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Methylated Mercury Species in Marine Waters of the Canadian High and Sub Arctic

JANE L. KIRK,^{*,†} VINCENT L. ST. LOUIS,[†]
HOLGER HINTELMANN,[‡]
IGOR LEHNHERR,[†] BRENT ELSE,[§] AND
LAURIER POISSANT[¶]

Department of Biological Sciences, University of Alberta, Edmonton, Alberta Canada T6G 2E9, Department of Chemistry, Trent University, Peterborough, Ontario, Canada K9J 7B8, Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2, Centre St-Laurent, Aquatic Ecosystem Protection Research Division, Water Science and Technology Directorate, Science and Technology Branch, Environment Canada, 105 rue McGill, Montréal, Québec, Canada H2Y 2E7

Received June 18, 2008. Revised manuscript received August 11, 2008. Accepted September 01, 2008.

Distribution of total mercury (THg), gaseous elemental Hg(0) (GEM), monomethyl Hg (MMHg), and dimethyl Hg (DMHg) was examined in marine waters of the Canadian Arctic Archipelago (CAA), Hudson Strait, and Hudson Bay. Concentrations of THg were low throughout the water column in all regions sampled (mean \pm standard deviation; $0.40 \pm 0.47 \text{ ng L}^{-1}$). Concentrations of MMHg were also generally low at the surface ($23.8 \pm 9.9 \text{ pg L}^{-1}$); however at mid- and bottom depths, MMHg was present at concentrations sufficient to initiate bioaccumulation of MMHg through Arctic marine foodwebs (maximum 178 pg L^{-1} ; $70.3 \pm 37.3 \text{ pg L}^{-1}$). In addition, at mid- and bottom depths, the % of THg that was MMHg was high (maximum 66%; $28 \pm 16\%$), suggesting that active methylation of inorganic Hg(II) occurs in deep Arctic marine waters. Interestingly, there was a constant, near 1:1, ratio between concentrations of MMHg and DMHg at all sites and depths, suggesting that methylated Hg species are in equilibrium with each other and/or are produced by similar processes throughout the water column. Our results also demonstrate that oceanographic processes, such as water regeneration and vertical mixing, affect Hg distribution in marine waters. Vertical mixing, for example, likely transported MMHg and DMHg upward from production zones at some sites, resulting in elevated concentrations of these species in surface waters (up to 68.0 pg L^{-1}) where primary production and thus uptake of MMHg by biota is potentially highest. Finally, calculated instantaneous ocean–atmosphere fluxes of gaseous Hg species demonstrated that Arctic marine waters are a substantial source of DMHg and GEM to the atmosphere (27.3 ± 47.8 and $130 \pm 138 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively) during the ice-free season.

* Corresponding author phone: (780) 492-1288; fax: (780) 492-9234; e-mail: jkirk@ualberta.ca.

† University of Alberta.

‡ Trent University.

§ University of Manitoba.

¶ Environment Canada.

Introduction

Monomethyl mercury (MMHg), a toxic form of Hg that bioaccumulates through foodwebs, is present in some Arctic marine mammals at concentrations above the Canadian fish commercial sale limit of $0.5 \mu\text{g g}^{-1}$ wet weight (ww) (1). In the North Open Water (NOW), for example, a large productive polynya in the Canadian Arctic, concentrations of MMHg in muscle of ringed seals are $0.56 \pm 0.25 \mu\text{g g}^{-1}$ ww (2). At this average concentration, Northern people could eat $\sim 90 \text{ g}$ of seal meat per week before consuming the U.S. Environmental Protection Agency's maximum MMHg limit of $50 \mu\text{g}$. Although there is some evidence that concentrations of MMHg in Arctic marine mammals have increased since industrialization (3), sources of MMHg to Arctic marine foodwebs are not known.

Gaseous elemental Hg(0) (GEM) is the predominant form of Hg in the atmosphere (4). Since industrialization, atmospheric concentrations of GEM have increased as activities such as coal burning and metal smelting release GEM to the atmosphere (5). Due to its high vapor pressure and low oxidation potential, GEM is stable in the atmosphere and therefore undergoes long-range transport (4). Strong oxidants in the troposphere, such as halogen radicals and ozone, may transform GEM to ionic forms of Hg(II), termed reactive gaseous Hg (RGM) and particulate Hg (pHg), which have low vapor pressures and are therefore scrubbed from the atmosphere and deposited to landscapes and water bodies (6, 7). In the Arctic, oxidation of tropospheric GEM and subsequent deposition of Hg(II) is enhanced during springtime by atmospheric mercury depletion events (AMDEs) which are catalyzed by halide radicals over sea ice (8–10). Although it has been hypothesized that AMDEs are an important source of Hg to Arctic ecosystems (9, 10), the quantity of Hg(II) entering marine waters from AMDEs is not known (8) as a large portion of Hg(II) deposited during AMDEs may be rapidly (photo)reduced and re-emitted to the atmosphere (11). It is also not known how Hg(II) in Arctic marine ecosystems, deposited during AMDEs or otherwise, is methylated to MMHg, which is the key step initiating the bioaccumulation of Hg in foodwebs. In estuaries (12, 13) and contaminated coastal marine areas (14, 15), Hg(II) is methylated to MMHg primarily by sulfate-reducing bacteria in anoxic surface sediments. However, MMHg is likely produced by different mechanisms in remote open oceans, where methylation likely occurs throughout the water column (16–19) and dimethyl Hg (DMHg), a volatile form of gaseous Hg, is typically the dominant methylated Hg species found below the thermocline (19–21). Furthermore, Hg cycling in polar marine waters is likely different than in more temperate regions as persistent ice cover and relatively low primary productivity affect photochemically and biologically mediated Hg reduction, oxidation, and degradation processes, and thus rates of atmosphere–ocean exchange, as well as methylation and demethylation rates.

Here we present an extensive examination of Hg speciation in Canadian Arctic marine waters. Distribution of total Hg (THg), MMHg, DMHg, and GEM throughout the water column of the Canadian Arctic Archipelago (CAA), including the NOW and Northwest (NW) Passage, Hudson Strait, and Hudson Bay (Figure 1) were examined to determine potential zones of reduction and/or destruction of the different Hg species. Ocean–atmosphere fluxes of DMHg and GEM were also quantified.

Materials and Methods

Study Design. All samples were collected between August 16 and October 13, 2005 from aboard the Canadian Coast Guard

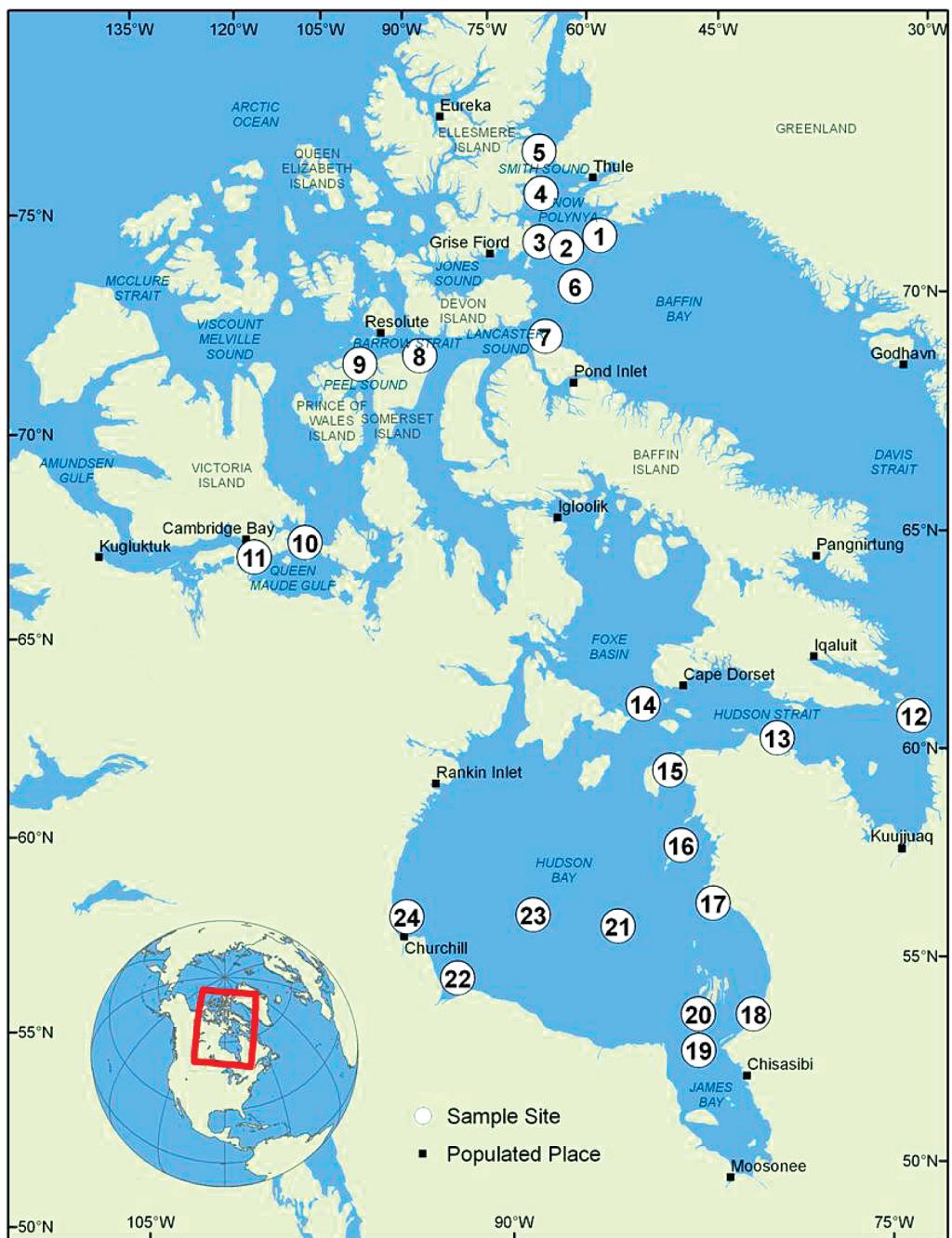


FIGURE 1. Sites in the Canadian Arctic Archipelago (CAA), including the North Open Water (NOW) polynya and Northwest (NW) Passage, Hudson Strait, and Hudson Bay where seawater was sampled from the surface, bottom, and midway through the water column for concentrations of total Hg (THg), gaseous elemental Hg(0) (GEM), monomethyl Hg (MMHg), and dimethyl Hg (DMHg).

Ship (CCGS) *Amundsen*. The spatial distribution of THg, GEM, MMHg, and DMHg in Canadian high and sub Arctic marine waters was assessed by quantifying concentrations of these Hg species at 24 sites throughout the CAA and Hudson Bay region (Figure 1). To determine potential zones of production and/or destruction of the different Hg species, seawater was collected from different depths of the water column (the surface or top ~2–5 m, a mid-depth ~half way between the surface and bottom, and ~5–15 m above the bottom) at each site. All sites were ice free during the sampling period and air temperatures ranged between -3.7 and 12°C .

Water Mass Characterization. Water masses at our sampling sites were characterized by examining temperature, salinity, and oxygen profiles measured along the *Amundsen* cruise. Temperature, salinity, and oxygen were measured using a Seabird 911+CTD equipped with Seabird model 3+,

4C, and 43 sensors, respectively. Chlorophyll a (*chl a*) concentrations were also measured onboard the *Amundsen* using a Turner Designs model 10-AU fluorometer (22).

Collection and Analyses of Hg Samples. Seawater samples for Hg analyses were collected in acid-cleaned 12 L Teflon-lined Niskin bottles installed on a SeaBird Carousel Rosette water sampler with SeaBird 911+ controller. Seawater was subsampled from the Niskin bottles immediately after collection using “clean hands–dirty hands” Hg sampling protocol (11).

Concentrations of THg and MMHg in Seawater. Water samples for THg (includes all of the Hg(II) and MMHg and perhaps a small portion of the GEM and DMHg in a sample) and MMHg analyses were collected into acid-washed 125 and 250 mL Teflon bottles and preserved with concentrated trace-metal grade HCl and H_2SO_4 equal to 0.2% and 0.4% of

sample volume, respectively. Analysis was performed at the University of Alberta Low-level Hg Analytical Laboratory using standard protocols detailed in the Supporting Information.

Concentrations of GEM and DMHg in Seawater. Seawater for GEM and DMHg analyses was collected into 1.2 and 2.2 L acid-washed glass bottles, respectively, and processed using standard purge and trap techniques. Dissolved gaseous Hg (DGM; includes both GEM and DMHg) (17) and DMHg were collected onto gold and Carbo traps, respectively. Gold traps were analyzed on board the *Amundsen* whereas Carbo traps were analyzed at the Trent University Worsfold Water Quality Centre. Concentrations of DGM and DMHg were calculated by dividing pg of Hg on each trap by the sample volume. Dissolved GEM concentrations were then determined by subtracting DMHg concentrations from DGM concentrations. Further analytical details are provided in the Supporting Information.

Instantaneous Diffusive Fluxes of GEM and DMHg from Seawater to the Atmosphere. To determine if high and sub Arctic marine waters are a source of gaseous Hg species to the atmosphere, diffusive flux rates of GEM and DMHg from water to the atmosphere were calculated as in ref 23 using the following formula:

$$\text{Flux} = k(C_w - C_{\text{eq}}) \quad (1)$$

where k is the gas transfer velocity (cm hr^{-1}), C_w is the measured gaseous Hg concentration (pg L^{-1}) in water near the air–water interface, and C_{eq} is the gaseous Hg concentration (pg L^{-1}) in water at solubility equilibrium with the atmosphere. Procedures used to calculate k and C_{aq} are described in the Supporting Information.

Results and Discussion

Water Mass Characterization. Temperature and salinity profiles (Figure S1 for example) were used to identify water masses sampled for concentrations of Hg in the CAA (which included sites in the NOW and NW Passage), Hudson Strait, and Hudson Bay. The CAA receives inflow of Atlantic, Arctic, and Pacific-origin water masses which undergo mixing and modification as they circulate through the numerous straits and basins of the CAA (24, 25). In the NOW (Figure 1, sites 1–5), unique water masses form from mixing of Arctic or Northern Assemblage water, which enters through Smith and Jones Sound, with Atlantic or Southern Assemblage water, which enters via the West Greenland Current (WGC) (26). A branch of the WGC also enters the NW Passage through Lancaster Sound (sites 6–7) (26), mixing in Barrow Strait (site 8) with eastward flowing Canada Basin water composed of fresh, cool Pacific water overlying warm, salty Atlantic water (25, 27). Restricted by shallow sills, the upper Pacific layer loops southward into Peel Sound (site 9) before flowing eastward toward Baffin Bay (28). Sites 10 and 11, located in Queen Maude Gulf, are shallow sites (~50 and 100 m deep, respectively) composed of fresh, cool Pacific-origin surface water which enters the NW Passage through the Amundsen Gulf (25).

Hudson Bay is comprised of three main water masses termed Hudson Bay Summer Surface Water (HBSSW), Hudson Bay Winter Surface Water (HBWSW), and Hudson Bay Intermediate Water (HBIW) (29). HBSSW constitutes the top ~40 m of the water column and forms in summer from mixing of river runoff and sea ice melt with HBWSW, formed during sea ice formation in the fall (29, 30). Between ~100–175 m lies HBIW, formed from mixing of HBWSW with inflowing Hudson Strait Bottom Water (HSBW) (29, 30). HSBW forms at the eastern end of Hudson Strait, where intense vertical mixing of Baffin Bay and Intermediate Labrador Sea water produces a homogeneous, westward flowing water mass (sites 12 and 13) (31).

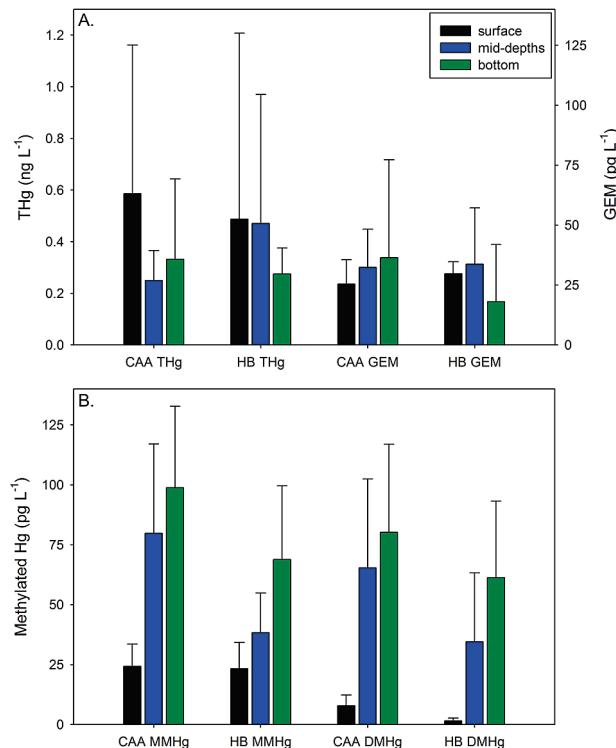


FIGURE 2. Average concentrations of THg (ng L^{-1}), GEM, MMHg, and DMHg (pg L^{-1}) at the surface, bottom, and midway through the water column at sites in the CAA and Hudson Bay (HB) region. Error bars represent standard deviation.

Concentrations of THg and GEM in Seawater. Concentrations of THg were low throughout the water column in both the CAA and Hudson Bay region (mean \pm standard deviation 0.39 ± 0.40 and $0.42 \pm 0.53 \text{ ng L}^{-1}$, respectively) (Table S1, Figure 2a). These concentrations are similar to those measured in other remote oceans such as the north Atlantic ($0.48 \pm 0.32 \text{ ng L}^{-1}$) (17), north Pacific ($0.23 \pm 0.17 \text{ ng L}^{-1}$) (32), and Mediterranean ($0.51 \pm 0.25 \text{ ng L}^{-1}$) (20).

Concentrations of GEM were quite low in surface waters and varied little among sites, averaging $25.4 \pm 10.2 \text{ pg L}^{-1}$ in the CAA and $29.6 \pm 5.0 \text{ pg L}^{-1}$ in the Hudson Bay region (Figure 2a). Although some (33) have suggested that GEM in marine surface waters is produced mostly from photochemically mediated reduction of Hg(II), reduction of Hg(II) by marine microorganisms (34, 35) has also been demonstrated. Elevated concentrations of GEM in surface waters often coincided with elevated concentrations of *chl a* measured at the *chl a* maximum (between 10–50 m) (Figure S2), suggesting that a portion of GEM is produced biotically and/or by biotically mediated processes. As has been previously observed in the North Atlantic (17, 21), concentrations of GEM at some sites were lower than expected based on the relationship between GEM and *chl a* observed at most sites (e.g., site 7 (Figure S3)), likely due to degassing of the surface mixed layer by strong winds. At site 7, for example, average wind velocity 3 h prior to sampling was 39.3 km h^{-1} (Table S2), one of the highest values observed throughout the cruise. In surface waters of the Baltic Sea, Kuss and Schneider (37) also recently observed higher concentrations of GEM during summer compared to other seasons and a significant relationship between GEM and particulate organic carbon which they attributed to biologically mediated reduction of reactive Hg(II).

In deeper regions of the water column, concentrations of GEM were variable, ranging from <MDL to 133 pg L^{-1} and averaging $34.3 \pm 29.7 \text{ pg L}^{-1}$ in the CAA and $26.5 \pm 24.5 \text{ pg L}^{-1}$ in the Hudson Bay region (Figure 2a). In addition,

concentrations of GEM at different depths within the same site often varied greatly, indicating that the biotic and/or abiotic processes responsible for net GEM production varied from site to site and throughout the water column. Although reduction of Hg(II) is likely the dominant source of GEM in marine waters, photodegradation of MMHg (37) and DMHg at the surface and biotically and/or abiotically mediated reductive demethylation may also produce GEM deep in the water column (17).

Concentrations of MMHg and DMHg in Seawater. At most sites in the CAA and Hudson Bay region, concentrations of both MMHg and DMHg were low in the surface waters but increased with depth (to maximum concentrations of 178 pg L^{-1}), suggesting that methylated Hg species are produced in deep Arctic marine waters and/or sediments (Figures 2b and S3). In the CAA (except site 9 discussed below), concentrations of MMHg and DMHg averaged only 24.3 ± 9.2 and $7.9 \pm 4.4 \text{ pg L}^{-1}$, respectively, in the surface polar mixed layer (Table S1). Similarly, in the Hudson Bay region, concentrations of MMHg and DMHg in surface waters, generally composed of fresh HBSSW, averaged only 23.3 ± 11.0 and $1.6 \pm 1.1 \text{ pg L}^{-1}$, respectively (with the exception of site 12 discussed below). Interestingly, although concentrations of MMHg at the surface were similar in the CAA and Hudson Bay region, average concentrations of DMHg in surface waters of the CAA were significantly higher than those in the Hudson Bay region ($t = 4.48$, $p < 0.005$), possibly due to the large influence of river input on HBSSW. Although rivers are a known source of MMHg to downstream water bodies, freshwaters do not contain large quantities of DMHg (21) and therefore likely dilute DMHg transported to the surface from deeper regions of the water column and/or produced in HBSSW. Sites 9 and 12, located in Peel Sound and at the eastern end of Hudson Strait, had high concentrations of MMHg (68.0 and 24.4 pg L^{-1} , respectively) and DMHg (52.3 and 32.0 pg L^{-1} , respectively) at the surface (Figure S3). Water column mixing during the ice-free season at these sites, at site 9 likely from water rushing through the narrow channel of Peel Sound and at site 12 from vertical mixing of Baffin Bay and Intermediate Labrador Sea Water (31), likely transported MMHg and DMHg to the surface (Figure S1c–f). This may be an important source of MMHg to organisms feeding in the surface polar mixed layer, where primary production is generally greatest (24), and to surrounding landmasses as DMHg in surface water is evaded to the atmosphere where it may then be photolyzed to MMHg (23, 38, 39). High concentrations of MMHg and DMHg (up to $\sim 160 \text{ pg L}^{-1}$) have also been measured in surface waters of Fram Strait and the Greenland Sea (18). However in remote regions of the north Atlantic (17) and equatorial Pacific (19), concentrations of methylated Hg species in surface waters are generally $<\text{MDL}$.

At mid-depths of the water column in the CAA, concentrations of MMHg and DMHg averaged 79.8 ± 37.3 and $65.4 \pm 37.1 \text{ pg L}^{-1}$, respectively, and increased to 98.8 ± 33.9 and $80.2 \pm 36.7 \text{ pg L}^{-1}$, respectively, at the bottom (Figure 2). Similarly, in the Hudson Bay region, concentrations of MMHg and DMHg averaged 38.3 ± 16.6 and $34.6 \pm 28.7 \text{ pg L}^{-1}$, respectively, midway through the water column, and 68.8 ± 30.7 and $61.3 \pm 31.9 \text{ pg L}^{-1}$, respectively, at the bottom. Concentrations at depth are comparable to those measured in deep waters of the equatorial Pacific (maximum MMHg and DMHg concentrations 116 and 134 pg L^{-1} , respectively) (19) but are higher than those measured in the western Mediterranean (concentrations of MMHg and DMHg there were $<30 \text{ pg L}^{-1}$ and $<60 \text{ pg L}^{-1}$, respectively) (20). Interestingly, in deep north Atlantic waters (17) average concentrations of DMHg were lower than those reported here ($26 \pm 16 \text{ pg L}^{-1}$), but concentrations of MMHg there were higher, averaging $208 \pm 216 \text{ pg L}^{-1}$. Perhaps more importantly than concentrations of methylated Hg species, the % of THg that

was in the MMHg form (or % MMHg) was generally high at mid- and bottom depths of the water column in both the CAA (maximum 66%, 36 ± 17 and $38 \pm 16\%$, respectively) and Hudson Bay region (16 ± 11 and $27 \pm 13\%$, respectively) (Table S1). High percentages of MMHg typically reflect high methylation rates and low demethylation rates (40). However, in Arctic marine waters where concentrations of THg are low, high % MMHg may reflect limitation of MMHg production by Hg(II) supply.

At mid- and bottom depths of the water column, the variation in concentrations of methylated Hg species observed can be explained by examining oceanographic processes at individual sites. Concentrations of methylated Hg species varied little among sites of the NOW, Lancaster Sound, and Barrow Strait, for example, (1–8), likely because water column composition was similar there (Figure S1a–d). Concentrations of MMHg and DMHg at the bottom of the water column, composed of WGC water, were high (104 ± 19.0 and $76.0 \pm 21.3 \text{ pg L}^{-1}$, respectively). However, at mid-depths, in the warm halocline, concentrations were slightly lower, averaging 78.1 ± 9.6 and $60.1 \pm 19.3 \text{ pg L}^{-1}$, respectively. The highest concentrations of methylated Hg species and % MMHg were measured at Peel Sound (site 9) (concentrations of MMHg and DMHg were 178 and 161 pg L^{-1} , respectively, at mid-depth and 158 and 170 pg L^{-1} , respectively, at the bottom). Interestingly, Pacific-origin water, which is generally far richer in nutrients than WGC water of Atlantic origin (24), comprised the water column at site 9 suggesting that this site may be a methylation “hot spot”. Alternatively, high concentrations of MMHg and DMHg at Peel Sound may represent a slow build up of these species. In fact, bottom waters are regenerated slowly in Peel Sound because sill depths to the north and south are $<160 \text{ m}$ (28). During the brief ice-free season, a portion of the accumulated MMHg and DMHg was likely transported to the surface by vertical mixing as described above. At shallow sites in Queen Maude Gulf (10, 11), where the water column was composed of fresh (salinity <29.3) Pacific-origin surface water, concentrations of MMHg and DMHg both increased with depth (37.7 ± 8.8 and $38.8 \pm 20.9 \text{ pg L}^{-1}$, respectively, at mid-depths and 47.4 ± 1.5 and $51.7 \pm 21.6 \text{ pg L}^{-1}$, respectively, at the bottom), suggesting that methylated Hg species were produced at these sites. However at sites 10 and 11, concentrations of methylated Hg species were \sim half those measured at deeper sites of the CAA (Figure S3a and b and Table S1), suggesting that methylation rates are lower in fresh, oxygen-rich waters or that faster water regeneration times of shallow water prevent long-term buildup of methylated Hg species there.

In Hudson Strait (sites 12–14) concentrations of MMHg and DMHg were slightly lower than at most sites of the CAA (39.9 ± 14.6 and $22.5 \pm 18.8 \text{ pg L}^{-1}$, respectively, at mid-depths, and 62.5 ± 33.4 and $39.0 \pm 12.9 \text{ pg L}^{-1}$, respectively, at the bottom), again likely due to the fast regeneration of deep waters there (31). In addition, concentrations of methylated Hg species did not always increase with depth (Figure 2c and d), likely due to the intense vertical mixing in Hudson Strait. In Hudson Bay, we sampled shallow, coastal sites (sites 18–20, 22, and 24, depths $<100 \text{ m}$) and deeper, open water sites (sites 15–17, 21, and 23, depths ~ 100 – 200 m). At sites 18–20, located in southwestern Hudson Bay, concentrations of MMHg and DMHg were comparable to those measured in shallow sites of the CAA (33.5 ± 12.3 and $36.5 \pm 4.1 \text{ pg L}^{-1}$, respectively, at mid-depths, and 50.6 ± 16.6 and $61.3 \pm 18.9 \text{ pg L}^{-1}$, respectively, at the bottom). However, at sites 22 and 24, located at the mouths of the Nelson and Churchill Rivers, respectively, concentrations of MMHg and DMHg in subsurface samples were low and did not increase with depth (26.1 ± 2.2 and $2.3 \pm 1.2 \text{ pg L}^{-1}$ at the bottom, respectively). These results suggest that methylated Hg species are not produced at sites 22 and 24, possibly

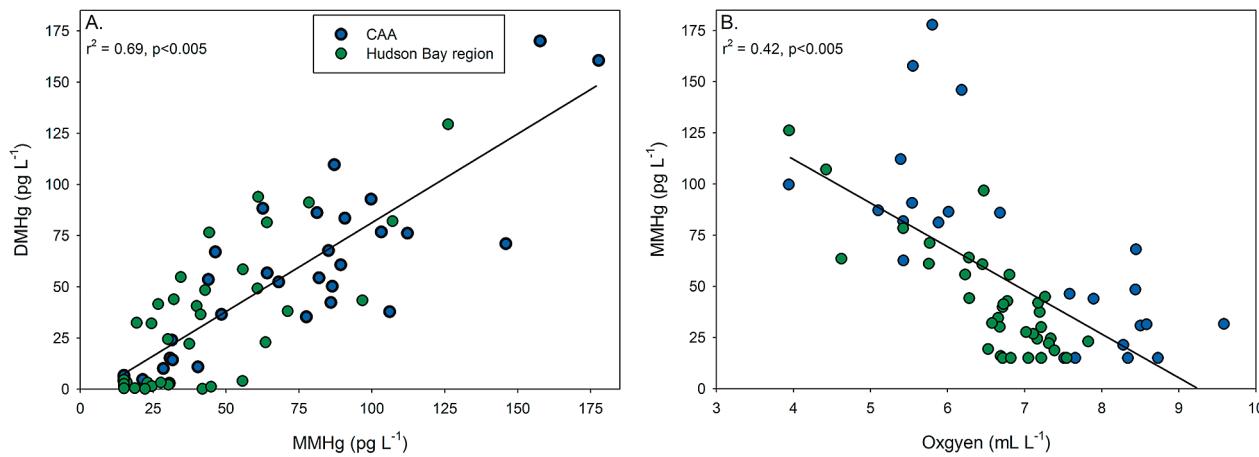


FIGURE 3. Relationship between MMHg and DMHg (pg L^{-1}) (a) and MMHg and oxygen (mL L^{-1}) (b) throughout the water column at sites in the CAA and Hudson Bay region.

because the water columns there were composed of fresh river input mixing with Hudson Bay seawater (e.g., Figure S1g and h). MMHg concentrations at sites 22 and 24 may therefore reflect dilution of Nelson and Churchill River discharge, which generally contains high concentrations of MMHg (in fall 2005 concentrations of MMHg at the mouths of the Nelson and Churchill Rivers were 168 ± 89.0 and $98.6 \pm 26.9 \text{ pg L}^{-1}$, respectively (Kirk unpublished data)) with Hudson Bay seawater of lower concentration. Not surprisingly, at deeper, open water sites (15–17, 21, and 23), concentrations of MMHg and DMHg at mid- and bottom depths, generally composed of HBWSW and slow moving HBIW, were higher than in other parts of Hudson Bay (45.2 ± 22.1 and $53.6 \pm 34.6 \text{ pg L}^{-1}$, respectively at mid-depths, and 83.6 ± 33.4 and $74.8 \pm 40.9 \text{ pg L}^{-1}$, respectively, at the bottom). In addition, concentrations of MMHg and DMHg were much higher in deep, Hudson Bay waters than in the in-flowing waters of Hudson Strait (sites 12 and 13), demonstrating that methylation occurs in Hudson Bay.

Due to the ubiquitous presence and overall similarity in concentrations of MMHg and DMHg in deep regions of the water column throughout the CAA and Hudson Bay region, we hypothesize that *net* methylation rates vary little among regions and that oceanographic processes, such as regeneration time and vertical mixing, are important controls on the distribution of methylated Hg species throughout the water column. Furthermore, it is unlikely that the concentrations of MMHg and DMHg observed throughout the water column can be explained by production of these species predominantly in the sediments, as is seen in contaminated coastal marine sediments (14, 15) and estuaries (12, 13). If production of MMHg and DMHg occurs solely in sediments, transport of these two species would have to be fast to supply mid-depths of the water column, often $>200 \text{ m}$ away, with the concentrations observed here. For example, at site 7 concentrations of MMHg and DMHg at 200 m were 62.6 and 88.3 pg L^{-1} , respectively, and were only slightly greater 400 m below at the bottom (99.7 and 92.8 pg L^{-1} , respectively). Furthermore, we observed a strong, significant relationship between concentrations of DMHg and MMHg throughout the water column at all sites (Figure 3a, $r^2 = 0.69, p < 0.005$) indicating that these two species are produced by similar mechanisms and/or that one species is produced from the other. If methylated Hg species are produced solely in marine sediments, transport of these two species from sediments would also have to occur at nearly identical rates to preserve the constant ratio of MMHg/DMHg observed throughout the water column. It seems more likely that transport of methylated Hg species is slow (unless there is vertical mixing) and that concentrations at each site and depth are dictated

by production and decomposition processes which are in equilibrium. In fact, others have hypothesized that DMHg can decompose to MMHg in deep regions of the water column (19, 21). We therefore hypothesize that a large portion of methylated Hg species in Arctic marine waters is produced directly in the water column, as has been suggested previously for the Arctic and Antarctic Oceans (18), the north Atlantic (21), and the Mediterranean Sea (16). Unfortunately, with measurement at only three depths per site, it cannot be assessed if Hg methylation occurs throughout the entire water column as low concentrations of MMHg observed at the surface may reflect rapid loss via photochemically and/or biologically induced demethylation, as demonstrated in the Mediterranean (16). Similarly, DMHg produced in surface waters may be lost to the atmosphere via gas exchange. Production of both MMHg and DMHg by pure cultures of marine bacteria collected from Antarctic surface waters (42) and macroalgae from an Arctic fjord (43) has also been demonstrated. However, the strong relationship we observed between concentrations of MMHg and dissolved oxygen throughout the water column (Figure 3b, $r^2 = 0.42, p < 0.005$) suggests that Hg methylation rates are higher in deep, low-oxygen regions of the water column. Alternatively, low oxygen concentrations may reflect water mass age and therefore the build up of MMHg over time. Regardless of the mechanism by which methylated Hg species are produced in Arctic seawater, the concentrations of MMHg reported here are sufficient to initiate biomagnification of MMHg through Arctic marine foodwebs (23).

Instantaneous Diffusive Fluxes of GEM and DMHg from Water to the Atmosphere. Marine waters of the CAA and Hudson Bay region were always a source of GEM and DMHg to the atmosphere (ranges $2.6\text{--}388$ and $0.2\text{--}176 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively; averages 130 ± 138 and $27.3 \pm 47.8 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively) (Table S2). Because concentrations of GEM in surface waters were similar at all sites (Figure 2a), flux magnitude was primarily driven by wind velocity (Figure S4a). In contrast, surface concentrations of DMHg varied among regions, resulting in fluxes of DMHg that were greater in the CAA ($39.7 \pm 54.6 \text{ ng m}^{-2} \text{ day}^{-1}$) compared to the Hudson Bay region ($16.9 \pm 35.7 \text{ ng m}^{-2} \text{ day}^{-1}$), although due to the large variation the difference was not statistically significant (Figure S4b). Even at deep, open water sites of Hudson Bay (15–17, 21, and 23), where concentrations of DMHg at depth were comparable to those measured in the CAA, low concentrations of DMHg at the surface ($<3.4 \text{ pg L}^{-1}$) resulted in low ocean-atmosphere fluxes. The only flux over $20.5 \text{ ng m}^{-2} \text{ day}^{-1}$ in the Hudson Bay region was measured at the eastern end of Hudson Strait (site 12) where vertical mixing likely

transported DMHg to the surface from production zones as described above. Interestingly, average ocean–atmosphere GEM fluxes reported here are higher than those calculated previously for north Atlantic ($94.7 \text{ ng m}^{-2} \text{ day}^{-1}$) (44), Mediterranean ($2.8 \text{ ng m}^{-2} \text{ day}^{-1}$) (20), and Baltic waters ($50 \text{ ng m}^{-2} \text{ day}^{-1}$) (36)). Our average ocean–atmosphere DMHg fluxes are also higher than previous estimates for the Arctic ($4.7 \text{ ng m}^{-2} \text{ day}^{-1}$), Antarctic ($2.8 \text{ ng m}^{-2} \text{ day}^{-1}$), and Atlantic Ocean ($4.9 \text{ ng m}^{-2} \text{ day}^{-1}$) (18). Finally, ocean–atmosphere fluxes of both GEM and DMHg reported here are likely lower than fluxes directly after ice-out when substantial degassing of gaseous Hg species trapped under the sea ice throughout winter (23) may occur. In fact, concentrations of DMHg ($11.1 \pm 4.1 \text{ pg L}^{-1}$) and GEM ($129 \pm 36 \text{ pg L}^{-1}$) measured under the sea ice near Resolute, Nunavut, Canada are higher than those reported here for ice-free surface waters of the CAA and Hudson Bay region.

Acknowledgments

We acknowledge the following for providing funding: ArcticNet, Manitoba Hydro, NSERC Collaborative Research and Development program, and the Canadian Circumpolar Institute Circumpolar/Boreal Alberta Research (C/BAR) and Northern Scientific Training (NSTP) grant programs. We would also like to thank Yves Gratton and Marie Emmanuelle Rail for providing CTD data, Johannie Martin and Jean-Eric Tremblay for providing chlorophyll a data, Tim Papakyriakou for providing wind velocity and air temperature, Sara Berkel, Micheal Gaulois, and Khaled Al-Badani for laboratory help, and Charlene Nielson for making Figure 1.

Note Added after ASAP Publication

There was an error in the last sentence of the abstract in the version published ASAP October 22, 2008; the corrected version published ASAP November 13, 2008.

Supporting Information Available

Analytical details, three figures, and two tables. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Arctic Monitoring and Assessment Programme (AMAP). *AMAP Assessment 2002 (Heavy metals in the Arctic)*; AMAP: Oslo, 2005.
- (2) Campbell, L. M.; Norstrom, R. J.; Hobson, K. A.; Muir, D. C. G.; Backus, S.; Fisk, A. T. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Sci. Total Environ.* **2005**, *351–352*, 247–263.
- (3) Outridge, P. M.; Hobson, K. A.; Savelle, J. M. Changes in mercury and cadmium concentrations and the feeding behavior of beluga (*Delphinapterus leucas*) near Somerset Island, Canada, during the 20th century. *Sci. Total Environ.* **2005**, *350*, 106–118.
- (4) Schroeder, W. H.; Munthe, J. Atmospheric mercury - an overview. *Atmos. Environ.* **1998**, *32*, 809–822.
- (5) Pacyna, E. G.; Pacyna, J. M.; Fudala, J.; Strzelecka-Jastrzab, E.; Hlawiczka, S.; Panasiuk, D. Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. *Sci. Total Environ.* **2006**, *370*, 147–156.
- (6) Mason, R. P.; Sheu, G. -R. Role of the ocean in the global mercury cycle. *Global Biogeochem. Cycl.* **2002**, *16*, 109b., 10.1029/2001GB001440.
- (7) Shia, R. -L.; Seigneur, C.; Pai, P.; Ko, M.; Sze, N. -D. Global simulation of atmospheric mercury concentrations and depositional fluxes. *J. Geophys. Res.* **1999**, *104*, 747–760.
- (8) Steffen, A.; Douglas, T.; Amyot, M.; Ariya, P.; Aspmo, K.; Berg, T.; Bottenheim, J.; Brooks, S.; Cobbett, F.; Dastoor, A.; Dommergue, A.; Ebinghaus, R.; Ferrari, C.; Gardfelt, K.; Goodsite, M. E.; Lean, D.; Poulain, A. J.; Sherz, C.; Skov, H.; Sommar, J.; Temme, C. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.* **2008**, *8*, 1445–1482.
- (9) Lindberg, S. E.; Brooks, S.; Lin, C. J.; Scott, K. J.; Landis, M. S.; Stevens, R. K.; Goodsite, M.; Richter, A. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **2002**, *36*, 1245–1256.
- (10) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. A.; Lu, J. Y.; Steffen, A.; Schneeberger, D. R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394*, 331–332.
- (11) Kirk, J. L.; St. Louis, V. L.; Sharp, M. J. Rapid reduction and reemission of mercury deposited into snowpacks during Atmospheric Mercury Depletion Events at Churchill, Manitoba, Canada. *Environ. Sci. Technol.* **2006**, *40*, 7590–7596.
- (12) Gilmour, C. C.; Riedel, G. S. Measurement of Hg methylation in sediments using high specific-activity ^{203}Hg and ambient incubation. *Water, Air, Soil Pollut.* **1995**, *80*, 747–756.
- (13) Compeau, G. C.; Bartha, R. Sulphate-reducing bacterial principle methylators of mercury in anoxic estuarine sediments. *Appl. Environ. Microbiol.* **1985**, *50*, 498–502.
- (14) Sunderland, E. M.; Gobas, F. A. P. C.; Branfireun, B. A.; Heyes, A. Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.* **2006**, *102*, 111–123.
- (15) Hammerschmidt, C. R.; Fitzgerald, W. F.; Lamborg, C. H.; Balcom, P. H.; Visscher, P. T. Biogeochemistry of methylmercury in sediments of Long Island Sound. *Mar. Chem.* **2004**, *90*, 31–52.
- (16) Monperrus, M.; Tessier, E.; Amouroux, D.; Leynaert, A.; Huonnic, P.; Donard, O. F. X. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. *Mar. Chem.* **2007**, *107*, 49–63.
- (17) Mason, R. P.; Rolfhus, K. R.; Fitzgerald, W. F. Mercury in the North Atlantic. *Mar. Chem.* **1998**, *61*, 37–53.
- (18) Pongratz, R.; Heumann, K. G. Determination of concentration profiles of methyl mercury compounds in surface waters of polar and other remote oceans by GC-AFD. *Int. J. Environ. Anal. Chem.* **1998**, *71*, 41–56.
- (19) Mason, R. P.; Fitzgerald, W. F. The distribution and biogeochemical cycling of mercury in the equatorial Pacific. *Deep-Sea Res.* **1993**, *40*, 1897–1924.
- (20) Cossa, D.; Martin, J. -M.; Kazufumi, T.; Sanjuan, J. The distribution and cycling of mercury species in the western Mediterranean. *Deep-Sea Res. II* **1997**, *44*, 721–740.
- (21) Mason, R. P.; Rolfhus, K. R.; Fitzgerald, W. F. Methylated and elemental mercury cycling in surface and deep ocean waters of the North Atlantic. *Water, Air, Soil Pollut.* **1995**, *80*, 665–677.
- (22) Falkowski, P. G. Molecular ecology of phytoplankton photosynthesis. In *Primary Productivity and Biogeochemical Cycles in the Sea*; Falkowski, P. G., Woodhead, A. D., Eds.; Plenum Press: New York, 1992.
- (23) St Louis, V. L.; Hintelmann, H.; Graydon, J. A.; Kirk, J. L.; Barker, J.; Dimock, B.; Sharp, M. J.; Lehnher, I. Methylated mercury species in Canadian high Arctic marine surface waters and snowpacks. *Environ. Sci. Technol.* **2007**, *41*, 6433–6441.
- (24) Michel, C.; Ingram, R. G.; Harris, L. R. Variability in oceanographic and ecological processes in the Canadian Arctic Archipelago. *Prog. Oceanogr.* **2006**, *71*, 379–401.
- (25) Melling, H.; Lake, R. A.; Topham, D. R.; Fissel, D. B. Oceanic thermal structure in the western Canadian Arctic. *Cont. Shelf Res.* **1984**, *3*, 233–258.
- (26) Melling, H.; Gratton, Y.; Ingram, G. Ocean circulation within the North Water Polynya of Baffin Bay. *Atmos. Ocean* **2001**, *39*, 301–325.
- (27) Prinsenberg, S. J.; Bennett, E. B. Mixing and transports in Barrow Strait, the central part of the Northwest Passage. *Cont. Shelf Res.* **1987**, *7*, 913–935.
- (28) Prinsenberg, S. J.; Bennett, E. B. Transport between Peel Sound and Barrow Strait in the Canadian Arctic. *Cont. Shelf Res.* **1989**, *9*, 427–444.
- (29) Jones, P. E.; Anderson, L. G. Northern Hudson Bay and Foxe Basin: Water masses, circulation and productivity. *Atmos. Ocean* **1994**, *32*, 361–374.
- (30) Prinsenberg, S. J. Salinity and temperature distributions of Hudson Bay and James Bay. In *Canadian Inland Seas*; Martini, I. P., Ed.; Elsevier: New York, 1986.
- (31) Drinkwater, K. F. Physical oceanography of Hudson Strait and Ungava Bay. In *Canadian Inland Seas*; Martini, I. P., Ed; Elsevier: New York, 1986.
- (32) Laurier, F. J. G.; Mason, R. P.; Gill, G. A.; Whalin, L. Mercury distributions in the North Pacific Ocean - 20 years of observations. *Mar. Chem.* **2004**, *90*, 3–19.
- (33) Whalin, L.; Kim, E. -H.; Mason, R. Factors influencing the oxidation, reduction, methylation, and demethylation of mercury species in coastal waters. *Mar. Chem.* **2007**, *107*, 278–294.

- (34) Poulain, A. J.; Chadhain, S. M. N.; Ariaya, P.; Amyot, M.; Garcia, E.; Campbell, P. G. C.; Zylstra, G. J.; Barkay, T. Potential for mercury reduction by microbes in the high Arctic. *Appl. Environ. Microbiol.* **2007**, *73*, 2230–2238.
- (35) Mason, R. P.; Morel, F. M. M.; Hemond, H. F. The role of microorganisms in elemental mercury formation in natural waters. *Water, Air, Soil Pollut.* **1995**, *80*, 775–787.
- (36) Kuss, J.; Schneider, B. Variability of the gaseous elemental mercury sea-air flux of the Baltic Sea. *Environ. Sci. Technol.* **2007**, *41*, 8018–8023.
- (37) Chen, J.; Pehkonen, S. O.; Lin, C. -J. Degredation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. *Water Res.* **2003**, *37*, 2496–2504.
- (38) Niki, H.; Maker, P. S.; Savage, C. M.; Breitenbach, L. P. A fourier transform infrared study of the kinetics and mechanism for the reaction of Cl + CH₃HgCH₃. *J. Phys. Chem.* **1983**, *87*, 3722–3724.
- (39) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. A long-path Fourier transform infrared study of the kinetics and mechanism for the HO-radical initiated oxidation of dimethylmercury. *J. Phys. Chem.* **1983**, *87*, 4978–4981.
- (40) Rudd, J. W. M. Sources of methylmercury in freshwater ecosystems: a review. *Water, Air, Soil Pollut.* **1995**, *80*, 697–713.
- (41) Bodaly, R. A.; Jansen, W. A.; Majewski, A. R.; Fudge, R. J. P.; Strange, N. E.; Derksen, A. J.; Green, D. J. Postimpoundment time course of increased mercury concentrations in fish in hydroelectric reservoirs of northeastern Manitoba, Canada. *Arch. Environ. Contam. Toxicol.* **2007**, *53*, 379–389.
- (42) Pongratz, R.; Heumann, G. Production of methylated mercury, lead, and cadmium by marine bacteria as a significant natural source for atmospheric heavy metals in polar regions. *Chemosphere* **1999**, *39*, 89–102.
- (43) Pongratz, R.; Heumann, K. G. Production of methylated mercury and lead by polar macroalgae - a significant natural source for atmospheric heavy metals in clean room compartments. *Chemosphere* **1998**, *36*, 1935–1946.
- (44) Mason, R. P.; Lawson, N. M.; Sheu, G. -R. Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters. *Deep-Sea Res. II* **2001**, *48*, 2829–2823.

ES801635M