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Biogeochemical Cycling of Methylmercury in Lakes and Tundra Watersheds of Arctic Alaska

CHAD R. HAMMERSCHMIDT,^{*,†,‡}
WILLIAM F. FITZGERALD,[†]
CARL H. LAMBORG,[‡]
PRENTISS H. BALCOM,[†] AND
C.-MAO TSENG[§]

Department of Marine Sciences, University of Connecticut, Groton, Connecticut 06340, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, and National Center for Ocean Research, Taipei, Taiwan, Republic of China

The fate of atmospherically deposited and environmentally active Hg is uncertain in the Arctic, and of greatest toxicological concern is the transformation to monomethylmercury (MMHg). Lake/watershed mass balances were developed to examine MMHg cycling in four northern Alaska lakes near the ecological research station at Toolik Lake (68° 38' N, 149° 36' W). Primary features of the cycle are watershed runoff, sedimentary production and mobilization, burial, and photodecomposition in the water column. The principal source of MMHg is in situ benthic production with 80–91% of total inputs provided by diffusion from sediments. The production and contribution of MMHg from tundra watersheds is modest. Photodecomposition, though confined to a short ice-free season, provides the primary control for MMHg (66–88% of total inputs) and greatly attenuates bioaccumulation. Solid-phase MMHg and gross potential rates of Hg methylation, assayed with an isotopic tracer, vary positively with the level of inorganic Hg in filtered pore water, indicating that MMHg production is Hg-limited in these lakes. Moreover, sediment–water fluxes of MMHg (i.e., net production at steady state) are related to sediment Hg loadings from the atmosphere. These results suggest that loadings of Hg derived from atmospheric deposition are a major factor affecting MMHg cycling in arctic ecosystems. However, environmental changes associated with warming of the Arctic (e.g., increased weathering, temperature, productivity, and organic loadings) may enhance MMHg bioaccumulation by stimulating Hg methylation and inhibiting photodecomposition.

Introduction

There is increasing interest and concern related to Hg cycling and contamination in the Arctic. This is driven in part by evidence for pan-Arctic springtime Hg depletion events (e.g., 1, 2), and worries related to potential effects from climate change on the behavior and fate of monomethylmercury

(MMHg) in polar ecosystems (3). However, current knowledge about the biogeochemistry of MMHg in arctic lakes and watersheds is limited. The aquatic MMHg cycle is balanced by competing production/source and removal processes. Important sources include MMHg production in lacustrine and wetland sediments, where sulfate-reducing bacteria (SRB) are the presumed primary methylators of Hg (4). In temperate lakes, in situ sedimentary production and mobilization is a major source of MMHg (5, 6), and watersheds can also contribute modest amounts depending upon physicochemical characteristics and the relative area of the wetlands they contain (e.g., 7–10). MMHg from these sources has several fates, namely export (outflow), demethylation, and scavenging and bioaccumulation with eventual burial in sediments. Among these processes, bioaccumulation is most well-known. Public health concerns related to consumption of contaminated fish have prompted extensive surveys of fish Hg levels and studies of MMHg in aquatic food webs (11). However, the significance of bioaccumulation and its relationship to the sources and sinks of MMHg is not well defined, especially in the Arctic.

Here, we address quantitatively the relative significance of these sources and sinks by developing mass balances for MMHg in four arctic Alaskan lakes. Such an approach provides a broad biogeochemical framework for experimental design and permits inter-system comparisons. Characterization of the major fluxes in arctic ecosystems is critical for assessment of anticipated climate change in the Arctic on the cycling of MMHg. Multiple aspects of the aquatic MMHg cycle were examined, including (1) Hg speciation in surface water, pore water, and sediment, (2) in situ Hg methylation potentials, (3) production and runoff of MMHg from tundra watersheds, (4) MMHg photodecomposition (12), and (5) bioaccumulation. The results of this study provide a first-order view of the major processes affecting MMHg in arctic Alaskan lakes, and show in situ sedimentary production to be the primary source and photodecomposition to be the principal sink. Moreover, MMHg production in sediments is limited by the availability of inorganic Hg. Gross potential rates of Hg methylation, assayed with an isotopic tracer, are related to the level of inorganic Hg in pore water, and net rates of MMHg production (i.e., sediment–water flux) vary positively with sediment Hg loadings from the atmosphere.

Experimental Section

Study Lakes. The cycling of MMHg was examined in four arctic Alaskan lakes near the long-term ecological research (LTER) site at Toolik Field Station (68° 38' N, 149° 36' W), which is about 250 km south of the Arctic Ocean (Figure 1). There is permafrost under the entire area, and the regional vegetation is treeless tussock tundra (13). The study lakes included Toolik Lake, which is adjacent to the field station, and three others within a 25 km radius (Lakes E1, E5, and F2; Figure 1). These lakes were selected because they span a range in physicochemical characteristics and lake and watershed sizes that are typical of most other lakes in arctic Alaska (13), and their biogeochemistry and ecology have been investigated as part of the LTER program (14). The study lakes have a circumneutral pH, contain low levels of sulfate, are moderately dilute, and span a relatively wide range in lake/watershed area ratios (Table 1). They also are oligotrophic; primary production in Toolik Lake, for example, is about 14 g C m⁻² y⁻¹ (15). Investigations of MMHg cycling in the lakes and their watersheds were conducted in July 2003.

* Corresponding author phone: 508-289-3551; e-mail: methylhg@whoi.edu.

† University of Connecticut.

‡ Woods Hole Oceanographic Institution.

§ National Center for Ocean Research.

TABLE 1. Limnological Characteristics of the Study Lakes^a

lake	location	watershed area (ha)	lake area (ha)	watershed/lake area	mean depth (m)	pH	conductivity ($\mu\text{S cm}^{-1}$)	sulfate (μM)	K_a^b (m^{-1})
E1	68°38'N, 149°33'W	100	2.99	33.4	2.3	7.1	43	36	0.62
E5	68°39'N, 149°27'W	134	11.3	11.9	6.2	6.8	7	3	0.83
F2	68°41'N, 149°06'W	35	5.65	6.2	8.3	8.2	120	43	0.31
Toolik	68°38'N, 149°36'W	6760	149	45.5	11.1	7.6	40	12	0.65

^a pH, specific conductivity, and sulfate values are for epilimnetic water. Conductivity and sulfate data are from Arctic LTER (14). ^b Attenuation coefficient for downward irradiance of photosynthetically active radiation (PAR).

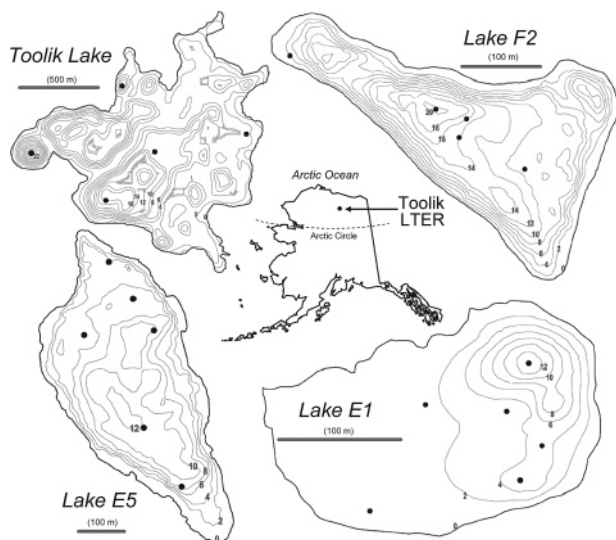


FIGURE 1. Bathymetric maps of the four study lakes near the Toolik LTER site in arctic Alaska. Locations of sediment coring sites are indicated by closed circles on the lake maps. Variable length scales are shown for each lake, and depth contours are 2-m intervals.

Lake Water. Water samples were collected for Hg speciation analysis from each of the study lakes. Surface waters (~ 0.2 m depth) were collected in Teflon bottles with gloved hands, and hypolimnetic waters were sampled 1–2 m above the sediment–water interface with a Go-Flo bottle suspended on a Kevlar line. Water samples were collected on only one occasion. Trace-metal clean procedures were employed throughout sample collection and analysis (16). Water samples were kept in a darkened container until they were filtered ($0.2 \mu\text{m}$) inside a laminar flow hood, typically within 4 h of collection. Total Hg and MMHg were measured in the $0.2\text{-}\mu\text{m}$ filtered fraction of surface waters because this portion presumably is most available for biogeochemical transformation and, on average, 80% of total Hg was in the filtrate.

Sediments. Surface sediments were sampled at 5–6 locations that spanned a range in water depth within each of the study lakes (Figure 1). Intact sediment cores were collected with a gravity corer that did not disturb the sediment–water interface. Cores were kept in the dark until they were sectioned inside a N_2 -filled glovebag within 6 h of collection. Cores were sectioned in 1-cm vertical increments to 4 cm depth, and sections were transferred to polyethylene syringes fitted with $0.45\text{-}\mu\text{m}$ hydrophilic Teflon filters for pore water extraction. Filtered pore water (acidified to 0.2% HCl) and sediment were frozen promptly after filtration and transported on dry ice to the University of Connecticut where they were analyzed for MMHg and total Hg. Sediments were freeze-dried before Hg analysis and measured for organic content (as loss on ignition, LOI; 17).

Watershed/Precipitation. Production and runoff of MMHg from tundra watersheds were estimated from concentrations in the outflow of a 2-ha experimental subcatchment in the

watershed of Toolik Lake. The vegetation and geology of the subcatchment are comparable to watersheds of the study lakes. Outflow water was sampled from a gauged weir on seven occasions over a range of flow rates (one sample per occasion). Two samples of rain were collected in Teflon bottles with an automated collector (18) and analyzed for MMHg to verify that direct deposition was a trivial source to the study lakes.

In-Lake Decomposition. Degradation of MMHg in the epilimnion of the study lakes was estimated from experiments conducted in Toolik Lake (12). MMHg photodecomposition fluxes for whole-lake mass balances were estimated from a relationship between photodecomposition rate, MMHg concentration, and intensity of photosynthetically active radiation (PAR, 400–700 nm) in Toolik Lake (equation 3 in ref 12), as well as measured epilimnetic MMHg levels and PAR extinction coefficients for each of the study lakes.

Bioaccumulation. The food web of arctic Alaskan lakes is based on benthic resources (19), so epilithon, snails (*Gyrinus* spp.), chironomid larvae, and fish were sampled to examine MMHg bioaccumulation in the study lakes. Arctic grayling *Thymallus arcticus* ($n = 27$) were angled from Toolik Lake, and Arctic char *Salvelinus alpinus* were sampled similarly from Lakes F2 ($n = 4$) and E5 ($n = 8$). A minimal number of Arctic char were collected because of their low density in these isolated lakes. Fish were dissected with clean protocols (20) to remove a sample of skinless axial muscle for analysis. Chironomid larvae were sampled from three locations in each lake with a ponar grab. Epilithon (typically a brown slime) and snails were removed from submerged rocks at two or three locations in each lake. Frozen biological samples were transported to the University of Connecticut where they were freeze-dried and analyzed for MMHg.

Hg Methylation Potentials. Gross potential rates of MMHg production in surface sediments were assayed by adding isotopically enriched ^{200}Hg (96.41% ^{200}Hg ; Oak Ridge National Laboratory, TN) to two intact sediment cores from each of four coring locations in each lake. These sediments were collected at the same location and time as those analyzed for Hg speciation. Our methods for ^{200}Hg spike preparation, sediment incubation, MMHg extraction, and analysis of Hg isotopes are detailed in Hammerschmidt and Fitzgerald (21). The only methodological differences between the current study and our previous work were that (1) added ^{200}Hg increased the ambient Hg burden in sediments by about 5%, and (2) cores were incubated 7–9 h at in situ conditions (dark, 5°C) before the upper 4 cm of sediment was extruded and frozen to terminate the incubation (i.e., one sample per core). Measured rates of ^{200}Hg methylation are considered *methylation potentials* because the added Hg, having undetermined chemical speciation and sediment–water partitioning, may be more available for methylation than ambient inorganic Hg (22). The precision (relative standard deviation, RSD) of ^{200}Hg methylation potential measurements averaged 10% ($n = 14$), based on analyses of methodically replicated subsamples. The relative percent difference (RPD) in ^{200}Hg methylation potentials between replicate cores from each location averaged 25%.

Hg Analysis. Lake water, watershed runoff, and precipitation were analyzed for Hg speciation within 24 h of collection at the field station. Total Hg was determined by cold-vapor atomic fluorescence spectrometry (CVAFS; 23) after digestion with BrCl (21). MMHg was measured by flow injection gas chromatographic CVAFS (24) after direct ethylation of sample MMHg with sodium tetraethylborate, which results in quantitative recovery from these dilute waters (12). Estimated detection limits for a 200-mL sample were about 0.010 ng L⁻¹ for total Hg and about 0.004 ng L⁻¹ for MMHg.

Sediments and filtered pore waters were analyzed at the University of Connecticut. Total Hg and MMHg in the solid phase of sediment were defined as the fraction of each species remaining after pore water removal. Total Hg in pore water was quantified by CVAFS after BrCl digestion (21). Total Hg in sediment was measured with a Milestone DMA-80 pyrolytic Hg analyzer (25). MMHg was extracted from sediment and pore water by aqueous distillation (21) and determined by CVAFS (24). Biological samples were analyzed for MMHg after digestion with dilute HNO₃ (26). Estimated detection limits (ng g⁻¹ dry weight) for a 0.5-g sediment sample were about 0.2 for total Hg and 0.01 for MMHg. Detection limits for 5-mL aliquots of pore water were about 0.4 ng L⁻¹ for total Hg and 0.1 ng L⁻¹ for MMHg. We defined the difference between total Hg and MMHg as Hg(II). Thus, Hg(II) represents the sum of all Hg²⁺ species that are complexed with inorganic and organic ligands. All analyses were subject to a rigorous quality control protocol that included calibration with standards traceable to the National Institute of Standards and Technology as well as analyses of procedural and field blanks, certified reference materials, replicate subsamples, and samples with known Hg additions.

Results and Discussion

Hg Speciation in Lake Water. Hg species in 0.2- μ m filtered water in arctic Alaskan lakes ranged from 0.17 to 1.36 ng L⁻¹ for total Hg and 0.010–0.063 ng L⁻¹ for MMHg (see Table A in Supporting Information). These concentrations are comparable to those in lakes in the Canadian Arctic (10, 27). MMHg (epilimnion/hypolimnion, ng L⁻¹) was homogeneous with depth in Toolik (0.051/0.055) and E1 (0.042/0.042), but enhanced in bottom water of Lakes E5 (0.022/0.063) and F2 (0.010/0.019).

Watershed Contributions. *MMHg in Runoff.* Export of MMHg from tundra watersheds was examined in an experimental subcatchment. The concentration of MMHg (<0.2 μ m) in subcatchment outflow ($MMHg_{Runoff}$, ng L⁻¹) was related inversely to the flow rate through a gauged weir (Q , L min⁻¹) and described by the equation (Figure 2, $r^2 = 0.97$)

$$MMHg_{Runoff} = 0.016 + 0.154e^{-(0.039Q)} \quad (1)$$

MMHg was greatest during drier conditions and decreased exponentially to an asymptotic value of 0.016 ng L⁻¹ when flow rates exceeded about 100 L min⁻¹. This concentration is comparable to the mean level of MMHg measured in two rain events (0.025 ± 0.010 ng L⁻¹; Figure 2), and suggests that MMHg is produced in the tundra and flushed during precipitation events. Watershed production accounts for the relatively high levels during low flow, and the asymptotic concentration at greater flow rates may reflect runoff of atmospherically derived MMHg.

Watershed MMHg Production. Net production of MMHg in the Alaskan tundra is low compared to that in temperate watersheds. The estimated average level of MMHg in tundra runoff is 0.048 ng L⁻¹, based on eq 1 and a mean flow rate of about 40 L min⁻¹ from the subcatchment during the ice-free season (personal communication; George Kling, University of Michigan, Ann Arbor, MI). This concentration

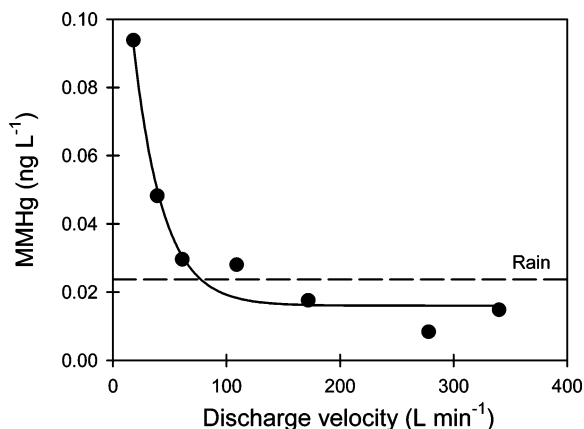


FIGURE 2. Relationship between MMHg (<0.2 μ m filtered) and water discharge velocity from an experimental subcatchment in the watershed of Toolik Lake. The dashed reference line is the mean concentration of MMHg in two rain samples.

includes MMHg from both atmospheric deposition and in situ production, and is comparable to levels measured in the inlet streams of E1 and Toolik Lakes (0.038–0.040 ng L⁻¹), which provide an integrated measure of MMHg runoff from the expansive watersheds. The tundra-specific concentration is 0.032 ng L⁻¹ when corrected for MMHg contributed from precipitation (0.016 ng L⁻¹; asymptote of eq 1). The product of the tundra-specific MMHg concentration and water discharge (about 50% of annual precipitation; 18) results in an estimated net production of about 0.005 μ g MMHg m⁻² y⁻¹ for the subcatchment. This rate is at the lower range of similar estimates for temperate watersheds (0.01–0.44 μ g m⁻² y⁻¹; 7–9), but 5-fold greater than that in watersheds of the Canadian High Arctic (10). In temperate systems, net MMHg production/export is reduced in watersheds where water flow is restricted and has limited interaction with mineral substrate (9). This may also be the case in the Arctic where water permeation is restricted by permafrost.

Watershed MMHg Flux. The annual watershed export of MMHg to arctic lakes can be estimated using results from the experimental subcatchment. Fluxes of MMHg from watershed runoff (precipitation + in situ production; F_{Runoff} , μ g m⁻² lake area y⁻¹) were calculated for each of the study lakes with the following equation:

$$F_{Runoff} = MMHg_{Runoff} \frac{([A_W - A_L] \times 0.5V_{Precip})}{A_L} \quad (2)$$

where $MMHg_{Runoff}$ is the estimated average concentration of MMHg in tundra runoff (0.048 μ g m⁻³), A_W and A_L are areas of the watershed and lake (m², Table 1), and V_{Precip} is the mean wet deposition velocity (0.31 m y⁻¹; 13). This assumes that (1) 50% of precipitation to the watersheds is lost to evapotranspiration or sublimation (18), (2) the remaining water enters the lake, and (3) MMHg in outflow from the subcatchment is representative of watershed runoff to the study lakes, which, as noted, ranged 0.038–0.040 ng L⁻¹ for two of the lakes. Annual watershed fluxes of MMHg should be represented reasonably by this approximation ($\pm 50\%$) because (1) most ($\sim 70\%$) of the precipitation occurs between June and September, when lakes and the active layer of the tundra are not frozen, and (2) levels of MMHg in arctic Alaskan snow (<0.036 ng L⁻¹; 28) are comparable to or less than those in watershed runoff during the summer. Estimated watershed fluxes of MMHg to the study lakes ranged from 0.04 to 0.33 μ g m⁻² y⁻¹, and are summarized and compared to other fluxes

TABLE 2. Mean Characteristics of Surface Sediments (Upper 1 cm) in the Four Study Lakes, and Spearman Correlation Coefficients between Characteristics of Surface Sediments in Each Lake

lake	water content (%)	bulk density (g cm ⁻³)	organic content (%LOI)	Hg(II) (ng g ⁻¹ dry wt)	MMHg (ng g ⁻¹ dry wt)	pair of variables in correlation ^a		
						Z:Hg(II)	Z:OM	Hg(II):OM
E1	93.3 (89.4–98.2)	1.04 (1.02–1.06)	25.0 (22.0–26.3)	239 (184–327)	1.37 (1.03–1.60)	0.91	0.64	0.38
E5	90.7 (87.8–92.6)	1.05 (1.04–1.08)	19.8 (12.9–22.2)	159 (110–190)	0.33 (0.26–0.41)	0.86	–0.56	–0.38
F2	92.9 (90.4–95.3)	1.04 (1.02–1.06)	27.2 (20.2–36.6)	102 (87–108)	0.78 (0.55–1.33)	0.60	–0.77	–0.02
Toolik	90.4 (87.6–92.0)	1.06 (1.05–1.09)	20.7 (17.3–25.2)	244 (135–316)	2.38 (1.62–3.40)	0.93	0.00	–0.12

^a Z = water depth (m), Hg(II) = Hg(II) concentration (ng g⁻¹ dry weight), OM = concentration of organic matter (%LOI).

later in the discussion. If MMHg in snowmelt near Toolik were as high as that in the Canadian High Arctic (0.15 ng L⁻¹; 10, 27), then watershed fluxes could be as much as 50% greater than those estimated above.

Lake Export MMHg Flux. The outflow of MMHg with surface water through lake outlets was estimated similarly. For this calculation, the area of the entire watershed (A_w) was substituted for $[A_w - A_L]$ in eq 2 and the concentration of MMHg in epilimnetic water was used in lieu of that in watershed runoff. Accordingly, the outflow flux is the product of epilimnetic MMHg concentration and annual water outflow. Although epilimnetic MMHg was measured only once in each of the lakes, a recent study suggests little variation of MMHg in arctic surface waters during the summer (about 30% RSD; 10).

Precipitation MMHg Flux. MMHg also is deposited directly to the lake surface with precipitation. As noted, the mean level of MMHg in July rain was 0.025 ng L⁻¹. This concentration is comparable to levels found in precipitation at temperate North American locations (e.g., 29), but greater than that in oceanic rain (e.g., 30). With an average annual precipitation depth of 0.31 m, the estimated atmospheric deposition of MMHg is 0.01 $\mu\text{g m}^{-2} \text{y}^{-1}$. Although this flux could be as high as 0.02 $\mu\text{g m}^{-2} \text{y}^{-1}$ if precipitation at Toolik has the same average concentration as that in the Canadian High Arctic (0.06 ng L⁻¹; 27), direct deposition is a trivial source of MMHg to these Alaskan lakes.

Sediment Hg Cycling. *Hg(II).* In each lake, as noted, sediment cores were collected at 5–6 locations that span a range in water depth (Figure 1) and, potentially, biogeochemical characteristics associated with sediment focusing. Among all surface deposits (uppermost cm), Hg(II) ranged from 87 to 330 ng g⁻¹ dry weight (Table 2), concentrations within the range of those measured in nearby lakes (18). Hg(II) in surface sediments was correlated positively with water depth in lakes where Hg(II) varied by at least a factor of 1.5 among locations (Table 2). The relationship was not as pronounced in Lake F2, where Hg(II) was relatively homogeneous (Table 2). Increasing sediment Hg(II) with water column depth can be attributed to focusing of fine-grain particles and associated Hg toward greater depths (31). Hg species have a high affinity for organic matter (e.g., 32), however, the general pattern of increasing sediment Hg(II) with water depth was unrelated to organic material. There were no consistent relationships between either sediment organic content and water depth or Hg(II) and organic matter in surface deposits (Table 2). Hence, the distribution of Hg(II) was influenced strongly by factors other than sorting of organic-rich particles. The absence of a relationship between sediment Hg(II) and organic content may be attributed to erosion and input of unweathered soils that are enriched with Hg (18).

A relationship between watershed/lake area ratio and Hg(II) in surface sediments suggests that unweathered soils

contribute a major fraction of the Hg(II) in sediments of the study lakes. The relationship between the mean concentration of Hg(II) in sediments ($Hg(II)_{\text{sed}}$, ng g⁻¹ dry weight; Table 2) and watershed/lake area ratio (A_w/A_L , Table 1) is described by the following equation:

$$Hg(II)_{\text{sed}} = 101 + 3.53 \left(\frac{A_w}{A_L} \right) \quad (3)$$

which has a coefficient of determination (r^2) of 0.90. By eq 3, sediments in a lake with no watershed would contain about 101 ng Hg g⁻¹ dry weight. We have reported recently that mercury depletion events (MDEs) and/or year-round deposition of reactive gaseous mercury (RGM) species may deposit $1.2 \pm 0.7 \mu\text{g m}^{-2} \text{y}^{-1}$ of total Hg to the study area, in addition to an annual wet depositional flux of $1.5 \pm 0.6 \mu\text{g m}^{-2} \text{y}^{-1}$ (18). If direct deposition to the lake surface were the only source of Hg, then sediments should contain 27 ng g⁻¹, given an average sediment accumulation rate of about 100 g m⁻² y⁻¹ in arctic Alaskan lakes (18). The difference in these estimates (74 ng g⁻¹) can be attributed to erosion of unweathered soil in the watershed, which is in agreement with the Hg content of soil-parent material in four nearby watersheds (64–80 ng g⁻¹; 18).

MMHg. The sedimentary distribution of MMHg, in contrast to Hg(II), appears to be governed primarily by organic matter. MMHg was related positively to the organic content of sediments in Toolik Lake ($r^2 = 0.65$) and F2 ($r^2 = 0.77$), where MMHg varied by at least a factor of 3 among locations (see Figure A in Supporting Information). There was relatively little variation in either the MMHg or organic content of sediments in E5 and E1 (Table 2), and only modest relationships between these variables ($r^2 = 0.16$ – 0.20). The relative significance of organic matter–MMHg interactions is supported by a positive relationship between the distribution coefficient (K_D , L kg⁻¹) of MMHg and concentration of sedimentary organic material ($r^2 = 0.66$; see Figure B in Supporting Information). The K_D of Hg(II), in contrast, was related less strongly to the organic content of sediments ($r^2 = 0.40$), and as noted, the distribution of Hg(II) in surface sediments was unrelated to that of organic matter. Again, this may be attributed to the presence of Hg(II) associated with unweathered mineral, which would be unable to partition between solid and pore water phases. MMHg averaged 0.5% (range 0.08–1.44%) of total Hg in the solid phase and 15% of total Hg in pore water (range 3.7–37%).

Hg Methylation. Potential gross rates of ²⁰⁰Hg methylation in surface sediments were related positively to the concentration of Hg(II) in filtered pore water ($r^2 = 0.60$, $p < 0.001$; see Figure C in Supporting Information). ²⁰⁰Hg methylation potentials were determined from a homogenate of the upper 4 cm of sediment, and the pore water Hg(II) concentration is the mean value from the 0–1, 1–2, 2–3, and 3–4 cm depth

horizons at each location. This relationship suggests that availability of Hg(II), having undetermined complexation, is an important factor influencing MMHg production in arctic lake sediments. Hg(II) exists as complexes with sulfide in pore water, and the concentration of dissolved sulfide determines the speciation (33). HgS^0 is the Hg–S complex presumed most available to methylating bacteria in pore water (34), and it is the dominant species when dissolved sulfide is between 1 pM and 10 μM (33). Although dissolved sulfide was not measured, it is likely that pore water concentrations do not exceed 10 μM given that sulfate, the substrate for microbial sulfide production, ranged from 3 to 43 μM among lakes (Table 1). This would suggest that HgS^0 was a major Hg–S complex in these pore waters, and that much of the Hg(II) was available for methylation. Comparable relationships between ^{200}Hg methylation potential and Hg(II) in pore water have been observed in other sediments having <10 μM dissolved sulfide (21, 35).

Sediment MMHg was related positively to potential rates of ^{200}Hg methylation ($r^2 = 0.41$, $p < 0.01$). This relationship, in addition to the one between ^{200}Hg methylation potential and Hg(II) in pore water, suggests a connection between Hg(II) availability, the rate of Hg methylation, and solid-phase accumulation of MMHg in these sediments. Comparable relationships between in situ MMHg concentration and short-term Hg methylation potentials have been observed in other freshwater systems (22). Furthermore, solid-phase MMHg was correlated with pore water Hg(II) in the same samples ($r^2 = 0.52$, $p < 0.001$). Hence, the production of MMHg is influenced by processes affecting the level of Hg(II) in pore water.

Sedimentation Flux. At steady state, the net sedimentation (burial) flux can be estimated as the product of solid-phase MMHg concentration and sedimentation rate. Burial fluxes were estimated from the mean MMHg concentration in surface sediment (Table 2) and the average rate of sedimentation determined for comparable nearby lakes ($\sim 100 \pm 50 \text{ g m}^{-2} \text{ y}^{-1}$; 18). Estimated burial fluxes of MMHg ($\pm 50\%$) ranged from 0.03 to 0.24 $\mu\text{g m}^{-2} \text{ y}^{-1}$ among lakes.

Sediment–Water MMHg Fluxes. Sediment–water fluxes of MMHg were estimated assuming Fickian diffusion and using the concentration gradient between pore water in surface sediment and hypolimnetic water (32). The mean level of MMHg in filtered pore water in the 0–1 and 1–2 cm horizons of surface sediment was used for the pore water value, applying the mean to 1.0 cm depth for the flux calculation. The estimated diffusion coefficient of CH_3HgSH^0 ($1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C; 32), the presumed dominant complex of MMHg in pore fluids (36), was corrected to an average annual sediment temperature of 3 °C for the flux estimates (37). The mean annual sediment temperature of these lakes is uncertain, but estimated annual fluxes vary less than 6% from the 3 °C estimates if the average temperature is 0.5 °C or 5 °C.

Estimated diffusive fluxes of MMHg from sediment varied within and among lakes. Sediment–water fluxes ranged from 0.8 to 11 $\text{ng m}^{-2} \text{ d}^{-1}$, and in general, were greatest in profundal sediments, followed by the littoral zone, and least at intermediate water depths (see Figure D in Supporting Information). The average flux from arctic lake sediments, 3.1 $\text{ng m}^{-2} \text{ d}^{-1}$, is comparable to those estimated from budgets for temperate lakes (2.8–8.5 $\text{ng m}^{-2} \text{ d}^{-1}$; 5, 6). As the physical properties (e.g., porosity) of all surface sediments in the arctic lakes were comparable and levels in overlying water were low compared to pore fluids, fluxes were driven mostly by the concentration of MMHg in filtered pore water, which in turn, was influenced largely by partitioning with the solid phase. Indeed, sediment–water fluxes were correlated positively with MMHg in the solid phase among all surface sediments ($r^2 = 0.80$, $p < 0.001$).

Because sediment–water fluxes varied with water depth in E1, F2, and Toolik, whole-lake benthic fluxes of MMHg were estimated by spatially categorizing estimates according to water depth and scaling to the entire lake. In Lake F2, for example, 0.42 of the sediment area was in less than 8 m of water (mean flux, 1.3 $\text{ng m}^{-2} \text{ d}^{-1}$), 0.35 was between 8 and 14 m depth (1.0 $\text{ng m}^{-2} \text{ d}^{-1}$), and 0.23 was greater than 14 m depth (2.3 $\text{ng m}^{-2} \text{ d}^{-1}$), based on detailed analysis of lake bathymetry (Figure 1). The whole-lake flux from sediments is the sum of area ratio \times sediment–water flux for each depth range. The benthic flux for E5 was estimated from the average of the six cores because there was little variation among locations and depths. Estimated sediment–water MMHg fluxes were 1.01, 0.53, 0.53, and 1.64 $\mu\text{g m}^{-2} \text{ y}^{-1}$ for E1, E5, F2, and Toolik Lakes, respectively. Temperature is an important factor influencing bacterial MMHg production in sediments (21, 38). It is presumed that there is little seasonal variation in the benthic production and efflux of MMHg in arctic lakes because the temperature of most sediments in the summer (4–7 °C) is not much greater than those expected in the winter (1–4 °C).

Photodecomposition. Photodecomposition of MMHg in the study lakes was estimated with results from experiments conducted in Toolik Lake (12). We assumed the kinetics of MMHg photodecomposition in the study lakes were comparable to those in Toolik Lake, which is supported by the good agreement between Toolik and a physicochemically disparate lake in northwest Ontario (12). We also assumed that the average surface intensity of PAR (62 $\text{E m}^{-2} \text{ d}^{-1}$), PAR extinction coefficients (Table 1), and mean epilimnetic MMHg concentrations measured during our sampling period were representative of average conditions throughout the ice-free season, which is typically from mid-June to mid-September (about 100 d). Accordingly, estimated depth-integrated photodecomposition fluxes ($\pm 50\%$) were 0.89, 0.46, 0.51, and 1.31 $\mu\text{g m}^{-2} \text{ y}^{-1}$ for E1, E5, F2, and Toolik, respectively.

Bioaccumulation. Dry-weight concentrations of MMHg in biota were comparable among the four study lakes (see Table B in Supporting Information). Sedimentary organic matter and epilithic detritus/bacteria/algae are the foundation of these benthos-based food webs (19). Levels of MMHg in epilithon were similar among lakes (2.2–2.5 ng g^{-1} dry weight). Snails graze on epilithon (19), and MMHg is biomagnified 7-fold between epilithon and the soft tissue of snails (17–18 ng g^{-1}). Chironomid larvae forage mostly on detritus (39), and although there was considerable variability within each lake, mean (± 1 SD) levels of MMHg in larvae (3.2 ± 1.7 to $4.4 \pm 4.8 \text{ ng g}^{-1}$) were comparable among lakes and 2- to 10-fold greater than those in surface sediments. Fish forage mostly on benthic invertebrates in these lakes (19, 40). Mean (± 1 SD) levels of MMHg in fish muscle (ng g^{-1} dry weight) were comparable between Arctic grayling in Toolik Lake (297 ± 122) and Arctic char in E5 (265 ± 116) and F2 (408 ± 137). Overall, biomagnification results in more than a 10^2 increase in MMHg concentration between sedimentary organic matter/epilithon and fish muscle, comparable to the increase between seston and small fish in other systems (11).

Bioaccumulation Flux. Without removal of fish from a lake, MMHg bioaccumulation is not a net sink because MMHg is deposited to the benthos when organisms die, and thus is a part of a burial flux, which we have considered already. Accordingly, bioaccumulation fluxes were not included in our steady-state mass balances, but the annual uptake of MMHg by fish in arctic lakes was estimated for comparison to MMHg photodecomposition.

In contrast to pelagic-based food webs, where uptake from water by seston constrains the bioaccumulation flux of MMHg (5, 41), lacustrine ecosystems in arctic Alaska are founded in the benthos. This means that MMHg accumulated by seston,

TABLE 3. Mass Balances for MMHg in the Study Lakes ($\mu\text{g m}^{-2} \text{y}^{-1}$)

lake	sources			sinks				
	direct wet deposition	watershed runoff ^a	sediment flux	sedimentation	outflow	photodecomposition	net	bioaccumulation ^b
E1	0.01	0.24	1.01	0.14	0.22	0.89	+0.01	0.03
E5	0.01	0.08	0.53	0.03	0.04	0.46	+0.09	0.03
F2	0.01	0.04	0.53	0.08	0.01	0.51	−0.02	0.08
Toolik	0.01	0.33	1.64	0.24	0.36	1.31	+0.07	0.10

^a Includes both precipitation and production in the watershed. ^b Not included in the steady-state mass balance; includes only bioaccumulation by slimy sculpin, Arctic char (Lakes E5 and F2 only), and Arctic grayling (Toolik Lake only).

in the absence of significant predation by fish (19, 40), contributes only to the burial flux, part of which is re-assimilated into the food web by detritivores. MMHg also enters the benthic food web through aqueous uptake by epilithic organisms. Accordingly, and without knowledge of the absolute or relative contributions of MMHg from either of these sources, bioaccumulation was assessed for fish only, the principal reservoir for MMHg in temperate lakes (5), and which provide an integrated measure of biological uptake from all sources. Although multiple species of fish exist in each of the lakes (40), bioaccumulation of MMHg by fish was assessed with Arctic char (E5 and F2 only), Arctic grayling (Toolik only), and slimy sculpin *Cottus cognatus* (all lakes). Arctic char and slimy sculpin are major species in E5 and F2, whereas Arctic grayling are important in Toolik Lake (14). The fishery in E1 is unknown.

The bioaccumulation flux by Arctic char was estimated for Lakes E5 and F2 with the following lake-specific information: (1) average mass of Arctic char, (2) the mean concentration of MMHg in axial muscle, and (3) their estimated density and growth rate. Estimates of char density and growth were determined from tagging studies (personal communication; Chris Luecke, Utah State University, Logan, UT). The estimated bioaccumulation of MMHg by Arctic char in E5 and F2 is 0.01 and 0.06 $\mu\text{g m}^{-2} \text{y}^{-1}$, respectively. Growth rate and abundance estimates are not available for Arctic grayling in Toolik Lake; however, MMHg bioaccumulation by these fish can be estimated assuming their average growth and density is comparable to that of Arctic char in Lakes E5 and F2. Accordingly, the estimated bioaccumulation of MMHg by Arctic grayling Toolik Lake is 0.08 $\mu\text{g m}^{-2} \text{y}^{-1}$.

Slimy sculpin forage principally on chironomid larvae and are present in each of the study lakes. Although we did not measure MMHg in slimy sculpin, their bioaccumulation can be estimated from the following information: (1) the estimated density of slimy sculpin (42), (2) their average consumption rate of chironomid larvae (43), and (3) the mean burden of MMHg in individual larvae. The estimated rate of MMHg bioaccumulation by slimy sculpin is about 0.02 $\mu\text{g m}^{-2} \text{y}^{-1}$ in each of the lakes, assuming the sculpin assimilate all of the MMHg in their diet (44).

Lake–Watershed Mass Balance. Mass balances for MMHg in the study lakes are presented in Table 3. In-lake processes dominate the cycling of MMHg, and as illustrated, sedimentary production and mobilization is the primary source (Table 3). Although the benthic flux of MMHg varies 3-fold among lakes, it accounts for 80–91% of total inputs. Catchment runoff, including both precipitation and production in the tundra, is less than 20% of total inputs and dependent on watershed/lake area ratio. Although sedimentation and outflow are important sinks for MMHg, in-lake photodecomposition is the major removal process. Photochemical degradation during the 100-d ice-free period results in destruction of 80–96% of the MMHg mobilized from sediments and 66–88% of total annual inputs. Even with widely varying fluxes for each of the mass balance components among lakes, there was little discrepancy

between total sources and sinks in each of the lakes. The “net” term in Table 3 is less than the error associated with either of the major source or sink fluxes in these budgets.

Mass balance evaluations of lacustrine systems that examine only external sources (e.g., watershed input, direct deposition) and outflow underestimate the significance of in-lake MMHg cycling. Based only on watershed runoff and outflow flux estimates for these lakes, which are comparable (Table 3), it would appear that there is little in-lake production or decomposition of MMHg. However, estimates of MMHg mobilization from sediments and photodecomposition in the water column indicate that these two processes dominate the cycling of MMHg and are comparable.

Bioaccumulation is a strikingly minor component of the MMHg cycle in these lakes. Our estimates of MMHg bioaccumulation by fish were only 2–14% of total inputs (Table 3). These estimates are limited and likely underestimate the actual amount bioaccumulated, but they are constrained by the sedimentation flux, which at steady state, includes bioaccumulation. The small percentage accumulated by fish is surprising given that more than half of the MMHg entering other lacustrine and coastal marine systems presumably is assimilated into the food web (e.g., 5, 41). This suggests that these lakes are MMHg-limited with regard to bioaccumulation. Photodecomposition has a major role in the cycling of MMHg in these lakes, and it appears to reduce significantly the pool of MMHg that is available for biological uptake.

Net MMHg Production and Hg Loadings. Production and mobilization of MMHg from sediments in these arctic lakes is related to atmospheric Hg deposition. As noted, the level of Hg(II) in pore water influences the gross potential rate of Hg methylation, which subsequently affects the solid-phase MMHg concentration and, by partitioning with sedimentary organic matter, the pore water concentration and efflux of MMHg. Accordingly, and if availability of Hg(II) were a primary constraint on MMHg production, then the flux of MMHg from sediments (i.e., net production at steady state) may be related to sedimentary loadings of Hg(II). Among these four lakes, the whole-basin sediment-water flux of MMHg (F_{MMHg} , $\mu\text{g m}^{-2} \text{y}^{-1}$; Table 3) is related positively to sediment Hg loadings from the atmosphere (Hg_{load} , $\mu\text{g m}^{-2} \text{y}^{-1}$) and described by the following equation ($r^2 = 0.93$, $p = 0.04$; see Figure E in Supporting Information):

$$F_{\text{MMHg}} = 0.045 + 0.078Hg_{\text{load}} \quad (4)$$

Atmospheric Hg loadings were estimated from the slope of eq 3 and watershed/lake area ratios in Table 1, assuming an average sediment accumulation rate of 100 $\text{g m}^{-2} \text{y}^{-1}$ (18), with an additional 2.7 $\mu\text{g m}^{-2} \text{y}^{-1}$ deposited directly to the lake from wet deposition (1.5 $\mu\text{g m}^{-2} \text{y}^{-1}$) and MDEs and/or RGM (1.2 $\mu\text{g m}^{-2} \text{y}^{-1}$; 18). Loadings of Hg associated with unweathered soil from the watershed were not considered in this analysis because, and as noted, they appear to be trapped in solid mineral phases and are therefore inactive environmentally. Accordingly, systems with larger watershed/

lake area ratios have proportionately greater loadings of atmospherically derived Hg, and the flux of MMHg from sediments is enhanced. The slope of the relationship in eq 4 indicates that the net benthic methylation flux is about 8% of Hg loadings from the atmosphere.

Implications for the Arctic. Warming of the Arctic may increase MMHg bioaccumulation by both enhancing Hg methylation and reducing the role of photodecomposition. Temperature enhances Hg methylation (21, 38), so MMHg production should increase as the tundra and lake sediments warm. Moreover, MMHg bioaccumulation may be heightened by a decline in photodecomposition. Increases in primary production as well as allochthonous inputs of photoactive dissolved organic matter (DOM) may accompany continued warming in the Arctic (45, 46), and these would attenuate the in-lake photon flux and photodecomposition of MMHg, although the duration of the ice-free season may increase.

Another potential consequence of warming in the Arctic is enhanced weathering of watersheds. Weathering liberates ions, including SO_4^{2-} , from the mineral phase. Microbial sulfate reduction can be sulfate-limited (47), and in studies of temperate lakes, experimental additions of SO_4^{2-} increase Hg methylation (e.g., 4). These results point to SO_4^{2-} availability as a potentially important factor affecting MMHg production in low-sulfate systems (48), which would include arctic lakes (Table 1). However, and although SO_4^{2-} varied 10-fold among the study lakes (Table 1), there were no relationships between SO_4^{2-} and either ^{200}Hg methylation potential, sediment MMHg concentration, or benthic MMHg flux. Loadings of Hg(II) may be the principal control on MMHg production in these arctic lakes, and if this were the case, stimulating SRB activity may not enhance Hg methylation. Gross potential rates of Hg methylation and solid-phase concentrations of MMHg are related positively to levels of Hg(II) in pore water. Furthermore, net sedimentary production of MMHg (i.e., sediment–water flux) is correlated with Hg(II) loadings from the atmosphere. These results suggest that MMHg production in arctic lake sediments is limited by the availability of Hg(II), loadings of which may increase as a result of enhanced precipitation and weathering in the Arctic.

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Supporting Information Available

Five figures and two tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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