BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:	)	
	)	
PROPOSED NEW 35 ILL. ADM. CODE 225	)	R06-25
CONTROL OF EMISSIONS FROM	)	(Rulemaking – Air)
LARGE COMBUSTION SOURCES (MERCURY)	)	

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PLEASE TAKE NOTICE that the Environmental Law and Policy Center has electronically filed the attached MICHAEL MURRAY ADDITIONAL REFERENCES IN SUPPORT OF TESTIMONY.

s/ Faith E. Bugel
Faith E. Bugel
Counsel for Environmental Law and Policy Center

DATED: August 11, 2006

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MICHAEL MURRAY ADDITIONAL REFERENCES IN SUPPORT OF TESTIMONY

The following documents are additional references in support of the testimony of Michael Murray which was filed in PCB R06-25 on July 24, 2006.

s/ Faith E. Bugel
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Mercury in the Aquatic Environment: A Review of Factors Affecting Methylation

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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

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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

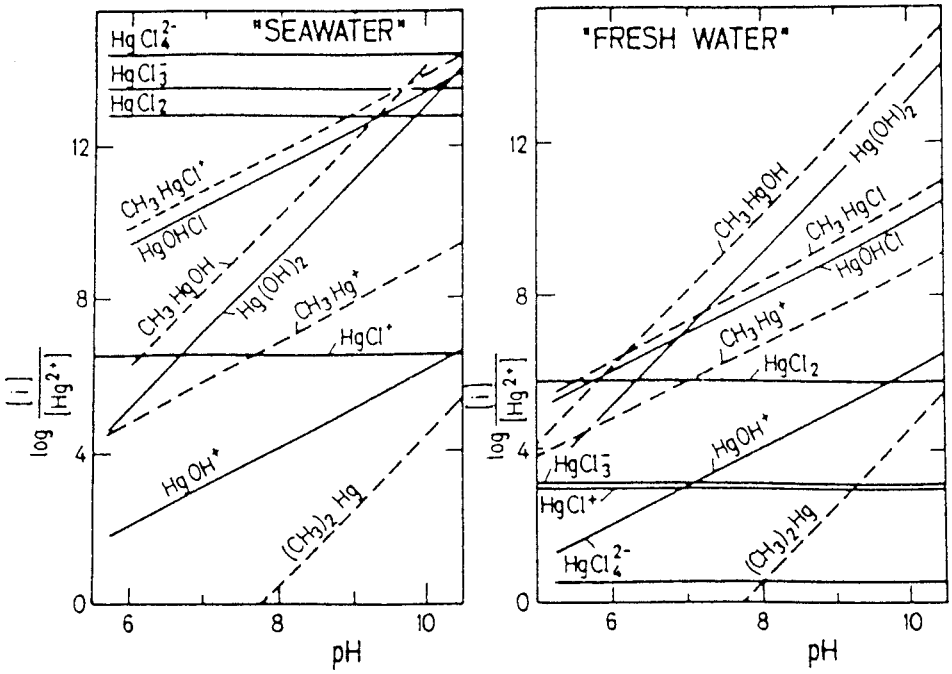

FIGURE 1. Concentration ratio diagrams illustrating the relative thermodynamic stability of mercury species in fresh water and sea water. Conditions: sea water [Cl^-] = 0.6 *M*, [$CH_{4(aq)}$] = 10^{-4} *M*: fresh water [Cl^-] = 2×10^{-4} *M* [$CH_{4(aq)}$] = 10^{-4} *M*. (Source: Stumm and Morgan.[304] 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 40ºC between pH 3 and 7. At 35ºC, up to 160 pg could still be formed. In the river sediment itself, however, methylation was only detected at 40ºC, 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 μg 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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Critical Review

The Case for Atmospheric Mercury Contamination in Remote Areas

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Elevated levels of mercury in aquatic environments remote from industrial sources have been broadly attributed to long-range atmospheric transport and deposition of anthropogenic Hg. Evidence in support of this prevailing scientific view—global biogeochemical Hg models, sedimentary archives of historic Hg fluxes, and geographic trends in soil Hg—have been challenged as being insufficiently rigorous to rule out the alternative explanation that natural geologic sources are the principal contributors of Hg in remote locations. In this review, we examine the weaknesses in interpretation and the choice of information that has been used to argue against atmospheric Hg contamination. Analytical advances in measuring trace levels of environmental Hg have greatly narrowed estimates of natural Hg fluxes, providing a clear measure of the relative magnitude of anthropogenic Hg emissions and deposition. Recent experimental results indicate that diagenetic processes cannot explain the mounting number of lake sediment and peat profiles showing substantial increases in Hg flux during the past century. Geologic sources of Hg may be important in specific localities but cannot explain corresponding geographic trends in soil Hg and industrial emission sources. Despite uncertainties in current understanding, there is a broad and geochemically consistent data base indicating that, over large regions of the globe, human-related Hg emissions have increased relative to natural sources since the onset of the industrial period.

Introduction

Human exposure to monomethylmercury (MMHg) through the consumption of freshwater and marine fish is the principal public health concern with Hg in the environment. Alkylated Hg species such as MMHg and dimethylmercury (DMHg) are integral components of the Hg cycle. Their distribution and fate at the earth's surface will be affected by natural and anthropogenic sources and processes. Elevated MMHg concentrations in fish are common even in the oceans and terrestrial waters distant from point sources. Long-range atmospheric transport and deposition of anthropogenically-derived Hg has been implicated (e.g., refs 1−4). Much of the recent work appears in the conference volumes from three international conferences on "Mercury as a Global Pollutant" (*5*−*7*).

However, in a recent *Environ. Sci. Technol.* critical review of the subject, Rasmussen (*8*) argues that the underlying assumptions linking anthropogenic Hg emissions to the atmosphere and to subsequent Hg deposition in remote continental and oceanic settings "deserve careful scrutiny" because the "conclusions hold serious implications to both government and industry". In Rasmussen's view, recent investigations suggesting that atmospheric transport and deposition of human-related Hg emissions dominate the cycling and bioaccumulation of Hg in systems distant from anthropogenic point sources underestimate the influence of natural geological sources. Evidence in support of anthropogenic interruption of the global Hg cycle such as historic records of Hg accumulation in lake sediments and peat cores or geographic gradients in soil Hg concentrations are dismissed as diagenetic artifacts or the product of underlying geologic variation.

The purpose of this review is to provide the "careful scrutiny" that such controversial conclusions demand. It is our contention that the case for atmospheric Hg contamination in remote areas is stronger than ever, having been advanced by worldwide improvements in analytical methods, sampling techniques, and experimental design over the past decade. Much of the earlier uncertainty regarding Hg contributions from natural sources has been replaced by a convergence of data that points unequivocally toward significant human-related Hg emissions and deposition over large regions of the globe.

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In contrast to previous views, it has become evident that atmospheric and aquatic cycling of Hg and the bioaccumulation of MMHg in aquatic systems are driven by complex chemical and biological reactions involving exceedingly small quantities of Hg. Accordingly, environmental investigations of Hg require an ultraclean trace metal analytical approach that was rarely used during the 1960s to the mid-1980s. Thus, one must carefully evaluate the Hg literature for analytical quality and the assurance that the findings are geochemically consistent. In the following review, we address the weaknesses in interpretation and the choices of information used to support the contention that geological sources of Hg are the principal contributors of Hg in remote locations. We consider first the geological fluxes associated with the global cycle of Hg, then examine the reliability of lake sediments and peat cores as recorders of past Hg deposition, and finally explore geographic gradients in soil Hg relative to industrial emission sources.

Global Hg Cycle

The global biogeochemical cycling of Hg has been described often using mass balance formulations (e.g., refs 1−3 and 9−18). These simulations, in general, show the prominent role of the atmosphere in mobilizing and depositing Hg at the earth's surface and indicate that anthropogenic Hg emissions to the atmosphere represent a significant interference in the modern Hg cycle. Environmental assessments of source strengths for natural and anthropogenic processes have often been in error due to the inclusion of inaccurate published information and the limited availability of accurate data for important aspects of the Hg cycle. The geochemical picture of the global mercury cycle has improved significantly during the past decade. Present estimates for mercury fluxes to the earth's surface and for the mercury content of active reservoirs (e.g., natural waters; atmosphere) are converging. Continued improvements are expected from the large number of on-going high-quality studies concerning the emissions, chemical speciation, and reactivity of Hg in the environment. Indeed, the field is so active that a fourth international conference on "Mercury as a Global Pollutant" (since 1990) was held in Hamburg in August 1996.

A scrupulously critical approach must be employed in evaluating environmental Hg measurements, especially those obtained prior to the mid-1980s. Unfortunately, Rasmussen (*8*) was not discriminating in her tabulation of global estimates of annual Hg emissions from natural sources. By including results from the early work by Lantzy and MacKenzie (*12*) and alluding to others, she concludes that estimates for natural global Hg emissions to the atmosphere vary by orders of magnitude. While modern values for average annual natural Hg flows to the air range from 8 to 20 Mmol (*1*, *2*, *18*), the estimate of 29 325 Mg yr^{-1} (150 Mmol yr^{-1}) reached by Lantzy and MacKenzie (*12*) is much larger and certainly wrong. This value, which is derived using a global Hg model developed by MacKenzie and Wollast (*11*), is in gross error because it is based on inaccurate Hg measurements of the Hg content of Greenland ice that were published by Weiss and co-workers (*19*) in 1971. Weiss et al. reported that the average Hg concentration in ice between 800 BC and 1952 was 60 ± 20 pg g^{-1} and 130 ± 50 pg g^{-1} for the period between 1952 and 1965. The enhanced levels were attributed to anthropogenic Hg emissions, which were determined by Lantzy and Mackenzie (*12*) to be 15 800 Mg yr^{-1} (79 Mmol yr^{-1}), which is also an erroneously large value.

The Greenland Icesheet studies illustrate the need for scrupulous attention to analytical methodology and field sampling protocols in ultratrace studies of Hg. They also show clearly the need to evaluate critically the literature for accuracy and geochemical consistency. Historically, Hg measurements in the Greenland Icesheet range from <1 to 880 pg g^{-1}, approximately 3 orders of magnitude. The highest levels were reported by Weiss and co-workers in 1971 (*19*) and in 1977 (*20*). These concentrations reflect gross contamination acquired during sample collection, processing, and analysis. Using improved techniques, later work by investigators from the Danish Isotope Center (*21*) reported Hg concentrations between 2 and 19 pg g^{-1} over the time period of 1727−1971. Most recently, Vandal et al. (*22*) found a range in between (<1−1.5 pg g^{-1}) for samples within any one year for the past 30 years that have been analyzed thus far. These collections were made using extraordinarily careful and ultratrace metal free techniques developed especially for depositional studies in polar regions by C. Boutron and co-workers at the Laboratoire de Glaciologie et Géophysique de l'Environnement, France (see refs 23 and 24 for technical details). These latter results are the order of magnitude consistent with recent measurements of Hg in snows from the mid-continental lakes region in northcentral Wisconsin, which show concentrations between 2.3 and 8.2 pg g^{-1} (*25*, *26*). Thus, an estimate of natural Hg emission to the atmosphere of 150 Mmol is not supported by modern data. Indeed, using modern data, Mason et al. (*2*) have applied a model similar to the one developed by Lantzy and MacKenzie (*11*) to assess the role of anthropogenic emissions within the global cycle of Hg. Their estimate for annual average Hg emissions from natural sources at 8 Mmol is nearly 20-fold lower.

Geological Hg Fluxes to the Oceans

Global tectonic theory may provide a useful framework for evaluating natural Hg fluxes. However, the suggestion (in Table 3, ref 8) that there are extraordinarily large geothermal Hg fluxes from ocean ridges and oceanic crust at 9.3−18.6 Mmol yr^{-1} (1860−3720 Mg yr^{-1}) and 36.7−73.4 Mmol yr^{-1} (7340 −14 680 Mg yr^{-1}) respectively, that affect the oceanic concentration of Hg is not supported by oceanic profiles of Hg. Deep ocean profiles (e.g., ref 27) do not show any significant increase in concentration with depth, which would be expected if inputs from the ocean floor exceeded the rate of vertical mixing. Thus, this source cannot exceed the rate of vertical mixing. Use of a vertical mixing coefficient of 3 m/yr (*28*) and 2 pM Hg concentration (a conservatively high value) yields a flux of 6 nmol m^{-2} yr^{-1}. Eddy diffusion calculations yield a value of the same order. This is equivalent to a (maximum) flux of 1.8 Mmol yr^{-1} or 360 Mg yr^{-1}. These field data negate the heat flow-based flux estimate suggesting that a geothermal Hg input to the oceans that would be 20−40 times larger **(*8*)**. Furthermore, many trace metals such as Hg are scavenged by precipitating hydrous oxides of Fe and Mn and trapped close to their hydrothermal entry points. Accordingly, elevated concentrations of Hg are found in hydrothermally derived metal-rich sediments of the East Pacific Rise (*29*) and the Gorda Ridge (*30*).

Unfortunately, erroneous data from the literature were published by Camargo (*31*). He gives a value of 100 ng/L or 500 pM as the ocean concentration. Oceanic concentrations of Hg range between <1 and 10 pM (<0.2 and 2 ng/L) (*27*, *32*−*34*; see recent review in ref 35). This gross error invalidates arguments that the ocean reservoir is so large that anthropogenic inputs are undetectable. It also ignores ocean mixing processes and the rapid recycling of mercury to the atmosphere due to volatilization (*2*). Estimates for the annual volatilization of Hg from the oceans are large ranging between 6 (*3*) and 10 Mmol (*2*). Moreover, a substantial fraction of these oceanic emissions represents the recycling of Hg that entered the marine environment from anthropogenic sources.

Lake Sediments and Peat Bogs as Historical Archives

Lake-Sediment Records. Anthropogenic Hg emissions on a global scale have been increasing for at least 100−150 years, which is a short period as compared to processes occurring over geological time. For example, it takes about 500−1000 years to mix the oceans (*28*, *36*). Indeed, geological sources of Hg have varied very little during this modern industrial interval because large-scale geologic processes associated with plate tectonics are essentially constant over such short time intervals. In contrast, there is much evidence from the tabulation of various emission sources and from the historical record of Hg as preserved in lake sediments and peat bogs that indicate that significant human-related Hg interferences have been impressed on the Hg cycle over a broad geographic area.

An estimate of the potential impact from human-related Hg emissions to the atmosphere on a national basis can be developed for the United States. In an extensive recent effort, the Environmental Protection Agency (EPA) determined the overall annual fluxes (1990) of Hg from U.S. anthropogenic sources to the atmosphere to be ca. 1 Mmol (205 t yr^{-1}; *37*). These amounts are considerably smaller (50−70%) than Watson's (*38*) estimate of 2.4 Mmol for the year 1975. Nevertheless, even 1 Mmol from the United States alone appears as a very large interference (ca. 20%) as compared to the annual worldwide natural terrestrial Hg emissions, which were estimated to be about 5 Mmol (*2*).

Lake-sediment records provide the most compelling evidence thus far that remote regions receive significant inputs of anthropogenic Hg by long-range atmospheric transport. Although numerous studies from European (*39*−*42*) and North American (*43*−*51*) sites show consistently elevated Hg levels (and fluxes) in recent sediments as compared to deeper preindustrial strata, Rasmussen (*8*) suggests that many (if not all) such profiles are generated by post-depositional diagenesis and diffusion (or advection) of Hg. As we argue elsewhere, such assertions, in general, are clearly not supported by recent experimental studies. Moreover, the lake-sediment records themselves show a pattern of recent Hg enrichment that is spatially and temporally coherent and not easily explained by either diagenetic processes or local geological sources.

In almost every well-dated sediment core from the midwestern United States, Hg concentrations (or fluxes) increase above background in the mid-19th century, shortly after the start of the industrial period (*48*, *52*, *53*). These sediment profiles range in length from <20 cm (Thrush L.) to more than 90 cm (Wirth L.), yet the timing of the increase is the same. Although Hg levels rise somewhat later in cores from northern Canada and Scandinavia (*40*, *42*, *51*), the chronology is again consistent among lakes within each geographic area. In lakes where multiple sediment cores have been analyzed, Hg increases are likewise synchronous, though sediment depth may vary by a factor of 2 or more (*54*). It seems highly improbable that temporally concordant patterns of Hg accumulation could be generated in numerous sediment profiles of varying thickness by post-depositional sedimentary processes.

Not only is the timing of Hg increase synchronous among sites, but also the magnitude of the change is remarkably similar across a large geographic area. In mid-continental North America, four studies of 40 U.S. and Canadian lakes (*45*−*48*) show modern Hg concentrations (or fluxes) elevated over background values by a ratio of 2.7 ± 0.9 (SD). A similar range of enrichments (modern/background) has been reported for northern Canada (2.3 ± 0.6, $n = 10$) (*51*) and Scandinavia (mean = 2.0−2.6) (*39*, *41*), although ratios become higher for sites closer to industrialized areas of eastern Europe (mean = 5.0−6.3) where direct measurements of atmospheric Hg deposition are also higher (*55*). It is difficult to imagine how sediment diagenesis and Hg diffusion could generate such a convergence of enrichment ratios or the north−south increase that parallels measured Hg deposition in the Nordic countries. There is clearly variability in Hg loading among lakes [in some cases attributable to differences in local geology; e.g., Coker et al. (*56*)], but the similar timing and magnitude of recent increases and a concordance with spatial trends in measured Hg deposition argue strongly that long-distance transport of anthropogenic Hg is the cause of increasing Hg concentrations and fluxes in the sediments of lakes in sparsely populated regions that are not impacted by localized human-related sources of Hg.

A particularly convincing case for the utility of lake sediments in preserving the anthropogenic perturbation to the background Hg pattern is found in the work of Swain et al. (*48*) and Fitzgerald et al. (*25*, *57*). Swain and co-workers (*48*) employed an innovatively simple but effective multiple core mass-balance approach to obtain modern and historical Hg flux information from the sediment record of seven "relatively undisturbed" lakes in Minnesota and Wisconsin. Regression analysis using the seven lakes yielded an average value for present atmospheric deposition of 12.5 $\mu g\ m^{-2}\ yr^{-1}$ and a preindustrial value of 3.7 $\mu g\ m^{-2}\ yr^{-1}$. This represents an average enrichment ratio of 3.4. The recent depositional determination is similar to the estimate for atmospheric Hg deposition of 11.5 ± 3.8 $\mu g\ m^{-2}\ yr^{-1}$ for the period of 1988−1990 (*57*). This estimate was established by Fitzgerald and co-workers for the Little Rock Lake region (one of the study lakes in the Swain et al. work) in Wisconsin. The good agreement between these two independent measures of modern Hg deposition is a strong indication that the Hg accumulating in lake sediments is not significantly affected by diagenetic processes and the anthropogenic signal is preserved.

An additional example of the utility of lake sediments to preserve the Hg accumulation signal is evident at a relatively unusual core site in Clay Lake, Northwestern Ontario. This lake received inputs of a chloralkali plant at Dryden, Ontario, during the 1960's, but Hg emissions ceased in 1970. A core was taken in 1971 by Armstrong and Hamilton (*58*), and it showed a peak at the surface of the sediment, consistent with recent inputs. In 1978, another core was taken by Rudd et al. (*59*), which showed the peak a few centimeters deeper, consistent with cleaner recent inputs. The latest core was obtained in 1995, and it shows the peak several centimeters lower than observed in 1978 (*60*).Thus, the three cores preserved accurate records of mercury consistent with known history. This is similar to the experience of Smith and Loring (*61*), but the availability of three cores from Clay Lake provides convincing evidence that diagenetic factors are not major influences on the Hg accumulation pattern in lake sediments.

Geological Context. High variability in background Hg concentrations in lake sediments has been offered as evidence that local geology, not long-distance atmospheric transport, controls the natural distribution of Hg in Canadian lakes (*8*). However, much of this variability may be explained by differences in sediment flux among lakes and by spatial variability in Hg sedimentation within lakes. Most of the Hg data in the studies Rasmussen (*8*) cites are based on single sediment collections from which Hg concentrations are calculated on a dry-weight basis (*62*). Concentration data, however, are very sensitive to differences in dilution by the flux of the sediment matrix, which is known to vary considerably among and within lakes (*63*−*66*). Mercury concentrations are also highly variable (by a factor of 10 or more) within lake basins because of density-dependent particle settling (focusing) (*44*, *54*, *67*). When these factors (sediment flux and focusing) are taken into account, either by the calculation of Hg flux ratios for individual cores or by

multiple-core studies of whole-basin Hg accumulation (*54*), much of the between-lake variability evident in raw concentration data vanishes. Variations of Hg concentrations in surface sediments do not automatically imply local differences in geological Hg supply as some have claimed (*8*, *68*).

Diagenetic Questions. The main argument against the use of sediments as historical records of atmospheric pollution is that diagenetic processes may bring Hg up to the sediment surface (as organo-mercury complexes, mercury organosulfide complexes, or vapor-phase Hg), followed by adsorption on oxides and hydroxides (Fe, Mn) with higher redox potential (*8*). Support for this view is contained in a study of Hg in slowly accumulating deep lake sediments and porewaters of four depositional environments in Lake Superior and Lake Michigan (*69*). However, if this were generally true, we should find (1) approximately the same kind of profiles for Fe, Mn, and Hg, (2) a probable correlation of Hg with Fe and Mn in surface sediments when comparing several lakes, and (3) no clear geographical pattern for Hg. None of these points are valid in several studies conducted by Verta and co-workers in Finland (*40*, *41*, *70*).

These researchers studied 25 lake profiles from 16 lakes for all major elements including Fe, Mn, Hg, Cu, Zn, Pb, and Cd (*40*, *41*, *70*). They found that the geographical patterns for Pb, Cd, Hg, and Zn in surface sediments (uppermost 5−10 cm) were very similar with the higher concentrations in the southern more industrialized areas. This distribution is preserved at depth in sediments deposited after the late 1800s (and shows an earlier increase in Pb deposition than other elements). In general, no such geographical or vertical pattern was found for Fe or Mn. Large variations in Fe and Mn occurred among lakes, and in most lakes a surface or subsurface maximum for Fe was found with no increase in Hg (*70*). There was also a positive correlation of sulfate in lake water with surface sediment Hg concentrations.

These observations are consistent with the measured higher atmospheric Hg deposition rates in southern Scandinavia (including one station in Finland) than in the north and with positive correlation of rainwater sulfate and rainwater Hg in the area (*55*). They do not support indications of any major effects of diagenetic processes on Hg partitioning and vertical movement in sediments.

Lucotte and co-workers (*51*) studied Hg in 12 oligotrophic lakes in northern Quebec, where the redox boundary layer lies at or very close to the water−sediment interface. Below this sharp redox gradient, sedimentary iron is reduced and liberated in pore waters and diffuses upward toward the water column. Only in rare cases could they identify a layer of iron re-precipitation at the very interface between the water column and the sediment (*71*, *72*). Along with these early diagenetic reactions, loss of detrital organic matter through biodegradation does not appear to be measurable within the sediments as all profiles of organic carbon remain fairly constant below the immediate surface of the sediment (*51*, *71*, *72*). At the same time, all mercury profiles decrease progressively with depth to baseline concentrations in sediments older than about 1940. These trends appear totally decoupled from the iron or the carbon profiles (*51*, *71*, *72*) and thus clearly contrast with the Hg profiles reported for marine sediments (*73*). On the other hand, Dmytriw et al. (*71*) demonstrated that most Hg in a lake sediment (85%) was bound to NaOH-extractable organic matter. As the organic matter load remains fairly stable in the sampled sediments, the surficial increases of mercury concentrations in the sedimentary profiles thus represent larger Hg fluxes in the recent years.

It can also be argued that the inference of historic Hg fluxes from sediment cores requires that there has been no loss of Hg to pore water during the decomposition of humic material, no transport within the sediment column, and no Hg transfer between the sediment pore water and overlying waters. However, recent experimental studies indicate that these restrictions are overstated. Because gross sedimentation of Hg to the sediment surface exceeds net accumulation, there is likely to be recycling of Hg prior to incorporation in the permanent sediment record. The important factor is the depth of the zone of recycling. Gobeil and Cossa (*73*) found that post-depositional migration of Hg in pore waters in estuarine environments could not account for the surface enrichment. Similarly, and in lacustrine experiments, Hurley et al. (*52*) observed K_d values between sediments and pore waters to be about 10^4, suggesting a strong affinity for the particulate phase. Additionally, in long-term (12 and 27 month) sediment mixing−incubation experiments, Henning (*74*) and Hurley et al. (*75*) found little post-depositional redistribution of Hg due to diffusion in pore water. Hurley et al. (*75*) reported little or no diffusion below 2−4 cm, concluding that any pore water release to overlying waters must occur above the 2 cm sediment depth.

If deep pore water release were important in regulating hypolimnetic increases in anoxic lakes, pore water Hg concentrations of several hundred nanograms per liter would be necessary to create a diffusion gradient in sediments (*52*). No such levels have been reported by researchers using ultratrace metal clean techniques. Montgomery et al. (*76*) in their northern Quebec study, for example, report the absence of gradients in the profiles of dissolved Hg in sediment pore water, and the concentrations were found to be in equilibrium with the water column.

The work of Krabbenhoft and Babiarz (*77*) can be considered as an example where advection obscures Hg profiles in sediments. However, it must be stressed that the Krabbenhoft and Babiarz (*77*) study was not one designed for interpretation of historical profiles, but was rather a study of transport of Hg through a sandy, shallow aquifer. A sediment core for use in evaluating historical accumulation would never be taken in shallow, sandy sediments. In deep, high organic matter sediments (where cores for historical evaluation are commonly taken), advective processes are usually minimal.

Peat Bogs. The use of ombrotrophic peat bogs as depositional archives of Hg has been criticized on the basis of potential *in situ* diagenetic remobilization of Hg and contributions to the peat record that may be derived from localized gaseous evasion of elemental Hg from soils (*8*). However, a number of studies on the adsorptive capacity of mosses suggest high retention of Hg in peat (*78*−*82*). Speciation calculations for Fe, Al, and Mn show that the vertical distribution of metals in ombrotrophic bogs can be explained by the redox potential gradient in peat and seasonal fluctuations in water table depth (*83*). A geochemical model for metal mobility indicates that the Hg (and Pb) profiles in peat cores cannot readily be explained by redistribution processes but that they probably reflect changes in deposition to the bog over time (*83*). In this study, total Hg inventories (μg m^{-2}) for the past several hundred years were extremely consistent among hummocks, which indicates no significant horizontal movement of Hg as water drains laterally through the surface peat. Similarly, Urban et al. (*82*) found that Pb-210 inventories from Minnesota peatlands were similar to that expected from atmospheric deposition and that there was little evidence of transport of Pb from hummocks to hollows.

With respect to local gaseous evasion of Hg from soils, we note that the residence time of Hg^0 in the atmosphere is about 1 yr (*2*, *13*, *14*, *84*). This long residence time allows for hemispheric-scale mixing of this gas before it is returned to the soil via precipitation and dry deposition. Furthermore, there is no evidence of large-scale temporal changes in the

magnitude of soil degassing of Hg^0 over time. This is analogous to the gaseous evasion of ^{222}Rn from soils. The deposition of ^{210}Pb (derived from ^{222}Rn), which has remained fairly constant over the past several hundred years, indicates that ^{222}Rn emissions from soils have also been relatively stable with time (85).

The discussion of peat cores from ombrotrophic bogs in Rasmussen's (*8*) review uses the Scandinavian study of Jensen and Jensen (*86*) as a case study. It is implied that soil Hg concentrations varying from one geological setting to another may partly explain the variability of Hg shown in these bogs. If instead another Scandinavian study (*87*; also referenced in ref 8) had been chosen to discuss the origin of Hg in these bogs, a different conclusion would have seemed more reasonable. Data from that study showed a uniform Hg level of 31 ± 8 ng g^{-1} (mean $\pm$ SD) at 50 cm depth in 13 ombrotrophic bogs distributed all over Norway, reflecting a general pre-industrial level. In recent peat layers, the Hg concentration had increased to 169 ± 32 ng g^{-1} in four bogs along the southern coast where the general impact of long-range atmospheric transport of pollutants from Europe is considerable (*88*). In central Norway (which is much less exposed to air pollution), the corresponding figure for four bogs was 66 ± 10 ng g^{-1}. These figures are very difficult to explain on the basis of soil-derived Hg, which might be expected to vary considerably with geological setting but not so much with time.

As documented, Hg accumulation trends in surface sediments are similar in a great variety of biological and geographical settings and seem independent of local geological conditions. For example, chronologies for Hg from lower latitude subtropical Florida wetlands (*89*) corresponded well with reported trends in lacustrine systems in Scandinavia, the northern United States, and Canada. Rood and coworkers (*89*) studied a total of 18 sediment cores from four major hydrologic units in the Florida Everglades and a dynamic linear wetland system along Florida's Atlantic coast (Savannas Marsh). The field sites varied from organic peat to predominantly marl spanning a wide range of geological conditions. Post-1985 Hg accumulation rates averaged 53 (23−141) μg m^{-2} yr^{-1} with pre-1900 rates generally below 10 μg m^{-2} yr^{-1}. Recent Hg fluxes were an average of 4.9 times higher than those of ca. 1900 and appeared to be unrelated to geochemical conditions. Rates increased starting about 1940, coinciding with mid-century alterations of the hydrology of these wetlands and increased regional agricultural and urban development.

Geographic Gradients in Soils

Nater and Grigal (*90*) inferred a regional gradient in atmospheric Hg deposition and anthropogenic impact based on observation of a gradient in Hg burdens in forest floor (a partially-decomposed surficial organic layer) and surface mineral soils (0−25 cm depth) along a transect from northwestern Minnesota to northeastern Michigan. Rasmussen (*8*) has questioned the assumption that Hg in soil organic matter originates from the atmosphere and argues for the possibility that "... geological variations override regional deposition effects".

Concerning these objections, we note that atmospheric Hg deposition directly to soils, complexation of Hg by organic matter (*91*), and atmospheric inputs to leaves (*92*−*94*) and hence to surface soils are well-documented processes (*95*). Significant plant uptake of Hg directly from deeper geological materials is unlikely because of limited root uptake of Hg (*96*) and the lack of a trend in Hg burdens in subsoils (75−100 cm depths) along the transect (*90*). Deeper geological materials are beyond the rooting zone. Consequently, for deeper geological sources to affect the Hg accumulation in soil, as discussed by Rasmussen (*8*), there must be an indirect pathway requiring (1) volatilization/emission of Hg from the geological substrate as Hg^0; (2) diffusion to the soil−atmosphere interface; (3) Hg^0 uptake and/or Hg^0 oxidation and capture by leaves; (4) leaf senescence and deposition of Hg to the soil surface; and (5) retention by soil.

Such an indirect pathway may exist, and while we agree with Rasmussen (*8*) that it is possible that deep geological sources may be responsible for part of the Hg trends observed in forest litter and surficial mineral soils, the magnitude of this geological contribution would be small as compared with that from other atmospheric sources. The 155 study sites from Nater and Grigal (*90*) were located across a large region on a wide variety of bedrock and surficial materials, where the distributional pattern for Hg corresponded well with similar trends for Cd and Pb that were found in the same samples (*97*, *98*). Pb and Cd are elements known to be atmospheric deposition products of anthropogenic activity. In addition, the metal distribution corresponded with known patterns of acid sulfate deposition across this region (*99*, *100*) and with a general increase in anthropogenic activity toward the southeast. The high correspondence between Hg and other known atmospheric pollutants in this region strongly supports a regional gradient in anthropogenic atmospheric Hg deposition rather than undetermined trends in deep geological sources. The statistically significant trend produced by the 155 samples measured, by definition, shows that the regional trend was sufficiently clear to override local scale variability.

Summary

In summary, there is much published literature on the Hg cycle. While the quality of the data has improved dramatically over the past decade, one must be most diligent in evaluating the quality of published data for the cycling of Hg in the environment. Inaccurate results plague the Hg literature and mislead the unwary researcher. There has been much recent research on Hg in nature that has been reported and published especially in association with the 1990, 1992, 1994, and 1996 international conferences on "Mercury as a Global Pollutant". Nevertheless, critical information is lacking concerning natural and anthropogenic emissions, chemical speciation, and reactivity of Hg in the environment. This discussion stresses appropriately that, while our understanding of the biogeochemical cycling of Hg and assessments of the impact from anthropogenic Hg releases are as yet limited by many "uncertainties" in current knowledge, there is a broad and geochemically consistent data base indicating that, over large regions of the globe, human-related emissions and deposition during the past century have increased relative to natural sources (*5*−*7*). Moreover, the signal is evident in remote regions. The results demonstrate that (carefully selected) lake sediments, bogs, and soils can be used as indicators of airborne Hg pollution.

We have noted that the critical concern associated with Hg in the environment is human exposure to MMHg through the consumption of fish and fish products. Current studies show the insidiously complex nature of the biogeochemical cycle of Hg. The production and bioaccumulation of MMHg in aquatic systems (especially piscivorous fish) and the resultant exposure to humans and wildlife are driven by chemical reactions and biologically-mediated transformations involving ultratrace amounts of Hg in the atmosphere and natural waters. It is apparent from the modern high quality work we have summarized that human-related Hg emissions are significant and that plausible linkages between the releases of Hg to the atmosphere from anthropogenic sources and the exposure to humans and wildlife to MMHg can be drawn. At present, however, a comprehensive quantitative assessment of the relationship between anthropogenic Hg releases to the atmosphere and the potential

exposure to people, wildlife, and terrestrial and aqueous systems is not possible. For example, deposition is critically dependent on the chemical form of Hg. Yet, there are few data on the physical and chemical species of Hg emitted from various sources (e.g., refs 101 and 102); near-source contamination is most likely related to the emission of ionic and particulate forms of Hg, while the farther field effects are associated with elemental Hg (*2*, *103*, *104*). There is much research to be done. Modern studies are providing a scientifically reasonable blueprint to use in designing and conducting experimental research on Hg in the environment. It does not appear that large natural sources of Hg have been missed, and there is evidence for the impact of atmospherically transported human-related Hg emissions in remote regions of the globe.

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METHYLMERCURY ACCUMULATION IN TISSUES AND ITS EFFECTS ON GROWTH AND APPETITE IN CAPTIVE GREAT EGRETS

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ABSTRACT: To test the hypothesis that fledging wading birds would be more at risk from mercury toxicosis than younger nestlings, captive great egret nestlings were maintained as controls or were dosed from 1- to 14-wk-old with 0.5 or 5 mg methylmercury chloride/kg wet weight in fish. Birds dosed with 5 mg/kg suffered from subacute toxicosis at wk 10–12. Growing feather concentrations were the most closely correlated with cumulative mercury consumed per weight. Blood concentrations of mercury increased more rapidly after 9 wk in all groups when feathers stopped growing. Total mercury accumulated in tissues in concentrations in the following order: growing scapular feathers > powderdown > mature scapular feathers > liver > kidney > blood > muscle > pancreas > brain > bile > fat > eye. The proportion of total mercury that was methylated depended upon tissue type and dose group. Selenium accumulated in liver in direct proportion to liver mercury concentrations. After wk 9, appetite and weight index (weight/bill length) declined significantly in both dosed groups. At current exposure levels in the Everglades (Florida, USA) mercury deposited in rapidly growing feathers may protect nestlings from adverse effects on growth until feathers cease growing.

Key words: Appetite, *Ardea albus*, bioaccumulation, captive, contaminants, feathers, great egret, growth, methylmercury, tissue accumulation.

INTRODUCTION

Methylmercury contamination of wetland food chains has been suspected to cause reduced survival and/or reproduction in top carnivores (Fimreite, 1974; Van der Molen et al., 1982; Barr, 1986; Facemire et al., 1995; Meyer et al., 1998) and has been suggested as one of the possible causes for reduced reproduction of long-legged wading birds (Ciconiiformes) in the Everglades (Florida, USA) in recent decades (Frederick and Spalding, 1994; Spalding et al., 1994; Sundlof et al., 1994). One mechanism by which methylmercury might affect reproduction would be to directly alter the development of nestlings. A few authors have documented reduced appetite and/or reduced weight gain in captive juvenile raptors and ducks dosed with relatively high concentrations of methylmercury (Borg et al., 1970; Fimreite and Karstad, 1971; Pass et al., 1975; Bhatnagar et al., 1982) and Hoffman et al. (1998) found reduced weights in wild diving ducks with higher liver mercury concentrations. Williams (1997) and Sepulveda et al. (1999b) found effects of mercury on appetite, but not on survival of wild great egret young that were dosed with methylmercury in the Everglades. In their study dosing was confined to the fastest growth period for the chicks. It seemed likely that a large proportion of mercury would be shunted into growing feathers during that time, where it might be unavailable to other tissues (Furness et al., 1986). For this reason, we hypothesized that young chicks with rapidly growing feathers would be protected from the effects of dietary methylmercury and that chicks that continued to receive methylmercury after feather growth ceased would be more likely to exhibit the signs of methylmercury toxicosis.

In the present study, we raised captive great egret nestlings from hatching to 14-wk-old, well after the time that they would normally fledge and be independent in the

wild (9–11 wk, Sepulveda et al., 1999b), on control diets and diets containing 0.5, and 5 mg methylmercury/kg food. The main purpose of this paper is to report the accumulation of mercury in various tissues of these birds and the effects of mercury on growth and appetite. The effects on behavior and foraging skills (Bouton et al., 1999), tissue and plasma biochemistry (D. J. Hoffman et al., unpubl. data), and health and histologic changes (Spalding et al., 2000) are or will be published elsewhere.

METHODS

On 16 March 1996 we collected first-hatched great egret nestlings from broods of 23 different nests in Alley North colony (26°11.25'N, 80°31.05'W) in Water Conservation Area 3 of the central Everglades. This colony is located within an area where high mercury concentrations have been measured in wading birds and fish (Sundlof et al., 1994; Frederick et al., 1999). They were taken from nests of three eggs that had been monitored throughout incubation. Some were collected as pipped eggs, which took several days to hatch, and others were as old as 5 days. The range in ages was 7 days. Seven birds were excluded from the experiment due to early mortality. The birds were transported to the Florida Field Station of the National Wildlife Research Center (United States Department of Agriculture, Gainesville, Florida, USA). Chicks were assigned to group randomly and 5, 5, and 6 birds were in control, low dose, and high dose groups respectively. Initially birds were housed indoors in individual 65 × 40 cm plastic boxes with artificial stick nests. All birds were kept in the same heated room during the first 2 wk of life, and heating pads were applied to the bottoms of the boxes for the first wk of life. Boxes were cleaned daily. At 5 wk, birds were moved to outdoor housing. The plastic boxes were attached to perches within each outdoor cage, and removed after the birds stopped using the boxes for perching and resting. Cages were 3m × 3m × 2m enclosures constructed of chickenwire supported by PVC plastic tubing. The cages had sand floors and each contained a water dish, perches, and, during the latter third of the experiment, one shallowly flooded plastic wading pool. Cages were grouped into blocks of three with common walls between adjacent cages. Each block contained one bird from each dose group, and dose group cage assignment was random with respect to location within a block. An electrified fence to keep terrestrial predators away surrounded the entire group of pens. The outdoor housing units were surrounded by pine flatwoods forest, and were not subject to any routine disturbance other than our visits.

All birds received the same diet of thawed Atlantic silversides (*Menidia menidia*), with small but regular (ca. 10% by weight) additions of capelin (*Mallotus villosus*). Food was provided in dishes for 0.5 hr four to two times daily, depending on age, on a modified *ad libitum* basis. Uneaten fish were removed and weighed. *Ad libitum* feeding for the first wk allowed us to establish the initial amount to feed each bird. We offered that amount of food to each bird until it either ate all food offered for three consecutive meals, or left any amount of food uneaten for three consecutive meals. We then either increased or decreased food by 10 g, respectively. During the trials on hunting behavior, wk 10–14, the birds were also allowed to forage on live fish (see Bouton et al., 1999). Methylmercury dosing was based upon total daily food offered, including the live fish.

Gelatin dosing capsules were made three times a week from solutions that contained 0, 3, or 30 μg reagent grade methylmercury chloride/μl in acetone. Each gelatin capsule received 0.17 μl solution/g food offered, which was equivalent to 0, 0.5, or 5.0 mg/kg food offered for that day. In addition to the controls, we used a low dose of 0.5 mg/kg in fish because it was similar to what great egret nestlings in the Everglades currently eat (Frederick et al., 1999) and a high dose of 5 mg/kg because that would be expected to produce clinical toxicity. The acetone was evaporated from the capsules and they were stored in sealed containers until time of dosing. Capsules were given to the birds daily just prior to the evening meal by manipulating the capsules within the esophagus to the base of the neck. We never saw birds regurgitate the capsules and never found any capsules in the cages. Assignment to methylmercury dose groups was random and blind to researchers working on the experiment. Only 8 of the original 23 birds were male. Of the birds included in the study, 1 of 5, 2 of 5, and 2 of 6, were male in the control, low, and high dose groups respectively.

Birds were dosed every 3 days starting at about 8 days of age. Dosing then changed to a daily regime beginning on day 20, and continued until the end of the experiment (wk 14). The high dose group received 0.5 mg/kg food until wk 6 due to an error in handling solutions. This error was confirmed by examining blood, feather, and fecal data. Birds were captured weekly for examination, to collect blood and feather samples, and to perform various tests.

Twenty-four hour fecal collections were made during wk 5 and 13, for 1 and 2 birds respectively, from each group. Feces, including embedded fragments of feather sheath, were collected every 8 hr from the individual boxes or from plastic placed on the ground. The sample was mixed thoroughly and an aliquot submitted for total mercury analysis. To determine the conversion ratio for wet to dry weight, feces were dried in an oven to constant mass at 58 C. Birds were killed humanely by an overdose of sodium pentobarbital when they could no longer stand [birds in the high dose group were killed at wk 10 (1 individual), 11 (2), and 12 (3)], and all remaining birds were killed at the end of the experiment (wk 14).

The Department of Environmental Protection Chemistry Laboratory (Tallahassee, Florida) determined total and methylmercury concentrations in tissues of great egrets. Total mercury concentrations were detected by cold vapor atomic absorption spectrophotometry as described by Sepulveda et al. (1999a). Methylmercury concentrations were determined for two birds from each group using aqueous phase ethylation followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection (Bloom, 1989). Unless specified otherwise, reported values are total mercury or methylmercury concentrations on a wet weight basis (ww) for blood and other tissue samples and on a dry weight basis (dw) for feathers and feces. Selenium concentrations in liver were measured using a fluorometric method (Whetter and Ullrey, 1978) and are reported on a dry weight basis.

We used repeated measures analysis of variance (ANOVA) to test for effects of dose group on various responses (SAS, 1988). The responses were all tissue concentrations, weight, weight index (weight divided by bill length), tarsometatarsus length, bill length, tail length, length of the most distal primary feather (emerged portion), primary sheath length (as a proportion of total primary feather length), daily food consumed (food averaged over the 3 days prior to blood collection), and food/weight (daily food divided by body weight). We included age as a covariant in these analyses because there was a 7 day difference in age among individuals. We also included gender as a covariant, since great egrets are somewhat sexually dimorphic in body measurements even during the pre-fledging stage (Palmer, 1962). Measurements were made either weekly or biweekly, and the effect of wk was included as a covariant in all models. Significant effect of group × wk interactions were interpreted as evidence of an effect of methylmercury dose. Probabilities <0.05 were considered significant, and probabilities of 0.10–0.05 were considered marginally significant. A multiple comparisons test using a probability of <0.01 was used to determine weeks during which effects differed from the control group.

RESULTS

Fish used to feed the birds contained an average (adjusted for proportions of each species fed) of 0.025 mg/kg of total mercury (0.022 mg/kg in silversides, 0.046 mg/kg in capelin). Selenium measured in the fish used to feed the great egrets was 0.87 mg/kg dryweight (dw) for silversides and 1.14 mg/kg dw for capelin. The adjusted average for the diet was 0.90 mg/kg dw selenium. Selenium accumulated in liver in direct proportion to mercury ($n = 20$, $P < 0.001$, $r^2 = 0.93$) (Fig. 1).

The proportion of total mercury that was methylmercury varied depending on the tissue and on the dose group. In some cases the methylmercury measurement exceeded the measurement of total mercury (>100%). In livers the mean proportion of methylated mercury increased with dose group ranging from 56% (range = 51 to 59%) in the control group, to 61% (55 to 67%) in the low dose group to 73% (69 to 80%) in the high dose group. The proportion of mercury that was in the methyl form in the kidneys was similar, mean = 58% (range = 43 to 69%) in the control group, 61% (49 to 70%) in the low dose group, and 90% (74 to 145%) in the high dose group. Virtually all of the mercury in feathers from two birds in each of the dosed groups was methylmercury; mean = 120% (range = 93 to 150%).

Between 11 and 15% of the mercury administered to low dose birds was recovered in feces during a 24 hr period. Although lower concentrations of mercury were recovered in the feces of control birds, the percent excreted was much higher. Large quantities of shed feather sheath fragments contaminated the feces, especially at 5 wk, and probably account for these higher than expected percentages in the control birds. The percent excretion rate for the low dose birds is also

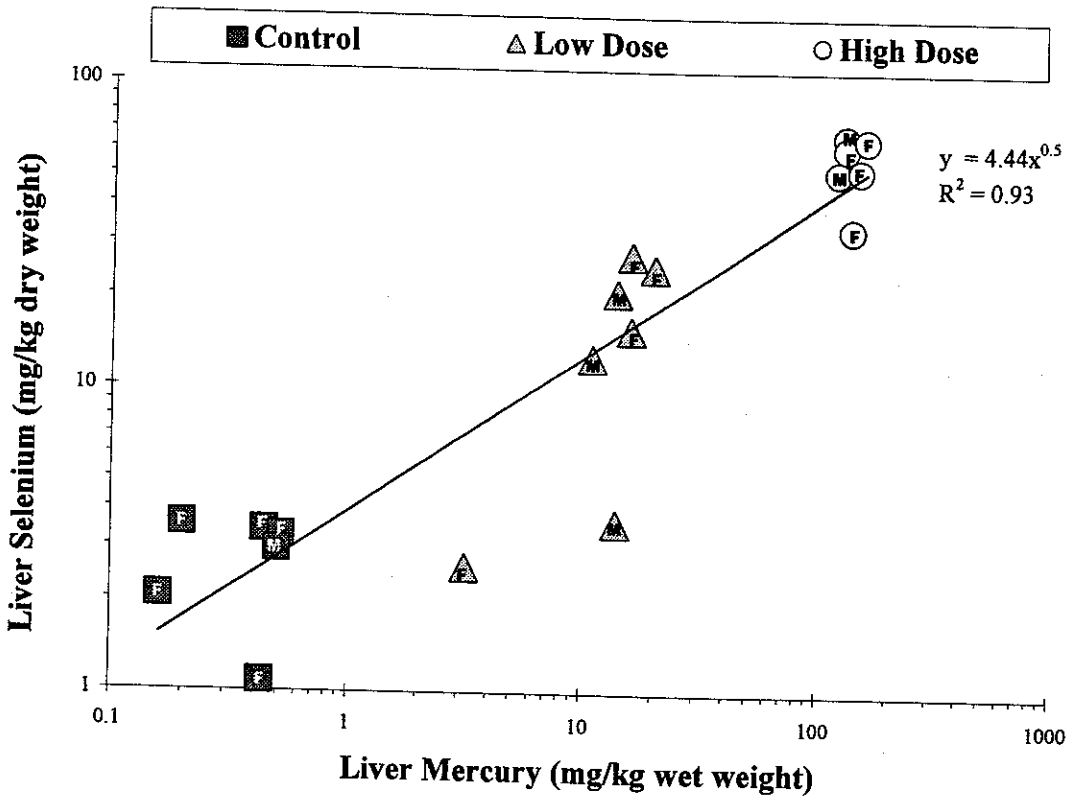

FIGURE 1. Liver selenium (mg/kg dry weight) and total mercury concentrations (mg/kg wet weight) graphed on a log scale for great egrets dosed with methylmercury. M = male, F = female.

undoubtedly artificially increased by this same phenomenon.

We found that mercury concentrations in growing scapular feathers and powderdown were similar. Because growing scapular feathers could not always be found, especially later in the study, the data for these feather categories were combined and are referred to as "growing feather".

Mercury concentrations in blood and growing feathers increased significantly with time over the course of the experiment for all three groups (Fig. 2). In the control group, where background concentrations in the embryo were probably higher than in the food offered, there was an initial decline in blood and feather mercury concentrations.

Concentrations of mercury in various tissues collected at death are listed in Table 1. All tissue concentrations, including those collected repeatedly during the experiment, increased significantly with the amount of mercury administered (CumHg/Weight, ANOVA, $P < 0.05$). Except for bile and fat, all tissues were also significantly correlated with each other (Pearson correlation coefficient, $P < 0.05$). Generally, mercury concentrated in tissues in the following decreasing order: growing scapular feathers > powderdown > mature scapular feathers > liver > kidney > blood > muscle > pancreas > brain > bile > fat > eye.

We compared mercury concentrations in those tissues that could be sampled repeatedly (blood, mature scapulars, and growing feathers), with several measures of mercury intake to obtain a better understanding of the dynamics of accumulation. These included cumulative methylmercury consumed, cumulative methylmercury consumed divided by weight of the bird (CumHg/Weight), daily methylmercury consumed, and daily methylmer-

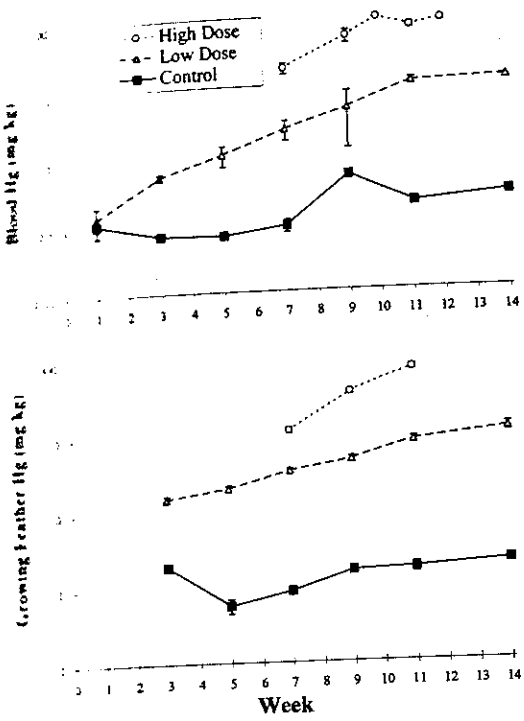

FIGURE 2. Blood and growing feather total mercury concentrations for great egrets dosed with methylmercury at control, 0.5, and 5 mg/kg graphed on a log scale during the course of experiment. Dosing with the high dose began at week 6.

cury consumed divided by weight of the bird. CumHg/Weight was the best predictor of tissue concentration, and growing feather was the best predictor of CumHg/Weight. For all groups, blood concentrations lagged below the regression line early in the experiment, and then rose above it at about 9 wk when feathers ceased to grow (Fig. 3).

The greatest 3-day-average daily food consumed per body weight (Food/Weight) ranged between 6 and 27% of body weight, and peaked during the third wk for all groups (Fig. 4). Methylmercury chloride consumed (mg/kg body weight) varied with amount of food consumed and ranged from a high of 0.135 mg/kg/day during wk 3 to a low of 0.048 mg/kg/day during wk 13. We found a significant effect of dose group on Food/Weight (ANOVA, $P = 0.007$). Food intake differed significantly between the control and low dose birds during wk 11 and between the control and high dose birds during wk 10–11. Note that only two birds remained in the high dose group during wk 12.

We found a significant effect of gender on weight (ANOVA, $P = 0.007$). Weight index (weight/bill length) differed significantly between groups (ANOVA, $P = 0.008$), being lower in the low dose group during wk 11–14, and in the high dose group during wk 10–11 (Fig. 5). Bill length, tarsometatarsus length, primary length, primary sheath, tail length, and tail sheath did not differ significantly between the groups.

TABLE 1. Mean total mercury concentrations in tissues of control, low-dosed, and high-dosed great egrets at death. The mean total methylmercury chloride administered was 0.35, 8.0, and 45 mg/kg for the control, low-dose, and high-dose groups respectively.

	Mean ± standard error		
Tissue	Control	Low-dose	High-dose
Growing feather	2.0 ± 0.16	110 ± 14	810 ± 46
Mature scapular feather	6.6 ± 5.6	40 ± 3.2	150 ± 15
Liver	0.42 ± 0.057	15 ± 1.5	140 ± 6.0
Kidney	0.33 ± 0.0080	8.4 ± 1.3	120 ± 7.6
Blood	0.25 ± 0.0093	12 ± 1.2	93 ± 3.7
Pancreas	0.20 ± 0.0071	5.4 ± 1.3	52 ± 1.5
Muscle	0.17 ± 0.012	18 ± 11	45 ± 3.3
Brain	0.21 ± 0.014	3.4 ± 0.25	35 ± 1.5
Bile	0.45 ± 0.39	3.5 ± 1.7	14 ± 5.0
Eye	0.031 ± 0.0063	0.43 ± 0.096	4.8 ± 0.20
Fat	0.027 ± 0.0021	0.25 ± 0.022	3.6 ± 1.5

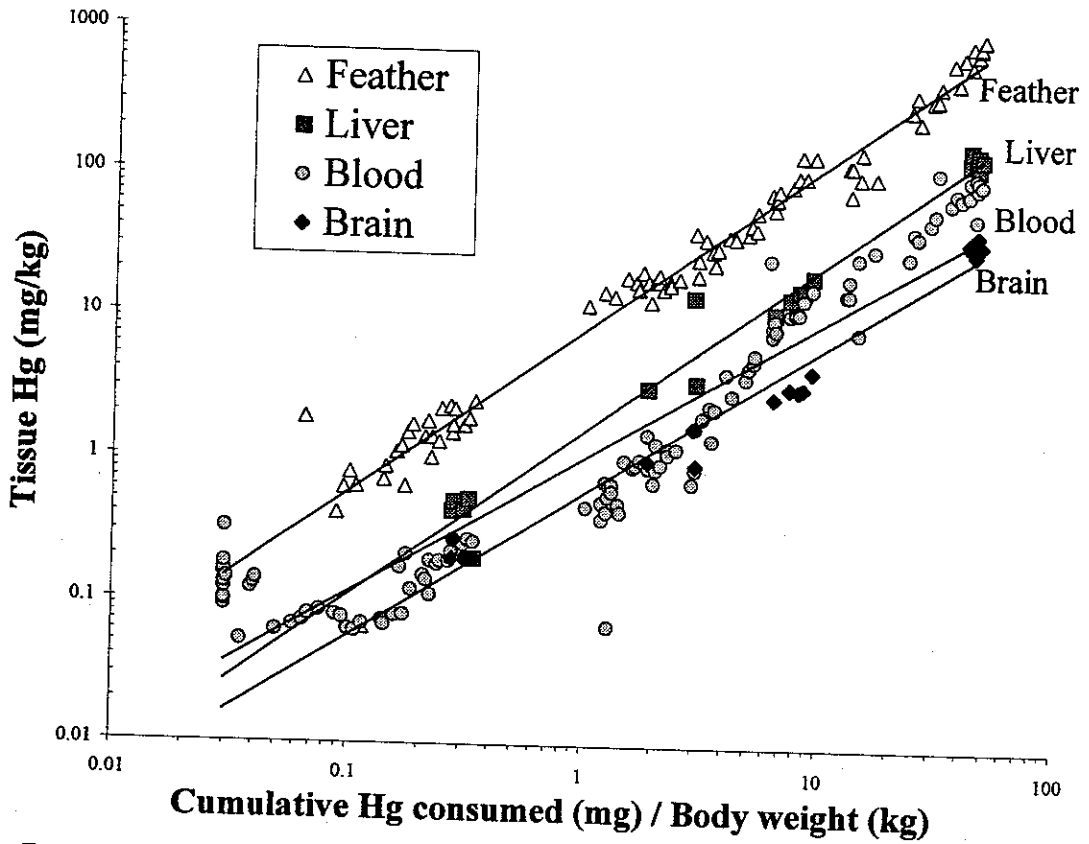

FIGURE 3. Tissue concentrations of total mercury plotted against cumulative mercury ingested/body weight (mg/kg) graphed on a log scale for great egret chicks dosed with methylmercury. Growing feather concentration = $8.0599x^{1.1456}$, blood concentration = $1.0188x^{0.9494}$, liver concentration = $1.5798x^{1.1602}$, and brain concentration = $0.9754x^{1.0136}$, were x = CumHg/Weight in mg/kg.

DISCUSSION

Methylmercury is generally well absorbed by the intestinal tract (Lewis and Furness, 1991), and although we were not able to accurately measure the proportion of methylmercury assimilated in this study due to contamination of feces by feather sheaths, our data generally agree. Based upon estimated food intake for wild nestlings (Frederick et al., 1999) tissue concentrations in our study were similar to those of naturally exposed great egrets in Florida (Sepulveda et al., 1999a).

In our study, although we administered methylmercury chloride, the bulk of the tissue analysis was for total mercury. Several authors have reported that most of the mercury in fish is methylated, and this is true for the Everglades ecosystem (Gardner et al., 1978; Bloom, 1992; Frederick et al., 1999). Essentially all of the mercury in the egret feathers was methylated, concurring with the findings of Thompson and Furness (1989) for seabirds. Only a proportion of mercury that was in liver and kidney was methylated, and that proportion increased with dosing level. This observation supports the hypothesis that birds are capable of demethylating mercury (Thompson and Furness, 1989). It appears that this process is more efficient at lower mercury concentrations than at higher mercury concentrations, or that there are limitations to the demethylation process, such as might occur with cell damage or inadequate materials for detoxification (possibly selenium). Thompson et al. (1991) reported that all mercury in the

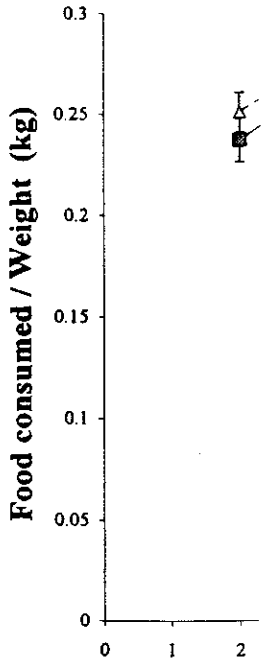

FIGURE 4. Three-day
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birds remained in the hig

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Mercury was not
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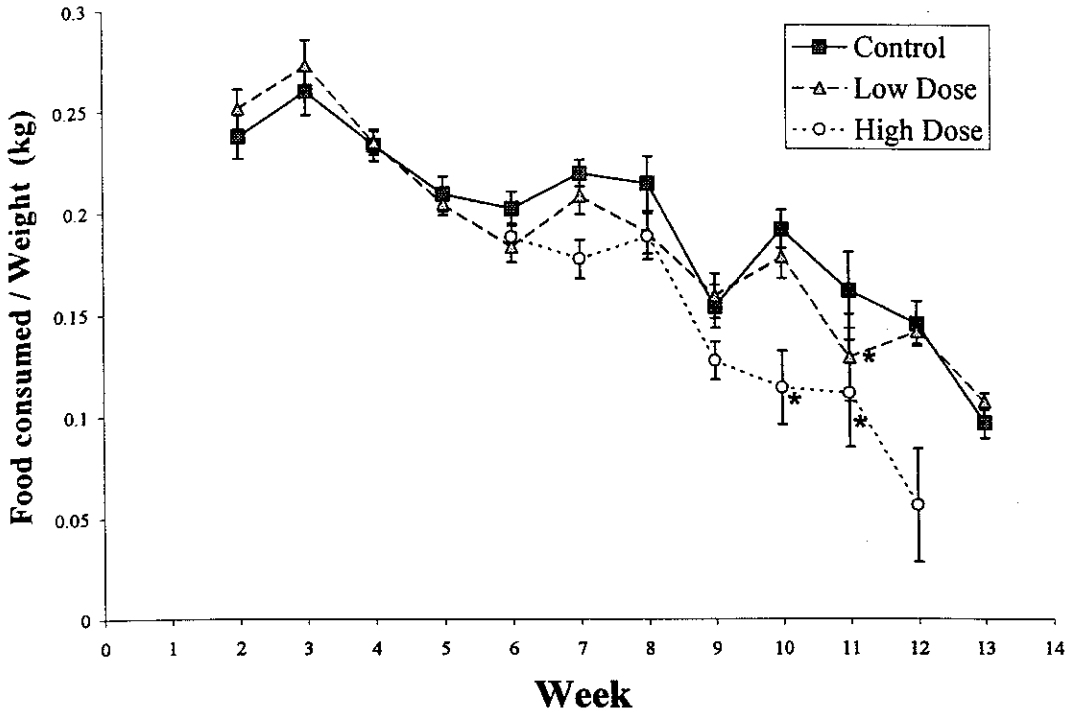

FIGURE 4. Three-day average daily food consumed per weight for great egrets dosed as control, 0.5, and 5 mg/kg methylmercury in their diet. * = values that differ significantly from controls ($P < 0.01$). Only two birds remained in the high dose group by wk 12.

muscles of great skuas (*Catharacta skua*) was methylated, whereas, approximately half that in liver and kidney was. Gardner et al. (1978) found that 40% and 20% of mercury in livers of snowy egrets (*Egretta thula*) and tricolored herons (*Egretta tricolor*) respectively, was methylated. Contrary to our findings, several authors have reported an inverse relationship between the total mercury concentration and the proportion that is methylated in liver and kidney (Norheim and Froslie, 1978 in raptors; Thompson and Furness, 1989 in seabirds; Kim et al., 1996 in seabirds).

Mercury was not distributed uniformly among tissues and our findings generally are similar to other studies of fish-eating birds. (Hesse et al., 1975; Osborn et al., 1979; Nicholson, 1981; Frank et al., 1983; Honda et al., 1985, 1986; Furness et al., 1986; Thompson et al., 1991; Lewis and Furness, 1991; Lock et al., 1992; Elbert and Anderson, 1998; Evers et al., 1998; Wolfe and Norman, 1998). The tight correlations we observed between tissue concentrations and dose and among tissue types were undoubtedly due to the very controlled nature of this study and would not necessarily apply directly to field situations where dosing would be irregular in duration, magnitude, and chemical form. In a number of experimental dosing studies in captive seabirds, mercury concentrations were higher in kidney than in liver, whereas the opposite was found in wild seabirds (summarized by Lewis and Furness, 1991). We have not observed this in herons and egrets in Florida (M. E. Spalding and M. S. Sepulveda, unpubl. data). In grebes, Elbert and Anderson (1998) found correlations between kidney, muscle and brain concentrations, but not liver, contrary to our findings.

A positive correlation between mercury and selenium in liver has been reported for other piscivorous species (Van der Mo-

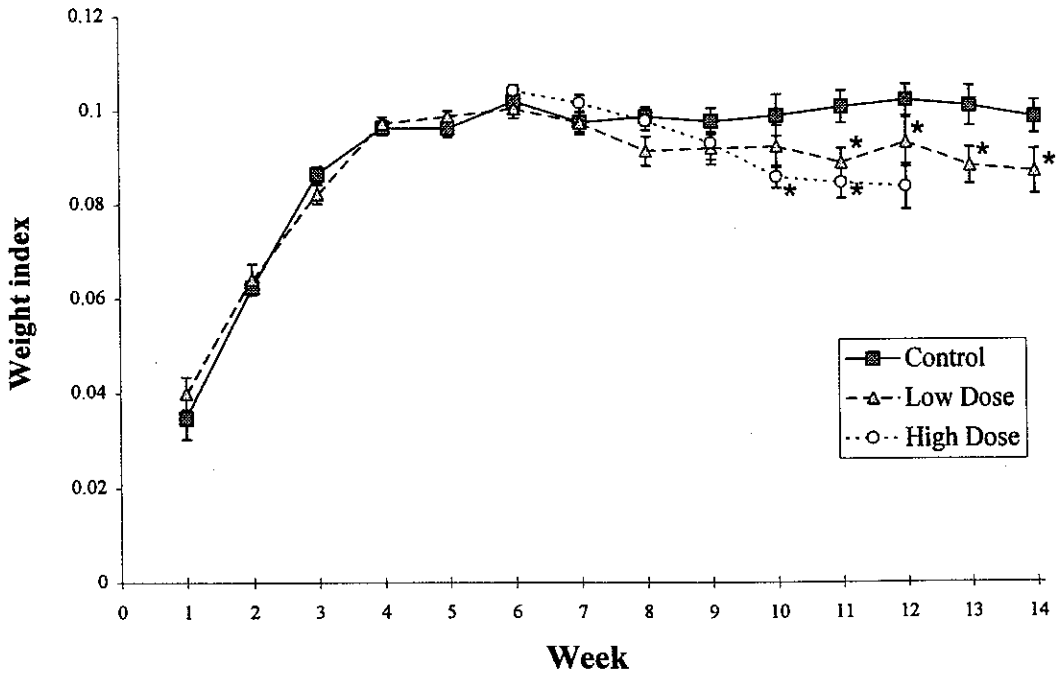

FIGURE 5. Weight index (weight/bill length) for great egrets dosed as control, 0.5, and 5 mg/kg methylmercury in their diet. * = values that differ significantly from controls ($P < 0.01$). Only two birds remained in the high dose group by wk 12.

len, et al., 1982; Sepulveda et al., 1998; Scheuhammer et al., 1998b), and it has been hypothesized that selenium plays an important role in the reduction of the toxic effects of methylmercury (Change et al., 1977; Cuvin-Aralar and Furness, 1991; Hoffman and Heinz, 1998; Heinz and Hoffman, 1998; Scheuhammer et al., 1998b). When methylmercury was fed to adult mallards (*Anas platyrhynchos*), selenium accumulated in liver at a greater rate than in controls, and accumulated at three times the rate in laying females, and 19 times the rate in males (Heinz and Hoffman, 1998). We did not observe any difference in selenium concentrations due to gender in our study of young birds (Fig. 1). Liver selenium concentrations in the high dose group exceeded the 66 ppm dry weight suggested for selenium toxicosis by Heinz (1996) however we did not observe all of the criteria for selenium toxicosis listed by Albers et al. (1996). We could not rule out the possibility that some of our experimental results were due to the effects of selenium directly, or possibly in concert with the methylmercury.

As reported previously for great egrets and for other fish-eating birds, feather and blood concentrations were highly correlated with each other, and mercury concentrated in feathers at a greater rate than in blood (Gochfield, 1980; Evers et al., 1998; Scheuhammer et al., 1998a; Sepulveda et al., 1999a). Overall, we found concentrations in growing feathers to be roughly eight times those in blood, but this relationship varied with age. We found that growing feathers were excellent predictors of other tissue concentrations and of the cumulative mercury consumed. Blood mercury concentrations, on the other hand, varied relative to the molt status. It seems likely that molt in adult birds would also act to decrease mercury concentrations in blood and other storage organs.

Our finding of increasing feather mercury concentration with age supports the

reports of Furness et al. (1986) and Braune and Gaskin (1987) that feather mercury reflects the cumulative amount of mercury stored in body tissues rather than the dietary intake at the time that the feather grew. Mature feathers collected near the end of the experiment had lower mercury concentrations than growing feathers collected at the same time. This is probably because mature feathers ceased to grow at about 9 wk, whereas growing feathers were exposed to the higher blood and other tissue concentrations near the end of the experiment. Although Lewis and Furness (1991) found higher concentrations in primary feathers grown first in gull chicks, all dosing in their experiment occurred prior to the initiation of feather growth. Therefore, the timing of feather growth in relation to mercury exposure and maturity of feather are important factors when comparing birds or locations, or simply evaluating the exposure history of a single bird of interest. The combination of a mature feather, a growing feather, a blood sample, and knowledge of the molt stage may provide the most comprehensive information about contamination history for a bird.

Even though chicks were ingesting food (and methylmercury, 0.135 mg/kg/day) at the highest rate relative to body size during wk 3, the effects of mercury on appetite and growth were not apparent until much later. In all three groups mercury began to accumulate in blood in higher concentrations relative to dosing after wk 9. This corresponded with the time that feathers stopped growing (wk 9–11 for primary feathers, and wk 9 for tail feathers) and was just before the time that birds also began to show obvious deficits in appetite and growth.

Although appetite declined in both dosed groups, we could find no good explanation for why it occurred after consumption of 6.4 mg/kg in the low dose group, and but not until 44.5 mg/kg had been consumed in the high dose group (Spalding et al., 2000, Table 1). In wild dosed great egrets (1.8 mg Hg/kg in fish) declines in appetite were detected when feather concentrations were 49 mg/kg (=4.8 CumHg/body weight using regression in Fig. 3, see Williams, 1997). These findings support the hypothesis that wild nestlings might be more sensitive to methylmercury than captive nestlings because of uncontrolled factors that might interact to affect appetite.

The weight loss that occurred in both dose groups was a logical consequence of the methylmercury-induced reduction in appetite. The magnitude of weight loss was small and all birds had abundant body fat at the end of the experiment. The lack of food stress in these captive birds may have masked some of the effects that methylmercury contamination would have caused had the birds been hunting on their own. Williams (1997) could find no evidence of weight declines or changes in skeletal measurements in wild great egret nestlings dosed in the field.

It appears that growing feathers, and possibly other storage organs, provide a sink for mercury during the nestling period that protects chicks from mercury poisoning. When feathers ceased to grow and this sink was no longer available, mercury increased more rapidly in blood. Our findings support the conclusion that there is a period of higher risk of chronic mercury toxicity for young birds when feathers stop growing. This period of elevated risk usually would occur as feathers are finishing their growth which coincides with the time that young birds also encounter the multiple risk factors of having to forage on their own, leave the natal colony, and become exposed to novel predation and disease factors.

We conclude that methylmercury affected appetite and growth of great egrets, even at the 0.5 mg/kg dose rate, a dose similar to current exposure in the Everglades (Frederick et al., 1999). We caution against using these data to designate a lowest observable adverse affect level (LOAEL) for two reasons. Selenium avail-

ability was high in our experiment, and we suspect that in a system where it is less available poisoning might occur earlier. In wild birds with lower nutritional reserves, a reduction of appetite could more quickly result in loss of weight and body condition given the rigors of competition between siblings for limited food resources (Mock et al., 1987), learning to forage, and other stressors. Since the consequences of poor body condition can initiate a downward trend in health due to poorer foraging success, compromised immune system (Grasman and Scanlon, 1995) and increased disease susceptibility, we suggest that the effects of mercury on body condition will lead to higher mortality rates for juveniles in the wild.

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Atmospheric Mercury Deposition during the Last 270 Years: A Glacial Ice Core Record of Natural and Anthropogenic Sources

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Mercury (Hg) contamination of aquatic ecosystems and subsequent methylmercury bioaccumulation are significant environmental problems of global extent. At regional to global scales, the primary mechanism of Hg contamination is atmospheric Hg transport. Thus, a better understanding of the long-term history of atmospheric Hg cycling and quantification of the sources is critical for assessing the regional and global impact of anthropogenic Hg emissions. Ice cores collected from the Upper Fremont Glacier (UFG), Wyoming, contain a high-resolution record of total atmospheric Hg deposition (ca. 1720−1993). Total Hg in 97 ice-core samples was determined with trace-metal clean handling methods and low-level analytical procedures to reconstruct the first and most comprehensive atmospheric Hg deposition record of its kind yet available from North America. The record indicates major atmospheric releases of both natural and anthropogenic Hg from regional and global sources. Integrated over the past 270-year ice-core history, anthropogenic inputs contributed 52%, volcanic events 6%, and background sources 42%. More significantly, during the last 100 years, anthropogenic sources contributed 70% of the total Hg input. Unlike the 2−7-fold increase observed from preindustrial times (before 1840) to the mid-1980s in sediment-core records, the UFG record indicates a 20-fold increase for the same period. The sediment-core records, however, are in agreement with the last 10 years of this ice-core record, indicating declines in atmospheric Hg deposition.

Introduction

Atmospheric transport and fate of mercury (Hg) and subsequent methylmercury bioaccumulation in the environment are critical contamination issues (*1*). Of continuing debate is whether atmospheric Hg deposition is due to local, regional, or global sources (*2*, *3*). Recent estimates indicate that anthropogenic emissions of Hg have exceeded natural inputs since the onset of the industrial period (*4*). The potential effectiveness of proposed Hg emission reductions hinges on an accurate estimate of the function of current atmospheric deposition from "manageable" sources. A significant question facing scientists and environmental agencies is the relative contribution of natural and anthropogenic sources to atmospheric Hg. Mercury concentrations in glacial ice provide a direct measurement and historic record of atmospheric Hg deposition (*5*−*7*). Research on total Hg in glacial ice, especially in the midlatitudes, is scarce. Although some polar ice cores have provided a limited record of past Hg deposition, polar ice cores are, at best, proxy indicators of historic Hg deposition in the midlatitudes.

Increasingly, ice cores from low- and midlatitudes are becoming recognized as valuable tools for reconstructing paleoclimatic and paleoenvironmental records (*8*−*15*). These records, however, are uncommon; the Hg record presented here is the first and most comprehensive of its kind yet to be available in North America. To underscore the importance and uniqueness of these records, increasing global temperatures are threatening the existence and integrity of low- and midlatitude glaciers, which are receding rapidly. If recession continues at these rates, the Dinwoody Glacier, about 3 km north of the Upper Fremont Glacier (UFG), will be gone in about 20 years (*16*). Other estimates show that the remaining glaciers in Glacier National Park, Montana, will no longer exist in 50−70 years (*17*) and that high alpine glaciers in the Andies of South America (i.e., Quelccaya) will be severely compromised by meltwater processes (*13*). This irreplaceable paleoenvironmental resource may literally melt away in the near future, releasing an additional and potentially large reservoir of Hg trapped in snow and ice to the environment.

The dynamics of Hg in glacial ice are not well-known. Although Hg deposition to polar cores has been investigated (*5*−*7*), it is recognized that, unlike polar ice cores, meltwater processes can influence the chemical stratigraphy of alpine glaciers. This process is described in terms of an elution sequence (*18*) and may "dampen" or complicate the environmental signal by mobilizing or removing solutes. A complete removal of chemical signal from the ice by meltwater processes limits paleoenvironmental interpretation in that it is impossible to know if an environmental signal initially existed. Therefore, any chemical signal preserved in the ice, albeit possibly stratigraphically shifted, may have potentially been much larger during deposition. To date, there has been no work to place metals such as Hg in the elution sequence. Thus, the mobility of Hg in temperate ice, in relation to other ions, is largely unknown. Despite these potential problems, previous studies (*8*−*11*, *19*) indicate that the UFG preserves chemical stratigraphy with sufficient resolution to support the interpretation of valuable paleoenvironmental records. Moreover, Hg concentrations in ice cores are not subject to controversial diagenetic processes that may affect Hg concentrations in sediment cores, peat bogs, and soils (*20*−*21*). Hg(0) is sparingly soluble (equilibrium concentrations with typical air concentrations are about 2−6 pg/L) and, with respect to other solutes, the solubility of Hg(II) and HgO is low, suggesting that movement in glacial ice due to meltwater is minimal.

Experimental Section

Continuous ice cores were collected from UFG in the Wind River Range, Wyoming (Figure 1), in 1991 and again in 1998.

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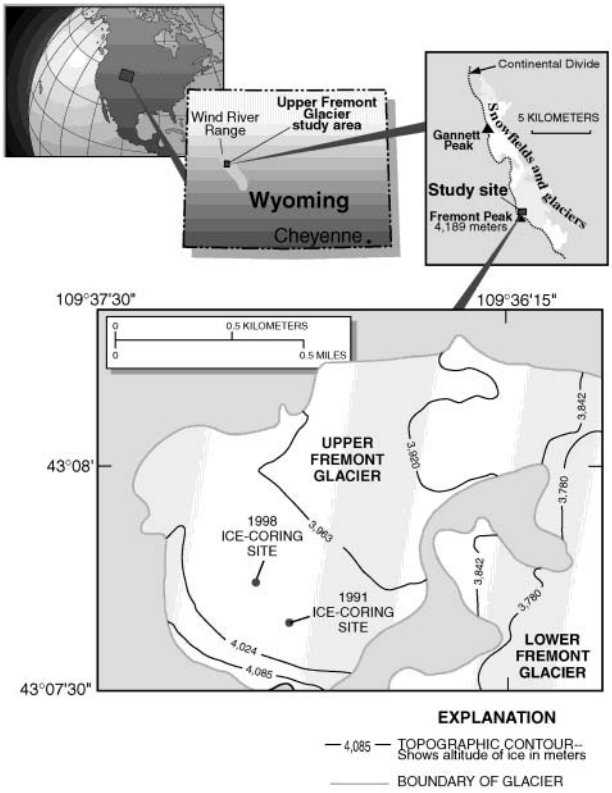

FIGURE 1. Map showing the location of the 1991 and 1998 ice-core drilling sites. Each site was located at about the same altitude separated by about 220 m.

For a temperate glacier, the UFG has some unique qualifications conducive to preserving paleoenvironmental signal. The drill site elevation is 4100 m. Minimum, maximum, and average annual air temperatures during 5 years of record were −36, 13, and −7 °C, respectively. Temperature profiles from snow pits, conducted on an intermittent basis, on the UFG indicated that the snowpack was typically isothermal at 0 °C during the summer months. During the winter months, the snowpack was below 0 °C, ranging from −7 to −2 °C. The net accumulation rate is 96 cm ice equivalent/year, based on the 29-m depth of ice (the 1963 tritium peak) divided by time. The glacial surface gradient is near level, reducing crevassing and fracturing of the ice strata (*9*). These characteristics reduce the potential for meltwater to alter any paleoenvironmental signal. Because the remoteness of the site limits the influence of local sources of atmospheric Hg deposition to the UFG, the location is favorable for measuring historical regional and global deposition of total Hg from the atmosphere (Figure 2) (*22*).

Typically, ice cores are recovered with electromechanical drills, and deep polar cores require the use of liquid lubricants such as fuel oil or antifreeze to keep the drill hole open. The UFG cores, located about 220 m apart roughly along the same contour elevation, were recovered with a 7.6-cm diameter thermally heated aluminum coring device (*9*). The thermal drilling process excludes the use of lubricants, reducing the potential for Hg contamination. The drill winch cable was a Kevlar braid protected by an outer Nylon braid. All bolts on the core barrel were stainless steel, and silver was a major component of the thermal blade. The metals exposed to the ice-core surface during recovery and processing were composed of aluminum and stainless steel. To assess possible Hg contamination from these metals, "veneer experiments" similar to those reported for polar ice (*23*) were performed on a 20-cm piece of archived UFG ice (ca. 1855) from a depth of 103 m. Four successive ~1 cm layers (i.e., concentrai rings) were scraped from the sample using a titanium blade onto a Teflon working platform inside a laminar-flow hood. Powder-free Latex gloves were worn throughout the procedure (*24*). The scrapings were collected into acid-boiled 250-mL Teflon bottles and allowed to melt at room temperature. The melted samples, ranging in volume from 51 to 71 mL, were analyzed for Hg using internationally adopted and proven analytical methods (*25*). Rinse water from the titanium blade was measured at 0.35 ng/L. Selected metal concentrations (including rare earths) were measured by ICP-MS. Mercury concentrations from the veneer experiment ranged from 9.3 to 11.2 ng/L with no obvious trend in those data, and the average concentration was within 6% of the composite sample taken from the same horizon for the development of the Hg profile. The uniform concentrations through the thickness of this ice-core sample suggest two possibilities: (1) the source of Hg is from atmospheric deposition and represents an uncontaminated signal, or (2) an Hg source from the core barrel has penetrated the entire thickness of the core. The latter is unlikely for three reasons: (1) Hg(0) is sparingly soluble and, with respect to other solutes, the solubility of Hg(II) and HgO is low, and reducing movement in ice, a solid-phase exchange process would be required; (2) the significant variations in Hg concentrations observed throughout the length of the core would be masked or dampened by a constant source of contamination; and most significantly, (3) if a contamination source existed, concentrations of these constituents would decrease from outer to inner core (*23*); this trend was not observed in the UFG ice core. Aluminum and zinc, two major components of the core barrel and saw blade, also showed no decreasing trends from the outer layers to the ice-core center. Moreover, silver, a major component of the thermal blade, and chromium, a component in stainless steel, were not detected. Aluminum did not correlate with the rare earth elements La, Ce, and Nd in the outermost layer as a function of radius from the center, suggesting that a fraction of this aluminum is from the core barrel. The next five layers to the center of the core, however, show that aluminum is correlated to these rare earth elements, indicating that the source is natural or crustal earth. Although the potential for Hg contamination exists, based on these results, removal of the outer layer of the ice-core samples (discussed next) greatly reduces the potential for Hg contamination from recovery and processing techniques used for the UGF ice cores.

After the ice core was removed from the aluminum core barrel, 1-m sections were quickly sealed in polyethylene bags and placed in core tubes by personnel wearing Tyvek suits and powder-free Latex gloves. During the entire process, "clean hands" protocol was used (*24*). To prevent melting,

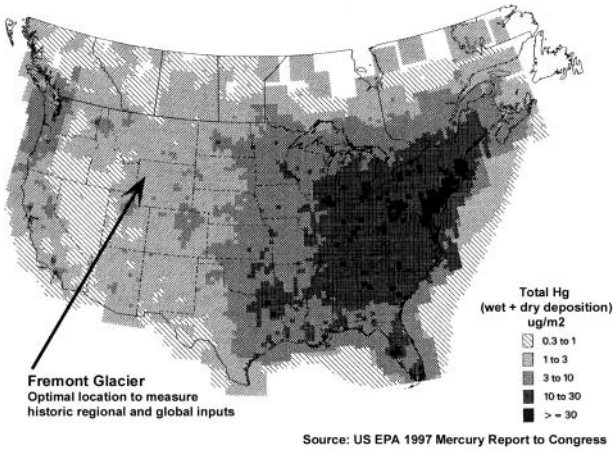

FIGURE 2. Location of the Upper Fremont Glacier showing very little impact from upwind local sources of atmospheric Hg.

the core tubes were stored at 0 °C in snow vaults on the glacier. Immediately after drilling was complete, the cores were transported to a freezer truck via a 10-min helicopter flight to storage in the National Ice Core Lab (NICL) storage room (−36 °C) in Denver, CO, until processing and analysis.

All processing took place in the clean −24 °C environment of NICL. The cores, totaling 160 m in length, were cut into 7-cm sections with a stainless steel band saw cleaned with methanol. A total of 57 samples and 40 samples were removed from the 1991 and 1998 cores, respectively. The sections were placed in Hg-free clean polyethylene bags and shipped frozen on dry ice overnight to the U.S. Geological Survey's Wisconsin District Mercury Research Lab (WDMRL) in Middleton, WI. Temperature recorders were placed in the shipping containers, and the temperature inside the containers during shipment did not exceed 0 °C.

At the WDMRL, ice samples were removed from the bags with gloved hands and rinsed with about 50 mL of WDML deionized water (total Hg ≤0.1 ng/L) to remove any potential contamination from field procedures. After rinsing, the samples were placed in Hg-clean (*25*) Teflon jars. Four milliliters of bromine monochloride (BrCl) was added to oxidize all species of Hg to Hg(II), the jars were capped, and the samples were allowed to thaw at room temperature. Samples ranged in volume from 25 to 75 mL. Although there are small variations in ice density, this is not the main reason for sample-volume variation. In some sections of the ice core, demands for ice to address other research interests (i.e., chlorine-36 studies and paleoclimate and paleoenvironmental studies) limited the volume of ice available for Hg research. Because all samples were run in duplicate for Hg analysis and the likely possibility Hg concentrations would be relatively low in many preindustrial samples (<1 μg/L), creating further demand for a maximum volume needed for accurate Hg analysis, 50 mL of rinse water was used to remove the potentially contaminated outer core layer. Once thawed, the liquid was transferred to Hg-clean Teflon bottles that were placed in an oven at 50 °C overnight to ensure complete oxidation of all mercury species. Analysis for total Hg was performed with dual amalgamation cold vapor atomic fluorescence spectrometry (*25*) with a method detection limit (MDL) of 0.04 ng/L (*26*).

Quality control (QC) check samples were analyzed at the beginning of the run, at least every 10th sample, and at the end of the run to establish daily statistical control. QC checks were prepared with WDMRL deionized water and a known amount of Hg standard from a source other than that used for standardization. The QC standards measure any possible instrument drift and provide an external check on the accuracy of the calibration standards. Four jar blanks (process blanks) were run during the period of analysis. A jar blank consisted of brominated deionized water that was allowed to sit in a clean jar for the time it took for the ice to melt and then was transferred into a Teflon bottle and treated like a sample. Results from the jar blanks were used to determine the contribution of Hg from the oxidant BrCl and any Hg sources from the jars. The blanks ranged in concentration from 0.30 to 0.86 ng/L (mean = 0.66, std dev = 0.25, $n = 4$). After blank subtraction of the mean blank value, the lowest total Hg concentration from 97 samples was 1.21 ng/L, which is still significantly above the highest blank value. All samples were analyzed in duplicate. If the percent difference between the two duplicates was greater than 10%, the sample was analyzed a third time. In all cases, the relative standard deviation between the three replicates was less than 10%. On each work day, at least one sample was spiked and the percent recoveries ranged from 90 to 111 (mean = 99, std dev = 6, $n = 15$).

Results and Discussion

Ice Core Chronology. Accurate ice-core chronology is essential to paleoenvironmental interpretation. Unlike polar ice cores from Greenland and Antarctica, which are more likely to preserve visual stratigraphy in the form of annual summer dust layers (*27*, *28*), annual dust layers in the UFG were not always visible, thereby making visual age-dating methods unreliable. Although long-term trends in the water isotopes appear to be preserved, there is no evidence that seasonal isotopic signatures have been preserved in the UFG ice (*8*, *9*). Instead, the chronology of the UFG was determined using other isotopic and chemical age-dating techniques. The 1963 tritium (*8*) and 1958 chlorine-36 (*10*) peaks were found at depths of 28 and 32 m respectively. A carbon-14 value from a grasshopper leg found at 152 m yielded a most probable age of 221 ± 95 years (*8*). These dates, in combination with estimated snow accumulation and ablation measurements (*9*), established a low-resolution chronology for the UFG cores. Additional time markers of volcanic origin at 88 and 123 m were identified through electrical conductivity measurements (ECM), establishing a confident age−depth relationship and refining the ice-core chronology to prediction limits of ±10 years (90% confidence level) and confidence limits of 2−3 years (*11*). Although the resolution of the UFG ice cores is considered low by polar ice-core research standards, it provides a chronology of sufficient resolution over its 270-year record to support the conclusions made about historical changes in Hg deposition. Development of the UFG ice-core chronology is described in detail in other work (*8*, *9*, *11*, *29*).

Hg Concentrations in the UFG. The remote location and high elevation of the UFG (Figure 1) most likely reduce the contributions from local anthropogenic influences of atmospheric Hg (Figure 2) (*22*). As such, Hg concentrations in ice cores from the UFG reflect regional and global atmospheric inputs. Although the range of Hg concentrations found in the UGF ice cores (Figure 3) were much greater than those found in Antarctic and Greenland ice, preindustrial or background concentrations not influenced by volcanic activity, however, were similar to those found in Antarctic ice and Greenland ice (*5*, *6*), indicating that the large ranges of Hg concentrations found in the UFG are not an artifact of contamination but rather reflect natural and anthropogenic deposition of atmospheric Hg at this latitude. Total Hg measured in 97 ice-core samples spanning 160 m provided an average Hg profile resolution of 3 years. The detailed chronology of the UFG cores, coupled with analytical advances in measuring trace levels of Hg, together with a 3-year profile resolution, provide a clear and direct measure of historical natural and anthropogenic contributions to atmospheric Hg deposition. Furthermore, the continuity of the Hg profile from the 1991 core to the 1998 core indicates that Hg is preserved in the ice (Figure 3).

By integrating the peak areas identified as separate atmospheric sources of Hg, the relative contributions of these sources were quantified. Eighteen preindustrial (before 1840) measurements of Hg were used to extrapolate a background value (3 ng/L) through the ice-core record. Background concentrations contributed 42% of the total Hg in the ice core during its 270-year record.

Volcanic Sources of Hg. Volcanic eruptions are a known atmospheric Hg source (*30*, *31*); however, their importance on a global scale has remained unresolved. Three distinct peaks in the ice-core Hg profile are coincident (within the chronology prediction limits of ±10 years) with increased chloride and sulfate concentrations and ECM (Figure 4) (*11*). ECM is a direct measurement of the acidity of the ice (*32*). Volcanic eruptions increase the acidity of precipitation, resulting in increased ECM of the ice. Strong ECM signals,

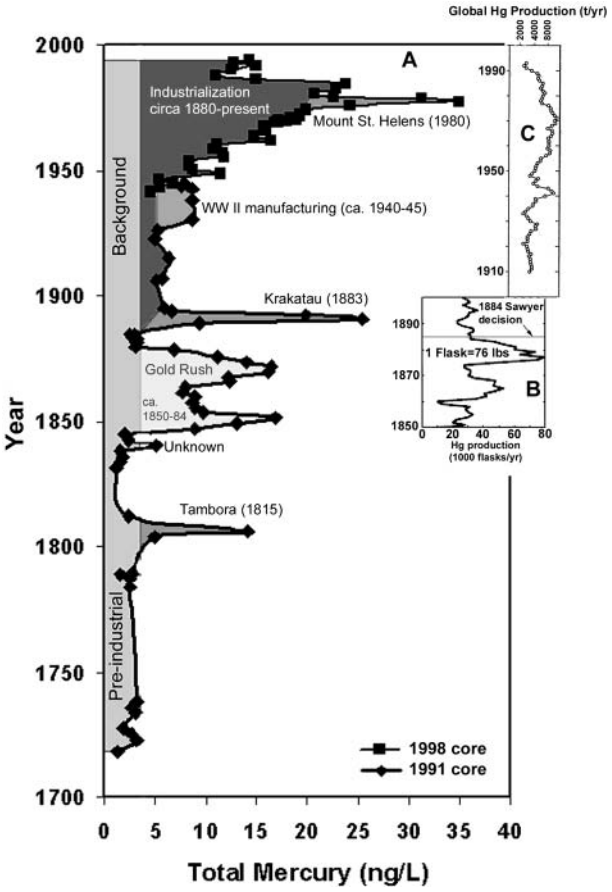

FIGURE 3. (A) Profile of historic concentrations of Hg in the Upper Fremont Glacier. A conservative concentration of 4 ng/L was estimated as preindustrial inputs and extrapolated to 1993 as a background concentration. Age−depth prediction limits are ±10 years (90% confidence level); confidence limits are 2−3 years (*11*). (Inset B) Hg production during the California Gold Rush (adapted from Figure 5 in ref *39*). (Inset C) World production of Hg in tons per year during the last century (adapted from Figure 4B in ref *43*).

along with increased chloride and sulfate concentrations in the ice-core profile suggest that the snow falling on the glacier surface at that time contained volcanic fallout.

The two largest eruptions in recorded history, Krakatau (1883 AD) and Tambora (1815 AD), albeit in the southern hemisphere 20 000 km from the UFG, reached well into the stratosphere with global effects. The ship, Medea, measured the Krakatau eruption column height to be up to 26 km (*33*). The Tambora event, perhaps the largest eruption in the last 10 000 years, injected volcanic material to a height estimated to be as high as 44 km into the stratosphere (*34*). Historical observations of remarkable sunsets in Europe, North America, and Hawaii and optical effects for up to 2 years after each eruption were another indication that the dust columns reached the stratosphere (*35*). Fallout from the Tambora and Krakatau events has been identified in Antarctic and Greenland ice cores (*36*, *37*). These natural geologic events were point sources in terms of Hg origin but were followed by global scale deposition. The Mount St. Helens eruption (1980), although orders of magnitude smaller in scale, was only 600-km distant and directly upwind of the UFG, blanketing the region with volcanic ash (*9*). The proximity of Mount St. Helens to the UFG qualifies the corresponding Hg peak as a regional Hg source. The peak's superposition on elevated concentrations due to near-peak anthropogenic Hg emissions resulted in the profile's highest measured Hg concentrations (Figure 3). Differences in Hg loads among the three volcanic peaks may have been due to differences in volcanic dust compositions as indicated by differences in chloride, sulfate, and ECM peaks. Whether the volcanic source of Hg was regional, global, or altered by postdepositional processes, it is clear that these globally impacting natural events have "punctuated" the historical Hg record in the UFG and likely elsewhere.

Integrating the peak areas attributed to volcanic activity with global impact (Figure 3), these natural atmospheric Hg sources were quantified. During the past 270 years, three major volcanic events (Tambora, Krakatau, and Mount St. Helens) contributed 6% of the total Hg measured in the ice cores. It is likely, however, that 6% is an underestimate. There are three main possibilities for this underestimate. (1) There have been numerous smaller volcanic events (*38*) during the past 270 years. Some of these events undoubtedly had some global impact, but the volcanic signal was likely masked by the background or anthropogenic signal. (2) Only 6.7 m of a total length of 160 m of ice was sampled for Hg throughout the length of the core. The Hg signal from a volcanic source is of short duration (1−2 years). Thus, it is likely that some volcanic events were not sampled. (3) It is also possible that elution processes (described earlier) dampened the volcanic Hg signal of the three major volcanic eruptions identified in the UFG ice core.

Anthropogenic Sources of Hg. Mercury was used on a large scale to recover gold from mining operations throughout the western United States beginning around 1850. These activities peaked around 1860 and then again around 1877 (Figure 3, inset B) (*39*). The bimodal nature of these activities was reflected in the ice-core Hg profile, showing significant increases coincident with peak Hg production in California during this period. The age−depth prediction limit for the UFG ice cores is ±10 years, thus accounting for the slight offsets among Figure 3A and insets B and C. Mercury production decreased significantly in 1884 with the introduction of legislation (The Sawyer Decision) (*39*) that greatly reduced the use of Hg for gold extraction in California. A precipitous drop in UFG ice-core Hg concentrations coincided with this period.

Most sediment-core studies do not indicate an increase in Hg concentrations coincident with the start of the California Gold Rush. There are some studies, however, that do record a "jump" in the sediment Hg profile ca. 1850 (*40*, *41*). Nriagu (*42*) explains that most of the Hg would have blown west, describing this transport as a "grasshopper-like dispersal pattern". The mercury−gold amalgamation practices during the California gold rush during the mid-to-late 1800's were unregulated and unrivaled by any other mining activity up to that time (*39*). During this time, unknown amounts of Hg were volatilized to the atmosphere. The depositional pattern of atmospheric Hg from this source would be, in a large part, dependent on storm trajectories and jet stream patterns for which there is obviously no data for that period. On the basis of (1) today's general knowledge that it is not uncommon for storm trajectories and the jet stream to migrate north and south, (2) the UFG's proximity to the California mining belts, and (3) the magnitude of the estimates of Hg volatilized into the atmosphere for 30 years (ca. 1849−1884), it is suggested that the source of elevated Hg concentrations measured in the UFG ice core coincident with the same time period is Hg from California mining activities (Figure 3). If the source of these elevated Hg concentrations is from California gold-mining activities, as suggested by Figure 3, then the integration of the profile indicates that the mercury−gold amalgamation activities during the California Gold Rush contributed 13% of the total Hg in the 270-year ice-core record. These data suggest that

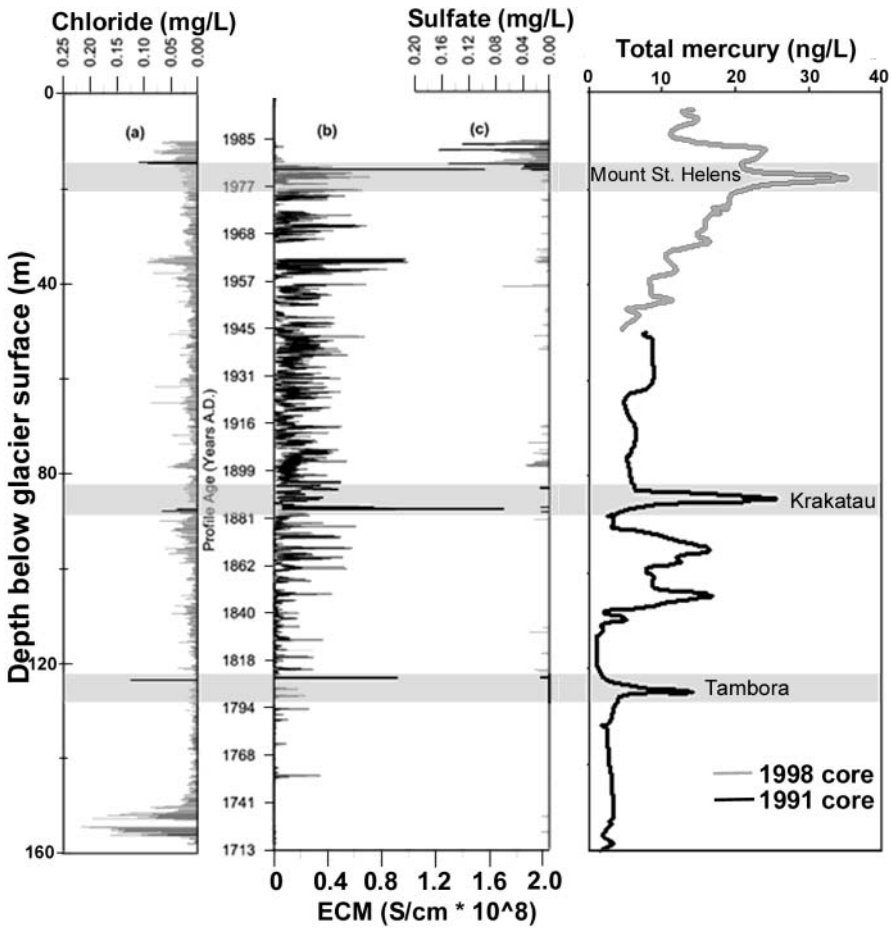

FIGURE 4. Profiles for Hg compared to chloride, sulfate, and electrical conductivity measurements (ECM). The *y* axis is scaled with the age−depth relation ship, thus giving the Hg profile a slightly different appearance from Figure 3. ECM is a measure of the acidity of the ice. A correlation among chloride, sulfate ECM, and Hg is a strong indication of a volcanic source. Age−depth prediction limits are ±10 years (90% confidence level); confidence limits are 2−3 years (*10*) (adapted from Figure 3 in ref *11*).

the California Gold Rush had a significant regional impact in terms of atmospheric Hg deposition in the western United States.

At the turn of the 20th century, atmospheric Hg levels remained elevated as compared to preindustrial (before ca. 1840 AD) or background values. Increases in anthropogenic Hg emissions during the past century have been attributed mainly to coal-burning power plants, waste incineration, and chlor-alkali plants (*3*, *43*, *44*). The next significant increase in ice-core Hg concentrations coincided (within the ±10 year prediction limits) with increased global Hg production (Figure 3, inset C), most likely in response to industrial mobilization for World War II. There was a post-WWII decline in global Hg production, once again coincident with decreases in ice-core Hg concentrations. The last half of the 20th century up until 1990 shows a consistent increase in both global Hg production and Hg concentrations in the UFG ice cores.

Volcanic eruptions contributed to the global Hg pool for brief periods (<2 years) and, thus, cannot account for the substantial increase in ice-core Hg concentrations during the last century. The volcanic inputs, albeit competitive with industrial inputs, were short in comparison to the chronic levels of elevated Hg concentrations during the last 100 years, indicating that anthropogenic inputs have had the greatest influence on the atmospheric Hg deposition record in the UFG. During the past 270 years, anthropogenic inputs contributed 52% of the Hg accumulation in the core. More significantly, during the last 100 years, anthropogenic sources contributed 70% of the total Hg input. A post-1990 decline in the ice-core Hg concentrations is discussed next.

Hg Deposition Rates to the UFG. Historical Hg deposition rates were calculated from Hg concentrations measured in the ice cores (Table 1). The calculated rates of deposition assume an average accumulation rate of 1 m of ice equivalent to the UFG per year. Obviously, this rate varies from year to year. However, on the basis of average measurements of accumulation and ablation rates (*8*, *9*) this estimate is not unreasonable. Moreover, up to 50% of seasonal snowfall accumulation is lost through ablation (*9*). This process, although difficult to quantify, would, most likely, lead to an underestimate of Hg deposition calculated from concentrations in the ice core.

There is a down-core change in the age−depth relationship due mostly to glacial flow processes leading to layer thinning with depth. Basically, the same 7-cm section of ice-core sample represents more time with depth. Considering the calculation of Hg deposition rates and utilizing the age−depth relationship (*11*), a ratio (change in age/change in depth) was calculated and applied to Hg deposition results to develop corrected Hg deposition rates using eq 1

$$(A_i - A_{i-1})/(D_i - D_{i-1}) \quad (1)$$

where A is the calculated age (years) (*10*), D is the ice-core depth (meters), and i denotes the sequential Hg sample (1−97). At the base of the core (the 97th Hg sample), the ratio is 2.88. Thus, at this depth, 1 m of ice represents approximately 2.88 years. Equation 1 was applied to Hg deposition rates as a correction factor to compensate for down-core changes of

TABLE 1. Mercury (Hg) Deposition Measured among Three Sample Media

site	sample media	episode (reference)	year(s) (AD)	average [Hg] (ng/L)	deposition[a] (μg/m^2/year)	change from preindustrial (fold)
UFG	ice	Clean Air Act	1986−1993	9	11.4	11
UFG	ice	industrial max	1984	20	20.3	20
UFG	ice	Mt. St. Helens	1980	11[b]	12.7§	12
UFG	ice	industrial	1900−1993	10	11.0	11
UFG	ice	WWII	1938−1946	7	4.73	5
UFG	ice	Krakatau	1883	21[c]	18.2§	18
UFG	ice	Gold Rush	1850−1878	8	4.84	5
UFG	ice	Tambora	1815	10[c]	8.60§	8
UFG	ice	preindustrial	1719−1847	3	0.78	na[d]
Minnesota	wet ppt[e]	(*49*)	1997−1999	14	6.99	7
Colorado	wet ppt	(*49*)	1999	10	9.20	9
			<1880	na	80.0	na
Minnesota	lake sed**	(*48*)	>1880	na	170	2[#]
			<1850	na	3.70	na
Minnesota	lake sed	(*45*)	modern	na	12.5	3
			<1750	na	2.00	na
Arctic	lake sed	(*47*)	1980	na	12.5	6
			<1850	na	5.00	na
New York	lake sed	(*46*)	modern	na	8.90	2
			<1850	na	7.60	na
California	lake sed	(*40*)	>1980	na	38.0	5

[a] Deposition calculated using age−depth correction factor. [b] Preindustrial and industrial inputs subtracted to isolate volcanic signal; maximum input reported. [c] Preindustrial input subtracted to isolate volcanic signal; maximum input reported. [d] Not applicable or not available. [e] Wet precipitation. § Age−depth correction factor not used to calculate deposition rate. ** Sediment. # Change measured from "preindustrial" dated cores from cited study.

the age−depth relationship (due to thinning) on each 7-cm sample.

The ratio attained one at about 35 m. It is assumed there is no change in the age−depth relationship (due to thinning) from 35 m to the top of the core (1 m of ice ∼ 1 year). The residence time of Hg(0) in the atmosphere is on the order of a year (*1*). Thus, deposition from volcanic sources represents, at most, a 1-year period. Therefore, volcanic deposition values were calculated and reported without age−depth correction factors. Also, preindustrial (background) and industrial inputs were subtracted from the calculated volcanic deposition to isolate the volcanic signal. Using maximum input from each volcanic event and the conditions described previously, deposition rates from the volcanic events identified here indicate an 8−18-fold increase in Hg deposition over background due to globally impacting volcanic activity.

Again, assuming an accumulation rate of 1 m of ice/year (*9*) at the top of the ice core and accounting for changes in the age−depth relation down-core (*11*), there was a 20-fold increase from preindustrial times to an "industrial maximum" ca. 1984. During the last century, the average increase due to industrialization was 11-fold. Analysis of sediment cores from lakes (*40*, *45*−*48*) and precipitation (*49*) also indicate increases in atmospheric Hg deposition (2−9-fold) since the 1700s. The increase in Hg deposition rates from preindustrial times to the mid-1980s, as indicated by the ice cores, are up to 10 times higher than increases determined from sediment cores and precipitation. Recent work indicates that ice-core response to changes in global atmospheric cycling masses and deposition may be amplified for snow (*50*). Although the mechanisms are unclear, the work concluded there is a positive relationship of altitude to Hg loading in snow. A more recent study, however, indicates that Hg in snow packs is susceptible to reemission due to photochemical redox reactions, resulting in reductions of Hg levels by 54% within 24 h after deposition (*51*). If this process does occur at the UFG, the estimated Hg deposition rates calculated from the UGF ice cores could be underestimated by as much as one-half. On the other hand, recent work has also shown that mercury deposition may be affected by altitude, resulting in increases in atmospheric Hg deposition. Work in the Wasatch and Teton ranges near the UFG indicate that annual Hg accumulation rates increase from 100% to 175%, with an elevation gain of 1000 m (*50*). In addition, recent work on Denali (Mt. McKinley) in Alaska (Krabbenhoft, to be submitted for publication) showed a 30−75-fold increase in Hg concentrations in the surface snow with an elevation gain of about 5500 m; the ice-core site on the UFG is at an elevation of 4100 m (Figure 1). It appears that the altitude effect is much larger than the reemission processes indicated by LaLonde (*51*). This may by why there are measurable and distinct volcanic and anthropogenic Hg signals in the UFG ice cores and why this profile differs greatly from those found in sediment cores. The nearly 50% decline in mercury accumulation at the top of the ice core compares very favorably in magnitude with independent estimates of recent global declines of mercury production and use (*43*, *52*). Lake sediments, on the other hand, retain only a small fraction of the total Hg deposition, and the remainder is generally recycled back to the lake (*53*). Moreover, uncertainties such as sediment focusing associated with using sediment cores to estimate accumulation rates prevent simple comparisons of the two methods.

Estimation of "Global Impact" Volcanic Hg Deposition. An estimated 21 km^3 of volcanic material was ejected during the 1883 Krakatau eruption (*54*). The 1815 Tambora event produced a bulk volume of approximately 150 km^3 of pumice and ash (*55*). Assuming that the ejecta and gases reached the stratosphere and were distributed evenly over the earth's hemisphere (*56*), an estimation of the atmospheric deposition attributed to these globally impacting volcanic events was calculated by eq 2

$$\mathrm{Hg_{vol}}(\mu\mathrm{g/m^2}) = [V_{\mathrm{eje}}(\mathrm{cm^3})\rho_{\mathrm{plu}}(\mathrm{g/cm^3})1/\rho_{\mathrm{str}}(\mathrm{g/m^3})\mathrm{Hg_{plu}}(\mu\mathrm{g/m^3})]/A_{\mathrm{hem}}(\mathrm{m^2}) \quad (2)$$

where $\mathrm{Hg_{vol}}$ is the atmospheric deposition from a globally impacting volcanic eruption, V_{eje} is the volume of volcanic ejecta, ρ_{plu} is the density of the volcanic plume, ρ_{str} is the

density of air at 5000-m elevation (pressure ~ 0.4 atm, and average air temperature in the volcanic plume is ~ −20 °C (*57*)), Hg_{plu} is the concentration of Hg in the plume, and A_{hem} is the area of the earth's hemisphere.

On the basis of previous work (*58*−*62*), the concentration of Hg in an atmospheric volcanic plume or volcanic fumarolic gases can range from 1 to >7000 $\mu g/m^3$. For the sake of argument, a conservative value of 48 $\mu g/m^3$ (*61*) and a fine ash density of 1 g/cm^3 (*56*) were used in eq 2. Assuming conditions at 5000-m elevation (the approximate lower limit of the stratosphere), the estimated Hg deposition for the Tambora eruption is 25.6 $\mu g/m^2$; approximately 3 times the estimated Hg deposition calculated from Hg concentrations in the ice core (8.6 $\mu g/m^2$). In eq 2, if the atmospheric deposition (Hg_{vol}) is set equal to the estimated value from the ice core and the equation solved for the concentration of Hg in the volcanic plume (Hg_{plu}), a value of 16 $\mu g/m^3$ is calculated. When the same assumptions are applied to the Krakatau eruption, atmospheric Hg deposition is estimated to be 3.6 $\mu g/m^2$, almost 5 times less than the deposition calculated from ice-core Hg concentrations (18.2 $\mu g/m^2$). Again, setting atmospheric deposition equal to the Hg deposition estimated from the ice core in the equation and solving for the concentration of Hg in the volcanic plume (Hg_{plu}), a value of 244 $\mu g/m^3$ is calculated. On the basis of a limited number of studies measuring Hg concentrations in volcanic plumes, the volcanic plume estimate for the Krakatau eruption is comparatively high. The measurements made in previous studies (*58*−*62*), however, suggest that large ranges of Hg concentrations in volcanic ash plumes are possible. This estimation, although basic and oversimplified, demonstrates that the Hg deposition calculated from concentrations in the ice core attributed to the globally impacting volcanic eruptions of Tambora and Krakatau are not unreasonable. While individual volcanic events lead to short-term deposition rates similar to the industrial maximum (Table 1), the brief duration of the events limits their importance in overall deposition.

Recent Declines in Atmospheric Hg Deposition. Since the industrial maximum (ca. 1984), Hg concentrations in the UFG ice core have declined from the 20-fold increase since preindustrial times to an 11-fold increase during the 1990s. This decline is corroborated by recent declining trends observed in dated sediment cores (*41*, *43*, *63*) and precipitation (*50*). The declining trends recorded during the last 10 years are consistent with the last 7 years of precipitation data (*22*). The top 10 m of the ice core have a calculated average deposition rate of about 1 $\mu g/m^2$. Figure 2 shows the UGF region receiving 1−3 $\mu g/m^2$. The recent declines may be in response to emission controls implemented through the United States Clean Air Act of 1970 and the Clean Air Amendment of 1990 requiring pollutant scrubbers that also likely remove a fraction of the Hg in flue gases. If so, the results presented here suggest that further reductions are achievable.

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Reproductive Performance of Two Generations of Female Semidomesticated Mink Fed Diets Containing Organic Mercury Contaminated Freshwater Fish

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Abstract. Semidomesticated female mink (*Mustela vison*) were fed daily diets containing 0.1 ppm, 0.5 ppm, and 1.0 ppm of total mercury. Piscivorous and nonpiscivorous fish naturally contaminated with organic mercury were used to prepare the diets. Twenty-month-old females (G1 generation) that were exposed to the experimental diets for approximately 400 days in 1994 and 1995 and their 10-month-old female offspring (G2 generation) that were exposed to mercury for approximately 300 days in 1995, were all mated to 10-month-old males. Males were fed the diet containing 0.1 ppm mercury 60 days prior to the mating season. Diets containing 0.1 ppm and 0.5 ppm were not lethal to G1 and G2 females for an exposure period of up to 704 days. At the age of 11 months, mortalities occurred in 1994 for G1 females (30/50) and in 1995 for G2 females (6/7) fed the 1.0 ppm mercury diet after 90 days and 330 days of exposure, respectively. The length of the gestation periods and the number of kits born per female were not different among dietary groups for the two generations of females. The proportion of females giving birth was low for all groups, except for the G1 females fed the 0.1 ppm diet. There was an inverse relationship between whelping proportion and exposure group, but was not statistically significant. There was evidence that kits were exposed to mercury both *in utero* and/or during lactation as indicated by the presence of mercury in their livers. Mercury exposure did not influence the survival and growth of neonatal kits.

It is well documented that the creation of hydroelectric reservoirs in Canada, Sweden, and the United States caused an increase in Hg levels in water and aquatic biota (Hydro-Québec 1993). Mercury, in its inorganic form, is first released from the soil and plants by submersion of the land from the creation of the reservoir. Inorganic mercury is transformed by bacterial activity into methylmercury (MeHg). Methylmercury is then taken up by aquatic biota and passed on in the food chain.

By consuming contaminated fish on a regular basis, piscivorous mammals can bioaccumulate MeHg. Therefore, it is important to evaluate the possible risks associated with a natural chronic exposure to MeHg in regard to survival and reproduction.

Mink (*Mustela vison*) and river otter (*Lutra canadensis*) are reported to be sensitive to MeHg. Wobeser and Swift (1976) reported a case of intoxication in a wild female mink located near a river known to be polluted with mercury. Farm-bred female mink receiving 1.0 ppm died after 70 days (Wren *et al.* 1987a) and mink fed 5.0 ppm died after 30 days of exposure (Aulerich *et al.* 1974). No signs of toxicity were reported in female mink exposed for 90 days to 0.5 ppm MeHg originating from fish (Kirk 1971).

Reproduction is a biological process very sensitive to low levels of toxins (Kihlström 1983); therefore, MeHg could affect the reproductive performance of various mammalian species because of its ability to cross the placental barrier and to be passed on in maternal milk (Goyer 1986). Very few studies have examined the impact of MeHg on the reproduction of fish-eating mammals following chronic exposure. Wren *et al.* (1987b) carried out a study on the effects of MeHg contamination on reproduction of semidomesticated mink that received a diet supplemented with 1.0 ppm of MeHg every other day. At the time of parturition, the females had been exposed to MeHg for 150 days. No effects on reproduction (litter size, kit survival, or kit development) were noted.

In order to evaluate the effects of a chronic exposure targeting the reproductive system of fish-eating mammals, the semidomesticated mink was used as a model. The main objective of our study was to examine the reproductive effects of methylmercury with diets containing 0.1 ppm, 0.5 ppm, or 1.0 ppm of total mercury (ww) in two generations of female mink (G1 and G2) exposed for approximately 400 and 300 days, respectively, before mating. Mercury levels were also assessed in some dead kits.

Materials and Methods

Animals

Male and female pastel mink were housed individually at a mink farm (Morrow Furs, St-Paul d'Abbotsford, Québec, Canada). They were

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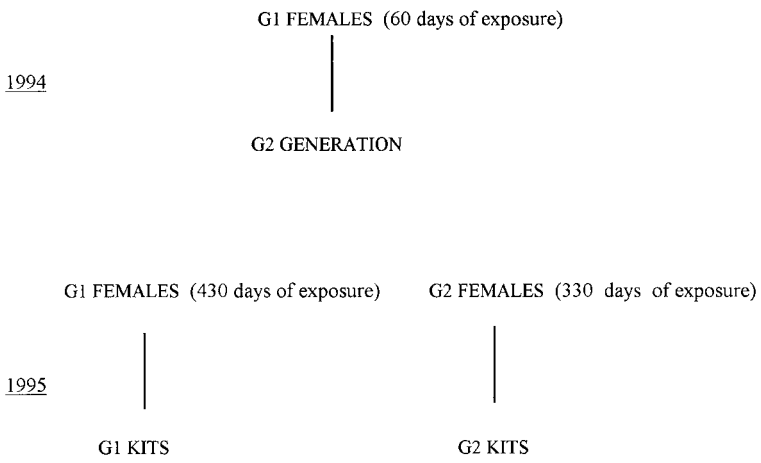

Fig. 1. Reproduction calendar for 1994 and 1995 for G1 and G2 females mated in March to 10-month-old males fed a diet containing 0.1 ppm Hg.

subjected to natural variations in temperature and photoperiod. All were vaccinated annually for canine distemper, botulism, and viral enteritis.[1] Each individual was identified with a subcutaneous implant.[2] The experiment was conducted between January 1994 and July 1995.

Diet

The diets were composed of 40% eviscerated chicken carcasses free of contaminants, 40% whole ground freshwater fish, 20% commercial mink feed, a supplement of thiamin and minerals, and water. The fish naturally contaminated with mercury was caught from the Robert Bourassa Reservoir (La Grande Hydroelectric Complex), Quebec, in the fall of 1994 and 1995.

Three diets were prepared to provide mercury concentrations of 0.1 ppm, 0.5 ppm, and 1.0 ppm. The 0.1 ppm mercury diet was constituted from nonpredatory fish, the lake whitefish (*Coregonus clupeaformis*), whose average total Hg concentration was 0.5 ppm. The 1.0 ppm diet was formulated by incorporating a predatory fish, the northern pike (*Esox lucius*), whose average total Hg concentration was 3.0 ppm. The intermediary diet (0.5 ppm) was obtained through a mixture of 50% northern pike and 50% lake whitefish. No free mercury diet was constituted due to the nonavailability of noncontaminated fish of the same species.

Diet Analysis and Total Mercury Concentration in Tissue

Samples of whole ground fish were taken for mercury analysis in both 1994 and 1995. Samples of the experimental diets were collected between February 2, 1994, and July 24, 1995, for mercury analysis. Some nutrient analysis was done by the Center for Nutrition and Environment of Indigenous Peoples (McGill University, Macdonald Campus, Montréal, Québec, Canada). Livers were collected from adult G1 and G2 females killed at the beginning of April 1995 after 430 and 330 days of exposure. These were not part of the reproductive cohort, except for some mated females that died during this period. Livers were also taken from kits born from G1 and G2 females in 1995 that died accidentally at 29–30 days of age. Total Hg (ww) concentrations in liver, fish, and in experimental diets were determined by acid digestion and reduction of the samples prior to analysis by cold-vapor flameless atomic absorption spectrophotometry by Le Centre de Toxicologie du Québec (CHUL, Sainte-Foy, Québec, Canada). Even though total mercury (inorganic and organic form) was determined from samples, it is known that its organic form (MeHg) constituted the large portion of mercury in tissue (Hydro-Québec 1993). A toxic screen test was also performed on many samples of the three experimental diets (Michigan State University, Animal Health Diagnostic Laboratory, East Lansing, MI).

Generations Description

Description of the G1: At the beginning of January 1994, 50 female mink were randomly assigned to each of the three dietary groups. At the beginning of March, 20 females were randomly selected from each group to participate in the reproductive study. The 10-month-old primiparous females from the three dietary groups were mated to males of the same age fed a diet contained 0.1 ppm Hg for 60 days prior to mating.

Description of the G2: At 8 to 10 weeks of age, the kits born from the G1 groups, identified as G2, were weaned. They were exposed to MeHg *in utero* and/or throughout lactation. They also ingested mercury when they began to eat solid food at around 30–35 days via their mother's food. They continued to receive the same diet as their mothers after the weaning.

Reproductive Season for 1995 (G1 and G2 Females)

Ten-month-old males, chosen from the farm colony and not originally exposed to Hg, received a diet containing 0.1 ppm Hg for 2 months prior to the mating period. The males had their testes checked by palpation just before the breeding season for abnormalities. One male was dismissed from the experiment because he showed unilateral cryptorchidism. In all, 29 males participated in the breeding process.

Mating: In March 1995, G1 females, now 20 months old, and their offspring, the 10-month-old G2 females, were mated after a period of 400 and 300 days of exposure, respectively, to the 0.1 ppm Hg males (Figure 1). Only six G1 and seven G2 females of the 1.0 ppm dietary group were mated, whereas there were 20 females in each of the other dietary groups. Each female was brought to the cage of a randomly chosen male and was remated 8 days after the initial mating with the same male. If a female refused her first partner, she was introduced to another male. Females that were not mated a second time were omitted from the experiment. In all, 78 females were mated twice (Table 1).

[1] Biocom ^{Mc}—D, United Vaccines Inc. Madison, WI, USA.

[2] Implants T-IS 6110, Datamars SA. Systèmes Idelec, Inc., Québec, Canada.

Table 1. Number of G1 (20-month-old) and G2 (10-month-old) females mated twice in the 1995 breeding season and fed experimental diets containing various concentrations of mercury

Dietary Mercury (ppm)	G1 Generation # Females Mated Twice/ Total # Females	G2 Generation # Females Mated Twice/ Total # Females
0.1	16/20	16/20
0.5	17/20	16/20
1.0	6/6	7/7

Birth Period and Weaning: Near the whelping period (April 29–May 18, 1995), the mink farm was visited each day to verify new births. The number of kits born alive and dead and the number of deaths subsequent was noted daily. Each kit was sexed, and weighed with an electronic scale (±0.1 g) twice weekly starting the day following birth (day 1) until the age of 35 days. Each kit was identified with a subcutaneous implant. Kits were weaned at around 10 weeks of age.

Statistical Analyses

Data were processed by the BMDP (BMDP Statistical Software Inc., Los Angeles, CA) and the SAS programs (SAS Institute Inc., Cary, NC). No statistical comparisons between data from the G1 and G2 were made because females of the two generations were not of the same age, the length of mercury exposure was different, and most likely, G2 females had been exposed to mercury *in utero.* Reproduction data for the G2 at 1.0 ppm were not included in the statistical analysis because only one female from this group survived until parturition.

Values from the nutrient analysis were initially expressed as a percentage. In order to compare each variable (moisture, fat, protein, ash, HCO_3, energy) among dietary groups, the percentage values were submitted to the following transformation (known as the angular transformation):

$$y = \arcsin(\times^{1/2}) \quad (1)$$

where y is the transformed values and x is the nutrient values (%) (Sokal and Rohlf 1995).

Nutrient data for 0.1 ppm, 0.5 ppm, and 1.0 ppm mercury groups were then analyzed by a nonparametric analysis of variance test (Kruskal-Wallis) as were the data for the mercury content in experimental diets.

Statistical comparisons of gestation length and the number of kits per female were made by the Kruskal-Wallis test for the G1 generation and the Wilcoxon rank sum test for the G2 generation. Groups that were statistically different were compared by pairs by experiment-wise error rate (Scherrer 1984). Proportions of females giving birth were analyzed by the heterogeneity G-test. Simultaneous test procedure (STP) was used as *a posteriori* procedure (Sokal and Rohlf 1995).

The overall analysis of G1 and G2 kit survival (day 0 to weaning at 70 days) was done by a nonparametric life table using the Kaplan-Meier procedure. The Mantel-Cox test was used to compare the survival functions across the dietary groups. Proportions of mortality (day 1 to weaning) were described according to two categorized variables, *i.e.*, kit weight ($<$10g, $\geq$10g) and litter size (1–3, 4–6, 7–9) at day 1.

An ANOVA procedure for repeated measures could not be used for analyzing the postnatal kit growth data because of insufficient data points. Therefore, in order to analyze kit growth, we used a linear regression of natural logarithm weight against age for two randomly chosen individuals within each family, one male and one female, that had survived at least 35 days. We used the intercept and the slope from each regression line to characterize the growth of each individual. We analyzed separately the relationship between the intercept and the slope and the following variables: dietary groups, generation of mother, litter size at day 1 (categorized 1–5 and 6–9). The analysis was done separately for males and females. Growth data of kits born to G1 females fed 1.0 ppm mercury were excluded from the analysis because the sample was too small.

The level of statistical significance was set at alpha = 0.05 for all analyses. However, for the growth data, a 0.025 level was used since we divided the statistical analysis in two to maintain the experiment-wise error rate at 0.05 (Bonferroni method) (Sokal and Rohlf 1995).

Table 2. Comparison of the mean (±standard deviation) nutrient and mercury content (Hg) in experimental diets

	Diets Containing Hg (ppm)			
	0.1	0.5	1.0	p
Nutrient analysis				
% moisture	65.4 ± 3.16	63.8 ± 3.79	65.0	0.5130
% fat	6.95 ± 0.79	7.79 ± 1.28	6.64	0.3208
% protein	13.4 ± 1.29	14.0 ± 1.43	13.3	0.5252
% ash	3.11 ± 0.44	2.96 ± 0.45	3.37	0.3511
% HCO_3	10.8 ± 1.67	11.5 ± 1.54	11.7	0.3208
energy (Kcal)	159.2 ± 11.2	172.0 ± 20.1	159.8	0.2614
n	10	7	1	
Hg analysis				
Hg (ppm)	0.12 ± 0.06	0.56 ± 0.19	0.9 ± 0.26	0.0001
n	25	18	5	

Results

Diet

As shown in Table 2, no significant statistical difference was found according to the various nutrient factors: % moisture ($p = 0.51$), % fat ($p = 0.32$), % protein ($p = 0.53$), % ash ($p = 0.35$), % HCO_3 ($p = 0.32$), and energy ($p = 0.26$) between the 0.1 ppm, 0.5 ppm and 1.0 ppm diets.

The actual means Hg concentration for the three types of rations: 0.12 ppm, 0.56 ppm, and 0.9 ppm are very close to the expected Hg concentration (0.1 ppm, 0.5 ppm, 1.0 ppm). The Hg concentration statistically differed from one diet to the other ($p = 0.0001$). No toxic compounds other than mercury were detected.

Adult Mortality, 1994 and 1995

In 1994, 30 out of the 50 G1 females initially assigned to the 1.0 ppm mercury diet died at the age of 11 months after demonstrating neurological clinical signs between 75–100 days of exposure. Six of 20 females survived until the 1995 breeding season and no subsequent deaths followed. Since few 1.0 ppm G1 females gave birth in 1994, only 11 G2 females were born. Seven of these females survived until the mating period of 1995; the causes of the four that died are unknown.

Mortality of six G2 females (1.0 ppm) out of seven occurred at the beginning of April 1995 after 330 days of exposure at the age of 11 months before whelping. They exhibited weight loss, weakness, lethargy, incoordination, and splaying of the hind

Table 3. Reproductive performance in 1995 of G1 and G2 female mink fed experimental diets containing various concentration of mercury

Generation	Dietary Mercury (ppm)	# Females Mated Twice	# Females Whelped	Females Whelped/ Mated (%)	Gestation Length[1] (days)
G1	0.1	16	15	93.7[a]	50.4 ± 4.7[a]
	0.5	17	9	52.0[b]	47.9 ± 1.9[a]
	1.0	6	2	33.0[b]	50.0 ± 1.4[a]
G2	0.1	16	12	73.0[a]	47.6 ± 4.0[a]
	0.5	16	10	62.5[a]	49.0 ± 2.9[a]
	1.0	7	1	14.3*	51.0*

[1] Mean ± standard deviation. Based on date of final mating
* Not included in statistical test
[a,b] Groups with different letters within columns and generations are considered statistically different ($p \leq 0.05$)

Table 4. Litter size in 1995 of G1 and G2 female mink fed experimental diets containing various concentrations of mercury (including stillbirths)

Generation	Dietary Mercury (ppm)	Total of Kits Born (Alive and Dead)	Kits per Litter,[1] Day 0[2]
G1	0.1	90	6.0 ± 2.2[a]
	0.5	49	5.4 ± 2.0[a]
	1.0	11	5.5 ± 0.7[a]
G2	0.1	71	5.9 ± 2.2[a]
	0.5	51	5.7 ± 2.4[a]
	1.0	2	2.0*

[1] Mean ± standard deviation
[2] Stillbirths are included
* Not included in statistical test
[a,b] Groups with different letters within columns and generations are considered statistically different ($p \leq 0.05$)

legs and died approximately 7 days after the initial clinical signs. Only one female reached parturition even though she presented the same signs. She died a few hours after giving birth. The clinical signs observed prior to death were consistent with MeHg intoxication (Aulerich *et al.* 1974; Wren *et al.* 1987a).

Nine G1 and G2 females receiving 0.1 ppm and 0.5 ppm died. They exhibited loss of appetite and apathy, but didn't demonstrate any neurological clinical signs.

Total Hg Concentration (ww) in Adult Female Livers, April 1995

The Hg concentrations in the liver of G1 females were analyzed after 430 days of exposure. Means were as follows: 28.2 ± 8.88 ppm, 80.4 ± 59.9 ppm, and 96.6 ppm for the 0.1 ppm ($n = 4$), the 0.5 ppm ($n = 3$), and the 1.0 ppm ($n = 1$) groups, respectively. The average Hg concentration of the G2 female livers after 330 days of exposure were 15.2 ppm, 49.5 ± 9.96 ppm, and 99.8 ± 27.6 ppm for the 0.1 ppm ($n = 1$), the 0.5 ppm ($n = 6$), and the 1.0 ppm ($n = 5$) groups, respectively.

Reproduction

The mean gestation length for G1 females was 49.5 days and was not significantly different among the three dietary groups ($p = 0.26$). Neither was there a significant difference in the mean gestation length (48.3 days) between the two dietary groups for the G2 females ($p = 0.09$) (Table 3).

The proportion of females giving birth was statistically higher for the G1 females exposed to 0.1 ppm (93.7%) than the females receiving 0.5 ppm (52.0%) or 1.0 ppm of mercury (33.0%) ($p = 0.005$). The proportion of G2 females giving birth did not differ statistically between those exposed to 0.1 ppm (73.0%) or 0.5 ppm of mercury (62.5%) ($p = 0.704$) (Table 3).

The G1 and G2 females gave birth to an average of 5.7 kits per litter (including stillbirths) with the exception of a G2 female exposed to 1.0 ppm of mercury that gave birth to two kits that died within 24 h. There was no significant difference between the litter size (including stillbirths) per female at day 0 among dietary groups for G1 ($p = 0.70$) and G2 ($p = 0.88$) (Table 4).

Kit Mortality

Most kit mortalities occurred during the first 3 days of life (21.9%) including stillbirths. Twelve percent died within 24 h and 30.6% of the kits died from day 0 to weaning time (70 days).

The overall survival according to the life table for kits born to G1 females in the 0.5 ppm dietary group was statistically higher ($p = 0.02$) than for kits from the 0.1 ppm and 1.0 ppm groups. There was no significant difference in overall postnatal survival according to the life table between G2 kits from the 0.1 ppm and 0.5 ppm dietary groups ($p = 0.72$). No statistical difference was found between the overall survival of males and females kits born from G1 females ($p = 0.39$) and also for kits born from G2 females ($p = 0.43$).

Tables 5 and 6 show the distribution of G1 and G2 kit mortality between day 1 to weaning (70 days) in relation to litter size and kit weight on day 1. Mortality of 0.1 ppm G1 kits occurred primarily in groups with lower body weights (<10 g) and in litters of 4–6 kits in size (Table 5). Mortality of G2 kits born to females receiving 0.1 ppm and 0.5 ppm of mercury appeared in the largest litters (7–9). Body weight did not seem to influence the mortality distribution for G2 kits (Table 6).

Kit Growth (Day 1 to 35 Days)

The overall postnatal growth for the male and female kits was not significantly affected, as shown in Table 7, by the generation of females, dietary mercury, or litter size. Even though the growth data of kits born from G1 females at 1.0 ppm of mercury were not analyzed, gross observation indicated that their growth was similar to any of the kits of the other dietary mercury.

Total Hg Concentration (ww) in Kit Liver

Mercury concentrations in livers of kits that died accidentally at the age of 29–30 days were analyzed before the kits began to eat

Table 5. Mortality of mink kits born to G1 females between day 1 to weaning time (70 days) in relation to litter size and kit weight recorded on day 1

Dietary Mercury (ppm)	Weight (g) <10 % Mortality	(# Kits Born)	≥10 % Mortality	(# Kits Born)	Total % Mortality	(# Kits Born)
Litter size: 1–3						
0.1	0	(6)	0	(3)	0	(9)
0.5	0	(1)	0	(0)	0	(1)
1.0	0	(3)	0	(0)	0	(3)
Litter size: 4–6						
0.1	50	(16)	0	(8)	33	(24)
0.5	6.7	(15)	20	(10)	12	(25)
1.0	0	(0)	33	(6)	33	(6)
Litter size: 7–9						
0.1	26	(19)	4.3	(23)	14	(42)
0.5	25	(4)	5.9	(17)	9.5	(21)
1.0	0	(0)	0	(0)	0	(0)

Table 6. Mortality of mink kits born to G2 females between day 1 to weaning time (70 days) in relation to litter size and kit weight recorded on day 1

Dietary Mercury (ppm)	Weight (g) <10 % Mortality	(# Kits Born)	≥10 % Mortality	(# Kits Born)	Total % Mortality	(# Kits Born)
Litter size: 1–3						
0.1	17	(6)	100	(1)	29	(7)
0.5	0	(0)	0	(2)	0	(8)
Litter size: 4–6						
0.1	33	(6)	10	(10)	19	(16)
0.5	29	(14)	0	(1)	27	(15)
Litter size: 7–9						
0.1	44	(16)	95	(21)	73	(37)
0.5	86	(7)	86	(7)	86	(14)

solid food at around 33 days according to our observation. Mean were 0.10 ± 0.007 ppm, 0.10 ± 0.02 ppm, and 0.69 ± 0.23 ppm for G1 kits at 0.1 ppm (n = 2), for G2 kits at 0.1 ppm (n = 6), and for G2 kits at 0.5 ppm (n = 8), respectively.

Discussion

The concentrations of Hg used in this study did not affect the gestation length of G1 and G2 females. The mean gestation length was similar to the 51-day average period reported by Enders (1952), Eagle and Whitman (1987), Sundqvist *et al.* (1989), and Murphy (1996) for untreated female mink. Wren *et al.* (1987b) reported no difference in gestation length for females fed a diet containing 1.0 ppm of MeHg added in the diet every other day for 150 days relative to the control group.

The whelping percentages for the G1 and G2 females, except for the 0.1 ppm G1 group (93.7%), were all low relative to the reported performance of untreated female mink (around 90%) (Bleavins *et al.* 1984; Wren *et al.* 1987b). Wren *et al.* (1987b) reported a diminution of the whelping percentage between the treatment group at 1.0 ppm of MeHg (75%) and the control group (93.3%). Despite the fact that our protocol of reproduction is different from a commercial setting, which might explain the overall lower whelping performance, the linear decrease of performance with increasing mercury exposure, may suggest a certain effect (negative) of mercury on the reproduction process. However, statistically, we could not show a significant difference.

Table 7. Factors influencing mink kit growth between day 1 until the age of 35 days

Variables	Categories	Female Kits (n = 35) Intercept p	Slope p	Male Kits (n = 28) Intercept p	Slope p
Generation	G1 (2 years old) G2 (1 year old)	0.3856	0.1974	0.9416	0.8409
Dietary mercury	0.1 ppm 0.5 ppm	0.9263	0.9025	0.7211	0.1499
Litter size	1–5 6–9	0.5682	0.3778	0.8970	0.5464

Hg levels in experimental diets did not influence the litter size at day 0. G1 and G2 females gave birth to an average of 5.7 kits per litter (including stillbirths), which concurred with the average of four to five kits per litter (including stillbirths) reported by Enders (1952), Eagle and Whitman (1987), Sundqvist *et al.* (1989), and Wren (1991) for unexposed female mink. No difference in litter size between exposed females and the control group was reported by Wren *et al.* (1987b).

This study showed that most kit mortalities occurred within the first 3 days of life (21.9%) which is a high risk period for mortality in unexposed farm-bred mink (Villemin 1956). The percentage of G1 and G2 kit mortalities within 24 h of birth (12%) or between day 0 and weaning time (70 days) (30.6%) was only slightly greater than the percentages for nonexposed kits (11.5% and 25%, respectively) (Martino and Villar 1990; Korhonen 1992).

The survival of kits born from G1 and G2 females between birth and weaning (70 days) was not influenced by the Hg level in the diets, but most likely by other factors such as kit body weight and litter size at birth. Kits in G1 generation that were lighter tended to die more. According to the study of Martino and Villar (1990), kit body weights at birth may influence survival. However, for G2 kits, mortality occurred primarily in large litters (7–9). Mortality of G2 kits could be attributed to a lack of experience of the young mothers having to take care of that many kits. It has been observed in pigs and many rodents species that multiparous females were better mothers because of their greater parenting experience (Mason 1994). Wren *et al.* (1987b) reported that there was no difference in kit survival between the control kits and kits in the 1.0 ppm mercury group at 5 weeks of age.

The concentrations of Hg that females received in this experiment did not have an impact on kit growth between day 1 and day 35 for G1 and G2 kits. According to our observation, kits before eating solid food, at 29–30 days old, had higher liver Hg (range 0.10–0.69 ppm) than nonexposed kits in the study of Wren *et al.* (1987a) killed at 35 days of age (mean 0.06 ppm). It is apparent that mercury passed the placental barrier and/or was

passed on through the maternal milk, but the transfer of mercury from the dam to the kit did not affect neonatal growth. Kit growth was not affected by either litter size or generation of female. The study of Wren *et al.* (1987b) did not show any difference in growth between kits born in the 1.0 ppm group and kits in the control group.

No negative control group was present in this study because it was not possible to make a diet with freshwater fish noncontaminated by MeHg. However, the 1.0 ppm diet level was regarded as a kind of positive control group because this Hg concentration in the diet is considered to be toxic for mink. The study of Kirk (1971) showed that female mink died 2 months after being fed a daily diet of 1.0 ppm of mercury. Wren *et al.* (1987a) also reported adult mortalities in mink exposed daily to 1.0 ppm of MeHg. In the present study an exposure of 1.0 ppm of mercury for a period of more than 330 days was toxic to G2 females. In fact, clinical signs prior to death support MeHg intoxication as the cause of death for the G2 adult females in this dietary group (Aulerich *et al.* 1974; Wren *et al.* 1987a). The survival and consequently the reproduction of the G2 females fed 1.0 ppm Hg diet were therefore affected.

It is interesting to note that the death of G1 females at 1.0 ppm Hg in 1994 (30/50) occurred at the age of 11 months after 90 days of exposure after showing neurological clinical signs consistent with mercury toxicity and that the females that reproduced successfully in 1995 survived up to 704 days of exposure (end of the study). The role of the genetics relative to mercury tolerance was not explored in this study, and to our knowledge, it has not been shown. However, their descendants (G2) all died after a longer time of exposure than the G1 females the previous year but at about the same age.

The 0.1 ppm and 0.5 ppm Hg diets were not lethal to G1 and G2 female mink and no females showed neurological signs. In the study of Kirk (1971), a daily exposure of 0.5 ppm of mercury for a 90-day period did not result in female mink death. In our study, even an exposure period for as long as 704 days for the G1 (July 1995) did not affect female survival.

Another aspect of the validation of our model, besides the deaths from the 1.0 ppm Hg group, is the level of accumulation of mercury in adults female livers, which was exposure group-related (range of 28.2 to 96.6 ppm for G1 females and 15.2 to 99.8 ppm for G2 females in April 1995). Normally, for untreated semidomesticated female mink, the Hg concentrations in the liver is approximately 0.02 ppm (Wren *et al.* 1987a).

In conclusion, our present findings indicate that the survival and overall reproductive performance of semidomesticated female mink, was not affected by chronic exposure to mercury. The 1.0 ppm diet was toxic relative to survival for G1 and G2 females around the reproduction season in 1994 and 1995, respectively. Even though mercury crossed the placental barrier and/or was present in maternal milk as demonstrated by the kit liver Hg concentrations, survival and growth of neonate kits were unaffected. The impact of MeHg on the reproduction of wild fish-eating mammals following chronic exposure are unknown. Moreover, the reproductive function of wild female and male mink exposed to Hg could interact with other environmental risk factors.

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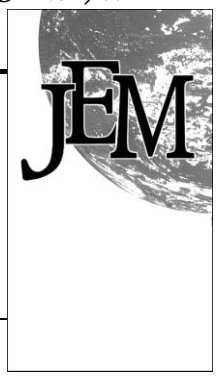

Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years)

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Peat cores from three bogs in southern Ontario provide a complete, quantitative record of net rates of atmospheric Hg accumulation since pre-industrial times. For comparison with modern values, a peat core extending back 8000 years was used to quantify the natural variations in Hg fluxes for this region, and their dependence on climatic change and land use history. The net mercury accumulation rates were separated into "natural" and "excess" components by comparing the Hg/Br ratios of modern samples with the long-term, pre-anthropogenic average Hg/Br. The average background mercury accumulation rate during the pre-anthropogenic period (from 5700 years BC to 1470 AD) was 1.4 ± 1.0 μg m^{-2} per year ($n = 197$). The beginning of Hg contamination from anthropogenic sources dates from AD 1475 at the Luther Bog, corresponding to biomass burning for agricultural activities by Native North Americans. During the late 17th and 18th centuries, deposition of anthropogenic Hg was at least equal to that of Hg from natural sources. Anthropogenic inputs of Hg to the bogs have dominated continuously since the beginning of the 19th century. The maximum Hg accumulation rates decrease in the order Sifton Bog, in the City of London, Ontario (141 μg Hg m^{-2} per year), Luther Bog in an agricultural region (89 μg Hg m^{-2} per year), and Spruce Bog which is in a comparatively remote, forested region (54 μg Hg m^{-2} per year). Accurate age dating of recent peat samples using the bomb pulse curve of ^{14}C shows that the maximum rate of atmospheric Hg accumulation occurred during AD 1956 and 1959 at all sites. In these (modern) samples, the Hg concentration profiles resemble those of Pb, an element which is known to be immobile in peat bogs. The correlation between these two metals, together with sulfur, suggests that the predominant anthropogenic source of Hg (and Pb) was coal burning. While Hg accumulation rates have gone into strong decline since the late 1950's, Hg deposition rates today still exceed the average natural background values by 7 to 13 times.

1. Introduction

Mercury is a potentially toxic trace metal which is released from the Earth to the atmosphere, biosphere, and hydrosphere from a variety of natural processes. Degassing from hydrothermal systems, volcanism, soil erosion, biomass burning, and marine emissions are believed to dominate natural sources of Hg to the air.[1] By far the majority of Hg emitted from these natural sources is gaseous, elemental mercury (Hg^0). Because Hg is used in many industrial applications and also present in coal, natural gas and industrial and domestic waste, it is also emitted to the atmosphere during combustion for energy production or waste incineration. In contrast to the natural sources, at least one-half of anthropogenic Hg is emitted in various particulate forms.[2] Most of the mercury deposited from the atmosphere is either Hg^{II} or particulate mercury. Whereas particulate Hg is mainly deposited in the vicinity of its sources, Hg^0 is added to the global pool of atmospheric Hg: the volatility and low solubility of Hg^0, combined with its comparative stability in the atmosphere, are factors which contribute to the long atmospheric residence time ($\sim$1–2 years) of gaseous elemental Hg.[3] Eventually, this species also will be deposited, but only after oxidation and washout, including non-industrial regions far from the original source. Because of the relatively rapid atmospheric scavenging and deposition of particulate mercury, Hg^0 is preferentially enriched in the air and, on average, accounts for 98% of atmospheric mercury.[4] These facts, combined with the potential of methylated forms of Hg to bioaccumulate in aquatic ecosystems, renders Hg a trace metal of global environmental concern.[5]

Increases in the accumulation rates of Hg have been observed in the uppermost, modern layers of lake sediment cores[6,7] and ombrotrophic bogs[8] in northeastern North America, and these have been attributed to recent increases in atmospheric Hg emissions (and deposition) related to human activities. In these studies, estimates of the "natural background" atmospheric deposition rates of Hg are poorly constrained, as they are derived from relatively short cores (less than one meter), which typically span only the last few hundred years of accumulation. These natural background accumulation rates of Hg are then assumed to represent the "pre-industrial" accumulation rates. However, age dating these materials is difficult, as the peats/sediments are usually too old to be age dated reliably using ^{210}Pb, and too young to be dated using ^{14}C. Not only are the natural background Hg accumulation rates inadequately quantified using this approach, but the extent to which these natural background

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accumulation rates have varied with time, and the natural processes which control this variation, often are not adequately considered. To quantify the effects of human activities on atmospheric Hg deposition in southeastern Canada, an improved understanding is needed of the long-term, natural variations in the concentrations, fluxes and sources of Hg for this industrial region.

Ombrotrophic[9] peat bogs receive metals only from the atmosphere. Because Hg supplied to peat bogs from the air is very well preserved in the peat column[10,11] peat cores from bogs can be used as long-term archives of atmospheric Hg deposition.[8,12–16] Peat cores were collected from three ombrotrophic peat deposits in Southern Ontario: Sifton Bog in the City of London, Ontario, Luther Bog which is in a rural location, and Spruce Bog which is comparatively remote, in Algonquin Provincial Park. The main goal of this study was to quantify the changing rates of atmospheric Hg accumulation from the modern period through the pre-industrial period, into pre-European times. To help put these results into perspective, the entire peat profile from Luther Bog (representing *ca.* 8000 years of peat accumulation) has been studied in detail, to quantify the long-term, natural variation in atmospheric Hg accumulation rates. Radiocarbon dating methods (the atmospheric bomb pulse of ^{14}C and conventional ^{14}C age dating) have been combined with ^{210}Pb to allow reliable age–depth models to be constructed for each of the peat profiles. To bridge the gap between ^{210}Pb and ^{14}C age dating, the probability distribution of ^{14}C age dates was used to model the age–depth relationship. In an effort to distinguish between natural and anthropogenic sources of Hg, the natural variation in Hg to bromine (Br) in ancient samples is used to calculate the amount of "excess" mercury in modern samples. Taken together, this is the first comprehensive, long-term study of changes in atmospheric Hg accumulation rates for this part of northeastern North America.

To compare with mercury in the three peat profiles, we have measured lead (Pb) which is transported primarily in the fine aerosol fraction.[17] Lead is known to be well preserved in ombrotrophic bogs,[18–20] with bogs recording Pb chronologies which are comparable to lake sediment archives[12,21] and historical records of ancient Pb mining.[22] Here, Pb is used to help identify the predominant source of anthropogenic Hg contamination.

2. Material

2.1. Luther Bog

Situated along a headwater tributary of the Grand River, Luther Marsh Provincial Wildlife Area lies near the southern fringe of the Dundalk Plateau, about 25 km west of the town of Orangeville, in a predominately agricultural region of southern Ontario. The Dundalk plateau, with an elevation of approximately 480 m above sea level, is the coldest off-shield region of southern Ontario, with temperatures and precipitation similar to those of Algonquin Park, 300 km to the northeast.[23]

Historically, Luther Marsh was a large peatland complex surrounding two small lakes and containing several streams. In 1954 the Grand River Conservation Commission constructed a dam across Black Creek, a headwater tributary of the Grand River, which created Luther Lake. Peat cores were collected on July 26, 2000 at a site (43° 54′30N, 80° 24′36W) which is characterised by vegetation typical of continental, ombrotrophic *Sphagnum* bogs. Visual inspection of the modern vegetation growing on the surface of the bog today, as well as the peat cores collected at this site, provided no botanical evidence that flooding had affected the ombrotrophic zone of the bog in any way. A visit to the same site to collect peat cores in 1984 had drawn the same conclusion (W.S., personal observation). However, to overcome the uncertainty of possible impacts by past flooding at this site, peat cores were also collected at two other *Sphagnum* bogs in southern Ontario.

2.2. Spruce Bog Trail

Spruce Bog Trail is situated in Algonquin Park, a 3000 km^2 nature reserve in a predominately recreational region of rural southern Ontario, at an elevation of about 410 m above sea level. Samples were collected on the northwest side, directly across from the boardwalk, on the far side of the peatland. The core was taken on July 10, 2000 in a very small (*ca.* 50 cm wide) *Sphagnum* lawn within a zone of dense growth of dwarf shrubs. This zone is between the floating mat and the forest, and the core was removed from the edge of the floating mat. This coring area (45° 35′51N, 78° 22′16W) was chosen because it is still open with respect to the surrounding forest and because it was firm and stable compared to the floating mat.

2.3. Sifton Bog

The Sifton Bog is an acidic *Sphagnum* peat bog located within the city of London, Ontario (population *ca.* 300 000). The bog covers an area of about 28 hectares and is formed in a large depression, left behind as a glacial block melted about 13 000 years ago. This bog rests on about 25 m of glacial deposits of sands and gravels, which overlies Devonian limestones. The peatland today consists of a small pond surrounded by a floating mat of *Sphagnum* moss, flanked by a marginal hardwood swamp. Beyond the swamp are lowland and upland forest, respectively. The central portion of the bog contains as much as 10 m of peat accumulation.[24] The sampling site (42° 58′31N, 81° 19′48W) was chosen in an area between the floating mat and the damp woods. The thickness of peat accumulation at the sampling site was about 6 m at the time of collection (27 July, 2000).

3. Methods

3.1. Sample collection and preparation

The topmost layers of peat were collected using a 1 m titanium Wardenaar corer as a 15 × 15 cm monolith.[25] In addition to the short peat cores collected at all sites, a complete peat profile was taken at Luther Bog (*ca.* 600 cm) in 50 cm sections using a stainless steel Belarus corer.[26] Unfortunately, a 50 cm section was lost during the coring session. Peat cores were removed from two holes, approximately 30 cm apart, in parallel overlapping fashion. The Luther Bog profile was reconstructed by correlating depth to depth using the bog surface as reference, assuming that samples from equal depths, but different hole, were the same distance from the bog surface. All samples were frozen at −18 °C for storage and transport to Berne, Switzerland.

The Wardenaar and Belarus cores were cut in the laboratory (while frozen) into 1 cm and 2 cm slices respectively using a stainless steel band saw. The outside edges of each slice were cut away, dried overnight at 105 °C in a drying oven and milled in a centrifugal mill with titanium sieve. The powdered samples (used for XRF and ^{14}C analyses) were manually homogenized and stored in airtight plastic beakers.

3.2 Analysis

One gram of dried, milled powder was analyzed for 22 selected major and trace elements, including lead, calcium (Ca), strontium (Sr), manganese (Mn), iron (Fe), Br and selenium (Se), using the EMMA XRF spectrometer.[27] Titanium (Ti) was measured using a new analytical spectrometer for Ti (NASTIA), which was described earlier.[28] The instruments were calibrated and checked for accuracy and precision as described elsewhere.[29] The XRF methods were validated using

Table 1 Summary of measurements of Hg, Br, Se, and Ti in certified, Standard Reference Materials. Information values are indicated by *

Element	Method	SRM	Measured value	Certified value
Hg	AAS	NIST 1515	31.8 ± 0.8 ng g^{-1}, $n = 27$	31 ± 7 ng g^{-1}
Hg	AAS	NIST 1547	43.0 ± 0.7 ng g^{-1}, $n = 45$	44 ± 4 ng g^{-1}
Br	Emma XRF	NIST 1515	2.0 ± 0.2 μg g^{-1}, $n = 3$	1.8* μg g^{-1}
Br	Emma XRF	NIST 1547	12.9 ± 0.2 μg g^{-1}, $n = 2$	11* μg g^{-1}
Br	Emma XRF	NIST 1575	9.3 ± 1.1 μg g^{-1}, $n = 9$	9* μg g^{-1}
Se	Emma XRF	NIST 1632b	1.3 ± 0.4 μg g^{-1}, $n = 3$	1.29 ± 0.11 μg g^{-1}
Pb	Emma XRF	NIST 1575	12.0 ± 1.1 μg g^{-1}, $n = 3$	10.8 ± 0.5 μg g^{-1}
Ti	Nastia XRF	NIST 1635	189 ± 14 μg g^{-1}, $n = 11$	200* μg g^{-1}

standard reference materials (Table 1). Ca and Sr can be used to identify mineral weathering reactions in peat profiles, Mn and Fe redox processes, Br and Se atmospheric aerosols of marine origin, and Ti atmospheric aerosols of continental origin.

Four plugs were subsampled from the middle of each slice with a sharpened stainless steel tube (16 mm diameter). Three of them were used for Hg analyses. These were air-dried overnight at room temperature in a class 100 laminar flow clean air cabinet. Mercury concentrations were measured by atomic absorption spectrometry (AAS) in solid peat samples[30] using the LECO AMA 254 as described in detail elsewhere.[31] The instrument was calibrated using liquid standards prepared from a Merck 1000 mg l^{-1} Hg standard solution. Precision was determined by measuring replicates of international standard reference materials, either NIST 1515 (Apple Leaves) or NIST 1547 (Peach Leaves), after every 10th sample (Table 1). The mean relative standard deviation of the determination of Hg within a peat slice was 11.7% ($n = 3$) which is primarily a reflection of the heterogeneity of the slices. The fourth plug was use to determine the dry bulk density. The height of each plug was measured to an accuracy of 0.1 mm and the volume calculated. After recording wet weights, plugs were dried at 105 °C overnight and the dry mass was weighed to 1 mg.

The degree of decomposition of the peat was measured by colorimetry on alkaline peat extracts at 550 nm using a Cary 50 UV-visible spectrophotometer. The powdered peat samples (0.02 g) were placed in test tubes and 8% NaOH solution (10 ml) was added. The samples were shaken then heated 95 ± 5 °C for 1 h, then made up to 20 ml with deionised water, shaken and left to stand for 1 h before being re-shaken and filtered through Whatman no. 1 filter papers. Samples were diluted with an equal quantity of deionised water directly before colorimetric measurement. The percentage of light absorption (% absorbance) in these extracts was used as a proxy of peat humification.[32]

3.3. Age dating

Macrofossils of *Sphagnum* moss were collected, cleaned, and submitted for ^{14}C age dating by Acceleration Mass Spectrometry (AMS) at Århus University, Denmark, and at the ETH Zurich, Switzerland. In cases when it was not possible to identify macrofossils, bulk peat samples were used. Samples dated using AMS were prepared using a standard procedure for plant material (washed, acid-base-acid treatment) which removes humic matter that could overestimate the ^{14}C ages.[33] Selected bulk peat samples were also age dated using decay counting at the Institute of Environmental Physics, University of Heidelberg, Germany.

Age dates of plant macrofossils younger than AD 1950 can be obtained using ^{14}C by directly comparing the absolute concentration of ^{14}C in the sample to the general-purpose curve derived from annually averaged atmospheric $^{14}CO_2$ values in the northernmost northern hemisphere: post-1950 ^{14}C concentrations in the atmosphere are elevated compared to natural levels due to atomic weapons testing. This approach which effectively matches the ^{14}C concentrations (percent modern carbon, or PMC) in successive plant macrofossils to the increase (since AD 1950) and subsequent decrease (since AD 1963) in ^{14}C concentrations is the so called "bomb pulse curve of ^{14}C" and has been successfully used to date peat accumulation in Denmark and in southern Greenland.[34] This comparatively new dating method has been found to provide high-resolution age dates which are accurate to ±2 years.

The other ^{14}C calibrated ages were calculated using the Seattle CALIB program[35] version 4.0 (Århus University) and version 4.3 (University of Heidelberg), and the program calibETH (ETH Zurich). The calibration curves used for the calibration were taken from Stuiver *et al.*[36] and Niklaus *et al.*[37] respectively. Due to irregular multimodal shapes of probability distributions of the major part of these dates, it was decided to present the results in the form of 95% confidence intervals (2σ-ranges) of the highest probability (narrowest 95% confidence intervals). The results of calibration of individual dates are presented in Table 2, 3 and 4.

In addition to the ^{14}C age dating using the bomb pulse curve, the uppermost layers of the Spruce bog core were also age dated down to 65 cm using the ^{210}Pb (CRS) model.[38]

4. Results

4.1. Peat chronologies

Absolute chronologies were reconstructed for each of the three peat profiles (Fig. 1) using calibrated ^{14}C dates (Luther and Sifton bogs), and both calibrated ^{14}C and ^{210}Pb dates (Algonquin bog); in each case, it is assumed that peat accumulation was continuous. The points included in the age–depth models were specified by taking the average depth of the peat slice together with the mid-point of the calibrated age. A significant challenge in dating peat accumulation is the gap which exists between the oldest reliable ^{14}C bomb pulse date (late 1950s) or ^{210}Pb date (*ca.* mid 19th century) to the first reliable conventional ^{14}C date (*ca.* 17th century). To bridge these gaps, composite probability distributions were used: for a given sample, these provide an estimate of the probability of each ^{14}C age. Assuming that the overlying samples are younger than the deeper samples, a best fit can be made using polynomial regression, linking the uppermost ^{14}C ages (obtained using the bomb pulse curve) to the deeper, conventional ^{14}C ages. Calibrated age ranges were considered only in visually assessing the fit of the regression line through the data. Moreover, the age of the top sample (the date of core collection, AD 2000) was used as a fixed point with 100% confidence interval. A series of regression models were used to fit the age–depth plots. The choice of the model finally selected was based on best fit (r^2 values) of available age dates, and a consideration of the published range of peat accumulation rates.

For the Luther Bog profile (Fig. 1a), the age-depth relationship was constructed from the dated points using a third-degree polynomial regression from 0 to 45 cm and a sixth-degree polynomial regression from 45 cm to ~535 cm. The gap from the beginning of the oldest reliable ^{14}C bomb pulse date (AD 1956 at 20.0 cm) to the first reliable conventional radiocarbon

Table 2 Radiocarbon age dates (conventional ^{14}C years BP (before the present era)) and calibrated ages (calendar years AD/BC) obtained from bulk peat samples and *Sphagnum* moss in selected samples from the Luther Bog profile (calendar dates calculated from Niklaus *et al.* 1992 (ETH) and Stuiver *et al.* 1993 (Hd))

Average depth/cm	Material dated	Dating method	Laboratory No.	Date (^{14}C years BP)	$\delta^{13}C$ (‰)	Date (calendar years AD/BC)
0+		Year of collection				AD 2000
6.7	*Sphagnum*	^{14}C bomb pulse	ETH-26042	−1065 ± 45	−23.0 ± 1.2	AD 1992–1993
9.1	*Sphagnum*	^{14}C bomb pulse	ETH-26043	−1030 ± 45	−19.5 ± 1.2	AD 1993
12.7	*Sphagnum*	^{14}C bomb pulse	ETH-26044	−1985 ± 45	−23.1 ± 1.2	AD 1979–1980
15.2	*Sphagnum*	^{14}C bomb pulse	ETH-26045	−3980 ± 40	−27.3 ± 1.2	AD 1967
17.6	*Sphagnum*	^{14}C bomb pulse	ETH-26046	−1470 ± 45	−29.9 ± 1.2	AD 1958–9
20.0	*Sphagnum*	^{14}C bomb pulse	ETH-26047	−480 ± 45	−29.9 ± 1.2	AD 1956
24.9	*Sphagnum*	Conventional ^{14}C	ETH-26049	245 ± 45	−26.8 ± 1.2	AD 1617–1692
44.3	*Sphagnum*	Conventional ^{14}C	ETH-26052	220 ± 50	−30.0 ± 1.2	AD 1631–1822
51.6	*Sphagnum*	Conventional ^{14}C	ETH-26053	315 ± 50	−28.7 ± 1.2	AD 1459–1666
68.6	*Sphagnum*	Conventional ^{14}C	ETH-26055	630 ± 50	−30.1 ± 1.2	AD 1290–1408
83.6	Bulk peat sample	Conventional ^{14}C	ETH-25977	1130 ± 50	−28.3 ± 1.2	AD 800–1010
96.1	Bulk peat sample	Conventional ^{14}C	ETH-25978	1310 ± 50	−31.6 ± 1.2	AD 649–829
116.9	Bulk peat sample	Conventional ^{14}C	ETH-25941	1670 ± 50	−21.6 ± 1.2	AD 317–532
139.9	Bulk peat sample	Conventional ^{14}C	ETH-25942	2150 ± 50	−21.9 ± 1.2	260–44 BC
160.7	Bulk peat sample	Conventional ^{14}C	ETH-25943	2280 ± 50	−23.4 ± 1.2	328–200 BC
216.9	Bulk peat sample	Conventional ^{14}C	ETH-25944	2825 ± 50	−25.9 ± 1.2	1088–890 BC
248.4	Bulk peat sample	^{14}C decay counting	Hd-21554	3486 ± 24		1834–1739 BC
268.4	Bulk peat sample	^{14}C decay counting	Hd-21553	3557 ± 37		1979–1855 BC
308.6	Bulk peat sample	Conventional ^{14}C	ETH-25945	3935 ± 55	−24.5 ± 1.2	2508–2275 BC
366.3	Bulk peat sample	Conventional ^{14}C	ETH-25946	4930 ± 60	−29.3 ± 1.2	3810–3629 BC
427.4	Bulk peat sample	Conventional ^{14}C	ETH-25947	5815 ± 60	−26.2 ± 1.2	4807–4520 BC
498.2	Bulk peat sample	Conventional ^{14}C	ETH-25948	6720 ± 65	−27.3 ± 1.2	5686–5474 BC
535.1	Bulk peat sample	^{14}C decay counting	Hd-21694	8175 ± 71		7355–7052 BC

Table 3 Radiocarbon age dates (conventional ^{14}C years BP) and calibrated ages (calendar years AD/BC) obtained from bulk peat samples and *Sphagnum* moss in selected samples from the Spruce Bog profile (calendar dates calculated from Stuiver *et al.* 1998)

Average depth/cm	Material dated	Dating method	Laboratory No.	Date (^{14}C years BP)	$\delta\ ^{13}C$ (‰)	Date (calendar years AD/BC)
0+		Year of collection				AD 2000
1.7	*Sphagnum*	^{14}C bomb pulse	AAR-7536	−880 ± 32	−28.90	AD 1996–8
7.5	*Sphagnum*	^{14}C bomb pulse	AAR-7537	−997 ± 39	−30.38	AD 1994
14.5	*Sphagnum*	^{14}C bomb pulse	AAR-7538	−1565 ± 37	−29.5	AD 1984–5
21.5	*Sphagnum*	^{14}C bomb pulse	AAR-7539	−2966 ± 29	−27.17	AD 1972–3
25.0	*Sphagnum*	^{14}C bomb pulse	AAR-7540	−3641 ± 30	−28.20	AD 1968
27.3	*Sphagnum*	^{14}C bomb pulse	AAR-7541	−3704 ± 32	−28.31	AD 1962–3
29.6	*Sphagnum*	^{14}C bomb pulse	AAR-7542	−1124 ± 36	−28.76	AD 1957–8
33.1	*Sphagnum*	^{14}C bomb pulse	AAR-7543	−899 ± 34	−28.74	AD 1957
35.4	*Sphagnum*	Conventional ^{14}C	AAR-7544	133 ± 37	−29.20	AD 1676–1779
37.7	*Sphagnum*	Conventional ^{14}C	AAR-7545	87 ± 41	−29.05	AD 1804–1939
45.9	*Sphagnum*	Conventional ^{14}C	AAR-7547	124 ± 37	−28.48	AD 1802–1839
56.3	*Sphagnum*	Conventional ^{14}C	AAR-7549	97 ± 34	−25.59	AD 1805–1935
65.6	*Sphagnum*	Conventional ^{14}C	AAR-7551	138 ± 37	−26.22	AD 1670–1780

Table 4 Radiocarbon age dates (conventional ^{14}C years BP) and calibrated ages (calendar years AD/BC) obtained from from bulk peat samples and *Sphagnum* moss in selected samples from the Sifton Bog profile (calendar dates calculated from Niklaus *et al.* 1992 (ETH) and Stuiver *et al.* 1993 (Hd))

Average depth/cm	Material dated	Dating method	Laboratory No.	Date (^{14}C years BP)	$\delta\ ^{13}C$ (‰)	Date (calendar years AD/BC)
0+		Year of collection				AD 2000
0.5	*Sphagnum*	^{14}C bomb pulse	ETH-26273	−785 ± 45	−32.0 ± 1.2	AD 1999–2000
4.8	*Sphagnum*	^{14}C bomb pulse	ETH-26274	−1050 ± 45	−32.8 ± 1.2	AD 1992–3
6.9	*Sphagnum*	^{14}C bomb pulse	ETH-26275	−1580 ± 50	−30.3 ± 1.2	AD 1985
9.0	*Sphagnum*	^{14}C bomb pulse	ETH-26276	−2025 ± 50	−29.5 ± 1.2	AD 1979–80
11.2	*Sphagnum*	^{14}C bomb pulse	ETH-26277	−3140 ± 50	−30.0 ± 1.2	AD 1972
13.3	*Sphagnum*	^{14}C bomb pulse	ETH-26278	−3345 ± 45	−28.7 ± 1.2	AD 1962–3
15.4	*Sphagnum*	^{14}C bomb pulse	ETH-26279	−1460 ± 55	−28.2 ± 1.2	AD 1958–9
17.5	*Sphagnum*	Conventional ^{14}C	ETH-26280	70 ± 50	−30.1 ± 1.2	AD 1804–1937
22.8	*Sphagnum*	Conventional ^{14}C	ETH-26281	175 ± 55	−31.1 ± 1.2	AD 1656–1891
36.7	*Sphagnum*	Conventional ^{14}C	ETH-26282	105 ± 45	−33.4 ± 1.2	AD 1802–1939
51.5	*Sphagnum*	Conventional ^{14}C	ETH-26283	105 ± 45	−28.6 ± 1.2	AD 1802–1939
66.4	*Sphagnum*	Conventional ^{14}C	ETH-26284	25 ± 45	−29.1 ± 1.2	AD 1813–1925
66.4+	Bulk peat sample	^{14}C decay counting	Hd-21686	206 ± 24		AD 1738–1805

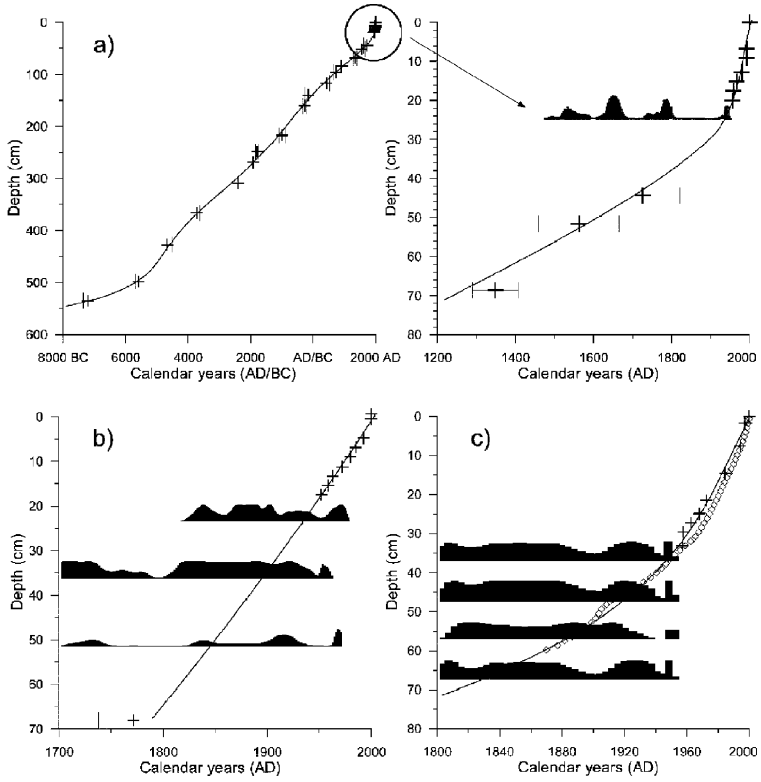

Fig. 1 Age–depth relationship for Luther Bog (a), Sifton Bog (b) and Spruce Bog (c). Calibrated age dates (obtained using ^{14}C) and their errors are reported as crosses (+), or as a composite of the probability distribution. Radiometric age dates obtained using ^{210}Pb (CRS model) are indicated by the diamonds (◇).

date (AD 1631 to 1822; average age AD 1727 at 44.3 cm) was bridged by using the probability distribution for the sample from 24.9 cm. Specifically, the probability distribution of this sample shows that four age dates are possible (Fig. 1a). Of these four age dates, the three oldest ones do not lie on the age–depth trend. Therefore, the youngest age (AD 1935) was selected as being the most reasonable of the four, and this age was used to construct the age–depth relationship.

The age–depth relationship for Sifton Bog (Fig. 1b) was reconstructed using a second-degree polynomial regression from nine reliable points. Between 15.4 to 66.4 cm depths, the probability distribution profiles of three conventional radiocarbon dates were used. For Spruce Bog (Fig. 1c), the age–depth relationship was reconstructed using a third-degree polynomial regression from the reliable age dated points from the surface to 33.1 cm depth. Below, the probability distributions of four conventional radiocarbon dates were used. Using this approach, sample depths for each peat profile were converted into calendar dates using the age–depth relationships.

4.2. Trophic status of the profiles

Visual inspection of the Luther bog core indicates that the profile consists of clay-rich sediments up to 560 cm; gyttja (a lacustrine organic-rich sediment), from 560 to 490 cm; and peat above 490 cm (Fig. 2). The concentrations of Ti and ash provide an index of the amount of mineral matter in the peat[16] which can be used to help distinguish between ombrotrophic peat (mineral matter supplied exclusively from the air) from minerotrophic peat (mineral matter from the air, as well as terrestrial and aquatic inputs). Calcium and Sr may be used to describe the trophic status of the peat profile,[39] and are also sensitive indicators of inputs to the peat profile from mineral-fluid interactions subsequent to peat formation. The concentrations of these parameters allow the following zones to be distinguished within the peat column, in ascending order (Fig. 2): clay, gyttja, minerotrophic fen peat, transitional peat, ombrogenic peat, and ombrotrophic peat. "Ombrogenic" peat consists of organic matter derived from ombrotrophic bog plants, but has since been overprinted with a minerotrophic signature because of the upward diffusion of Ca and Sr derived from chemical weathering of the underlying sediments. Taken together, the geochemical data, briefly summarised here, show that the uppermost 165 cm of the Luther profile are ombrotrophic and therefore that all elements were supplied to the peat in this section of the bog exclusively *via* the atmosphere.

The abundance and distribution of Ca, Sr, Ti and ash in the Spruce bog and Sifton peat cores are comparable to those in the ombrotrophic section of the Luther bog profile. In the peat cores from Spruce and Sifton bogs, therefore, these cores also have received their inputs from the atmosphere. As observed in the ombrotrophic section of the Luther bog profile, there is an exceptional zone of elevated ash content and lithogenic elements concentration in the uppermost layer of Spruce bog and Sifton bog at 35 and 20 cm respectively.

4.3. Mercury and lead concentration profiles in the three Wardenaar peat cores

Mercury concentrations are lowest in the top and bottom layers of the Wardenaar cores, with the maximum concentrations (189, 251 and 333 ng g^{-1} in Spruce Bog, Luther Bog and Sifton Bog respectively) at intermediate depths. Each peat core shows a unique variation in Hg concentrations with respect to depth (Fig. 3), with peaks in Hg concentration found at depths varying between 15 and 35 cm. Despite this, the chronologies of the changing Hg concentrations are remarkably similar, with maximum Hg concentrations dating from the late 1950's in each core (Fig. 3). The Pb concentration profiles resemble the Hg concentration profiles (r^2 = 0.72, 0.77 and 0.82 in the Luther bog, Spruce bog and Sifton bog profiles respectively) in the sense that the zones which contain elevated Hg concentrations, also are elevated with respect to Pb. As is true of Hg, therefore, Pb displays a similar chronology in each of the cores,

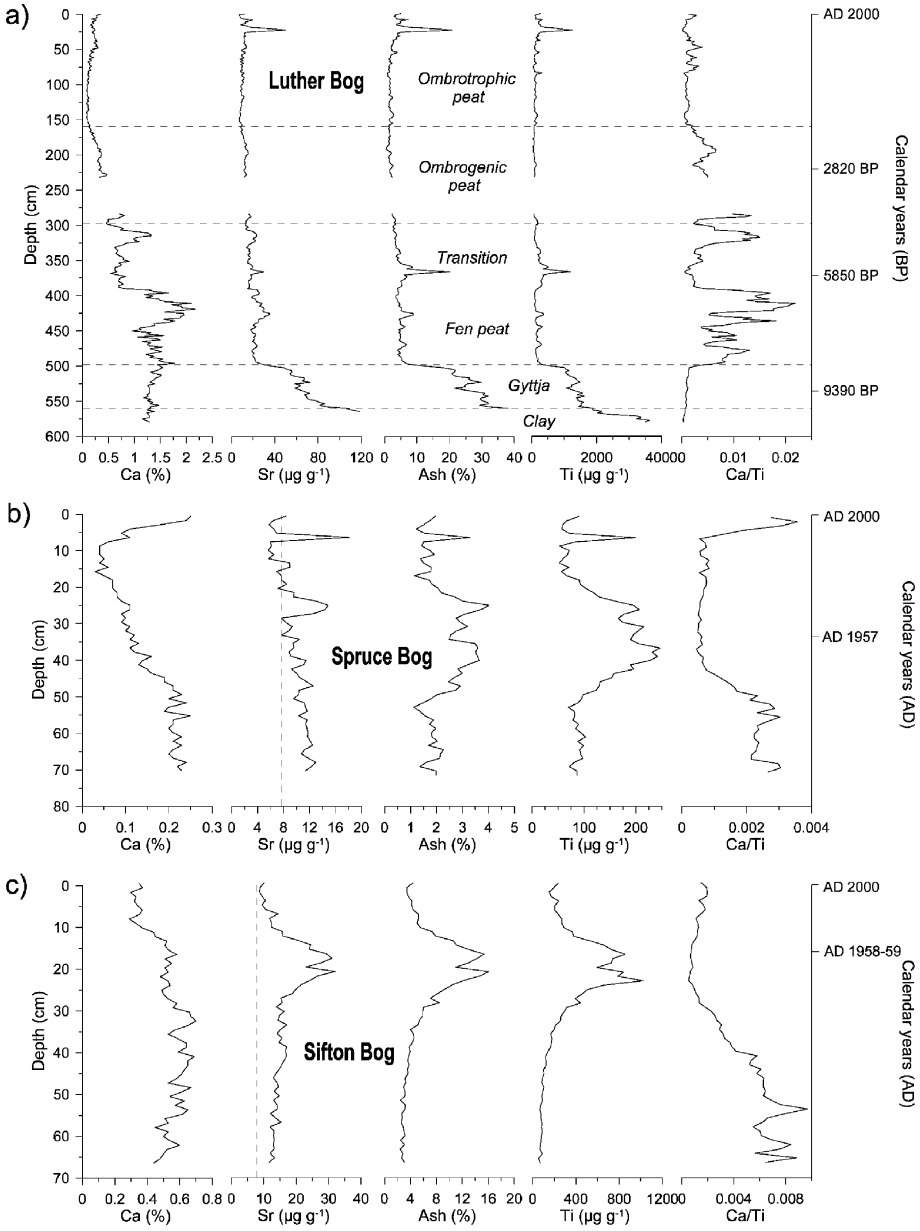

Fig. 2 Concentration profiles of elements discussed in the text and ash content in the Luther Bog (a), Spruce Bog (b) and Sifton Bog (c) profiles and assigned peat/sediment type. The year of collection and selected calibrated age dates obtained by ^{14}C AMS are shown for convenience. The vertical dashed line indicates the average Sr concentration in the ombrotrophic zone of Etang de la Gruère, a continental bog in the Jura Mountains of Switzerland.

with the maximum Pb concentration dating from the late 1950's in each case. The coincidence of the Hg and Pb concentrations in the modern peat samples from the surface layers of all three bogs suggests that either these elements have a predominant source in common, that they behave similarly in peat bogs, or both.

4.4. "Background" Hg concentrations in the Luther Bog profile

For comparison with the Hg concentrations in modern peat samples from the surface layers of each of the bogs, it is important to establish the "natural background" Hg concentration for peat in this region. Analysis of the peat core from Luther Bog shows low and quite stable Hg concentrations below 150 cm, even in the transitional and minerotrophic peat sections, with values in the range of 13 to 35 ng g^{-1} from 150 to 495 cm (Fig. 4). Again, the peat samples from the fen, transitional, and ombrogenic zones are rich in Ca, out of proportion with Ti (Fig. 2); these peats, therefore, have been overprinted with chemical signatures indicating pronounced mineral–water interactions (Fig. 2). However, these reactions and processes have not measurably contributed Hg to the profile, and Hg concentrations are effectively constant (22.3 $\pm$ 4.0 ng g^{-1}) from 300 to 500 cm (Fig. 4). Because the concentrations of Hg in the transitional and minerotrophic peats are not significantly different from the ombrotrophic peat (which has received Hg only from the atmosphere), even in the transitional and minerotrophic, Hg was supplied exclusively by the atmosphere. Assuming that the Hg concentrations between 150 and 495 cm at Luther (13 to 35 ng g^{-1}) reflect the range in natural concentrations of Hg in ombrotrophic peat, the maximum Hg concentrations at Spruce Bog, Luther Bog and Sifton Bog exceed this range by factors of 6–13, 8–18, and 10–23 respectively.

5. Discussion

5.1. Effects of natural biogeochemical processes on Hg concentration profiles

Diagenesis of Fe and Mn within the peat profile. It has previously been shown that redox-related transformation of Fe

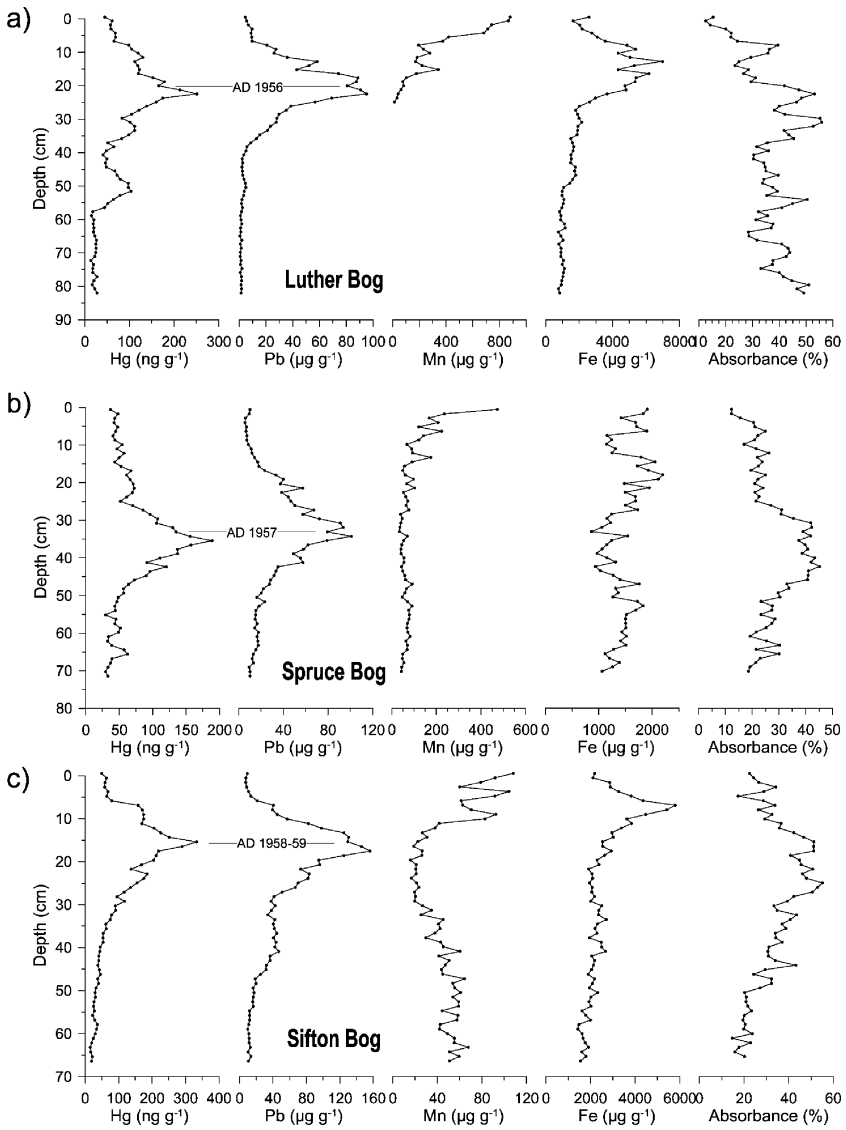

Fig. 3 Concentrations of Hg (ng g^{-1}), Pb (µg g^{-1}), Mn (µg g^{-1}) and Fe (µg g^{-1}), and degree of humification (corrected absorbance) for the Wardenaar peat profiles from Luther (a), Spruce (b) and Sifton bogs (c). The age dates represent those ^{14}C bomb pulse age dates (± 2 years) which are closest to the peaks in Hg concentration and are included for convenience.

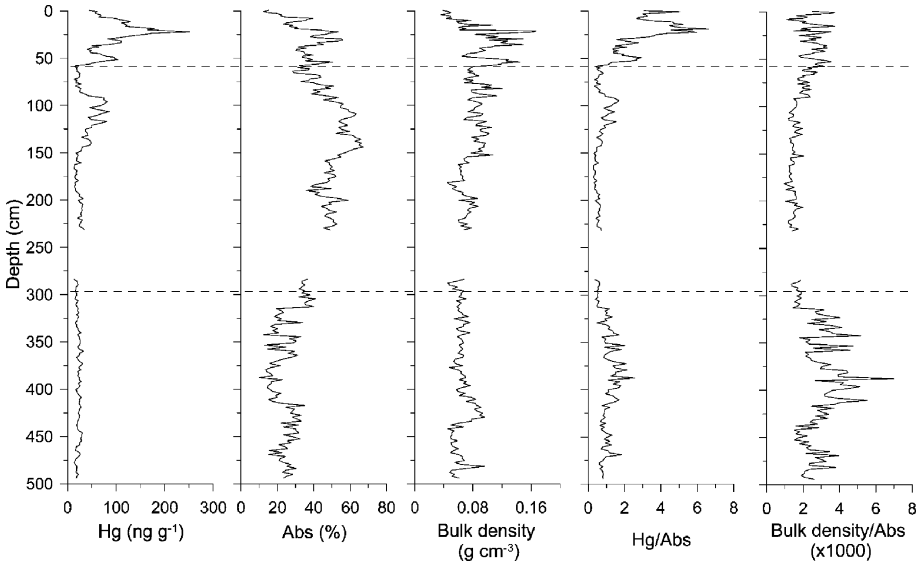

Fig. 4 Mercury concentrations (ng g^{-1}), degree of humification (corrected absorbance) and bulk density (g cm^{-3}) in the peat profile from Luther Bog. The ratio Hg/Abs is also shown to compensate the Hg concentrations for changes in peat decay. The ratio bulk density/Abs shows that these parameters provide a comparable index of the degree of humification for *Sphagnum*-dominated bog peats (above *ca.* 180 cm) but not for *Carex*-dominated fen peats (below *ca.* 250 cm).

and Mn in marine and lacustrine sediments may contribute significantly to Hg enrichments in the surface layers of these sediments, and it is important to know if these processes may have affected the Hg concentration profiles near the surface layers of the peat bogs. At the bog surface, Fe and Mn are deposited as soil dust particles, primarily as oxides and hydroxides derived from the chemical weathering of soils. In acidic, anoxic peat, these will react *via* reductive dissolution, releasing Fe(II) and Mn(II) to the porewaters which will diffuse upward into the oxic zone, become oxidised and precipitate.[40] It is conceivable, therefore, that Hg may have become enriched in the surface layers of the peat profiles *via* absorption onto the reactive surfaces of Fe and Mn oxides in the anoxic zone.[41] To evaluate this hypothesis, the distribution of Fe and Mn in the three Wardenaar cores is shown along with that of Hg in Fig. 3. The surface layers of each core are clearly enriched in Mn: given the LLD (lower limit of detection) of Mn in peat using the EMMA XRF (12 μg g^{-1}), the Mn concentration profile shows that Mn concentrations in the top of each core may be as much as two orders of magnitude greater than the underlying peat layers. However, these pronounced Mn enrichments are restricted to the top of the peat core, and in each peat core they clearly overlie the zone of elevated Hg concentrations (Fig. 3). Thus, the distribution of Hg and the distribution of Mn are clearly separated in space and time at all sites. With respect to Fe, the maximum in Hg concentrations in each core also is below the maximum Fe concentration (Fig. 3). Thus, in each of the three profiles, the maximum concentrations of Fe and Mn are separated in both space and time with respect to Hg (Fig. 3). The onset of changing Hg concentrations, therefore, precedes and pre-dates the changes in Mn and Fe concentrations.

Normalizing Mn and Fe to Ti emphasizes the change in Mn and Fe abundance, relative to the abundance of mineral matter (Fig. 5). In the peat core from Sifton Bog (Fig. 5b) and in the core from Spruce Bog (Fig. 5c), the maximum concentration of Hg corresponds to the minimum in Fe/Ti and Mn/Ti ratios. In these two peat profiles, therefore, there is no indication that the distribution of Hg has been affected in any way by redox-related transformations of either Fe or Mn.

Even in the case of the Luther bog (where a dam was constructed in 1954), the distribution of Hg does not correspond to that of Fe/Ti or Mn/Ti (Fig. 5a). The construction of the dam may have affected the hydrology of the bog by changing the level of the water table and therefore the depths at which redox processes take place within the peat column. The peaks in Fe/Ti at *ca.* 75 cm, 65 cm, and 45 cm may somehow be related to these hydrological changes to the peatland. However, even in these cases, the changes in Fe/Ti do not have a corresponding change in Hg concentration. The maximum Hg concentration, for example, at a depth of *ca.* 22 cm, corresponds to the minimum in Fe/Ti (Fig. 5a). Therefore, the distribution of Fe and Mn has not noticeably influenced the Hg concentration profiles in any of the cores. Although reductive dissolution of Mn and Fe in the peat cores is probably taking place (as seen in their chemical separation from Ti subsequent to deposition from the air as dust particles) this process has not discernibly affected the distribution of Hg.

Other diagenetic processes. There are other factors which argue that the peaks in Hg concentration have not been caused by chemical diagenesis within the peat profile. First, given the differences in the structure and morphology of the three peat bogs studied, and the spatial variability within each peatland, each peat core shows a unique variation in Hg concentrations with respect to *depth*: the maximum Hg concentrations are found at depths of *ca.* 15 cm (Sifton Bog), 22 cm (Luther Bog), and 35 cm (Spruce Bog). Each of the peat bogs is a naturally acidic, organic-rich, ombrotrophic ecosystem. Considering that the climate regime is reasonably similar at all sites, the average

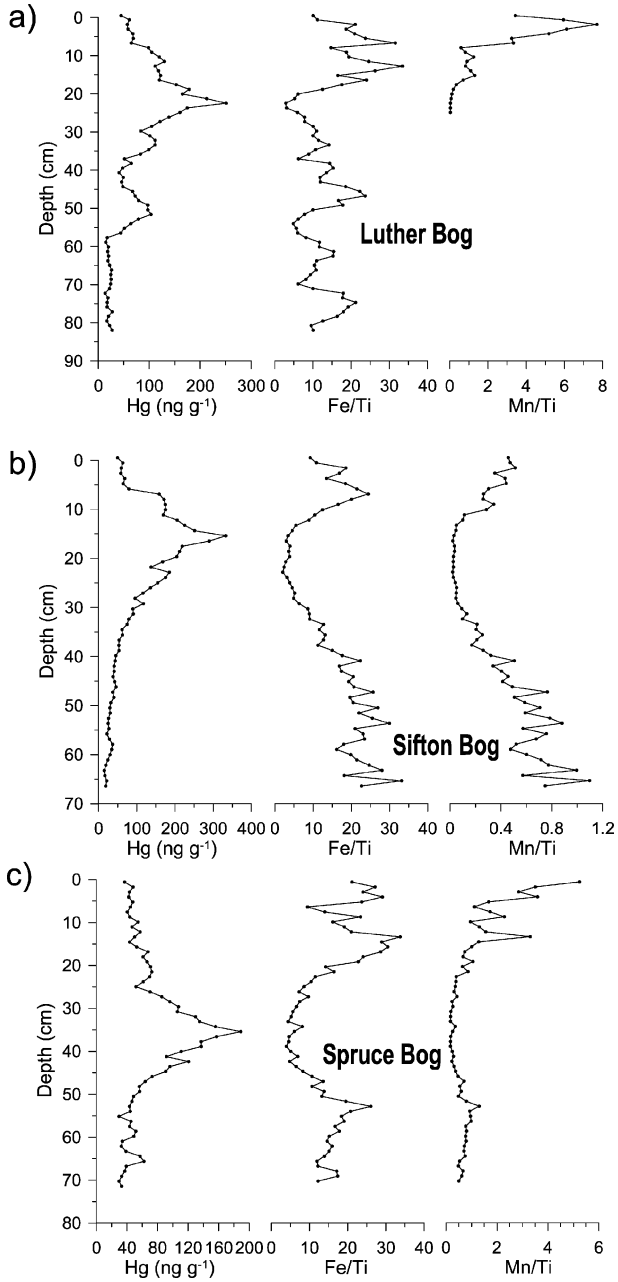

Fig. 5 Concentrations of Hg (ng g^{-1}), Fe/Ti and Mn/Ti ratio for the Wardenaar peat cores from (a) Luther Bog, (b) Sifton Bog, and (c) Spruce Bog. Note that the peaks in Hg concentrations correspond to minima in Fe/Ti in all three cores.

depth to water table should also be similar in each of the bogs. Therefore, if the distribution of Hg concentrations within the peat profiles was controlled or dominated by geochemical processes, there is no obvious reason why the maximum Hg concentrations should be found at different depths at each of the sites. However, the change in Hg concentrations with respect to *time* are similar, with Hg concentrations having reached their maximum concentrations during the late 1950's at each site. The similar chronologies of Hg accumulation in the three peat cores, therefore, suggest that the changing rate of atmospheric Hg deposition is the dominating process affecting the Hg concentration profiles.

Second, many published studies have concluded that Pb is effectively immobile in acidic, ombrotrophic peat bogs, and that these bogs faithfully preserve a record of atmospheric Pb deposition.[18–20] Given the pronounced differences between the geochemical behaviour of Hg and Pb, the correlation between the peaks in Hg and Pb concentrations (Fig. 3) cannot be mere

coincidence. In fact, taking Pb to represent an immobile reference element, the similar distribution of Hg and Pb in these peat cores suggests that Hg too, is well preserved, and that these bogs do indeed serve as archives of atmospheric Hg deposition. Taken together, the available evidence suggests that:

(i) the Hg concentrations measured in the peat core were supplied exclusively by the atmosphere,

(ii) there has been no significant diagenetic remobilisation of Hg, and

(iii) the peat bog has faithfully preserved a record of atmospheric Hg accumulation.

Effect of organic matter decay on Hg concentration profiles. In a recent study about Hg accumulation rates in Patagonian peat cores,[42] it has been suggested that humification processes and mass losses during the diagenesis of peat might have a strong influence on Hg concentrations or accumulation rates. Moreover, those authors suggested that bulk density is not an adequate parameter to express changes in peat humification, and that Hg accumulation rates should be corrected for humification to take into account mass loss during peat decay. In the present study, absorbance of alkaline extracts of peat was used as a measure of decay, and these data are compared with the Hg concentration profiles for the three Wardenaar cores in Fig. 3. These data show that the changes in Hg concentration within the profile are disproportional to the changes in peat humification (as reflected by the absorbance measurements). For example, at the Luther Bog the peat samples between 100 and 150 cm are clearly more decomposed than the peat samples above 50 cm (Fig. 4); however, the peat samples above 50 cm contain far higher Hg concentrations (Fig. 4). Thus, the variation in degree of decomposition of peats from the Luther bog profile alone cannot explain the most significant changes in the Hg concentration profile (Fig. 4). To emphasise this, the Hg concentrations have been normalised to absorbance and this ratio (Hg/Abs) is found to be elevated in three zones: in the *Carex* fen peat (*ca.* 450 to 300 cm), around 100 to 150 cm (to be discussed later), and above 50 cm (Fig. 4). In contrast to the small changes in absorbance within the peat profile, the changes in Hg concentrations relative to absorbance (Hg/Abs) are far greater. As a result, physical processes such as organic matter decomposition cannot explain the magnitude of the variation in Hg concentrations with depth in these peat bog profiles. Also, the small variation in the ratio between bulk density and absorbance in the *Sphagnum* peats (Fig. 4) shows that other physical processes such as compaction also cannot explain the magnitude of the Hg concentration differences.

5.2. Predominant sources of atmospheric Hg

Lithogenic sources of Hg and Pb. In the upper part of all three profiles, Hg, Pb and Ti have some peaks in common (Figs. 2 and 3) and it is necessary to quantify to what extent atmospheric soil dust may be a potential source of Hg (and Pb) and to the bog. Recent research, for example, has demonstrated that mineralised bedrock or/and bedrock with high natural background concentration in Hg and Pb constitutes significant sources of these elements to lake sediments in the south-eastern part of the Canadian Shield.[43] The lithogenic Hg and Pb fractions derived from atmospheric mineral matter can be estimated as the product of the concentrations of a conservative lithogenic element in a given profile (*e.g.* Ti), and the Hg/Ti or Pb/Ti ratio of the pre-anthropogenic, background period of the Luther bog profile. The pre-anthropogenic, natural background values of Hg/Ti and Pb/Ti are taken from the 60–290 cm section of the Luther bog profile which is ombrotrophic with respect to all three elements. These values are more representative of the pre-anthropogenic ratio of Hg/Ti and Pb/Ti ratios in atmospheric aerosols of southern Ontario than ratios obtained from compiled values published in the literature for the Upper Continental Crust.[44] Calculations of lithogenic Hg using the background Hg/Ti values, show the atmospheric deposition of mineral matter cannot explain more than 0.2% of the peak Hg concentrations, and no more than 15.5% of the Pb. Clearly, natural inputs of Hg from soil dust represent a negligible source of Hg to the peat bog profiles. Further evidence supporting this conclusion is the notable peak in Ti concentration at a depth of *ca.* 375 cm in the Luther profile which has no corresponding peak in Hg concentration (Figs. 2 and 4).

The elevated Ti concentrations seen in all three peat cores (Fig. 2) indicate recent increases in the deposition of dust particles from the atmosphere. These changes are most likely caused by soil dust because of the extensive forest clearance for agriculture. During the period *ca.* AD 1800 to 1900, southern Ontario was more or less deforested by European settlers, and the increased rate of soil erosion would have created a significant increase in the release of dust particles to the air; the surface layers of these bogs bear witness to this process. Again, however, these inputs are not a significant source of Hg to the bogs. While there certainly are elevated concentrations of Hg and Pb in the samples which are enriched in Ti, these three elements only share a common chronology, and not a common source. In other words, the processes which have enhanced Ti inputs to the bog (enhanced fluxes of soil dust) are independent of those providing Hg and Pb (mainly coal-burning; see below): however, the *chronology* of the changing importance of these two processes is similar.

If the changing Hg concentrations seen in the recent peat layers of all three peat cores cannot be explained by chemical processes operating within the peat profiles, and if the changing rates of atmospheric soil dust cannot explain their distribution, then anthropogenic sources of Hg must be invoked to explain the increased rate of deposition of this element.

Distinguishing between natural and anthropogenic mercury sources. *Hg in relation to Br and Se.* To distinguish between natural and anthropogenic Pb in peat bog profiles, we have previously used scandium (Sc) as a conservative reference element to represent the natural Pb component contributed by atmospheric soil dust.[19] This approach is valid because atmospheric Pb deposition in pre-anthropogenic times was dominated by inputs of soil dust, and because Sc behaves conservatively both during chemical weathering in soil profiles, but also subsequent to deposition in the bog.[16] It is highly desirable to have an analogous "reference element" for Hg, to quantify the natural inputs of Hg to the bog. In the case of Hg, however, the data and arguments given above show that soil dust inputs of Hg were insignificant in pre-anthropogenic times, and therefore that a reference element is needed whose inputs to the bog are independent of soil dust.

Bromine and selenium are two elements whose supply to the bog is independent of soil dust. The chemistry of Br and Se is very different to that of Hg: Br is probably supplied to the bog primarily as ionic bromide and Se perhaps as dimethyl selenide; both are ultimately supplied by the oceans. In contrast, Hg in the atmosphere in pre-anthropogenic times must have been present primarily as the volatile, unreactive, gaseous elemental form.[1,2] The physical and chemical processes which affect and control their atmospheric transport and deposition also are very different. Despite these great differences, Hg/Br and Hg/Se ratios in ombrotrophic peat dating from pre-anthropogenic times were remarkably constant for thousands of years (Fig. 6): from 495 to 150 cm, the Hg/Br and Hg/Se ratios averaged 0.0010 ± 0.0003 and 0.021 ± 0.007, respectively ($n = 144$). Therefore, even though these elements may have different atmospheric sources, chemical properties, and different modes of transport and deposition, their rates of accumulation in

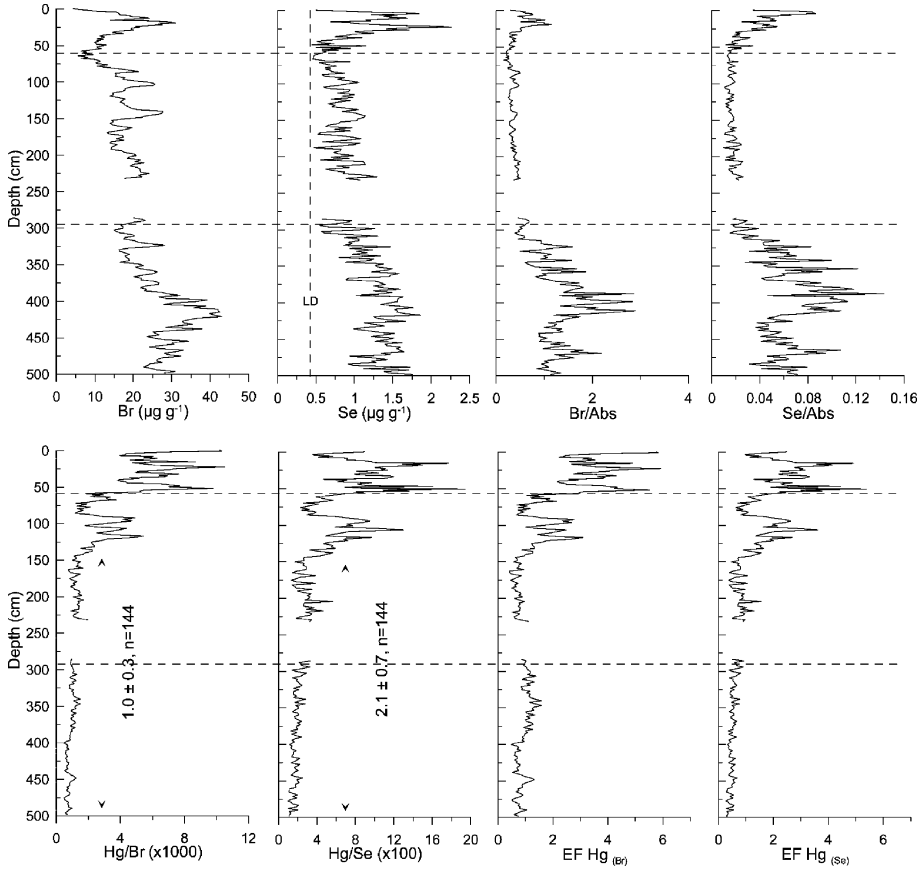

Fig. 6 Bromine and selenium concentration profiles (μg g^{-1}) for the Luther Bog peat profile. The Br/Abs and Se/Abs ratios show that the surface peat layers are enriched in Br and Se, out of proportion with the extent of humification. The Hg/Br and Hg/Se ratios show that these values were relatively constant for many thousands of years. The vertical dashed line indicates the analytical limit of detection for Se (0.4 ppm). Mercury enrichment factors (EF Hg) have been calculated using both the pre-anthropogenic Hg/Br and Hg/Se ratios to calculate the extent of enrichment (no. of times) relative to these pre-anthropogenic, background values.

pre-anthropogenic peat were in constant proportions for thousands of years. The constant "background" ratios warrants an attempt to use Hg/Br and Hg/Se to try to quantify anthropogenic Hg. Further support for this approach is provided by the peat core collected at Etang de la Gruère in the Jura Mountains of Switzerland, where the natural "background" Hg/Br ratio[14,29] was constant for several thousand years (average 0.0012 $\pm$ 0.0002 from *ca.* 14 500 to 800 years BP).

Relative to the "background" values, the ratios Hg/Br and Hg/Se increase below 495 cm where the profile consists of gyttja and clays, as well as in samples from 150 to 85 cm and in all samples above 70 cm depth. The increases in Hg/Br and Hg/Se in the peat samples above 70 cm (dating from recent times) are of particular interest.

If Hg, Br and Se in peat are conserved during decomposition, then they will increase in concentration with increasing humification (as measured using corrected absorbance). In the Luther Bog profile from 300 cm to 60 cm depth, there is a constant botanical composition of peat, but variable degree of humification (Fig. 4): here, the Br/Abs and Se/Abs ratios are low and constant (Fig. 6). Thus, during decomposition, these elements appear to behave similarly and become enriched to the same extent; this is true also of Hg (Fig. 4). Humification processes operating with the peatland, therefore, affect Hg, Br and Se to the same extent, and as a first approximation, they are conserved during organic matter decay. In the *Carex* fen peat layers, the Br/Abs and Se/Abs ratios are clearly elevated, but here emphasis is placed on the corresponding ratios in ombrotrophic peat which are constant from *ca.* 200 to 50 cm (Fig. 6).

Calculating an enrichment factor for Hg (EF Hg) using Hg/Br and Hg/Se. Enrichment factors have been calculated for Hg (EF Hg) using the constant, pre-anthropogenic values for Hg/Br and Hg/Se. These EF calculations (Fig. 6) show that Hg is enriched in the Luther profile by a factor of up to 6 times, relative to "background" values. In the uppermost peat samples, however, the Br/Abs and Se/Abs profiles show that both Br and Se themselves are enriched, relative to "background" values (Fig. 6). Thus, the EF calculations underestimate the true extent of anthropogenic enrichment of Hg. The enrichments of Br and Se may be due to natural processes, anthropogenic inputs, or both. The topmost sample of the core is made up of living plant matter, but here the Br and Se concentrations are lower than in underlying samples (Fig. 6). Therefore, biological uptake of Br and Se by plants does not appear to be the dominant cause of the elevated Br/Abs and Se/Abs values in the surface layers of the bog. Possible anthropogenic sources of Br[45] and Se[46] include Br compounds added as gasoline Pb additives (to scavenge Pb from motors) and Se release during coal burning and metal sulfide refining. The calculated EF values for Hg, therefore, are at best rather conservative estimates of anthropogenic Hg.

Separating total Hg into natural and anthropogenic components using Br. Because the ratio Hg/Br and Hg/Se in peat dating from pre-anthropogenic times was effectively constant, these ratios can be used to separate total Hg into its natural and anthropogenic components. With respect to Se, the concentrations of Se in the pre-anthropogenic section of the peat profile are typically *ca.* 5$\times$ the LLD provided by EMMA XRF (0.4 ppm), but in some cases the Se concentrations in peat approach the LLD. In contrast, Br concentrations in the same peats are always at least a factor of ten above the LLD (0.7 ppm). Because measurements of element concentrations

10 × LLD are more accurate than those approaching the LLD, Br was selected as the better reference element for Hg. Therefore, the natural Hg component in the peat cores was calculated using the Hg/Br ratio. Here, "excess Hg" is defined as the difference between the natural Hg component and the total Hg concentration:

$$[Hg]_{excess} = [Hg]_{total} - [Hg]_{natural} \quad (1)$$

where

$$[Hg]_{natural} = [Br]_{sample} \times [Hg]/[Br]_{background} \quad (2)$$

A similar approach was used previously to separate Pb in peat cores into its natural and anthropogenic components using the background Pb/Sc or Pb/Ti ratio.[28] Excess Hg calculated in this way cannot be attributed to the residual enrichment of Hg during the decomposition of organic matter because this effect is already taken into account by the Br concentrations: the Br concentrations (Fig. 6) vary with peat humification (Fig. 3) and by normalising the Hg concentrations to Br, therefore, this process is already considered. In the uppermost peat layer where Br/Abs reveals an enrichment of Br, out of proportion with humification (Fig. 6), however, excess Hg calculated as described above will certainly be underestimated. To have a better measure of excess Hg in the surface peat layers, a reference element for atmospheric Hg deposition is needed which has no significant anthropogenic contribution: we are not aware of any such element. For the moment, therefore, there is no choice but to use Br as a reference element for atmospheric Hg inputs, as imperfect as this may be.

Excess Hg in the peat core consists of Hg in a concentration range which exceeds that which can be attributed to the natural ratio of Hg to Br. This excess Hg may be due to Hg inputs from volcanic emissions,[29] changes in intensity of biogenic emissions including biomass burning, climate changes such as variations in temperature or rainfall,[29] or anthropogenic Hg inputs. Previous studies using peat cores from Swiss bogs[29] have shown excess Hg due to climate change and volcanic emissions are small compared to the concentrations of excess Hg in modern peat samples dating from the Industrial Period.

Below 495 cm in the Luther Bog profile, excess Hg cannot be interpreted with respect to atmospheric inputs because the peat core at these depths consists of gyttja, a nutrient-rich sedimentary peat dominated by plankton and other plant and animal residues. The Hg/Br and Hg/Se ratios are elevated in this zone of the peat profile (not shown), as well as the Hg concentrations, possibly reflecting other Hg enrichment processes related to intense bacterial activity (bioaccumulation) at the gyttja/water interface during sedimentation in a quiet water environment. These natural Hg enrichment processes are beyond the scope of this paper.

5.3. Calculating net atmospheric Hg accumulation rates

To estimate the atmospheric Hg fluxes, net Hg accumulation rates (AR) were calculated using:

$$AR = 10 \times [Hg] \times BD \times GR \quad (3)$$

where AR is the net accumulation rate of Hg (μg m^{-2} per year), [Hg] the Hg concentration (ng g^{-1}), BD the bulk density of the peat (g cm^{-3}) and GR the growth rate (cm per year). Growth rates were determined using ages calculated for each layer by the age–depth relationship of each core. The net rate of Hg accumulation (Hg AR) for the past 8000 years derived from the Luther Bog peat profile is shown in Fig. 7 and for the three Wardenaar peat cores in Fig. 8. The error associated with the mercury accumulation rates for the last 50 years is calculated to be 21%, based on conservative estimates of the errors associated with ^{14}C dates (*ca.* 5%), Hg concentrations (*ca.* 5%), and bulk density measurements (*ca.* 20%). The error range for the samples pre-dating AD 1950 and too young to be dated using ^{14}C is more difficult to quantify because the age–depth model does not permit uncertainties to be calculated; however, these are assumed to be comparable to the others.

Natural background Hg accumulation rates. The Hg AR profile for Luther Bog shows total Hg deposition for the last 8000 years (Fig. 7). Here, the net rate of atmospheric Hg accumulation during the Holocene (past ten thousand years) varied between 0.4 and 7.7 μg m^{-2} per year with an average accumulation rate of 1.4 ± 1.0 μg m^{-2} per year (n = 197) from 5700 years BC to AD 1470. These values are consistent with natural Hg AR measured in peat cores from bogs in Sweden,[15] Switzerland,[14,29] Greenland.[16] and Maine, USA.[47] The variation exhibited by Hg AR is thought to be primarily due to Holocene climate change. For example, during a warm, dry period in southern Ontario[48] from *ca.* 3600 to 200 calendar years BC, the natural rate of atmospheric Hg accumulation was

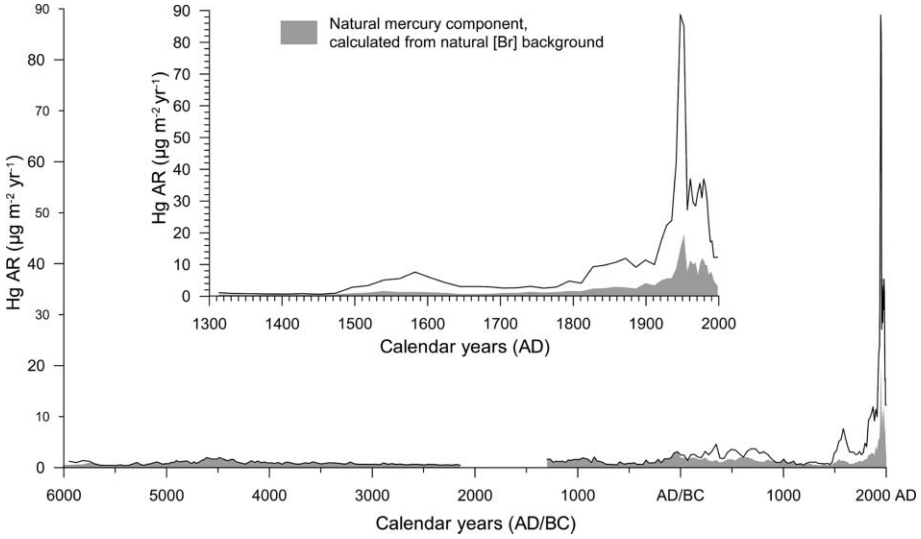

Fig. 7 Total (solid line) and natural (shaded area) Hg accumulation rates (past 8000 years) in the Luther Bog profile calculated using the background Hg–Br relationship. Inset: past 700 years.

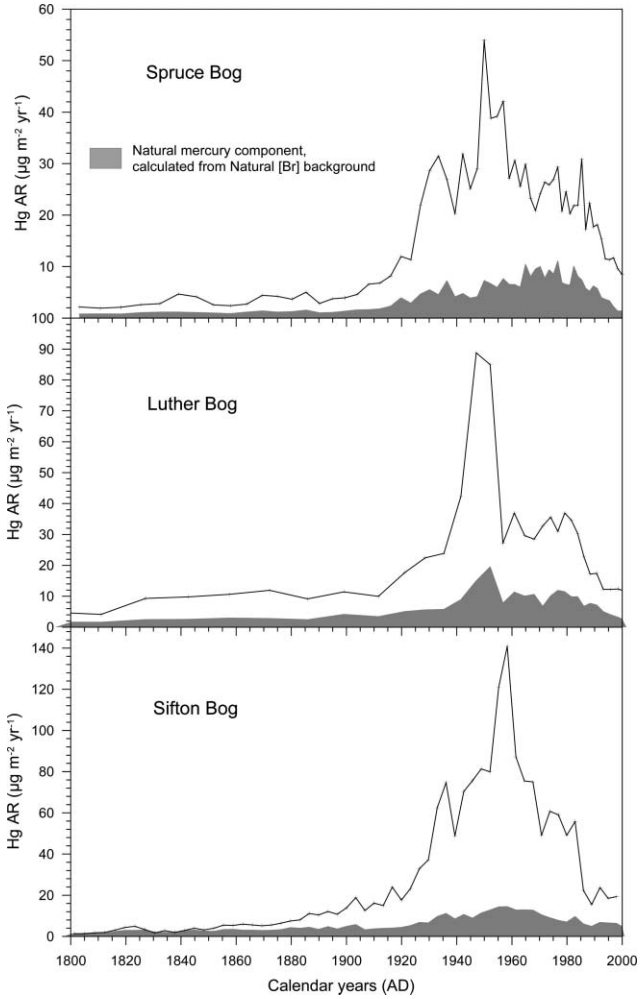

Fig. 8 Chronologies of total (solid line) and natural (shaded area) Hg accumulation rates for Spruce Bog, Luther Bog and Sifton bog. The difference between the total AR and the natural AR is an estimate of the anthropogenic contribution.

particularly low and constant (Fig. 7). During the pre-anthropogenic period, an excess of Hg occurred only once, in peat from *ca.* 72 to 135 cm and dating from *ca.* 200 calendar years BC to AD 1200 (Fig. 7).

Several physical and chemical properties of peat from ombrotrophic bogs have been used as proxy climate indicators,[49] including the degree of peat decomposition.[32] The increase in the absorbance values (degree of humification) of the Luther Bog peat core (Fig. 3) from 4000 to 0 calendar years BC (385 cm to 135 cm) reflects an increase in the degree of peat decomposition; this, in turn, indicates a period of low effective precipitation. The occurrence of this climate phase in the Luther Bog is consistent in timing (from other archival records) with the late middle Holocene warm and dry period in Ontario.[48] Recent paleohydrological studies of water levels at other sites in eastern North America indicate similar dry climate periods which are thought to be due to more frequent incursions of drier Pacific air into the northeast of North America.[50,51]

Following this warm, dry phase, the subsequent period (*ca.* 200 calendar years BC to AD 1200) shows a decrease in the degree of humification which reflects a shift in climatic conditions to a period of higher effective precipitation. Lake sediment records throughout the northeast USA document increasing lake levels by 2000 BP which suggests increased humidity and colder conditions; this has been interpreted as a response to a more southward displacement of the Arctic front relative to it's modern position.[52,53] Of special interest here, an excess of Hg is observed throughout this period, with the Hg AR increasing by more than a factor of three from 1.4 to 4.6 μg m^{-2} per year. These changes reflect an increase in atmospheric humidity in southern Ontario at that time, following the preceding warm and dry period: this must have led to a corresponding increase in wet deposition of atmospheric Hg which is recorded by the peat core from Luther Bog (Fig. 7). The elevated Hg fluxes for this period (Fig. 7), and the elevated Hg/Br and Hg/Se ratios (Fig. 6), are therefore interpreted as a direct reflection of climate change. The magnitude of the change in Hg AR from this period (a factor of three times) documents the sensitivity of natural 'background'' Hg accumulation rates to Holocene climate change. Clearly, these variations must be duly considered when quantifying modern Hg accumulation rates for comparison with background values. Similar climate-driven Hg accumulation rate phenomena have been seen in others bogs.[13,29]

In addition to direct effects of climate change on Hg accumulation rates, there are several possible indirect effects. For example, the change in climate may have led to changes in the relative abundance of dominant plant species growing on the bog surface at that time. Some bog plant species are particularly efficient at retaining Hg compared to others[14] such that small differences in net rates of Hg accumulation may be partly due to changes in the abundance of predominant plant species. For example, the deposition of Hg associated with litterfall and throughfall may provide up to 60% of the total Hg deposited beneath a spruce forest canopy.[54] Therefore, a change in vegetation such as a change of the relative abundance of bog plant species or greater tree cover, may have led to a long-term change in the efficiency by which Hg was deposited, captured and/or retained by the bog. While differential retention or release of Hg during organic matter decay may also play a role, this seems far less likely to be important because the relationship between Hg concentration and absorbance (Figs. 3, 4) suggests that Hg is very well retained by the peat. Also, experimental studies have shown that little of the Hg deposited on peat bog surfaces is re-emitted to the air.[55]

The fluctuations in Hg AR due to Holocene climate change are dwarfed by the dramatic increases in Hg AR in peat samples dating from the modern period; these more recent changes are discussed in more detail below.

Excess Hg beginning in peat dating from the 15th century AD. A notable peak of Hg AR (up to 5× relative to ''background'') occurs from AD 1475 to AD 1650 and reaches a maximum flux of 7.7 μg m^{-2} per year (Fig. 7, inset). Since AD 1475, Hg AR has been elevated and the Hg/Br and Hg/Se ratios have continuously been outside of their long-term average range. This excess of Hg relative to both Br and Se may be an entirely natural phenomenon such as enhanced Hg deposition from the global cycle of gaseous elemental Hg due to increased atmospheric humidity and its effects on Hg oxidation and precipitation scavenging, or an anthropogenic process such as local or regional scale changes in Hg emission rates due to gold and silver mining.

There are at least two regional anthropogenic sources of Hg which may have resulted in Hg contamination of the Luther bog profile in the late 15th century. First, this enrichment may be a reflection of Hg consumed and emitted by amalgamation associated with silver mining activities in Spanish America. Hylander *et al.*[56] have recently reported that the onset of Hg use in South America dates from around AD 1550. The impact of fugitive Hg release from industrial silver production in Spanish America may explain part of the peak in Hg contamination observed in Luther profile from AD 1475 to AD 1650 (Fig. 7). However, at Caribou bog in Maine, about 1000 km east of the Luther bog, onset of Hg contamination from anthropogenic sources began during the nineteenth century.[47] No peak of HgAR is observed at that site in the period of industrial Hg use for silver recovery in South

America. In addition, the peak in Hg concentration and Hg AR in the Luther Bog correlates with smaller but significant peaks in Pb (Fig. 3) and sulfur (S, not shown) concentrations during the same period. Taken together, those two observations suggest that a local source of anthropogenic Hg is probably needed to explain the Hg, Pb and S contamination observed in the Luther profile from AD 1475 to AD 1650.

Second, southern Ontario has its own unique record of regional scale human impacts. It is known from archaeological evidence that Iroquoians settled in the Grand River watershed of southern Ontario from AD 1370 to AD 1650. Although paleoecological evidence for impact of Iroquois farmers on the forests of southern Ontario is limited to few sites,[57–59] there is abundant archaeological evidence for their presence in the period between AD 900 and AD 1600.[60] High-resolution pollen and charcoal analyses from Crawford Lake (30 km SE of Luther Bog) by McAndrews and others[57,59,61] reveal a pronounced change in the composition of upland forests around 1500 AD which was caused by deliberate forest burning by Iroquois for maize cultivation. The Iroquoian practiced long-fallow cultivation which involved clearing a plot of land by cutting the underbrush and girdling large trees, burning the residue, and planting crops for several years until the soluble nutrients supplied from the wood ashes became depleted. The cycle was repeated on other sections of land over a number of years until all the arable soils within a reasonable distance to the village were exhausted. Once this point had been reached, the village would be relocated to a new area and the process would begin over again.[60]

Published studies from Manitoba, Canada, and the Amazon basin of Brazil have shown that forest fires can be significant sources of Hg emissions.[62] It is quite possible, therefore, that the increase in Hg AR seen in the Luther Bog reflects biomass burning by Native North Americans. The peak in excess Hg dates from *ca.* AD 1580 when the Neutral population is estimated to have reached its maximum. The population of the Neutral has been variously estimated to range from 12 000 to 40 000 people.[63] The lower estimates may reflect the devastating effects of European diseases and periods of famine which swept through the region between AD 1634 and 1640.[64] The introduction of European diseases, for which native populations had little immunity, and intensified warfare during the beginning of the 17th century led to the collapse of the Huron and Neutral tribes in 1649.[65] The Hg AR recorded by the peat core decreased from AD 1580 to reach a plateau around AD 1650 and may reflect well the decline of biomass burning by at that time.

The partitioning of Hg released from biomass burning remains controversial. Combustion gases from fires would resemble those from fossil fuel burning,[62] with up to 50% of total Hg in the form of water-soluble Hg^{II}.[66] Recent laboratory experiments,[67] however, report that during biomass burning, mercury is emitted almost exclusively as elemental Hg ($>95\%$) and $<5\%$ as particulate mercury. Thus, it remains unclear how the Hg released from regional biomass burning for native agriculture gave rise to the peak in Hg accumulation rate (AD 1580) in the Luther Bog. However, if 50 to 95% of the Hg released was in the form of Hg^0, then the Hg recorded by the bog probably only reflects a fraction of the total emission flux, with much of the emitted Hg having been dispersed globally.

Modern Hg accumulation rates. During the late 17th and 18th centuries, the approach used here to calculate anthropogenic Hg in the Luther Bog profile indicates that the accumulation of Hg from anthropogenic sources was equivalent to or exceeded the inputs of Hg from natural sources (Fig. 7). All three bogs show that Hg contamination increased again at the beginning of the 19th century, with the greatest change seen at the beginning of the 20th century (Fig. 8). The chronology of Hg accumulation recorded by the three ombrotrophic bogs in southern Ontario is similar, with maximum rates of accumulation of anthropogenic Hg dating from the 1950–60s at all three sites (Fig. 8). At that time, anthropogenic mercury contributed at least to 85% of the total Hg AR and the greatest accumulation rates recorded by the bogs (54, 89 and 141 $\mu g\ m^{-2}$ per year at Spruce Bog, Luther Bog and Sifton Bog, respectively) are up to 39, 63 and 101 times greater than the average natural background rates. Clearly, there is a gradient within southern Ontario of the intensity in anthropogenic Hg inputs, with Hg AR increasing in the order remote $<$ rural $<$ urban site. Assuming that inputs to the relatively remote Spruce Bog are more indicative of global changes in the atmospheric Hg cycle, the much greater Hg AR recorded by the Sifton bog in London, Ontario reflects the importance of regional and local sources.

The Hg AR values today (10, 12 and 18 $\mu g\ m^{-2}$ per year at Spruce Bog, Luther Bog and Sifton Bog, respectively), are approximately 7, 9 and 13 times the average natural background values. The modern fluxes obtained using these peat cores can be compared with the direct measurements of atmospheric Hg deposition at regional Mercury Deposition Network (MDN) monitoring sites in southern Ontario. Wet deposition of mercury monitored at regional MDN sites in Ontario reported values of 7.4 $\mu g\ m^{-2}$ per year in 1998 at the Dorset site and 4.7 $\mu g\ m^{-2}$ per year in 2001 at the Edbergt site. Assuming that dry deposition constitutes no more than $40 \pm 50\%$ of wet deposition,[68] these direct measurements indicate total mercury deposition rates ranging from 5.6 to 13.3 $\mu g\ m^{-2}$ per year which is in good agreement with the values reported by this study for the same period of time. The agreement between the two independent methods for quantifying atmospheric Hg deposition rates suggests that the approach described here (using peat cores from ombrotrophic bogs to reconstruct accumulation rates) is reasonable. Moreover, the retrospective approach using peat cores from bogs is especially valuable because it not only provides a detailed chronology of the changes extending back in time, but also because it yields the "natural background" rate of atmospheric Hg accumulation, against which modern values may be compared.

Because Br and Se have also been emitted by anthropogenic sources[69] such as gasoline additives (to scavenge Pb) and coal burning, respectively, the natural Hg component for the modern period has been overestimated by the peat cores. Given the changes in Br/Abs and Se/Abs seen in the top layers of the Luther Bog (Fig. 6), we estimate that the natural Hg component found in modern peats has been overestimated by at least a factor of two, compared to the pre-anthropogenic period. As a result, the rates of anthropogenic Hg accumulation which we have calculated for the modern period in each of the peat cores (Fig. 8) represent conservative estimates.

Identifying the predominant source of anthropogenic Hg during the 20th century. The similarities in Hg accumulation chronologies among the three peat bogs from southern Ontario (Fig. 8) imply a common, predominant source. We note that the peat samples containing the greatest Hg concentrations and Hg accumulation rates (Fig. 8) are also the samples containing the highest Pb concentrations (Fig. 3). While traditional chloro-alkali plants were the predominant source of anthropogenic Hg to the global atmosphere in the recent past,[70] these did not emit Pb. While leaded gasoline was the single most important source of anthropogenic Pb to the global atmosphere[71] until recently, this was not a source of Hg. In fact, the predominant anthropogenic source that these two elements have in common is coal burning. In southern Ontario, therefore, the maximum rates of atmospheric Hg and Pb deposition, and the maximum contributions of these metals from anthropogenic sources, was due to coal burning, and this source peaked in the late 1950's. Support for this hypothesis is provided by the sulfur concentration profiles (not shown)

which show that the maximum S concentrations in all three peat cores coincide with the peaks in Hg and Pb; coal is enriched in all three of these elements. We note further that a peat bog in Denmark and a minerotrophic fen in southern Greenland provide very similar chronologies of both metals,[16] with maximum accumulation rates (also obtained using the bomb pulse curve of ^{14}C) dating from AD 1953. In that study,[16] the isotopic composition of Pb in the most contaminated section of the Danish peat bog profile was found to be comparable with that of British coals lending further support to the importance of coal burning as a source of both metals.

5.4. Comparison with other archives

For comparison with the results presented here, we know of no published studies providing a record of atmospheric Hg deposition for North America extending so far back in time. However, there are several published chronologies of Hg contamination for the modern period, and the results presented here are generally in good agreement with those studies. For example, data from lake sediments in Minnesota[72] indicate that mercury deposition peaked in the 1960's, with recent declines appearing in both rural and urban sites. The emission budget by Pirrone[7] suggests that atmospheric Hg deposition from local sources dominated from 1940 to 1960, with deposition subsequently dominated by long-range atmospheric transport. The results presented here also are consistent with other findings that indicate that a substantial fraction of anthropogenic Hg emissions are deposited locally near the source of pollution.[2]

The Upper Fremont Glacier (UFG) has yielded a high-resolution record of total atmospheric mercury deposition for the past *ca.* three centuries.[73] The ice core taken from this site indicates a 20-fold increase in Hg accumulation rates between pre-industrial (*ca.* AD 1720) and industrial times which is comparable to the peat records from southern Ontario for the same period of time. The UGC core is the only other high-resolution record, along with the present study, reporting atmospheric mercury deposition in North America as far back in time as AD 1720. Without long-term records of atmospheric mercury deposition, it is difficult if not impossible to determine pre-industrial rates of atmospheric Hg accumulation, and to quantify the natural variation in "background" fluxes. Many of the studies published to date appear to have overestimated the natural "background" rates of atmospheric Hg deposition, and therefore may have underestimated the true impact of human activities on the geochemical cycle of mercury.

For example, lake sediment archives document smaller differences between anthropogenic and natural Hg fluxes. In many studies of peat and lake sediments archives by authors mentioned previously, accumulation rates of atmospheric mercury are reported to be in the range of 4 to 7 $\mu g\ m^{-2}$ per year for the "natural background" and ranging between 10 and 50 $\mu g\ m^{-2}$ per year for the modern period. In contrast, the peat cores studied here suggest that the maximum rates of net Hg deposition are between 54 and 141 $\mu g\ Hg\ m^{-2}$ per year, compared with a natural background of approximately 1.4 $\mu g\ m^{-2}$ per year which was fairly constant for thousands of years. We see two important reasons for the discrepancies. First, unlike lake sediments, peat bogs receive Hg only from the atmosphere. Thus, the total amount of Hg retained by a peat core is a reasonable approximation of the total atmospheric input. In contrast, the Hg concentrations in lake sediments reflect not only direct inputs from the atmosphere, but also terrestrial and aquatic inputs. Second, many of the lake sediment Hg records do not provide high-resolution reconstructions. As a consequence, Hg concentrations are often averaged over longer time intervals which tends to "flatten" any peaks in concentration change (or flux). As a consequence, it is difficult to compare in detail the trace metal accumulation chronologies when there are large differences in the time increments being examined.

The results presented here and other recent studies using peat bog archives dated using the bomb pulse curve of ^{14}C have shown that undisturbed peat bogs are excellent paleoenvironmental archives. These bogs certainly do record in a faithful way the changing chronologies of atmospheric mercury deposition. In fact, the historical records of net atmospheric Hg deposition appear to be so well preserved in the peat profiles that our ability to read and interpret these records is much less dependent upon physical and chemical processes taking place within the bog, and more dependent on appropriate and accurate methods for peat core sampling, handling, sectioning, sub-sampling, preparation, and age dating.

5.5. Implications for the global atmospheric Hg cycle

The changing fluxes of atmospheric Hg accumulation recorded by the peat bogs in southern Ontario, especially the decline since the 1960's (Fig. 8), is probably related to the introduction and growth of nuclear power, but also the regulatory developments or/and industrial process changes, including the introduction of filter technologies which retain particulate Hg.[74] In addition, residential home heating evolved from coal to oil and then to natural gas. While these trends are certainly positive and encouraging, they must also be viewed with caution and concern. Even though the various filtration technologies deal effectively with the removal of particulate Hg from flue gas streams, more volatile species such as gaseous elemental Hg are largely unaffected.[72,75] As a result, the changing fluxes of atmospheric Hg accumulation recorded by the peat bogs (Fig. 8) do not necessarily document a decrease in *total* Hg emissions. Most likely, these changes primarily reflect strong declines in atmospheric emission of *particulate* Hg. The large differences in Hg AR between the three sites demonstrate the quantitative importance of local inputs of particulate and ionic Hg: the decline in Hg AR since the late 1950's recorded by all three bogs certainly reflects a decrease in deposition of this fraction. However, these peat cores may provide little information about the changes in emissions of gaseous elemental Hg because it is volatile, much less reactive, and has a long atmospheric residence time. Peat cores from bogs in remote areas of Canada, for comparison with the results shown here, might provide more insight into the changing rates of atmospheric deposition of elemental Hg from anthropogenic sources. The effect of particle size distribution plays an important role in transferring Hg from the atmosphere to lakes[76] and this phenomenon may have important implications for atmospheric Hg accumulation in remote areas such the Arctic.

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Mercury Concentrations in Bicknell's Thrush and Other Insectivorous Passerines in Montane Forests of Northeastern North America

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Abstract. Anthropogenic input of mercury (Hg) into the environment has elevated risk to fish and wildlife, particularly in northeastern North America. Investigations into the transfer and fate of Hg have focused on inhabitants of freshwater aquatic ecosystems, as these are the habitats at greatest risk for methylmercury (MeHg) biomagnification. Deviating from such an approach, we documented MeHg availability in a terrestrial montane ecosystem using a suite of insectivorous passerines. Intensive and extensive sampling of Bicknell's thrush (*Catharus bicknelli*) indicated significant heterogeneity in MeHg availability across 21 mountaintops in northeastern North America. Southern parts of the breeding range tended to be at greater risk than northern parts. Mean blood Hg concentrations for Bicknell's thrush at 21 distinct breeding sites ranged from 0.08 to 0.38 ug/g (ww) and at seven Greater Antillean wintering sites ranged from 0.03 to 0.42 ug/g (ww). Overall concentrations were significantly greater in wintering than in breeding areas. Mercury exposure profiles for four passerine species on Mt. Mansfield, Vermont indicated greatest MeHg uptake in Bicknell's thrush and yellow-rumped warbler (*Dendroica coronata*) and lowest in blackpoll warbler *(Dendroica striata)* and white-throated sparrow *(Zonotrichia albicollis)*. The MeHg and total Hg ratio in blood in these four species was nearly 1:1. There was no correlation between blood and feather Hg concentrations in breeding Bicknell's thrush, in part because of apparent retention of winter Hg body burdens, within-season variation of MeHg availability, and confounding factors such as influences from age. Adult thrushes had significantly higher concentrations of feather Hg than did young-of-the-year. Although individual patterns of inter-year feather Hg concentrations were disordered, some individuals exhibited bioaccumulation of MeHg. Female blood Hg concentrations were significantly lower than males', in part because females have additional depurating mechanisms through eggs. Older male Bicknell's thrushes that breed in New England are therefore likely at greatest risk. Mechanisms for Hg methylation in montane areas without standing water are not yet fully understood. However, recent studies indicate that

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MeHg is present in forest tree leaves and leaf detritus; saturated soils and other moist microhabitats may also contribute to MeHg availability. Our finding of a correlation between regional litterfall Hg flux patterns and Bicknell's thrush blood Hg concentrations demonstrates on-site availability of MeHg. Further investigations into MeHg availability in montane environments are recommended to assess risk to insectivorous passerines, particularly the Bicknell's thrush.

Keywords: Songbirds; Catharus bicknelli; Nearctic-neotropical migratory birds; methylmercury

Introduction

It is well established that elevated levels of atmospheric mercury (Hg) deposition and methylmercury (MeHg) bioavailability in the northeastern United States influence wildlife populations. Investigations have focused on multiple trophic levels of freshwater aquatic ecosystems (Evers et al., 2004; Bank et al., 2005; Chen et al., 2005; Kamman et al., 2005; Pennuto et al., 2005), where converted MeHg biomagnifies through the aquatic foodweb, from phytoplankton and zooplankton to invertebrates, amphibians, fish, and piscivorous vertebrates. Particular emphasis has been on higher trophic piscivorous wildlife, which are most at risk from mercury's ability to bioaccumulate and biomagnify (Thompson, 1996; USEPA, 1997; Evers et al., 2005).

Little is known about MeHg availability or toxicity in passerine birds, especially those species not associated with aquatic systems (Thompson, 1996; Wolfe and Norman, 1998; Wiener et al., 2003). Further, exceedingly few data exist on MeHg burdens in migratory passerine birds, which are potentially exposed to varying environmental levels of Hg during their breeding, migration, and wintering periods. Birds are an important taxon for sampling because they are well-established bioindicators of MeHg availability (Burger, 1993; Furness and Greenwood, 1993; Bowerman et al., 2002; Mason et al., 2005), they are relatively easily sampled, and commonly used matrices reflect $>95\%$ of the total body burden of Hg (Evers et al., 2005). Among passerines, obligate insectivorous species are most likely to be at risk from Hg toxicity, although established impact thresholds are only now being developed at the individual level (G. Heinz, pers. com.) and no published studies have investigated population level risk.

While pathways for Hg uptake and bioaccumulation in terrestrial ecosystems are not well understood, recent research has shown that Hg deposition varies by a factor of three at both regional and local scales due to proximity of emissions sources, climatic effects, and variations in surface characteristics that influence dry deposition (Miller et al., 2005; VanArsdale et al., 2005). Mercury loading is significantly (2–5×) higher in montane areas of the Northeast than in surrounding low elevation areas (Lawson, 1999; Miller et al., 2005). Orographically enhanced precipitation and interception of acidic, pollutant-laden cloud water contribute to increased Hg deposition in high elevation ecosystems. However, the possible toxic effects of such deposition on montane biota are largely unknown. Numerous studies have demonstrated that MeHg is present in both live and recently senesced forest foliage in proportions of approximately 1% of the total Hg content (e.g. Lee et al., 2000; Schwesig and Matzner, 2000; St. Louis et al., 2001; Ericksen et al., 2003; see earlier studies reviewed by Grigal, 2002). It is not clear at this time if this MeHg is methylated within the leaf or if it represents direct deposition of atmospheric gas-phase MeHg. Evergreen species have both higher total Hg concentrations and higher proportions of MeHg than deciduous species. Using their model of Hg accumulation in leaves, Miller et al. (2005) estimated that MeHg made available to terrestrial food webs by forest foliage ranges from 5 to 135 ng m^{-2} y^{-1} in northeastern North American forests. Baseline data on total Hg levels and ratios of MeHg:Hg in wildlife from terrestrial habitats are needed to address this issue.

In this paper, we present data on Hg concentrations in terrestrial passerine birds of montane forests in the northeastern United States and adjacent Canada. We focus on the Bicknell's thrush *(Catharus bicknelli)*, a 25–30 g passerine that breeds from southern Quebec and the Maritime provinces south through New York and New England, where it is

restricted to coniferous forest typically above 900 m (Ouellet, 1993; Atwood et al., 1996; Rimmer et al., 2001). It winters in the Greater Antilles from sea level to > 2000 m, chiefly in mesic and wet broadleaf forest (Rimmer et al., 2001). Due to its small global population, estimated at < 50,000 individuals (Rimmer et al., 2001), its geographically restricted breeding range, and its dwindling winter habitat, Bicknell's Thrush is considered among the Nearctic-Neotropical migrant species of highest conservation priority in the Northeast (Pashley et al., 2000; Rosenberg and Wells, 2000). Its specialization on high elevation fir-dominated forests suggests that it might be an appropriate bioindicator of MeHg bioavailability in these habitats.

Study area and methods

Field sampling

We sampled passerines in montane forests at two spatial scales, intensive (sites with ≥ 10 samples) and extensive (sites with < 10 samples). We sampled 28 sites overall (Fig. 1). Of these, 21 were on breeding areas and included two sites in Maine (ME), five sites in New Brunswick (NB), two sites in New Hampshire (NH), one site in New York (NY), one site in Nova Scotia (NS), three sites in Quebec (PQ), and seven sites in Vermont (VT). We sampled an additional seven sites within the wintering range of Bicknell's thrush. These included two sites in Cuba, four sites in the Dominican Republic (DR), and one site in Haiti.

Intensive sampling was conducted on two US peaks, Mt. Mansfield (hereafter "Mansfield") in north-central Vermont and Stratton Mountain (hereafter "Stratton") in southwestern Vermont. Both are sites of long-term demographic research on montane forest bird populations. We collected Hg samples on Mansfield during June and July of 2000–2003, and on Stratton in late May to July 2001–2003. Vegetation at these and other breeding sites (see below) is dominated by balsam fir *(Abies balsamea)*, with scattered red spruce *(Picea rubra)*, heart-leafed paper birch *(Betula papyrifera* var. *cordifolia)* and mountain ash *(Sorbus americana)*. This vegetation is stunted by chronic exposure to high winds and heavy winter ice loads, and it is extremely dense. Canopy heights on the Mansfield study site average 1–4 m (mean 2.2 m) and stem densities average 8274/ha (Rimmer and McFarland, 2000); these are typical characteristics of montane fir forests in the northeastern US and Canada.

On Stratton, we sampled Hg levels only in Bicknell's thrush, while on Mansfield, we sampled this and three additional breeding passerines: blackpoll warbler (*Dendroica striata*), yellow-rumped warbler (*Dendroica coronota coronota*), and white-throated sparrow (*Zonotrichia albicollis*). Bicknell's thrush and blackpoll warbler are near-obligate breeding residents of montane forests in the Northeast (Hunt and Eliason, 1999; Rimmer et al., 2001), while yellow-rumped warbler and white-throated sparrow breed at high densities in these forests, but are also common in a variety of low elevation forested habitats throughout the Northeast (Falls and Kopachena, 1994; Hunt and Flaspohler, 1998). All four species are primarily insectivorous during the breeding season with Bicknell's thrush and white-throated sparrow foraging mainly on or close to the ground, blackpoll warblers mainly gleaning foliage, and yellow-rumped warblers capturing insect prey both by foliage gleaning and fly-catching. Bicknell's thrush and blackpoll warbler are long-distance migrants to the Greater Antilles and northern South America, respectively, while yellow-rumped warbler and white-throated sparrow are short- to medium-distance migrants, wintering primarily in the southeastern US. These four species thus represent a diverse array of habitat specialization, foraging guilds, and migration strategies.

We conducted additional intensive sampling of Bicknell's thrush during 2003 at three montane sites in Canada: two in southern Quebec and one on Cape Breton Island, NS. Mont Gosford (hereafter "Gosford"), adjacent to the Maine border, is dominated by 35-year old balsam fir stands, many of which were thinned in the 1980s and 1990s for timber production. Mine Madeleine (hereafter "Gaspé") is located on the Gaspé Peninsula, 475 km northeast of Quebec City and adjacent to the Gaspèsie National Conservation Park. This mountainous study area is characterized by steep rocky slopes covered with dense balsam fir forest interspersed with white birch, balsam poplar *(Populus balsamifera)*, and alder *(Alnus* spp.*)* stands. Cape North is located on the extreme

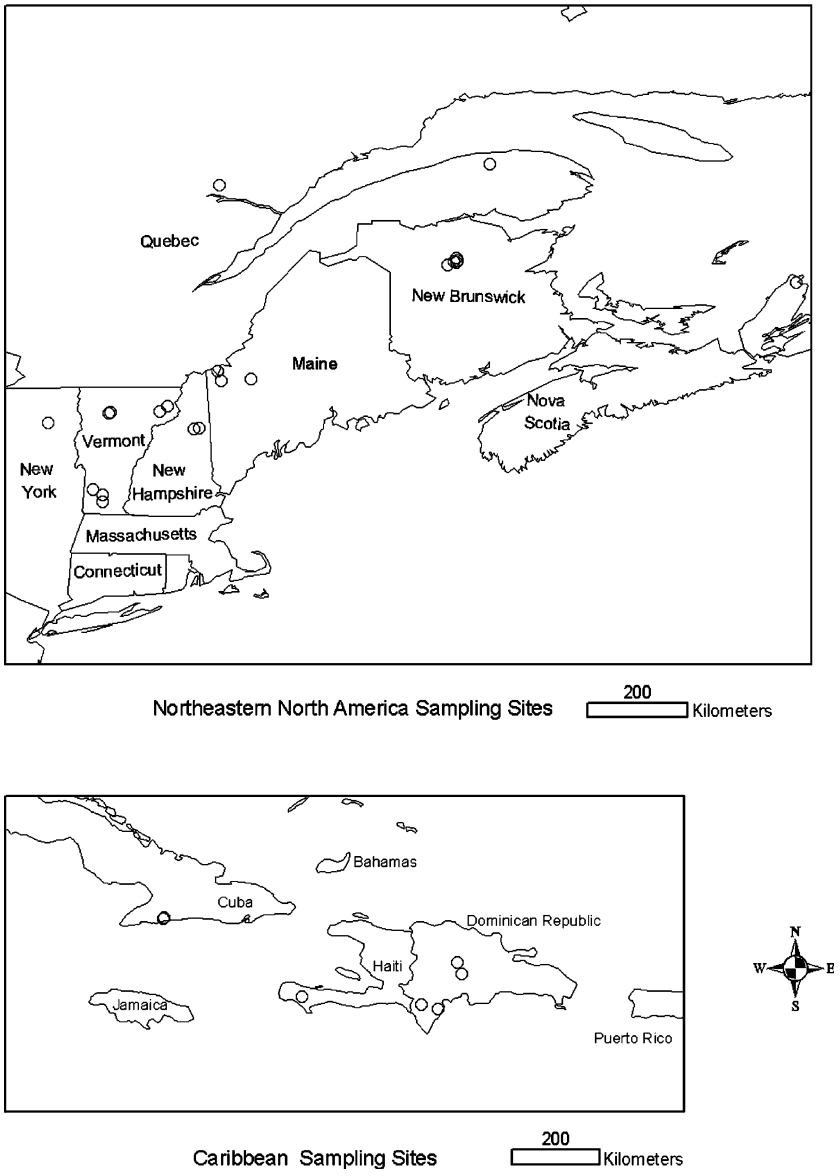

Figure 1. Distribution of sampling locations for the Bicknell's thrush.

northern tip of Cape Breton Island, covering an extensive plateau that projects into the Cabot Strait. The dense habitat at this site consists primarily of balsam fir, paper birch and mountain ash, ranging from 2 to 5 m in height. The forests at Gaspé and Cape North contain many dead standing trees and are stunted due to heavy winter snow cover, ice loading, and chronically harsh winds.

Our extensive sampling included only Bicknell's thrush and was conducted during 2000–2004 at 10 additional peaks in the northeastern US, six additional sites in eastern Canada, and seven sites on the species' Greater Antillean wintering range (Table 1). Preferred winter habitats of this species are mesic to wet broadleaf forests with a dense understory, mainly at high elevations (Rimmer et al., 2001). At all sampling sites in North America and the Caribbean, birds were captured in nylon mist nets (12×2.6 m, 36-mm mesh), either passively or using vocal playbacks as lures. Each

Table 1. Montane forest sites sampled for Bicknell's thrush blood and feather Hg levels, 2000–2004

Site name	State/ Province	Geographic cluster[a]	Lat-long	Elevation (s) Sampled (m)	Feather Hg (ug/g, fw) Mean ± SD (*n*)[b]	Blood Hg (ug/g, ww) Mean ± SD (*n*)
Canada						
Cape North (Cape Breton Island)	NS	8	46°53′ N, 60°31′ W	344–426		0.13 ± 0.03 (12)
Mt. DesBarres	NB	5	47°19′ N, 66°35′ W	668–683		0.13 ± 0.05 (2)
Fisher Ridge	NB	5	47°15′ N, 66°38′ W	654		0.08 (1)
Gaspé Peninsula	PQ	2	49°00′ N, 66°00′ W	1040	0.37 ± 0.2 (18)	0.09 ± 0.02 (21)
Mt. Gosford	PQ	9	45°18′ N, 70°52′ W	1192	0.64 ± 0.23 (24)	0.11 ± 0.04 (26)
Mt. Mitchell	NB	5	47°16′ N, 66°34′ W	688		0.15 (1)
Mt. Nalaisk	NB	5	47°12′ N, 66°45′ W	621		0.12 ± 0.04 (2)
Mt. Valin	PQ	7	48°37′ N, 70°50′ W	860	0.46 ± 0.18 (6)	0.08 ± 0.14 (5)
Unnamed Mtn. near Mt. Mitchell	NB	5	47°14′ N, 66°35′ W	645–664		0.11 ± 0.01 (3)
United States						
Avery Peak	ME	9	45°09′ N, 70°16′ W	900–990	0.29 ± 0.09 (4)	0.27 ± 0.28 (6)
Burke Mtn.	VT	6	44°34′ N, 71°54′ W	930		0.18 ± 0.05 (4)
Carter Notch	NH		44°16′ N, 71°12′ W	1025	0.48 (1)	
East Mtn.	VT	6	44°40′ N, 71°46′ W	1010–1030		0.15 ± 0.08 (5)
Equinox Mtn.	VT	3	43°10′ N, 73°06′ W	1122		0.09 (1)
Mt. Mansfield	VT	4	44°32′ N, 72°49′ W	990–1175	0.70 ± 0.23 (34)	0.10 ± 0.04 (56)
Mt. Snow	VT	3	42°57′ N, 72°55′ W	1025		0.141 (1)
Spruce Peak	VT	4	44°33′ N, 72°47′ W	1000	0.75 ± 0.45 (2)	0.06 ± 0.01 (3)
Stratton Mtn.	VT	3	43°05′ N, 72°55′ W	1065–1200	0.81 ± 0.36 (12)	0.12 ± 0.04 (45)
Mt. Washington	NH	1	44°15′ N, 71°17′ W	1350	0.91 (1)	0.09 (1)
W. Kennebago Mtn.	ME	9	45°07′ N, 70°48′ W	1060		0.38 (1)
Whiteface Mtn.	NY	4	44°22′ N, 73°54′ W	1275–1330	1.21 ± 0.39 (5)	0.08 ± 0.004 (5)
Hispaniola						
Pueblo Viejo	DR	n/a	18°12′ N, 71°32′ W	1400		0.34 ± 0.14 (21)
Cienaga de Manabao	DR	n/a	19°04′ N, 70°47′ W	900		0.03 (1)
Valle Nuevo	DR	n/a	18°50′ N, 70°42′ W	1935		0.10 ± 0.05 (2)
El Cachote	DR	n/a	18°06′ N, 71°11′ W	1190–1240		0.13 ± 0.05 (5)
Plaine Boeuf	Haiti	n/a	18°21′ N, 73°59′ W	1824–1901		0.28 ± 0.57 (8)
Cuba						
Pico Cuba	Cuba	n/a	19°58′ N, 76°51′ W	1426–1800		0.42 ± 0.28 (3)
Pico Suecia	Cuba	n/a	19°59′ N, 76°49′ W	1763		0.21 (1)

[a]Geographic clusters of North American sites reflect spatial proximity (see Fig. 1), which is useful for comparing an abiotic compartment (models of litterfall Hg flux) (Miller et al., 2005) and a biotic compartment (thrush blood Hg) (Fig. 6): 1 = White Mts. (NH); 2 = Gaspé (PQ); 3 = southern VT; 4 = northern Green Mts. (VT) and Adirondack Mt. (NY); 5 = northern NB; 6 = northeastern VT; 7 = northern PQ; 8 = NS; and 9 = northwest ME and southern PQ.

[b]Includes all adult age and sex classes. Individuals sampled in more than one year are counted separately for each year, while only the first sample is included for birds sampled more than twice in a single year.

individual was banded, aged, sexed, measured, and weighed. A 30–50 µl blood sample from the subcutaneous ulnar (brachial) vein was collected in a heparinized capillary tube, refrigerated in a vaccutainer in the field, and frozen within 12–48 h. Samples were frozen until contamination analyses were conducted. We collected both fifth secondary wing feathers from most birds by clipping the calamus close to its insertion point; these were stored in glassine envelopes prior to Hg analyses.

Laboratory analyses

Analysis of tissue samples from 2000 was conducted at the Environmental Chemistry Laboratory of the Sawyer Research Center, Orono, Maine, while all 2001–2003 samples from the US, Dominican Republic, and Haiti were analyzed at Texas A & M Trace Element Research Laboratory (TERL), College Station, Texas. Analysis of Canadian and Cuban samples was performed at

Table 2. Mercury concentrations and blood MeHg:Hg ratios in four species of montane forest breeding birds (adults only) sampled in 2000 and 2001 on Mt. Mansfield, VT. Data presented as arithmetic mean ± SD in ug/g (ww)

Species[a]	Total blood Hg (*n*)	Blood MeHg:Hg ratio (*n*)	Total feather Hg (*n*)
BITH	0.094 ± 0.47 (43)	0.983 ± 0.254 (39)	0.699 ± 0.25 (38)
BLPW	0.055 ± 0.017 (10)	0.895 ± 0.21 (12)	0.397 ± 0.237 (5)
YRWA	0.091 ± 0.055 (13)	0.959 ± 0.189 (15)	1.099 ± 1.119 (4)
WTSP	0.062 ± 0.026 (12)	1.091 ± 0.372 (14)	0.502 (1)

[a]BITH = Bicknell's thrush; BLPW = blackpoll warbler; YRWA = yellow-rumped warbler; WTSP = white-throated sparrow.

the National Wildlife Research Centre of Environment Canada, Ottawa, Ontario.

Blood samples were expressed from sealed capillary tubes and diluted with 2 ml of double deionized water, then homogenized and aliquoted into total Hg and MeHg fractions. Samples were prepared for total Hg according to TERL SOP-ST16, with volumes reduced to accommodate the small volumes available. This method incorporated digestion with nitric acid, sulfuric acid, potassium permanganate, and potassium persulfate. Digest solutions were reduced with hydroxylamine hydrochloride to eliminate excess MnO_2. Samples were prepared for MeHg analysis according to TERL SOP-9712, again with volumes reduced to accommodate sample size limitations. In this method, MeHg was extracted from an acid bromide sample into an organic solvent and prepared for analysis by a permanganate digestion. Feathers were analyzed only for total Hg; using the same digestion process and reagents as were used for blood samples.

Prior to 2003, total Hg and MeHg were both analyzed by element-specific cold vapor atomic absorption using an LDC Mercury Monitor equipped with a 30 cm path cell (SOP-9024). Samples were quantified based on peak height compared with external calibration standards. Quality assurance samples accompanying sample batches included method blanks, laboratory control samples (LCS), certified reference materials (NRCC DOLT-2), matrix spike samples, and duplicate samples. All analytes are reported in units of parts per million (ppm or ug/g), on a wet weight (ww) basis for blood and a fresh weight (fw) basis for feathers. Detection limits were dependent upon sample weights and dilution factors but averaged approximately 0.009 ug/g for both total Hg and MeHg and 0.04 ug/g for total Hg in feathers.

In 2003 and 2004, blood and feather samples were analyzed for total Hg according to TERL SOP-0301. This method utilized a Milestone DMA 80 to combust blood and feather samples in nickel boats in an oxygen-rich atmosphere. Combustion products were passed through a heated catalyst to complete oxidation and then through a gold column which trapped Hg. Upon completion of combustion, the gold trap was heated and the Hg released for analysis by atomic absorption. Some blood samples were analyzed for moisture content prior to Hg analysis. Moisture loss was determined via freeze drying blood samples in aluminum cups, and the cups were then placed in the DMA 80s nickel boats in order to determine Hg content.

Statistical analyses

We examined all data for normality. Non-normal data were log-transformed prior to analyses. Because samples from Canada were collected only in 2003, we examined blood and feather Hg data from Mansfield and Stratton for effects of year; there were no year effects or interactions of year with other variables (ANOVA for year: $F_{2,67} = 1.86$, $p = 0.164$). We thus combined data across years for all North American sites. Statistical analyses were performed on SYSTAT 10.2 (SYSTAT, 2002). Data are presented as arithmetic means and standard deviations (SD).

For population-level analyses of blood Hg levels, we used only the first sample obtained from each individual in each year, although we treated samples from individual thrushes obtained in multiple years independently. This avoided potential problems of within-year autocorrelation, as blood samples reflect short-term dietary Hg uptake (Evers et al., 2005) and thus cannot be considered independent within the same season.

Further, because individuals sampled in both June and July within a single year invariably showed significantly higher blood Hg concentrations in June (see below), we excluded all July samples in our population-level analyses. For feather Hg analyses from individuals that provided samples in multiple years, we used only those samples obtained in the first year. Feathers reflect chronic Hg body burdens (Burger, 1993), such that between-year samples can not be treated independently. We examined differences in blood and feather Hg samples from the five intensive breeding sites using ANOVA with sex, age, sample site, and their interactions as independent variables.

To correlate Bicknell's thrush Hg levels at Mansfield and Stratton with those of regional atmospherically-deposited Hg, we calculated average values for the aggregate presumed breeding home ranges of sampled birds from modeled data (Miller et al., 2005). We selected deposition data for two of eight available habitat classes within this sampling area on each mountain, balsam fir-red spruce-white birch and balsam fir-red spruce, as Bicknell's thrush is most closely associated with these two montane forest types (Rimmer et al., 2001). We considered total deposition rates as well as three different Hg deposition modes (wet, reactive gaseous, and litterfall) that might reflect different degrees of bioavailability of atmospherically-borne Hg to Bicknell's thrush (Miller et al., 2005). Mercury deposited with litterfall is thought to represent primarily elemental mercury vapor that has been assimilated by leaves. Reactive gaseous mercury is $HgCl_2$ that deposits to the surface of leaves.

Results

MeHg: total Hg ratio

The mean ratio of total blood Hg to blood MeHg was close to 1:1 in each of the four species sampled on Mansfield (Table 2). This ratio did not significantly differ among the four species ($\chi^2 = 3.344$, $df = 3$, $p = 0.342$).

Species patterns of Hg levels

Mean blood Hg concentrations were significantly different among the four species sampled on Mansfield (ANOVA: $F_{3,56} = 4.35$, $p = 0.008$; Table 2). Overall mean blood Hg concentrations were highest in Bicknell's thrush, and these were significantly higher than levels of blackpoll warbler and white-throated sparrow (*post-hoc* pairwise comparisons with Bonferroni adjustment: $p = 0.028$ for blackpoll warbler, $p = 0.046$ for white-throated sparrow). Excluding one yellow-rumped warbler with aberrantly high feather Hg of 2.62 ug/g, mean feather Hg concentrations were highest in Bicknell's thrush, but small samples sizes for the three other species limit comparisons (Table 2). Excluding this one yellow-rumped warbler outlier, Bicknell's thrush demonstrated the greatest overall variability in both blood and feather Hg concentrations.

Geographic patterns in Hg levels of Bicknell's thrush

Among the five intensively-sampled sites, blood Hg concentrations differed significantly (ANOVA: $F_{4,92} = 3.66$, $p = 0.02$), being highest at the two most geographically disparate sites, Cape North and Stratton, and lowest at Gaspé (Table 1). There was no significant interaction of either age or sex and site. Although small sample sizes precluded statistical testing of geographic trends among all 21 breeding sites, within New England, blood Hg levels were markedly higher in northeastern Vermont (Burke and East mountains) and Maine than elsewhere in Vermont or in New York (Table 1). Canada lacked a clear pattern, although Quebec samples tended to exhibit lower blood Hg concentrations than in New Brunswick and Nova Scotia.

Our initial comparison of feather Hg concentrations among the four sites that yielded feather samples showed significant between-site differences ($F_{3,76} = 8.37$, $p < 0.001$), but also a significant interaction between age and sampling site ($F_{3,76} = 11.86$, $p < 0.001$). This interaction likely resulted from our unequal samples of age-sex cohorts among sites, with the two Quebec sites strongly skewed by males >2 years old. We therefore pooled feather Hg data from all sites for demographic analyses (below), but were unable to test for differences among sites. Qualitatively, feather Hg concentrations at the four sites showed a similar trend to that of blood, being highest at Stratton and lowest at Gaspé (Table 1). Unlike

blood, however, feather Hg data from all sampling sites increased along an East–West gradient, with levels highest in New York and lowest in Maine and Canada (Table 1).

Blood Hg concentrations of Bicknell's Thrush from breeding areas in North America (Cape North, Gaspé, Gosford, Mansfield, and Stratton) and wintering areas in the Greater Antilles (Dominican Republic and Haiti) were compared using an ANOVA with sample site nested within season. Significant effects were found between season ($F_{1,182} = 149.55$, $p < 0.00001$) and site(season) ($F_{5,182} = 4.96$, $p = 0.00028$). Blood Hg concentrations in wintering birds were generally 2–3 times higher than in birds sampled on their breeding sites. Although small sample sizes limit statistical comparisons among wintering sites, birds from more western locations (Cuba, Haiti, and western Sierra de Bahoruco [Pueblo Viejo]) tended to have higher blood Hg concentrations than birds further east in the Dominican Republic (eastern Sierra de Bahoruco [El Cachote] and Cordillera Central [Valle Nuevo and Cienaga de Manabao]; Table 1).

Bicknell's thrush Hg levels and regional deposition patterns

The significantly higher Hg blood concentrations of thrushes on Stratton versus Mansfield paralleled modeled deposition patterns at the two sites. In the two forest types used by Bicknell's thrush at each site, deposition was consistently higher at Stratton for the three deposition modes we examined (Table 3). Both absolute and relative differences were higher for total Hg deposition than for the other three Hg deposition modes.

Bicknell's thrush demographic Hg profile

Among the five intensively-sampled North American sites, male Bicknell's thrushes had a significantly higher mean blood Hg concentration (0.11 ug/g ± 0.05; SD range 0.04–0.29) than females (0.09 ug/g ± 0.04; SD range 0.02–0.23) (ANOVA: $F_{1,92} = 4.9$, $p = 0.04$). Mean feather Hg concentrations did not differ significantly between males and females (ANOVA: $F_{1,84} = 0$, $p = 0.96$). The relationship between blood and feather Hg concentrations for Bicknell's thrushes from which we obtained both samples in a given year was only weakly positive and not significant (Fig. 2).

Mean feather Hg concentrations of ≥ 2-year old (after second-year [ASY]) Bicknell's thrushes were significantly higher overall than those of yearling (second-year [SY]) birds (ANOVA: $F_{1,84} = 16.63$, $p < 0.0001$), although this was not the case at Gaspé (Table 4). However, among ASY individuals of precisely known age at Mansfield and Stratton, based on multi-year banding histories, no relationship existed between feather Hg concentrations and age. Similarly, no consistent trend was evident among the 20 individuals from which we obtained feathers in multiple years (Fig. 3). Of these birds, from which we obtained samples 1–3 years apart, nine had increased feather Hg concentrations between first and last captures, while the concentrations of 11 individuals decreased. The overall population mean rate of Hg accumulation was −0.01 ug/g ± 0.51 SD (range −0.81 to 1.55). Males ($n = 13$) accumulated feather Hg at an overall mean rate of −0.13 ug/g ± 0.37 (range −0.81 to 0.44), while the mean overall accumulation rate of females ($n = 7$)

Table 3. Modeled atmospheric Hg deposition for Stratton and Mansfield. Data presented as $\mu g/m^2/yr$ (extracted from maps described in Miller et al., 2005)

Deposition mode	Fir-spruce-birch zone		Fir-spruce zone	
	Mansfield	Stratton	Mansfield	Stratton
Reactive gaseous Hg	10.8	12.9	10.8	12.6
Litterfall Hg	13.8	13.9	15.4	15.6
Wet (rain + cloud)	9.3	12.9	13.5	20.7
Total Hg[a]	35.2	42.4	41.2	51.5

[a]Includes dry particulate deposition.

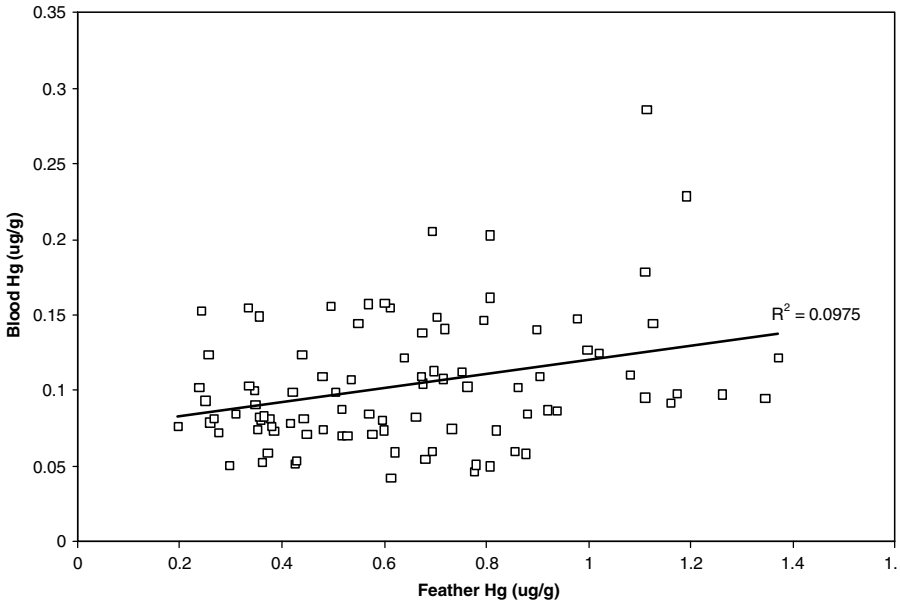

Figure 2. Relationship between blood (ug/g, ww) and feather Hg (ug/g, fw) concentrations in Bicknell's thrushes on Mt. Mansfield and Stratton Mtn., Vermont.

Table 4. Mean feather Hg levels (ug/g, fw) ± SD (*n*) by age class in Bicknell's thrush

Age class[a]	Stratton	Mansfield	Gosford	Gaspé
SY	0.322 ± 0.041 (3)	0.485 ± 0.12 (11)	0.49 ± 0.129 (6)	0.463 ± 0.297 (7)
ASY	0.974 ± 0.231 (9)	0.796 ± 0.193 (23)	0.687 ± 0.236 (18)	0.309 ± 0.079 (11)

[a]SY = second-year (yearling); ASY = after second-year (≥ 2 years old).

was 0.22 ug/g ± 0.68 SD (range −0.56 to 1.55). Of thrushes examined in consecutive years, representing 26 accumulation-years, the mean annual accumulation rate was −0.03 ug/g ± 0.48 SD (range = −0.94 to 0.87). Of 13 males representing 23 accumulation-years, 12 of those years showed an increase, and the mean annual accumulation rate in males was −0.04 ug/g ± 0.51 SD. Of five recaptured females representing six accumulation-years, Hg feather levels increased in four years, and the mean annual accumulation rate for females was 0.02 ± 0.36 ug/g.

Mean blood Hg concentrations of individual Bicknell's thrushes examined on Mansfield and Stratton in multiple years did not show a clear pattern (Fig. 4). We used only those birds sampled during June in each year to limit within-season variability (see below). Of the 16 individuals that provided data in at least two years, representing 20 between-year changes, blood Hg concentrations increased between 11 successive-year captures and declined between nine. Of four birds examined in three consecutive years, none showed a consistent trend over all three years. Mean blood Hg concentrations of males ($n = 10$) increased 0.004 ug/g + 0.06 SD between successive years, while those of females ($n = 3$) declined 0.05 ug/g + 0.09 SD.

To examine within-season variability in Hg blood concentrations, we sampled 13 Bicknell's thrushes at three- to four-week intervals during a single breeding season. Every bird showed a decrease in Hg blood concentration between its first and subsequent capture. The mean Hg blood concentration of first captures was 0.14 ug/g ± 0.05 SD, while later-captured birds had mean levels of 0.09 ug/g ± 0.03 SD. This difference was

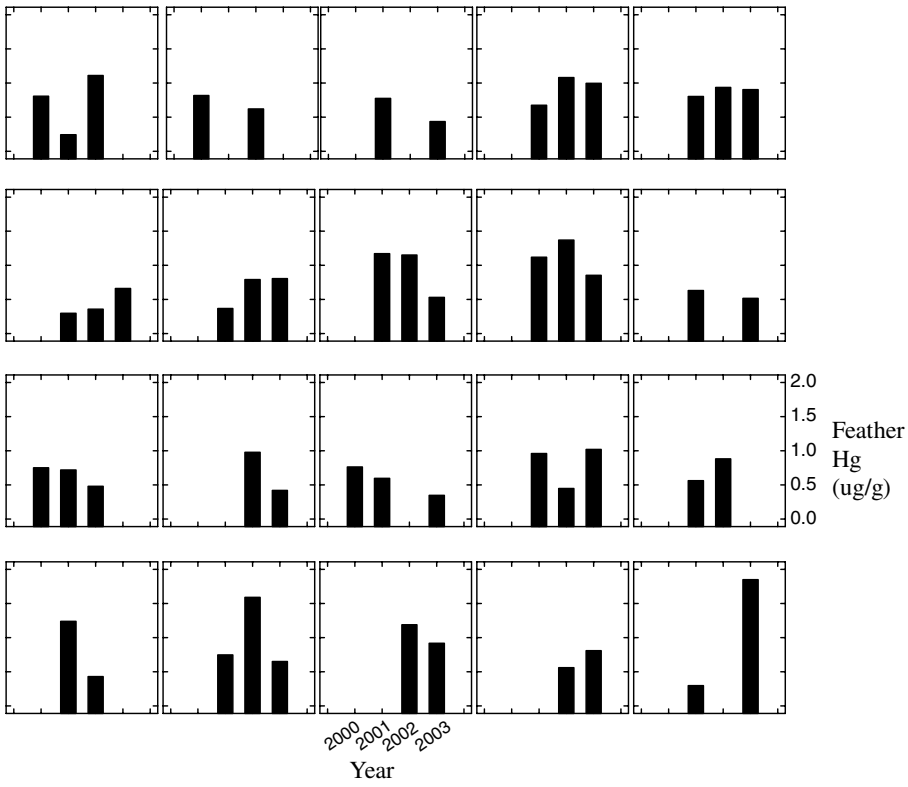

Figure 3. Feather Hg concentrations (ug/g, fw) of Bicknell's thrushes examined in multiple years on Mt. Mansfield and Stratton Mtn., Vermont.

significant (paired t-test: $t = 4.41$, $df = 12$, $p < 0.001$). The mean change in Hg blood concentrations between first and subsequent samples was −0.05 ug/g ± 0.04 SD. A less pronounced seasonal decline in Hg blood concentrations of Bicknell's thrush on Mansfield and Stratton is reflected by population-level data, which show weakly negative relationships between blood Hg concentrations and date on both mountains (Fig. 5).

Discussion

The data presented here for Bicknell's thrush are the most comprehensive and detailed yet available for a strictly terrestrial, insectivorous passerine. The Hg concentrations in this and the other three montane forest species are relatively low compared to those documented in other free-ranging North American birds. However, nearly all species examined to date are associated with aquatic-based systems and are at the top of piscivorous or aquatic insectivorous trophic webs (Thompson, 1996; Evers et al., 2005). Bicknell's thrushes inhabit conifer-dominated forests and are not closely tied to aquatic habitats at any phase of their annual cycle. Methylation dynamics and MeHg availability in terrestrial systems are not well understood, but our results indicate that a mechanism for biotic uptake of MeHg exists in montane forests.

Total Hg and MeHg relationships in blood

All four species sampled on Mansfield exhibited MeHg:Hg ratios of nearly 1:1 (Table 2). Such a ratio in blood is well-established in piscivorous birds (Scheuhammer, 1991; Thompson, 1996; Evers et al., 1998; Fournier et al., 2002), however, it is less well known for insectivorous passerines. The high proportion (90–100%) of MeHg in blood from our suite of montane insectivorous passerines

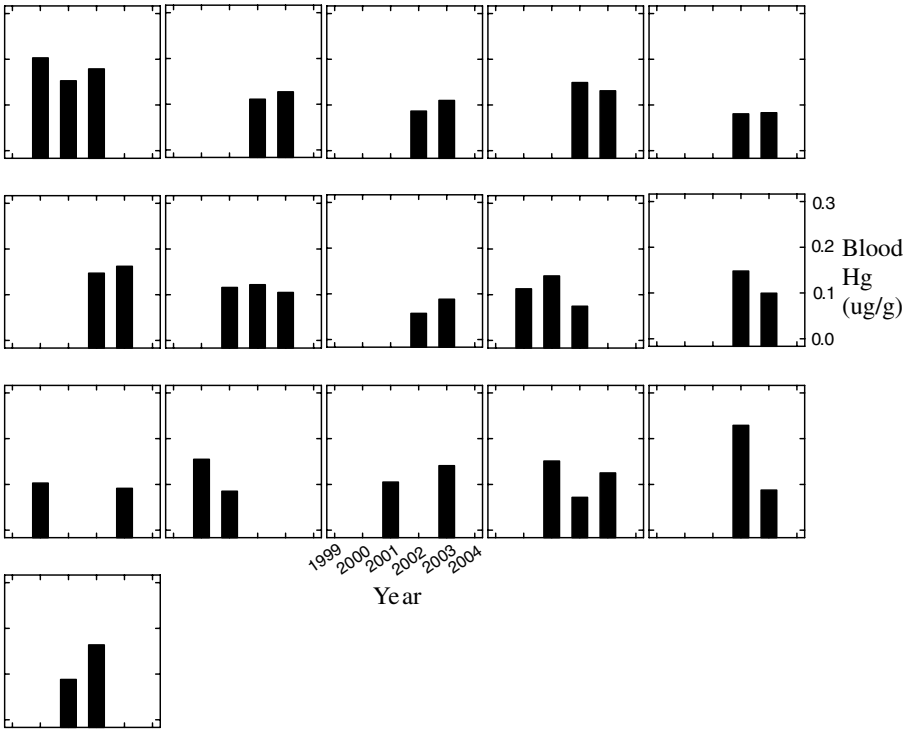

Figure 4. Blood Hg concentrations (ug/g, ww) of Bicknell's thrushes examined during June in multiple years on Mt. Mansfield and Stratton Mtn., Vermont.

was expected, even though there are species-specific differences in how MeHg is absorbed into the blood (Monteiro and Furness, 2001). Unlike fish, which form the dietary basis for piscivorous birds and generally have whole body content >85% MeHg (Wiener and Spry, 1996), insects generally have far less MeHg content (average ~65%; Pennuto et al., 2005), but exhibit a broad range with lowest levels in detritivores (20–25%) and highest levels in predatory insects like dragonflies (95%) (Tremblay et al., 1996; Tremblay and Lucotte, 1997). However, the transfer of more limited MeHg concentrations in insect prey to insectivorous birds does not appear to be significantly different than in piscivorous birds. Both Gerrard and St. Louis (2001) and Wolfe and Norman (1998) found high MeHg:Hg ratios in the tissues of various insectivorous passerines. Our analysis indicates that even insectivorous birds dependent on terrestrial food-webs are susceptible to MeHg availability and bioaccumulation.

Comparisons of Hg exposure during the breeding season

Blood Hg concentrations of four montane breeding birds at Mansfield fell into two general groups: higher exposure (pooled mean, 0.09 ug/g) in Bicknell's thrush and yellow-rumped warbler and lower exposure in blackpoll warbler and white-throated sparrow (pooled mean, 0.06 ug/g). Compared to other sampling sites in northeastern North America, Bicknell's thrush blood Hg concentrations were 34% lower at Mansfield than elsewhere (unweighted, arithmetic mean = 0.14 ± 0.08 SD, n = 18 sampling locations). Because there are few studies documenting insectivorous passerine Hg exposure (Bishop et al., 1995; Wolfe and Norman, 1998; Gerrard and St. Louis, 2001; Reynolds et al., 2001; Adair et al., 2003) and because none of the existing studies sampled blood for Hg analysis, few comparisons are available. Two exceptions are from northeastern North America. Shriver et al. (2002) sampled and

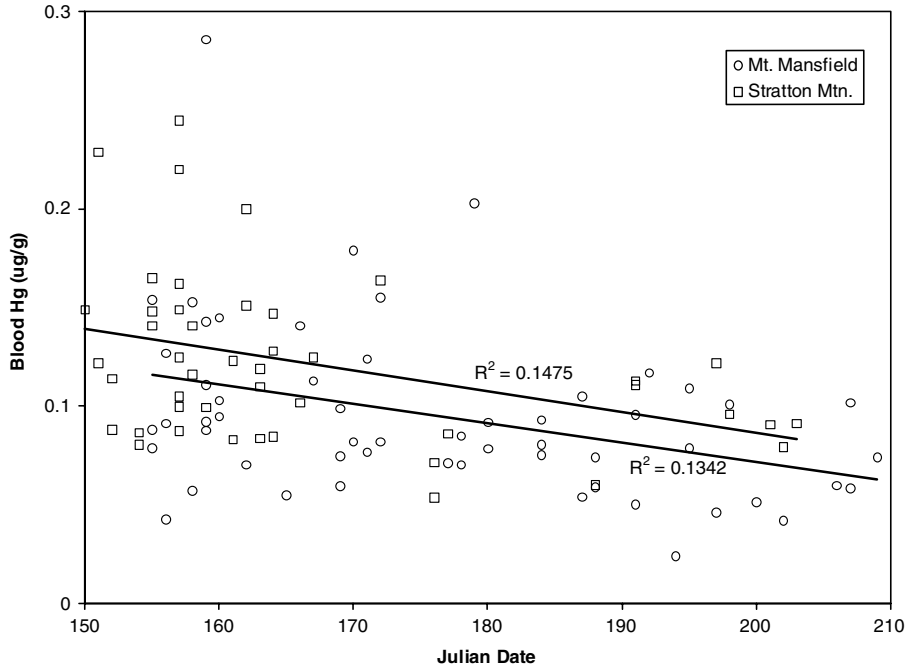

Figure. 5. Relationship of blood Hg concentrations (ug/g, ww) in Bicknell's thrush by Julian date (150 = 31 May, 180 = 30 June, 210 = 30 July) on Mt. Mansfield and Stratton Mtn., Vermont. Mt. Mansfield = lowerline, Stratton Mtn. = upperline.

analyzed the blood Hg concentrations of saltmarsh and Nelson's sharp-tailed sparrows (*Ammodramus caudacutus* and *A. nelsoni*, respectively) at five Maine estuaries and found relatively high Hg levels. Mean concentrations for the saltmarsh sharp-tailed sparrow (0.69 ug/g) were significantly higher than for the closely related Nelson's sharp-tailed sparrow (0.41 ug/g), and both were higher than the mean concentrations found in Bicknell's thrush from 21 distinct breeding sites (Table 1). Blood Hg concentrations in 10 insectivorous passerines associated with riverine habitats on the Sudbury River, Massachusetts varied from 0.04 ug/g in the yellow warbler (*Dendroica petechia*) to 0.92 ug/g in the northern waterthrush (*Seiurus noveboracensis*) (Evers et al., 2005). In that study, adult mean Hg blood concentrations were lower than those of Bicknell's thrush for three of the 10 species (barn swallow [*Hirundo rustica*], gray catbird [*Dumetella carolinensis*], and yellow warbler).

The causes of intra-site differences in the blood Hg concentrations of insectivorous passerines likely parallel patterns found in piscivorous birds. Evers et al. (2005) identified differences among species within the same habitat as primarily related to trophic level. Biomagnification of MeHg in aquatic systems is largely dictated by the diversity and density of the planktivorous community (Chen et al., 2005). An analogous community of terrestrially-based microorganisms is likely present in montane habitats, as passerine blood Hg concentrations average only one order of magnitude less than concentrations in small piscivores such as the belted kingfisher (*Ceryle alycon*) (Evers et al., 2005). The trophic level of MeHg in the diet of a Bicknell's thrush is likely higher than in a blackpoll warbler because thrushes are larger-bodied and feed on larger arthropods (Hunt and Eliason, 1999; Rimmer et al., 2001) that tend to be more predaceous and have higher levels of MeHg than smaller arthropods (Tremblay and Lucotte, 1997). While Bicknell's thrush and blackpoll warbler follow the regression model by Evers et al. (2005) that predicts $>70\%$ of the variation in passerine blood Hg levels as a function of body weight, the yellow-rumped warbler and white-throated sparrow deviate from this model. The white-throated sparrow has a lower component of insects in its breeding season diet (Falls and Kopachena, 1994), and this may contribute to

lower blood and feather Hg concentrations than those in thrushes and even smaller species such as warblers. The relatively high and variable mean Hg concentrations in yellow-rumped warbler blood may be an artifact of small sample size, a more varied diet, and preference toward black flies (*Simulus* spp.), which have an aquatic larval phase that is likely more exposed to MeHg availability than terrestrial insects.

Geographic patterns in Bicknell's thrush

The lack of a clear geographic pattern in Hg levels of Bicknell's thrush by individual mountain is not surprising, given the heterogeneity of Hg deposition across northeastern North America (Miller et al., 2005; VanArsdale et al., 2005). However, the overall trend of higher Hg blood and feather concentrations in thrushes in the southern part of the species' breeding range and lower concentrations in northern areas implies a linkage between atmospherically-deposited Hg and MeHg availability. This is reinforced by the strong correlation of deposition and thrush blood data on Stratton and Mansfield. Higher modeled deposition data from Stratton reflect a plume of atmospheric-borne Hg from the southwestern part of the study area (Miller et al., 2005), which decreases northward and eastward. The significantly higher blood and feather Hg concentrations of Bicknell's thrushes on Stratton versus Mansfield further suggest linkages with regional MeHg availability.

The markedly higher mean blood Hg concentrations of thrushes in the Greater Antilles versus the northeastern North America sampling sites is counter to expected lower levels. Sampling of birds in marine (Burger and Gochfeld, 1991) and estuarine (Burger et al., 1992) environments in Puerto Rico in the late 1980s found relatively low body burdens of Hg. Significant local or regional industrial sources of Hg are unknown for the Greater Antilles. Because the global pool of Hg is increasing (UNEP, 2003), isolated islands and other areas disconnected from local and regional emission sources may be increasingly important for long-term monitoring (Mason et al., 2005). Until biogeochemical processes can be quantified in the breeding and wintering habitats of Bicknell's thrush, determining differences in MeHg availability between the two areas will remain problematic.

Interpreting blood-feather Hg relationships

We used two matrices, blood and feathers, to better understand spatiotemporal pathways of Hg exposure and potential effects on Bicknell's thrush. The lack of a correlation between blood and feather Hg concentrations and the disordered patterns in repeated measurements of feather Hg among individual birds demonstrate the dynamic complexity of MeHg availability for the Bicknell's thrush. Although adult Bicknell's thrushes undergo a complete remigial molt in August in their breeding areas (Rimmer et al., 2001), blood Hg concentrations measured in June and July are not predictive of August feather Hg levels (albeit, representing MeHg depuration 12 months prior). Confounding factors contributing to a decoupling of the two tissues are (1) within-summer changes in MeHg availability, (2) annual differences in Hg deposition and potentially in MeHg availability, (3) dietary changes within-summer and among years, (4) depuration of MeHg in eggs, (5) gender and (6) age differences in MeHg uptake, and (7) MeHg bioaccumulation.

Atmospheric deposition of Hg is not consistent within or between years (VanArsdale et al., 2005). The relationship of available inorganic Hg and associated methylation is also inconsistent and often non-linear, and is therefore difficult to predict even in well-studied freshwater aquatic systems (Wiener et al., 2003). Prey availability may be the most important driving factor in MeHg availability in montane systems. Precipitation events and sudden temperature drops can rapidly alter the composition of the montane forest insect community (Rimmer and McFarland, unpubl. data), which may subsequently affect trophic level representation of MeHg. Because predaceous insects generally have significantly higher MeHg levels than non-predaceous insects (Tremblay et al., 1996), rapid change in trophic structure and therefore MeHg availability is likely. Variations in the relative abundance of folivores and detritivores further complicate patterns of MeHg availability.

Eggs provide a short-term pathway of MeHg sequestration (Thompson, 1996). Depending on the success of initial nesting attempts, female Bicknell's thrushes may produce up to three clutches in a single breeding season (Rimmer et al., 2001). Because a rapid equilibrium between dietary

uptake of MeHg and blood MeHg is typical (Kambamandi-Dimou et al., 1991) and because egg MeHg primarily reflects blood MeHg levels (Evers et al., 2003), the influence of egg MeHg depuration on blood-feather decoupling of Hg levels is likely not a driving factor. However, loss of Hg through eggs may at least partly contribute to gender differences in Hg levels of Bicknell's Thrush, particularly because the species exhibits no significant sexual dimorphism in body mass or bill size (important metrics for dimorphism) (Rimmer et al., 2001) that might account for niche partitioning of prey.

Age responses to MeHg availability are well quantified with this study. One-year-old (SY) thrushes had significantly lower feather Hg concentrations than adults (ASY) at both intensively sampled Vermont sites and one of two Quebec sites (Table 1). Other studies have documented similarly significant differences in Hg body burdens between unfledged young and adult birds (Thompson, 1996), including passerines (Evers et al., 2005). However, differences in Hg levels among age classes of adult passerines have not previously been described. In our study, some known-age adult thrushes exhibited a significant increase in feather Hg concentrations with increasing age, while other individuals did not. Feather Hg concentrations were highly variable among individual birds examined in multiple years, likely reflecting the variable dynamics of MeHg availability in wintering and breeding areas. Because feathers provide one of the most effective pathways of MeHg depuration (70–93% of the body burden; Burger, 1993), it appears that the elimination of Hg through feathers is greater in some years than others.

Linking blood Hg levels with litterfall Hg deposition

Greater exposure to MeHg availability in wintering versus breeding areas likely contributes to body burdens of Hg in spring arrivals that exceed those of late-summer residents. The parallel decline of blood Hg levels in Bicknell's thrush during the breeding season on both Mansfield and Stratton suggests that much of the Hg blood and feather concentrations represent dietary uptake in wintering areas. The half-life of MeHg in the blood of non-molting adults is 40–60 days in Cory's shearwater (*Calonectris diomedea*) (Monteiro and Furness, 2001) and 84 days in mallards (*Anas platyrhynchos*) (Heinz and Hoffman, 2004). The retention of MeHg in the blood of Bicknell's thrush during its two to four week spring migration is therefore a potentially important contributor to blood Hg concentrations documented in the earlier part of the breeding season. Such a geographically disjunct influence on blood Hg levels of spring arrivals assumes that MeHg availability is static over the breeding season. In freshwater aquatic systems, MeHg availability increases throughout the summer as the sulphur-reducing bacteria responsible for methylation show a positive correlation with water temperature; however, the mechanisms that drive methylation in montane environments without standing water are poorly known (Wiener et al., 2003).

While these mechanisms remain uncertain (atmospheric deposition or bio-methylation), it appears that autotrophs make significant amounts of MeHg directly available to the terrestrial food web. Assuming a constant ratio of MeHg:Hg in leaves, the model for total Hg accumulation presented by Miller et al. (2005) suggests that MeHg made available via the leaf pathway would be lowest in spring and would increase five-fold (day 20 through day 140) during the growing season as leaves assimilate mercury from the atmosphere. Average MeHg concentrations might range from 0.02 (0.11) to 0.12 (0.54) ng/g in first-year evergreen leaves. Food webs deriving energy from the detrital leaf layer representing the previous year's leaf crop can be expected to be exposed to MeHg concentrations >0.5 ng/g. In Germany, Schwesig and Matzner (2000) measured MeHg concentrations in the Oi layer of soils of approximately 0.8–1.0 ng/g, in forests where fresh leaf litter concentrations ranged from 0.07 to 1.49 ng/g.

The availability of MeHg based on this process may partly explain the link with metrics related to atmospheric deposition. Miller et al. (2005) established deposition and concentration patterns of leaf, litterfall, precipitation (wet and dry), and particulate Hg. Regional comparisons of these patterns and nine geographic clusters of mean blood Hg concentrations of Bicknell's

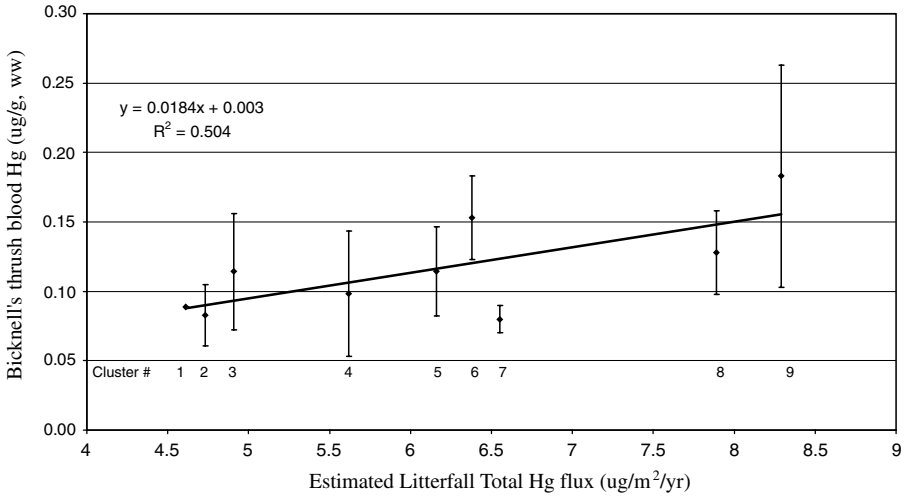

Figure 6. Relationship between modeled litterfall Hg flux (ug/m^2/yr) and the geometric mean +/− SE of Bicknell's thrush blood Hg concentrations (ug/g, ww). Clusters represent geographical grouping of thrush blood Hg samples from 21 different mountains.

thrush (see Table 1 for how sampling sites were grouped) demonstrated a significant correlation with litterfall Hg deposition ($r^2 = 0.49$, $p < 0.05$) (Fig. 6).

Conservation of Bicknell's thrush and the montane bird community

Biogeochemical factors that dictate MeHg availability in terrestrial montane habitats of northeastern North American and in the Greater Antilles are poorly known and warrant further investigation. The issue is of particular concern because the Bicknell's thrush is the most highly ranked Nearctic-Neotropical migrant passerine for conservation priority in the northeastern US (Pashley et al., 2000), where it is restricted to high elevation forests for breeding. Unlike migratory piscivorous birds, such as the common loon (*Gavia immer*), that breed on freshwater lakes and winter in marine systems, where MeHg availability is three times lower (Evers et al., 1998), the Bicknell's thrush is exposed to significantly higher Hg levels on its wintering grounds. Our finding of elevated MeHg availability in the Greater Antilles is unexpected based on previous avian Hg studies in subtropical areas (Burger and Gochfeld, 1991; Burger et al., 1992), and it heightens conservation concerns for the Bicknell's Thrush, which is also exposed to elevated Hg levels in its montane forest breeding areas. Such chronic exposure to Hg throughout its annual cycle, in combination with potential synergistic impacts from calcium deficiencies in areas of northeastern North America (Hames et al., 2002), might exert population level impacts in Bicknell's Thrush. Effects-based research to elucidate the relationship of MeHg burdens to demographics and reproductive success in this and other insectivorous migratory passerines is needed.

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Estimating the Natural Background Atmospheric Deposition Rate of Mercury Utilizing Ombrotrophic Bogs in Southern Sweden

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A critical gap in the understanding of the global cycling of mercury is the limited data describing the natural background atmospheric deposition rate of mercury before the advent of pollution. Existing estimates of the natural deposition rate are typically about 2−5 μg of Hg m^{-2} $year^{-1}$ (see, for example, Swain et al. *Science* **1992**, *257*, 784−787), based on studies that generally rely on short, ^{210}Pb-dated lake sediment and peat cores that span the past 150 years. Analyses of mercury in long peat cores in southcentral Sweden indicate that natural mercury deposition rates in the period 4000−500 BP were lower, about 0.5−1 μg of Hg m^{-2} $year^{-1}$. This suggests that recent mercury accumulation rates in the peat (15−25 μg of Hg m^{-2} $year^{-1}$) and measured atmospheric deposition rates of mercury in Sweden over the past 3 decades (5−30 μg of Hg m^{-2} $year^{-1}$) (Munthe et al. *Water, Air, Soil Pollut.: Focus* **2001**, *1*, 299−310) are at least an order of magnitude greater than the prepollution deposition rate, rather than representing only a 3−5-fold increase, as has generally been estimated.

Introduction

In Sweden, as elsewhere, direct measurements of atmospheric deposition rates of mercury (Hg) are limited in terms of both time and space. Time-series data on Hg deposition rates usually span less than the past 30 years for direct instrumental measurements of deposition (*6*, *7*), as well as for indirect measurements such as biomonitoring programs based on forest mosses (*8*). The limited data on historical trends of atmospheric Hg deposition, and especially on the natural conditions preceding the advent of pollution, represent an important gap in the understanding of large-scale Hg pollution and global Hg cycling in general. This is a critical gap that can only be filled through paleo-studies that examine natural archives such as peat bogs, lake sediments, or glacial ice.

Mercury is introduced into the environment primarily via the atmosphere (*9*); it is emitted naturally via outgassing of the earth's crust (volcanic and geothermal activity) and evasion from the terrestrial environment (soils and vegetation) and water bodies. Estimates for the natural Hg emission rates vary considerably. Superimposed over these natural sources is a substantial anthropogenic component derived from fossil-fuel combustion, waste incineration, metal production and diffuse sources. In southern Sweden, Hg deposition is strongly influenced by the long-range transport of pollutants from emission sources in mainland Europe, which was evidenced by the 50% decline in Hg deposition from the late 1980s to the early 1990s, following the reunification of Germany and economic downturn in Eastern Europe (*6*)

Because of the continued concerns over Hg contamination, there is great interest in determining the relative contribution of natural versus anthropogenic sources. Because ombrotrophic peat bogs receive their pollutants only from the atmosphere, they offer the potential of reconstructing atmospheric deposition rates for nonmobile elements. Thus far, the consensus is that Hg and also Pb are immobile in peat (*4*, *10*), because of the strong affinity of these metals for organic matter; consequently, ombrotrophic peat is considered to contain a reliable archive for the atmospheric deposition of these metals (*11*, *12*). Further support for the viability of peat deposits as an archive is provided indirectly by the temporal cohesiveness of the Pb pollution record in Europe over the past few millennia among the different natural archives, namely, peat, lake sediments, and glacial ice (*13*−*18*).

The important lesson learned from analyses of the long-term record of Pb in peat bogs, and the other natural archives, is that human impacts on the atmospheric transport and cycling of heavy metals must be viewed from a long-term perspective. In the case of Pb, preanthropogenic (natural) values in Europe are only found in layers older than 3500 years. The natural Pb deposition rate in these preanthropogenic layers is 1000-fold lower than the maximum deposition rates in the 1970s (10^{-2} versus 10 mg of Pb m^{-2} $year^{-1}$) (*13*, *18*).

Typically, estimates for the natural background atmospheric deposition rate of Hg are based on analyses of short cores (ca. 25−30 cm in length) from peat bogs or lake sediments, records that generally span only the past 200−300 years. The older layers of these short cores, which were only deposited just prior to modern industrialization, are frequently considered to represent natural preanthropogenic background conditions (*1*, *12*, *19*−*22*).

In the case of Hg, the first unambiguous evidence that a long-term perspective also needs to be employed comes from a peat core from an ombrotrophic bog, Penido Vello, in northwestern Spain (*23*). Spain is home to one of the historically most important Hg mining regions at Almadén, where mining began some 2500 years ago. Martínez-Cortizas and colleagues found a clear Hg-pollution signal from about 1500 years ago, with potential traces of Hg pollution as early as 2000−2500 years ago (*23*). Supporting evidence for a preindustrial anthropogenic impact on atmospheric Hg has also come from studies of Swiss sites (*24*) and from a few studies of sediment cores from high-latitude lakes, where a pre-1800 increase in Hg has also been suggested (*25*−*27*).

Here, the concentrations of Hg in complete peat profiles from two ombrotrophic bogs in south Sweden and limited analyses from a third site are presented. In particular, focus is directed toward deriving a realistic estimate of the natural background atmospheric deposition rate of Hg.

Materials and Methods

Site Descriptions and Sampling. Dumme Mosse (57°30′ N, 14°02′ E) and Limbergsmosse (59°45′ N, 15°30′ E) are classic, ombrotrophic raised bogs that developed initially as *Carex* fens (Figure 1). The individual coring sites were situated in *Sphagnum* hummocks in the raised area of each bog. For the top approximately 1 m of peat, a Wardenaar box-type corer

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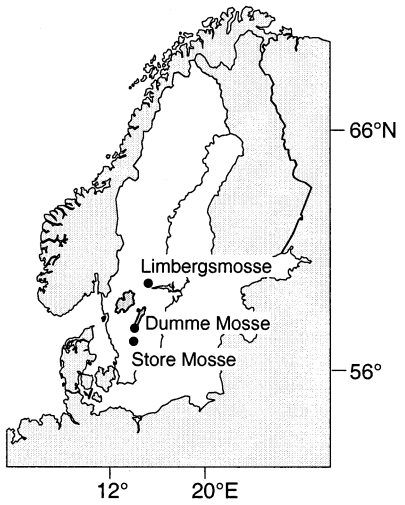

FIGURE 1. Locations of the three peat bogs Dumme Mosse, Limbergsmosse, and Store Mosse, in southern Sweden.

(*28*) was used (length 100 cm, area 10 cm × 10 cm), and for deeper layers, a Russian peat corer (length 50 cm, diameter 5 cm) was used. To ensure retrieval of a complete peat profile, two parallel drives were taken ≤50 cm apart in alternating sequence, with an overlap of 25 cm. The cores were wrapped in plastic and then aluminum foil, transported back to the laboratory, and stored in the dark at 4 °C. The cores for the Hg study were collected in 1998, and a replicate core from Dumme Mosse was collected in 2000.

Dumme Mosse is a large mire complex encompassing ca. 2000 ha, most of which is currently protected as a nature reserve. The ontogeny of Dumme Mosse has not been the subject of specific study, but according to analyses of the peat (humification, ash content, and other unpublished analyses) and radiocarbon dating of the replicate core, the site was fully ombrotrophic by 4100 calibrated-year BP (*29*). A 2-km-long, 19-core transect of the bog in 1994 indicates a fairly uniform stratigraphy across the bog plain (*30*): The top 1−1.5 m of the bog is composed of a low-humified *Sphagnum* peat. Below this lies a more-humified *Sphagnum* peat section about 0.25−0.5 m thick, followed by a ca. 1.5-m-thick, less-humified *Sphagnum* peat, and finally a more-humified *Carex* fen peat. The complete peat sequence collected for the current study was 525 cm thick.

Limbergsmosse is a small bog, 18 ha, with an adjoining fen of 18 ha. The peat profile extends to a depth of 470 cm. The coring site on Limbergsmosse was located near the center of an 8-core transect by Almquist-Jacobson and Foster (*31*), who examined bog initiation and development at this and other sites in central Sweden. The initiation of the *Carex* fen began ca. 9500 BP, and the transition from fen to *Sphagnum* peat is dated in the central area of the bog to ca. 4500−4000 BP, which they suggested was correlated with regional changes in lake levels in central Sweden. This fen-to-bog transition also corresponds approximately in time with the transition in Dumme Mosse.

A smaller number of samples were also included in this study from Store Mosse (57°15′ N, 13°55′ E), a ca. 8500-ha bog complex. This 620-cm-long profile was previously radiocarbon-dated and analyzed for Pb (concentrations and isotopic composition) (*32*) as well as Sc, Ti, and ash content in 1996.

Analyses. The cores from Dumme Mosse and Limbergsmosse were subsampled in continuous 5-cm sections for the uppermost 50 cm and continuous 10-cm sections for the remainder of each profile. The ash content of the complete peat profiles (with a few gaps where there was insufficient quantities of peat) was determined by combusting oven-dried samples (80 °C) at 450 °C for 6 h.

For Hg analyses, all samples from the top 1-m and every other 10-cm section thereafter were included. After being freeze-dried, the larger fragments, e.g., twigs, roots, and woody fragments, were removed. The samples were digested using strong acids (HNO_3/H_2SO_4) and analyzed for Hg concentration using cold-vapor atomic fluorescence spectrometry (CVAFS) at the Swedish Environmental Research Institute (IVL) in 1998. All results from analyses of standard reference material were within the certified range (BCR-142 light sandy soil, certified 104 ± 12.3 ng of Hg g^{-1}; measured 99.5 ± 5.5 ng of Hg g^{-1}). Analytical uncertainty was ≤10%, whereas the actual relative standard error of replicate analyses was ≤5%.

For Dumme Mosse, a more-detailed analysis of the same 1998 Wardenaar monolith analyzed for CVAFS (5-cm sections) was also carried out in 2002. For this analysis, the peat core was frozen (−18 °C), the outer few centimeters was cut away, and the surfaces of the frozen core were hand-planed, leaving an inner section of the core with a length of 47.5 cm and a surface dimension of 4 cm × 4.5 cm. This inner core was cut into precise 2.5-cm-thick sections, freeze-dried, and homogenized. These samples were analyzed for Hg using automated thermal decomposition atomic adsorption spectrophotometry (TD-AAS, Leco AMA254), which eliminates the need for sample pretreatment (modified from U.S. EPA Method 7473). Results from analyses of standard reference materials were within the certified ranges (NIST-1515 apple leaves, certified 44 ± 4 ng of Hg g^{-1}, measured 43.6 ± 2.5 ng of Hg g^{-1}, $n = 8$). The relative standard error of replicate analyses was ≤5%. All Hg concentrations are reported on a dry mass basis, nanograms of Hg per gram. Samples previously analyzed using CVAFS are also included for comparison.

In addition to the analyses of Dumme Mosse and Limbergsmosse, a smaller number of freeze-dried peat samples from Store Mosse were analyzed using either CVAFS or TD-AAS. The subsamples for CVAFS analyses represented about a 1-cm-thick section of peat, whereas the samples for TD-AAS were bulk samples representing a larger section of peat (the vertical bars in Figure 2c indicate the section of peat represented by each of these samples).

Dating of the Peat. The recent peat (the 2.5-cm sections from the 1998 Waardenaar core) from Dumme Mosse was ^{210}Pb-dated (Flett Research Ltd., Manitoba, Canada) based on its granddaughter ^{210}Po. Samples were digested in a nitric hydrochloric acid medium, evaporated and converted to the chloride salt, plated out onto silver, and then counted by alpha spectroscopy. Recovery was monitored by concurrent measurement of the activity of a ^{209}Po spike added at the beginning of sample processing. Detection limits are ~0.1 DPM/g (0.0017 Bq/g) for about an 8-h counting period and a 0.5-g sample mass. Ages were calculated using the CRS model (*33*), and error bars in the modeled ages are based on counting-error propagation (*34*).

Dating of the deeper peat from Dumme Mosse is based on age−depth modeling of the replicate profile collected in 2000 (*29*) and stratigraphic correlation between this radiocarbon-dated profile and the 1998 core used for Hg analyses. The age−depth model for Dumme Mosse used in this paper combines the CRS model for the recent peat from the 1998 profile with the dating results from the 2000 profile, which includes three radiocarbon ages (a fourth value, shown in the results, is excluded) and one inferred age, ca. 0 AD for the Pb concentration peak corresponding to the Roman peak in lead (*14*) (Table 1). The radiocarbon dates are based on analyses of *Sphagnum* leaves, which were first rinsed with distilled water. Radiocarbon dates for Dumme Mosse are given here as calibrated years BP (1950) (Calib 4.3) (*35*).

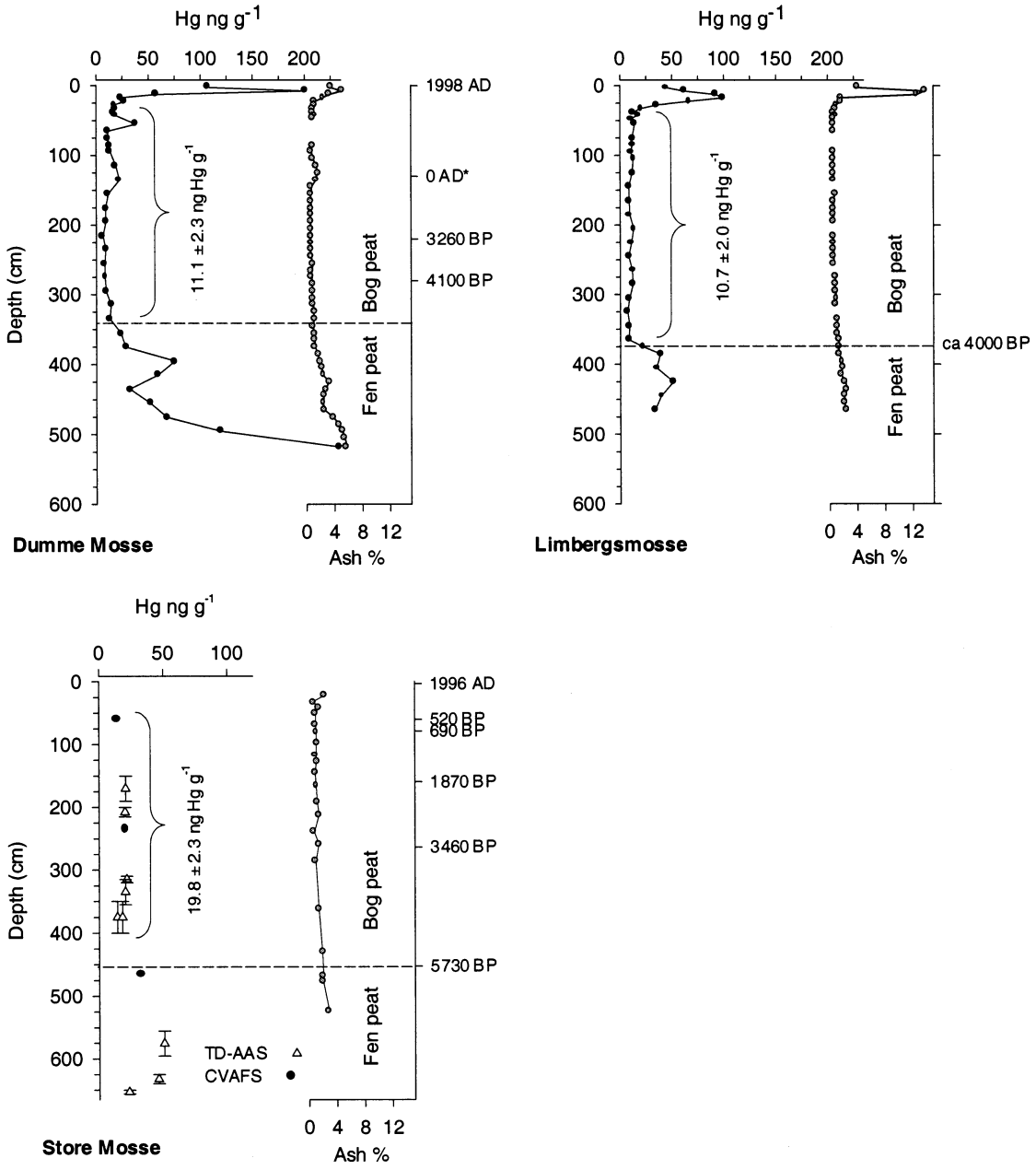

FIGURE 2. Depth profiles of mercury concentration and ash content from (a) Dumme Mosse (CVAFS Hg analyses only), (b) Limbergsmosse, and (c) Store Mosse. The mean background Hg concentration in the ombrotrophic peat is indicated for each bog. Calibrated radiocarbon ages and inferred ages are indicated on the right axis of each profile.

TABLE 1. Dating Results of the Deeper Peat in the Replicate Core (2000) from Dumme Mosse (*29*)

depth (cm)	^{14}C year BP	calibrated year BP[a]	notes
130		1950 ± 150	inferred age: Roman Pb peak (*14*)
220	3070 ± 55	3435−3079	Ua-18824
280	3640 ± 75	4217−3721	Ua-14791; excluded from age model
343	3700 ± 50	4222−3890	Ua-18454
345	3805 ± 75	4412−3983	Ua-14792

[a] Calibrated year BP for the ^{14}C dates represents the 2σ age range.

Results

Ash Content. The ash content and Hg concentration profiles of Dumme Mosse and Limbergsmosse are quite similar (Figure 2a,b). The ash content in each profile follows a general pattern expected for ombrotrophic bogs. For the main part of the each peat profile, i.e., from about 350 cm depth upward to about 25 cm depth below the peat surface, the *Sphagnum* bog peat has a very low ash content (≤1.5% ash), whereas the ash content is higher in both the surface peat and the underlying *Carex* fen peat.

The higher ash content in the fen peat of each bog is the combined result of a greater degree of decomposition in the *Carex* fen peat [humification grade ≥ 6 in Dumme Mosse and also Store Mosse (*36*)], the minerogenic character of fen peat, and the potential for translocation and upward diffusion of metals from underlying sediments (*37*). In Dumme Mosse, the decline in ash content at 350 cm depth coincides with the botanical transition from fen peat to ombrotrophic peat (*29*). The higher ash content of the surface/near-surface peat can be attributed to nutrient retention and cycling (*38*, *39*) and possibly also to an increased atmospheric influx of soil dust, as indicated by elevated Sc and Ti inputs (in relation to ash content) in the nearby bog, Store Mosse. In both

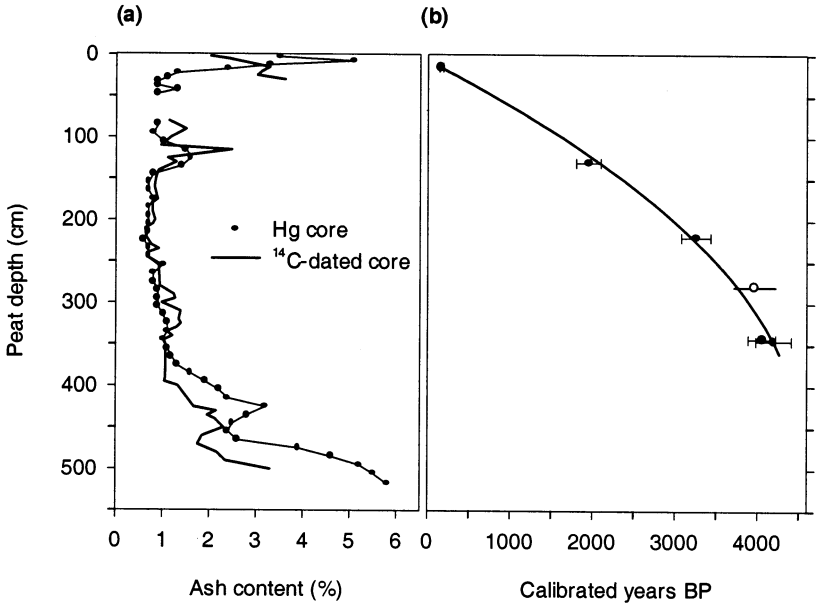

FIGURE 3. (a) Ash content of the 1998 core used for Hg and the 2000 radiocarbon-dated core and (b) age−depth modeling of the Dumme Mosse record. The open circle indicates a radiocarbon date excluded in the model: the ^{14}C age at 280 cm has a calibrated age similar to the calibrated ages at 343 and 345 cm depth.

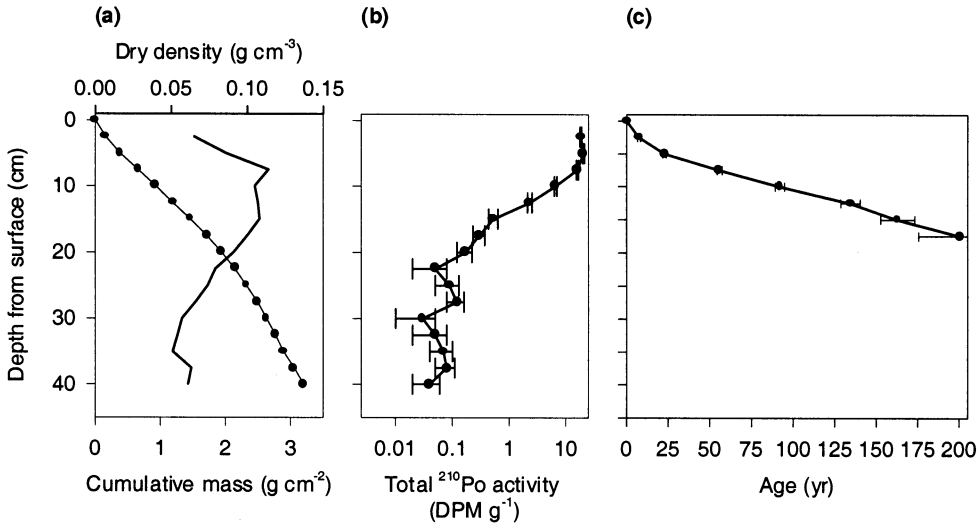

FIGURE 4. (a) Bulk density (g of dry mass cm^{-3}) and cumulative peat mass (g cm^{-2}) (line and filled circles, respectively), (b) ^{210}Pb activity (measured as total activity of ^{210}Po) versus depth, and (c) the CRS age−depth modeling of the surface core from Dumme Mosse.

Dumme Mosse peat profiles, i.e., the 1998 and the 2000 profiles, there is an increase in ash content between 100 and 140 cm depth (Figure 3a) that is related to a zone of increased humification (humification grade ≥ 6), whereas the peat above and below is less humified (grade 3−4), which is a layer found across the entire bog plain (*30*). This zone likely corresponds approximately with a bog-phase transition in Store Mosse, also indicated by increased humification and increased ash content, that is dated to ca. 2500 BP (*40*).

Peat Accumulation Rates. The age−depth model for Dumme Mosse (Figure 3b) indicates fairly typical bog development and peat accumulation rates as compared to other Swedish bogs. In the surface peat, ^{210}Pb dating indicates that the uppermost 15 cm of peat, which includes the living plant material (top ~1 cm), represents approximately 160 years of peat accumulation (AD 1835 ± 25 year at 15 cm depth) (Figure 4b). Although the average peat mass accumulation rate for this period is 77 g m^{-2} $year^{-1}$ (0.92 mm $year^{-1}$), the rapid decomposition of organic material below the litter deposition layer causes the accumulation rate to decline sharply from 220 g m^{-2} $year^{-1}$ in the top 2.5-cm section to 70 g m^{-2} $year^{-1}$ in the 10−12.5-cm section. The mass accumulation rate is estimated to decline even further to ca. 40 g m^{-2} $year^{-1}$ in the 17.5−20-cm section.

For the peat between 160 and 4100 years old, the average vertical growth rate is 0.80 mm $year^{-1}$, although the age−depth model shows that the vertical growth rate has gradually declined over this period (Figure 3b), from >1 mm $year^{-1}$ before 3500 BP to <0.6 mm $year^{-1}$ in the past millennium. Likewise, the modeled mass accumulation rate has gradually declined from 90 g m^{-2} $year^{-1}$ before 3500 BP to 40 g m^{-2} $year^{-1}$, with the average over the past 4100 years being 50 g m^{-2} $year^{-1}$. These values for the accumulation rate in Dumme Mosse are within the range of typical accumulation rates shown for other Swedish ombrotrophic bogs (*18*, *29*, *40*, *41*). The generally declining peat mass accumulation rate in Dumme Mosse over the past few thousand years is found in many Swedish bogs and mires (*39*, *41*). Importantly, the age−depth model describes only the smoothed, long-term growth

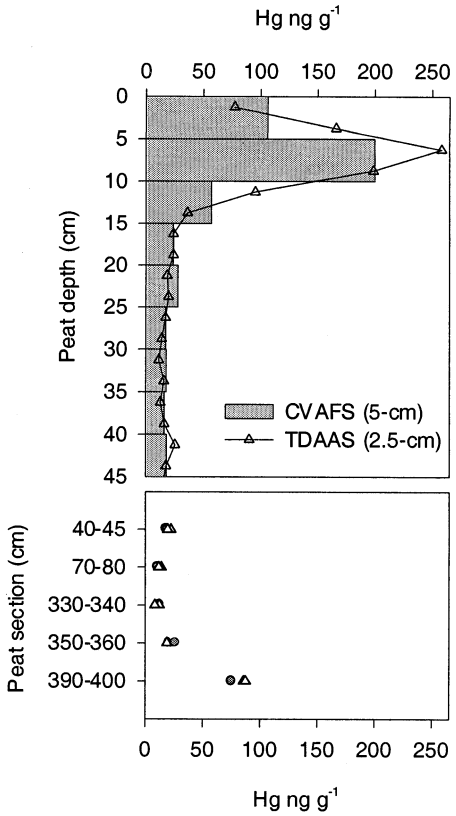

FIGURE 5. Comparison of the CVAFS analyses of the 5-cm-thick sections and the TD-AAS analyses of the 2.5-cm-thick sections from the Wardenaar surface peat core from Dumme Mosse and additional peat sections measured using both methods.

of the bog and does not incorporate significant short-term variations in bog growth rate that have likely occurred.

Comparison of the 1998 and 2000 profiles from Dumme Mosse indicates that the ombrotrophic section of the 1998 profile is 15 cm thinner, which indicates that the average vertical accumulation rate is slightly lower, i.e., 0.77 mm year^{-1}. This small difference (4%) in vertical growth rates between the two profiles is not likely to introduce a significant source of error in further calculations. Although the emphasis here is placed on Dumme Mosse, it is also reasonable to assume that a comparable average peat mass accumulation rate can be expected for Limbergsmosse, based on the similarities in ash content with Dumme Mosse and other bogs, the thickness of the *Sphagnum* peat, and the ontogeny of the bog (*31*).

Hg. *CVAFS vs TD-AAS Hg Analyses.* As described in the Materials and Methods section, the 1998 Wardenaar surface core from Dumme Mosse was analyzed for Hg using two separate methods, CVAFS and TD-AAS. A comparison of the results of the two analyses, along with several samples from deeper peat layers that were analyzed using both methods, shows remarkable consistency between the methods (Figure 5).

Hg Profiles in the Peat. As with the ash content, the concentration of Hg is higher in the *Carex* fen peat, probably as a result of the greater decomposition of the fen peat, the minerogenic nature of fen peat, and the influence of groundwater (Figure 2). In Dumme Mosse, the maximum Hg concentration (230 ng of Hg g^{-1}) occurs in the deepest layers of the *Carex* peat (510−525 cm depth), and the concentration declines continuously upward through the *Carex* peat and into the transition toward *Sphagnum* peat. In the *Carex* peat from Limbergsmosse, the Hg concentrations are also elevated, although only to 30−50 ng of Hg g^{-1}. For the bulk of the *Sphagnum* peat in both Dumme Mosse and Limbergsmosse, i.e., from 350 cm upward to about 50 cm depth, the concentration of Hg is quite low and varies little, 11 ± 2 ng of Hg g^{-1}. There is an excursion away from this low background value in Dumme Mosse, from 120 to 140 cm depth, where the Hg concentration increases about 2-fold. This increase is clearly related to the increase in the degree of humification; a 2-fold increase in peat decomposition would cause the observed 2-fold increase in both ash content and Hg concentration. Similarly, there is a second Hg concentration excursion in the 50−60-cm section (38 ng g^{-1}) also related to an increase in humification.

The concentration of Hg is elevated about 2-fold (16−28 ng of Hg g^{-1}) over background in the peat sections (15−45 cm depth) that are below the ca. 1840 AD horizon (15 cm depth), and it increases further above 15 cm and reaches the peak value of 260 ng of Hg g^{-1} in the 5−7.5 cm peat section. In Limbergsmosse, located farther north, Hg concentrations increase 10-fold in the near-surface peat, with the maximum value of 100 ng of Hg g^{-1} in the 15−20-cm section.

As in the other bogs, the average Hg concentration in the *Sphagnum* peat (from 400 upward to 60 cm depth) in Store Mosse is low and shows only a small variation; however, the concentrations are higher than in the other two peat records, 20 ± 2 ng of Hg g^{-1} ($n = 8$ samples). Also, similarly to the other two bogs, the Hg concentration in the deeper *Carex* peat of Store Mosse is elevated as compared to that in the ombrotrophic peat, 25−50 ng of Hg g^{-1} ($n = 3$ samples).

Discussion

Recent Hg Deposition Rates. Given the calculated peat mass accumulation rates in the surface peat sections of Dumme Mosse, the maximum Hg concentrations in the recent peat correspond to a maximum net Hg accumulation rate of 23−25 μg of Hg m^{-2} year^{-1} in the two peat sections dating to AD 1942−1975 and 1975−1991 (Figure 6a). In the surface 2.5-cm section, AD 1991−1998, the accumulation rate has declined by about 30% to 17 μg of Hg m^{-2} year^{-1}. Assuming that recent peat accumulation rates for Limbergsmosse are similar to those for other Swedish bogs, 100−200 g peat m^{-2} year^{-1}, the Hg accumulation rate there would be in the range of 5−20 μg of Hg m^{-2} year^{-1}. By comparison, the measured Hg wet-deposition rates in Sweden in 1987−1989 were 27 and 10 μg of Hg m^{-2} year^{-1}, for the western (Rörvik) and eastern (Aspvreten) coasts of Sweden, respectively, which declined to 9 and 6 μg of Hg m^{-2} year^{-1} during the 1990s (*6*) (Figure 6b).

Although more detailed dating is necessary to determine the onset of increased Hg accumulation accurately, the age−depth model for Dumme Mosse indicates that the Hg accumulation rate began to increase over background levels in about the 17th century and has increased continuously until the most recent decade. This preindustrial (pre-1850) increase is not as early as indicated by bogs located closer to preindustrial centers of metallurgy, e.g., the Penido Vello bog in Spain (*23*) or Etang de la Gruère in Switzerland (*24*)

Background Concentrations and Preanthropogenic Hg Deposition Rates. The low background Hg concentrations measured in the three Swedish bogs (10−20 ng of Hg g^{-1}) are similar to reported concentrations in longer peat profiles from other ombrotrophic bogs, for example, 5−20 ng of Hg g^{-1} for Storelungmose in Denmark (*42*) and 10−30 ng of Hg g^{-1} for Etang de la Gruère in Switzerland (*24*). Background concentrations are slightly higher in the Penido Vello bog in northwest Spain, 20−40 ng of Hg g^{-1} for the period 4000−1500 BP (*23*). The background Hg concentrations in the above bogs are lower than those generally reported from other bog sites in Scandinavia (*21, 22*)—studies that have relied on only short cores (i.e., 35−50 cm in length). Although it is not expected that all bogs should have equally low background

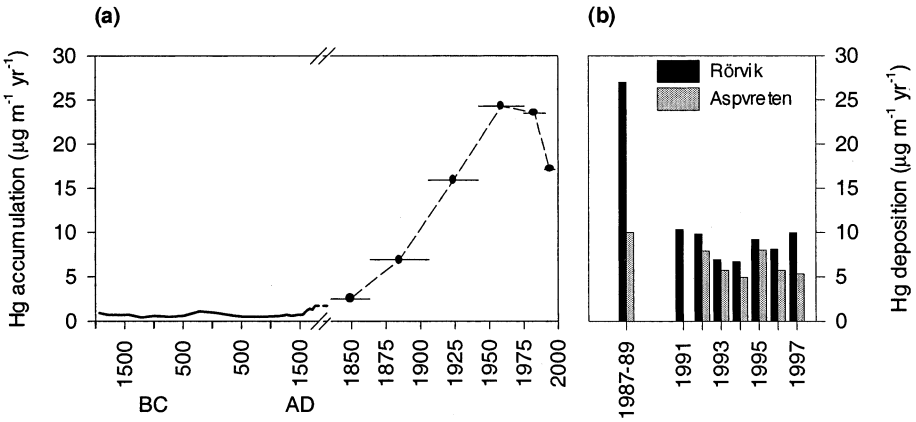

FIGURE 6. (a) Hg accumulation rate in Dumme Mosse and (b) measured Hg wet-deposition rates at two stations in southern Sweden (Rörvik on the west coast and Aspvreten on the southeast coast) (*6*). Horizontal bars in the left panel for the flux values of the two most-recent centuries represent the time period covered by each of the 2.5-cm peat sections.

concentrations (for example, the difference between Store Mosse and both Dumme Mosse and Limbergsmosse), collection and analysis of longer records are preferable to ensure that representative background values are captured.

In addition to performing a brilliant demonstration of the existence of pre-1800 atmospheric Hg pollution, Martínez-Cortizas and co-workers have suggested that there might be a climatic influence on the retention of Hg in peat (*23*). Although this might be important to some degree (although it has not yet been independently validated), current evidence from peat and soil studies (*4, 5, 12, 43*−*46*) indicates that the loss of Hg from peat through revolatilization or other diagenetic losses is small. A second complicating factor is the variable temporal response of bogs to climate changes, which is, in part, site-specific (*31*). Consequently, it is assumed in this paper that the loss of Hg from the peat is minor and, therefore, that the net Hg accumulation rate in the peat corresponds approximately to an open-field atmospheric deposition rate of Hg. The general agreement between modern accumulation rates in Dumme Mosse and recent measured wet-deposition rates of Hg elsewhere in Sweden suggests that this approximation between peat accumulation and atmospheric deposition is reasonable.

On the basis of the modeled peat accumulation rate in Dumme Mosse, the natural background Hg accumulation rate in Dumme Mosse is estimated to be 0.6 ± 0.2 μg of Hg m^{-2} $year^{-1}$. It is likely that the background range includes both higher and lower excursions from this average estimate, as this Hg accumulation rate is based on a smoothed model of peat growth.

For Store Mosse, where the average peat accumulation rate is similar to that at Dumme Mosse (50 g m^{-2} $year^{-1}$ in Store Mosse for the period ca. 3500−500 BP) but the Hg concentrations are 20 ng of Hg g^{-1}, the estimated background Hg accumulation rate is slightly higher, about 1 μg of Hg m^{-2} $year^{-1}$. At present, it is not possible to explain why Store Mosse has a higher background Hg concentration and apparently higher Hg accumulation rate than Dumme Mosse. Other questions would have to be addressed before making a critical assessment of the specific differences between the individual bog records, such as how representative a single peat profile is for the bog as a whole. Factors such as the microtopography of individual coring sites are known to be important (*12, 39*). Therefore, it is possible that the difference in background concentrations in Store Mosse versus Dumme Mosse, which are less than 50 km apart, is no greater than the potential difference within each of the bogs. This is an important issue for future research to address.

The significance of the current study is that this estimated range for the natural, background Hg accumulation rate, 0.5−1 μg of Hg m^{-2} $year^{-1}$, based on Dumme Mosse and Store Mosse, and by inference also Limbergsmosse, is at a level that is less than existing estimates for the background atmospheric deposition rate, ca. 2−5 μg of Hg m^{-2} $year^{-1}$ (*1, 3*−*5, 23, 47, 48*). Similarly to the data from the Swedish bogs, a study of two adjacent bogs in the Swiss Jura Mountains, one ombrotrophic and the other minerotrophic, shows calculated mean background net Hg accumulation rates of 0.7 and 1.6 μg of Hg m^{-2} $year^{-1}$, respectively, in the two bogs (*24*). As with Dumme Mosse, the Swiss sites record approximately a 30-fold increase in Hg accumulation rates in recent versus preanthropogenic levels.

Some variation in the natural background deposition rate of Hg between regions can be expected given differences in precipitation and geology, and it might be that the low values derived from the Swedish and Swiss bogs are related to such factors. The higher estimated value from the Spanish bog (3.3 μg m^{-2} $year^{-1}$) (*23*) is likely related to the presence of extensive Hg mineral deposits in Spain, for example, whereas for midcontinental sites in North America (3−4 μg of Hg m^{-2} $year^{-1}$) (*1, 4, 47*), atmospheric chemistry is strongly influenced by the significantly longer distances that air masses must travel over land.

Further studies of the long-term records preserved in other peat bogs and other paleo-archives would strengthen the estimates of preanthropogenic Hg deposition rates. Other issues that should be addressed in interpreting reconstructions from peat include a better understanding of (i) the potential long-term losses that might affect the quantitative record in peat in response to decay losses of organic matter [25−85% of the litter input may be lost in the acrotelm, with further gradual losses in the catotelm (*40, 49*)]; (ii) the ways in which Hg concentrations might vary simply as a function of bog development, as well as varying as a function of more complex ecosystem−climate interactions; and (iii) the representativity of single cores within a bog for making detailed reconstructions. However, just as the peat record has provided new insights into long-term changes in atmospheric Pb deposition, especially regarding preanthropogenic deposition rates (*13, 18*), studies of the Hg record in peat are providing new insights into preanthropogenic Hg cycling and long-term atmospheric pollution.

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Mercury in Livers of Wading Birds (Ciconiiformes) in Southern Florida

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Abstract. Mercury was measured in livers from 144 wading birds representing seven species collected from four different areas in southern Flordia, including the Everglades National Park. Significant differences in hepatic mercury concentrations were identified between birds collected from different geographic locations, birds of different ages, dietary factors, and relative amounts of body fat. Birds collected from an area encompassing the central Everglades and eastern Florida Bay had significantly greater concentrations of hepatic mercury than did birds from other collection areas. Livers from fledgling and young adult birds contained approximately three times the concentration of mercury as livers from nestling birds. Bird species whose prey base consists of larger fish were found to have approximately four times the hepatic concentration of mercury as did those species which consume smaller fish or crustaceans. Birds with minimal to moderate amounts of body fat had two to three times the concentration of hepatic mercury as birds with relatively abundant body fat reserves. Four great blue herons collected from the central Everglades contained liver mercury at concentrations typically associated with overt neurologic signs ($\geq$30 μg/g). Between 30% and 80% of potential breeding-age birds collected from this area contained hepatic mercury at concentrations associated with reproductive impairment in ducks and pheasants. These data suggest that declining numbers of nesting ciconiiform birds in Florida may be due, in part, to mecury contamination of their food supply.

Since the early 1980s, mercury has been recognized as a major contaminant of various watersheds throughout the state of Florida, especially in certain areas of the Everglades National Park (Cabbage 1989; Hand and Friedemann 1990). By sampling Everglades wetland sediments at progressively deeper levels it has been estimated that rate of mecury accumulation has increased 6.4-fold since the beginning of the 20th century (Delfino *et al.* 1993). Although the precise sources of mercury have not been established, recent studies suggest that 61% of the mecury in the Everglades is due to atmospheric deposition from anthropogenic sources. The largest single contributor to environmental mercury is municipal solid waste combustion facilities (14.6%), followed by medical waste incinerators (14.0%), paint manufacturing, and application (11.1%), the electric utility industries through the combustion of fossil fuels (10.7%), electrical apparatus including fluorescent, mercury vapor, metal halide, and sodium lights (5.9%), and other fossil fuel combustion sources including industrial residential sources (1.7%). All other anthropogenic sources combined including sugar cane processing, the dental industry, open burning, and sewage sludge disposal accounted for only 3% of the total mercury emitted to the environment (KBN, 1993). Natural sources of mercury were estimated to contribute 39% of the annual total emitted to the Everglades. Virtually all of the mercury from natural sources (38.9% of the total emissions from both anthropogenic and natural sources) is attributed to release from the soil through natural processes including microbial transformation of inorganic and organic mercury to methylmercury (KBN 1993).

State health officials have issued advisories to prohibit consumptions of largemouth bass (*Micropterus salmoides*) in southern Florida, and the entire Everglades watershed has been closed to hunting of alligators due to excessive mecury in edible tissues (Royals and Lange 1990). The imminent threat of mercury to wildlife was recognized in 1989 when an endangered Florida panther (*Felis concolor coryi*) was discovered deceased in the Everglades National Park. Death of the animal was attributed to mercury intoxication as evidenced by liver mercury concentration of 110 μg/g based on wet tissue weight (Jordan 1990). Since 1989, mercury has been strongly implicated in the deaths of at least two other panthers (Roelke *et al.* 1991). The impact of mercury on less intensely studied wildlife species and populations in southern Florida has not been determined.

Mercury undergoes bioaccumulation in aquatic food webs such that species which are long-lived and occupy the upper trophic levels accumulate the highest concentrations of mercury and are at greatest risk of intoxication (Clarkson and Marsh

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Table 1. Numbers and classification of ciconiiform birds by geographic area where collected, relative age, and diet

		Numbers of birds collected												
		Area 1[a]			Area 2			Area 3			Area 4			
Species	Diet[b]	SN[c]	LN[c]	FA[c]	FN	LN	FA	SN	LN	FA	SN	LN	FA	Total
Great blue heron	A	5	2	2	2	4	1	0	14	18	0	0	11	59
Great egret	A	4	5	0	5	6	1	0	1	0	0	0	2	25
Little blue heron	B	3	1	0	1	0	2	0	0	0	0	0	0	7
Snowy egret	B	0	3	0	0	7	0	1	0	0	0	0	0	11
Tricolored heron	B	3	1	0	5	1	0	2	2	1	0	0	0	15
Roseate spoonbill	C	0	0	0	1	3	0	1	7	1	0	0	0	13
White ibis	C	9	1	2	0	0	1	2	0	0	0	0	0	15
All species		24	13	4	14	21	5	6	24	20	0	0	13	144

[a] See Figure 1 for visual representation of geographic areas 1–4

[b] Dietary group A consists of those species which consume large fish as a major portion of the diet; group B consists of species which consume small fish as a major dietary component; group C consists of species which consume small fish, crustacea, and insects as major dietary components

[c] SN = small nestling birds, LN = large nestlings, FA = fledglings/young adults

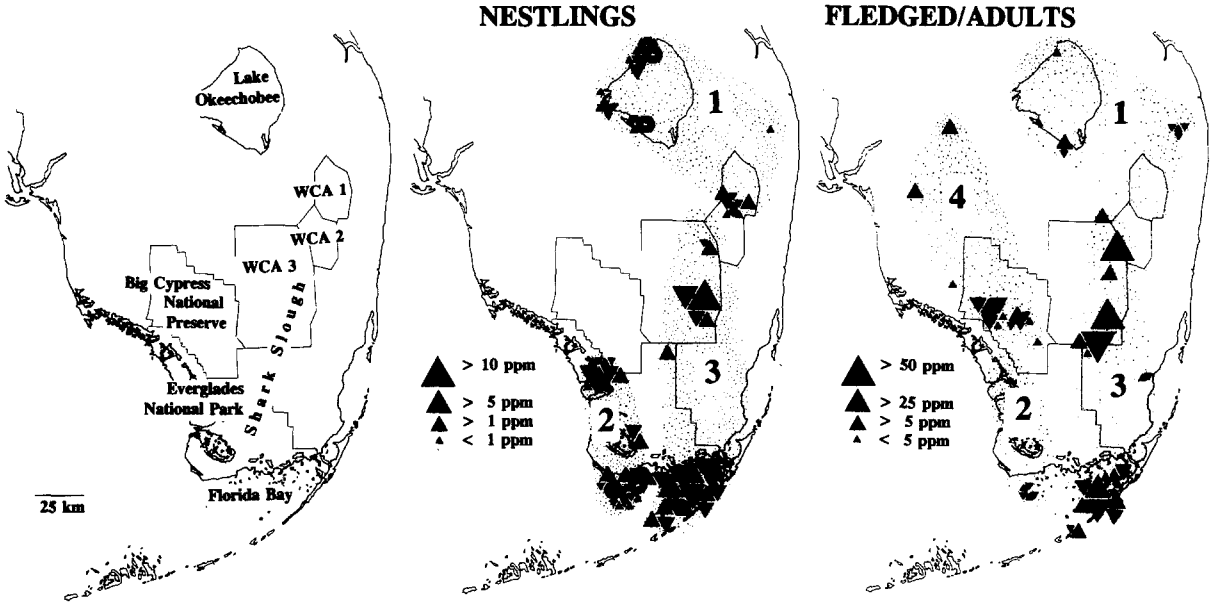

Fig. 1. Geographic location of sites where ciconiiform birds were collected (collection areas 1–4). Each triangle represents an individual bird. The size of the triangle indicates the approximate concentration of mercury in the liver of each bird. Only fledged or adult birds were collected from Area 4. Map on the right is for orientation. WCA = water conservation area

1982). Wading birds (order Ciconiiformes) including herons, egrets, ibis, and spoonbills, are upper trophic level aquatic feeders and may be at potential risk from mecury intoxication in those watershed areas of Florida with high ambient mercury. Populations of these birds have been declining in southern Florida for reasons which are not well understood (Ogden 1994). The purpose of this study was to compare mercury concentrations in livers of young ciconiiform birds collected from various geographic locations in southern Florida.

Materials and Methods

Collection of Birds and Sampling of Tissues

Wading birds (n = 144) representing seven ciconiiform species and one subspecies were collected from four geographic areas of southern Florida from 1987 through 1991 (Table 1). The species included: great blue heron (*Ardea herodias*) including a color morph—the great white heron (*A. h. occidentalis*), great egret (*Casmerodius albus*), snowy egret (*Egretta thula*), tricolored heron (*E. tricolor*), little blue heron (*E. caerulea*), white ibis (*Eudocimus albus*), and roseate spoonbill (*Ajaia ajaja*).

Collection Area 1 (Figure 1) encompasses Lake Okeechobee and Water Conservation Area 1 (WCA 1). Colonies were situated in tree islands on the shores of Lake Okeechobee, in small willow-heads and bay islands in fresh-water marsh in WCA 1, and on spoil islands in an abandoned shell mine in Palm Beach County. Area 2 includes the estuarine mangrove area of the western portion of the Everglades National Park including western Florida Bay. All colonies were on mangrove islands in estuarine or marine areas. Area 3 includes WCA 3, eastern Shark Slough, and eastern Florida Bay. Colonies on the mainland were on willow-heads and bay islands in freshwater marsh and on mangrove islands in marine Florida Bay. Area 4 includes the Big Cypress National Preserve and areas north and west of it. None of the birds collected from Area 4 were nestlings.

Table 2. Effects of geographic location on mercury concentrations (μg/g) in livers of ciconiiform birds from south Florida. Values represent the geometric mean and range (in parentheses)

	Liver mercury (μg/g)			
Species	Area 1	Area 2	Area 3	Area 4[a]
Great blue heron	0.60 (0.32–5.82)	0.80 (0.21–2.70)	4.25 (0.22–74.54)	7.62 (2.99–17.51)
Great egret	0.50 (0.18–1.60)	1.24 (0.38–4.27)	18.84[d]	1.13 (0.64–2.01)
Little blue heron	0.38 (0.29–0.73)	0.29 (0.23–0.41)	ND[c]	ND
Snowy egret	0.37 (0.29–0.42)	0.38 (0.15–1.43)	5.38[b]	ND
Tricolored heron	0.57 (0.20–4.96)	0.32 (0.12–0.58)	1.93 (0.67–4.70)	ND
Roseate spoonbill	ND	0.27 (0.16–0.35)	0.74 (0.31–5.38)	ND
White ibis	0.34 (0.05–1.15)	1.28[d]	1.06 (0.77–1.46)	ND
All species[e]	0.44 (0.32–0.61)	0.55 (0.40–0.76)	2.63[f] (1.96–3.54)	

[a] Area 4 birds were not included in any statistical analysis because only adult birds of dietary group A were represented
[b] Geometric mean and range (in parentheses)
[c] ND = no data available
[d] Value represents datum from a single bird
[e] Least squares mean and 95% confidence interval (in parentheses)
[f] Least squares mean from Area 3 birds is significantly different from Area 1 or Area 2 ($P < 0.001$)

Deceased birds were collected during periodic visits to colonies during the nesting cycle and when found dead along roadsides. Upon postmortem examination, the nutritional condition of each bird was noted and scored such that birds were classified as having abundant body fat, moderate body fat, or minimal to no observable body fat relative to the amount of fat expected for a bird of that age. Following postmortem examination the liver was removed and frozen at −20°C. Birds were assigned size/age classification based on bill length and plumage. Nestlings with bill length less than 60% of an average adult bill length were placed in the small nestling category. Nestlings with larger bills were placed in the large nestling category. Fledglings collected away from the nesting colony and adults were placed in the fledgling/adult category (Table 1).

Bird species were designated to one of three diet groups (Table 1). Group A consisted of those species which consume large fish as a part of their diet and included great blue herons and great egrets. Group B consisted of the following species which consume predominantly small fish: little blue herons, snowy egrets, and tricolored herons. Group C included white ibis and roseate spoonbills, which eat both fish and arthropods (Collopy and Jelks 1989).

Analysis of Mercury in Liver

Livers were thawed and the outer exposed layer of tissue removed to minimize the effects of potential contamination by exogenous mercury, and dehydration due to frozen storage. Samples of liver tissue (1 g) were accurately weighed and transferred to pre-weighed, metal-free, glass tubes. The sample-containing tubes were heated to dryness and subsequently digested in 1 ml of concentrated nitric acid until the solution became clear. Hydrogen peroxide (2 ml) was added to each tube and the tube heated at 95°C for 2 h after which the volume of the tube was adjusted to 10 ml with deionized water. After mixing, a 1 ml aliquot was placed into a hydride reaction tube along with 0.1 ml of 5% $KMnO_4$, and the volume adjusted to 10 ml with 1.5% nitric acid. Mercury was measured by cold vapor atomic absorption spectrophotometry on a Perkin Elmer Model 2380 (Perkin Elmer Corp, Norwalk, CT). All unknowns were compared with commericially available mecury standards (Fisher Scientific, 7464 Chancellor Drive, Orlando, Florida 32809). The lower limit of detection was 0.05 ppm, and recovery of mercury from mercury-fortified liver samples was 93%.

Statistical Analysis

Data from birds collected in Area 4 were excluded from any statistical analysis because only adult and fledged great blue herons and great egrets were obtained. Data (mercury concentrations) from all remaining birds were logarithmically transformed to better meet the assumption of homogeneity of variance of the residuals. An analysis of variance (SAS 6.07) was conducted on the transformed data using a linear model containing all main effects (area, diet, age, and body fat) and all first-order interactions. Because none of the first-order interactions were statistically significant ($P > 0.10$), a simpler model containing only the main effects was used. Least square means were calculated and pairwise t-tests were performed to determine significant differences between levels of each of the main effects. The reported least square means and 95% confidence intervals were transformed (antilogarithm) to the original scale and reported as μg of mercury per gram of liver.

Results

The geographic location of the nest site had a significant effect on mercury concentrations in ciconiiforms ($P < 0.0001$). Livers from birds collected in the area south of Lake Okeechobee and southward to the northern Everglades (Area 1) and birds collected from the western mangrove and western Florida Bay region (Area 2) contained significantly lower concentrations of mercury than livers from birds collected from the central Everglades and eastern Florida Bay region (Area 3) (Table 2). The highest concentration of mercury (74.54 μg/g) was observed in a great blue heron from Area 3. This value was more than 12 times the highest liver mercury value for any bird collected from Area 1 or Area 2.

Differences in mercury concentrations were also associated with age of the bird. Although mercury concentrations in birds from the two nestling age groups were not significantly different from one another, birds from the oldest group (fledged/adult) contained mercury at concentrations averaging approximately 3 times those of the younger birds (Table 3). Of all samples analyzed, the five highest in mecury were from fledged/adult birds.

Ciconiiform species which consume large fish as a major component of the diet (great blue herons and great egrets) were found to accumulate greater amounts of mercury than those species which eat primarily smaller fish or arthropods (Table 4). No differences in liver concentrations of mercury were observed between those species which consume small fish

Table 3. Effects of age on mercury concentrations (μg/g) in livers of ciconiiform birds from south Florida. Values represent the geometric mean and range (in parentheses)

	Liver mercury (μg/g)		
Species	Small nestlings	Large nestlings	Fledgling/Young adult
Great blue heron	0.31 (0.21–0.36)	1.53 (0.22–7.33)	6.65 (0.07–74.54)
Great egret	0.77 (0.31–1.85)	1.10 (0.18–18.84)	1.70[a]
Little blue heron	0.33 (0.29–0.41)	0.73[a]	0.24 (0.23–0.26)
Snowy egret	5.38[a]	0.38 (0.15–1.43)	ND[b]
Tricolored heron	0.73 (0.20–4.96)	0.74 (0.12–2.69)	0.67[a]
Roseate spoonbill	0.34 (0.16–0.74)	0.61 (0.26–5.38)	0.84[a]
White ibis	0.50 (0.23–1.46)	0.52[a]	0.25 (0.05–1.28)
All species[c]	0.62 (0.46–0.83)	0.62 (0.47–0.82)	1.68[d] (1.15–2.47)

[a] Value represents datum from a single bird
[b] ND = not available
[c] Least squares mean and 95% confidence interval (in parentheses)
[d] Value is significantly different from small nestling or large nestling birds ($P = 0.0001$)

Table 4. Effects of diet on mercury concentrations (μg/g) in livers of ciconiiform birds from south Florida. Values represent the geometric mean and range (in parentheses)

	Liver mercury (μg/g)		
Species	Diet A[a]	Diet B	Diet C
Great blue heron	2.31 (0.21–74.54)		
Great egret	0.97 (0.18–18.84)		
Little blue heron		0.43 (0.23–0.73)	
Snowy egret		0.48 (0.15–5.38)	
Tricolored heron		0.72 (0.12–4.96)	
Roseate spoonbill			0.55 (0.16–5.38)
White ibis			0.42 (0.05–1.46)
All species[b]	1.39[c] (1.10–1.77)	0.73 (0.52–1.01)	0.64 (0.44–0.92)

[a] Dietary group A consists of those species which consume large fish as a major portion of the diet; group B consists of species which consume small fish as a dietary component; group C consists of species which consume small fish, crustacea, and insects as major dietary components
[b] Least squares mean and 95% confidence interval (in parentheses)
[c] Value is significantly different from those of dietary groups B ($P < 0.004$) or C ($P < 0.006$)

(small herons and egrets) and those which consume both fish and arthropods (roseate spoonbills and white ibis). On average, mercury concentrations in the large herons and egrets were two times those of species feeding at lower trophic levels of the aquatic food web.

Hepatic mercury concentrations were inversely related to the relative amount of body fat (Table 5). Birds with only minimal to moderate amounts of body fat had an average of two to three times the concentrations of hepatic mercury compared to birds with abundant amounts of fat ($P < 0.007$).

Discussion

A relationship was observed between hepatic mercury concentrations and geographic location, dietary habits, age, and nutritional condition of wading birds collected from southern Florida. Birds containing the greatest concentrations of mercury were collected from the central Everglades and eastern Flordia Bay. Similar regional patterns of mecury contamination have been observed by others in other species on mainland southern Florida, particularly in fish and fish consumers in the area (Hand and Friedemann 1990; Roelke *et al.* 1991). In the present study, mercury concentrations in nestling ciconiiform birds reflected regional differences in the degree of contamination of aquatic food sources. In addition, the data suggest that mercury contamination may extend into eastern Florida Bay. When the same species and age groups were compared, mercury concentrations reported in this study were similar to those in birds collected in Ohio (Hoffman and Curnow 1979) and South Dakota (Hesse *et al.* 1975), but lower than those in birds collected in the Netherlands (Van der Molen *et al.* 1982), Ontario (Fimreite 1974), Lake St. Clair (Dustman *et al.* 1972), and California (Faber *et al.* 1972).

Although most of the ciconiiform species nesting in southern Florida migrate from distant locations to breed there, concentrations of mercury in livers of adult birds had the same regional relationships as did nestlings. In areas where nestlings had low hepatic mercury, adult birds also had low levels of mercury compared to adults collected in regions where nestlings had higher liver concentrations of mercury. This suggests that concentrations in livers may reflect a recent exposure to mercury rather than long term exposure elsewhere.

Hepatic mercury increased in concentration as a function of the bird's age. This direct relationship between animal age and mercury accumulation in tissues is consistent with numerous

Table 5. Relationship between amount of body fat and mercury concentrations (μg/g) in livers of ciconiiform birds from south Florida. Values represent the geometric mean and range (in parentheses)

	Liver mercury (μg/g)		
	Relative amount of body fat present at time of death		
Species	Abundant	Moderate	Minimal
Great blue heron	2.76 (0.22–59.41)	4.33 (0.32–74.54)	1.47 (0.21–52.09)
Great egret	1.48 (1.28–1.70)	1.14 (0.70–1.85)	0.91 (0.18–18.84
Little blue heron	0.24 (0.23–0.26)	0.48 (0.32–0.73)	0.34 (0.29–0.41)
Snowy egret	ND[a]	ND	0.48 (0.15–5.38)
Tricolored heron	0.67 (0.22–2.01)	0.32 (0.21–0.58)	0.95 (0.20–4.96)
Roseate spoonbill	0.68 (0.31–5.38)	ND	0.32 (0.16–0.74)
White ibis	0.34 (0.05–1.28)	0.24[b]	0.57 (0.27–1.46)
All species	0.47[d] (0.34–0.64)	1.21 (0.78–1.90)	1.14 (0.88–1.46)

[a]ND = no data available
[b]Value represents datum from a single bird
[c]Least squares mean and 95% confidence interval (in parentheses)
[d]Value is significantly different from that of birds with moderate fat ($P < 0.0007$) or minimal fat ($P < 0.0001$)

other reports (Burger 1993; Burger *et al.* 1992; Frank *et al.* 1983; Hoffman and Curnow 1979). Honda *et al.* (1986) have shown that mercury accumulates rapidly in young stages of the eastern great white egret downy chick. This accumulation is partially diluted by growth of the chick, but body burdens are reduced substantially during the first moult as mercury is lost through the down. Hepatic mercury concentrations in the eastern great white egret undergo a substantial decline shortly after hatching and remain low for the first 30–40 days of life. After this time, mercury accumulates in the liver in an age-related fashion (Honda *et al.* 1986). Finding no differences in hepatic mercury between small and large nestlings is consistent with observations reported by Honda (1986).

Trophic level is important in the bioaccumulation of mercury by wading birds. Species which consume larger predatory fish accumulated greater concentrations of hepatic mercury than did those species which consume smaller fish and invertebrates. Hoffman and Curnow (1979) reported a similar relationship between trophic level of prey species and bioaccumulation of mercury in egrets and herons.

Birds with subnormal amounts of body fat concentrated hepatic mercury to a greater degree than did birds with abundant amounts of body fat. Frank *et al.* (1983) observed a similar inverse relationship between amount of body fat and brain concentrations of mercury in common loons. Subnormal body fat in nestlings can result from poor absorption of nutrients or, more likely, from the inability of the parents to adequately provide for the nutritional needs of their offspring. Furthermore, natural stresses including food shortages may enhance the toxicity of mercury (Wren *et al.* 1987). Van der Molen *et al.* (1982) found an association between high mercury concentrations and poor nutritional condition in fledged grey herons. Inorganic mercury added to the drinking water of chickens caused decreased growth rate (Grissom and Thaxton 1985). Anorexia was observed in pigeons fed methylmercury (Evans and Kostyniak 1972). Mallard ducks fed methylmercury and their offspring showed both behavioral changes such as laying eggs outside of the nest and decreased responsiveness to adult calls by ducklings (Heinz 1979). Such behavioral changes potentially could result in less food delivered to nestling wading birds. An association between mercury contamination and chronic disease causing death was determined in some of the great white herons included in the present study (Spalding *et al.* in press).

All of the birds included in this study were found deceased, injured, or terminally ill when collected. As a result, it was not possible to compare these results with those of living birds to determine whether mercury may have contributed to morbidity and mortality. Hoffman and Curnow (1979) suggested that mercury did not contribute to mortality in the great blue heron nestlings collected in their study because concentrations were greater in birds collected alive than those found deceased. Hepatic mercury concentrations reported by Hoffman and Curnow (1979) ranged from 0.56 to 2.31 μg/g (median = 0.96 μg/g) in nestling great blue herons compared to values of 0.21 to 7.33 μg/g (median = 1.10 μg/g) in the present study. However, mercury concentrations in great egret nestlings were greater in the present study (0.18–18.84 μg/g, median = 0.86 μg/g) compared to those reported by Hoffman and Curnow (0.26–1.13 μg/g, median = 0.55 μg/g).

It has been estimated that the wading bird population has decreased by 90% in southern Florida (Robertson and Kushlan 1984). Although much of this decline can be attributed to loss of habitat and changing hydroperiods, recent attention has focused on the impact of mercury on wading birds and other high level aquatic feeders (Jurczyk 1993). In a risk assessment of the impact of mercury on five indicator species (largemouth bass, great egrets, raccoons, panthers, and alligators), great egrets were placed at the highest risk of adverse health effects (Jurczyk 1993). Scheuhammer (1991) reported that neurologic signs are typically associated with liver mercury concentrations of 30 μg/g in birds in general. He did not indicate whether there were species differences in susceptibility to the neurotoxic effects of mercury. In the present study four birds, all great blue herons and all from Area 3, had hepatic mercury concentrations at or above 30 μg/g. Tissue mercury concentrations associated with significant reproductive impairment are typically much lower than those causing overt neurologic impairment (Scheuhammer 1991). Reproductive success in captive ducks can decrease by 35–50% through dietary ingestion of mercury at

concentrations insufficient to cause neurologic signs (Heinz 1974). Hepatic mercury concentrations of 2–12 μg/g in adult pheasants and mallard ducks were associated with egg shell thinning and decreased hatchability (Fimreite 1971; Heinz 1976). If ciconiiform birds are as sensitive to the reproductive effects of mercury as are pheasants or ducks, the data presented in this paper suggest that wading bird populations in southern Florida are at imminent risk of further declines. However, other studies have failed to demonstrate an effect of mercury on egg shell thickness (Eisler 1987). Of the 144 birds in the present study, 45 (31%) had hepatic mercury in excess of 2 μg/g whereas 11 (7.6%) had liver mercury concentrations greater than 12 μg/g. Considering only those birds of potential breeding age (fledgling and young adults), 67% had liver concentrations above 2 μg/g, and 24% had concentrations greater than 12 μg/g. In the central Everglades and eastern Florida Bay (Area 3) where mercury concentrations were significantly greater than in the other collection areas, 80% of potential breeding-age birds had hepatic mercury concentrations in excess of 2 μg/g and 30% had concentrations greater than 12 μg/g.

It is estimated that the nesting wading bird population in Florida has declined to 10% of its original size (Runde 1991). The effects on reproduction of constant low-level exposure of wading birds to mercury in the diet may be mediated primarily through changes in reproductive behavior rather than the direct toxic effects on fertility, embryonic development or hatchling viability (Scheuhammer 1991). A recent quantitative risk assessment indicates that the great egret population in southern Florida is suffering a decrease in reproductive success due to the effects of mercury in the food supply (Jurczyk 1993). The risk assessment was based on the assumptions that great egrets weighing 1 kg consume 195 g of prey per day, the diet is composed of small fish (75%) and crayfish (25%), the average concentration of mercury in small fish and crayfish in the Everglades is 0.72 μg/g and 2.4 μg/g, respectively, all mercury in prey items is present as methylmercury, and methylmercury is 100% bioavailable following ingestion. Based on these assumptions, great egrets would be expected to consume a daily dose of 0.233 mg mercury. For the risk model, Jurczyk (1993) selected a Lowest Observable Adverse Effect Level (LOAEL) for mercury of 0.059 mg/kg/day based on the dose required to produce adverse reproductive effects in loons as reported by Scheuhammer (1991). Jurczyk concluded that great egrets are consuming mercury at a daily rate of 3.9 times the LOAEL thus placing the population at risk of mercury-induced adverse reproductive effects. Jurczyk performed similar risk assessments for largemouth bass, raccoons, Florida panthers, and American alligators inhabiting the Everglades. Great egrets were considered to be at greatest risk of adverse health effects than any of the other species studied. The data reported in the present study provide additional evidence in support of this conclusion.

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Inputs and outputs of mercury from terrestrial watersheds: a review

D.F. Grigal

Abstract: This review focuses on mercury (Hg) inputs and outputs in temperate and boreal terrestrial systems. It covers deposition via throughfall and litterfall, whose sum (ca. 38 μg m^{-2} a^{-1}) is greater than that via precipitation (ca. 10 μg m^{-2} a^{-1}). Outputs considered include volatilization, soil sequestration, and streamflow. The former is highly uncertain, but the mean rate (11 ng m^{-2} h^{-1}) over a growing season is equivalent to about 32 μg m^{-2} a^{-1}. Modern rates of soil sequestration (ca. 5 μg m^{-2} a^{-1}) and streamflow fluxes (ca. 2 μg m^{-2} a^{-1}) balance the annual budget. The majority of the uncertainty in the budget is related to volatilization. Nonetheless, a large fraction of atmospheric Hg is likely a product of continuing deposition and volatilization. Watershed characteristics related to streamflow fluxes of both Hg and methylmercury (MeHg) are discussed. Both runoff concentration and flux of Hg are weakly and inversely related to watershed size. Dissolved organic carbon (DOC) and particulates are important carriers of Hg; watershed activities that affect either affect Hg flux. Runoff flux of MeHg is skewed with about 80% of observations less than 0.15 μg m^{-2} a^{-1}. Although there is no pattern of MeHg flux with watershed size, there is a strong positive relationship between flux and wetland area. Wetlands are a site of MeHg production and their presence increases water residence time; both increase MeHg flux. Concentrations of MeHg in streamflow from watersheds with wetlands are near the current water quality criterion, and effective control measures in those watersheds appear problematic.

Key words: deposition, non-point pollution, methylmercury, wetlands, dissolved organic carbon (DOC).

Résumé : Cette revue porte sur les entrées et sorties de mercure (Hg) dans les systèmes boréaux et tempérés. Elle couvre les dépositions via la canopée et la chute des litières, dont la somme (ca. 38 μg m^{-2} an^{-1}) est plus grande que la précipitation au sol (ca. 10 μg m^{-2} an^{-1}). Les sorties prises en compte incluent la volatilisation, la séquestration au sol et le lessivage. Ce dernier est très peu certain, mais le taux moyen (11 ng m^{-2} h^{-1}) au cours d'une saison de croissance est l'équivalent de 32 μg m^{-2} an^{-1}. Les taux modernes de séquestration au sol (ca. 5 μg $m^{-2}an^{-1}$) et les flux par lessivage (ca. 2 μg m^{-2} an^{-1}) balancent le budget annuel. La majeure partie de l'incertitude dans le budget implique la volatilisation. Néanmoins, une forte proportion du Hg atmosphérique résulte vraisemblablement de dépositions et de volatilisations continues. On discute les caractéristiques des bassins versants reliées aux flux de lessivage du Hg aussi bien que du mercure méthylé (MeHg). La teneur du ruissellement ainsi que le flux de Hg sont faiblement et inversement reliés à la dimension du bassin versant. Le carbone organique dissout (DOC) et les particules sont d'importants vecteurs du Hg, et les activités des bassins versants qui les affectent, affectent également le flux de Hg. Le flux par ruissellement du MeHg est biaisé, avec environ 80 % des observations inférieures à 0.15 μg m^{-2} an^{-1}. Bien qu'il n'y ait pas de

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patron de flux du MeHg selon la dimension du bassin de drainage, il y a une forte relation positive entre le flux et la surface de terrain humide. Les terres humides constituent un site de production de MeHg et leur présence augmente le temps de résidence de l'eau; les deux augmentent le flux de MeHg. Les teneurs en MeHg dans les ruisseaux provenant de bassins versants bordés de terres humides rencontrent les critères usuels de qualité de l'eau, et les mesures correctives efficaces dans ces bassins versants apparaissent problématiques.

Mots clés: déposition, pollution non-ponctuelle, mercure méthylé, terres humides, carbone organique dissout (DOC).

Introduction

Mercury (Hg) occurs in two oxidation states in environmental media: Hg^0 (metallic, Hg(0)) and Hg^{2+} (mercuric, Hg(II)). Under ordinary conditions, Hg(0) vaporizes readily and is easily transported in the atmosphere. Natural sources of Hg to the atmosphere include degassing of the earth's crust through volcanos and diffusion from ore bodies (Nriagu 1979). Human activities such as mining and associated smelting, burning of fossil fuels, and industrial uses of Hg in chloralkali plants, paints, batteries, medicine, and dentistry have significantly increased the global reservoir of atmospheric mercury since the beginning of the industrialized period (Fitzgerald et al. 1998). This Hg is widely distributed via atmospheric processes, and deposition from the atmosphere to terrestrial and aquatic systems, even those in remote areas, has led to the recognition of Hg as a toxic global pollutant (Fitzgerald et al. 1998; Jackson 1997).

Aquatic systems are considered most sensitive to Hg toxicity, with nearly all concern directed at methylmercury (MeHg). It can be concentrated more than a million-fold in the aquatic food chain. It can cross the barrier that normally protects the brain from toxins in the blood stream and is a potent neurotoxin, penetrating the placenta and exposing the fetus. Point sources are important in delivering Hg to aquatic systems, but atmospheric Hg deposition, either directly to the aquatic system or indirectly via deposition to terrestrial watersheds and its subsequent transport, is also significant (Fitzgerald et al. 1998; Schroeder and Munthe 1998). Fish far from obvious sources of Hg emissions have been found to have MeHg levels of concern to human health (U.S. EPA 1997), leading to fish consumption guidelines and health advisories in Scandinavia, North America, and elsewhere. For example, 35 states in the U.S.A. have at least one waterbody under an Hg advisory, and six states have statewide advisories (U.S. EPA 1997). Although nearly all Hg in fish is MeHg (U.S. EPA 1997), the cycling of total Hg (HgT) is of concern because an important environmental source of MeHg is biological methylation, first shown by Jernelöv (Schroeder and Munthe 1998).

Regulation of pollutants in aquatic systems has historically emphasized point sources. More recently, non-point or diffuse sources have received increasing attention, as illustrated by the U.S. Environmental Protection Agency's concept of total maximum daily load (TMDL) (U.S. EPA 1999). Atmospheric deposition of Hg is a classic example of a non-point source of a contaminant. Although direct Hg deposition from the atmosphere can be important, terrestrial watersheds are the proximate source for most Hg in aquatic systems. Simply on an areal basis, terrestrial watersheds receive more Hg from the atmosphere than do aquatic systems. Between 5 and 25% of atmospheric Hg deposited on upland terrestrial basins reaches the associated lakes (Krabbenhoft and Babiarz 1992; Krabbenhoft et al. 1995; Lorey and Driscoll 1999; Swain et al. 1992), contributing between 5 and 85% of the total Hg loading depending on the terrestrial-to-lake surface area ratio (Krabbenhoft et al. 1995; Lindqvist et al. 1991; Lorey and Driscoll 1999; Swain et al. 1992). There is some evidence that the proportional contribution of Hg by terrestrial watersheds has increased as Hg loadings to the watersheds have increased with time (Lorey and Driscoll 1999).

The significance of the non-point contribution of Hg from terrestrial watersheds to aquatic systems depends on biogeochemical processes in the watershed, including deposition of atmospheric Hg, its storage in ecosystem components, its transfer among components, and its loss either as a gas or in solution. Although biogeochemical behavior of some non-point pollutants such as nitrogen and phosphorus

is fairly well understood in terrestrial watersheds, understanding of Hg behavior is incomplete. Fluxes of Hg both in and out of terrestrial watersheds can be as solids, liquids, or gases, and their measurement, especially of the gaseous pathways, is challenging. System pools usually are considerably larger than are fluxes so that uncertainties in their measurements leads to an inability to draw any firm conclusions about short-term trends in pool sizes and of fluxes influencing them. Elemental budgets of Hg in terrestrial systems are often "balanced" by an unmeasured residual term.

Although Hg contamination in remote areas is generally considered to be the result of atmospheric deposition (Fitzgerald et al. 1998), there is an opposing view that emphasizes the importance of natural geologic sources (Rasmussen 1994*a*). Part of the disagreement is based on conflicting reports of Hg concentrations and amounts. One of the keys to understanding Hg in the environment is cognizance of the level of technical sophistication required for analysis of the low levels of Hg found in many environmental media. Ultra-clean analytical approaches were rare before the mid-1980s, and hence reports published before that time must be approached cautiously (Fitzgerald et al. 1998). Some early techniques such as neutron activation analysis (Låg and Steinnes 1978) or radiotracers (Landa 1978*a*) have provided valid data.

This review will focus on Hg cycling, especially inputs and outputs, in terrestrial systems in the temperate and boreal zones. It will cover wet deposition and a detailed discussion of various forms of dry deposition that result in Hg in both throughfall and litterfall. Outputs considered include soil sequestration, volatilization, and losses in solution, primarily in streamflow. In the latter case, watershed characteristics that are related to fluxes of both Hg and MeHg will be discussed. The role of disturbance in altering Hg loss will also be evaluated. The data collected in the review will be synthesized to create a nominal input–output budget for Hg in terrestrial systems, and this budget will be related to both current concerns about Hg pollution of aquatic systems and to global Hg cycling.

There will be no attempt to review all papers on the topic; the literature is very large and continues to grow. Instead, the emphasis will be on representative studies and especially those focused on watersheds that are not near point sources of atmospheric Hg. Most research has been carried out on forested watersheds, but available data from other land uses, such as agriculture, will also be included. Information from studies in systems with high concentrations and contents of Hg, usually as a result of industrial activity, will be included only where relevant. Because of the plethora of reports, in many cases data will be aggregated from pertinent reviews rather than from original literature.

Histograms have been used to summarize the literature, providing a succinct description of the data, including its central tendency and variability. Many distributions are skewed and are often lognormal, and the geometric mean is used as a more appropriate measure of central tendency than the arithmetic mean. If distributions are more nearly normal, the geometric and arithmetic means are numerically similar. Some empirical relationships have been developed. These may reflect an underlying mechanism or principle or may simply reflect a coincidence of numbers. The authenticity of general trends that transcend sites and dates, albeit with high uncertainty, gains credibility when the plethora of other factors that influence the individual response of a unique site or date is considered. In all cases, however, such relationships should be considered to be hypotheses and not facts.

Inputs

Atmospheric concentrations

The three major Hg species in the atmosphere are elemental Hg(0) in the vapor phase, gaseous inorganic Hg(II) compounds (also termed reactive gaseous Hg; RGM), and particulate-phase Hg (Hg(p)) (Shroeder and Munthe 1998). Elemental Hg is capable of being aerially transported for tens of thousands of kilometres from its source, Hg(II) for a few tens to hundreds of kilometers, and Hg(p) at intermediate distances depending on particulate size and mass (Schroeder and Munthe 1998). Nearly all the Hg in the atmosphere occurs as Hg(0) (>95%), but the relative amounts of Hg species can be altered by oxidation–reduction reactions (Iverfeldt and Lindqvist 1986; Munthe 1992; Munthe et al. 1991). Total

gaseous Hg (TGM) concentrations over the open ocean show a general linear increase from south to north from about 1 ng m^{-3} at 40°S to about 2.2 ng m^{-3} at 45°N (data from Fitzgerald and Mason (1996)). Concentrations over land are similar although somewhat higher (Gill et al. 1995; Iverfeldt et al. 1995; Kvietkus et al. 1995; Lindberg et al. 1992; Schroeder 1994; Schroeder et al. 1995) and are influenced by both location, such as distance to point sources, and methodological issues, such as season of sampling, the period of time over which a sample was collected, and the number of observations included in a reported value.

There is some evidence for a long-term decrease in TGM and hence related decreases in deposition to terrestrial surfaces. There has been about a 2% decline per year in TGM on the west coast of Sweden over the period 1980 to 1992, and more recent observations are more nearly normally distributed compared to earlier lognormal distributions, implying fewer episodes of high TGM (Iverfeldt et al. 1995). Wet deposition of HgT has declined even more, about 7% per year (Iverfeldt et al. 1995). These declines are consistent with declines in Hg concentrations in ryegrass leaves (*Lolium multiflorum*), used as a biological monitor for Hg deposition in south Sweden, of about 10% per year over the period 1990 to 1994 (Xiao et al. 1998).

Atmospheric concentrations of Hg(p) are about two orders of magnitude lower than those of TGM (Guentzel et al. 1995; Keeler et al. 1994; Keeler et al. 1995; Lamborg et al. 1994; Lamborg et al. 1995). Because Hg(p) is subject to both washout by precipitation and dry deposition, its low atmospheric concentrations are not indicative of the role it can play in creating regional patterns of Hg deposition. Such patterns depend on both the size and mass of the particulates (Schroeder and Munthe 1998), precipitation frequency (for washout), and the nature of the receiving surface (for dry deposition). All these variables make the role of Hg(p) in total Hg deposition very site-specific.

Precipitation

Although atmospheric Hg is dominated by Hg(0), gaseous Hg(II) is much more soluble and is the dominant form in precipitation (Fitzgerald and Mason 1996; Porcella 1994). In a global pattern similar to that of atmospheric TGM concentrations, Hg concentration in precipitation over land generally increases from south to north (Mason et al. 1994). Although Hg deposition in precipitation depends on both volume and Hg concentration, it follows a trend similar to that of concentration (Mason et al. 1994). These generalized trends obscure a great deal of variation. Both gaseous and particulate forms of Hg(II) may contribute to the regional differences in wet deposition in spite of the well-mixed atmospheric load of Hg(0) (Fitzgerald and Mason 1996). Although concentrations of Hg in precipitation vary widely, from less than 1 to more than 1000 ng L^{-1} (Downs et al. 1998), the extremes are likely due to variation associated with sampling over short time periods or with samples collected near point sources of Hg.

A compilation of reports from unpolluted North Temperate areas indicates that most volume-weighted annual average concentrations of HgT in precipitation are in the range of 5 to 20 ng L^{-1}, with a mean of 16 ng L^{-1} (Fig. 1). Annual precipitation does not vary widely over most areas where Hg has been studied in terrestrial watersheds because most are forested and in temperate or boreal zones. The distribution of reports of wet deposition of Hg (Fig. 2), therefore, looks similar to that of precipitation concentration (Fig. 1), with about 60% of observations in the range of 5 to 15 μg m^{-2} a^{-1} and a mean of 10 μg m^{-2} a^{-1}. The average concentration of MeHg in precipitation is about 1% of that of HgT (Downs et al. 1998; Fitzgerald et al. 1994; Hultberg et al. 1994; Iverfeldt et al. 1996; Lamborg et al. 1995; Meuleman et al. 1995; Munthe et al. 1995; Schwesig and Matzner 2000; St. Louis et al. 1995), as is its average reported wet deposition (Driscoll et al. 1998; Fitzgerald et al. 1994; Hultberg et al. 1994; Iverfeldt et al. 1996; Lamborg et al. 1995; Lee et al. 2000; Munthe et al. 1995; Rudd 1995; Schwesig and Matzner 2000; St. Louis et al. 1995; St. Louis et al. 1996). Loadings of MeHg in wet deposition in Scandinavia, especially from the Gårdsjön watershed in southern Sweden, are at the high end of the distribution and are related either directly or indirectly to industrial activity (Rudd 1995). Variations in MeHg to HgT ratios in inputs to watersheds are not related to variations in ratios in streamflow (Lee et

Fig. 1. Volume-weighted mean annual Hg concentration in precipitation reported in studies from Ontario (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), northern U.S.A. (Burke et al. 1995; Glass and Sorensen 1999; Hoyer et al. 1995; Kolka et al. 1999*a*; Lamborg et al. 1995), Florida (Guentzel et al. 1995), Siberia (Meuleman et al. 1995), central Europe (Schwesig and Matzner 2000), and Scandinavia (Jensen and Iverfeldt 1994; Munthe et al. 1995) ($n = 54$).

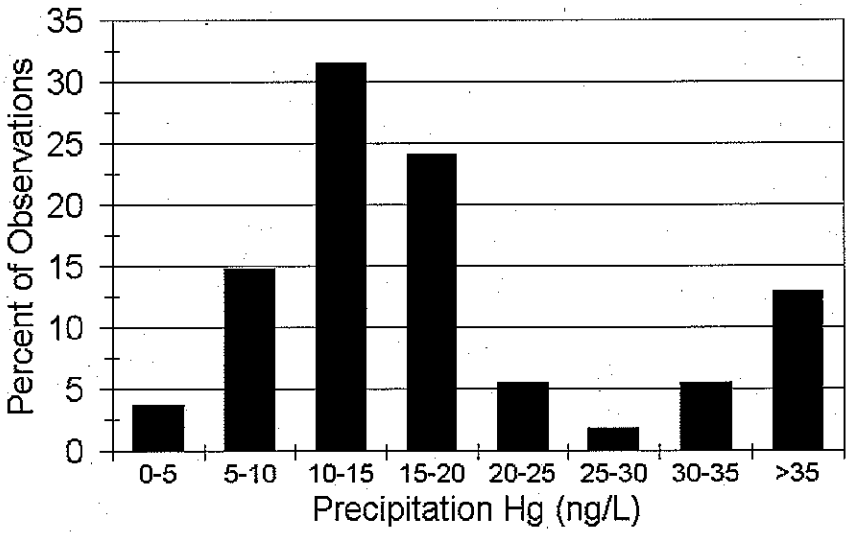
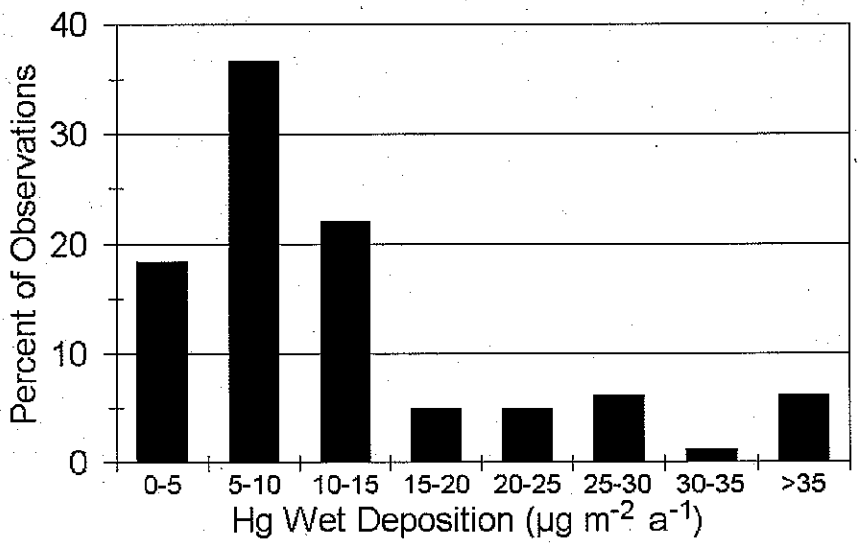
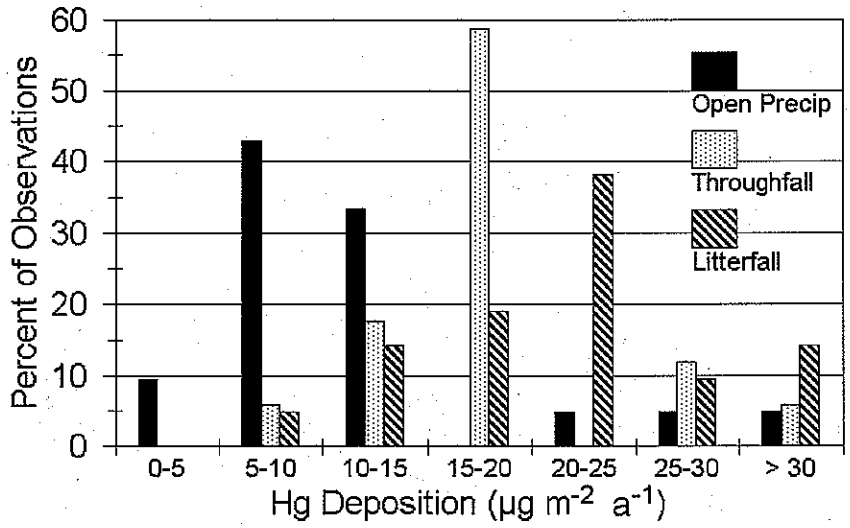


Fig. 2. Annual wet deposition of Hg to terrestrial systems reported in individual studies from Ontario (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), northern U.S.A. (Burke et al. 1995; Fitzgerald et al. 1994; Glass and Sorensen 1999; Hoyer et al. 1995; Kolka et al. 1999*a*; Lamborg et al. 1995), Florida (Guentzel et al. 1995), central Europe (Schwesig and Matzner 2000), Scandinavia (Iverfeldt 1991*a*; Jensen and Iverfeldt 1994; Lee et al. 2000; Munthe et al. 1995), and as tabulated by Jensen and Iverfeldt (1994) and Kolka (1996) ($n = 82$).



al. 2000; Schwesig and Matzner 2000); differences in MeHg loadings are not as important to terrestrial as to aquatic systems.

Fig. 3. Annual deposition of Hg in open field precipitation, via throughfall, and via litterfall in forests in studies from Scandinavia (Driscoll et al. 1994*a*; Iverfeldt 1991*b*; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1995), central Europe (Schwesig and Matzner 2000), and the U.S.A. (Grigal et al. 2000; Guentzel et al. 1998; Kolka et al. 1999*a*; Lindberg 1996; Rea et al. 1996).



Dry deposition

Dry deposition, deposition to surfaces during precipitation-free periods, also contributes atmospheric Hg to terrestrial systems. About 25% of total Hg deposition directly to lakes in north central Wisconsin, U.S.A., was dry deposition of Hg(p) (Lamborg et al. 1995). Because of the large area of receptor surfaces, dry deposition of Hg is much more important in forests. Fluxes in throughfall, water reaching the ground under forest canopies during precipitation, have been used to directly estimate total wet plus dry deposition for atmospheric constituents such as the Na^+ cation and SO_4^{-2} anion (Johnson and Lindberg 1992). These estimates can be used if precipitation quantitatively removes previously deposited material and if foliar leaching of internal plant sources of the material is negligible (Lindberg et al. 1994). These conditions, but especially the latter, are satisfied in the case of Hg. Substantially more total Hg is deposited as throughfall in forests than is reported in open precipitation (Fig. 3). The ratio of the geometric means of inputs via throughfall (17 $\mu g\, m^{-2}\, a^{-1}$) to those from open precipitation (9.7 $\mu g\, m^{-2}\, a^{-1}$) (Fig. 3) is 1.8, slightly greater than the 1.5 suggested by Munthe et al. (1995). Simply to use that ratio to estimate Hg deposition to forests, however, obviates some important details about the process.

First, throughfall is not merely wet deposition plus washoff of adsorbed Hg(p). Measurement of atmospheric Hg(p) and assumptions of reasonable velocities for its dry deposition lead to significant underestimates of Hg in throughfall (<10% of measured) (Lindberg et al. 1994; Rea et al. 1996). The most likely sources of Hg in throughfall are considered to be adsorption of gaseous Hg(II) and capture and oxidation of Hg(0) by the canopy (Lindberg et al. 1994). Secondly, the use of a simple ratio erroneously assumes that all forest canopies are identical in their role in Hg deposition via throughfall. The deposition of Hg to a forest via throughfall depends on both the efficiency of the canopy in capturing Hg, whether gaseous or particulate, and the characteristics of the canopy that influence volume of both throughfall and related stemflow (water flowing down the branches and the bole of the tree to reach the ground) (Helvey 1971). The influence of these relationships on Hg can be illustrated by contrasting annual throughfall deposition under a black spruce (*Picea mariana*) canopy (19.5 $\mu g\, m^{-2}\, a^{-1}$) compared to under an adjacent deciduous aspen (*Populus tremuloides*) canopy (9.3 $\mu g\, m^{-2}\, a^{-1}$) (Kolka et al.

1999*a*). These large differences presumably arose because of the greater efficiency of the more dense spruce canopy in trapping atmospheric Hg. The ratio of Hg deposition in throughfall to that in the open was 1.4 for aspen but 3.0 for spruce, very different from the overall ratio of 1.5 suggested by Munthe et al. (1995).

In the few studies that have reported both MeHg and HgT in open precipitation and throughfall, the average ratio of MeHg to HgT in open precipitation is about 1.5 times higher than that in throughfall (1.5 vs. 0.9 %, respectively). Ratios are highest and differences are greatest in coniferous forests in southern Sweden (3 vs. 1.2%, Munthe et al. 1995; Munthe et al. 1998), differences are virtually non-existent in coniferous forests in northern Sweden (about 1.7%, Lee et al. 2000), and ratios are slightly lower in open precipitation in both coniferous and deciduous forests in central Europe (0.4 vs. 0.5%, Schwesig and Matzner 2000). As stated earlier, variations in MeHg to HgT ratios in inputs to watersheds are not related to variations in ratios in streamflow (Lee et al. 2000; Schwesig and Matzner 2000). Other factors, to be discussed later, much more strongly affect the ratio in streamflow.

Litterfall

If adsorption of gaseous Hg(II) and capture and oxidation of Hg(0) by the canopy are likely sources of Hg in throughfall (Lindberg et al. 1994), and if Hg strongly binds to organic matter (Meili 1991), it is unlikely that all of the adsorbed Hg will be removed from the canopy during precipitation events. It is therefore logical that litterfall, dropping of senescent leaves, is a major pathway of Hg flux from the atmosphere to forested terrestrial watersheds.

Foliar uptake

The source of foliar Hg appears to be almost exclusively the atmosphere. Several greenhouse and laboratory studies have indicated that Hg uptake from soil is limited, with roots acting as a significant adsorption site for Hg and hence a barrier for its further transport to foliage (Beauford et al. 1977; Godbold and Hüttermann 1988; Hogg et al. 1978*a*; Lindberg et al. 1979; Mosbæk et al. 1988; Rao et al. 1966). These studies are consistent with field observations. For example, foliar concentrations of Hg in red pine plantations were inversely related to Hg in soil, but positively related to length of the growing season and hence duration of plant physiological activity (Fleck et al. 1999), implying Hg uptake from the atmosphere rather than from soil. Similarly, although positive relationships were reported between Hg concentrations in the atmosphere and pine needles in an Hg mining area, no relationship existed between Hg concentrations in needles and roots, implying soil was not the source of the Hg (Barghigiani et al. 1991). Calculations based on annual transpiration and soil water Hg concentrations indicate that $<10\%$ of annual Hg deposition in litterfall is likely due to root uptake and subsequent sequestration in leaves (Johnson and Lindberg 1995; Lindberg 1996), and measurement of HgT and MeHg concentrations in xylem sap in mature spruce and pine in Sweden indicate that only about 10% of HgT and about 3% of MeHg in litterfall could be accounted for by root uptake and sequestration (Bishop et al. 1998).

Foliar uptake of Hg presumably occurs through open stomata, with subsequent binding and oxidation of the Hg(0) (Du and Fang 1982). Experimental data with graminaceous plants indicated that uptake of Hg(0) was not limited by stomatal resistance, but by the binding and oxidation step described by a residual term, mesophyll resistance (Du and Fang 1982). Modeling of Hg deposition to the surface of a forest canopy confirmed that mesophyll resistance dominated exchange (Lindberg et al. 1992). As a result, simple analogies of Hg(0) uptake with that of other common gases such as O_3, SO_2, and NO_2 are inappropriate (Lindberg et al. 1992). Another potential source of Hg is RGM (Stratton and Lindberg 1995). Because of its high deposition velocity, this Hg species would accumulate in foliage (Barton et al. 1981; Guentzel et al. 1998).

There is also evidence that foliar emission of Hg occurs. Maintaining Hg(0) atmospheric concentrations near ambient levels in gas exchange chambers, Hanson et al. (1995) observed that foliar exchange of Hg(0) was balanced around a critical atmospheric concentration or compensation point, with uptake

occurring at concentrations above that point and emissions below that point. The compensation point was species specific, but it ranged from about 10 to 25 ng m^{-3} for tree seedlings, considerably higher than observed average atmospheric TGM concentrations. Lindberg (1996) has measured substantial emissions of gas-phase Hg(0) from the forest canopy and suggested that the source is transport of the gas from soil to leaves via the transpiration stream. The very low solubility of Hg(0) in lakewaters and sediment porewaters, albeit up to 50 times higher than atmospheric concentrations (Lindqvist et al. 1984; Vandal et al. 1995; Watras et al. 1994; Watras et al. 1995), makes that source unlikely to lead to significant Hg(0) efflux, <0.2 $\mu g\ m^{-2}\ a^{-1}$. Siegel et al. (1974) also measured volatile Hg loss from vascular plant leaves at room temperature, but this was neither MeHg nor dimethyl Hg, nor was it gas-phase Hg(0). Fluxes from the canopy appear to be under stomatal control.

Although foliar emissions of Hg may occur, evidence is overwhelming that foliage is a net sink for atmospheric Hg. In conifers, Hg concentrations increase with needle age (Barghigiani et al. 1991; Bombosch 1983; Fleck et al. 1999; Rasmussen 1995), and in both coniferous (Rasmussen 1995) and deciduous trees (Lindberg 1996), Hg concentrations also increase over the growing season. As a general rule, conifer needles tend to have higher concentrations than deciduous leaves from trees at same location, perhaps because conifer collections usually include older needles (Rasmussen et al. 1991). There is also the suggestion that plants of lower stature have higher concentrations than trees from the same location (Rasmussen et al. 1991). This would be consistent with foliar uptake from a soil source of gaseous Hg(0) (Lindberg et al. 1992). Concentrations of Hg in non-vascular plants (mosses, fungi, and lichens) are nearly an order of magnitude higher than those in vascular plants (Moore et al. 1995). Whether these higher concentrations are related to increased adsorption of atmospheric Hg(0) or of soil-based gaseous Hg(0) is unclear.

Flux

Both the quantity of litterfall and its Hg concentration are important in affecting inputs to forested watersheds. Firstly, litterfall mass in forests has a strong positive relationship with actual evapotranspiration (AET) (Meentemeyer et al. 1982), an index of growing season length and quality. Forests in areas with longer growing seasons are likely to have both a greater quantity of litterfall and higher Hg litter concentrations as a consequence of a longer period of foliar uptake. Secondly, there are great contrasts in foliar concentrations of Hg, apparently depending upon atmospheric concentrations and differences in uptake efficiency. Although there is a general increase in Hg concentration with needle age, concentrations in needles from central Europe are much higher than those in needles from relatively remote North American sites (Barghigiani et al.1991; Bombosch 1983; Fleck et al. 1999; Rasmussen 1995). For example, in a Hg mining area in Italy, pine needle Hg concentrations were up to 4000 $\mu g\ kg^{-1}$, associated with TGM concentrations of 600 ng m^{-3} (Barghigiani et al. 1991). Most reported tree foliar concentrations are much lower, with the majority in the range 10 to 50 $\mu g\ kg^{-1}$ and a mean of those reports near the midpoint of that range (24 $\mu g\ kg^{-1}$) (Barghigiani et al. 1991; Bombosch 1983; Fleck et al. 1999; Grigal et al. 2000; Lindberg 1996; Moore et al. 1995; Rasmussen et al. 1991; Rasmussen 1994*b*; Rasmussen 1995; Zhang et al. 1995). Leaves in litterfall have concentrations 1.5 to 2 times those reported in foliage (Grigal et al. 2000; Lindberg 1996; Rea et al. 1996) because of Hg accumulation over the entire growing season compared to foliage collected near the midpoint of the season. Litterfall includes not only leaves but also bark, twigs, reproductive parts, and other overstory components; an average of about 70% is leaves (Meentemeyer et al. 1982). Concentrations of Hg in the other litterfall components have been rarely reported but can be much higher than in leaf litter (Grigal et al. 2000).

There is a consistent trend of higher inputs of Hg via litterfall than via either open precipitation or throughfall (Fig. 3). In co-located studies, the ratio of the mean annual Hg wet deposition in the open (9.7 $\mu g\ m^{-2}\ a^{-1}$), that in throughfall (17 $\mu g\ m^{-2}\ a^{-1}$), and that in litterfall (21 $\mu g\ m^{-2}\ a^{-1}$) (Fig. 3) is 1:1.8:2.2, not greatly different than the ratio of 1:1.5:3 suggested by Munthe et al. (1995). As explained earlier, however, those overall ratios of means may obscure many important differences

within and among sites. Atmospheric deposition of Hg to lakes is much less than that to forests in the same geographic location because the lakes lack the forest canopy and hence those surfaces for both dry deposition and foliar uptake. Deposition of Hg to lakes ranges from approximately equal to about 25% higher (Lamborg et al. 1995) than wet deposition in the open (Fig. 2), or only about one-fourth that of Hg deposition to forests (sum of throughfall and litterfall). Deposition to vegetation of low stature, such as to grasslands, is likely to be intermediate between that to lakes and to forests because of differences in total surface area for interception, but data are rare. Dry particulate deposition of Hg over an open field in Ontario, Canada, was non-detectable, but based on a limited number of vertical profiles deposition of RGM to vegetation was estimated as 40 to 110 $\mu g\ m^{-2}\ a^{-1}$, 1.5 to 3.5 times greater than wet deposition (Barton et al. 1981). Similarly, using grass as a bioindicator, annual dry deposition in southern Sweden was estimated to be 42 $\mu g\ m^{-2}\ a^{-1} \pm 40\%$ (Xiao et al. 1998), higher than most estimates of Hg deposition via litterfall (Fig. 3). The high uncertainty of both these estimates does little to clarify the question of Hg deposition to low-stature vegetation.

Litterfall may also be a source of MeHg to terrestrial ecosystems, either of atmospheric origin or produced in the plants (Rudd 1995). In northwestern Ontario, Canada, tree and shrub leaves had a low ratio of MeHg to HgT (1.1%, Moore et al. 1995). In the few studies that have reported both HgT and MeHg in litterfall, it appears that the average ratio of MeHg to HgT is nearly identical to that in open precipitation (1.5%) (Lee et al. 2000; Munthe et al. 1995; Munthe et al. 1998; Schwesig and Matzner 2000), but is higher than that in throughfall (0.9%). Because the ratio in precipitation and litterfall is so similar, an atmospheric origin of MeHg is more likely than is production within the plants. Higher ratios in litterfall than in throughfall can also lead to an inference that vegetation may preferentially adsorb MeHg as compared to HgT. As in many cases, the average obscures some important differences among sites. In some locations, the ratio of MeHg to HgT in litterfall was nearly twice that in open precipitation (1.7 vs. 1.1%, Lee et al. 2000; 0.8 vs. 0.4% , Schwesig and Matzner 2000), while in others the ratio was higher in open precipitation than litterfall (3 vs. 2.4%) and both ratios were higher than in throughfall (1.2%) (Hultberg et al. 1995). Litterfall does contribute MeHg to watersheds, but usually as a small proportion of HgT.

Summary

Deposition of Hg by direct precipitation in the open in unpolluted North Temperate areas is the range of 5 to 15 $\mu g\ m^{-2}\ a^{-1}$ (60% of observations) with an overall mean of 10 $\mu g\ m^{-2}\ a^{-1}$. Atmospheric deposition of Hg to forests is about four times open precipitation (38 $\mu g\ m^{-2}\ a^{-1}$) because of additions via throughfall, washoff of dry deposition, and litterfall, dropping of senescent leaves that have accumulated atmospheric Hg. Atmospheric deposition of Hg to lakes is only about one-fourth that to forests in the same geographic area because the lakes lack the forest canopy and hence surfaces for both dry deposition and foliar accumulation. Deposition of MeHg is only about 1% of HgT deposition, and variations in ratios of MeHg to HgT in deposition do not appear to be related to variations in ratios in streamflow from watersheds.

Outputs

Loss of Hg from terrestrial ecosystems can be either as a gas or in solution. The first pathway has implications for Hg in the atmosphere, including concentrations and deposition to other systems, while the latter has implications for aquatic systems and human health. The strong binding of Hg to organic matter, including dissolved organic matter (DOM) (or dissolved organic carbon (DOC)) in waters and soil organic matter (SOM), is critically important to its behavior in the environment (Meili 1991). Although ligands such as OH^- and Cl^- have some theoretical importance, in most cases "It is mainly the physical fractioning of soil organic matter (dissolved vs. adsorbed) that determines the behavior and distribution of Hg in soils." (Schuster 1991), and "... chloride complexation is not quantitatively important ... in most soil and fresh water systems ..." (Skyllberg et al. 2000). It is generally acknowledged, then, that

"Studies at the watershed level have shown that Hg^{2+} is the predominant form of Hg in soils and surface waters and that it is associated with organic substances." (Skyllberg et al. 2000). The binding of Hg to organic matter appears to be exclusively associated with reduced S groups whose concentration in natural systems is high enough to bind all Hg(II) (Xia et al. 1999; Skyllberg et al. 2000).

Volatilization

Because of the relatively high vapor pressure of Hg(0) at ambient conditions, Hg can be lost from terrestrial watersheds by volatilization. Most research has emphasized loss from soils, where volatilization is presumed to require three steps, reduction of Hg(II) to Hg(0), diffusion or mass transport of Hg(0) to the soil surface, and diffusion or mass transport of the Hg(0) across the soil–air boundary layer into the atmosphere (Zhang and Lindberg 1999). If Hg(0) is present in soil as a gas, in solution, or adsorbed, the first step is obviated. The reduction of Hg(II) can potentially be accomplished by both biotic and abiotic agents. In an adaptation to Hg toxicity, microbes can enzymatically reduce Hg(II) to Hg(0). This reduction is induced by toxic levels of Hg, and below the minimum Hg threshold concentration there is usually no induction and hence no reduction (Baldi 1997). Levels of Hg(II) found in uncontaminated environments are usually lower than that threshold (about 10 ng L^{-1} in solution, Morel et al. 1998). Microbial Hg reduction is also unlikely in anaerobic environments; presence of organic sulfides in such environments may strongly bind Hg, reducing its toxicity so that the microbial enzyme systems are not induced (Baldi 1997).

Both early and more recent laboratory work have shown that when Hg(II) is applied as salts to soils, a rapid loss of 10 to 30% of the Hg occurs within 10 to 15 days (Hogg et al. 1978*b*; Landa 1978*b*; Schlüter et al. 1995). The pattern of loss is a rapid initial rate followed by a sharp decline to low rates, suggesting an abiotic reduction mechanism because of lack of a lag phase characteristic of enzyme induction. The Hg(II) reduction has been attributed to a reaction with DOM in soil solution, with the rate decline attributed to the decreasing availability of Hg for reduction because of binding with SOM (Schlüter et al. 1995). Because of the much greater concentration of DOM than Hg(II) in soil solution, it can be described as a pseudo-first-order reaction with the rate linearly related to the Hg(II) concentration. Another potential agent of reduction is sunlight, either by direct photolysis of Hg compounds or by photolysis of other reactants that then reduce Hg(II) (Zhang and Lindberg 1999). Such reactions are unlikely in closed-canopy forests, but could be important in open agricultural areas. Because of the plethora of reactants and conditions in terrestrial environments, many other reduction reactions could also occur. In particular, wet areas in the landscape such as near stream channels or microtopographic depressions are usually strongly reducing environments and could provide conditions leading to significant Hg(II) reduction.

Many other factors can influence Hg volatilization. Both the vapor pressure of volatile Hg species and biotic or abiotic reaction rates are temperature dependent, and higher temperatures increase rates of Hg loss in the laboratory (Landa 1978*c*). Temperature dependence of volatilization in the field is more difficult to assess because of the interactions of temperature with other environmental factors. In general, however, highest rates of Hg volatilization have been reported in summer as compared to other seasons and during the day as compared to night (Schlüter 2000). In a boreal forest in Sweden, Hg that was deposited to the soil surface during the winter was apparently emitted or re-emitted during the remainder of the year (Schroeder and Munthe 1998). Similarly, Hg concentrations in the organic-rich aspen forest floor in Alberta, Canada, declined from high levels in spring following snowmelt through the summer to a minimum in August, and then increased in autumn, a time of both leaffall and cooler temperatures (Dudas and Cannon 1983). These observations could be interpreted as volatilization by higher summer temperatures of labile forms of Hg that were deposited during the winter. Finally, in portions of a peat core from an ombrotrophic bog in Spain that were deposited during periods of globally cool climate, up to 50% of the Hg was represented by Hg(0); in other parts of the core nearly all (>80%) Hg(II) was bound to organic matter (Martinez-Cortizas et al. 1999). The supposition was that cool temperatures

during peat formation retained the Hg(0), while warm temperatures led to volatilization of that species. All these data imply that a significant portion of Hg that is deposited on terrestrial landscapes may be extremely labile and that simply moderately warm temperatures are sufficient to volatilize that portion without any other mechanism being invoked.

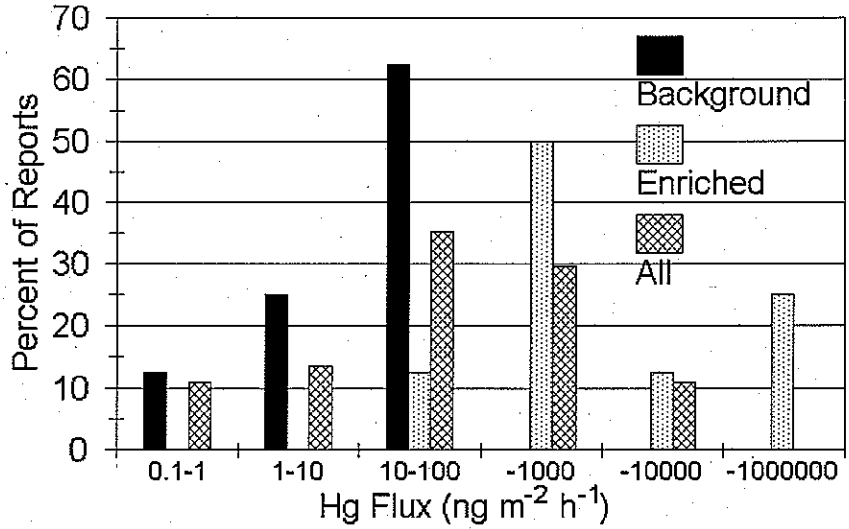
In addition to temperature, other soil properties also affect volatilization rates, including soil water content, pH, and clay and SOM content. In the laboratory, Hg losses from soils were maximized at field capacity compared to either air-dry or nearly saturated soils (Landa 1978*b*). Some field observations indicate increased rates of volatilization with increases in soil water content, such as following a rainfall event (Zhang and Lindberg 1999). This has been provisionally attributed to displacement of adsorbed Hg(0) by water molecules. The diffusion and mass transport of Hg(0) within the soil are affected by soil water. Saturation and filled soil pores would be expected to reduce both processes, whereas dry soils would be associated with higher transport rates. Reduction of Hg(II), however, may be inhibited in dry soils. Finally, as stated earlier, wet areas in the landscape could provide conditions leading to significant Hg(II) reduction. In general, Hg volatilization tends to increase with increase in soil pH (Schlüter 2000). Higher volatilization also seems to be associated with lower clay and SOM contents, associated both with lack of binding and therefore stabilizing sites for Hg(II) and with an increase in pathways for diffusion (Schlüter 2000). The movement of Hg(0) across the soil–air boundary layer into the atmosphere also depends on environmental conditions such as barometric pressure (or its change), wind speed, and turbulence (Kim et al. 1997). Another complicating factor in determining the magnitude of volatilization from soil is the evidence that Hg(0) vapor is also adsorbed by soils. Experimentally, such adsorption was roughly correlated with soil carbon (C) content, and retention was predominantly by organo-complexes. Little adsorbed Hg was subsequently lost under ambient conditions (Landa 1978*a*). Although undocumented, a possibility exists that Hg(0) could also be adsorbed by the abundant charcoal found in some soils, remnants of historical fires. The balance between Hg(0) production and adsorption ultimately determines the net flux of Hg from soil.

As might be expected when so many factors potentially affect Hg volatilization, reports of rates vary widely and have high uncertainty, from <1 ng m^{-2} h^{-1} to about 90 000 ng m^{-2} h^{-1} (Fig. 4). In those reports, the mean for sites enriched in Hg through mining or other contamination is 1300 ng m^{-2} h^{-1}, while that for unenriched background sites is 11 ng m^{-2} h^{-1} (Zhang and Lindberg 1999). Lindberg (1996) reported net emission flux from the soil at Walker Branch Watershed, Tennessee, during spring, summer, and fall to be about 7.5 ± 7.0 ng m^{-2} h^{-1}. This net flux was the summation of periods of fluxes from the atmosphere to the soil and of emissions from the soil.

The potential of foliar exchange of Hg(0) around a compensation point (Hanson et al. 1995) was discussed earlier. Using best-available though uncertain data, and including gas-phase exchange of Hg(0) between the atmosphere and both the forest canopy and the soil, Lindberg (1996) estimated that atmospheric deposition of Hg to Walker Branch Watershed, Tennessee, on a summer day was only about one-third of the losses, the largest of which were canopy emissions of gas-phase Hg(0). The source of the additional Hg was either the soil pool or deposition during the dormant season when canopy emissions would be absent. This conclusion is tentative because of both the history of the site, near industrial sources of Hg, and high uncertainty in the measurements. Although measured throughfall and litterfall were nearly equivalent to estimated atmospheric deposition to the canopy, gasous emissions from the canopy had a coefficient of variation of ±80%. As mentioned earlier, the very low solubility of Hg(0) makes transport of the gas from soil to leaves via the transpiration stream puzzling. If, however, these emissions are generalizable to other forests, then they have a significant impact on global Hg budgets (Lindberg 1996). The complexity of gaseous Hg flux to and from both terrestrial and aquatic systems can be summarized, "Because of its persistence in the environment and its proclivity to cycle ... a large portion of the mercury in the atmosphere today may consist of recycled mercury stemming from previous releases from both natural and anthropogenic sources." (Schroeder and Munthe 1998, p. 818).

The dynamics of MeHg volatilization from soils differs from that of Hg(0) because of the greater

Fig. 4. Frequency distribution of reported rates of Hg flux by volatilization measured over terrestrial surfaces. Rates over *Background* and *Enriched* surfaces from Zhang and Lindberg (1999) (n = 8 in each case), rates over *All* surfaces from Schlüter (2000) (n = 37).



toxicity of the compound, its lower binding to SOM, but also because of its relatively low abundance. Concurrent work with Hg(II) added as $HgCl_2$ and MeHg added to soil as CH_3HgCl showed characteristics of biotically induced reduction in the loss of MeHg, including presence of a lag phase (Schlüter et al. 1995). More Hg was volatilized when applied as MeHg than as $HgCl_2$, but the results must be interpreted cautiously because rates of application exceeded natural levels by five to six orders of magnitude. Both greater rates of biotic detoxification of MeHg and the lower binding of MeHg to SOM were cited as reasons for the difference in volatilization of the two Hg compounds (Schlüter et al. 1995).

Solution losses

Soil solution and groundwater

Presence and transport of Hg in soil solution and groundwater, both in temperate (Aastrup et al. 1991) and tropical soils (Roulet and Lucotte 1995), is closely related to the presence and mobility of DOC or DOM. In general, Hg concentrations are very low in soil solution and groundwater, and Hg transport in lower soil horizons and groundwater is limited. For example, in a boreal landscape in Sweden with glacial till over bedrock, there was a general decrease in Hg concentration in soil solution from the surface (14 ng L^{-1}) to groundwater samples at 100 to 165 cm (7 ng L^{-1}) (Aastrup et al. 1991). Dominant soil solution flux was horizontal, not vertical, in this landscape, and over three-fourths of the downslope transport of Hg occurred in the upper 50 cm. Similarly, soil solution concentrations decreased from near 5.5 to about 3 ng L^{-1} from 20 to 70 cm in depth in the Gårdsjön watershed, Sweden (Lee et al. 1994). In Germany, Hg concentrations in mineral soil solution were below detection limits of 15 ng L^{-1}, but concentrations in groundwater in nearby peatlands were about 20 ng L^{-1} and solutions from the upland forest floor were highly variable but ranged up to 130 ng L^{-1} (Schwesig et al. 1999). Similar high near-surface Hg concentrations in soil water were reported from northern Sweden, where HgT declined with depth from about 150 ng L^{-1} at the surface to about 18 ng L^{-1} at 50 cm (Bishop et al. 1998). The nearly order of magnitude range in concentrations over shallow depths is striking. Low soil water concentrations have also been reported in hardwood stands in Tennessee, U.S.A., 5 ng L^{-1} at 5 cm depth (Lindberg 1996). Concentrations of Hg in deeper groundwater have not been widely

reported, but data from the north-central U.S.A. indicate that they are even lower than those in soil solution (2–4 ng L^{-1}, Krabbenhoft and Babiarz 1992; 1 ng L^{-1}, Grigal et al. 2000).

Even extreme laboratory situations have failed to find significant vertical transport of Hg through soil. For example, following a high rate of Hg application in simulated acid rain (about 50 and 400 years of annual deposition of $HgCl_2$ over about 20 days), the uppermost 1 to 2 cm of soil cores contained 85 to 96% of the applied Hg (Schlüter et al. 1995). Similarly, Hogg et al. (1978*b*) applied $HgCl_2$ to undisturbed soil cores and leached them with sewage effluent of relatively high pH (8.5) and high concentrations of cations and anions compared to waters in undisturbed systems. They failed to find movement of Hg below 20 cm, but other cations including Ca^{2+}, Mg^{2+}, K^{+}, and Zn^{2+} were progressively leached in a similar experiment. A variety of moderate extractants failed to remove the applied Hg; only 6 N HCl, which progressively dissolves inorganic colloids and hydrolyzes organic matter, was effective (Hogg et al. 1978*b*). There are reports of vertical Hg movement in the field, but also under extreme conditions. Fifteen years following a single application of sewage sludge containing 3000 to 5000 $\mu g\ kg^{-1}$ Hg to an agricultural site in New York, U.S.A., the surface soil layer (upper 20 cm) had an Hg concentration of 640 $\mu g\ kg^{-1}$ compared to about 150 $\mu g\ kg^{-1}$ in the control (McBride et al. 1999). Total HgT loading to the site had been extremely high, 4.5 kg Hg ha^{-1} ($4.5 \times 10^5\ \mu g\ m^{-2}$) (McBride et al. 1997). Concentrations of Hg in soil solution at 60 cm in the control were below detection limits compared to 130 ng L^{-1} at the treated site. The transport of several heavy metals, including Hg, was presumably enhanced by high DOM in the sludge leachate (McBride et al. 1999).

In conclusion, groundwater and soil solution that are low in DOM are also likely to be low in Hg so that vertical transport of Hg is minimal. However, a caveat must be attached to that conclusion. There is the possibility that Hg, with DOM, could be transported quite deeply in highly structured soils through preferential flow paths (Jardine et al. 1989*a*). This Hg could reach groundwater, at least during storms (Jardine et al. 1990). There is also evidence, however, that in most cases this DOM and presumably associated Hg will be adsorbed by the soil matrix as the solutions move through the soil (Jardine et al. 1989*b*). Similarly, although vertical Hg flux was minimal in moist peat soils, drying led to shrinkage of the soils, and resulting cracks provided pathways for significant Hg flux (Lodenius et al. 1987).

There are limited data on MeHg concentrations in soil solution, including groundwater. Similar to HgT, MeHg is low in groundwater, ranging from below detection limits of 0.02 ng L^{-1} (Krabbenhoft et al. 1995) to about 0.2 ng L^{-1} (Branfireun et al. 1996). Observations of higher MeHg concentrations in soil solution near the surface (e.g., Branfireun et al. 1996) imply that the major source of MeHg is via surficial or near-surface processes. Relatively high ratios of MeHg to HgT in soil solution have been reported at Gårdsjön, southern Sweden, with an average of about 21% of Hg present as MeHg and nearly identical ratios in both discharge and recharge areas (Lee et al. 1994). These ratios are driven by relatively low HgT concentrations (4 ng L^{-1}) associated with high MeHg concentrations (about 0.9 ng L^{-1}). In northern Sweden, concentration of both HgT and MeHg in soil solution declined with depth, with MeHg about 0.24 ng L^{-1} at the surface to about 0.01 ng L^{-1} at 50 cm (Bishop et al. 1998), and ratios of MeHg to HgT ranging from 0.05 to 0.2%, with a tendency for a decrease with depth (Bishop et al. 1998). In contrast with Gårdsjön, high HgT concentrations (geometric mean about 40 ng L^{-1}) were associated with low MeHg (geometric mean about 0.07 ng L^{-1}). The high ratio of MeHg to HgT at Gårdsjön may be due to high levels of atmospheric deposition of MeHg (Hultberg et al. 1994), but data from either organic surface horizons of mineral soils or organic horizons in a fen and bog in Germany show MeHg concentrations similar to those reported at Gårdsjön (1.2 ng L^{-1}) (Schwesig et al. 1999). Concentrations of HgT in Germany, however, were much higher (25 ng L^{-1}) and therefore ratios of MeHg to HgT were only about 5%. Reports from Ontario, Canada, did not include HgT, but MeHg concentrations were lower in recharge than in discharge areas (0.4 versus 1.8 ng L^{-1}) (Branfireun et al. 1996). In summary, both the HgT and the MeHg concentrations in soil water are highly variable, as is the resulting ratio between them. From the limited available data, the ratio of MeHg to HgT in soil water can be expected to range from about 0.15 to 15%.

Streamflow

Water flux

Loss of Hg by streamflow is controlled by water flux from terrestrial watersheds. Baseflow, streamflow between storm or snowmelt periods, represents outflow from groundwater aquifers that are recharged by percolating soil water. Baseflow would be expected to be low in Hg. Runoff, synonymous with stormflow, is water the origin of which is storms or snowmelt. Runoff is derived from channel precipitation, precipitation falling directly on the flowing stream; overland flow, precipitation that has reached the stream without infiltrating into the soil surface at any point; and interflow, subsurface stormflow that has moved through the soil during at least part of its journey to the stream (Hewlett 1982). Overland flow, produced when rates of precipitation or snowmelt exceed soil infiltration rates, leads to very sharp peaks and recessions of stream hydrographs and is often considered to be the dominant source of runoff (Horton 1933). Although overland flow occurs in agricultural soils, roads, lawns, parking lots, areas subject to livestock trampling, and similar situations (Dunne 1978), it has not been observed or described in undisturbed humid forested areas except under unique conditions (Chorley 1978; Dunne 1978; Hewlett 1982).

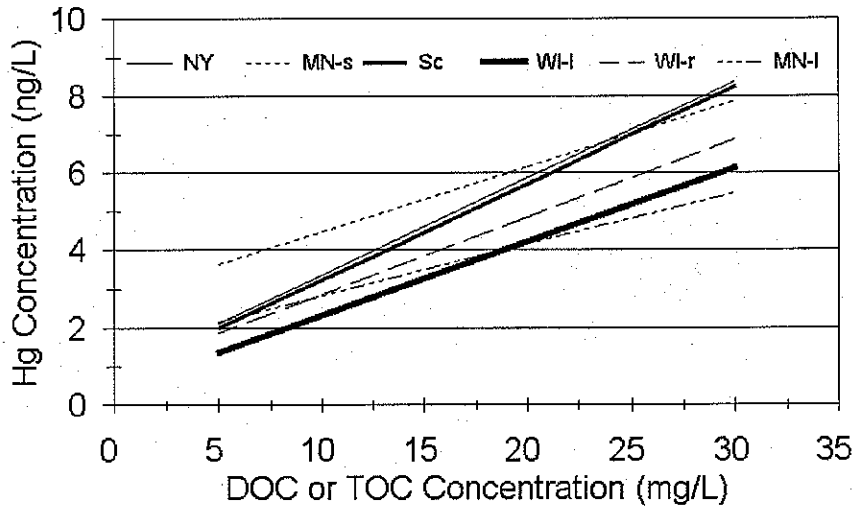
Interflow, common in humid forested watersheds, is caused by differential rates of vertical percolation through soil and may occur in more than one soil horizon (Hewlett 1982). The rapid stream response of many forested watersheds to storms is explained by preferential flow through soil macropores, which can occur even in very dry soils (Wilson et al. 1990), and by the development of a variable source area (Hewlett 1974). The variable source area is the part of the watershed that contributes to stormflow, varying in size with the storm and with antecedent conditions; entire watersheds do not contribute to stormflow. Many hydrologic characteristics of lower slope positions increase the importance of near-stream interflow (Helvey and Hewlett 1962). Interflow discharging directly into the stream bed increases streamflow, expands the stream channel network, and increases the size of the source area, often by overflowing temporarily flooded low areas (Hewlett and Nutter 1970). The concept of the variable source area is well established and has potential ramifications to Hg transport. Near-stream areas of the watershed are generally high in SOM and likely Hg and hence are sites where Hg–organic complexes will be mobilized to enter streams during storms. Because of high soil water content, these areas are also likely to have reducing conditions and be sites of both reduction of Hg(II) to Hg(0) and of methylation.

Dissolved Hg

The close relationship between Hg and DOC in solution is well documented (e.g., see citations in Joslin (1994), and many more recent) (Fig. 5). Relationships from around the Northern Hemisphere have similar slopes, about 0.2 ng Hg per 1 mg DOC, with differences in intercepts probably related to whether or not particulate Hg is included. The relationship between DOC and Hg is considered to have strong explanatory power for the transport of Hg from terrestrial to aquatic systems (Driscoll et al. 1995; Johansson and Iverfeldt 1994; Joslin 1994; Lee et al. 1998; Kolka et al. 1999*b*; Mierle and Ingram 1991). In spite of similarities (Fig. 5), there are regional (Johansson and Iverfeldt 1991) and local differences in the Hg–DOC relationship.

Data from a single location help demonstrate the variability that can be expected. Data were collected on the Marcell Experimental Forest, Minnesota, U.S.A., and included biweekly streamflow samples from six watersheds and concurrent interflow samples from the organic forest floor and from the top of the B mineral horizon at 40 cm (Fleck 1999). The change in Hg concentration with change in DOC is markedly different between the streamflow and interflow samples (Fig. 6), with streamflow very near that reported for other locations (0.17 ng Hg per 1 mg DOC) but interflow through both organic and mineral soil horizons having both greater change (about 0.40 ng Hg per 1 mg DOC) and greater intercept at 0 DOC (about 13 ng L^{-1} compared to 2.8 ng L^{-1}) (Fig. 6). The greater Hg enrichment of interflow than streamflow DOC may be associated with hydrophobic versus hydrophilic organic matter.

Fig. 5. Reported empirical relationships between total Hg concentration and dissolved or total carbon concentration in solution. NY = lakes in the Adirondack Mountains, New York, U.S.A. (Driscoll et al. 1995); MN-s = first-order streams in northen Minnesota, U.S.A. (data from Fleck 1999); Sc = forest streamflow in Sweden (from Meili 1991); WI-l = lakes in northern Wisconsin, U.S.A. (Watras et al. 1996); WI-*r* = rivers in Wisconsin, U.S.A. (Babiarz et al. 1998); MN-l = lakes in northern Minnesota (Sorensen et al. 1990).

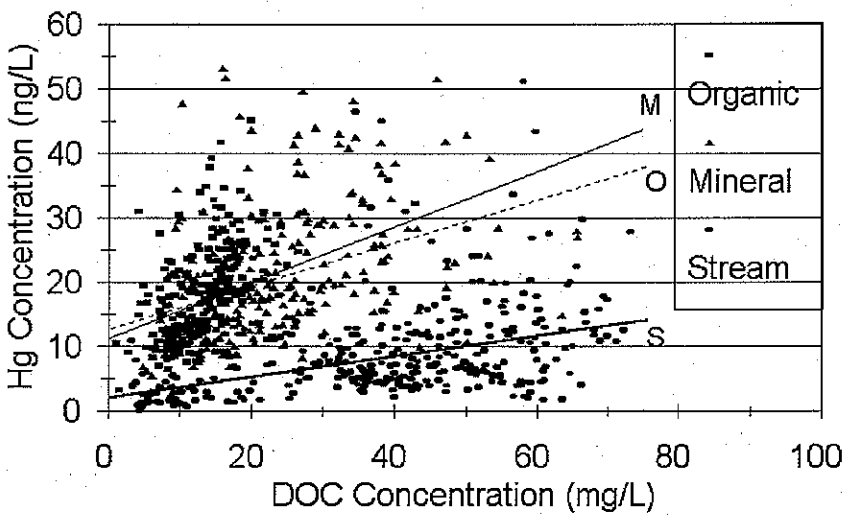


Concentration of hydrophobic organic matter is higher in interflow, with a positive relationship between it and HgT, while no such relationship exists in streamflow (Fleck 1999). Varshal et al. (1996) note that fulvate complexes dominate in the solution phase of river waters, while humic complexes dominate in soils or particulate organic carbon (POC). Export of HgT from watersheds in northern Ontario was very closely related ($r^2 = 0.95$) to the export of humic material (Mierle and Ingram 1991). The greater intercept of the interflow waters (Fig. 6) suggests the presence of other forms of Hg, either unlikely Cl salts (Skyllberg et al. 2000) or particulates, including POC. Interflow only occurs when soils are saturated, primarily during snowmelt with lesser occurrences during summer storms or autumnal rains, and these conditions are likely to mobilize particulates.

Particulate-bound Hg

In many systems, most of the annual Hg flux is transported during spring floods and high flow periods both because of an increase in Hg concentration and the contribution of these events to the annual water flux (Johansson and Iverfeldt 1994). Short periods during spring flow can carry 50 to 90% annual Hg flux of a watershed (Aastrup et al. 1991; Johansson et al 1991; Mason and Sullivan 1998; Sukhenko et al. 1992). The relationship between Hg and DOC degrades during these high flow events (Bishop et al. 1995*a*; Bishop et al. 1995*b*; Johansson et al. 1991; Mierle 1990; Pettersson et al. 1995; Sukhenko et al. 1992), and a major reason for the increase in Hg concentration is particulate transport. Aastrup et al. (1991) observed large organic particles in soil solution from upper soil horizons, but decreasing amounts downslope and none in deep groundwater, and they suggested that these particles could be the main carriers of Hg in the watershed. A single summer storm event in an agricultural watershed in Wisconsin transported 70 times more particulate matter and 20 times more Hg than normal flow (Babiarz et al. 1998). In a small, relatively steep (average slope 35%) hardwood watershed in New York, U.S.A., 60 to 75% of the annual Hg export from the watershed was by particulates during high-flow events (Scherbatskoy et al. 1998). Particulate Hg (total – dissolved) was highly correlated with the organic fraction of suspended sediment, suggesting that the Hg was associated with POC. In five small watersheds in Minnesota, U.S.A., Kolka et al. (1999*b*) found poor correlations between monthly

Fig. 6. Empirical relationships between total Hg concentration and dissolved organic carbon concentration in interflow through organic surface horizons (O, $n = 220$), mineral subsurface horizons (M, $n = 270$), and first-order streams (S, $n = 340$) in the Marcell Experimental Forest, Minnesota, U.S.A., from 1993–1998 (data from Fleck 1999).



HgT and DOC or total organic carbon (TOC), but significant positive relationships between HgT and POC, operationally defined as the difference between TOC and DOC. Although POC accounted for only 10 to 20% of the carbon transported from the watersheds, it was associated with 52 to 80% of the HgT transported. Others have also considered particulates to be important in Hg transport, with the Hg concentration curve following the hydrograph during frequent episodic events (Allan and Heyes 1998).

Particulates have also been implicated in Hg transport in large watersheds. Nearly three fourths of the Hg load of the St. Lawrence River Basin, Canada, 1.34×10^6 km^2, with a variety of land uses including agriculture, forest, and urban, was particulate (Quémerais et al. 1999). Similarly, virtually all the transport of Hg in the Minnesota River basin, draining about 44 000 km^2 of largely agricultural land, was by particulates assumed to be primarily mineral and derived from surface erosion (Balogh et al. 1997). The origin of this material was demonstrated by monitoring overland flow from a cultivated area in the watershed during snowmelt (Balogh et al. 2000). Due to particulates, concentrations of Hg were much higher in overland flow (about 20 ng L^{-1}) than in snow (1 ng L^{-1}). In this case, true overland flow (Hortonian) occurred and a minimum of 70% of the Hg particulate fraction was derived from soil. The Hg concentration of the particulates, 52 μg kg^{-1}, was very similar to that reported for particulates in the river system (46 μg kg^{-1}) (Balogh et al. 1998*a*) and for the silt plus clay soil fraction both across the north-central U.S.A. (52 μg kg^{-1}, Nater and Grigal (1992)) and the prairie soils of Alberta, Canada (53 μg kg^{-1}, Dudas and Pawluk (1976)). These data demonstrate that mobilization of soil materials is important to Hg transport in cultivated watersheds.

The ratio of particulate to dissolved Hg is affected by land use. Compared to export from the predominantly agricultural large river system (Balogh et al. 1997), there was about an order of magnitude lower annual-sediment-yield (particulates) per unit watershed area and only about one-third the annual Hg yield per unit watershed area in two adjacent large basins (20 000 and 51 500 km^2) (Balogh et al. 1998*a*). The smaller watershed, the St. Croix basin, is predominantly forested with wetlands; the larger watershed, the Upper Mississippi basin, has a mix of forest and agriculture. These differences in land use influenced both particulate and dissolved Hg, with both higher Hg concentrations in particulates (191 and 86 μg kg^{-1}, respectively, compared to 46 μg kg^{-1}) (Balogh et al. 1998*a*) and higher dissolved Hg (1.9 and 0.79 ng L^{-1} compared to 0.41 ng L^{-1}, Balogh et al. 1998*b*) in the other watersheds than in

Table 1. Distribution coefficients (particulate Hg (ng kg^{-1}) divided by dissolved Hg (ng L^{-1})) reported or calculated from the literature (all means or medians).

Location	log K_d (L kg^{-1})	Reference
Large rivers north-central U.S.A.	4.4	Balogh et al. 1998*a*
Minnesota 1st order streams	4.7	Fleck 1999
Wisconsin rivers (spring)	4.8	Hurley et al. 1995
Wisconsin rivers (fall)	4.9	Hurley et al. 1995
Wisconsin rivers	4.9	Babiarz et al. 1998
Texas estuaries	4.9	Stordal et al. 1996
Wisconsin lakes	5.2	Hurley et al. 1994
Lake Michigan tributaries	5.5	Hurley et al. 1996
St. Lawrence River and tributaries	5.5	Quémerais et al. 1999
Lake Michigan	5.7	Mason and Sullivan 1997

the agricultural watershed. In spite of lower concentrations, higher particulate flux led to higher Hg flux from the agricultural watershed. In a study of 39 river systems in Wisconsin, U.S.A., Hurley et al. (1995) associated elevated HgT flux with land use, with particulate Hg important in agricultural watersheds and dissolved Hg important in forested watersheds with wetlands. In an urban river near Washington, D.C., storm flow associated with particulates was the major vector for Hg transport (Mason and Sullivan 1998).

Although particulates are important in transporting Hg, there are difficulties in ascertaining their absolute importance. First, there are analytical difficulties associated with their determination, especially at low particulate concentrations. Another difficulty is measurement during appropriate times. To understand the actual contribution of particulates to Hg flux and the contributions of single events to the annual Hg load, samples must be collected during episodes of high flow. Simply using weekly or monthly grab samples for Hg and particulate determination will not appropriately weight the data for flux determination.

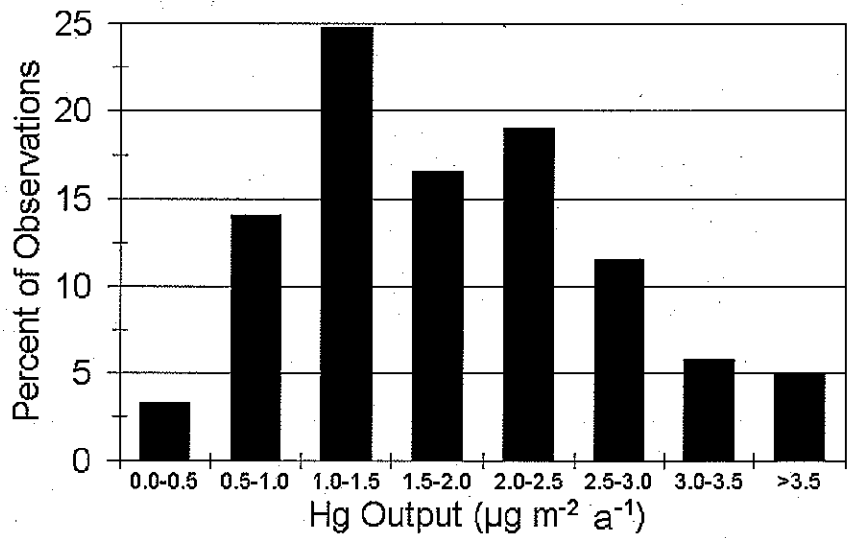
Despite these difficulties in determining the role of particulates in transport, it is interesting that the log of the distribution coefficient, K_d, is surprisingly uniform among a variety of studies and systems (Table 1). The mean of these studies, 5.1 ± 0.4 L kg^{-1}, indicates that the Hg concentration associated with particulates is generally high. However, in storm events from agricultural areas with significant mineral particulates, the values of log K_d are likely to be lower than this mean (2.8, Babiarz et al. 1998; 3.4, computed from Balogh et al. 2000). The ratio of organic to mineral matter in particulates affects both K_d and particulate Hg concentration, with stronger binding associated with higher organic content (e.g., Mason and Sullivan 1998).

Resulting flux

Overall patterns

Mean annual streamwater Hg concentrations from streams and rivers, collected over multiple years or sites ($n = 79$), ranges over one order of magnitude, from 1.2 to 20 ng L^{-1} (Babiarz et al. 1998; Johansson et al. 1991; Kolka 1996; St. Louis et al. 1996; Westling 1991). Annual fluxes of Hg, from an even wider variety of watersheds ranging from very small first-order watersheds (minimum 0.6 ha, Gårdsjön G1 (Munthe et al. 1998)) to very large river basins (maximum 1.34×10^8 ha, St. Lawrence River, Canada (Quémerais et al. 1999)), have a near-normal frequency distribution with about 75% of observations in the range of 1 to 3 μg m^{-2} a^{-1} and a mean of 1.7 μg m^{-2} a^{-1} (Fig. 7). This relatively small range of flux is surprising. Many scientists stress the importance of DOC, particulates, area of

Fig. 7. Frequency distributions of annual Hg flux from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A., (Balogh et al. 1998*b*); St. Lawrence River, Canada, (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern Minnesota, U.S.A. (Kolka 1996), Vermont, U.S.A. (Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; Mierle and Ingram 1991; St. Louis et al. 1996), Scandinavia (Driscoll et al. 1994*a*; Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1998), and central Europe (Schwesig and Matzner 2000); and miscellaneous reports tabulated by Bishop and Lee (1997, 6 reports), Driscoll et al. (1998, 6 reports), and Kolka (1996, 9 reports) ($n = 121$).



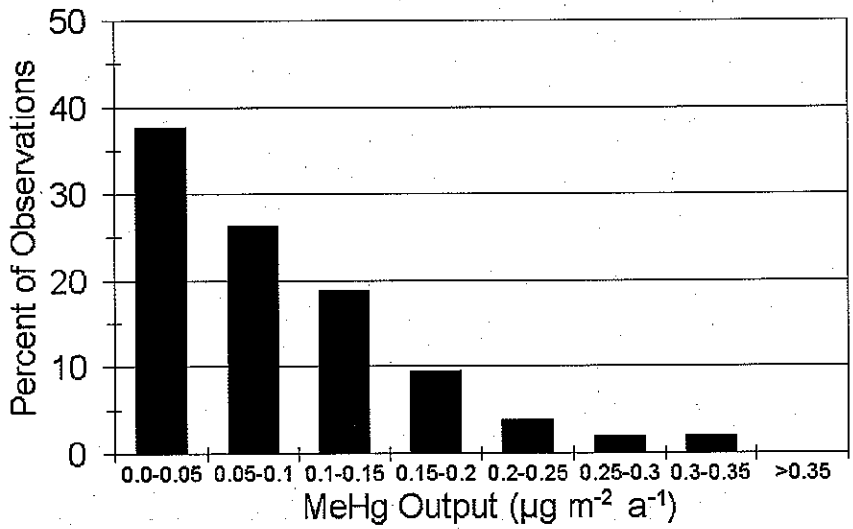
peatlands, frequency of episodic events, and other factors to explain variation among sites or years in their annual flux data. Although all these factors are likely to be important, these nuances are apparently averaged out to create a relatively uniform Hg flux from a variety of systems (Fig. 7).

Although the main concern involving toxicity of Hg is MeHg, as described above, only a small proportion of the Hg in both inputs and pools of the terrestrial Hg cycle is present as MeHg. In the case of MeHg flux from terrestrial to aquatic systems via streamflow, however, the situation becomes more complex. Flux of MeHg from watersheds is very skewed, with about 80% of observations $<0.15\ \mu g\ m^{-2}\ a^{-1}$ (mean = $0.06\ \mu g\ m^{-2}\ a^{-1}$) (Fig. 8). On the basis of averages, flux of MeHg is only about 4% of HgT flux. However, some of the measured MeHg fluxes are substantially higher than the mean (Fig. 8), and the explanation for those fluxes lies in watershed characteristics.

Watershed characteristics

Topography — Because of the close relationship between Hg and DOC, watershed factors that increase DOC export are also likely to enhance Hg export. The DOC concentrations of 337 lakes in the northern U.S.A. and in Canada were positively related to the ratio of drainage area to lake area and negatively related to watershed slope and both lake area and depth (Rasmussen et al. 1989). At the extremes, highest DOC was likely in small, shallow headwater lakes with relatively large, low-sloped watersheds and rapid water turnover, while the lowest DOC was associated with large, deep, higher-order lakes with small, steep, direct drainage areas and slow water turnover. Both thin, rocky soils and presence of coniferous vegetation led to increased DOC. Wetlands are also a major source of DOC (Eckhardt and Moore 1990). In general, long water residence times in terrestrial systems lead to higher DOC in associated lake waters and should also lead to higher Hg concentrations. Concentration of Hg in water, sediments, and fish from 81 lakes in northern Minnesota, U.S.A., was positively related to total organic

Fig. 8. Frequency distributions of mean annual MeHg flux from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in Ontario, Canada (St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Driscoll et al. 1994*a*; Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000; Munthe et al. 1998); and miscellaneous reports tabulated by Bishop and Lee (1997, 6 reports) and Driscoll et al. (1998, 6 reports) (n = 53).

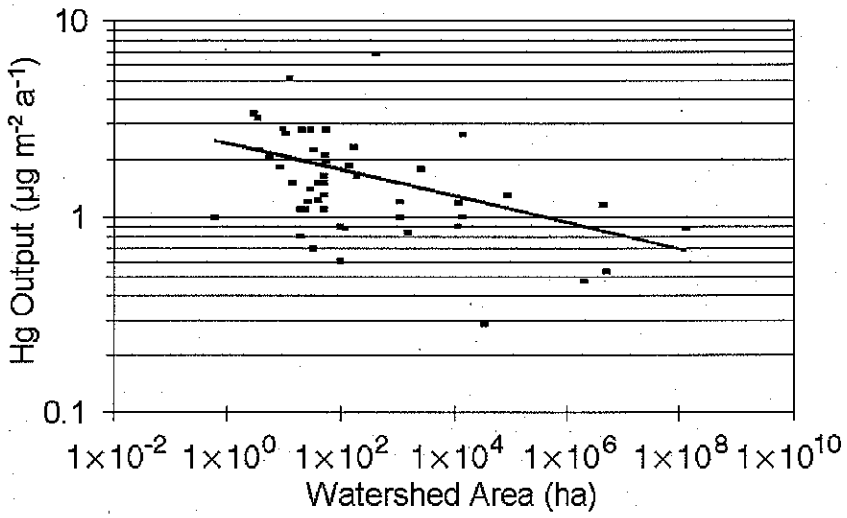


carbon (TOC) in solution (Sorensen et al. 1990) and to those watershed factors that could plausibly affect TOC, including positive relationships with the proportion of the watershed that was forested and lake water turnover time and a negative relationship with lake surface area. Similar positive relationships between lake water DOC and Hg and negative relationships with lake size have been reported from Wisconsin, U.S.A. (Watras et al. 1995). In the Adirondack Mountains, New York, U.S.A., Driscoll et al. (1994*b*) stressed that DOC in lakes and the watershed characteristics that influence it were the most obvious factors regulating the concentration and availability of both Hg and MeHg. Lee et al. (1998) summed up these characteristics with respect to Hg transport from the Svartberget watershed in Sweden, "... variation in the (total Hg) output was largely controlled by the major flow pathways and DOC levels in runoff." During periods of high flow, flow paths were surficial and passed through soils layers rich in Hg and C, leading to higher HgT and DOC than during low discharge periods when water flowed through deeper soil layers with lower Hg and C (Lee and Iverfeldt 1991; Lee et al. 1998).

Size — Flux of Hg via streamflow is weakly related to watershed size, with a clear tendency for lower annual flux with increasing watershed size (Fig. 9, $r^2 = 0.22$). Even though the relationship is weak, its existence over a range of about eight orders of magnitude of watershed size encompassing a broad range of systems lends it some credibility. Flux depends on both Hg concentration and on water yield, and size and water yield could co-vary. Concentration of HgT is also inversely related to watershed size, albeit more weakly, based on data from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A. (Balogh et al. 1998)); St. Lawrence River, Canada (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern U.S.A. (Kolka et al. 1999*b*; Krabbenhoft et al. 1995; Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Iverfeldt and Johansson 1988; Lee et al. 1995; Lee et al. 1998). The best-fit line, including the correction term for bias (Beauchamp and Olson 1973), is

$$[1] \quad \ln(\text{Hg concentration (ng L}^{-1})) = 2.02 - 0.063 \times \ln(\text{Area (ha)}),\ r^2 = 0.13,\ n = 47.$$

Fig. 9. Relationship of annual Hg flux and watershed area. Data from very large watersheds (Minnesota River, St. Croix River, Upper Mississippi River, U.S.A. (Balogh et al. 1998*b*); St. Lawrence River, Canada (Quémerais et al. 1999)); moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998); first-order streams in northern U.S.A. (Kolka et al. 1999*b*; Krabbenhoft et al. 1995; Scherbatskoy et al. 1998), Ontario, Canada (Mierle 1990; St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Iverfeldt and Johansson 1988; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000). Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(Hg flux (μg m^{-2} a^{-1})) = 0.89−0.068 × ln(Area (ha)), r^2 = 0.22, n = 49.



An algebraic solution for water yield, using the best-fit statistics for Hg flux and concentration, indicates less than a 7% change in water yield with increase in watershed size from 1 to 10^6 ha. In these data, size and water yield do not strongly co-vary and the decrease in both Hg concentration and flux with watershed size is therefore not simply due to change in water yield. One possible explanation for the decline in Hg may be less effective transport processes to streams and rivers in larger watersheds. Another possible explanation may be loss of Hg from the stream or river by in-stream processes such as volatilization and sedimentation. The rapid decrease in flux with watershed size, and hence with stream order, indicates more active processing of Hg in small systems, similar to the case of nitrogen export (Peterson et al. 2001). The data upon which this relationship is based were collected from systems that were not near significant sources of Hg contamination. In contrast, urban watersheds in New York, U.S.A. (Bigham and Vandal 1996) have Hg streamflow flux that is four to five times greater than predicted from the relationship with watershed size (Fig. 9). The higher flux in these watersheds is due to local sources of atmospheric Hg, reduced area of permeable soil due to paving, other non-point sources of Hg to the streams, and continual anthropogenic disturbance as compared to non-urban systems (Bigham and Vandal 1996).

There is no pattern of MeHg flux with watershed size (r^2 = 0.01, n = 22), based on data from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), central Europe (Schwesig and Matzner 2000), and Scandinavia (Iverfeldt et al. 1996; Lee et al. 1995; Lee et al. 1998; Lee et al. 2000).

Studies of HgT and MeHg flux are contradictory. St. Louis et al. (1996), for example, found no relationship between HgT and MeHg in waters from Ontario, while Watras et al. (1995) found such a relationship in Wisconsin. These contradictory results emphasize that export of HgT and MeHg are influenced differently by terrestrial factors such as DOC, particulates, area of peatlands, and frequency of episodic events (Lee et al. 1995). For example, two watersheds in Sweden that differed in wet MeHg inputs by a factor of three, associated with about a two-fold difference in both volume of precipitation and of streamflow, had comparable streamflow MeHg flux (0.12 μg m^{-2} a^{-1}) (Lee et al. 1995). Wet

deposition alone was not a good indicator of either MeHg concentrations or flux in streamflow (Lee et al. 1995).

Wetlands — Transport of Hg to lakes is frequently linked to presence of wetlands in the watershed. Because most studies have been conducted in northern forested watersheds, the term "wetlands" usually refers more specifically to peatlands. The role of peatlands in Hg transport is paradoxical. Budgets indicate significant Hg sequestration in peatlands (Benoit et al. 1994; Grigal et al. 2000). It is therefore logical to hypothesize that Hg flux from watersheds should be reduced when wetlands are present, and this hypothesis has support in the literature (Borg and Johansson 1989; Johansson et al. 1991; Lindqvist et al. 1991; Zillioux et al. 1993). Presence or absence of wetlands in watersheds in northwestern Ontario had no discernable effect on HgT retention, neither reducing nor enhancing it (St. Louis et al. 1996). Because wetlands (peatlands) are a major source of DOC (Eckhardt and Moore 1990), their presence may also be hypothesized to increase Hg streamflow flux. This hypothesis, too, has support in the literature (Babiarz et al. 1998; Driscoll et al. 1994*b*; Kolka et al. 1999*b*; Mierle and Ingram 1991; Watras et al. 1995). With a diverse data set from the literature, ranging from first-order basins (minimum about 3.5 ha, Paroninkorpi, Finland (Lee et al. 1998)) to very large watersheds (maximum 5.15×10^6 ha, Upper Mississippi basin (Balogh et al. 1998*a*)) and excluding watersheds reported as having no wetlands, there is a weak positive relationship between the percent of the watershed in wetlands and the annual HgT flux (Fig. 10, $r^2 = 0.19$, $n = 24$). One of the difficulties of determining such a general trend is assessing what is meant by the term wetlands in the literature. Some watersheds are clearly either wholly upland or wetland, but other descriptions are more problematic. For example, a watershed may be described as having no wetlands but "... low watershed slopes with thick organic soils." (Lee et al. 1998) or containing a "... riparian zone ... of deep peat" (Lee et al. 1995). Such areas may be functionally equivalent to wetlands in acting as a source of Hg and DOC, but no estimates of their area are provided. In addition, in very large watersheds wetlands are usually located nearer the headwaters, and their influence on Hg and DOC may become diluted as the waters reach higher-order rivers. It appears, however, that the role of wetlands as sources of DOC and associated Hg surpass their role as Hg sinks, so that Hg export is increased by wetlands in the watershed (Fig. 10).

The potential of wetlands and especially peatlands to act as sources of MeHg is reported so frequently that it is nearly axiomatic (Driscoll et al. 1994b; Hurley et al. 1995; Lee and Hultberg 1990; St. Louis et al. 1994; Watras et al. 1995). Such a relationship is confirmed over a diverse array of watersheds and indicates about a three-fold increase in MeHg flux with an increase in wetland area from 1 to 10% and a further three-fold increase from 10 to 50% (Fig. 11, $r^2 = 0.38$). This increase in flux is accompanied by a weak positive relationship between percent wetland and MeHg concentration (Fig. 12, $r^2 = 0.14$). In spite of the problem of defining wetlands, the relationship between wetlands and MeHg flux is quite strong. The increase in MeHg concentration with area of wetland in the watershed (about 0.01 ng L^{-1} per % in the range 1 to 10% wetland, Fig. 12) is similar to that reported for lakes in northern Wisconsin, U.S.A. (0.007 ng L^{-1} per %, Watras et al. 1995) but only about one-third that reported with area of near-shore wetlands for lakes in the Adirondack Mountains, U.S.A. (Driscoll et al. 1994*b*, 0.03 ng L^{-1} per % wetland). Wetlands located somewhere in the watershed are less significant sources of MeHg to lakes than are wetlands directly on the lakeshore. These empirical relationships do not directly address the mechanistic origin of the MeHg.

The increase in flux of MeHg with increase in wetland area (Fig. 11) is greater than the increase in flux of HgT (Fig. 10) and an algebraic solution of the two regressions yields the equation,

$$[2] \quad \ln(\text{MeHg/HgT}(\%)) = +1.1 + 0.3 \times \ln(\text{Wetland}\%).$$

Equation [2] indicates an increase in the ratio of MeHg to HgT from about 3% at 1% wetland to a maximum of about 12% at 100% wetland. These ratios are comparable to those reported in streamflow

Fig. 10. Relationship between the proportion of wetlands in a watershed and the annual Hg flux in streams and rivers from very large watersheds in the midwestern U.S.A. (Balogh et al. 1998), moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Minnesota, U.S.A. (Kolka et al. 1999*b*), Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(Hg flux (μg m^{-2} a^{-1})) = -0.21 + 0.26 × ln(Wetland %), r^2 = 0.19, n = 24.

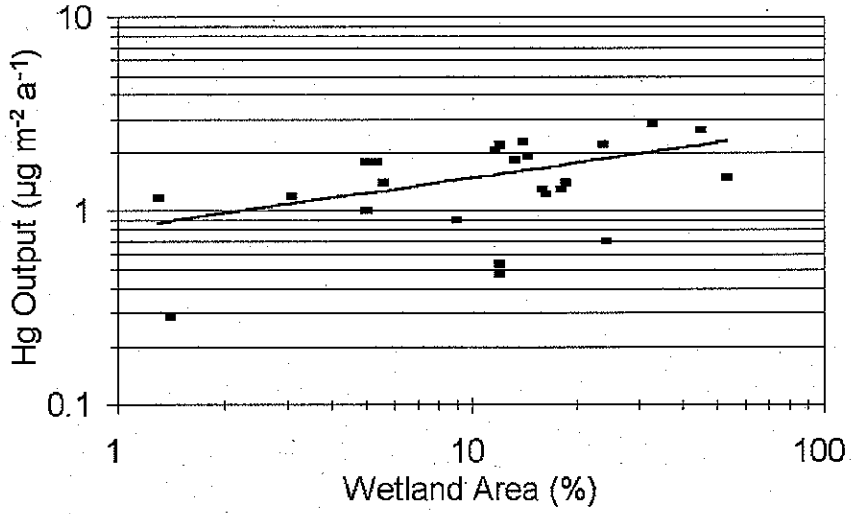
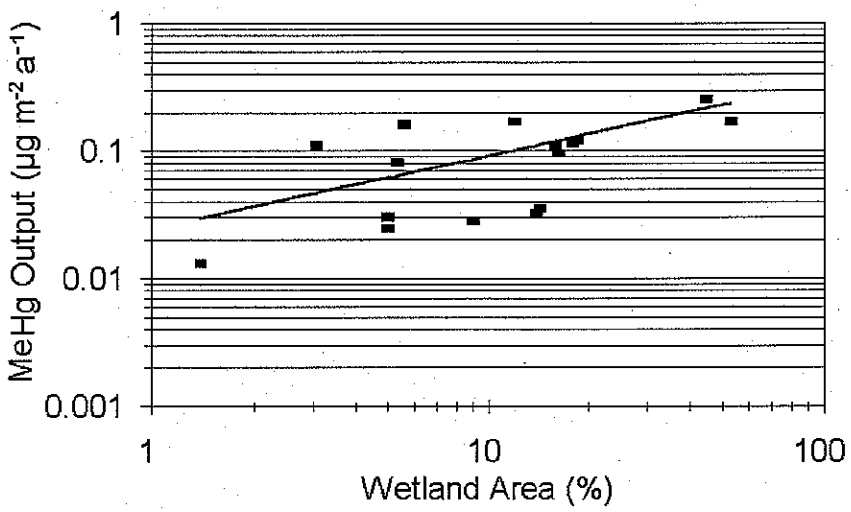


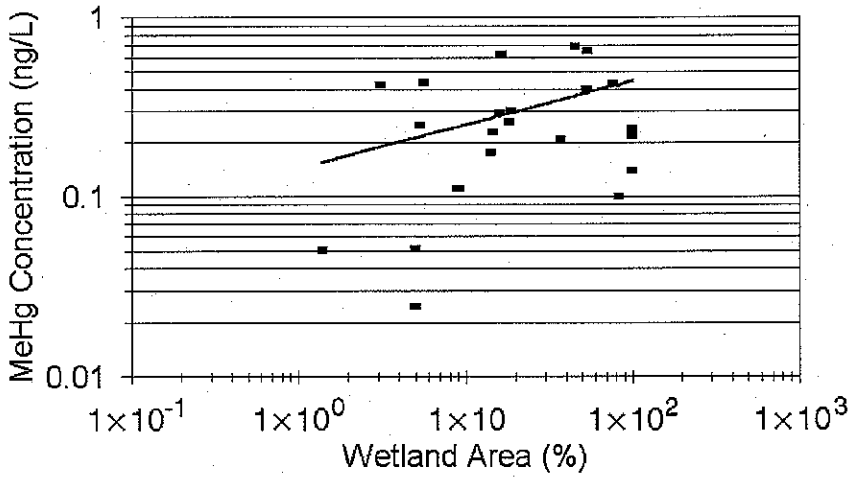
Fig. 11. Relationship between the proportion of wetlands in a watershed and the MeHg flux in rivers and streams from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(MeHg flux (μg m^{-2} a^{-1})) = -3.71 + 0.57 × ln(Wetland %), r^2 = 0.38, n = 16.



(Lee et al. 1995; St. Louis et al. 1996; Westling 1991) and may indicate an upper limit of about 10 to 15% in the ratio of MeHg to HgT, perhaps related to the balance between methylation and demethylation in terrestrial systems.

The flux of MeHg from watersheds has seasonality related to biological activity. Concentrations of MeHg are highest in flow from wetlands during midsummer (Rudd 1995). Although the runoff

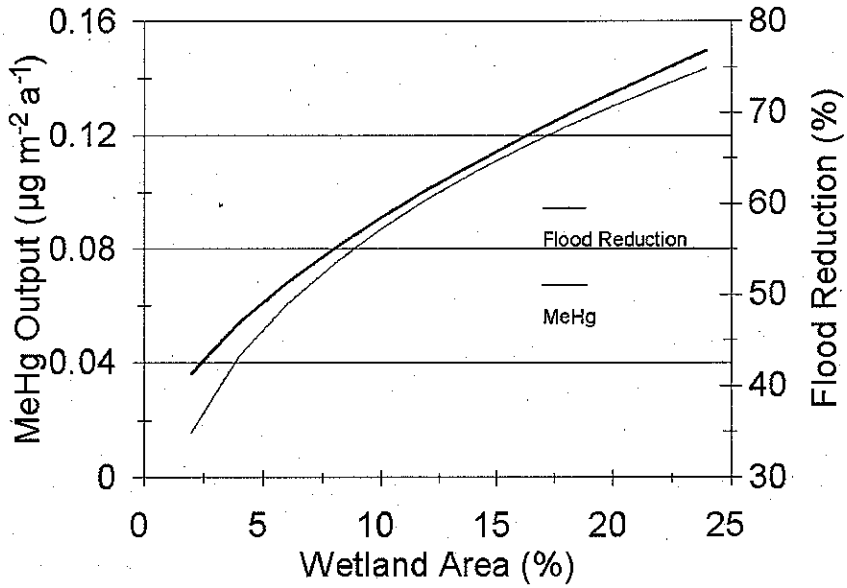
Fig. 12. Relationship between the proportion of wetlands in a watershed and the MeHg concentration in rivers and streams from moderate-sized watersheds in Wisconsin, U.S.A. (Babiarz et al. 1998) and first-order streams in Ontario, Canada (St. Louis et al. 1996), New York, U.S.A. (Driscoll et al. 1998), and Scandinavia (Lee et al. 1995; Lee et al. 1998, Westling 1991). Watersheds without wetlands not included. Best-fit line, including correction term for bias (Beauchamp and Olson 1973), ln(MeHg concentration (ng L^{-1})) = -1.95 + 0.25 × ln(Wetland %), r^2 = 0.14, n = 23.



associated with snowmelt in spring accounted for about one fourth of the water flux and about one third of annual output of HgT from a small watershed in northern Sweden, it only accounted for slightly >10% of the MeHg flux which continued to increase to a maximum in August (Bishop et al. 1995*b*). Less than 5% of HgT transported during the spring thaw from watersheds of seven rivers in Wisconsin, U.S.A., was MeHg, but that ratio increased to about 15% in autumn, presumably as a consequence of the flushing of soil pore waters in late summer (Babiarz et al. 1998). Concentration of MeHg in pore-water also increased from spring to summer in a watershed in Ontario, Canada (Branfireun et al. 1996). The highest concentration of MeHg in base flow was during a very warm dry period, and 53% of the annual mass flux of MeHg from the watershed occurred during one summer storm. Surface stream flow across a peatland was the most important flux path for MeHg, while groundwater discharge from the peat was an insignificant contributor because of both low water flux and MeHg concentration (Branfireun et al. 1996). Near-surface pore-water concentrations of MeHg were high in peatland discharge zones and lower in recharge and lateral flow zones. Annual production rates of MeHg in wetlands are about 0.3 μg m^{-2} a^{-1} compared to 0.5 to 3 μg m^{-2} a^{-1} for lakes and 13 μg m^{-2} a^{-1} for recently flooded areas (Rudd 1995). Driscoll et al. (1998) measured rates of MeHg production in a beaver pond of 0.45 μg m^{-2} a^{-1} of pond area, with highest rates during low-flow conditions. They suggest that the recent increased beaver populations in forested areas, rebounding from very low levels near 1900, may have led to increased MeHg production due to inundation of terrestrial landscapes, with a gradual decline to current rates of production as ponds matured.

Although wetlands provide suitable conditions for production of MeHg (Rudd 1995), they also affect the hydrologic response of a watershed. Both flow paths and residence times are extremely important for mobilization of MeHg (Bishop and Lee 1997; Branfireun et al. 1996). As the proportion of wetlands in a watershed increases, stormflow (flood) peaks are attenuated because of temporary water storage in those relatively flat landscape elements. The attenuation is proportional to the logarithm of percent of wetlands, and the shape of the relationship (Fig. 13) is very similar to that describing the increase in MeHg flux from watersheds (Fig. 11). The flood attenuation is equivalent to an increase in water residence time in the watershed, allowing greater interaction with the porewaters in the wetlands.

Fig. 13. Relationship between the proportion of wetlands in a watershed and both the reduction in flood peak flow (stormflow) from watersheds in the midwestern U.S.A. (Verry 1997) and the mean annual MeHg flux (see Fig. 11).



Wetlands therefore increase MeHg flux from terrestrial to aquatic systems both because they act as sites of production and because they increase water residence time. In a few cases, uplands, usually sinks for MeHg, have been reported to be sources (Rudd 1995). Although each watershed is unique in its streamflow regime and mix of land cover, as reflected in the lack of a relationship between MeHg flux and watershed size, wetlands are especially important as sources of MeHg. The flow of waters through them, its residence time, and the season of residence all affect MeHg transport to aquatic systems. It is ironic that wetlands, sacred landscape elements that both regulation and legislation attempt to protect from disturbance, are the single most identifiable source of MeHg from terrestrial to aquatic systems.

Fire or other disturbance

Fires are common in nearly all forests, particularly those in the boreal zone. High temperatures during burning of foliage and small twigs of trees should lead to volatile loss of associated Hg. Similarly, loss of soil C by fire should lead to loss of Hg because of the close association between soil C and Hg. For example, there was about a 50% loss of C from the forest floor following a spring forest fire when the soil was relatively moist from recent snowmelt (Slaughter et al. 1998), and even greater losses could be expected from fires in mid- to late-summer when soils are dryer. Fires are common in peatlands, creating layers of charcoal and reducing peat accumulation (Kuhry 1994) and also likely leading to loss of accumulated Hg. In the Okefenokee Swamp, Georgia, U.S.A., an inverse relationship between percent ash and Hg concentration with depth in peat contrasted with either no relationship or a positive relationship between ash and other metals (Casagrande and Erchull 1976). The increased ash content of the peat is an indicator of oxidizing conditions, either induced by warm dry climatic conditions or by fire, and its inverse relationship with Hg indicates Hg loss under those conditions in contrast with accumulation of other metals.

Fires can also alter the hydrology of the site, with effects varying with environment. A forest fire in semi-arid New Mexico, U.S.A., mobilized both organic matter and Hg and increased their transport to a reservoir (Caldwell et al. 2000). Concentrations of HgT increased six fold and of MeHg by about 30-fold in reservoir sediment compared to that deposited before the fire. In contrast, there was no increase

in MeHg in zooplankton in boreal lakes in Québec, Canada, associated with forest fire (Garcia and Carignan 1999). In this environment, burning did not increase transport of Hg, presumably because it did not increase transport of DOC from terrestrial watersheds to lakes (Garcia and Carignan 1999).

Reduced transport of DOC from a terrestrial watershed, by about 50% over a 20-year period, was attributed to a combination of dry, warm temperatures and associated forest fires in the Experimental Lakes Area, Ontario, Canada (Schindler et al. 1996). This reduction in DOC would be expected to reduce transport of Hg to the lakes and also to affect in-lake Hg reactions (Schindler et al. 1996). The reduction in DOC transport was ascribed almost wholly to reductions in water flux from the terrestrial watershed to the lake, about 11 mm per year over the 20-year period (Schindler et al. 1996).

Forest harvest also affects DOC transport, and should therefore affect Hg. Most studies have measured only DOC and not Hg, and results vary. In some cases, harvesting has had little effect on total DOC (McLaughlin et al. 1996; Meyer and Tate 1983), in others harvest has increased DOC export (Neal et al. 1992; Qualls et al. 2000), and in still others relatively little change has occurred (McDowell and Likens 1988). These differences in response emphasize the importance of hydrologic regime and soil properties in affecting DOC export (Moore 1987). In a study that measured Hg but not DOC, Garcia and Carignan (1999) reported an increase in MeHg in lake zooplankton associated with recent logging in Québec, presumably because of associated increased transport of DOC.

Other disturbances also affect Hg flux. Based on numerous studies, initial cultivation of previously undisturbed soils and attendant increased microbial activity and erosion leads to a loss of 30% or more of the original SOM (Mann 1986). A logical deduction would be that cultivation should similarly reduce Hg by a combination of volatile and particulate losses. Tillage of forest soils significantly increased Hg concentrations in understory plants in Finland compared to either harvested and untilled or unharvested areas (Leinonen 1989), implying increased volatilization of Hg(0) and subsequent foliar uptake following tillage. A logical deduction would be that cultivated soils should have reduced Hg compared to uncultivated soils. Reported differences in Hg between undisturbed and cultivated soils, however, do not appear to be large. For example, in Alberta, Canada, soils that had not been cultivated had Hg concentrations ranging from 20 to 35 μg kg^{-1} (Dudas and Pawluk 1976), while similar cultivated soils ranged from 20 to 40 μg kg^{-1} (Dudas and Pawluk 1977). In southwest Siberia, the range of Hg concentrations among different types of cultivated soils was from 21 to 33 μg kg^{-1} (Anoshin et al. 1996), not appreciably different than that in uncultivated soils. In both cases, however, cultivation significantly affected those horizons very high in SOM, appreciably altering the high-organic LFH horizons in Canada (Dudas and Pawluk 1976) and the A_o and A_s horizons in Siberia (Anoshin et al. 1996). For these horizons, at least, cultivation clearly enhanced the loss of SOM and Hg. Cultivation also is a major cause of erosion (particulate transport) in watersheds (Pimental et al. 1995); particulates are important for Hg flux in many systems.

Because wetlands are a major source of DOC (Eckhardt and Moore 1990), peatland drainage for forest production could lead to increased Hg flux. There was no clear evidence of greater HgT flux from drained as compared to undrained peatlands in central and south Sweden, but MeHg flux increased from drained peatlands with about 70% of the MeHg associated with humic materials (Westling 1991). The highest concentrations of both HgT and MeHg occurred in streamflow following dry periods with low ground water and low water flow, climatically induced water fluctuations. In contrast to that reported lack of difference in HgT flux with drainage, Simola and Lodenius (1982) used Hg accumulation in annual sediments in two comparable lakes to assess peatland drainage. Rates of Hg accumulation in sediments increased in the lake with drained peatlands in the watershed, from 30 μg m^{-2} a^{-1} to over 100 μg m^{-2} a^{-1} temporally associated with the drainage; there was no such increase in the lake whose watershed had no drainage.

Table 2. Literature values for important fluxes of the terrestrial Hg cycle as documented in this review.

Category	Units	Mean	25th Percentile	75th Percentile	N
Inputs					
Open Precipitation	$\mu g\ m^{-2}\ a^{-1}$	9.6	6	15	82
Throughfall	$\mu g\ m^{-2}\ a^{-1}$	17	15	19	17
Litterfall	$\mu g\ m^{-2}\ a^{-1}$	21	17	25	21
Outputs					
Volatilization	$ng\ m^{-2}\ h^{-1}$	11	8	28	8
Streamflow HgT	$\mu g\ m^{-2}\ a^{-1}$	1.7	1.2	2.4	121
Streamflow MeHg	$\mu g\ m^{-2}\ a^{-1}$	0.06	0.03	0.12	53

Summary

Volatilization is an important Hg flux from terrestrial systems. Its measurement is highly uncertain with measured rates from soils having a central tendency near 10 $ng\ m^{-2}\ h^{-1}$. Gas-phase exchange of Hg(0) between the atmosphere and the forest canopy may be the largest mechanism of loss of Hg from terrestrial systems, but data are limited and uncertain. Watershed factors that increase hydrologic export of DOC are likely to increase Hg export. Particulates are also important in Hg transport, especially in steep or erosive systems such as cultivated land, but their absolute significance is difficult to determine because their episodic nature makes measurement difficult. Transport of Hg in lower soil horizons and groundwater is minimal. Fluxes of Hg from a wide variety and size of watersheds do not range widely, with about 75% of observations in the range of 1 to 3 $\mu g\ m^{-2}\ a^{-1}$ and a mean of 1.7 $\mu g\ m^{-2}\ a^{-1}$. Concentration and flux of HgT from watersheds are weakly and inversely related to watershed size. Flux of MeHg from watersheds is very skewed with about 80% of observations less than 0.15 $\mu g\ m^{-2}\ a^{-1}$, but some fluxes are substantially higher. Although there is no pattern of MeHg flux with watershed size, there is a strong relationship between MeHg flux and wetland area. Finally, the degree and kind of disturbance in terrestrial watersheds can influence Hg flux. In most cases, it appears that disturbance increases Hg efflux via either volatilization or in runoff.

Synthesis and integration

A central question is what happens to the Hg that is deposited in terrestrial systems? Is it sequestered or is it quickly lost? What are the pathways of loss? The answer to this question has strong implications for the efficacy of measures to minimize both point and non-point sources of Hg to the atmosphere and to aquatic systems.

Budget balancing/volatilization

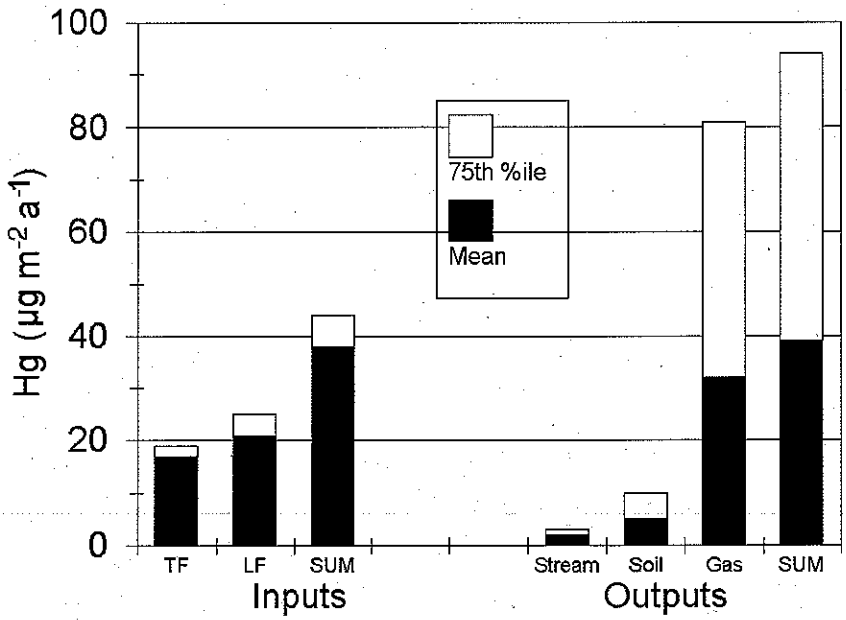
There are three possible fates for Hg inputs into terrestrial systems; they may be sequestered within the system, lost via hydrologic flux, or lost via volatilization. Before each of these fates is discussed in more detail, a simple exercise leads to an interesting conclusion. Using the means of the fluxes of Hg documented in this review (Table 2), annual input to forests, the sum of throughfall and litterfall, is about 38 $\mu g\ m^{-2}\ a^{-1}$. This input can be partially accounted for by streamflow output, about 2 $\mu g\ m^{-2}\ a^{-1}$, leaving a difference of 36 $\mu g\ m^{-2}\ a^{-1}$. Volatilization for a period of about 4.5 months at the mean rate, 11 $ng\ m^{-2}\ h^{-1}$ (Table 2), would balance the budget. If this computation is valid, then most of the Hg annually deposited on terrestrial ecosystems is simply returned to the atmosphere. Is this simple exercise valid?

Sequestration of Hg in terrestrial systems surely occurs, especially in peatlands, and some scientists believe that the forest floor layer in upland soils has sequestered nearly all the anthropogenically derived Hg (Aastrup et al. 1991; Borg and Johansson 1989; Johansson et al. 1991; Lee and Iverfeldt 1991). There are sufficient reduced S sites in SOM to bind all available Hg(II) (Skyllberg et al. 2000). Historical (pre-industrial) rates of Hg deposition can be estimated from the relative increase in Hg accumulation from the pre-industrial to the modern period in sediments in lakes and peatlands. A necessary assumption is that only the rate of deposition and not other factors influencing accumulation, such as the character of the basin, have changed over that time. Studies of sediment accumulation that have been carried out in north-temperate systems report an average ratio of modern to pre-industrial HgT accumulation of about 3.0 to 3.5 (Benoit et al. 1994; Engstrom and Swain 1997; Lorey and Driscoll 1999). Pre-industrial deposition to forests, including both throughfall and litterfall, would therefore be about 11 $\mu g\ m^{-2}\ a^{-1}$ (38 $\mu g\ m^{-2}\ a^{-1} \div 3.5$). If the modern period extends from 1850 to 2000, and the pre-industrial period is conservatively assumed to extend for 5000 years prior to that (well after deglaciation, which in most of the Northern Hemisphere was about 10 000 BP), then total deposition will have been about 61 mg m^{-2} (55 mg m^{-2} pre-industrial + 5.7 mg m^{-2} modern). Although this deposition compares fairly well with measured Hg accumulation in lakes and peatlands where multiple cores have been measured (lakes, 36 mg m^{-2} (Engstrom et al. 1994); 50 mg m^{-2} (Lorey and Driscoll 1999); peatlands, 40 mg m^{-2} (Benoit et al. 1994)), accumulation in upland soils in north-temperate areas is considerably less, about 8 mg m^{-2} (Lindqvist et al. 1991; Nater and Grigal 1992), although central European sites report accumulations over an order of magnitude higher (Schwesig et al. 1999). If sequestration is linearly related to deposition, then to achieve a current accumulation of 8 mg m^{-2} in upland soils, sequestration rates of 1.4 $\mu g\ m^{-2}\ a^{-1}$ (pre-industrial) and 5.0 $\mu g\ m^{-2}\ a^{-1}$ (modern) are necessary. Short-term studies, less than several decades, cannot detect these changes because pool sizes are too large.

Hydrologic flux is another possible fate for Hg inputs. Deep leaching to groundwater is an unlikely pathway of Hg loss, mainly because of its low Hg concentrations (Johnson and Lindberg 1995). Output of Hg in streamflow depends on both water flux and concentration. Water flux is unlikely to change appreciably because it is driven by the difference between precipitation and evapotranspiration, both of which can be assumed to be historically constant. At current rates of deposition, Hg flux is relatively uniform (Table 2). Assuming minimal groundwater loss, current hydrologic flux is at the mean of observations (Table 2, 2 $\mu g\ m^{-2}\ a^{-1}$). Because of the small variation in hydrologic flux (Fig. 7), pre-industrial flux could also be conservatively assumed to be about 2 $\mu g\ m^{-2}\ a^{-1}$.

Sequestration (5.0 $\mu g\ m^{-2}\ a^{-1}$) and hydrologic outputs (2 $\mu g\ m^{-2}\ a^{-1}$) therefore currently account for about 20% of annual Hg inputs (38 $\mu g\ m^{-2}a^{-1}$). Volatilization is the remaining possible fate for Hg inputs. In most studies of Hg budgets, Hg volatilization is estimated as a residual, assessed "indirectly" (Watras et al. 1996). In an overall Hg budget for a lake in southern Sweden, estimated volatilization losses from the terrestrial watershed ($<1\ \mu g\ m^{-2}\ a^{-1}$) were <5% of the inputs of 20 $\mu g\ m^{-2}\ a^{-1}$ (Lindqvist et al. 1991). If current net volatilization rates are at the mean of observations (11 ng $m^{-2}\ h^{-1}$, Table 2) and occur over a 4-month period, they would account for the remaining 80% of inputs (32 $\mu g\ m^{-2}\ a^{-1}$). As noted earlier, Lindberg (1996) reported net emission flux from the soil at Walker Branch Watershed, Tennessee, during spring, summer, and fall (6 to 9 months) to be about 7.5 ng $m^{-2}\ h^{-1}$. Such volatilization could range from rapid evaporation of deposited Hg(0) (Martinez-Cortez 1999) to reduction of Hg(II) by SOM (Schlüter et al. 1995) or microbes (Baldi 1997) and its subsequent loss. This estimated volatile loss does not include emissions of Hg(0) directly from the canopy to the atmosphere, which Lindberg (1996) considered an important flux in his conceptualization of the Hg cycle during a summer day in Walker Branch Watershed, Tennessee, U.S.A. Because of difficulties in measurement, reported volatilization rates are limited in number and range widely (Fig. 4, Table 2). If volatilization of 80% of the Hg that is deposited to terrestrial surfaces is incorporated into estimates of the global Hg cycle (Mason et al. 1994), then these fluxes to the atmosphere are

Fig. 14. Input–output budget of Hg in terrestrial watersheds. Mean rate refers to the geometric means as summarized in this review. Output by volatilization (gas) based on mean hourly rate extrapolated over 4 months per annum. Output via soil sequestration (soil) based on total soil accumulation of 8 mg m^{-2}. Uncertainty approximated by use of 75th percentile of values, with uncertainty in soil sequestration based on doubling of total accumulation. TF = throughfall; LF = litterfall; Stream = flux in streamflow.



comparable to anthropogenic fluxes. The magnitude of such re-emission has serious implications for control strategies (Jackson 1997).

This input–output budget of Hg in terrestrial watersheds and its associated uncertainties can be succinctly summarized (Fig. 14). At mean rates summarized in this review, the sum of inputs (38 $\mu g\ m^{-2}\ a^{-1}$) is nearly equal to the sum of outputs (39 $\mu g\ m^{-2}\ a^{-1}$) (Fig. 14). Uncertainty in these data is not easily defined, but a rough approximation for each of the inputs and outputs is the difference between the mean and the 75th percentile of values. In the case of soil sequestration, with few reports of total Hg accumulation, doubling of total accumulation yields a conservative 100% uncertainty. Using this metric, the uncertainty in volatilization rates is clearly much higher than that of any of the other fluxes (Fig. 14) and in fact is about an order of magnitude greater than that of any other flux. It is clear that terrestrial budgets will not be closed until volatilization is better understood.

Flux to lakes

Although a relatively small proportion of the Hg deposited on terrestrial watersheds reaches aquatic systems, that small fraction is of critical importance to health of those systems. Data from north-central (Swain et al. 1992) and northeastern U.S.A. (Lorey and Driscoll 1999) are consistent in showing that Hg accumulation in sediments increases 25% for each unit area increase in terrestrial watershed area per unit lake surface area. The accumulation rate extrapolated to a lake with no terrestrial watershed has been considered to be equivalent to Hg deposition to the lake surface (Swain et al. 1992; Lorey and Driscoll 1999). As discussed earlier, Hg deposition to lakes is approximately equivalent to open-field deposition; about one-fourth of total Hg deposition to forests. Forested watersheds therefore contribute about 6% of the annual Hg deposition they receive to lakes (25% of 1/4). This value serves as a check of the budget presented above, where hydrologic flux from forests was about 5% (2 ÷ 38) of annual deposition. The difference is trivial considering the uncertainty in all these empirical relationships. This

proportion is consistent with the 5 to 85% of total Hg loading to lakes from terrestrial watersheds, equivalent to lakes with virtually no terrestrial watershed to lakes with terrestrial watersheds nearly four times the lake size. Proportions are likely to level off in larger systems, consistent with the decline in Hg flux in streamflow with watershed size (Fig. 9).

Although 5 to 10% of terrestrial Hg loading reaches lakes, two watershed-specific factors appear to be most important in altering this overall proportion, DOC and particulates. Probably the best evidence for the role of differences in DOC influencing flux is the increase in annual HgT flux with the percent of the watershed in wetlands (Fig. 10), nearly a doubling of flux with an increase in wetland area from 1 to 10%. The probable cause of the increase is the DOC generated in the wetlands. Watersheds with wetlands, especially those wetlands that act as variable source areas, are likely to be disproportionately important sources of Hg to lakes. The importance of particulates in Hg flux is indicated by the degradation of the relationship between Hg and DOC during spring floods and high flow events. In watersheds without significant DOC, particulates can be especially important in transporting Hg to lakes. Watershed disturbances that mobilize particulates, including road-building, cultivation, and some logging practices will increase the flux of Hg to lakes.

In aquatic systems, attention is usually centered on MeHg. Sources of MeHg to lakes include direct precipitation, streamflow from terrestrial watersheds, and in-lake production (Rudd 1995). Simple models demonstrate that under different scenarios any of these sources can be important (Rudd 1995). With that caveat in mind, focus here will be on terrestrial streamflow. Even in that case, variations in MeHg to HgT ratios in atmospheric inputs to watersheds are not related to variations in ratios in streamflow. Internal watershed processes both produce and destroy MeHg, and it is the summation of those processes that ultimately reach lakes. As described earlier, the most important terrestrial watershed property affecting MeHg flux is the proportion of wetland in the watershed, affecting both production of MeHg and water residence time (Fig. 13). The U.S. Environmental Protection Agency has recently issued a water quality criterion for MeHg of 0.3 mg kg^{-1} of fish (wet weight) (U.S. EPA 2001). The criterion was based on a property of fish rather than of water because of the uncertainties associated with both Hg flux from terrestrial to aquatic systems and the bioaccumulation of mercury in aquatic biota. Translation of this criterion to concentration of MeHg in water is therefore tenuous, but it would correspond to an approximate concentration of 0.25 ng L^{-1} MeHg in streamwater using the default fish diet for the general population and about 0.11 ng L^{-1} if the diet is based only on predator fish such as northern pike (*Esox lucius*) and walleye (*Stizostedion vitreum*). In any specific application, actual concentrations would be influenced by site-specific properties such as water pH, temperature, and DOC, and by fish species, age, and trophic level.

Based on the empirical relationship of MeHg concentration with area of wetland in the watershed ($r^2 = 0.14$) (Fig. 12), the criterion based on consumption of all fish would be exceeded at 10% wetland and that based on consumption of predator fish would be exceeded for watersheds with only 1% wetland. Using the stronger relationship between MeHg flux and wetland area ($r^2 = 0.38$) (Fig. 11), and assuming annual streamflow of 50 cm per year, the all-fish criterion would be exceeded in watersheds with about 20% wetland and the predator fish criterion in watersheds with about 4% wetland. It is therefore likely that in many real-world situations, the new criterion is currently exceeded. An obvious method to reduce MeHg flux from terrestrial to aquatic systems would be to reduce the area of wetlands in watersheds. As stated earlier, it is ironic that wetlands, landscape elements that both regulation and legislation have attempted to protect from disturbance, are the single most identifiable source of MeHg in terrestrial systems.

Complexities influencing conclusions

Two factors further affect our ability to draw firm conclusions about Hg cycling. Because of scientific or political interest, and because Hg research requires well-equipped field sites and laboratories, much of the work dealing with Hg cycling has been carried out at relatively few locations. These locations,

such as the watershed of Lake Gårdsjön, southern Sweden; the Svartberget Watershed, northern Sweden; the Experimental Lakes Area in northwest Ontario; and Walker Branch Watershed, Tennessee; provide an important but narrow base upon which to generalize. Unique properties of each site, such as the presence of plumes with high concentrations of industrially generated Hg(0) (Kim et al. 1995), high concentrations of Hg in vegetation (Munthe et al. 1998), or very thin mineral soils associated with windstorms and forest fires (Schindler et al. 1996), illustrate the difficulty of generalizing from a few locations. Data are now being collected and published from many more sites, and those data are sorely needed in order to better allow us to generalize regarding Hg behavior in the terrestrial environment. The METAALICUS Study and other recent research initiatives (Sbick 2000) will help address many questions dealing with Hg and the environment, including some raised in this review.

Secondly, climatic fluctuations are very important to Hg cycling and affect interpretation of the data. For example, long-term studies of HgT and MeHg fluxes (Lee et al. 2000; Munthe et al. 1998) report significant inter-annual variations in fluxes, apparently related to climate. Where atmospheric deposition of Hg was experimentally curtailed, climatically driven variation in flux between the control and treated watersheds were too large to allow discernment of any effect of changes in deposition (Munthe et al. 1998). In an unmanipulated site, variations in output of Hg and MeHg from a watershed were much greater and did not follow the same trends as did variation in atmospheric deposition. Changes in climate had a stronger effect on flux of Hg from terrestrial to aquatic systems than did atmospheric deposition (Lee et al. 2000). Prediction of hydrologic flux of HgT and MeHg is difficult because of between-year variations related to climate and because of the large pool of Hg in soils. Global climate change, whether anthropogenically induced or not, could influence both rates of volatilization and hydrologic fluxes of Hg. Empirical relationships, in particular, can be undermined by change in conditions.

Major implications and limitations

Three major issues arise in this synthesis. First, the potential importance of volatilization, including fire, on Hg budgets of both terrestrial watersheds and of the globe must be better understood. The magnitude of this volatilization has serious implications for industrial control strategies. Secondly, although hydrologic flux of Hg from terrestrial watersheds is less than 10% of inputs, it is an important source of Hg to aquatic systems. Although reduction of Hg flux associated with particulates may be achievable in a few cases, most significant Hg flux is associated with naturally generated DOC. In systems with wetlands and associated DOC, concentrations of MeHg, in particular, already appear to be at or near the current water quality criterion. Finally, because all study sites are unique, and because climate strongly affects Hg cycling, only the most general conclusions about Hg cycling can be made and they must be critically evaluated. The overriding importance of climatic variation and the lack of representativeness of any short series of observations of ecosystems dynamics, including biogeochemical cycling, is cogently emphasized by 31 years of observations at Hubbard Brook, U.S.A. (Likens and Bormann 1995). Credibility is strengthened by relationships that encompass a broad range of systems and climatic variation.

Acknowledgments

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EFFECTS OF MERCURY ON WILDLIFE: A COMPREHENSIVE REVIEW

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Abstract—Wildlife may be exposed to mercury (Hg) and methylmercury (MeHg) from a variety of environmental sources, including mine tailings, industrial effluent, agricultural drainwater, impoundments, and atmospheric deposition from electric power generation. Terrestrial and aquatic wildlife may be at risk from exposure to waterborne Hg and MeHg. The transformation of inorganic Hg by anaerobic sediment microorganisms in the water column produces MeHg, which bioaccumulates at successive trophic levels in the food chain. If high trophic level feeders, such as piscivorous birds and mammals, ingest sufficient MeHg in prey and drinking water, Hg toxicoses, including damage to nervous, excretory and reproductive systems, result. Currently accepted no observed adverse effect levels (NOAELs) for waterborne Hg in wildlife have been developed from the piscivorous model in which most dietary Hg is in the methyl form. Such model are not applicable to omnivores, insectivores, and other potentially affected groups, and have not incorpotated data from other important matrices, such as eggs and muscle. The purpose of this paper is to present a comprehensive review of the Hg literature as it relates to effects on wildlife, including previously understudied groups. We present a critique of the current state of knowledge about effects of Hg on wildlife as an aid to identifying missing information and to planning research needed for conducting a complete assessment of Hg risks to wildlife. This review summarizes the toxicity of Hg to birds and mammals, the mechanisms of Hg toxicity, the measurement of Hg in biota, and interpretation of residue data.

Keywords—Review Wildlife Methylmercury Analytical methods

INTRODUCTION

The purpose of this review is to summarize the current state of knowledge about the effects of mercury (Hg) on wildlife, to provide an extensive reference list, and to add information from the literature about the cellular and biochemical mechanism of methylmercury (MeHg) toxicity from laboratory animal, aquatic animal, and in vitro work, when such findings are pertinent to impacts on wildlife. In this way, we hope to derive useful MeHg toxicologic benchmarks for wildlife, and to identify areas where adequate information is lacking. The literature search for this review drew on major computer databases for references concerning the effects of Hg on wildlife. The general search criterion was ''effects of MeHg on terrestrial wildlife.'' Using this search strategy, more than 800 references were retrieved and screened. Because MeHg is the form relevant to wildlife exposures, inorganic Hg effects have been included only for comparative or illustrative purposes. We preferentially selected studies reporting the results of dietary exposure, or oral administration at environmentally realistic doses. Residue-type field surveys are useful for documenting the extent of wildlife exposure, but have not been included here unless they help to provide a quantifiable exposure and effect. Studies conducted on wildlife species rarely are able to use large sample sizes; therefore, conclusions drawn from wildlife work are strengthened when supported and supplemented by similar investigations employing domestic or laboratory animals. Studies with domestic or laboratory species, aquatic organisms, or humans have been included if they provided information on a relevant toxicity endpoint for which no data was available from a wildlife species. Acceptable endpoints were those that affect growth, viability, or reproductive or developmental success, including behavior, immunologic effects, neurologic impairment and neurohistologic lesions, and teratology.

Reviews also have been presented recently by Heinz [1], and Thompson [2]. This review includes a discussion of the mechanisms of MeHg toxicity, which has not been included in previous wildlife reviews, and a overview of Hg and MeHg analysis methods in matrices of interest to wildlife toxicologists.

MECHANISM

Methylmercury toxicity in mammals is primarily manifested as central nervous system damage; including sensory and motor deficits and behavioral impairment [3,4] Animals initially become anorexic and lethargic. Muscle ataxia, motor control deficits, and visual impairment develop as toxicity progresses, with convulsions preceding death [5–7]. Smaller carnivores are more sensitive to MeHg toxicity than are larger species, as reflected in shorter time to onset of toxic signs and time to death. Dietary concentrations of 4.0 to 5.0 μg/g MeHg were lethal to mink and ferrets within 26 to 58 d, whereas otters receiving the same concentration survived an average of 117 days [3,8].

Methylmercury is readily transferred across the placenta, and concentrates selectively in the fetal brain. Mercury concentrations in the fetal brain were twice as high as in the maternal brain for rodents fed MeHg [9]. Reproductive effects of MeHg in mammals range from developmental alterations in the fetus, which produce physical or behavioral deficits after birth, to fetal death [10–14]. Sundberg and Oskarsson [15]

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reported speciation of Hg in the milk and offspring of rats exposed to dietary MeHg. The lack of comparable data from mammalian wildlife species certainly constitutes one of the more glaring gaps in our knowledge.

Neurotoxicity

Methylmercury damages primarily the cerebellum and cerebrum [16]. The neurotoxic effects of MeHg in adult mammals include ataxia, difficulty in locomotion, neurasthenia (a generalized weakness, impairment of hearing and vision, tremor, and finally loss of consciousness and death [1,14,17]. Lesions in the cerebral and cerebellar cortex accompany these clinical signs. Necrosis, lysis, and phagocytosis of neurons results in progressive destruction of cortical structures and cerebral edema. O'Connor and Nielsen [5] found necrosis, astrogliosis, and demyelination in the cerebral and cerebellar cortex of otters that received 0.09, 0.17, and 0.37 mg/kg/d MeHg for 45 to 229 d. In adult mammals MeHg is preferentially taken up by glial cells; these seem particularly susceptible to MeHg damage [18]. Low concentrations (10^{-5} M) of MeHg inhibit the ability of cultured rat brain astrocytes to maintain a transmembrane K^+ gradient, resulting in cellular swelling [19]. These findings support the suggestion of Clarkson [20] that inhibition of cell membrane Na^+, K^+, adenosine triphosphatase (ATPase) is the primary mechanism of MeHg toxicity. Aschner and his coworkers [21] further showed that the particular sensitivity of glial cells to MeHg was due to a neutral amino acid carrier system that enhances transport of MeHg into these cells. In an investigation of the protective effect of glutathione against MeHg toxicity in cultured mouse neuroblastoma cells, Kromidas et al. [22] proposed that MeHg causes damage to microtubules by oxidation of tubulin sulfhydryls and peroxidative injury.

The behavioral deficits produced by exposure to MeHg are known mostly from work with nonwildlife species, although an early article by Burton et al. [23] describes Hg-induced behavioral changes in *Peromyscus*. The behavioral teratology of MeHg in rodents was summarized by Shimai and Satoh [24]. Rats and mice exposed via the diet or by gavage at various times during gestation period showed retarded righting reflex, impaired or retarded swimming ability, decrease in spontaneous activities, impaired maze and avoidance learning, and deficits in operant learning [25]. Behavioral effects on a carnivorous species are reported only for the domestic cat [26]. The use of primates to study the behavioral teratology of MeHg has permitted more extensive investigations. Infant crab-eating macaques (*Macaca fascicularis*) born to females exposed to 50 or 70 μg/kg/d MeHg had blood MeHg levels of 1.69 ppm at birth and 1.04 ppm at the time of testing. The exposed macaques had significant deficits of visual recognition memory, compared to controls [27]. Cynomolgus monkeys (crab-eating macaques, *M. fascicularis*) born to females given by 50 μg/kg/d MeHg showed more nonsocial passive behavior, and less social play than nonexposed monkeys [28]. Adult macaques dosed with 0.24 to 1.0 mg/kg MeHg at twice-weekly intervals for up to 73 weeks first experienced constriction of the visual field, as has been reported by MeHg-intoxicated humans, an effect that was reversible if exposure was discontinued. At higher or more prolonged doses visual field constriction became permanent, and visual thresholds were altered, reflecting damage to neurons in the visual cortex [29]. Rice [30] exposed female monkeys to 10 to 50 μg/kg/d MeHg, bred them, then administered the same doses to the young, producing both a pre- and postnatal exposure. Infant Hg blood levels were 0.46 to 2.66 ppm at birth, decreasing to a steady-state concentration of 0.20 to 0.60 ppm by the time of behavioral assessment (fixed interval and discrimination reversal performance). Surprisingly, only small differences occurred in test performance in the young monkeys, even though the monkey receiving the highest doses exhibited clear signs of MeHg toxicity. Rice suggested that discrimination reversal might not be a sufficiently sensitive test in this species [30]. Cynomolgus monkeys to which Rice and Gilbert [31] administered 50 mg/kg/d MeHg for the first 7 years of life showed high-frequency hearing loss at 14 years, although no further exposure to MeHg occurred in the intervening 7 years. Ikeda et al. [32] reported that 100 to 300 μg/kg/d for 2 to 6 months was required to produce neurologic signs in rhesus monkeys (*macaca mulatta*). Although MeHg-induced behavioral impairments in birds have been documented (discussed below) comparable investigations with mammalian wildlife species have not been reported. Future effort should be directed to understanding the effect of low-level chronic MeHg exposure to sensory and behavioral function in wildlife species.

Biochemical and enzyme effects

Cholinesterase (ChE, acetylcholinesterase [AChE] and butyrylcholin esterase [BCE]) activities decreased in *Coturnix* quail receiving a diet containing 5 ppm MeHg for 18 weeks. Dietary concentrations of 0.05 or 0.5 ppm alone did not inhibit ChE activity, but potentiated the ChE inhibition of coadministered parathion. Quail receiving the highest concentration of MeHg had liver total Hg residues of 35.8 ppm, wet weigth [33,34]. Great blue heron nestlings were fed fish containing 0.31 to 0.87 ppm Hg in fish, resulting in liver Hg concentrations of 1.32 to 1.71 ppm by the end of the nesting period; however, no depression of brain ChE activity resulted from this exposure [35]. In rhesus monkeys given 0.4, 4.0, or 50 μg/kg/d MeHg for 150 d, no significant difference occurred in ChE activity, even at the highest dose [36].

Glutathione and glutathione enzymes

The MeHg-induced swelling of cultured rat brain astrocytes reported by Aschner et al. [19] mentioned earlier could be prevented if the cells were exposed to MeHg as its glutathione conjugate. Protection from MeHg-induced embryotoxicity in mice was provided by administering *N*-acetyl-L-cysteine, a precursor of glutathione, either simultaneously or following MeHg exposure [37]. Di Simplicio and coworkers [38] measured the activities of several glutathione enzymes in liver and kidney against a variety of substrates in mice given MeHg with or without the protective coadministration of sodium selenite. They described a complex interaction of glutathione in tissues in which MeHg-induced damage and tissue repair occurred together. Similar results in mice were reported by Yasutake and Hirayama [39]

Immunotoxicity

Mercuric compounds have been demonstrated to be immunotoxic in several investigations. In a study in which rat dams received 3.9 μg/g diet MeHg during pregnancy, natural killer cell activity was reduced 42% in offspring exposed in utero and via lactation. A decline in T-cell activity in some cell types was also noted [40]. Human peripheral blood cells exposed in vitro to low concentrations of both Hg and MeHg showed a dose-dependent reduction in T-cell proliferation, and

in monocyte and macrophage viability. Cell death was preceded by disruption of cell membranes and an increase in intracellular Ca^{2+}. The effect of MeHg was 5 to 10 times greater than the effect of Hg effect [41,42]. However, even inorganic Hg administered chronically to mice in drinking water as HgCl caused immune cell impairment and disruption of enzyme activity at doses too low produce kidney damage [43]. Methylmercury is more immunotoxic than Hg because MeHg exerts a double influence on Ca^{2+} modulation. In rat T lymphocytes, the rapid increase in Ca^{2+} concentration caused by MeHg resulted from both influx of extracellular Ca^{2+} and mobilization of Ca^{2+} from intracellular stores; the $HgCl_2$-induced slow rise in Ca^{2+} was due only to influx [44].

Chronic exposure to MeHg at levels too low to cause overt signs of toxicity may render an animal susceptible to infection that it might otherwise resist [43,45]. The finding by Spalding et al. [46] that great white herons dying of chronic, multiple diseases had greater body burdens of Hg than those dying of acute diseases suggests the importance for wildlife of mercurial compounds' immunotoxicity.

Genotoxicity

Both Hg and MeHg cause chromosome breakage, an effect that is mitigated by H_2SeO_3 [47,48]. In cultured lung and brain cells from rats, Chinese hamsters, and humans, brain cells were more susceptible to MeHg DNA strand breakage and cytotoxicity than were lung cells [47–50]. De Flora et al. [51] reported in an extensive review of the genotoxicity of mercury that Hg compounds often exerted clastogenic effects in eukaryotes, especially by binding SII groups and acting as spindle inhibitors, thus causing c-mitosis and resultant aneuploidy and/or polyploidy. Methylmercury compounds were more active than inorganic Hg salts.

MAMMALS

The results of studies of the effects of MeHg on mammals are summarized in Table 1. Controlled feeding studies employing wildlife species provide the highest quality data. O'Connor and Neilsen [5] fed rations with 2, 4, or 8 ppm MeHg to 11 adult male river otters, 3 per dose level and 2 controls. Actual MeHg consumption was quantified as 0.09, 0.17, and 0.37 mg/kg body weight/d. At the lowest observed adverse effect level (LOAEL) dose of 0.09 mg/kg/d, two of three otters developed anorexia and ataxia between day 168 and day 199. Histologic findings included neuronal necrosis and demyelination, mainly in the neocortex and cerebellum. Wobeser et al. [6] fed mink feed contaminated with fish containing 0.44 ppm MeHg for 145 days. The fish comprised either 50% (0.22 ppm) or 75% (0.33 ppm) of the diet. No MeHg toxicosis was observed at these exposures. Using a mink body weight of 1.3 kg and food ingestion rate of 0.18 kg/d, the no observed adverse effect level (NOAEL) from this study was calculated to be 0.046 mg/kg/d. In a follow-up study, Wobeser and coworkers [52] fed adult female mink rations containing 1.1, 1.8, 4.8, and 8.3 and 15 ppm MeHg for 93 d. Mink receiving 1.8 ppm and greater concentrations developed the same signs of Hg toxicosis, irrespective of dose, but the time to onset of signs was proportional to dose received. Mink receiving 1.1 ppm did not display clinical signs during the observation period, but at necropsy were found to have neurologic lesions. The authors maintained that clinical manifestations of MeHg toxicity would have developed at this those had the exposure period been longer. This argument is supported by the findings of Wren et al. [14], who fed diets containing 1 ppm MeHg to mink to determine the effects of chronic exposure. The diet was fed daily until a female mink died at 10 to 12 weeks, after which the diet was fed to the surviving mink on alternate days, effectively reducing the dose to 0.5 ppm/d. These findings suggest that 1.0 ppm should be regarded as the dietary LOAEL for mink and that a brain or muscle concentration of 5.0 ppm is the criterion for MeHg toxicity in mink. Ronald and coworkers [53] fed fish containg 0.25 or 25 mg/kg MeHg to harp seals. The 0.25 mg/kg exposure produced lethargy and weight loss in the seals; 25 mg/kg was lethal to seals exposed for 20 to 26 d.

Toxicokinetics and biotransformation

Ingested Hg may be either inorganic or organic, although it is usually in the form of MeHg in higher trophic level feeders. Inorganic Hg may be monovalent (mercurous) or divalent (mercuric). Methylmercury is readily absorbed from the gastrointestinal tract (90–95%), whereas inorganic salts of Hg are less readily absorbed (7–15%). In the liver, Hg binds to glutathione, cysteine, and other sulfhydryl-containing ligands. These complexes are secreted in the bile, releasing the Hg for reabsorption from the gut [54]. In blood, MeHg distributes 90% to red blood cells and 10% to plasma. Inorganic Hg distributes approximately evenly or with a cell : plasma ratio of ≥ 2 [55]. O'Connor and Nielsen [5] found that length of exposure was a better predictor of tissue residue level than dose in otters, but that higher doses produced an earlier onset of clinical signs.

Methylmercury readily crosses the blood–brain barrier, whereas inorganic Hg does so poorly. The transport of MeHg into the brain is mediated by its affinity for the anionic form of sulfhydryl groups. This led Aschner and Aschner [56] to propose a mechanism of molecular mimicry in which the carrier was an amino acid. Transport of MeHg across the blood–brain barrier in the rat as MeHg-L-cysteine complex has since been described [57]. Demethylation occurs in brain tissue, as evidenced by the observation that the longer the time period between exposure to MeHg and measurement of brain tissue residue, the greater the proportion of inorganic Hg [58–60]. Methylmercury is converted to mercuric Hg in other tissues, but the rate of demethylation varies with tissue. In humans exposed to dietary MeHg for 2 months, inorganic Hg constituted 16 to 40% of total Hg in lever, 7% in blood, and 22% in plasma. In monkeys (*M. fascicularis*) given 50 μg/kg body weight MeHg for 12 months, the half-life ($t_{1/2}$) in brain was 35 d. However, the proportion of inorganic Hg increased with increasing time after exposure [61]. Rice et al. [62] determined the $t_{1/2}$ of MeHg in macaque blood to be 14 d, and estimated the brain $t_{1/2}$ to be between 38 and 56 d. Chen et al. [63] administered MeHg to rhesus monkeys for 3.5 to 12 months. As the time between dosing and sacrifice increased, liver Hg declined and kidney Hg increased. Under these exposure conditions, the monkeys of Chen and coworkers did not exhibit neurologic symptoms, and blood chemistry remained within normal limits.

Both inorganic and organic Hg are excreted primarily in feces; 98 d after administration of a radiolabeled dose of MeHg to rats, 65% of the dose was recovered in the feces as inorganic Hg and 15% was recovered as organic Hg. Urinary excretion accounted for less than 5% of the dose, although urinary excretion of inorganic Hg increased with increasing time after exposure. Incorporation into fur or hair is also an important

route of excretion for both methyl and mercuric Hg [64]. On an average of species and tissues, the biological half-life of MeHg in mammals is about 70 d; for inorganic Hg the half-life is about 40 d.

All forms of Hg cross the placenta, but MeHg concentrates selectively in the fetal brain. Fetal red blood cells contain 30% more MeHg than do maternal red blood cells [65]. Methylmercury concentrations in the fetal brain were twice as high as in the maternal brain in rodents fed MeHg [9]. Reproductive effects of MeHg in mammals include developmental alterations that produce behavioral deficits after birth, impaired fertility, and fetal death. Chang and Annau [11], Eccles and Annau [12], and Shimai and Satoh [24] reviewed the behavioral toxicology of MeHg in mammals. Swimming ability, operant learning, avoidance, maze learning, and development of reflexes were affected at the lowest dosages, followed by changes in spontaneous activity, visual function, vocalization, and convulsions at successively higher exposures.

Further exposure may occur after birth. When hamster females were given 1.6 μmol/kg/d of radiolabeled MeHg the day after giving birth to young, 0.12 nmol/g of radiolabeled Hg was recovered in the milk 1 d later, 80 to 90% as MeHg. Pups continued to accumulate Hg in the tissues for 10 to 12 days, after which tissue concentrations declined, except in fur and kidneys, where concentrations increased throughout the 4-week study period. The investigators calculated that 5% of the dose administered to the dam passed to the young in the milk [66].

BIRDS

Mercury concentrations in avian eggs and tissues and related effects are summarized in Table 2. The biokinetics and toxicology of organomercurials in birds, particularly of MeHg, have been more extensively studied than those of Hg in the inorganic form. This is due to the greater toxicity and bioaccumulation of the methylated form compared to inorganic forms. Intestinal absorption of inorganic Hg is limited to a few percent, whereas absorption of MeHg is nearly complete [67]. The half-life of Hg in seabirds has been estimated to be about 60 d [68]. Inorganic Hg exerts its greatest effect on the kidneys, whereas MeHg is a potent embryo and nervous system toxicant. Methylmercury readily penetrates the blood–brain barrier in birds, as in mammals, producing brain lesions, spinal cord degeneration, and central nervous system dysfunctions. Symptoms of acute MeHg poisoning in birds include reduced food intake leading to weight loss; progressive weakness in wings and legs; difficulty flying, walking, and standing; and an inability to coordinate muscle movements [67]. Brain residues are most diagnostic for acute Hg poisoning. Kidney disease and kidney lesions also are strongly associated with elevated dietary Hg [46, 69–71]. Determination of Hg concentrations in brain, liver, and kidney of birds found dead is desirable if Hg poisoning is suspected. In some species, especially Procellariformes, demethylation of Hg appears to be a significant detoxification strategy.

In addition to well-identified acute effects of Hg at high concentrations, significant adverse effects also occur at lower tissue Hg concentrations representing chronic Hg exposures. In great white herons liver Hg contamination >6 ppm correlated with mortality from chronic diseases [72]. Reproduction is one of the most sensitive toxicologic responses, with very low dietary concentrations causing effects [73–76]. Concentrations in the egg are typically most predictive of Hg risk to avian reproduction, but concentrations in liver have also been evaluated for predicting reproductive risk. The documented effects of Hg on reproduction range from embryo lethality to sublethal behavioral changes in juveniles at low dietary levels: Effects of Hg include reduced hatchability due to increases in early mortality of embryos, eggshell thinning, reduced clutch size, increased numbers of eggs laid outside the nest, and aberrant behavior of juveniles, and potentially may include impaired hearing of juveniles [73,77–80].

Hg in avian diets

Barr [75] indicated that reductions in egg laying and territorial fidelity were associated with mean prey Hg concentrations of 0.3 to 0.4 ppm fresh weight; common loons established few territories, laid no eggs, or one egg and raised no progeny in waters where the mean Hg concentrations of prey exceeded 0.4 ppm fresh weight. The dietary concentrations of MeHg that are required to produce significant reproductive impairment are about 1.5-fold those required to produce overt toxicity in adult birds of the same species [81]. Overall reproductive success in birds can decrease by 35 to 50% due to dietary MeHg exposure insufficient to cause obvious signs of intoxication in adults. Heinz [73] fed 0.5 mg/kg dry weight MeHg (0.1 mg/kg wet weight) to three generations of mallards. Females laid fewer eggs and produced fewer ducklings. Barr [75] made the same observations in the field study mentioned previously where reductions in egg laying and in nest-site and territorial fidelity of the common loon in northwestern Ontario were associated with maximum Hg residues in eggs of 1.39 mg/kg wet weight. The loon diet contained from 0.2 to 0.3 mg/kg wet weight Hg. Heinz [73] also found that ducklings in his multigeneration laboratory feeding study were less responsive to taped maternal warning calls and were hypersensitive to fright stimulus.

Hg in avian liver, brain, and kidney

Correct interpretation of tissue residue data requires characterization of the various species of Hg. The kidney is a major reservoir of inorganic Hg in birds as well as in mammals. In renal tissue Hg will bind to metallothionein. Not surprisingly, the major toxic effects of inorganic Hg are kidney damage when Hg-induced necrosis of proximal tubular cells occurs [82]. Spalding et al. [46] found that liver Hg concentrations >6 ppm correlated with malnutrition and mortality from chronic disease in great white herons; however, the authors cautioned against overinterpreting these results because only dead birds were examined. Zillioux and coauthors [83], in their review of the literature, found that concentrations in liver between 1 and 2 ppm (wet weight) Hg may be associated with behavioral effects, whereas liver Hg concentrations of about 11 ppm (wet weight) and above were associated with high embryo/duckling mortality and brain lesions. Spalding and Forrester [84] suggested that neurologic effects may be associated with liver Hg levels in birds as low as 5 ppm (wet weight). Gochfeld [85] reported abnormal feather loss in the young of common terns having liver concentrations of 3 to 14 ppm. Zillioux et al. [83] concluded that a conservative residue threshold for major toxic effects in waterbirds is 5 ppm (wet weight) in liver. In contrast, apparently normal seabirds have been found with extraordinarily high Hg concentrations in liver, but these concentrations have been primarily inorganic Hg [86]. In the majority of wild birds sampled, liver concentrations of Hg are usually higher than kidney concentrations. However, in Hg poisoning some

Table 1. Effects of mercury and methylmercury (MeHg) on mammals and associated tissue residues

Species	Tissue	Tissue concn. (ppm, wet wt.)	Dose (mg/kg or ppm)	Route/form	Exposure/ duration	Effect/comments	Reference
Dog (*Canis familiaris*)		0.1–0.25 mg/kg		Oral, during pregnancy		Stillbirths	[13]
Cat (*Felis catus*)	Liver (total Hg)	40.2	0.25 mg/kg/d, 5 of 7 d	MeHg, in caps with food	90 d	First convulsions 68 d after dosing, mean survival 78 d	[17]
	Liver (MeHg)	18.1					
	Hair	170					
	Liver	40.2					
	Kidney	21.6					
	Brain	11.3					
	Muscle	15.1					
	Heart	8.92					
	Lung	10.8					
Cat	Brain	0.85	0.55 with 2.9 mg/kg selenium	Dietary, 93.5–154 μg/d	188 d	No difference in maze learning or handling response but less than half object contact on open field test	[26]
	Kidney	1.27					
	Liver	11.9					
	Muscle	1.59					
Cat			0.5	Dietary	7–11 months	Proliferation of smooth endoplasmic reticulum; degeneration of hepatic mitochondria	[10]
Pig (*Sus* spp.)			0.5	Oral, during pregnancy		Stillbirths	[13]
Crab-eating macaque (*Macaca fascicularis*)			0.4 μg/kg body wt.	MeHg, in apple juice	150 d	No clinical symptoms, no significant difference in cholinesterase activity	[36]
			4.0 μg/kg body wt.				
			50 μg/kg body wt.				
Rhesus monkey (*Macaca mulatta*)			0.5 mg/kg	Oral, d 20 to 30 of pregnancy		Abortions, maternal toxicity	[13]
Rhesus monkey	Liver	22.91	125 μg/kg body wt./d	MeHg, in apple juice	3.5 months	No clearance period; liver and kidney histologic alterations	[62]
	Kidney	21.32					
	Liver	26.4	80 μg/kg body wt./d		7 months	No clearance period; liver and kidney histologic alterations	
	Kidney	30.32					
	Liver	14.45	80 μg/kg body wt./d		12 months	No clearance period; liver and kidney histologic alterations	
	Kidney	46.93					
	Liver	1.12	100 μg/kg body wt./d		10 months	Five-month clearance period; liver normal, kidney effects persisted	
	Kidney	10.34					
	Liver	2.51	80–100 μg/kg body wt./d		15 months	Two and one-half-month clearance period; liver normal, kidney effects persisted	
	Kidney	29.54					
	Liver	2.73	90 μg/kg body wt./d		10 months	Four and one-half-month clearance period; liver normal, kidney effects persisted	
	Kidney	11.76					

Table 1. Continued

Species	Tissue	Tissue concn. (ppm, wet wt.)	Dose (mg/kg or ppm)	Route/form	Exposure/ duration	Effect/comments	Reference
Mink (*Mustela vison*)	Liver	30.1	1	$MeHgCl_2$	6 months	Sublethal, synergistic effect with polychlorinated biphenyls caused reduced kit survival	[14]
	Brain	8.6	Experimental diet fed every other day after mortalities occurred at 10–12 weeks				
	Kidney	36.2					
Mink	Liver	44.1	1		6 months	Lethal (females only)	[14]
	Brain	15.3					
	Kidney	28.4					
Mink	Liver	55.6	5	MeHg in diet		Ataxia, anorexia, paralysis, death between day 30 and day 37	[7]
	Kidney	37.7					
	Brain	19.9					
	Muscle	25.2					
	Fur	1.22					
	Spleen	24.8					
	Lung	17.1					
	Heart	16.7					
Mink	Liver	4.2	0.44	Contaminated fish as 50% or 75% of total diet (0.33 ppm)	120 d	No clinical or pathologic effect	[6]
	Kidney	2.6	No observed adverse effect level (NOAEL)				
	Brain	3.4	0.073 mg/kg/d (male) 0.046 mg/kg/d (female)				
Mink	Liver	0.45	0.1	MeHg, dietary	93 d	No effect	[6]
	Kidney	0.75					
	Brain	0.1					
	Muscle	0.2					
	Fur	0.9					
	Liver	25.3	1.1 Lowest observed adverse effect level (LOAEL)			Nerve tissue lesions, no clinical signs	
	Kidney	22.4	0.24 mg/kg/d (male)				
	Brain	8.2	0.15 mg/kg/d (female)				
	Muscle	7.8					
	Fur	1.8					
	Liver	21.3	1.8			Anorexia, ataxia at 50–80 d, death at 59–79 d	
	Kidney	22.3					
	Brain	18.1					
	Muscle	4.9					
	Fur	2.3					
Mink	Liver	20.5	4.8			Anorexia, ataxia at 23–32 d; death at 26–36 d	
	Kidney	22.3					
	Brain	10.5					
	Muscle	14.1					
	Fur	1.7					

Table 1. Continued

Species	Tissue	Tissue concn. (ppm, wet wt.)	Dose (mg/kg or ppm)	Route/form	Exposure/ duration	Effect/comments	Reference
	Liver	31.7	8.3			Anorexia, ataxia at 16–21 d; death at 19–26 d	
	Kidney	21.5					
	Brain	13.3					
	Muscle	17.4					
	Fur	1.2					
	Liver	23.6	15			Anorexia, ataxia at 16–18 d; death at 18–20 d	
	Kidney	26.4					
	Brain	15.6					
	Muscle	22					
	Fur	1.2					
Otter (*Lutra canadensis*)	Liver, total Hg	1.85	0 ppm	MeHg, dietary	210 d		[5]
	Liver, organic Hg	1.03					
	Kidney, total Hg	2.1					
	Kidney, organic Hg	1.62					
	Muscle, total Hg	0.93					
	Muscle, organic Hg	0.77					
	Brain, total Hg	0.38					
	Brain, organic Hg	0.3					
	Liver, total Hg	32.6	2 ppm (0.09 mg/kg)		Average 181 d	Anorexia, ataxia in two of three, day 168 to day 199	
	Liver, organic Hg	17.3					
	Kidney, total Hg	37.6					
	Kidney, organic Hg	23.6					
	Muscle, total Hg	13.3					
	Muscle, organic Hg	12					
	Brain, total Hg	13.3					
	Brain, organic Hg	10.3					
Otter	Liver, total Hg	35.3	4 ppm		Average 116 d	Anorexia, ataxia in three of three, day 101 to day 120; nephrotic and neurologic lesions	
	Liver, organic Hg	17.3					
	Kidney, total Hg	39.6					
	Kidney, organic Hg	31.6					
	Muscle, total Hg	17.3					
	Muscle, organic Hg	16.3					
	Brain, total Hg	21					
	Brain, organic Hg	18.5					
	Liver, total Hg	32.3	8 ppm		Average 50 d	Lethal; mean time to death, 54 d; nephrotic and neurologic lesions	
	Liver, organic Hg	17.3					
	Kidney, total Hg	40.3					
	Kidney, organic Hg	28.5					
	Muscle, total Hg	21.6					
	Muscle, organic Hg	15.2					
	Brain, total Hg	23.7					
	Brain, organic Hg	14					
Peromyscus	Hair	10.8				Impaired swimming, open field	[23]
	Hair	0.31					
Rat, Sprague–Dawley (*Rattus norvegicus*)			3.9	MeHg, dietary	Fed to dam, 11 weeks prior to mating; during gestation and lactation		[15]

Table 1. Continued

Species	Tissue	Tissue concn. (ppm, wet wt.)	Dose (mg/kg or ppm)	Route/form	Exposure/ duration	Effect/comments	Reference
	Milk	0.16				No effect on maternal body weight, or litter size	
	Adult brain	2.9				Four percent lower body weight in offspring	
	Adult blood	32				No effect on behavior of dams or offspring	
	Pup brain	0.44				Reduced natural killer cell activity	
	Pup blood	1.52				Slight increase in cerebellar noradrenaline	
	Pup brain	0.35					
	Pup blood	0.98					
	Pup brain	0.092					
	Pup blood	0.42					
Harp seal (*Pagophilus groenlandicus*)	Brain	14.8	0.25	In gel caps, in fish	60 d	Decline in appetite, body weight	[53]
	Kidney	69.5					
	Liver	64					
	Blood (MeHg)	8.85					
	Blood (total Hg)	9.93					
	Brain	21.8			90 d	Reduced activity after 60 d	
	Kidney	50.6					
	Liver	82.5					
	Blood (MeHg)	12.5					
	Blood (total Hg)	13.1					
	Brain	33.3	25			Lethargy, weight loss from day 3; death on day 20 to day 26	
	Kidney	110					
	Liver	126					
	Blood (MeHg)	21.3					
	Blood (total Hg)	28.5					

Table 2. Mercury concentrations in avian eggs and tissues and related effects

Tissue	Concn. (ppm)	Wet (w) or dry (d)	Endpoint	Species	Reference
Liver	1.06	w	No effect	Common tern	[85]
Liver	22.2	w	Abnormal feather loss in juveniles	Common tern	[85]
Liver	3–13.7		Decreased hatchability	Common loon	[75]
Liver	*5*	*w*	*Conservative threshold for major toxic effects*	*Water birds*	[83]
Liver	>6	w	Correlated mortality from chronic disease	Great white heron	[46]
Liver	7.2	w	Increased disease and emaciation	Great white heron	[84]
Liver	9.08	w	Nesting success	Common tern	[76]
Liver	20.7	w	Hatching success	Common tern	[76]
Liver	27.5	w	10–12% fledge rate	Common tern	[46]
Liver	29.7	w	Reduced nesting success	Common loon	[75]
Liver	30	w	Neurologic effects	Birds in general	[92]
Liver	35	w	Death	Osprey	[96]
Liver	51.9	w	Reduced hatching success	Common loon	[75]
Liver	54.5	w	LD33[a]	Common grackle	[89]
Liver	97.7	w	Death	Gannet	
Liver	103.6	w	LD33	European starling	[89]
Liver	126.5	w	LD33	Red-winged blackbird	[89]
Liver	306 total/20.4 MeHg	d	No adverse effects observed	Black-footed albatross	[86]
Brain	>2	w	Reduced egg laying, and decreased nest and territory fidelity	Common loon	[75]
Brain	4–6	w	Failure to hatch	Black duck	[93]
Brain	20	w	25% mortality	Zebra finch	[88]
Egg	1–5/0.2–1.0	d	Reduced productivity in one half of the population	Merlin	[95]
Egg	0.5–1.5	w	Decreased hatchability	Pheasant	[73]
Egg	0.86	w	Aberrant nesting behavior	Common loon	[73]
Egg	1.0	w	Successful reproduction	Common tern	[76]
Egg	*1.0–3.6*	*w*	*Residue threshold for significant toxic effects*	*Variety of water birds*	[83]
Egg	2–16	w	No decreased hatchability	Herring gull	[76]
Egg	3.65	w	27% hatching, 10–12% fledging	Common tern	[76]
Kidney	37.4 total/6.2 MeHg	d	No adverse effect observed	Black-footed albatross	[86]
Kidney	40.4	w	LD33	Grackle	[89]
Kidney	74.3	w	LD33	Red-winged blackbird	[89]
Kidney	86.4	w	LD33	European starling	[89]

[a] LD33 = lethal dose, 33%.

indication exists that kidney concentrations may be elevated to near the liver concentration [87]. Kidney concentrations of 20 ppm have been found in birds found dead in Hg-contaminated environments [87]. It should be noted that birds differ from mammals in having a renal portal system; venous blood from the terminal portion of the digestive tract flows to the kidney rather than the liver, as in mammals. This may make the avian kidney more vulnerable. Brain Hg as low as 3 to 7 ppm can be lethal to ducklings. Four times these values are required to cause direct mortality in adults. The lowest concentration of Hg in brain found to produce obvious signs of intoxication in adults was 5 ppm dry weight or 1 to 1.6 ppm wet weight [88]. Brains of dead mallard ducklings with lesions in the brain contained an average of 6.17 and 5.19 ppm on 2 successive years [78]. Passerines are poorly represented in Hg studies; however, Finley et al. [89] found liver Hg concentrations between 50 and 150 ppm in four species of songbirds exposed to levels of Hg fatal to one third of the test group, and Scheuhammer [88] reported that Hg exposure lethal to 25% of exposed zebra finches resulted in brain Hg residues of 20 ppm [88].

Reproductive effects and egg concentrations

Toxic effects of Hg in bird eggs have been documented by many investigators in both laboratory and field studies [73,75,76,78,90–96]. Mercury is an extremely potent embryo toxicant and dietary Hg is dose-dependently transferred to avian eggs. Reproduction is one of the most sensitive endpoints of Hg toxicity. Mercury accumulates particularly in the egg-white proteins, which derive from serum proteins; egg concentrations thus apparently more closely reflect Hg from recent dietary uptake than from accumulated tissue stores. According to Walsh [97], evidence exists that the ovalbumin fraction of egg white has a specific affinity for dietary Hg, whereas the globulin fraction tends to accumulate low levels of nondietary Hg. Because of the strong dietary connection, Walsh suggested that eggs provide a particularly good indicator of Hg exposure in the vicinity of the nesting site in the immediate prelaying season. Methylmercury can be expected to predominate in eggs, particularly within the albumin fraction. Because Hg is predominantly deposited in albumin, more intraclutch variation in Hg content is also to be expected than in contaminants preferentially distributed to yolk. Becker [98] reported that the last egg of a clutch in Charadriiformes had lower Hg than the first egg. The first egg laid contained up to 39% more Hg than the second or third egg. Becker [98] predicted that the toxic effects of Hg would be more pronounced in the chick from the first-laid egg (a-chicks). In elevated Hg environments this will result in abnormally high losses of a-chicks, a reversal of

the normal situation. Barr [75] documented adverse effects on common loons associated with egg concentrations of 1.39 mg/kg wet weight.

Hoffman and Moore [93] treated mallard eggs with externally applied MeHg chloride. Effects were dose related and included decreased embryo weights, developmental abnormalities, and embryonic death. With increasing concentrations abnormalities progressed in severity from mostly minor skeletal deformities to gross external ones such as micromelia, gastroschisis, and eye and brain defects as well as internal defects such as reduction in liver size. Such laboratory work is useful because it may efficiently elucidate the types of effects that can be produced, but an extrapolation of dosages in Hoffman and Moore to the field situation would be inappropriate. External Hg exposures by Hoffman and Moore had more pronounced effects at lower doses than organic Hg incorporated into the egg from diet [92], presumably because of less binding to the ovalbumin and ovoglobulin.

Reproductive effects may extend beyond the embryo to adversely affect juvenile survival rates. Mercury in the eggs of mallards caused brain lesions in hatched ducklings. Mallards were fed 3.0 ppm MeHg dicyandiamide over 2 successive years. Mercury accumulated in the eggs to an average of 7.18 and 5.46 ppm (wet weight) in 2 successive years. Lesions included demyelination, neuron shrinkage, necrosis, and hemorrhage in the meninges overlying the cerebellum [92]. In a laboratory study with pheasants, Fimreite [77] estimated the threshold concentration in eggs for adverse effects on hatchability to be between 0.5 and 1.5 ppm. The low end of this effect range continues to be the LOAEL for Hg in the avian egg. In a field study of common terns, Fimreite [91] estimated the threshold level for toxic effects to be between 1.0 and 3.6 ppm. Heinz [92] was able to examine more subtle behavioral effects in mallard ducklings fed MeHg. Heinz fed ducks 0.5 ppm Hg over three generations and found decreased reproductive success and altered behavior of ducklings. The mean Hg concentration in eggs associated with these observations was 0.86 mg/kg (wet weight). Hoffman and Moore applied Hg externally to mallard eggs and found dose-related effects on survival, growth, and abnormal development. The lowest dose applied that affected survival was 27 μg. Given an average mallard egg weight of 55 g, this dose corresponds to about 0.5 mg/kg.

Hg in feathers: A potential monitoring tool and avian route of excretion

Almost all feather Hg is in the organic form [99]. Establishing effect levels using Hg concentrations in feathers must be considered with caution. Feathers represent a route of excretion and not a target organ. Mercury is deposited in feathers at the time of molt when feathers are actively growing and have a corresponding blood supply [100–102]. Once Hg is in feathers it is bound to the sulfide bonds of feather keratin and is not physiologically available for redistribution to target organs. Mercury content of feathers will vary with time to last molt, feather type, and age and species of the bird [103]. Feathers have the advantage of being a nondestructive exposure assessment matrix that may be resampled in the same individual, and that may also be compared with museum specimens [104]. The concentration of Hg in tissues may actually decrease during molting as Hg is mobilized from tissues into feathers [101]. In sequential feather loss patterns the first primary feather to be grown back has the greatest Hg concentration, with decreasing concentrations following [87,102,105]. Becker et al. [106] found results in three species of larids that implied that Hg in the first down of chicks was a consequence of Hg levels in the egg, whereas levels in feathers of chicks were largely due to Hg ingested in food. Lewis and Furness [107] found that in laboratory reared black-headed gulls 49% of the administered Hg was accumulated in the plumage independent of the dose administered. The percentage of the Hg body burden found in the plumage of different species has been found to vary. Species that are effective in demethylating Hg, such as members of the Procellariiformes, will tend to have a lower percentage of their total Hg body burden partitioned into the feather compartment as compared to other species. This has been interpreted as an adaptation to the slow molt of feathers in Procellariiformes with the consequent reduced opportunity for sequestration and ultimate excretion of MeHg via feathers [86]. The molt pattern of any given species will have a significant influence on variation in feather Hg concentrations between different feathers within an individual bird [104]. More variation in Hg with feather type should also be expected in more contaminated environments [106]. The exposure relative to season and feather growth may also have an important influence on Hg accumulation in other tissues if birds experience significant differences in Hg exposure between wintering and breeding grounds. For meaningful quantitative monitoring of Hg using feathers the feather/Hg pattern for a species should be established and similarly sampled among those individuals or populations that are to be compared. For historic comparisons using older museum specimens determinations of both total and MeHg in feathers may be prudent to evaluate the relative contribution of mercurials used in specimen preservation of avian study skins, if preservation methods are only vaguely recorded. In a review of effects related to Hg concentrations in feathers, Eisler [107] reported that concentrations between 5 and 40 mg/kg in feathers were linked to impaired reproduction. Sterility was observed in the Finnish sparrow hawk (*Accipiter nisus*) at feather Hg concentrations of 40 mg/kg. A great deal of variation is likely in feather Hg concentrations associated with adverse effects between species and between geographic areas due to Hg exposure patterns related to feather molt. Bowerman et al. [108] found mean Hg in feathers of bald eagles in the Great Lakes region of 13 to 21 mg/kg but no association between Hg concentrations and bald eagle reproduction could be made. Scheuhammer [81] suggests that feather Hg concentrations >20 mg/kg can result from diets containing Hg concentrations >1 μg/g and that these concentrations should be considered as indicative of a wetland that poses an Hg risk to birds. Scheuhammer estimated normal background of Hg in feathers of raptorial birds to be 1 to 5 μg/g.

REPTILES AND AMPHIBIANS

The toxicity of Hg and MeHg to reptiles and amphibians is almost unknown. A dose of 50 ppb applied to the embryos of the frog *Xenopis laevis* reduced survival by 50% after 4 d of treatment, and to 0% after 7 d. Surviving embryos showed disruption of morphogenesis, neurophysiology, and neuroimmune regulation [109]. Rao and Madhyastha [110] reported that the median lethal concentration (LC50) of HgCl to the tadpoles of *Microhyla ornata* ranged from 2.04 ppm (24 h) to 1.12 ppm (96 h). Wolfe (unpublished data) fed MeHg to garter snakes (*Thamnophis sirtalis*) in concentrations up to 200 μg/g food in the range-finding phase of a proposed feeding

Table 3. Summary of mercury (Hg) and methylmercury (MeHg) analytical methods

Method	Species	Detection limits (ng/g)	Advantages	Disadvantages
Cold-vapor atomic fluorescence spectroscopy (CVAFS)	Total Hg	0.005	Less cross-contamination concern	
	MeHg	0.001	Most sensitive	Costly, requires special lab
Ethylation/cold-vapor atomic absorption spectroscopy	Total Hg	0.05	Sensitive, routine analysis	Not as sensitive as CVAFS
	MeHg	0.01	Sensitive, routine analysis	Not as sensitive as CVAFS
Inductively coupled plasma–mass spectroscopy	Total Hg only	1.0	Low cost	Risk of cross-contamination with reagents or standards
High-performance liquid chromatography–atomic absorption	MeHg	0.6	Relatively fast	Fewer steps, higher yield
Gas–liquid chromatography–electron-capture detection	MeHg	0.001	Direct measurement	Many steps, lower yield
Gas–liquid chromatography–microwave-induced plasma detection (GC-MIP)	MeHg	0.001	Hg-specific detector	Many steps, lower yield
Headspace-injected–GC-MIP	MeHg	0.003	Sensitive	
Direct atomic absorption spectroscopy	Total Hg	0.005	Simple procedure	Many steps, lower yield
	MeHg	0.005	Simple procedure	MeHg determined by difference

study. The snakes displayed no sign of MeHg toxicity, no decrease in food consumption, and later gave birth to apparently normal young. Because no effect was seen at these high doses in the range-finding trials, the study was not completed.

Hg AND MeHg ANALYTICAL METHODS

Sample preparation

A summary of analytical methods for determination of Hg and MeHG is presented in Table 3. Biological samples such as muscle and liver tissues, hair or fur, eggshell, and body feathers have been used to determine the Hg body burden of wildlife species [111–114]. Most biological samples are obtained from wildlife captured in their habitats. Organ tissues such as skin, liver, muscle, and brain tissues are excised in the field and shipped on ice to the laboratory [113]. Normally the samples are stored in clear glass containers; however, the use of polyethylene terephthalate containers has proven to be as suitable as glass bottles [115] for shipping purposes. Eggs can be collected in the field and the contents stored under refrigeration for 2 to 3 months before analysis [111,112]. The samples are usually freeze-dried, ball-milled, and homogenized prior to digestion with a mixture of nitric and sulfuric acids.

Hair or fur samples may either be unwashed [116], or washed with acetone to reduce the fat content [117]. Some investigators have found that washing is not effective in removing naturally occurring Hg from exogenous deposition [118,119] The digestive process may include submersion of hair or fur in a mixture of concentrated acid extractive solvents such as nitric and sulfuric acid or acetonitrile–water and sodium pyrrolidinedithiocarbamate. After a period of time the prepared extracted solvent can be used in Hg analysis.

Feather and eggshell samples

Feathers can be collected from dead or live birds. Feather and eggshell samples are treated similarly. Some investigators do not wash the surface to eliminate external contamination [106], whereas others include washing the feather vigorously in deionized water alternately with acetone to remove loosely adherent external contamination [114,120] Without washing, surface Hg from the use of Hg in the preservation of older specimens may present a compounding variable. The washing process is followed by digestion in warm nitric acid with the addition of 50% hydrogen peroxide. The samples are diluted in deionized water before analysis.

Fish and shellfish samples

Fish and shellfish samples must be collected and analyzed when investigating Hg exposure in piscivorous species. Historically, high detection limits have caused limitations in measurement of total Hg and MeHg in aqueous and biological samples. Large amounts of organic matter and other substances accompanying biological specimens as well as contamination of samples during handling can potentially interfere with total Hg determination because of the ubiquitous presence of Hg in the laboratory environment [121].

Hg determination

The most commonly used technique for total Hg determination is cold-vapor atomic absorption spectroscopy (CVAAS) using electrochemical detection [122–126]. The basic approach of all cold-vapor methods is to convert the Hg in a small sample to mercuric ion, then reduce it to elemental Hg with a reductant such as stannous chloride. The Hg vapor is then measured in a modified atomic absorption spectrophotometer. Various acid mixtures have been used for the digestive process. The use of a high-pressure and high-temperature feedback microwave system has reduced the digestion time significantly [126]. The CVAAS method is applicable for drinking water, brackish water, domestic and industrial wastes, and biological samples. Other detection methods, such as inductively coupled plasma–mass spectrometry (ICP-MS), become feasible once the Hg has been released to mercuric vapor [127].

The most recent cold-vapor atomic fluorescence spectros-

copy (CVAFS) method [128] has become increasingly important compared to CVAAS, because the instrumental detection limit of CVAFS is about 1 picogram or less and at least one order of magnitude better than CVAAS [129]. Total Hg analysis by this method requires sample digestion by a strong acid (nitric–sulfuric or nitric–perchloric–hydrofluoric) that results in conversion of organic Hg to inorganic Hg. The digested samples are introduced to the cold-vapor generator, at which point tin (II) chloride is used to effectively reduce inorganic Hg to its elemental gaseous form prior to detection by atomic fluorescence. This method can attain 95 to 105% recovery efficiency for elemental Hg [130].

Several enrichment techniques have been proposed to improve on the sensitivity of the CVAFS method. Some techniques require preconcentration of Hg on copper wire or platinum [131] and preconcentration of volatilized Hg on gold or silver [132]. Very low detection limits for total Hg in biological and environmental samples have been successfully determined by the application of a high-temperature, high-pressure microwave system combined with Hg amalgamation tube systems that reduce the amount of time, the amount of acids, and the sample size required [133].

MeHg determination

Indirect measurement. The most common indirect measurement technique is a selective digestion that allows for determination of total Hg and inorganic Hg (II) directly, and MeHg by difference [134]. The method is based on the rapid conversion of organomercurials into inorganic Hg and then followed by conversion into atomic Hg suitable for aspiration through the gas cell of a Hg vapor concentration meter (atomic absorption) by a strong alkaline solution (tin (II) chloride–cadmium chloride). Alternatively, a two-step digestion method may be performed in which total Hg is determined on nitric acid–hydrogen sulfate and Hg (II) is determined as above [128]. These methods are simple but lack species specificity and are operationally defined.

Direct measurement. Following one of several isolation techniques (extraction, ion exchange, volatilization, separation, distillation, and digestion), final determination of MeHg is accomplished by various spectrophotometry detectors. The most common MeHg determination is performed by solvent extraction combined with separation using gas–liquid chromatography followed by electron-capture detection (GC-ECD) a technique developed by Westöö [135]. A variation of this method replaces the ECD with microwave-induced plasma detection (GC-MIP) because this can be used as an Hg-specific detector [136,137]. These methods are typically tedious and complex because the MeHg bound to the tissue sample has to be extracted and purified into a small volume of solvent suitable for GC injection. The multiple steps required can reduce the yield. In addition, the EC detector, which measures the halide rather than the Hg atom, is prone to matrix interference from known and unknown halogen-containing species in the typical laboratory [138].

To overcome the difficulty with sample preparation prior to GC separation, the headspace sampling analysis method to determine MeHg was developed [136] and modified further [139,140]. These methods involve MeHg extraction from the biological sample and conversion of the MeHg into the iodide form, the most volatile MeHg halide salt. These reaction steps take place in a closed headspace vial where the MeHg iodide is then headspace-injected into a gas chromatograph equipped with a microwave-induced plasma detector (HS-GC-MIP). Quantitation is accomplished by standard addition. This method is also prone to decreased yield due to matrix interferences.

As discussed previously, the most commonly used technique for total Hg determination is by CVAAS using electrochemical detection [122]. A similar detection method was also developed by Holak [141] for MeHg determination. Methylmercury is converted into MeHg (II) chloride by hydrochloric acid treatment and isolated from the sample by elution with chloroform from a diatomaceous earth column. Prior to high-performance liquid chromatographic (HPLC) separation, the sample is back-extracted into aqueous phase as sodium thiosulfate complex. Detection is accomplished either electrochemically or by atomic absorption (AA) in a specifically constructed apparatus [141]. A few methods use CVAAS detection combined with various isolation techniques [142–145]. Some of the methods can determine total Hg and MeHg from the same aliquots. For example, Gutiérrez et al. [145] conducted an experiment that utilized a mixed solution of sodium hydroxide, sodium chloride, and cysteine to digest fish tissue followed by a selective reduction with tin (II) chloride–cadmium chloride reagent. The inorganic and organic Hg in the same sample are sequentially reduced, volatilized, and measured by CVAAS.

All of the above methods have potential problems because they lack species specificity or because matrix interferences decrease the yields. In addition, all methods that employ an acid extraction step convert dimethylmercury to the monomethylmercury form, thus diminishing the speciation information gained from that analysis [138].

The most current technique being used to determine MeHg involves aqueous phase ethylation with cryogenic GC separation and atomic fluorescence detection [128,146,147]. In this method sodium tetraethyl borate converts the nonvolatile monomethyl Hg to gaseous methyl ethyl Hg. The volatile adduct is then thermally desorbed from the column and analyzed by cryogenic GC with a highly sensitive CVAFS detection. The detection limit of this method is about 1 picogram or less and at least one order of magnitude better than for CVAAS [129,147]. Atomic fluorescence is also less prone to matrix interferences [147]. Detection limits are less critical in determination of Hg in animal tissue; however, the use of a more sensitive detector such as CVAFS allows for smaller sample size, thereby reducing matrix interference.

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CERTIFICATE OF SERVICE

I, Faith Bugel, certify that on August 11, 2006, I filed the attached MICHAEL MURRAY ADDITIONAL REFERENCES IN SUPPORT OF TESTIMONY. An electronic version was filed with the Illinois Pollution Control Board and copies were served via United States Mail to those individuals on the included service list.

s/ Faith E. Bugel
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