

# Methylated Mercury Species in Canadian High Arctic Marine Surface Waters and Snowpacks

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We sampled seawater and snowpacks in the Canadian high Arctic for methylated species of mercury (Hg). We discovered that, although seawater sampled under the sea ice had very low concentrations of total Hg (THg, all forms of Hg in a sample; on average 0.14–0.24 ng L<sup>-1</sup>), 30–45% of the THg was in the monomethyl Hg (MMHg) form (on average 0.057–0.095 ng L<sup>-1</sup>), making seawater itself a direct source of MMHg for biomagnification through marine food webs. Seawater under the ice also contained high concentrations of gaseous elemental Hg (GEM; 129 ± 36 pg L<sup>-1</sup>), suggesting that open water regions such as polynyas and ice leads were a net source of ~130 ± 30 ng Hg m<sup>-2</sup> day<sup>-1</sup> to the atmosphere. We also found 11.1 ± 4.1 pg L<sup>-1</sup> of dimethyl Hg (DMHg) in seawater and calculated that there could be a significant flux of DMHg to the atmosphere from open water regions. This flux could then result in MMHg deposition into nearby snowpacks via oxidation of DMHg to MMHg in the atmosphere. In fact, we found high concentrations of MMHg in a few snowpacks near regions of open water. Interestingly, we discovered a significant log–log relationship between Cl<sup>-</sup> concentrations in snowpacks and concentrations of THg. We hypothesize that as Cl<sup>-</sup> concentrations in snowpacks increase, inorganic Hg(II) occurs principally as less reducible chloro complexes and, hence, remains in an oxidized state. As a result, snowpacks that receive both marine aerosol deposition of Cl<sup>-</sup> and deposition of Hg(II) via springtime atmospheric Hg depletion events, for example, may contain significant loads of Hg(II). Overall, though, the median wet/dry loads of Hg in the snowpacks we sampled in the high Arctic (5.2 mg THg ha<sup>-1</sup> and 0.03 mg MMHg ha<sup>-1</sup>) were far below wet-only annual THg loadings throughout southern Canada and most of the U.S. (22–200 mg ha<sup>-1</sup>). Therefore, most Arctic snowpacks contribute

relatively little to marine pools of both Hg(II) and MMHg at snowmelt.

## Introduction

Organisms at the top of Arctic marine food webs often contain elevated concentrations of monomethyl mercury (MMHg), a toxic and bioaccumulative form of Hg (1). In fact, some marine mammals and fishes contain concentrations of this neurotoxin high enough to cause exposure risks to northern peoples consuming them as traditional country foods (1, 2). It has been speculated that springtime atmospheric Hg depletion events (AMDEs), first discovered in the mid 1990s (3), are the ultimate source of this contamination. AMDEs result from sunlight-induced catalytic reactions of gaseous elemental Hg(0) (GEM) with the marine halogens Br and Cl to form oxidized Hg species, often operationally defined as reactive gaseous Hg and particulate Hg (4, 5). Both of these oxidized forms of Hg have dry-deposition velocities greater than GEM and thus fall out into snowpacks. In fact, AMDEs have been implicated as the source of elevated concentrations of Hg(II) (sometimes exceeding 100 ng L<sup>-1</sup>) found in snowpack surfaces in the Arctic, and models have estimated a potential gross loading of up to 325 tons of Hg(II) to the Arctic ecoregion each year (6). However, Kirk et al. (7) recently showed that the majority of the Hg(II) deposited to snowpacks during individual AMDEs at Churchill, Manitoba, Canada, was rapidly photoreduced to GEM and lost back to the atmosphere, whereas other studies have demonstrated that there is little Hg(II) in meltwater on sea ice following the total cessation of AMDEs each spring (4, 8, 9). Even if some portion of the Hg(II) deposited during AMDEs entered the marine ecosystem at ice out, a crucial question remains to be answered: Where does the MMHg that accumulates through Arctic food webs originate?

Interestingly, some studies recently found high concentrations of MMHg in Arctic snowpacks (for example, refs 10–12), and in some cases, a significant proportion of the total Hg pool was in the methylated form (11). St. Louis et al. (11) found a positive relationship between concentrations of MMHg and Cl<sup>-</sup> in snowpacks on the Prince of Wales icefield on the east coast of Ellesmere Island, Nunavut, Canada, suggesting a marine source of MMHg because Cl<sup>-</sup> in those snowpacks likely originated from sea salt aerosols. They hypothesized that MMHg found in snowpacks on the icefield originated from gaseous dimethyl Hg (DMHg) that had fluxed through open water regions in the sea, in particular, the large North Open Water (NOW) polynya located between Ellesmere Island and Greenland (Figure 1). Once in the atmosphere, radical species such as OH and Cl can initiate the oxidation of DMHg to MMHg (13–15). It is estimated that the tropospheric lifetime of DMHg is on the order of 1 day (15), making the ocean a potential source of MMHg to nearby snowpacks or the open water itself.

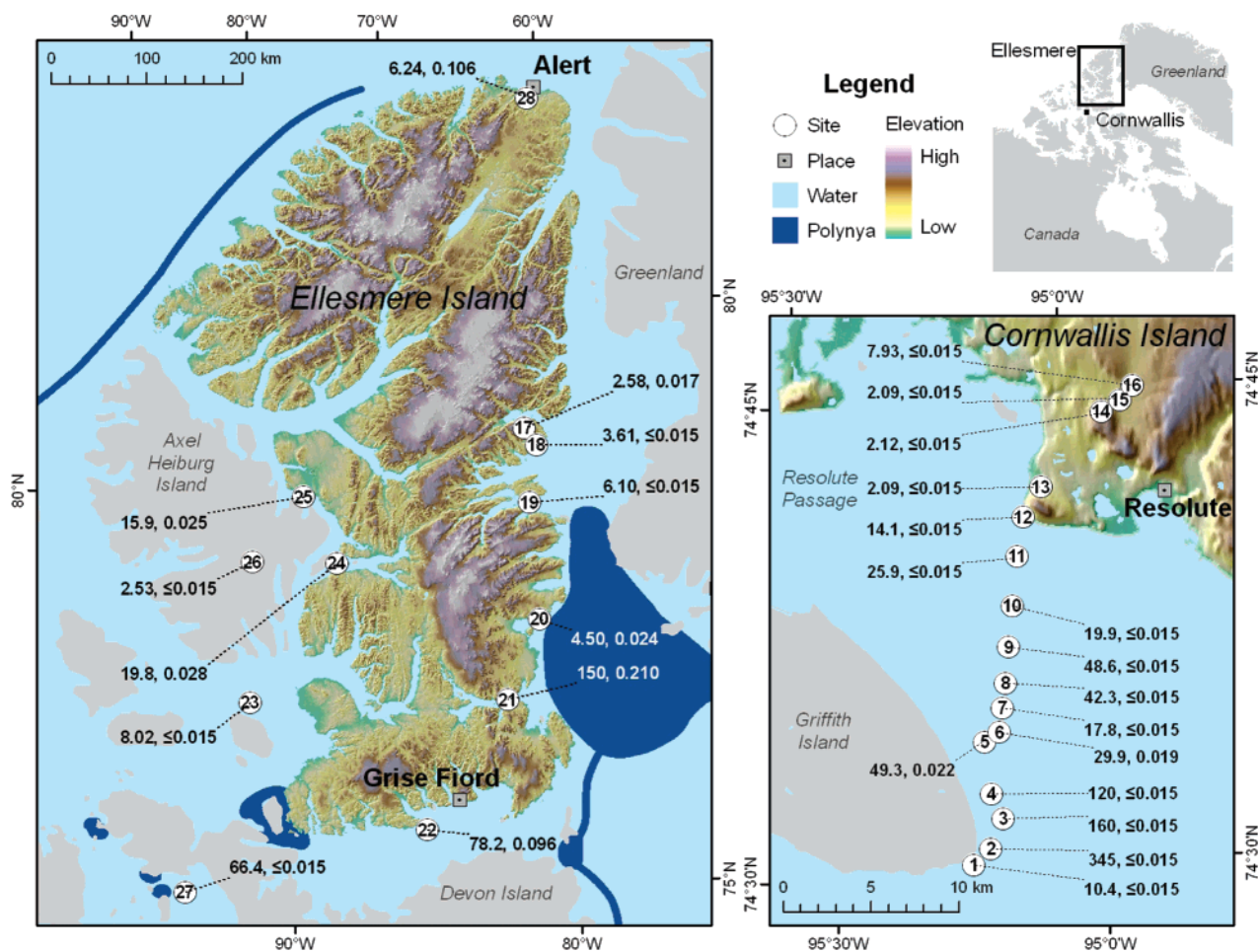
Methylated Hg species including DMHg have been found in subthermocline North Atlantic waters (16). In regions of deep-water upwelling or winter thermocline mixing, DMHg can be brought to the surface and subsequently lost to the atmosphere by gas exchange. To begin determining where the MMHg that accumulates through Arctic food webs originates, we sampled seawater under sea ice in the Canadian high Arctic for concentrations of DMHg and MMHg, as well as dissolved GEM and total Hg (THg, all forms of Hg in a sample). We also sampled snowpacks in the high Arctic to determine net loads of MMHg and THg in snowpacks in relation to their proximity to open water regions.

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**FIGURE 1.** Snow sampling sites in the Canadian high Arctic. Lower right map: Concentrations ( $\text{ng L}^{-1}$ ) of THg and MMHg (first and second number, respectively) in surface snow collected at 16 sites moving away from an open water lead at the tip of Griffith Island (site 1) to sites inland on Cornwallis Island  $\sim 20$  km away (sites 13–16). Map on left: THg and MMHg concentrations in surface snow collected over the sea ice at numerous sites around Ellesmere Island, as well as inland at Alert (site 28), John Evans Glacier (site 17), and on Axel Heiberg Island (Site 26).

## Methods

**Sampling Sites in General.** Sampling was based out of the Polar Continental Shelf Project (PCSP, Natural Resources Canada) station in Resolute Bay, Nunavut, in the Canadian high Arctic. From there, we accessed sampling sites both near and far from polynyas and open water leads in the sea ice near Cornwallis and Ellesmere Islands (Figure 1; also see Figure 1 in Supporting Information section). On 9 May 2004, on a relative microscale, using snowmobiles, we collected snow every 1.5–2 km along a transect from an open water lead at the SE tip of Griffith Island across the sea ice to  $\sim 5$  km inland on Cornwallis Island. Seawater was also collected along this transect in 2004, whereas between 8 and 9 May 2005, in addition to this site, seawater was collected from both Jones Sound and Wellington Channel accessed by Twin Otter aircraft. On a macroscale, we circumnavigated Ellesmere Island by Twin Otter between 10 and 16 May 2004, landing at numerous sites primarily on the sea ice to collect snow samples (Figure 1). In particular, we were interested in sampling in close proximity to the NOW polynya because it is the largest region of perennial open water in the Canadian high Arctic, and previous sampling efforts on the Prince of Wales icefield suggested that it was the ultimate source of the MMHg found in snowpacks there (11). Snow samples were also collected on different occasions between 31 May and 10 June 2004 at the Global Atmospheric Watch Laboratory

in Alert (Figure 1). This laboratory is located 6 km south of the northern Ellesmere Island coastline at 205 m above sea level.

**Concentrations of THg, MMHg, DMHg, and GEM in Seawater Under the Sea Ice.** In 2004, seawater was collected at  $\sim 3$  m depth along the edge of the open lead at the SE tip of Griffith Island (Figure 1, site 1) and through a seal breathing hole in Resolute Passage (Figure 1,  $\sim$  site 10) using an acid-washed 2.5 L Teflon-lined General Oceanics Go-Flo bottle. At each site, the Go-Flo bottle was deployed 2–3 times to collect independent sets of unfiltered water samples into acid-washed 125 mL and 250 mL Teflon bottles for analyses of THg and MMHg, respectively. The Go-Flo bottle was then deployed another nine times to collect seawater samples for total dissolved gaseous Hg (DGM) analyses (4 samples) and DMHg analyses (5 samples). Seawater was decanted slowly from the Go-Flo bottle into 2.2 L glass bottles and sealed with no headspace. Samples were transported back to the PCSP laboratory inside coolers.

At the PCSP laboratory, THg samples were preserved with concentrated trace metal grade HCl equal to 0.2% of sample volume, whereas MMHg samples were preserved with concentrated trace metal grade  $\text{H}_2\text{SO}_4$  equal to 0.4% of sample volume. At the University of Alberta Low-level Hg Analytical Laboratory, concentrations of THg and MMHg in seawater were determined using standard analytical protocols detailed in the Supporting Information section.

**TABLE 1. Average ( $\pm$ SD) (sample Size in Parenthesis) Concentrations of THg and MMHg in Seawater and Average Percent of the THg That Was in the MMHg Form**

site	May 2004			May 2005		
	THg (ng L <sup>-1</sup> )	MMHg (ng L <sup>-1</sup> )	%MMHg	THg (ng L <sup>-1</sup> )	MMHg (ng L <sup>-1</sup> )	%MMHg
Resolute Passage	0.21 $\pm$ 0.01 (6)	0.095 $\pm$ 0.014 (6)	45.2	0.14 $\pm$ 0.03 (2)	0.057 $\pm$ 0.011 (3)	40.7
Wellington Channel				0.24 $\pm$ 0.16 (2)	0.091 (1)	37.9
Jones Sound				0.24 $\pm$ 0.00 (2)	0.073 $\pm$ 0.044 (2)	30.4

Also at the PCSP laboratory, gaseous Hg species were stripped from seawater by purge and trap techniques within 2 h of collection as described in the Supporting Information section. Gold traps were used to collect DGM (consisting of both GEM and DMHg), and carbotraps were used for collection of DMHg only (16). Prior to departure to the field, gold traps and carbotraps were cleaned in the Low-level Hg Analytical Laboratory by thermal desorption, sealed using Teflon plugs and Teflon tape, individually bagged, and stored under positive pressure in acid-washed mason jars using ultrahigh purity nitrogen. In the field, following sample collection, traps were again plugged, taped, individually bagged, and placed back in the jars for transport back south.

Gold traps were processed at the Low-level Hg Analytical Laboratory, whereas carbotraps were processed at the Trent University Worsfold Water Quality Centre, as described in the Supporting Information section. Concentrations of DGM and DMHg in the seawater were calculated by division of the total quantity of Hg (ng) on the traps by the volume of water purged (2 L). Dissolved GEM concentrations were calculated by subtraction of the DMHg concentrations from DGM concentrations.

In 2005, we returned to the high Arctic to determine interannual and spatial variation in concentrations of THg and MMHg in seawater. Samples were again collected under the sea ice in Resolute Passage, as well as in Jones Sound and Wellington Channel (near sites 22 and 27, respectively; Figure 1). At all three sites, we power-augured holes through the sea ice, through which the samples were collected as described above for 2004.

**Concentrations of THg and MMHg in Snowpacks.** To determine whether open water regions in the sea ice are potential sources of MMHg to snowpacks, we sampled snow both near and far from polynyas and open water leads in the sea ice near Cornwallis and Ellesmere Islands (Figure 1). Springtime snowpacks in polar regions typically contain a visually distinct coarse granular depth hoar layer deposited in the previous fall and subjected to temperature-gradient metamorphism during winter when further deposition is low (17, 18). Above the depth hoar layer, snowpacks consists of a mixture of snow reworked by wind during winter and snow deposited throughout the spring, including very recent snowfall (17, 18).

At each sampling site, pits were dug down to the bottom of level snowpacks, avoiding drifts. Once the face of the pit was cleaned using acid-washed Teflon scrapers, snow from the depth hoar and spring layers in snowpacks, and fresh surface snow, was collected by pushing acid washed 2 L Teflon jars into the face of the pit. All snow sampling was conducted by two people using the "clean hands, dirty hands" protocol to avoid contamination (19). Snow samples were stored frozen until melted in the dark in the Low-level Hg Analytical Laboratory and analyzed for concentrations of THg and MMHg using standard protocols detailed in the Supporting Information section.

Co-incident with each snow sample collected for Hg analyses, we also collected a snow sample for anion analyses, especially Cl<sup>-</sup>. Snow was collected in Ziploc bags and stored frozen in the dark until analysis in the Glacier Hydrochemistry Laboratory in the Department of Earth and Atmospheric

Sciences, University of Alberta, as described in the Supporting Information section.

**Areal Loads of THg and MMHg in Snowpacks.** At each sampling site, the average areal water volume of the entire snowpack (L m<sup>-2</sup>) was determined from the weight of two snow cores (1 g = 1 mL) collected using a 5.1 cm diameter (20.4 cm<sup>2</sup> area) core tube.

We then used the proportion of the snowpack depth (measured in the field) that was either depth hoar or snow accumulated above the depth hoar, to estimate the proportion of water that was in each of these two layers. Because the proportional depth of the depth hoar layer was similar among all sites (35  $\pm$  14%), any error associated with our load estimates is likely similar among sites.

Net areal load of THg and MMHg in snowpacks at the time of sampling was estimated by multiplying concentrations of THg and MMHg in different layers of snowpacks by the areal water volume of the snow. Depth hoar THg and MMHg concentrations were multiplied by the estimated water volume of the hoar layer. THg and MMHg concentrations measured in the surface and spring layers of the snowpack were averaged prior to multiplication by estimated water volume of the upper layers.

## Results and Discussion

**Concentrations of THg, MMHg, DMHg and GEM in Seawater Under the Sea Ice.** Seawater samples collected from under the sea ice generally had very low concentrations of THg but, on average, relatively high concentrations of MMHg. Average seawater concentrations of MMHg and THg in Resolute Passage in the Arctic were slightly higher in 2004 (0.095  $\pm$  0.014 and 0.21  $\pm$  0.01 ng L<sup>-1</sup>, respectively) than in 2005 (0.057  $\pm$  0.011 and 0.14  $\pm$  0.03 ng L<sup>-1</sup>, respectively) (Table 1). In 2005, average concentrations of MMHg in seawater from Jones Sound and Wellington Channel (0.091 and 0.073  $\pm$  0.044 ng L<sup>-1</sup>, respectively) were slightly higher than at Resolute Passage that year, as were concentrations of THg at these two sites (0.24 ng L<sup>-1</sup>, Table 1). The concentrations of THg in our samples were within the range of those measured previously in the North Atlantic (0.48  $\pm$  0.32 ng L<sup>-1</sup>), whereas MMHg concentrations were not comparable because their detection limit of 0.10 ng L<sup>-1</sup> was higher than our measured concentrations (16). However, the MMHg concentrations we measured in seawater were at times almost double average concentrations (0.043  $\pm$  0.030 ng L<sup>-1</sup>) measured in surface waters of pristine freshwater lakes scattered across northern Ellesmere Island, even though THg concentrations in seawater were four times lower than in the lakes (1.11  $\pm$  0.48 ng L<sup>-1</sup>) (11).

Surprisingly, on average, 30–45% of the THg was in the MMHg form at all our sites (Table 1). In aquatic ecosystems, both a high percentage of the THg methylated (%MMHg), as well as relatively high concentrations of MMHg, often indicate elevated rates of net methylation (20–22). For example, at the Experimental Lakes Area (ELA, northwestern Ontario), %MMHg was only ~1% in open precipitation entering catchments, but it was 3–15% in runoff from catchments containing wetlands, which are known natural sites of microbial MMHg production (19). Some of the highest



%MMHg ever recorded (averaging 30%, but reaching 70%) have been found in anoxic bottom waters of stratified lakes or in hydroelectric reservoirs where decomposition of flooded organic matter fuels high rates of microbial Hg(II) methylation (23, 24).

The origin of the observed MMHg in polar oceans is still uncertain. Two potential sources are (1) external inputs of MMHg (from the atmosphere and large rivers) and (2) in situ production of MMHg through methylation of Hg(II).

We estimate that external MMHg inputs alone could not maintain the lowest concentrations of MMHg we measured under sea ice ( $0.057 \text{ ng L}^{-1}$ , Table 1). We conclude this by first assuming that, in seawater, rates of MMHg input and removal are in steady state, although Hg concentrations may be increasing in certain polar marine organisms (1). In the North Atlantic, Mason et al. (25) modeled a net MMHg removal rate constant of  $0.18 \text{ year}^{-1}$  through demethylation and particulate scavenging, resulting in 98% of the MMHg being turned over every 20 years. We further predict that net MMHg removal via photodegradation would be low in polar oceans because they are deep and ice covered for a large portion of the year. If the  $0.057 \text{ ng L}^{-1}$  MMHg surface concentration was equally distributed throughout the  $\sim 200 \text{ m}$  water column at our sites (although higher concentrations of MMHg were found in deeper waters of the Atlantic Ocean than at the surface (14)), there would be a pool of  $\sim 114 \text{ mg MMHg ha}^{-1}$  of polar ocean surface area. If MMHg is turned over approximately every 20 years in polar oceans, then external MMHg inputs would need to be  $\sim 5.7 \text{ mg ha}^{-1} \text{ year}^{-1}$  to maintain our lowest measured concentration. This input rate, however, is  $\sim 63$  times higher than the highest areal load of MMHg we observed in snowpacks ( $0.09 \text{ mg ha}^{-1}$ ; see below and Table 2). Although there are no major rivers flowing into the marine regions we sampled, terrestrial river runoff may contribute to marine pools of MMHg in general. For example, it was recently estimated that the Mackenzie River discharges  $\sim 15 \text{ kg}$  of MMHg and  $\sim 2200 \text{ kg}$  of THg ( $0.7\%$  MMHg) annually into the Beaufort Sea (26).

In situ methylation of Hg(II) in anaerobic environments such as sediments can be a major source of MMHg to freshwater ecosystems. When the same reasoning as above is used, *net* Hg(II) methylation rates in cold ocean sediments would need to be  $\sim 5.7 \text{ mg ha}^{-1} \text{ year}^{-1}$  to maintain water column concentrations of  $0.057 \text{ ng L}^{-1}$ . However, this is within the range of Hg(II) methylation rates measured in wetlands at the ELA ( $1\text{--}20 \text{ mg ha}^{-1} \text{ year}^{-1}$ ) where Hg(II) methylation during warm summer months is known to be extremely high for a pristine ecoregion (19). There could also be in situ methylation of Hg(II) to MMHg or the in situ production of DMHg and subsequent decomposition to MMHg as has been hypothesized elsewhere (16, 25), in the water column of polar oceans. If 41% of the total Hg pool is methylated at maximum (Table 1), a very slow methylation rate of  $0.11\% \text{ day}^{-1}$  would be required to produce the MMHg annually, even if MMHg was stable for only 1 year in marine waters. This methylation rate is low compared to that measured in anoxic freshwaters ( $0.5\text{--}14\% \text{ day}^{-1}$ ) (27).

Although our calculations are inconsistent with the hypothesis of atmospheric MMHg inputs and in situ methylation of Hg(II) to MMHg in sediments being major sources of MMHg to polar oceans, they are based only on a limited number of surface water MMHg concentrations measured under the sea ice in May 2004 and 2005. Much more research is required to determine the relative importance of both external inputs of MMHg and in situ production of MMHg to the marine MMHg pool. Regardless of the MMHg source, though, our results suggest that concentrations of MMHg in polar ocean waters ( $0.057\text{--}0.095 \text{ ng L}^{-1}$ , Table 1) are high enough to initiate the biomagnification of MMHg documented in, for example, the NOW marine food web, where

TABLE 2. Concentrations of THg and MMHg in Different Layers of High Arctic Snowpacks, and Total Loadings of Hg in Those Snowpacks

site <sup>a</sup>	date	surface snow			spring snow			depth hoar snow			areal load	
		THg (ng L <sup>-1</sup> )	MMHg (ng L <sup>-1</sup> )	%MMHg	THg (ng L <sup>-1</sup> )	MMHg (ng L <sup>-1</sup> )	%MMHg	THg (ng L <sup>-1</sup> )	MMHg (ng L <sup>-1</sup> )	%MMHg	THg (mg ha <sup>-1</sup> )	MMHg (mg ha <sup>-1</sup> )
17 John Evans Glacier	10 May 04	2.58	0.017	0.7	0.37	0.019	5.1	0.19	0.035	18.2	0.5	0.016
18 Allman Bay	10 May 04	3.61	$\leq 0.015$	0.4	0.29	$\leq 0.015$	5.1	0.56	0.095	17.1	0.8	0.033
19 Buchannan Bay	10 May 04	6.10	$\leq 0.015$	0.2	1.26	0.028	2.2	5.42	$\leq 0.015$	0.3	3.6	0.017
20 Talbot Inlet	10 May 04	4.49	0.024	0.5	0.40	$\leq 0.015$	3.8	7.86	$\leq 0.015$	0.2	1.8	0.007
21 Makinson Inlet	10 May 04	150	0.210	0.1	253	$\leq 0.015$	0.0	281	$\leq 0.015$	0.0	250	0.085
22 Jones Sound	11 May 04	78.2	0.096	0.1	8.02	$\leq 0.015$	0.2	17.1	$\leq 0.015$	0.1	29	0.036
23 Norveigian Bay	16 May 04	8.02	$\leq 0.015$	0.2	8.06	0.018	0.2	1.23	$\leq 0.015$	1.2	6.7	0.022
24 Bay Flord	16 May 04	19.8	0.028	0.1	18.1	0.058	0.3	48.6	0.089	0.2	22	0.046
25 Eureka Sound	16 May 04	15.9	0.025	0.2	1.40	0.042	3.0	9.79	$\leq 0.015$	0.2	13	0.043
26 Axel Heiberg Island	16 May 04	2.53	$\leq 0.015$	0.6	0.29	0.022	7.6	0.08	$\leq 0.015$	0.6	1.9	0.024
27 Wellington Channel	16 May 04	66.4	$\leq 0.015$	0.0	3.33	0.022	0.6	2.32	$\leq 0.015$	0.6	37	0.024
28 Alert	31 May 04	6.24	0.106	1.7	1.23	0.021	1.7	1.41	$\leq 0.015$	1.1	3.3	0.050
av $\pm$ SD		$30.3 \pm 5.5$	$0.048 \pm 0.060$	$0.4 \pm 0.5$	$24.6 \pm 72.0$	$0.024 \pm 0.013$	$2.5 \pm 2.5$	$31.3 \pm 79.8$	$0.031 \pm 0.031$	$3.6 \pm 7.0$	$31 \pm 70$	$0.034 \pm 0.021$
median		7.13	0.020	0.2	1.33	0.020	3.0	3.87	$< 0.015$	0.3	5.18	0.028

<sup>a</sup> Site numbers refer to those in Figure 1.

MMHg concentrations in lower food chain organisms (e.g., zooplankton) were  $4.0 \pm 3.0 \text{ ng g}^{-1} \text{ ww}$  (28). Using our measured seawater MMHg concentrations, we calculate log bioaccumulation factors (log BAFs), defined as the ratio of the concentration of MMHg in zooplankton ( $\text{ng g}^{-1} \text{ ww}$ ) and the concentration of MMHg in water ( $\text{ng mL}^{-1}$ ), of between 4.6 and 4.8 for the NOW zooplankton, identical to log BAFs quantified from zooplankton in freshwater systems at the ELA (4.4 to 4.8; assuming zooplankton dw was  $\sim 15\% \text{ ww}$  (29)).

DMHg concentrations in seawater under the ice were  $11.1 \pm 4.1 \text{ pg L}^{-1}$  ( $n = 10$ ), compared to MMHg concentrations of  $95 \pm 14 \text{ pg L}^{-1}$  at the same sites (Table 1). These DMHg concentrations are similar to those measured in deep northern Atlantic seawaters (16). Because radical species such as OH and Cl can initiate the oxidation of gaseous DMHg to MMHg in the atmosphere (13–15), fluxes of DMHg from open water regions make the ocean a potential source of MMHg to nearby snowpacks or the open water itself. In the Supporting Information section, equations required to calculate a diffusive flux of both DMHg and GEM from marine and fresh water surfaces are described in detail. Assuming maximum concentrations of DMHg in the atmosphere of  $0.5 \text{ pg L}^{-1}$ , seawater at  $0^\circ \text{C}$  and  $35\text{‰}$  salinity, a gas transfer velocity ( $k$ ) of  $3.7 \text{ cm hr}^{-1}$  derived for  $\text{CO}_2$  in the NOW polynya (30), and a Schmidt number for  $\text{CO}_2$  ( $\text{Sc}_{\text{CO}_2}$ ) of 2073.1, we calculate a diffusive DMHg flux of  $4.8 \pm 0.6 \text{ ng m}^{-2} \text{ day}^{-1}$  to the atmosphere from open water regions in the sea ice. From the NOW polynya, which had a surface area of  $\sim 45\,000 \text{ km}^2$  on 9 May 2004, approximately the date when we were sampling snowpacks (Supporting Information, Figure 3), we estimate that  $0.22 \pm 0.03 \text{ kg DMHg}$  was being emitted to the atmosphere *daily*. Some of this DMHg could be deposited to nearby snowpacks as MMHg.

In 2004, GEM concentrations were extremely high in seawater under the ice, averaging  $129 \pm 36 \text{ pg L}^{-1}$  ( $n = 8$ ) for our sites. These dissolved GEM concentrations are significantly higher than background GEM concentrations of  $1.7 \text{ pg L}^{-1}$  measured in the atmosphere at Alert (31). Again using equations detailed in the Supporting Information section and assumptions outlined above for DMHg, we calculate a flux of  $129 \pm 28 \text{ ng m}^{-2} \text{ day}^{-1}$  from open water regions, clearly showing that polar oceans can be *net* sources of GEM to the atmosphere. These fluxes would be even larger during AMDEs when concentrations of GEM in the atmosphere frequently drop below  $1.0 \text{ pg L}^{-1}$ . Furthermore, these results also suggest that there could be a major efflux of GEM from polar oceans to the atmosphere at ice break-up and melt each spring, as was first hypothesized by Kirk et al. (7). In fact, a springtime increase or “hump” in atmospheric concentrations of GEM has been recorded following spring melt at Alert (3), Barrow, Alaska (4), and Churchill, Manitoba (7).

In summary, we present the first complete dataset on the four major Hg species (MMHg, THg, DMHg and GEM) naturally occurring in polar marine waters. These data, however, and the conclusions drawn from them, are limited both temporally and spatially. More research is required before we can fully understand the biogeochemical cycling of Hg in northern marine ecosystems.

#### Concentrations of THg and MMHg in Snowpacks.

Concentrations of THg in snow ranged between  $0.08 \text{ ng L}^{-1}$  in the depth hoar layer of a snowpack on an inland glacier on Axel Heiberg Island (Site 26; Figure 1, Table 2) to  $345 \text{ ng L}^{-1}$  in surface snow  $\sim 1 \text{ km}$  away from an open-water lead near Griffith Island in Resolute Passage (site 2; Figure 1, Table 2). Average concentrations of THg were similar in surface ( $30.3 \pm 45.5 \text{ ng L}^{-1}$ ), spring ( $24.6 \pm 72.0 \text{ ng L}^{-1}$ ), and depth hoar ( $31.3 \pm 79.8 \text{ ng L}^{-1}$ ) snow (Table 2). However, these average concentrations were primarily driven by high concentrations of THg ( $> 150 \text{ ng L}^{-1}$ ) throughout the snow-

pack at Makinson Inlet near the NOW polynya (site 21, Figure 1, Table 2). Median concentrations of THg were much lower at 7.13, 1.33, and  $3.87 \text{ ng L}^{-1}$  in surface, spring, and depth hoar snow, respectively.

There was an overall significant and positive correlation between log  $\text{Cl}^-$  concentrations and log THg concentrations in snow ( $R^2 = 0.538$ ,  $P < 0.001$ ; Figure 2). This log–log correlation was stronger for concentrations in fresh surface ( $R^2 = 0.758$ ,  $P < 0.001$ ), spring ( $R^2 = 0.750$ ,  $P < 0.001$ ), and depth hoar ( $R^2 = 0.747$ ,  $P < 0.001$ ) snow, separately. Furthermore, on a microscale, THg concentrations in surface snow generally decreased along a transect moving away from the open-water lead near Griffith Island to sites  $\sim 20 \text{ km}$  away inland on Cornwallis Island where THg concentrations averaged only  $3.55 \pm 2.91 \text{ ng L}^{-1}$  (Figure 1; note THg concentration in snow at the lead edge was only  $10.4 \text{ ng L}^{-1}$  where snow was saturated with seawater). These results suggest a marine influence on the deposition and/or stability of oxidized Hg(II) into snowpacks.

Indeed, marine halogens play an important role in the oxidation of GEM during AMDEs (5), which results in the deposition of oxidized Hg species into snowpacks. Furthermore, other studies have shown that  $\text{Cl}^-$  slows photoreduction of Hg(II) to GEM, both in temperate snowpacks (32) and in Arctic meltwater ponds (33). Because at high  $\text{Cl}^-$  concentrations of  $40\,000\text{--}50\,000 \mu\text{mol L}^{-1}$  concentrations of THg in our snowpacks range between  $2.32 \text{ ng L}^{-1}$  (in depth hoar snow at Wellington Channel; Site 27, Figure 1) to concentrations of  $345 \text{ ng L}^{-1}$  (in surface snow near an open water lead; Site 2, Figure 1), we hypothesize that in Arctic snowpacks, especially those on sea ice and in close proximity to open water regions in the sea ice,  $\text{Cl}^-$  plays a central role in the stabilization of oxidized Hg(II), *if* it is deposited there.

We began to test this hypothesis by modeling the potential chemical speciation of Hg in our snowpacks using the chemical equilibrium program Visual MINTEQ, version 2.50 (see Supporting Information section for details). As snow  $\text{Cl}^-$  concentrations were increased in the model, there was a shift in modeled Hg speciation from hydroxo complexes to less photoreducible chloro complexes (Supporting Information section, Figure 4). These results suggest that at higher  $\text{Cl}^-$  concentrations, Hg will be preserved in oxidized forms within snowpacks, as was previously demonstrated experimentally in Boreal snowpacks (32). Therefore, long-term loads of Hg(II) stored in Arctic snowpacks are determined first by the load of Hg(II) deposited there either by AMDEs or from other atmospheric sources, and then by snowpack  $\text{Cl}^-$  concentrations which stabilize the Hg(II) in less reducible forms. For example, in Kirk et al. (7), where a rapid photoreduction of Hg(II) was observed following the cessation of each AMDEs, snowpack  $\text{Cl}^-$  concentrations were on average only  $713 \pm 995 \mu\text{mol L}^{-1}$ , with a maximum concentration of  $3600 \mu\text{mol L}^{-1}$  (J. Kirk, unpublished data).

Unlike previously described (11), we found no relationship between  $\text{Cl}^-$  concentrations and MMHg concentrations in snowpacks ( $R^2 = 0.0002$ ,  $P = 0.921$ , Figure 2). This relationship did not exist in either surface ( $R^2 = 0.011$ ,  $P = 0.597$ ), spring ( $R^2 = 0.004$ ,  $P = 0.846$ ), or depth hoar ( $R^2 = 0.048$ ,  $P = 0.516$ ) snow. Average concentrations of MMHg were higher in surface snow ( $0.048 \pm 0.060 \text{ ng L}^{-1}$ ) than in spring ( $0.024 \pm 0.013 \text{ ng L}^{-1}$ ) and depth hoar ( $0.031 \pm 0.031 \text{ ng L}^{-1}$ ) snow (Table 2).

There are three potential sources of MMHg to snowpacks: (1) dry deposition of MMHg following the oxidation of DMHg, as previously hypothesized, (2) wet deposition of MMHg to snowpacks (which may not be mutually exclusive from 1), and (3) within snowpack microbial or abiotic methylation of Hg(II). There were only three sites with relatively high concentrations of MMHg in recently deposited surface snow: (1) Makinson Inlet near the NOW polynya

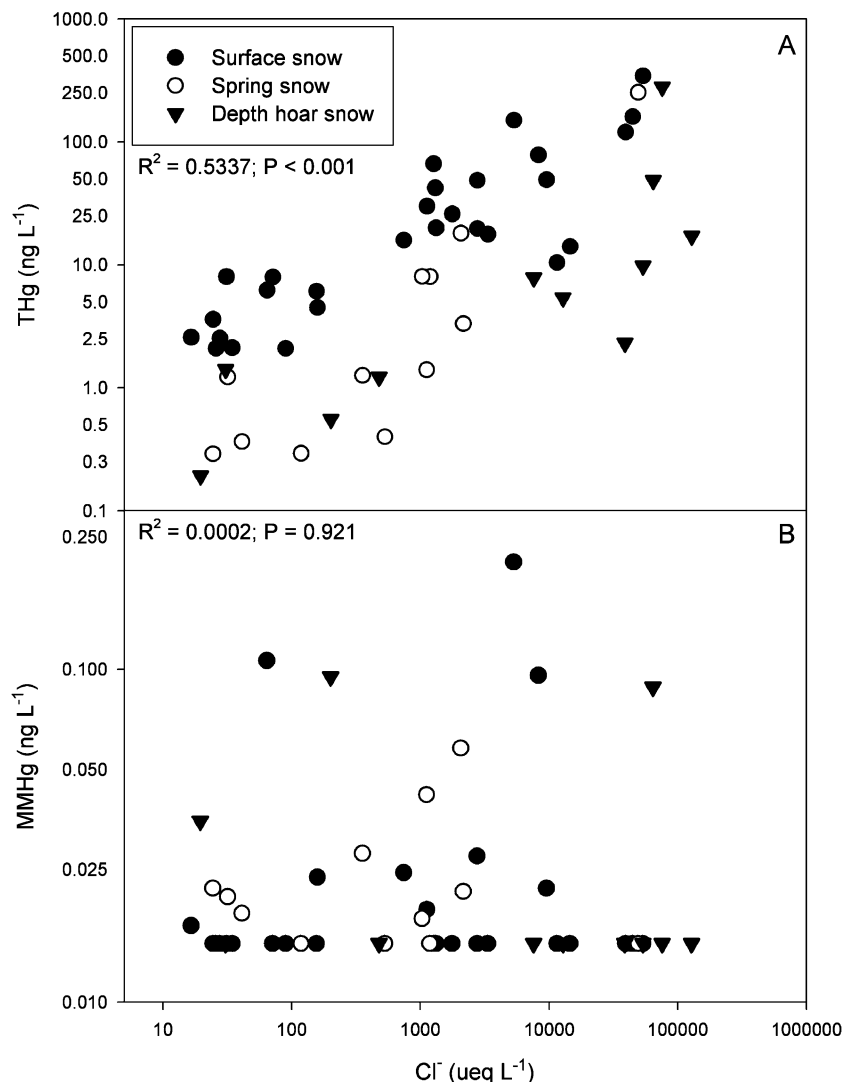


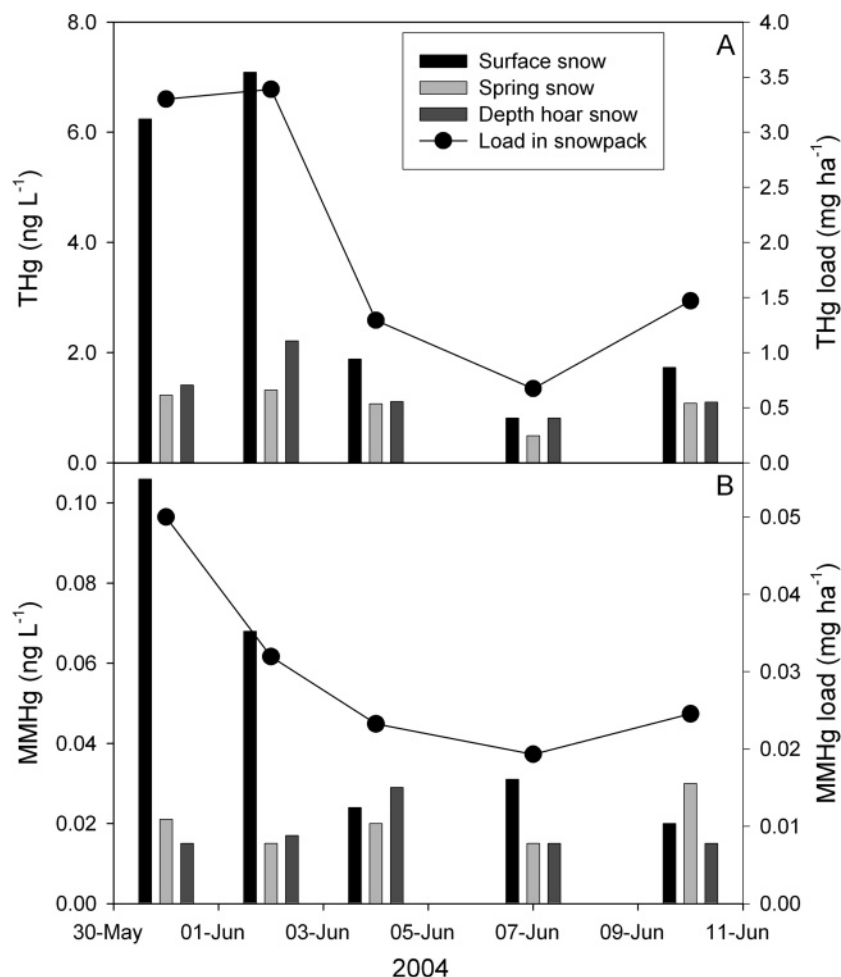
FIGURE 2. Log–log relationship between  $\text{Cl}^-$  concentrations and concentrations of THg (A) and MMHg (B) in snow.

(site 21,  $0.210 \text{ ng L}^{-1}$ , Figure 1), (2) Alert in relatively close proximity to an offshore lead in the sea ice to the north (site 28,  $0.106 \text{ ng L}^{-1}$ , Figure 1), and (3) Jones Sound between the NOW and Hell Gate Cardigan polynyas (site 22,  $0.096 \text{ ng L}^{-1}$ , Figure 1). Because these sites are all in close proximity to regions of open water, it is possible that the ultimate source of MMHg is the oxidation of DMHg emitted from ocean waters. Close proximity to open water, however, might not always result in MMHg deposition to nearby snowpacks, depending on prevailing winds in the region. For example, prevailing winds may possibly explain why MMHg concentrations in surface snow at Talbot Inlet (Site 20; Figure 1), which is equally close to the NOW polynya as Makinson Inlet, but further north, were approximately 10 times lower at  $0.024 \text{ ng L}^{-1}$ . Prevailing winter surface winds are north to south along the western coast of the NOW polynya, turning east at the southern margins of the open water (34).

It is also possible that MMHg in snow originates from long-range transport of MMHg from unknown sources elsewhere. However, at other locations such as the ELA, precipitation events containing high MMHg concentrations originated along the Pacific coast, prompting speculation that the ultimate source of the MMHg was DMHg fluxing from marine ecosystems (35). Precipitation events containing high Hg(II) concentrations at the ELA were traced back to industrial regions (35).

Although polar snowpacks may contain a diversity of microorganisms (e.g., 36), microbial Hg(II) methylation has never been shown to occur under aerobic conditions, such as those occurring in the upper layers of windswept snowpacks, where we observed some of our highest concentrations of MMHg (Figure 1). Abiotic methylation of Hg(II) has also been proposed (e.g., 37). However, abiotic Hg(II) methylation in freshwaters has been typically associated with high concentrations of both Hg(II) and organic matter such as dissolved organic carbon (DOC). We found no relationship between concentrations of inorganic Hg (IHg; THg minus MMHg) and MMHg in snowpacks ( $R^2 = 0.024$ ;  $P = 0.219$ ), and in fact, %MMHg was highest in snowpacks with very low concentrations of THg (Table 2). Furthermore, DOC concentrations in snowpacks sampled in 2005 from sites corresponding to sites 9, 22, and 27 (Figure 1) were very low, averaging only  $0.48 \pm 0.03$ ,  $0.53 \pm 0.10$ , and  $0.73 \pm 0.25$  in surface, spring, and depth hoar snow, respectively.

We continue to hypothesize that the ultimate source of MMHg to Arctic snowpacks is DMHg fluxing from open water regions in the sea ice, although we realize that more research is required to confirm this. Regardless of the origin of MMHg, though, the occurrence of high MMHg concentrations in snow is more a curiosity than a concern because overall MMHg loads in snowpacks are extremely small (see below).



**FIGURE 3.** Changes in concentrations and loads of THg (A) and MMHg (B) in the surface, spring and depth hoar layers of snowpacks at Alert (site 28, Figure 1) in May/June 2004.

**Areal Loads of THg and MMHg in Snowpacks.** Because of low MMHg concentrations in snow, loads of MMHg in high Arctic snowpacks were extremely low, averaging  $0.034 \pm 0.021 \text{ mg ha}^{-1}$  (Table 2). These loadings can be compared to annual wet deposition MMHg loadings of  $0.90 \text{ mg ha}^{-1}$  at the pristine ELA site (38).

Loads of THg in high Arctic snowpacks in May 2004 averaged  $31 \pm 70 \text{ mg ha}^{-1}$ , ranging between  $0.5 \text{ mg ha}^{-1}$  inland at John Evans Glacier (site 17, Figure 1) and  $250 \text{ mg ha}^{-1}$  on the sea ice in Makinson Inlet (site 21, Figure 1) near the NOW polynya, where there were also very high  $\text{Cl}^{-}$  concentrations in the snowpack (Table 2). In many snowpacks, THg concentrations were either consistently high or consistently low throughout the different layers, amplifying the observed differences in overall loads of THg. For example, at John Evan Glacier, THg concentrations were only 2.6, 0.37, and  $0.19 \text{ ng L}^{-1}$  in surface, spring, and depth hoar layers, respectively, whereas in the same three layers at Makinson Inlet, concentrations were 150, 253, and  $281 \text{ ng L}^{-1}$  (Table 2). The median THg load in Arctic snowpacks was only  $5.2 \text{ mg ha}^{-1}$ .

The average combined *wet/dry* THg loads in Arctic snowpacks were on the low end of *wet only* annual loadings across lower North America in 2004, which ranged between 22 and  $200 \text{ mg ha}^{-1}$  (39), suggesting that the Arctic is no more a sink for Hg than any other region. Furthermore, caution is warranted in using time-specific loads of Hg in snowpacks as the *net* loading of Hg to ecosystems because Hg loads in snowpacks change over time because of rapid

photoreduction (40). We sampled snowpacks at Alert (Site 28, Figure 1) for Hg concentrations five times between 31 May and 10 June 2004. Intense AMDEs have been recorded at this site since 1995. THg and MMHg concentrations in surface snow were elevated above concentrations in lower portions of the snowpack during the first two sampling times, suggesting recent deposition of these two species (Figure 3). During the final three sampling periods, THg and MMHg concentrations were fairly similar throughout the different layers of the snowpack. Loss of both THg and MMHg from surface snow is likely caused by photoreduction, as has been previously demonstrated in polar and temperate snowpacks. For example, Kirk et al. (7) found that over Hudson Bay, THg concentrations in surface snow averaged  $65 \text{ ng L}^{-1}$  during AMDEs, but only  $4.5 \text{ ng L}^{-1}$  4 days later. As a result, total loads of Hg in snowpacks changed over time. During the 11-day sampling period at Alert, loads of THg in the snowpack ranged from a high of  $3.4 \text{ mg ha}^{-1}$  to a low of  $0.67 \text{ mg ha}^{-1}$ , whereas loads of MMHg in the snowpack ranged between  $0.05 \text{ mg ha}^{-1}$  and a low of  $0.02 \text{ mg ha}^{-1}$ .

In conclusion, most snowpacks will annually contribute relatively little to marine pools of both MMHg and  $\text{Hg(II)}$ , and as a result, future research should focus more on other sources of MMHg to polar oceans (especially in situ production of MMHg in marine waters themselves) if we are to fully understand why organisms at the top of Arctic marine food webs often contain concentrations of MMHg elevated enough to be of concern for human consumers.



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## Supporting Information Available

Detailed procedures and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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