Methylmercury Cycling in High Arctic Wetland Ponds: Sources and Sinks

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Supporting Information

ABSTRACT: The sources of methylmercury (MeHg; the toxic form of mercury that is biomagnified through foodwebs) to Arctic freshwater organisms have not been clearly identified. We used a mass balance approach to quantify MeHg production in two wetland ponds in the Lake Hazen region of northern Ellesmere Island, NU, in the Canadian High Arctic and to evaluate the importance of these systems as sources of MeHg to Arctic foodwebs. We show that internal production (1.8−40 ng MeHg m⁻² d⁻¹) is a much larger source of MeHg than external inputs from direct atmospheric deposition (0.029−0.051 ng MeHg m⁻² d⁻¹), as expected. Furthermore, MeHg cycling in these systems is dominated by Hg(II) methylation and MeHg photodemethylation (2.0−33 ng MeHg m⁻² d⁻¹), which is a sink for a large proportion of the MeHg produced by Hg(II) methylation in these ponds. We also show that MeHg production in the two study ponds is comparable to what has previously been measured in numerous more southerly systems known to be important MeHg sources, such as temperate wetlands and lakes, demonstrating that wetland ponds in the High Arctic are important sources of MeHg to local aquatic foodwebs.

INTRODUCTION

Methylmercury (MeHg) is a potent neurotoxin¹ that has the ability to bioaccumulate and biomagnify in food webs, and the key step facilitating the transfer of this contaminant from physical to biological compartments is the methylation of inorganic Hg(II) to form MeHg.⁵ Unfortunately, the high concentrations of MeHg found in some Arctic marine mammals and freshwater fish, such as Arctic char (Salvelinus alpinus), may be harmful to Northern peoples harvesting these species as traditional food sources.³⁴ Moreover, in the past 20−30 years, MeHg concentrations have increased in certain Arctic fish populations.⁴ We recently showed that methylation of Hg(II) in Arctic marine waters is an important MeHg source to local foodwebs,⁵ but the sources of MeHg to Arctic freshwater systems are still poorly understood.

At temperate latitudes, inorganic Hg(II) can be microbially methylated in anaerobic lake sediments⁶ and hypolimnia,⁷ and wetlands have also been shown to be significant sources of MeHg to downstream ecosystems.⁸ Wetlands are relatively abundant in the north, covering approximately 5% of the Canadian Arctic landscape (15% if the sub-Arctic Hudson Plains are included),⁹ and therefore represent a potentially important MeHg source to Arctic freshwaters. However, the importance of wetlands to Hg(II) methylation in Arctic regions is not clear, and the limited data that is available is often contradictory. For example, while some Arctic wetlands appear to be sites of MeHg production, MeHg yields from snowmelt-fed tributaries can be more important in determining MeHg loads in downstream lakes.¹⁰¹¹ Similarly, experiments have indicated that soils from Arctic wetlands can methylate Hg(II) under laboratory conditions,¹¹¹² but in situ measurements showed a decline in MeHg over the summer season, suggesting that wetland soils are MeHg sinks, except perhaps for a short period during snowmelt.¹² Furthermore, small wetland ponds (<1 ha) on Ellesmere Island in the Canadian High Arctic have been shown to have higher concentrations of aqueous MeHg, and a higher percentage of total Hg (THg) that exists as MeHg (%MeHg), than larger ponds and lakes in the same area (% MeHg = 19.5% vs 4.5%), suggesting that these systems may be sources of MeHg.¹³ Finally, in a number of Alaskan watersheds with no wetland influence, Hammerschmidt et al.¹⁴ concluded that the major source of MeHg to lake water was in situ benthic production and subsequent diffusion from the sediments.

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MeHg concentrations in the environment are controlled not only by Hg(II) methylation processes but also by MeHg demethylation, which can be either microbially mediated in sediments or photolytically driven in surface waters. In fact, two independent mass balance studies conducted in a boreal lake and in Alaskan tundra lakes both demonstrated that photodemethylation is the largest sink of MeHg in lake ecosystems.

The objective of this study was to examine MeHg production in wetland ponds of the Canadian High Arctic (Ellsmere Island, Nunavut). The results are presented in two companion papers. Here we present mass balance budgets for two wetland ponds during the summer season, incorporating external MeHg inputs from atmospheric deposition, MeHg losses from photodemethylation, and changes in MeHg storage in the water column to quantify in-pond MeHg production. The second paper describes the results of methylation assays performed in sediment cores using Hg stable isotope tracers to examine the mechanisms controlling MeHg production in a series of wetland ponds in the same region.

**MATERIALS AND METHODS**

**Site Description.** The Lake Hazen region, located on northern Ellesmere Island within Quttinirpaaq National Park (Supplementary Figure S1), experiences anomalously warm summer conditions for its latitude due to its location on the lee side of the Grant Land Mountains. For example, mean July air temperature recorded in 2005 and 2008 at Lake Hazen camp (81° 49′ N, 71° 20′ W) was 6 °C, with average daily minimum/maximum temperatures of 2 and 10 °C, respectively (Campbell Scientific thermilinear probe, model 44212, data not shown). The summer growing season extends for 8–10 weeks, resulting in a greater diversity and abundance of vegetation compared to surrounding areas, even though the region is classified as a polar desert, receiving only ~95 mm of precipitation annually. Generally, wetland complexes in the vicinity of the Lake Hazen camp exhibit characteristics consistent with both marshes and shallow water wetlands, and are characterized by a central pond surrounded by a wet sedge meadow plant community. The two study sites, Pond 1 and Pond 2, are located along the shore of Lake Hazen and are representatives of the type of wetlands found in the region in terms of general characteristics, vegetation, and water chemistry. The ponds were generally shallow (0.3 and 0.5 m, respectively). However, water levels in both ponds were much higher in 2008 (Supplementary Figures S2–S3) due to very high water levels in adjacent Lake Hazen caused by temperature-induced increases in glacier melt and permafrost thaw that summer. This caused the wetlands to become flooded with Lake Hazen water and maximum depth increased to ~1 m at each site. This seasonal flooding of the wetlands by the end of summer has now occurred on an annual basis since 2008 as a result of warmer summer temperatures in recent years. The ponds provide seasonal habitat for Arctic char smolt at times when they are hydrologically connected to Lake Hazen (i.e., post-wetland flooding). The limnology of ponds in the Lake Hazen region has previously been described and ancillary data on sampled ponds, including water chemistry, wetland and sediment characteristics, are provided in Supplementary Tables S2 and S3 and in ref 18.

**Sample Collection and Experimental Designs.** The data presented here were collected over three field campaigns conducted in 2005 (July 4–24), 2007 (June 23–July 22), and 2008 (July 6–August 8). MeHg mass balance budgets were constructed for Pond 1 (2005, 2007, and 2008) and Pond 2 (2005, 2007) to quantify the net in-pond production of MeHg (Supplementary Figure S2). The two study systems (Supplementary Figures S3 and S4) were selected because they lacked inflow and outflow streams during the summer season (except in 2008, when the wetlands became flooded due to high water levels in adjacent Lake Hazen), therefore limiting the number of variables required to complete the mass balances and allowing the MeHg production term to be tightly constrained. The mass balance models incorporated MeHg inputs from wet atmospheric deposition (i.e., rainfall), the accumulation of MeHg in the water column pool, and the loss of MeHg via photodemethylation. Any change in the water column pool of MeHg that could not be accounted for by external inputs or sinks were attributed to in-pond production. The in-pond MeHg production measured in this fashion is analogous to the net transfer of MeHg into the water column from sediments where MeHg is produced, as we demonstrated using methylation assays performed with enriched Hg stable-isotope tracers in sediment core incubations. Thus, in-pond MeHg production reflects the net sum of Hg(II) methylation and MeHg demethylation in the sediments as well as MeHg transport across the sediment–water boundary.

As stated above, water levels in 2008 were much higher than in 2005 and 2007 and a mass balance could not be completed for Pond 2 due to the formation of a channel connecting Pond 2 (Supplementary Figure S3) to Lake Hazen that led to bidirectional water flow between the two water bodies and therefore unquantifiable exchange of MeHg. The 2008 mass balance for Pond 1 was restricted to the period July 21–27, because the rapidly changing water volume in Pond 1 (from the influx of Lake Hazen water) could not be accurately estimated outside of that time period. Bathymetric surveys were conducted on July 21 and 27 to quantify the volume of water within Pond 1, and the difference in water volume between the two dates was assumed to be equivalent to the influx of Lake Hazen water. The flow of water between Lake Hazen and Pond 1 was unidirectional because changes in water level in Pond 1 only occurred once water levels were significantly higher in Lake Hazen than in Pond 1. For the purpose of the mass balance calculations, Lake Hazen water flowing into Pond 1 was assumed to have a MeHg concentration of 0.020 ng L⁻¹, which is greater than the concentration measured in Lake Hazen water in 2005 (<0.015 ng L⁻¹) but equal to the concentration measured in 2003, and leads to a more conservative estimate of in-pond MeHg production.

Hg samples were collected into acid-cleaned containers using trace-metal sampling procedures. Pond water was collected from shore in Teflon bottles, keeping an unfiltered sample and filtering a second sample using a precleaned 0.45 μm nitrocellulose membrane. Precipitation was collected throughout each field campaign in 1 L wide-mouthed Teflon jars set out at the beginning of individual rain events and transferred into Teflon bottles immediately following each event. Precipitation volume was quantified using a standard rain gauge. Water samples were preserved with trace-metal grade HCl (0.2% of sample volume). Quantitative bulk zooplankton samples were collected by means of horizontal tows with a 19.5 cm diameter, 80 μm net. Zooplankton were transferred into whirl-paks and immediately frozen. Rates of MeHg photodemethylation were quantified using bottle incubations performed at three different depths in Pond 2 (surface, 17...
Sample Analysis. All analyses were performed at the University of Alberta Biogeochemistry Analytical Service Laboratory (BASL). All water samples collected in 2007 and 2008 were distilled and analyzed for MeHg using isotope-dilution gas chromatography inductively coupled plasma mass spectroscopy (GC-ICP-MS). Zooplankton samples were freeze-dried prior to analysis and analyzed similarly, using a nitric acid digestion instead of distillation to extract MeHg. Water samples collected in 2005 were analyzed for MeHg using cold vapor atomic fluorescence (CVAFS) detection instead of ICP-MS detection. THg concentrations in water samples were quantified by BrCl oxidation, SnCl2 reduction, gold trap amalgamation, and CVAFS detection. THg in zooplankton samples was quantified similarly, with the addition of an acid digestion step prior to analysis as previously described for plant tissues and detection of Hg isotope ratios by ICP-MS. Additional details on detection limits, reproducibility, QA/QC data, and the standard THg and MeHg analytical protocols employed are provided in the Supporting Information.

RESULTS AND DISCUSSION

MeHg in the Water Column and Zooplankton Pools. Concentrations of MeHg in unfiltered pond water ranged from 0.30 to 1.8 ng L⁻¹ in Pond 1 and 0.04–0.30 ng L⁻¹ in Pond 2 (Figure 1). The proportion of THg in the MeHg form (%MeHg) was high, ranging from 19% to 62% in Pond 1 and 2–34% in Pond 2 (Supplementary Table S4). Typically, oxic freshwaters have %MeHg values of ~10% (or less in the case of streams), and a high %MeHg can be interpreted as an indication that substantial Hg(II) methylation is occurring in the system. Overall, Ponds 1 and 2 were representative of the range of MeHg concentrations and %MeHg measured in other ponds in the Lake Hazen region, most of which exhibited either high MeHg concentrations and/or high %MeHg.

Water volumes in the ponds were lowest in 2007, followed by 2005 and 2008 (2007 < 2005 ≪ 2008). As a result, MeHg concentrations and %MeHg were much higher in 2005 and 2007 than in 2008 when high water levels resulted in greater dilution of the MeHg produced in sediments and exported into the water column. In 2008, Pond 2 was connected to Lake Hazen during the entire duration of the field campaign via a short channel cutting through the beach. During the same year,

Figure 1. Dissolved (open symbols) and unfiltered (closed symbols) concentrations of MeHg (circles) and THg (triangles), as well as pools of dissolved and particulate MeHg (bars) in Pond 1 (A, C, E) and Pond 2 (B, D, F) in 2005, 2007, and 2008. Note the scale change in panel F.
Lake Hazen water permeated the sand berm separating it from Pond 1, resulting in Pond 1 water levels progressively rising until the entire wetland was flooded. Eventually lake levels rose high enough that year to connect directly to Pond 1 via a short channel. Temporal variability in MeHg concentrations was also observed within a single summer, and in 2005 and 2007, unfiltered MeHg concentrations typically peaked in mid-July (Figure 1). Dissolved gaseous Hg (DGM) decreased throughout July when measured in 2005 (Supplementary Figure S5), despite mean wind velocities in the 12 h prior to sampling being very similar on all three sampling dates (1.6–2.0 m s\(^{-1}\)). These results indicate that the decrease in

Table 1. Summary of MeHg Storage Data

<table>
<thead>
<tr>
<th>site</th>
<th>year</th>
<th>(\Delta\text{MeHg})</th>
<th>external inputs</th>
<th>MeHg PD</th>
<th>MeHg production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond 1</td>
<td>(\mu g)</td>
<td>2005</td>
<td>46</td>
<td>0.31</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2007</td>
<td>−25</td>
<td>0.45</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2008</td>
<td>346</td>
<td>13.3(^b)</td>
<td>1571</td>
</tr>
<tr>
<td></td>
<td>ng m(^{-2}) d(^{-1})</td>
<td>2005</td>
<td>4.24</td>
<td>0.029</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2007</td>
<td>−1.98</td>
<td>0.036</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2008</td>
<td>7.26</td>
<td>0.28(^b)</td>
<td>32.9</td>
</tr>
<tr>
<td>Pond 2</td>
<td>(\mu g)</td>
<td>2005</td>
<td>−2.9</td>
<td>1.78</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2007</td>
<td>−21</td>
<td>2.09</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>ng m(^{-2}) d(^{-1})</td>
<td>2005</td>
<td>−0.047</td>
<td>0.029</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2007</td>
<td>−0.034</td>
<td>0.034</td>
<td>2.12</td>
</tr>
</tbody>
</table>

\(\Delta\text{MeHg}\), external inputs (from precipitation, and in 2008 from Lake Hazen water), MeHg losses from photodemethylation (MeHg PD), and in-pond MeHg production in Ponds 1 and 2 during 2005 (July 6–23), 2007 (Pond 1, June 25–July 18; Pond 2, June 24–July 19), and 2008 (July 21–27). Values are given both as total fluxes (\(\mu g\)) and average daily areal fluxes (ng m\(^{-2}\) d\(^{-1}\)). Exogenous inputs to Pond 1 in 2008 include inputs from the influx of Lake Hazen water (0.28 ng MeHg m\(^{-2}\) d\(^{-1}\)), assumed to have a concentration of 0.020 ng L\(^{-1}\) (see text for details).
concentration was not due to an increase in the water-to-atmosphere gas transfer velocities. Furthermore, no concurrent decreasing trend in THg concentrations, either in filtered or unfiltered waters, was observed (Figure 1, Supplementary Table S4), suggesting that the decreases in DGM concentrations were likely due to a combination of a decrease in the fraction of THg existing as reactive Hg(II) and/or decreases in net Hg(II) photoreduction, which is the process responsible for DGM production. If concentrations of reactive Hg(II) did decrease, this would have implications for Hg(II) methylation and might explain the decrease in MeHg concentrations observed after the mid-July peak.

The pool of MeHg in the water column was calculated by multiplying MeHg concentrations at each point in time by the water volume of the appropriate pond, which was in turn calculated from the area/volume curves obtained from bathymetric surveys conducted in 2005 and 2008 (Supplementary Figures S6 and S7). Due to their shallow nature, Ponds 1 and 2 remain well mixed and unstratified throughout the summer season, and therefore surface MeHg concentrations could be applied to the whole water column. In Pond 1, the pool of MeHg stored in the water column increased over the 2005 and 2008 field campaigns, (ΔMeHg = 4.2 and 7.3 ng m⁻² d⁻¹, respectively), whereas in 2007 there was a net loss of 2.0 ng m⁻² d⁻¹ (Table 1). There was also a loss of MeHg from the water column of Pond 2 in 2005 and 2007 (ΔMeHg = −0.05 and −0.03 ng m⁻² d⁻¹, respectively). However, the ΔMeHg values have to be interpreted with caution, and cannot be used as a metric for MeHg production in the same manner as the “MeHg production” term in eq 1 because they are highly dependent on the time period over which they are calculated. For example, in 2007, Pond 2 exhibited a net accumulation of MeHg between June 24 and July 8, but a net loss of MeHg between June 24 and July 19.

Bulk zooplankton samples collected in July 2005 in both Ponds 1 and 2 were composed primarily of cladocerans such as *Daphnia middendorffiana/tenebrosa* (>80%) and chydorids, with other major taxa present including anostracans (*Branchinecta paludosa*), notostracans (*Lepadus arcticus*), and cyclopoid copepods (*S. Arnott, Queen’s University, personal communication; see also ref 31). In Pond 1, zooplankton MeHg concentrations (MeHg_zoop) were usually between 700 and 900 ng g⁻¹ dw, except on July 19th when MeHg_zoop decreased to 267 ng g⁻¹ likely as a result of growth dilution following a 60% increase in biomass between July 16–19 (Figure 2, Supplementary Table S5). These MeHg concentrations are extremely high, approaching the maximum concentrations (~1000 ng g⁻¹ dw) measured in zooplankton from artificial reservoirs created by the flooding of boreal peatlands and uplands. Similar to MeHg concentrations in the water, MeHg_zoop was lower in Pond 2 (91–154 ng g⁻¹ dw) compared to Pond 1, but no growth dilution was observed even after biomass almost tripled in Pond 2 during July 12–16. Typically, %MeHg in zooplankton ranges from 30% to 50%, but values measured in this study ranged from 67% to >95%, demonstrating the high degree of MeHg availability and efficient trophic transfer in Ponds 1 and 2. By comparison, bulk zooplankton samples of similar taxonomic composition collected from ponds at another Arctic oasis in the Canadian Arctic (Truelove Lowland, Devon Island, NU) had %MeHg values of 78 ± 9% and MeHg concentrations ranging from 113 to 170 ng g⁻¹ dw, higher than for zooplankton collected in typical, (ultra)oligotrophic Canadian Arctic lakes. Log bioaccumulation factors (BAFs), calculated as the ratio of the MeHg concentration in zooplankton (in ng g⁻¹ dry weight) to the MeHg concentration in water (in ng g⁻¹ or ng mL⁻¹), ranged between 5.2 and 6.0, with the lowest value coinciding with and likely driven by the rapid increase in zooplankton biomass in Pond 1 during July 16–19, resulting in a lag in the bioaccumulation of MeHg. However, observed BAF values were typical of most aquatic habitats, where BAF ranges between 5.2 and 6.4.32

MeHg concentrations in zooplankton are controlled by multiple factors including MeHg concentrations in water, taxonomic composition, and growth rates. Chételat and Amyot34 attributed the higher %MeHg values and MeHg concentrations measured in zooplankton from the Truelove Lowland ponds, relative to other Arctic sites, to ecological interactions and the presence of *Daphnia middendorffiana* rather than abiotic factors such as differences in water MeHg concentrations. However, our data demonstrate that, other factors being equal (e.g., presence of *Daphnia middendorffiana*), differences in zooplankton MeHg concentrations between ponds primarily reflect differences in water MeHg concentrations. For example, MeHg concentrations in Pond 1 waters were about 10 times greater than in Pond 2, resulting in zooplankton MeHg concentrations that were seven times greater. The lower BAFs in Pond 1 compared to Pond 2 may potentially be the result of higher zooplankton densities in Pond 1. The combination of high %MeHg in zooplankton but “typical” BAF values observed in this study also supports that, in this particular case, the MeHg burden of zooplankton was controlled by the MeHg supply in the water more than by other factors such as foodweb/trophic dynamics. The benthic feeders *B. paludosa* and *D. middendorffiana* may also play an important role in Hg cycling in these ponds by providing a strong benthic-pelagic coupling, potentially mobilizing sediment MeHg.

The proportion of the water column MeHg pool stored in zooplankton (3–12%, Figure 2) was greater than is normally found in lentic freshwater systems (~1%) but similar to what has been observed in systems with high MeHg production, such as flooded peatland reservoirs (7–8%). While the proportion of the water column MeHg pool stored in zooplankton remained fairly constant in Pond 1, it increased over the 3-week sampling campaign in Pond 2. Overall, the proportion of the water column THg pool stored in zooplankton (0.6–6%) was lower than for MeHg (Wilcoxon Signed Ranks Test *p*= 0.005, *n*= 10, *α*= 0.05), but this value was higher in Pond 1 (2.5–5.8%) compared to Pond 2 (0.6–2.8%; Mann–Whitney U test *p*= 0.02, *n*= 5, *α*= 0.05), presumably because a greater portion of the water column THg in Pond 1 existed as MeHg, which is the more readily bioaccumulated and biomagnified form of Hg.

**MeHg Input (Precipitation).** Rainfall averaged 0.46, 0.29, and 0.75 mm/day during the 2005, 2007, and 2008 field campaigns, respectively, and MeHg concentrations in precipitation ranged from below detection (<0.015 ng L⁻¹) to 0.248 ng L⁻¹. Precipitation samples that were below detection limit were assigned a concentration of half the detection limit (0.0075 ng L⁻¹), and precipitation events for which the sample volume was insufficient to analyze for MeHg were assigned a MeHg concentration equal to the volume-weighted average concentration calculated for the same sampling season as per Graydon et al.55 MeHg inputs from precipitation ranged from 0.029 to 0.051 ng MeHg m⁻² d⁻¹ (Supplementary Table S6). No other estimates of MeHg inputs from rainfall exist for the Canadian Arctic; however, depositional fluxes quantified for the
Lake Hazen region during June–July are significantly lower than the long-term average of 0.11 ng m⁻² d⁻¹ reported for the Experimental Lakes Area (ELA) in the remote boreal ecoregion of Northwestern Ontario,³⁵ primarily due to the lower amount of rainfall in July at Lake Hazen compared to the ELA (rainfall in July at ELA ranged from 62 to 108 mm for the same years, with volume-weighted mean concentrations of 0.024–0.048 ng L⁻¹ and MeHg deposition of 0.05–0.14 ng m⁻² d⁻¹; J. Graydon, personal communication). Overall, inputs of MeHg from atmospheric deposition were negligible in the context of the whole-pond mass balances.

**MeHg Sink (Photodemethylation).** MeHg photodemethylation is the process by which MeHg is degraded photolytically by solar radiation,¹⁶,²² resulting in MeHg being converted to Hg(0) and Hg(II) (Supplementary Figure S2). MeHg concentration in water samples exposed to sunlight decreased over time, which is consistent with the abiotic process of MeHg photodemethylation,¹⁶,²² whereas MeHg concentrations remained constant in samples incubated in the dark (Figure 3), indicating no biotic demethylation in the water column. Rates of MeHg photodemethylation can be expressed as the loss of MeHg over time (t) as a function of the product of the photodemethylation rate constant (kpd), the MeHg concentration (MeHgconc), and the cumulative PAR photon flux during that time interval (PARcum):

\[
\text{rate} = \frac{d\text{(MeHg}_{\text{conc}})}{dt} = k_{pd} \cdot \text{MeHg}_{\text{conc}} \cdot \text{PAR}_{\text{cum}}
\]

kpd values were calculated and corrected for the attenuation of UV radiation by Teflon bottles, as in Lehnherr and St. Louis (see also the Supporting Information).²² kpd averaged 3.2 × 10⁻³ and 3.6 × 10⁻³ m² E⁻¹ at the surface of Ponds 1 and 2, respectively (Supplementary Table S7). These rate constants are similar to previous measurements made in boreal²² and tundra³⁶ lakes (4.4 × 10⁻³ and 3.7 × 10⁻³ m² E⁻¹, respectively). Photodemethylation rates in Pond 2 decreased significantly with depth and were controlled by the attenuation of UV-A radiation (Figures 4 and S8). Previous experimental and modeling considerations have also suggested that in waters that are not very transparent to visible light (attenuation coefficient ≥1 m⁻¹), UV radiation is the main driver of photodemethylation on an areal basis.²² Whole-pond photodemethylation was quantified by summing over the entire
water column the depth-specific photodemethylation rates. These were calculated using a simple model incorporating rate constants and light attenuation coefficients for each radiation waveband (UV-B, UV-A, and visible) as well as MeHg concentration, incident light, and water volume in each 2-cm slice of the water column. The experimentally determined $k_{p,d}$ value was separated into a UV-B, UV-A, and visible light component according to the previously reported contribution of each radiation waveband to the overall rate constant, and UV attenuation coefficients were calculated from dissolved organic carbon (DOC) concentrations, whereas visible light attenuation coefficients were measured by performing depth profiles of PAR in each pond.

Across the different sampling years, photodemethylation was a larger sink in Pond 1 (2.6−33 ng MeHg m$^{-2}$ d$^{-1}$) than in Pond 2 (2.0−2.1 ng MeHg m$^{-2}$ d$^{-1}$) due to higher MeHg concentrations in Pond 1 water resulting in higher photodemethylation rates (Table 1). In both ponds, photodemethylation was primarily mediated by UV-A radiation (Supplementary Figure S8). Water in Pond 1 was less optically transparent to UV and visible radiation than Pond 2 water, but this factor was less important than MeHg concentration in controlling photodemethylation rates. Few studies have included photodemethylation when building mass balance models for freshwater systems, but the magnitude of the photodemethylation sink in other systems is generally similar to the values reported here. Photodemethylation was reported to be a sink of 1.0 ng MeHg m$^{-2}$ d$^{-1}$ in a boreal lake and 5−13 ng MeHg m$^{-2}$ d$^{-1}$ in a series of Alaskan tundra lakes, although it should be noted that photodemethylation fluxes reported for the Alaskan lakes may be overestimated and not directly comparable as they were calculated using the assumption that photodemethylation is driven by visible light and not by UV radiation, as has now been demonstrated.

**MeHg Production Calculated from Mass Balance.** The in-pond production of MeHg, roughly equivalent to the net diffusion of MeHg into the water column from sediments where Hg(II) is methylated, was calculated as the quantity of MeHg required to balance the MeHg budget, taking into account water column storage ($\Delta$MeHg) and other inputs and sinks (eq 1): 

$$\text{MeHg production} = \Delta\text{MeHg} + \text{inputs(photodemethylation)} - \text{sinks}$$

For a given site, there was almost no difference in areal MeHg production between 2005 and 2007 (Table 1), but MeHg production was an order of magnitude higher in Pond 1 (14.4–18.5 ng MeHg m$^{-2}$ d$^{-1}$) than in Pond 2 (1.75–1.88 ng MeHg m$^{-2}$ d$^{-1}$). For both sites, the input of MeHg from precipitation was a much smaller MeHg source (<2%) than in-pond MeHg production (Table 1), as might be expected for a site that receives little precipitation. Furthermore, direct atmospheric deposition of MeHg usually accounts for a small percentage of all MeHg sources in lake mass balances. As described in the Materials and Methods section, the high water levels in Lake Hazen in 2008 resulted in the Pond 1 wetland becoming flooded. From a MeHg mass balance perspective, the influx of Lake Hazen water represented an almost negligible MeHg input (0.28 ng m$^{-2}$ d$^{-1}$), or less than 1% of the in-pond MeHg production over the same period (July 21−27). However, the flooding of woodland soils appeared to stimulate MeHg production in Pond 1, with the areal 2008 daily MeHg production flux value (39.9 ng m$^{-2}$ d$^{-1}$) more than twice as high as the 2005 and 2007 values. Flooding of wetlands is known to increase MeHg production, as was previously reported when a boreal wetland was experimentally flooded to form a reservoir, resulting in net annual MeHg yields of 3.8−19.2 ng m$^{-2}$ d$^{-1}$ in the decade post-flood. It is thought that flooding of soils and vegetation releases associated Hg(II) as well as organic matter and nutrients, thereby stimulating microbial methylation. Photodemethylation was a sink for 77−122% of the in-pond MeHg production, explaining why concentrations of MeHg did not keep increasing in the ponds over time, despite high rates of MeHg production. Because photodemethylation was such a large flux, the magnitude of the MeHg production term hinges largely on the photodemethylation term. Error propagation calculations taking into account MeHg analytical variability (10%) and uncertainty in the $k_{p,d}$ measurements (10%) and water volume calculations (25%) result in an uncertainty in the MeHg production term of 28%, suggesting that this term is fairly well constrained.

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and was therefore not measured in the seasonal mass balance budgets.

Recent evidence suggests that Hg(II) could be methylated within snowpacks and therefore meltwater-fed runoff and streams can be sources of MeHg to Arctic wetlands and lakes. However, it appears that snowmelt is not a large source of MeHg to the wetlands in the Lake Hazen region when compared to in-pond production. Snow THg concentrations measured on the ice-covered surface of Pond 1 and Lake Hazen in May 2009 ranged between 3.7 and 4.6 ng L$^{-1}$ (data not shown), while MeHg concentration in Pond 1 water measured on June 25, 2007 (or 2–3 weeks after snowmelt) were quite high (1.38 ng L$^{-1}$). For snow-fed runoff to reach these MeHg concentrations, and therefore be a significant source of MeHg, requires that approximately 30% of all THg in snow was methylated. Furthermore, considering that photodemethylation would remove ~0.6 ng L$^{-1}$ of MeHg during the 2–3 week period between the input of meltwater and sample collection on June 25, snowmelt runoff MeHg concentrations of ~2 ng/L are required, which is equivalent to the methylation of ~50% of snow THg. To put these numbers in perspective, the highest MeHg concentrations in snow meltwater reported in two studies conducted in Svalbard were 0.26 and 0.24 ng L$^{-1}$, with %MeHg values of ~10%.41,42

Conclusions. MeHg production in Pond 1 and Pond 2 varied by an order of magnitude, despite the superficial similarity of these two systems, suggesting the presence of important biogeochemical controls on net Hg(II) methylation. MeHg production rates measured using a mass balance approach have the advantage of being integrated over time and space (whole-pond) and therefore provide more realistic estimates of true rates. However, to gain insight into methylation mechanisms and controls, we performed, in sediment cores collected from eight ponds in the Lake Hazen region, methylation assays using enriched Hg stable-isotope tracers. Using this approach we were able to determine that the difference in internal MeHg production between Pond 1 and Pond 2 can be explained primarily by higher THg concentrations in Pond 1 sediments and water and to a lesser extent by somewhat higher methylation potentials in Pond 1 sediments. Factors that were important in controlling water column MeHg concentrations across all ponds were sediment MeHg concentrations, the dominance of anaerobic processes and conditions (estimated using dissolved CH$_4$ concentrations and NH$_4^+$$:\text{NO}_3^-$ ratios as proxies), and exposure to UV-A radiation. These findings are consistent with the mass balance results, which suggest that internal production in pond sediments is the main MeHg source, while UV-A mediated photodemethylation is a large MeHg sink. These wetland ponds provide important nesting and feeding habitat to many shore birds and waterfowl. Furthermore, when the ponds become hydrologically connected to Lake Hazen in the late summer, the ponds are inhabited by juvenile Arctic char in the late summer who feed on the abundant, and MeHg-rich, zooplankton before returning to Lake Hazen where they become prey to larger, older individuals. This in turn provides a mechanism by which MeHg produced in shoreline ponds can enter the Lake Hazen foodweb, although it is not clear how important this biotransportation of MeHg might be.

References


Supporting Information

Additional experimental and analytical details including tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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