to be linked with charged Hg-S complexes (cf. Section III.B.6). Gilmour and Henry[122] proposed an optimal sulfate concentration range of 0.2 to 0.5 m*M* SO_4^{2-} for Hg methylation by SRB in sediments, above which methylation is inhibited, and below which sulfate becomes limiting for methylation and sulfate-reduction processes. For comparison, seawater has ca. 28 m*M* or 2.7 g l^{-1} SO_4^{2-} (Ingvorsen et al.[155]), which may explain the typically low MMHg levels encountered in estuarine and marine environments (cf. Section III.B.7). Methylation is only partly inhibited by sulfur chemistry, however. For example, King et al.[177] have observed active MMHg formation in the presence of 30 m*M* sulfate and millimolar concentrations of dissolved sulfide. The addition of amorphous Fe(III) oxyhydroxide to sediments may inhibit both sulfate reduction and methanogenesis (Lovley and Phillips[204]), probably due to iron-reducing bacteria suppressing hydrogen and acetate concentrations. Whether this might lead to lower Hg methylation rates in Fe(III)-rich sediments still needs to be determined, however.

Many researchers have noted that net MMHg production in methylation experiments is highest in the first few days or weeks of equilibration (depending on study), after which accumulation apparently stops, and in some cases MMHg concentrations decline, and some studies have noted a cyclical production pattern for MMHg (Jacobs and Keeney;[162] Spangler et al.;[295] Hamdy and Noyes;[137] Olson;[253] Furutani and Rudd;[112] Ikingura and Akagi[153]). It has been suggested that cyclical variations in the supply of bacterial substrates may be the cause (Stary et al.[297]), but changes in the bacterial population may be a more likely explanation. Bacterial life stages can also affect the speciation and fate of Hg, but the available data appear contradictory. Ramamoorthy et al.[266] found growing bacterial cells promote Hg^0 formation, whereas living but nongrowing cells cause demethylation, and dead cells lead to the formation of MMHg. This would appear to agree with Parkman et al.,[258] who suggested Hg methylation is an accidental process that does not require the presence of living bacterial cells. In contrast, Ebinghaus et al.[96] observed active methylation during the phase of exponential growth of sediment bacteria, whereas demethylation became dominant when the bacterial population

began to die off, and Pongratz and Heumann[260] reported methylated Hg species were preferably formed in the stationary period of bacterial growth.

Compeau and Bartha[65] reported MMHg concentrations approached a steady state after 8 to 12 days of incubation, but renewed addition of Hg^{2+} resulted in MMHg synthesis at the previous rate. The percentage of total Hg converted to MMHg declined significantly with increasing spiking levels, however, a phenomenon that has also been noted by other authors (Berdichevsky et al.;[28] Jeffries;[164] Lexmond et al.;[197] Robinson and Tuovinen[277]). Chen et al.[59] observed an increase in methylation rates when the $HgCl_2$ spike was less than or equal to 15.3 $\mu g\ g^{-1}$ d.w., whereas microbial methylation activity appeared to be inhibited at concentrations exceeding this value. Sediments containing high levels of Hg have also shown higher rates of demethylation compared with less-contaminated sediments (Gilmour and Henry;[122] Oremland et al.[255]). The results suggest that high concentrations of inorganic Hg may depress MMHg production or may favor demethylation. In water samples, on the other hand, an increase in specific methylation rates that was proportionally greater than the increase in added Hg^{2+} was observed, possibly due to increased availability of Hg following the saturation of binding sites (Xun et al.[343]). The above results may explain why the ratio of methyl : total Hg in sediments or waters is frequently found to increase with increasing distance from the pollution source (e.g., Suchanek et al.;[305] Hines et al.[141]). The apparent cyclical nature of the methylation process together with a possible inverse relationship of net MMHg production with total Hg concentrations may be one reason why MMHg levels in sediments rarely exceed a threshold value of 1%.

The availability of nutrients is an important factor controlling microbial Hg methylation in aquatic systems (Jernelöv;[169] Langley;[189] Wright and Hamilton[339]). Methylation and sulfate reduction rates therefore are generally highest in the upper layers of sediments, where microbial activity and nutrient supply are greatest, and on suspended organic material (Jernelöv;[169] Callister and Winfrey;[55] Korthals and Winfrey;[180] Jorgensen and Bak;[172] Bubb et al.;[53] Choi and Bartha;[61] Gilmour et al.;[125] Bloom et al.;[41] Hines et al.[141]). Microbial DMHg formation in the ocean is also driven by the supply of labile organic matter (Mason and Sullivan[223]). Many studies have found a positive correlation between sediment organic matter content and MMHg production (Callister and Winfrey;[55] Jackson;[158] Choi and Bartha;[61] Hadjispyrou et al.;[133] Pak and Bartha[256]). Macalady et al.[207] observed a correlation between microbial community structure and organic carbon content and suggested that organic-rich sediments support microbial communities with higher Hg methylation activity per unit of microbial biomass. Because of the generally stimulating effect of organic matter on microbial activity, bacterial demethylation rates may also be increased (Ramlal et al.;[268] Pak and Bartha[256]). Ramlal et al.[268] found net MMHg production in organic-rich soils from a recently flooded reservoir was always higher compared with clay sites, but the organic sites also had rapid demethylation rates.

The creation of new hydroelectric reservoirs and enlargement of lakes significantly increases MMHg production, leading to elevated Hg concentrations in fish that can remain high for several decades (Morrison and Therien;[244] Jackson;[161] Bodaly et al.;[45] Schetagne et al.[286]). Kelly et al.[175] found that MMHg production increased by almost 40 times following the experimental flooding of a boreal forest wetland. Recent data by Montgomery et al.[241] indicate that dissolved MMHg concentrations in flooded environments are on average about four times greater than in natural lakes. It is thought that the flooding of vegetation and soils releases associated inorganic Hg as well as large amounts of organic matter and nutrients, thereby stimulating microbial methylation activity (Porvari and Verta;[261] Bodaly et al.[45]). The effect is enhanced further by the prevailing anaerobic conditions, but it may be mitigated by the provision of additional Hg-binding sites when an excess of organic substrates is supplied (Jackson[161]). Surprisingly, reservoir creation does not appear to increase microbial demethylation rates (Bodaly et al.[45]).

The availability of Hg to methylating bacteria is frequently believed to be determined by the concentration of free Hg^{2+} ions. However, microbial uptake of Hg involves diffusive transport of Hg across bacterial membranes, which are known to have higher permeability for uncharged molecules than for ionic species (e.g., Gutknecht[131,132]). Whereas uncharged $HgCl_2$ may diffuse rapidly through lipid bilayers, charged chloride complexes HgOHCl and $Hg(OH)_2$ do not cross membranes at a significant rate under physiological conditions, for example (Gutknecht[131]). Recent studies (Mason et al.;[219] Barkay et al.;[20] Benoit et al.;[26] Wright and Mason[340]) therefore have suggested that Hg bioavailability is controlled by the concentration of neutral dissolved Hg complexes. $HgCl_2$ may be the key chemical species determining cellular uptake of inorganic Hg in oxic waters (Morel et al.[243]), while uncharged HgS^0, bisulfide $Hg(SH)_2^0$, or polysulfide HgS_n^0 complexes may be important for bacterial uptake in anoxic waters (Hudson et al.;[148] Benoit et al.;[26] Jay et al.[163]). Wright and Mason[340] speculated that there may be other mechanisms of uptake besides passive diffusion, because bioavailability is reduced but not inhibited by organic complexation (Barkay et al.[20]).

Other factors that may affect microbial Hg methylation and/or demethylation are discussed in the following. In many cases these parameters appear to affect methylation by controlling the bioavailability of inorganic Hg. Net MMHg production rates in natural aquatic systems appear to depend to a large extent on the environmental conditions that determine whether bacterial methylation or demethylation will dominate.

2. Temperature

It has been observed frequently that Hg methylation rates in aquatic systems peak during the summer months (Jackson et al.;[157] Callister and Winfrey;[55] Korthals and Winfrey;[180] Bubb et al.;[53] Hintelmann and Wilken;[142] Watras et al.[326]). Most

studies have shown maximum methylation activity occurs during mid or late summer, although Bloom et al.[41] found a sharp peak in sediment MMHg production in early spring, followed by a slow decrease throughout the remainder of the year. Seasonal variations in MMHg production and decomposition generally have been attributed to temperature effects, but are probably also linked with seasonal changes in productivity/nutrient supply and redox conditions (cf. Section III.B.5).

Temperature most likely affects methylation as a result of its effect on the overall microbial activity (Bisogni and Lawrence[34]). Wright and Hamilton[339] noted that MMHg release from sediments at 4°C was only 50 to 70% of that observed at 20°C, suggesting that net MMHg production may be significantly decreased in winter due to lower rates of growth and metabolic activity, and Callister and Winfrey[55] reported microbial Hg methylation in surficial river sediments had a temperature optimum of 35°C. Korthals and Winfrey[180] found that while both temperature and anoxic conditions were important factors influencing net methylation, temperature alone accounted for about 30% of the variation. The data suggested that increased net MMHg production was partly due to decreased demethylation rather than an increase in the actual methylation rate, however. Several other workers have also found that demethylation is favored by low temperatures, whereas higher temperatures favor methylation, leading to a large increase in net MMHg production in the summer (Bodaly et al.;[44] Ramlal et al.[269]). Abiotic methylation by humic substances has also been shown to gain in importance with increasing temperature (cf. Section III.A.2), but it is probably of little/minor significance compared with biotic methylation. In contrast to the findings of Ramlal et al.[269] and Bodaly et al.[44], Matilainen et al.[229] found that the highest rates of *both* methylation and demethylation in surficial lake sediments coincided with maximum temperatures. Similarly, Matilainen and Verta[228] found microbial demethylation rates in aerobic surface waters of small forest lakes (up to 13.2% d^{-1}) were decreased by low temperatures.

Temperature is clearly an important factor controlling both methylation and demethylation. It appears that moderately high temperatures have a stimulating effect on Hg methylation, which is most likely due to increased microbial activity. Together with seasonal changes in oxygen levels and organic content/primary production, this seems to account for the increased MMHg production rates usually observed in the summer. The results for Hg demethylation are somewhat contradictory, but most workers found demethylation is favored by lower temperatures. It may be that the rate of methylation increases faster than the rate of demethylation with increasing temperature.

3. pH

The effect of pH on the methylation of Hg has received considerable attention over the last 2 decades, in particular with regard to lakewater acidification caused

by atmospheric deposition. Many workers have noted elevated Hg levels in fish from acidified lakes (e.g., Scheider et al.;[285] Akielaszek and Haines;[2] Wren and McCrimmon;[338] Lindqvist et al.;[199] Håkanson et al.;[135] Spry and Wiener[296]), and there has been concern that low pH values may lead to an increase in the production and/or bioaccumulation of MMHg. Modeling results suggest that observed inverse correlations between lakewater pH and fish Hg content are due to a combination of generally higher MMHg concentrations at low pH and lower bioconcentration factors at high pH (Hudson et al.[148]). There are, however, many ways in which pH changes may influence MMHg concentrations in aquatic systems, and the effect of pH is not necessarily a direct effect on methylation rates. The solubility and mobility of Hg and MMHg is pH dependent, for example, and acid rain/snow may increase Hg inputs from watersheds (Lee and Hultberg[193]). Furthermore, the added sulfate may stimulate MMHg production (Gilmour et al.;[123] Branfireun et al.[51]). Acid mine drainage, which typically is high in sulfate, has also been linked to elevated MMHg concentrations in lake water (Suchanek et al.[306]).

Low pH conditions generally facilitate the release of heavy metals from sediments and particulate matter, but data on the partitioning and mobility of Hg are somewhat contradictory. Some workers have noted that the mobility of Hg is higher in the acidic pH range (Beijer and Jernelöv;[23] Duarte et al.[94]), but Jackson et al.[156] found that Hg was not leached from sediments by HCl, and Schindler et al.[287] reported that lakewater acidification caused a higher proportion of Hg to bind to particulates, thereby decreasing the solubility of Hg in the water column. The amount of dissolved Hg in sediment porewater was also found to decrease with decreasing pH (Ramlal et al.[267]). The available data on the pH-dependent partitioning of MMHg between the sediment and water phases and the transport of MMHg in watersheds (cf. Sections II.C and II.D) strongly suggest that the solubility of MMHg is increased at low pH values. Thus, lakewater acidification probably does not result in the release of Hg^{2+} from organic sediments, but affects the partitioning of MMHg.

Several studies have indicated that the volatilization of Hg^0 may be positively correlated with lakewater pH (Winfrey and Rudd[335] after Rada et al., 1987, Hudson et al.;[148] Watras et al.[326]), which may decrease Hg(II) substrate concentrations for methylation in high pH waters (Fitzgerald et al.[103]). Modeling calculations by Hudson et al.[148] predict an increase in the ratio of Hg^0/Hg(II) and Hg^0 evasion rates with increasing pH, whereas low pH values favor methylation over Hg(II) reduction. In agreement with this, Watras et al.[326] observed an increase in Hg^0 and a corresponding decrease in MMHg with increasing pH values. High pH values also favor the formation of volatile DMHg (cf. Section III.A.3). Neutral and slightly alkaline conditions thus may reduce MMHg concentrations, whereas low pH waters may contain a relatively higher share of MMHg. This would appear to agree with Swedish field studies that have shown that the treatment of lakes with lime to raise lakewater pH can help reduce the Hg content of fish (e.g., Andersson and Håkanson[10]).

The effect of pH on Hg methylation has been studied both in waters and sediments. MMHg concentrations in lake water generally have been found to increase with decreasing pH (e.g., Xun et al.;[343] Bloom et al.;[40] Miskimmin et al.[240]). Xun et al.[343] reported that net MMHg production in lake water was about seven times faster at low pH (ca. 4.5) than at high pH (ca. 8.5), although in samples that were artificially acidified the observed effect may have been partly due to sulfate stimulation. A pH decrease at the aerobic sediment-water interface resulted in a two- to threefold increase in MMHg production. Miskimmin et al.[240] also reported that a reduction in lakewater pH from 7.0 to 5.0 led to significant increases in net methylation rates. In anaerobic sediments, on the other hand, net MMHg production was generally found to be decreased at low pH values (Steffan and Winfrey;[298] Furutani et al.;[113] Ramlal et al.;[267] Steffan et al.[299]). The acidification of surficial lake sediments always resulted in a significant decrease in ^{203}Hg methylation rates. Ramlal et al.[267] reported that the decrease in ^{203}Hg methylation with decreasing pH appeared to be linked to a reduction of available inorganic Hg in the sediment porewater, which may have been due to increased sorption to particles at low pH. Aerobic methylation in surface sediments was also found to decrease with decreasing water pH (Matilainen et al.[229]).

Demethylation rates are also pH sensitive. Matilainen et al.[229] observed a decrease in anaerobic demethylation in surface sediments with decreasing water pH and speculated that high MMHg concentrations found in the anoxic bottom waters of stratified, low pH lakes may be partly the result of a decrease in demethylation rather than an increase in methylation. Other workers have also found a decrease in demethylation activity at low pH values, but in general demethylation rates in both sediments and lake water were found to be much less affected by pH than methylation rates (Ramlal et al.;[267] Xun et al.;[343] Steffan et al.[299]), indicating that the changes observed in net MMHg production are largely due to an effect of pH on methylation rather than demethylation. However, the results of Ramlal et al.[267] and Steffan et al.[299] show that in sediments demethylation may gain in importance at low pH values. Steffan et al.[299] found little change in demethylation over the pH range 8.0 to 4.5, but methylation decreased sharply with decreasing pH, leading to a substantial increase in the relative importance of demethylation vs methylation under acidic conditions. This may also explain why Ramlal et al.[267] did not observe methylation below pH 5.0.

One of the ways in which pH might affect methylation may be by decreasing microbial activity under acidic conditions, causing a corresponding decrease in bacterial methylation rates. The published literature indicates that microbial activity in lakes is not reduced after acidification, however. Furutani et al.[113] and Kelly and Rudd[173] reported that acidification did not affect general microbial activity ($CO_2 + CH_4$ production) in sediments, and Miskimmin et al.[240] found that microbial respiration rates had only a very small effect on net MMHg production in lake water and were insensitive to pH changes between pH 5 and 7. However, there are indications that the activity of sulfate-reducing bacteria may be significantly

decreased in the acidic pH range (Connell and Patrick[68]), and Furutani et al.[113] observed a decrease in sulfate reduction at low pH that was independent of general microbial activity. It may also be that pH affects the population distribution of methylating vs. demethylating bacteria in sediments such that demethylation processes dominate at low pH values. This would agree with the results obtained by Ramlal et al.[267] and Steffan et al.[299] and might merit further investigation. It is also possible that pH affects cellular uptake of Hg, but Gutknecht[132] found that the diffusion of Hg^{2+} through lipid bilayer membranes was only dependent on Cl^- concentrations and not on pH.

In summary, it appears that acidic conditions generally favor Hg methylation in lake water and at the sediment/water interface, whereas methylation in anoxic sediments is decreased, possibly due to increased demethylation activity at low pH values. Lakewater acidification thus may lead to increased methylation in the water phase, but it is unlikely to substantially affect methylation in deeper sediments. The observed differences in the effect of pH on Hg methylation in waters and sediments may be related to differences in redox conditions: whereas sediments were generally studied under anoxic conditions, the water samples appear to have been oxygenated to some degree.

It is not clear whether the stimulation of methylation in lake water is a direct effect of low pH on the methylation process, or whether it is related to other factors that are influenced by pH, such as the loss of volatile Hg species from water surfaces, or changes in Hg solubility and partitioning. Winfrey and Rudd[335] hypothesized that the likely decrease in DOC binding sites at low pH values resulting from the protonation of functional groups may stimulate methylation by promoting Hg binding directly onto microbial cells. Increased MMHg concentrations in the water phase at low pH are also likely to be partly attributable to increased desorption of MMHg from surficial sediments (Miller and Akagi;[238] Hintelmann et al.[143]), and thus do not necessarily reflect increased methylation.

It should be mentioned briefly that the abiotic methylation of Hg by organic substances is also pH dependent, but the data are somewhat contradictory (Nagase et al.;[246,247] Varshal et al.;[315] Falter and Wilken[100]). Nagase et al.[246] reported that MMHg formation in fulvic acid solution was strongly enhanced at pH 4 and declined at higher pH values, whereas Varshal et al.[315] found MMHg production increased with increasing pH, for example. While the relative importance of abiotic mechanisms in the methylation of Hg under natural environmental conditions is still unclear, it is generally thought to be low.

4. Organic Material

The role of organic matter in the methylation of Hg is not well understood. Conversion rates of inorganic Hg to MMHg are generally much higher when sediments contain organic substances and can be very high in or near sewage

treatment plants (Jernelöv;[168] Jackson[158]). Observed increases in MMHg concentrations in water, sediments, or fish tissue with increasing levels of organic carbon (Olson and Cooper;[252] Furutani and Rudd;[112] Wright and Hamilton;[339] Lee and Hultberg;[193] Fjeld and Rognerud[107]) generally have been attributed to a stimulating effect of organic nutrients on microbial methylation activity (cf. Section III.B.1), but in some cases transport of (methyl)mercury-DOC complexes to surface waters with runoff (Section II.C) is likely to be an additional factor. Direct abiotic methylation by humic and fulvic acids generally is considered to be of minor importance (cf. Section III.A.2), although it is possible that its influence is increased in organic-rich lakes. However, the data of Porvari and Verta[261] indicate that although humic substances are chiefly responsible for the transport of MMHg, they are not themselves active methylating agents. To date it is not clear to what extent abiotic methylation contributes to MMHg production in organic-rich sediments and lake waters.

Many workers have reported decreased methylation at high concentrations of organic matter, and several studies have suggested that dissolved organic carbon (DOC) may have a mitigating effect on the production and/or bioaccumulation of MMHg in natural waters (Grieb et al.;[128] Jackson;[161] Miskimmin et al.;[240] Driscoll et al.;[93] Watras et al.;[326] Barkay et al.[20]). Miskimmin[239] reported that natural levels of DOC had no effect on the production of MMHg in sediments, although they enhanced the water solubility of MMHg. However, Miskimmin et al.[240] demonstrated that MMHg production in lake water is reduced at high DOC concentrations, presumably as a result of complexation of inorganic Hg with organic matter. A reduction in pH from 7.0 to 5.0 significantly increased methylation rates at both low and high DOC concentrations (500 to 2600 μM), possibly due to competition of H^+ with Hg^{2+} for negatively charged binding sites and increased bioavailability of Hg. Using a bioindicator that responds exclusively to bioavailable Hg^{2+}, Barkay et al.[20] demonstrated that DOC affects the rate of MMHg synthesis by reducing the availability of the Hg^{2+} substrate to methylating bacteria. The exact nature of the Hg-DOC interaction remains unknown, however. The reduction in bioavailable Hg was more pronounced under neutral (pH 7) than under acidic (pH 5) conditions, which is in good agreement with the study by Miskimmin et al.[240]

The availability of Hg for methylation reactions may also be decreased by complexation with sulfur ligands (cf. Section III.B.6). The degradation of organic matter in aquatic environments leads to the production of low-molecular-weight S compounds (Cutter and Krahforst[88]) that can potentially form complexes with Hg^{2+}. On the other hand, increased oxygen consumption during the degradation of organic matter causes progressively more anoxic conditions at the sediment/water interface, which may lead to the mobilization and potential methylation of inorganic Hg (Gagnon et al.;[115] Cossa and Gobeil[78]). DOC also significantly enhances the solubility of HgS (Ravichandran et al.[270]) and may inhibit the precipitation and aggregation of HgS even at low concentrations (Ravichandran et al.[271]).

Humic substances are capable of reducing Hg^{2+} to Hg^0 in aqueous systems (e.g., Miller[237]), which may lead not only to reduced availability of Hg^{2+} for methylation, but potentially also to a reduction in the overall Hg content. Allard and Arsenie[4] suggested Hg^0 production is highest in anaerobic systems in the absence of chloride at a pH of about 4.5, but it is considerably reduced by the presence of competing ions. In contrast to the findings of Miskimmin et al.,[240] Watras et al.[326] observed an increase in the MMHg fraction in Wisconsin lakewaters with increasing levels of DOC, in particular at DOC concentrations >5 mg l^{-1}, whereas the Hg^0 fraction decreased. This is in agreement with modeling calculations by Hudson et al.,[148] which predict that as DOC increases, the fraction of Hg(II) that is reduced declines, while the fraction that is methylated increases. The relative importance of Hg^0 evasion is increased in humic-rich lakes, however, despite the observed decrease in the Hg^0 fraction. Watras et al.[328] hypothesized that high DOC conditions in lakes favor either methylation (at low pH) or evasion (at high pH), whereas low pH low DOC conditions favor sedimentation processes.

The role of humic matter in the methylation of Hg remains unclear. It seems that, on the one hand, organic carbon can enhance methylation by stimulating the activity of heterotrophic microorganisms, or through direct abiotic methylation of Hg by humic or fulvic substances. On the other hand, Hg methylation may be inhibited at high DOC concentrations due to increased complexation of Hg with organic ligands, reducing Hg bioavailability to bacteria, particularly in the neutral pH range. The observed differences may partly reflect different methylation mechanisms. Anaerobic methylation was found to be enhanced by high concentrations of organic matter, presumably due to stimulated microbial growth, whereas aerobic methylation frequently has been observed to be suppressed by high organic matter or particulate concentrations and does not appear to be microbially mediated (cf. Section III.B.5).

5. Redox Conditions

Mercury methylation occurs in both aerobic and anaerobic environments. Early work based on pure culture studies showed that methylation was faster under aerobic conditions (Bisogni and Lawrence;[34] Hamdy and Noyes;[137] Ramamoorthy et al.[266]), but in the natural environment, methylation rates are highest in anoxic sediments and waters, and it is now generally accepted that Hg methylation takes place mainly in anaerobic conditions (Olson and Cooper;[252] Compeau and Bartha;[65] Callister and Winfrey;[55] Craig and Moreton;[87] Jackson;[159] Rudd et al.;[279] Matilainen et al.[229]). Both methylation rates and the stability of MMHg in sediments appear to be enhanced under anaerobic conditions (e.g., Olson and Cooper;[252] Compeau and Bartha[65]), whereas methylation rates are low under aerobic conditions, probably because of the reduced activity of anaerobic sulfate-reducing bacteria. Compeau and Bartha[65] found that Hg methylation in estuarine sediments was strongly

favored at low (-220 mV) E_h, for example, and Callister and Winfrey[55] reported that the oxygenation of sediments inhibited microbial methylation activity. Regnell and Tunlid[272] used radiolabeled $HgCl_2$ in model aquatic systems to demonstrate that Hg methylation in freshwater sediments and water is significantly higher under anaerobic than under aerobic conditions. MMHg concentrations in anaerobically incubated water and sediment samples from a Hg-contaminated lake were also at least an order of magnitude higher than in aerobic incubation (Regnell et al.[273]); both the production and water solubility of MMHg appeared to be increased under anaerobic conditions.

On the other hand, the degradation of MMHg appears to be generally favored by aerobic conditions. Although some workers have found demethylation rates in freshwater sediments were similar under aerobic and anaerobic conditions (Billen et al.;[32] Matilainen et al.[229]), most studies have shown that MMHg degradation is faster under aerobic/high E_h conditions (Olson and Cooper;[252] Compeau and Bartha;[65] Ramlal et al.;[268] Oremland et al.;[254] Ebinghaus et al.[96]). Oremland et al.[254] found that demethylation in estuarine sediments was more rapid and extensive under aerobic conditions, but anaerobic sulfate reducers were also important demethylators, suggesting that there are multiple degradation pathways (cf. Section III.A.4).

It may be that different mechanisms are responsible for Hg methylation under aerobic and anaerobic conditions. Anaerobic methylation was found to be enhanced by high concentrations of organic matter, presumably due to stimulated microbial growth (Olson and Cooper;[252] Compeau and Bartha[65]). Aerobic methylation on the other hand is frequently observed to be suppressed by high organic matter or particulate concentrations, and does not appear to be microbially mediated (Matilainen et al.;[229] Matilainen;[227] Matilainen and Verta[228]). Matilainen[227] found, for example, that aerobic methylation was abiotic and was suppressed by humic compounds and particulate matter, whereas methylation in the anaerobic hypolimnion was microbial. Matilainen et al.[229] reported that aerobic methylation in organic-rich surficial lake sediments was abiotic and was slow compared with anaerobic methylation, but increased in importance with increasing sediment mineral content. Aerobic methylation and the methylation/demethylation ratio correlated positively with the Fe and Mn content of the sediment. The authors suggested that sediments with high metal content may have more bioavailable Hg, owing to the interaction of these metals with sulfur, which would appear to agree with more recent results by Gagnon et al.,[114] who found that high dissolved Fe concentrations in sediment porewaters seem to limit the amount of dissolved H_2S that may potentially interfere with the methylation process. A possible catalytic effect of Fe on Hg methylation can also not be ruled out. Lee et al.[192] reported that Hg methylation in lake waters in the presence of fulvic acid was increased by the addition of metal ions, and in particular Fe.

In most aquatic sediments, only the upper few millimetres are aerobic, while the rest of the sediment is in an anaerobic state. MMHg concentrations are usually highest in the moderately anaerobic surface sediments and rapidly decline with

increasing sediment depth (Korthals and Winfrey;[180] Bubb et al.;[53] Hintelmann and Wilken;[142] Bloom et al.;[41] Hines et al.[141]). In sediment porewaters, MMHg concentrations were very low in the oxic zone, but were high in anoxic layers (Gagnon et al.[114]). Bubb et al.[53] suggested that subsurface maxima of methylation activity just below the sediment/water interface are caused by increased MMHg production under moderately anaerobic conditions, whereas bacterial degradation of MMHg dominates in the oxygenated surface zone, and in deeper sediment layers where conditions are strongly reducing sulfide limits the availability of Hg for methylation (cf. Section III.B.6). MMHg concentrations in sediments are also influenced by the redox cycling of Fe and Mn oxides that partly control dissolved Hg concentrations in sediment porewaters (Gobeil and Cossa;[126] Gagnon et al.[115]), thereby influencing Hg bioavailability. In the oxidized surface layers of marine sediments, Hg was found to be primarily associated with fresh particulate organic matter and Fe and/or Mn oxyhydroxides, which was limiting dissolved Hg concentrations (Gagnon et al.[115]). High dissolved Hg concentrations were observed at the redox boundary, however, due to the accumulation and subsequent dissolution of oxyhydroxides (Gagnon et al.[115]). Similarly, Gobeil and Cossa[126] found that dissolved Hg and Fe concentrations increased below 2 cm from the sediment/water interface.

In the water column, MMHg (and DMHg) production is also related to zones of low oxygen concentration (e.g., Bloom et al.;[40] Hurley et al.;[149] Verta and Matilainen;[316] Mason and Fitzgerald;[211,212] Mason et al.[214]), whereas levels are typically low in the oxic zone, both in freshwater lakes (Bloom et al.;[40] Cossa et al.;[74] Watras and Bloom[323]) and ocean waters (e.g., Mason and Fitzgerald[210,211]). In stratified lakes and estuaries, MMHg concentrations are usually highest in the oxic/anoxic boundary layer and in anoxic water layers (Bloom et al.;[40] Mason et al.;[213] Cossa et al.;[74] Parkman et al.;[258] Verta et al.;[317] Watras and Bloom;[323] Watras et al.;[324] Matilainen[227]). High MMHg concentrations at the oxic/anoxic boundary do not necessarily reflect *in situ* MMHg production, but could result from the accumulation of settling particulate matter. For instance, Matilainen[227] found MMHg concentrations were elevated in the particle-rich oxic/anoxic boundary layer despite low methylation rates (<0.1% d^{-1}), apparently as a result of the settling of particle bound MMHg from the epilimnion. The low net methylation rates were attributed to the binding of Hg to particles and demethylation by heterotrophic bacteria. Cossa et al.[74] also observed a peak in particulate MMHg in the upper region of the redoxcline. The results suggest that methylation occurs mainly in the low oxygen region, but the concentration and distribution of MMHg are strongly influenced by the redox cycling of Fe and Mn at the oxic/anoxic boundary.

Seasonal variations in MMHg concentrations are also strongly linked to changes in redox state. MMHg levels in hypolimnetic waters of seasonally stratified lakes and reservoirs generally increase during summer stratification, and decrease again following fall turnover (Bloom and Effler;[38] Bloom et al.;[40] Watras and Bloom;[323] Watras et al.;[324] Driscoll et al.;[93] Regnell et al.;[274] Canavan et al.[56]). Similar trends

are observed in surface sediments (Korthals and Winfrey[180]). The increased decomposition of organic matter and primary production during the summer months renders sediments and hypolimnetic waters progressively more anoxic, which together with the generally higher temperatures is thought to have a stimulating effect on bacterial methylation activity. Hypolimnetic enrichment of MMHg and Hg in (seasonally) anoxic lake waters may also be due to redox-controlled release of Hg from bottom sediments or sedimenting particles (Hurley et al.;[149,151] Mason et al.[224]). Meili[233] suggested that the build-up of MMHg in anoxic waters may be due to suppressed demethylation rather than enhanced methylation, however. Passive uptake of neutral $Hg(SH)_2^0$ and HgS^0 complexes by methylating bacteria may be another reason for increased Hg methylation in anoxic waters (Hudson et al.;[148] Benoit et al.[26]). Demethylation processes are expected to dominate when hypolimnetic waters are reaerated during lake turnover.

In summary, it is clear that microbially mediated methylation is generally favored by anaerobic conditions, while demethylation is favored by aerobic conditions. On the other hand, abiotic methylation appears to be largely aerobic. Sediment redox state also affects the partitioning of Hg species between the sediment and water phases. Other environmental factors can interact significantly with redox effects, in particular organic matter and pH.

6. Sulfide

Hydrogen sulfide plays an important role in the chemistry of anaerobic sediments where it is produced as a result of bacterial sulfate reduction. Conditions of high sulfide typically develop in anoxic, organic-rich sediments that are high in sulfate, but can also occur in surface waters as a result of industrial or domestic wastewater discharges. Early studies noted that high sulfide concentrations appear to inhibit MMHg formation in soils, sediments, and bacterial cultures (Fagerström and Jernelöv;[98] Bisogni and Lawrence;[34] Yamada and Tonomura;[346] Jacobs and Keeney;[162] Talmi and Mesmer[311]), and significant reductions of MMHg in fish were achieved in aquarium experiments by adding sulfides as S^{2-}, FeS, or FeS_2 (Jernelöv and Åséll[170]). An inverse relationship between (dissolved) sulfide concentration and MMHg production or concentration in sediments or sediment porewaters has also been noted in many more recent studies (e.g., Craig and Moreton;[85] Compeau and Bartha;[64,67] Winfrey and Rudd;[335] Gilmour et al.;[125] Benoit et al.[25,26]). Craig and Moreton[85] found MMHg levels in sediments were initially in direct proportion to sulfide concentrations, but declined sharply beyond a sulfide concentration of about 1.8 mg g^{-1}, and Berman and Bartha[29] observed that Hg added to sediments containing 7.06 mg g^{-1} (d.w.) acid labile and 1.98 mg g^{-1} (d.w.) free sulfide became rapidly unavailable for methylation, whereas increasing amounts of MMHg were formed when the sediment was diluted with a low-sulfide control sediment, or when it was partially depleted of sulfide.

The presence of sulfide clearly decreases the availability of Hg^{2+} for methylation. However, although MMHg production is generally greatly reduced at high sulfide concentrations, it is not usually completely inhibited. Furutani and Rudd[112] found that $^{203}Hg^{2+}$ was actively methylated in anaerobic sediments even in the presence of about 30 $\mu g\ g^{-1}$ of bound sulfide (d.w., as amorphous FeS), for example. Furthermore, MMHg levels in sediments are sometimes found to increase with increasing sulfide concentrations (Hintelmann and Wilken[142]), and in stratified lakes and estuaries high MMHg concentrations are frequently found in the sulfidic boundary layer (Bloom et al.;[40] Mason et al.;[213] Parkman et al.;[258] Verta et al.;[317] Watras et al.;[324] Matilainen[227]).

In the presence of sulfide, Hg forms insoluble HgS (cf. Section II.A). Several early reports indicated that mercury in the HgS form is not readily available for methylation under anaerobic conditions (Fagerström and Jernelöv;[98] Gillespie;[121] Yamada and Tonomura[344-346]). In aerobic conditions, the sulfide may be oxidized to sulfate, leading to increased solubility and greater availability of Hg^{2+} (Fagerström and Jernelöv;[98] Jensen and Jernelöv[166]), but aerobic methylation rates are several orders of magnitude lower compared to anaerobic conditions (Fagerström and Jernelöv;[98] Gillespie and Scott;[120] Jacobs and Keeney[162]). Nevertheless, exposure of contaminated sediments to aerobic conditions may lead to the remobilization and subsequent methylation of Hg (Berman and Bartha[29]).

It is commonly speculated that the inhibitory effect of sulfide on Hg methylation is the result of decreased solubility and bioavailability of Hg^{2+} due to HgS precipitation (e.g., Craig and Bartlett;[84] Gavis and Fergusson;[118] Blum and Bartha;[43]Compeau and Bartha;[64,67] Winfrey and Rudd;[335] Gilmour and Henry[122]). However, high dissolved Hg(II) concentrations in the porewater of sulfidic sediments (Gagnon et al.;[115] Benoit et al.;[25] Bloom et al.[41]) indicate that the solubility of Hg is actually increased in the presence of excess sulfide, most likely due to the formation of soluble sulfide complexes. Furthermore, the lack of a relationship between dissolved Hg(II) concentrations in porewater and MMHg production suggests that Hg^{2+} may not be the main species that is methylated (Benoit et al.[25]). The work of Benoit et al.[25-27] shows that sulfide affects the bioavailability of Hg by controlling Hg speciation. Benoit et al.[26] suggest that the bioavailability of Hg in sediments is determined by the concentration of neutral dissolved Hg complexes such as HgS^0, which may readily diffuse across bacterial cell membranes. Under sulfidic conditions, on the other hand, Hg methylation is inhibited due to the formation of charged disulfide complexes which are likely to be less bioavailable (Benoit et al.[27]). The formation of polysulfides (Paquette and Helz;[257] Jay et al.[163]) and complexes with dissolved organic matter (Ravichandran et al.[270,271]) may contribute to the solubility of Hg in sulfidic environments. Barkay et al.[20] have shown that DOC complexation reduces the availability of Hg to bacteria, but the effect of polysulfide formation on Hg methylation is not clear. Jay et al.[163] speculate that although the formation of charged polysulfide species may decrease the concentration of bioavailable HgS^0, bioavailability could potentially be increased

due to the formation of small concentrations of other lipid-soluble uncharged species such as HgS_5.

A number of studies have suggested that in the presence of high sulfide concentrations, MMHg may be converted to volatile DMHg (Craig and Bartlett;[84] Craig and Moreton;[86] Baldi et al.[16,18]). Craig and Bartlett[84] proposed that the reaction proceeds via the formation of an instable organomercury sulfide intermediate, $(CH_3Hg)_2S$, which decomposes into DMHg and HgS. The volatile hydrophobic DMHg produced may diffuse through the water column and be lost to the atmosphere, potentially leading to a significant reduction in the organic Hg content of sediments (Craig;[83] Craig and Moreton[85]). Craig and Moreton[86] demonstrated the evolution of DMHg from a sediment containing a natural unamended level of MMHg on exposure to sulfide. Baldi et al.[18] have shown that MMHg added to polluted sediments can also be converted to DMHg, but the study was performed under high sulfide and high MMHg conditions that would thermodynamically favor DMHg production. The formation of DMHg is considered a potentially important loss mechanism of MMHg from anaerobic sediments high in sulfide (Craig;[83] Baldi et al.[18]), but it is not clear to what extent it occurs in the natural environment.

7. Salinity

The methylating activity of marine and estuarine sediments is usually lower than that of freshwater sediments (e.g., Olson and Cooper;[251] Blum and Bartha;[43] Compeau and Bartha[67]), which generally has been attributed to salinity effects. Blum and Bartha[43] and Compeau and Bartha[67] observed a strong inverse relationship between the salinity of anaerobic sediments and their ability for Hg^{2+} methylation. High-salinity sediments methylated Hg at only 40% of the level observed in low-salinity sediments (Compeau and Bartha[67]). The inhibitory effect of salinity on Hg methylation is particularly pronounced under reducing conditions, and high-salinity conditions appear to promote demethylation processes (Compeau and Bartha[65]). Low-salinity coastal waters have also been found to contain a relatively higher proportion of MMHg (Coquery et al.[71]).

The negative effect of salinity on Hg methylation appears to be mainly linked with the microbial production of sulfide from sea salt sulfate. However, while MMHg production in sediments is often strongly reduced in the presence of sulfate (Baker et al.;[15] Compeau and Bartha;[67] Winfrey and Rudd[335]), methylation does not necessarily stop at high sulfate concentrations. Compeau and Bartha[67] reported that methylation still occurred at 2.4% salinity, corresponding to 19.5 m*M* sulfate per liter and 7.1 mg sulfide per gram of dry sediment, whereas the same level of sulfide had been found to almost completely inhibit methylation in a freshwater sediment (Berman and Bartha[29]). While it was previously believed that sulfide originating from sulfate-reduction processes limits the bioavailability of Hg in anaerobic

sediments due to HgS formation (Blum and Bartha;[43] Compeau and Bartha;[64,67] Winfrey and Rudd[335]), recent evidence suggests that methylation is inhibited at high sulfide concentrations due to changes in Hg speciation (cf. Section III.B.6).

Not only sulfate, but other sea salt anions may also affect Hg speciation and/or methylation in estuarine and marine environments. Compeau and Bartha[64] demonstrated that bicarbonate has a negative influence on Hg methylation under both aerobic and anaerobic conditions, possibly due to the formation of $HgCO_3$. The authors speculated that the availability of Hg for methylation may hence be higher in 'soft' than in 'hard' (i.e., bicarbonate rich) freshwater systems. Compeau and Bartha[64,67] found no noticeable effect of chloride on Hg methylation, but it has been suggested that the negative charge of mercuric chloride species may reduce their availability to methylating bacteria. Using a mercury-specific bioindicator, Barkay et al.[20] demonstrated that uncharged $HgCl_2$ is indeed more bioavailable than anionic forms. On the basis of the data available to date, it would appear that the formation of charged sulfide and chloride complexes offers the best explanation for the apparently reduced methylation activity in estuarine and marine environments.

IV. SUMMARY AND CONCLUSIONS

Mercury methylation is mainly a microbially mediated process with methylcobalamin being the most likely environmental methyl donor. Abiotic methylation appears to be of minor importance, although its influence may be increased in organic-rich lakes. The precise mechanism of MMHg and DMHg formation is still unclear. Although it is generally believed that DMHg is the final product of Hg methylation, MMHg in the ocean appears to be produced mainly by decomposition of DMHg, indicating that there may be more than one methylation mechanism. More research is also needed into the factors controlling bacterially mediated and abiotic demethylation processes.

Mercury methylation and demethylation rates in aquatic systems are clearly influenced by both the speciation and biochemical availability of Hg and by a large number of environmental variables, many of which are interrelated. Biological activity, nutrient availability, pH, temperature, redox potential, and the presence of inorganic and organic complexing agents all have significant effects, with the net rate of MMHg production being determined by their complex interaction. Which factors dominate is likely to differ from ecosystem to ecosystem. Furthermore, the distribution of Hg between the sediment and water phases as well as the gaseous evasion of volatile Hg species is also influenced by environmental factors. The interrelatedness of these processes has often hampered research into the factors controlling Hg methylation. Nevertheless, certain general trends are apparent. MMHg formation is generally favored under anaerobic conditions, whereas aerobic conditions promote demethylation processes. In stratified lakes and estuaries,

MMHg formation occurs primarily at the oxic/anoxic interface, whether this occurs in bottom waters or surface sediments. Methylation in the ocean is not confined to low-oxygen zones, however, which is another indicator that there may be more than one mechanism for MMHg/DMHg formation. Seasonal variations in MMHg production appear to be mainly related to temperature and redox effects, as well as seasonal changes in productivity and hence nutrient availability. Moderately high temperatures have a stimulating effect on methylation, whereas demethylation processes are favored by lower temperatures. Lakewater acidification may lead to increased methylation in the water column, but in sediments methylation is generally found to be decreased, which may be due to a reduction in the activity of sulfate-reducing bacteria, or increased demethylation. It may also be that different mechanisms are responsible for Hg methylation in waters and in sediments, and there are indications that methylation in the water column may be abiotic and linked to particles. Studies investigating the effect of pH on Hg methylation should consider that increased MMHg concentrations in the water phase are likely to be partly attributable to increased desorption of MMHg from sediments at low pH.

Sulfur chemistry is a particularly important factor controlling methylation. Sulfate-reducing bacteria are important methylators of Hg in anaerobic sediments, and sulfate stimulates microbial Hg methylation at the typically low sulfate concentrations prevailing in freshwater systems. However, at high levels in reducing conditions methylation is inhibited due to sulfide formation, which may be one reason why MMHg levels in sediments rarely exceed 1% of the total Hg concentration. Recent studies have shown that the inhibitory effect of sulfide on Hg methylation is not due to HgS precipitation, but that sulfide lowers the availability of Hg for bacterial methylation by formation of less bioavailable charged Hg-S complexes.

The role of organic matter in the methylation of Hg is not well understood. Humic matter is an important factor controlling the solubility and mobility of Hg in natural waters. Organic nutrients generally stimulate microbial activity and hence Hg methylation, although they may also have an effect on bacterial demethylation activity. Direct abiotic methylation of Hg by humic and fulvic acids has also been reported. On the other hand, high levels of dissolved organic carbon appear to have a mitigating effect on both the production and bioaccumulation of MMHg due to Hg complexation, particularly in the neutral pH range. The formation and dissolution of Hg-OM complexes is pH sensitive, with complexation being reduced at low pH.

Unfortunately, despite a vast body of literature on the subject, we are still unable to predict Hg methylation rates and the likely effects of environmental perturbations on methylation and demethylation processes in aquatic systems. Owing to the complexity of processes in the natural environment, it is difficult to directly compare the results of the studies that have been published to date. Future laboratory-based studies of methylation/demethylation rates that address not only

the direct effects of environmental variables but that place particular emphasis on understanding how these factors interact would be desirable. These studies should aim to quantify Hg transformation rates at environmentally relevant concentrations, thereby providing a more realistic assessment of *in situ* rates than the traditionally large Hg additions. The effect of pH under oxic compared with anoxic conditions should receive particular attention. Further research is also needed on the binding and partitioning of both inorganic and MMHg, which is also influenced by the above-mentioned factors and that may to a certain extent confound the primary effects of these variables on methylation/demethylation rates. This work is particularly important if we are to find more effective ways of minimizing the ecological risk of mercury in the aquatic environment.

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