

Some Sources and Sinks of Monomethyl and Inorganic Mercury on Ellesmere Island in the Canadian High Arctic

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We identified some of the sources and sinks of monomethyl mercury (MMHg) and inorganic mercury (Hg(II)) on Ellesmere Island in the Canadian High Arctic. Atmospheric Hg depletion events resulted in the deposition of Hg(II) into the upper layers of snowpacks, where concentrations of total Hg (all forms of Hg) reached over 20 ng/L. However, our data suggest that much of this deposited Hg(II) was rapidly photoreduced to Hg(0) which then evaded back to the atmosphere. As a result, we estimate that *net wet* and dry deposition of Hg(II) during winter was lower at our sites (0.4–5.9 mg/ha) than wet deposition in more southerly locations in Canada and the United States. We also found quite high concentrations of monomethyl Hg (MMHg) in snowpacks (up to 0.28 ng/L), and at times, most of the Hg in snowpacks was present as MMHg. On the Prince of Wales Icefield near the North Water Polynya, we observed a significant correlation between concentrations of Cl and MMHg in snow deposited in the spring, suggesting a marine source of MMHg. We hypothesize that dimethyl Hg fluxes from the ocean to the atmosphere through polynyas and open leads in ice, and is rapidly photolyzed to MMHg–Cl. We also found that concentrations of MMHg in initial snowmelt on John Evans Glacier (up to 0.24 ng/L) were higher than concentrations of MMHg in the snowpack (up to 0.11 ng/L), likely due to either sublimation of snow or preferential leaching of MMHg from snow during the initial melt phase. This springtime pulse of MMHg to the High Arctic, in conjunction with climate warming and the thinning and melting of sea ice, may be partially responsible for the increase in concentrations of Hg observed in certain

Arctic marine mammals in recent decades. Concentrations of MMHg in warm and shallow freshwater ponds on Ellesmere Island were also quite high (up to 3.0 ng/L), leading us to conclude that there are very active regions of microbial Hg(II) methylation in freshwater systems during the short summer season in the High Arctic.

Introduction

The number of fish and wildlife mercury (Hg) advisories in Canada and the United States has been steadily increasing (1). It is generally thought that increased emissions of Hg from human activities such as coal burning have led to the increase in advisories. Hg is considered a global pollutant because it can undergo long-range atmospheric transport to areas far from point source emissions (2). This behavior is due to the fact that Hg exists in the atmosphere primarily as gaseous elemental Hg(0), a relatively inert gas with a residence time of 6–24 months (2). Recent studies have demonstrated the importance of Hg exchange between the atmosphere and biosphere, and have shown that this exchange is more dynamic than previously hypothesized (e.g., 3–7). Atmospheric deposition is the dominant source of inorganic Hg(II) to most water bodies and terrestrial environments (8, 9). Once deposited, Hg(II) can be methylated to monomethyl mercury (MMHg), an organic and toxic form of Hg that bioaccumulates through food webs. It is generally believed that the primary methylating organisms are sulfate-reducing bacteria (13, 14), and that most methylation occurs at redox transition zones in environments such as lake sediments and wetlands (10–12) where rates of sulfate reduction are substantial and sulfide buildup is suppressed by reoxidation. MMHg is then available for bioaccumulation through food webs. Inorganic Hg(II) and MMHg can also be reduced photochemically or biologically to elemental Hg(0) and lost to the atmosphere (e.g., 15, 16). The amount of “re-emission” of Hg to the atmosphere influences the residence time of Hg in the biosphere, and hence the amount of Hg available for methylation.

Even in remote regions such as the Canadian High Arctic, there is increasing evidence of contamination by persistent, toxic substances including Hg (17). However, the degree of Hg deposition in certain regions of the High Arctic varies more seasonally than in more southern ecoregions, with a recently discovered pulse of deposition after polar sunrise (18). Gaseous elemental Hg(0) concentrations in the Arctic atmosphere normally range between 1 and 2 ng/m³ (18). However, for three months after polar sunrise (until the approximate timing of snowmelt), atmospheric Hg(0) levels frequently drop below 1 ng/m³, coinciding with a decrease in tropospheric ozone concentrations (18). It is now believed that gaseous Hg(0) is oxidized by sunlight-induced heterogeneous reactions with the marine halogens Br and Cl to become reactive gaseous Hg and/or particulate Hg (19–22). Both of these have dry-deposition velocities greater than gaseous Hg(0) and thus fall out into the snowpack. In fact, *atmospheric Hg depletion events* have been implicated as the source of elevated concentrations of Hg(II) (sometimes exceeding 100 ng/L) found in surface snow in the Arctic (23), and a potential gross loading of 50–300 T of Hg(II) to the Canadian archipelago each year (21, 23). It has been suggested that this Hg(II) loading is responsible for the recent increase in Hg levels in Arctic biota because it occurs at the onset of the spring pulse in biological activity in the High Arctic (21).

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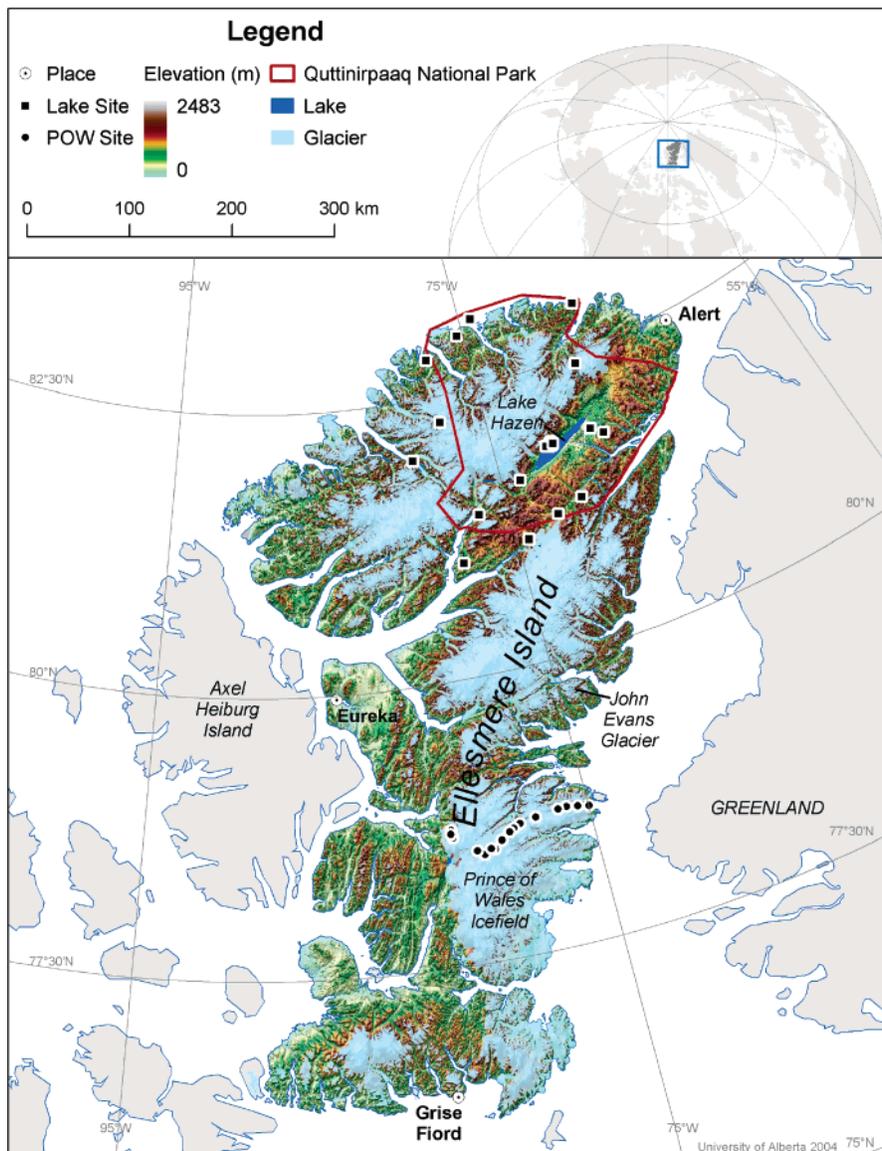


FIGURE 1. Samples were collected from numerous locations on Ellesmere Island in the Canadian High Arctic. Snow samples were collected along a transect traversing the northern part of the Prince of Wales Icefield in 2001, at Alert in 2001 and 2002, and on John Evans Glacier (Figure 2) in 2002. Snowmelt and glacial runoff samples were collected on John Evans Glacier in 2001 and 2002. The surface waters of 30 ponds and lakes in Quttinirpaaq National Park were sampled in 2003.

We acquired samples for total Hg (THg; the sum of all forms of Hg in a sample) and MMHg analyses from snowpacks, snowmelt, glacial runoff, ponds, and lakes on Ellesmere Island in the Canadian High Arctic between 2001 and 2003 to begin to address the following questions: (1) What is the short-term fate of Hg(II) deposited into snowpacks following springtime atmospheric Hg depletion events? (2) What are the sources of MMHg found in High Arctic snowpacks? (3) Where are the active sites of microbial Hg(II) methylation in the High Arctic? Addressing these questions is vital because it is MMHg, not oxidized Hg(II) directly deposited onto the Arctic landscape, that bioaccumulates through food webs.

Methods

Atmospheric Hg Depletion Events and Deposition of Hg(II) and MMHg into Snowpacks. In April 2001 and 2002, concentrations of gaseous elemental Hg(0) in air were monitored at the Global Atmospheric Watch laboratory, Alert, at the northern tip of Ellesmere Island, Nunavut, Canada (Figure 1). This laboratory is located 6 km south of the

coastline at 205 m above sea level. Concentrations of gaseous elemental Hg(0) in air were quantified using a Tekran 2537A mercury vapor analyzer (www.tekran.com). The analyzer measured concentrations of gaseous elemental Hg(0) in air by amalgamation onto gold cartridges with subsequent thermal desorption and cold vapor atomic fluorescence spectrophotometry (CVAFS) detection. Air was sampled at $1.5 \text{ L}/\text{min}^{-1}$ and concentrated on the gold cartridges for either 5 or 30 min. In 2001, during the period when snow samples were collected for THg and MMHg analyses, the Tekran 2537A was not operational. As a result, during this period gaseous elemental Hg(0) concentrations in air were inferred from measured atmospheric concentrations of ozone. The correlation between atmospheric concentrations of gaseous elemental Hg(0) and ozone was first calculated on a weekly basis for each of the six years from 1995 to 2000. For weeks 14 and 15, when snow samples were collected, average slopes and intercepts of the annual correlation equations from the 6 years were calculated, and these were used in a linear equation to interpolate hourly gaseous elemental Hg(0) concentrations from hourly ozone concentrations. For the

years 1995–2000, the average R^2 during week 14 was 0.825 (range 0.698–0.978) and during week 15 was 0.857 (range 0.740–0.967).

To determine if atmospheric Hg depletion events resulted in net deposition of Hg(II) into snowpacks, snow was collected for THg and MMHg analyses on a nearby plateau within 1 km of the laboratory where gaseous elemental Hg(0) in air was being monitored. In 2002 only, snow was also collected at the Ice Camp, located 1.4 km north of the nearest land on the frozen Arctic Ocean. The April–May snowpack in the Canadian High Arctic typically comprises three distinct layers (24, 25). The bottom layer of depth hoar consists of coarse granular snow that was deposited in the previous fall and subjected to temperature gradient metamorphism in winter. Snowfall on Ellesmere Island is quite low from November on, but accumulation begins again in April and May. The middle layer of the snowpack may consist of a mix of snow moved around by wind during winter and snow deposited in early spring. The surface layer, composed of recent snowfall, can be visually distinguished from the remaining underlying spring deposition because the crystal morphologies of fresh snow remain intact in the short-term. Depth hoar typically constitutes approximately half the total snowpack depth just prior to spring melt.

For the purposes of sampling, pits were dug down to the bottom of level snowpacks, avoiding drifts. The face of the pit was then cleaned using acid-washed Teflon scrapers. Snow from the spring and depth hoar layers in the snowpack, and often fresh surface snow, was collected into acid-washed 2-L Teflon jars by pushing them into the face of the pit. This sampling protocol allowed us to test the hypothesis that the Hg depleted from the atmosphere following polar sunrise is primarily found near the surface of the snowpack.

All snow sampling was conducted by two people using the “clean hands, dirty hands” ultraclean sampling protocol (12, 26). Snow samples were stored frozen in the dark until melted and processed in the Low-level Hg Analytical Laboratory at the University of Alberta. Because samples were kept frozen and not exposed to light, there was no photoreduction and loss of Hg(II) or MMHg from the snow during the storage period (unpublished data). In the laboratory, snow was melted in the dark and visually inspected to confirm that samples were not contaminated by pieces of large particulate matter such as soil. Samples for THg analyses were transferred slowly into 125-mL Teflon bottles and acidified with concentrated trace-metal-grade HCl equal to 0.2% of the sample volume. Samples for MMHg analyses were transferred to 250-mL Teflon bottles and frozen until analysis. THg in water was analyzed using a Tekran model 2500 CVAFS mercury detector as described in ref 27. Star Chromatography Workstation software (Varian Inc., Mississauga, ON) was used for peak integration. THg could be detected at concentrations of 0.05 ng/L at a blank level of 0.04–0.07 ng/L. MMHg in water was analyzed by CVAFS after distillation and aqueous phase ethylation (28, 29). MMHg could be detected at concentrations above 0.02 ng/L at blank levels of 0.05–0.10 ng/L. Samples in which MMHg concentrations were below our detection limit were assigned concentrations of 0.02 ng/L for statistical purposes. Almost all samples analyzed for THg, and 20% of samples analyzed for MMHg, were run in duplicate. Spike recoveries for THg and MMHg were generally >90% and >80%, respectively. Concentrations of THg and MMHg in a few snow samples that were split and analyzed in both the Low-level Hg Analytical Laboratory and at Flett Research Ltd. (Winnipeg, MB) agreed within 5% of each other.

Photoreduction of Hg in Surface Snow. To examine fine-scale temporal patterns of Hg deposition, surface snow samples were collected for THg analyses 1–3 times daily between May 4 and June 2, 2002 on John Evans Glacier located

on the east coast of Ellesmere Island (Figure 1). Surface snow samples were scooped into acid-washed 250-mL wide-mouth Teflon bottles from a cordoned off area 15 km up-glacier from its terminus using the clean hands, dirty hands sampling protocol. The samples were stored frozen and in the dark until melted and processed in the Low-level Hg Analytical Laboratory as described above.

Between May 9 and 17, we also sampled for concentrations of total gaseous Hg in the interstitial airspaces of the three layers of the snowpack to delineate zones of Hg(II) photoreduction, assuming that the majority of the total gaseous Hg was gaseous elemental Hg(0). On each sampling occasion, a snow pit was dug as described above within 3 km down-glacier from the site where surface snow was being collected daily to avoid overt disturbance of this site. Once a pit was dug, acid-cleaned “total gaseous Hg sniffers” were inserted at least 50 cm horizontally into the middle of the three different layers of the snowpack. The sniffer was constructed from a 75-cm-long, 1-cm-diameter quartz glass tube that was sealed and then perforated with tiny holes at one end. A gold-coated glass bead trap (gold trap) was then attached to the sniffer, using a Teflon PFA straight compression fitting, to strip gaseous Hg from the air that passed through it. The opposite end of the gold trap was then connected in-line first to a Cole Parmer stainless steel ball flow meter to measure instantaneous airflow through the gold traps, and then to a small vacuum pump (0–5 L/min capacity, TD-3, Brailsford & Co., www.brailsfordco.com) using 6.3-mm PTFE tubing. Air was vacuumed from the interstitial airspaces of the snowpack through the gold trap at ~1 L/min for approximately 30 min.

Prior to departure to the field, gold traps were cleaned in the Low-level Hg Analytical Laboratory. Hg was thermally desorbed from gold traps by heating them to 400 °C. The traps were then sealed using Teflon plugs and Teflon tape, individually bagged, and sealed in acid-washed mason jars flushed with ultrahigh purity (UHP) nitrogen. In the field, following sample collection, gold traps were again plugged, taped, individually bagged, and placed back in the mason jars (although jars could not be flushed with UHP nitrogen at this time). Upon return to the laboratory, Hg was thermally desorbed from the gold traps at 400 °C into an UHP argon carrier gas, and detected on a Tekran model 2500 CVAFS mercury detector. Gold traps shipped to John Evans Glacier and back, but not used (travel blanks), revealed that there was zero contamination of the gold traps during the ~1-month period they were at the field site.

Concentrations of total gaseous Hg in the interstitial airspaces of the snowpack were calculated by dividing the total quantity of Hg (ng) on the gold traps by the volume of air (L) passed through the gold traps during sampling.

Net Deposition of THg and MMHg in Snow. We conducted an intensive snow survey from May 5 to 19, 2001 at 16 sites on the Prince of Wales Icefield, south-eastern Ellesmere Island (Figure 1), to determine whether Hg(II) and MMHg deposition was related to proximity to the North Water Polynya of north Baffin Bay and to sources of marine halogens. Reactive halogen species, such as Cl and Br, produced through photochemically initiated autocatalytic reactions, are thought to catalyze atmospheric Hg depletion events (21, 22). During the sampling period, the snowpack was near its maximum annual depth, especially at lower elevations. Snowpits were dug as described above at 200-m elevation intervals over an elevation gradient of approximately 2000 m along an east to west transect from Rosse Bay across the northern part of the Icefield (Figure 1). At each site, snow was collected from the spring and depth hoar layers of the snowpack, and the thickness of each layer was recorded. Recently deposited surface snow was not collected during this survey. Samples were analyzed for THg and

MMHg in the Low-level Hg Analytical Laboratory as described above.

Net accumulation of THg and MMHg in snowpacks at the time of sampling was estimated by multiplying the concentrations of THg and MMHg in the spring and depth hoar layers of the snowpack by the water equivalent of each of these layers, determined using the following equation derived from measurements taken on John Evans Glacier just north of the Prince of Wales Icefield (Figure 1):

$$\text{snow water equivalent (kg/m}^2\text{)} = (0.282 \times \text{snow thickness (m)} - 0.0074) \times 1000 \quad (1)$$

In addition to the survey conducted on the Prince of Wales Icefield, we also used the concentrations of THg and MMHg measured in the different layers of snowpacks at Alert (see above) to estimate net accumulation of Hg in snowpacks when we sampled there. We also estimated net accumulation of Hg in snowpacks on John Evans Glacier from five snow pits dug on May 1 and 2, 2002 along a transect starting at the terminus of the glacier and moving up-glacier 7, 9, 12, and 15 km. At both Alert and John Evans Glacier in 2002, when all three layers of the snowpack were sampled, we first averaged concentrations of Hg measured in the surface and spring layers of the snowpack prior to multiplication by the water equivalents derived from the combined thickness of the upper layers of the snowpack. In 2002 at Alert, the average water equivalents determined using eq 1 and snow depths from eight snowpits we sampled over land and the sea ice ($155 \pm 39 \text{ kg/m}^2$) was very similar to the average water equivalents actually measured from snow cores taken at these same eight sites ($149 \pm 43 \text{ kg/m}^2$).

Coincident with each snow sample collected for Hg analyses, we also collected a snow sample for analyses of SO_4 , Na, Cl, and pH. Nonsea-salt sulfate (NSS SO_4) was calculated from the ratio of SO_4 :Na in sea salt and the concentrations of SO_4 and Na in snow. When marine sources of biogenic SO_4 are low, as is the case in the High Arctic, NSS SO_4 can be used as a proxy for industrial sources of solutes in snowpacks (30, 31), whereas Cl can be used to indicate marine origins of solutes. Cl and pH may further affect the stability and bioavailability of Hg(II) and MMHg in snowpacks (e.g., 32). Snow was collected in zippered plastic bags and stored frozen until analysis in the Glacier Hydrochemistry Laboratory, Department of Earth and Atmospheric Sciences, University of Alberta. Each snow sample was melted at room temperature. An aliquot of the sample was filtered through a $0.45\text{-}\mu\text{m}$ cellulose nitrate membrane. A 20-mL subsample of the filtrate was retained for analysis of SO_4 , Cl, and Na by ion chromatography (25), while the remaining filtrate was used to determine pH with a Ross Sure-Flow electrode and Orion 290A pH meter.

THg and MMHg in Snowmelt and Glacial Runoff. Water flow on the surface of John Evans Glacier (supraglacial runoff) begins each spring with the melting of snow and then the melting of glacier ice. Some of the surface water drains into the glacier through crevasses located approximately 4 km from the glacier terminus (33). Initially, outflow of this water is blocked because the glacier margin is frozen to the bed. As water inputs continue, however, subglacial water pressure builds up until an outburst is initiated either by an artesian fountain located on the ice surface within a few hundred meters of the glacier terminus, or by upwelling at the glacier margin (34). The first waters to be released are slightly turbid and highly solute rich (electrical conductivity up to $600 \mu\text{S/cm}$). Over 3–4 days, however, the solute-rich subglacial runoff waters are diluted by the new season's water input and electrical conductivity falls to $200 \mu\text{S/cm}$ or less (34).

In June 2001 and 2002, samples were collected from meltwater ponds and supra and subglacial runoff at John

Evans Glacier for THg and MMHg analyses (Figures 1 and 2). All samples were collected using the clean hands, dirty hands sampling protocol. Both unfiltered and filtered samples were collected at each site to determine the proportion of particle-bound THg and MMHg. Acid-cleaned 6.3-mm Teflon tubing was attached using acid-cleaned Cole Parmer C-flex tubing to a battery-operated Greylor Company model PQ-DC pump equipped with a Delrin housing and Teflon diaphragm and gears (CanSun Electronics, Winnipeg, MB; cansun@mts.net). We attached another shorter piece of Teflon tubing to the outlet of the pump. Water was pumped at approximately 2 L/min from the site for approximately 5 min to thoroughly flush all lines. Water was then pumped directly into 125-mL and 250-mL Teflon bottles for THg and MMHg analyses, respectively. To collect the filtered water samples we attached an acid-cleaned Meissner CSMF $0.4\text{-}\mu\text{m}$ inline capsule filter to the outlet line, and pumped filtered water directly into Teflon bottles. All samples were acidified in the field with concentrated trace-metal-grade HCl equal to 0.2% of the sample volume. Analyses were done in the Low-level Hg Analytical Laboratory as described above.

Coincident with each water sample collected for Hg analyses, we also collected water samples in Nalgene bottles for analyses of the same chemical parameters measured in snow. Water samples were analyzed in the Glacier Hydrochemistry Laboratory as described above.

Concentrations of THg and MMHg in Ponds and Lakes.

Surface waters from 30 ponds and lakes on northern Ellesmere Island were collected from July 9 to 18 2003 to determine the potential quantity of Hg available for accumulation through freshwater food webs following snowmelt and runoff. Fifteen sites in Quttinirpaq National Park (formerly Ellesmere Island National Park Reserve) were reached by helicopter (Figure 1). The other 15 sites were within walking distance of the base camp set up at Lake Hazen for this survey (Figure 1). At each site, unfiltered water samples were collected using the clean hands, dirty hands sampling protocol. Samples for THg and MMHg analyses were collected into acid-cleaned 125-mL and 250-mL Teflon bottles, respectively, by dipping the bottles just below the water surface while standing either on shore or in shallow water along the edge of the pond. All samples were preserved with concentrated trace-metal-grade HCl (as described above) the same day at base camp and stored in a cooler until shipped back to the Low-level Hg Analytical Laboratory where they were analyzed as described above.

Surface water pH was averaged from measurements taken at the time of sampling using three separate Hanna pHep3 meters. Samples for DOC analyses were first collected in a 1-L plastic Nalgene bottle, and then filtered through a $0.45\text{-}\mu\text{m}$ cellulose acetate filter at the base camp and stored in a glass bottle. Samples were analyzed for DOC at the National Laboratory for Environmental Testing (Canadian Centre for Inland Waters, Burlington, ON) using a Tekmar Dohrmann Phoenix 800 UV-Persulphate TOC analyzer. The surface area of lakes was estimated from topographic maps, whereas the surface area of small ponds was estimated using the equation for an oval, and the maximum length and width of the pond measured with a laser range finder.

Results and Discussion

Atmospheric Hg Depletion Events and Deposition of Hg(II) and MMHg into Snowpacks. *Atmospheric Hg Depletion Events and THg in Snow.* One atmospheric Hg depletion event occurred during the snow sampling period at Alert in 2001, and two occurred in 2002 (Figure 3). In 2001, the atmospheric Hg depletion event occurred from April 3 to 6. Two fresh surface snow samples collected on April 4 contained on average 5.3 ng/L THg (Figure 3). When snow was subsequently collected from the middle layer of the snowpack

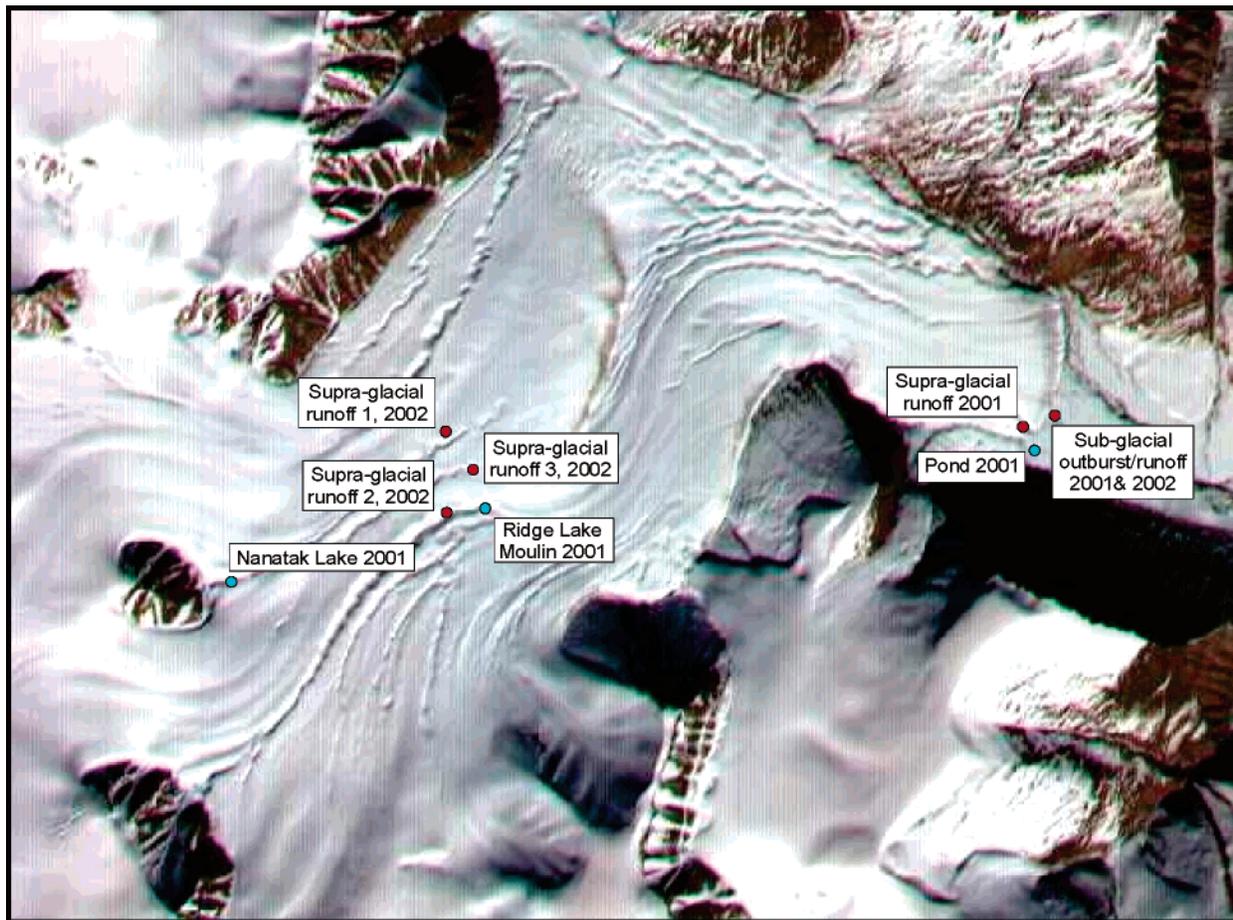


FIGURE 2. Aerial view of the snowmelt and glacial runoff sites sampled in 2001 and 2002 on John Evans Glacier.

following the cessation of this atmospheric Hg depletion event, concentrations of THg declined to 2.0 and 0.63 ng/L on April 9 and 12, respectively. Depth hoar contained on average only 0.59 ng/L THg on these two dates.

Average concentrations of THg in snow collected in the autumn of 2001 were 0.29 ± 0.04 ng/L THg (Table 1). This snow presumably became the depth hoar layer of the snowpack that was subsequently sampled in April 2002. Then, average concentrations of THg in the depth hoar were 0.89 ± 0.31 ng/L, three times higher than those observed when the snow was initially deposited, but still quite low (Table 1).

The first atmospheric Hg depletion event during our snow sampling campaign in 2002 lasted from April 11 to 14 (Figure 3). Snow was collected only at the Ice Camp during this event. Surface snow collected there on April 12 contained approximately 5.7 ng/L THg, very similar to concentrations measured in surface snow during the depletion event in 2001. Concentrations of THg in the spring snow and depth hoar layers on that date were 0.39 and 2.5 ng/L, respectively. When snow was again collected at the Ice Camp 3 days later on April 15, and on the plateau near the Global Atmospheric Watch laboratory 6 days later on April 18, concentrations of THg throughout the whole snowpack were similar and very low, averaging only 0.98 ng/L (Figure 3). The second depletion event in 2002 was detected at the Global Atmospheric Watch laboratory from April 23 to 25. Snow collected at the Ice Camp on April 22 contained high concentrations of THg in the very surface snow (11.1 ng/L) and the underlying spring snow layer (21.1 ng/L). The depth hoar on this sampling date contained only 1.3 ng/L THg. Interestingly, the snowpack on the plateau near the Global Atmospheric Watch laboratory on April 23 contained quite low concentrations of THg (average of 1.2 ng/L throughout). However, at this site 2 days

later on April 25 during a minor atmospheric Hg depletion event (Figure 3), surface snow and the underlying spring snow layer contained 7.3 ng/L and 19.2 ng/L THg, respectively. Snow from all layers of the snowpack subsequently collected at the Ice Camp (April 27) and on the plateau near the laboratory (April 30) contained less than 2.0 ng/L THg. Snow collected in November 2002 again contained very low concentrations of THg (0.35 ng/L).

Concentrations of THg in freshly fallen snow previously measured at Alert in 2000 following frequent atmospheric Hg depletion events were much higher than concentrations reported here, averaging 120 ng/L and 180 ng/L over land and sea ice, respectively (35). In 2000, however, concentrations of THg were measured in a thin layer of freshly fallen snow collected from the surface of a Teflon-coated "snow table," and not in the snowpack itself. Because Hg(II) deposited into snowpacks during atmospheric Hg depletion events appears to penetrate the whole upper portion of the snowpack (see second atmospheric Hg depletion event in 2002; Figure 3), it is possible that our concentrations were lower due to a dilution effect.

The quantity of Hg(II) measured in surface snow during a given atmospheric Hg depletion event is likely proportional to the abundance of reactive gaseous Hg and/or particulate Hg formed during the event (e.g., 21). Although atmospheric Hg depletion events resulted in the deposition of Hg(II) into the upper layers of the snowpacks we sampled, a large portion of the Hg(II) was gone from these snowpacks within days of deposition. This observation is inconsistent with other studies suggesting that Hg(II) accumulates in Arctic snowpacks from polar sunrise to just prior to snowmelt, at which time the majority of deposited Hg(II) is lost from meltwater due to photoreduction processes (21, 23). Although other studies

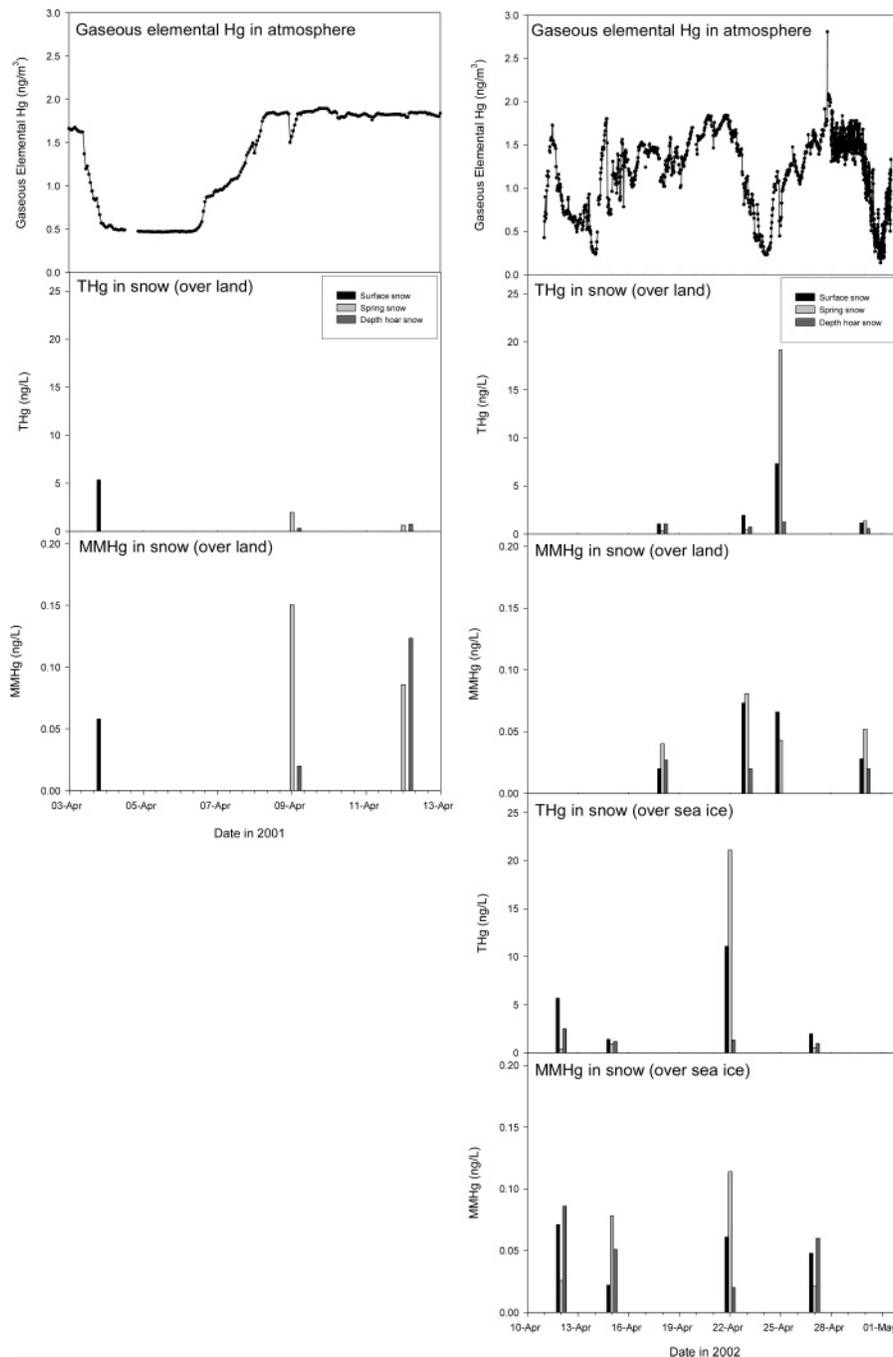


FIGURE 3. Concentrations of gaseous elemental Hg in air measured in 2001 and 2002 at the Global Atmospheric Watch laboratory located approximately 6 km south of the Arctic Ocean shoreline at Alert. Concentrations of gaseous elemental Hg in 2001 were interpolated from atmospheric concentrations of ozone (see methods). Concentrations of THg and MMHg in different layers of the snowpack. Snow was collected from snowpits dug near the Global Atmospheric Watch laboratory (over land) in 2001 and 2002, and at the Ice Camp (1.4 km out over the sea ice) (2002).

have measured higher concentrations of Hg(II) in snowpacks during atmospheric Hg depletion events than we have here (e.g., 21), no one else has yet examined the short-term fate of the deposited Hg(II) at these high latitudes. As a result, future research in the High Arctic should focus on the daily monitoring of Hg(II) concentrations in snowpacks not only during but between individual atmospheric Hg depletion events. Where did the majority of the Hg(II) in the snowpack go following the end of individual atmospheric Hg depletion events? At Alert it is possible that surface snow containing high concentrations of Hg(II) in the snowpack following deposition was redistributed by strong winds typical of this region. However, it would be expected that in an area

experiencing frequent atmospheric Hg depletion events, such as Alert, snow containing high concentrations of Hg(II) would replace that blown away. Furthermore, frequent atmospheric Hg depletion events, in conjunction with sublimation of the snowpack in this cold and xeric region, should result in concentrations of Hg(II) increasing, not decreasing, over time. More likely, much of the oxidized Hg(II) in the snowpack was photoreduced to gaseous elemental Hg(0), which then fluxed back to the atmosphere between atmospheric Hg depletion events. We provide evidence to support this hypothesis below.

Atmospheric Hg Depletion Events and MMHg in Snow. Although atmospheric Hg depletion events resulted in

TABLE 1. Concentrations of THg and MMHg, and Percent of the THg that Was MMHg, in Snow Collected from Different Layers in the Snowpits

site	date	THg (ng/L)	MMHg (ng/L)	%MMHg
Surface Snow				
Alert over land	April 2001	5.34 ± 1.32 (2)	0.058 ± 0.004 (2)	1.1 ± 0.4 (2)
Alert over land	April 2002	2.86 ± 2.99 (4)	0.049 ± 0.025 (4)	2.5 ± 1.3 (4)
Alert over sea ice	April 2002	5.03 ± 4.45 (4)	0.051 ± 0.021 (4)	1.5 ± 0.7 (4)
John Evans Glacier	May 2002	1.03 ± 0.24 (5)	0.050 ± 0.021 (5)	5.1 ± 2.7 (5)
Overall average		3.16 ± 3.10 (15)	0.051 ± 0.019 (15)	2.9 ± 2.3 (15)
Spring Snow				
Alert over land	April 2001	1.30 ± 1.42 (4)	0.118 ± 0.114 (4)	20.6 ± 22.4 (4)
Alert over land	April 2002	5.31 ± 9.24 (4)	0.054 ± 0.019 (4)	9.0 ± 8.8 (4)
Alert over sea ice	April 2002	5.74 ± 10.25 (4)	0.067 ± 0.057 (4)	4.9 ± 3.4 (4)
Prince of Wales Icefield	May 2001	0.38 ± 0.21 (16)	0.090 ± 0.064 (16)	28.7 ± 22.5 (16)
John Evans Glacier	May 2002	0.62 ± 0.34 (5)	0.085 ± 0.030 (5)	16.5 ± 8.4 (5)
Overall average		1.78 ± 4.78 (33)	0.086 ± 0.062 (33)	20.6 ± 19.6 (33)
Previous Autumn Snow				
Alert over land	April 2001	0.59 ± 0.28 (3)	0.089 ± 0.060 (3)	13.9 ± 7.8 (3)
Alert over land	April 2002	0.89 ± 0.31 (4)	0.022 ± 0.004 (3)	3.0 ± 0.5 (3)
Alert over sea ice	April 2002	1.49 ± 0.69 (4)	0.054 ± 0.027 (4)	3.9 ± 1.9 (4)
Prince of Wales Icefield	May 2001	0.23 ± 0.13 (13)	0.090 ± 0.068 (14)	48.0 ± 43.3 (13)
John Evans Glacier	May 2002	0.14 ± 0.02 (5)	0.052 ± 0.007 (5)	37.3 ± 6.5 (5)
Overall average		0.52 ± 0.54 (29)	0.071 ± 0.055 (29)	31.3 ± 34.9 (28)
Snow Collected in Autumn				
Alert over land	October 2001	0.29 ± 0.04 (4)	0.068 ± 0.024 (4)	24.7 ± 9.9 (4)
Alert over land	November 2002	0.35 ± 0.07 (3)	0.081 ± 0.009 (3)	24.4 ± 8.1 (3)
Overall average		0.31 ± 0.06 (7)	0.074 ± 0.019 (7)	24.6 ± 8.4 (7)

deposition of Hg(II) into the upper layers of the snowpack (Figure 3), we hypothesized that these events would not alter MMHg concentrations in snow because Hg(0) is not oxidized directly to MMHg. This hypothesis is supported at Alert where atmospheric Hg depletion events did not alter the concentrations of MMHg in snowpacks (Figure 3). Concentrations of MMHg in all layers of all snowpacks sampled at Alert in 2001 and 2002 ranged between our detection limit of 0.020 ng/L and 0.151 ng/L, averaging 0.063 ± 0.052 ng/L ($n = 32$) (Figure 3). In April 2002, when snow was collected from both the plateau near the Global Atmospheric Watch laboratory and near the Ice Camp, concentrations of MMHg were on average slightly higher, but not significantly so, in the snowpack over the sea ice (Table 1). There appeared to be no significant photoreduction or demethylation of MMHg to either Hg(II) or Hg(0) in the Alert snowpacks because MMHg concentrations remained fairly constant over time (Figure 3).

Photoreduction of Hg in Surface Snow. From May 2 to 14, 2002, concentrations of THg in surface snow on John Evans Glacier were low, averaging 1.8 ± 0.84 ng/L even following a heavy snowfall on May 13 which resulted in a dramatic decline in concentrations of NSS SO₄ and Cl in the snowpack, as well as a slight drop in the pH of the snow (Figure 4). However, during a snowfall event on May 15–16, concentrations of THg in surface snow reached 16 ng/L, averaging 8.6 ± 4.8 ng/L during this two-day period. Once the snowfall event ended, concentrations of THg decreased rapidly to 3.9 ± 1.8 ng/L until late on the 21st when THg concentrations in the surface snow again rose to 8.4 ng/L even though there was no new deposition of snow. Concentrations remained high at 9.8 ± 4.2 ng/L until the 23rd. The highest concentrations of Hg(II) in the surface snow during this period were 11.4 ng/L and 14.3 ng/L, measured late on May 22 and early on May 23 following heavy fog, rime icing, and moderate winds. Concentrations of THg in the surface snow then decreased to 2.6 ± 0.96 ng/L from May 24 until June 2 when sampling of surface snow ceased (Figure 4).

Unfortunately we do not have atmospheric gaseous elemental Hg(0) concentrations from this area (or Alert) during this sampling period to determine whether the two peaks of THg in surface snow were the result of dry deposition of Hg(II) following atmospheric Hg depletion events. The timing of the first peak of THg in surface snow coincided with the deposition of new snow and a spike in Cl concentrations, and therefore the Hg could have originated over northern Baffin Bay along the path of the storm trajectory that brought the snow to the region. The second peak in concentrations of THg in surface snow occurred despite no new snowfall, during a period of heavy fog and rime icing thought ideal for Hg(0) oxidation by sunlight-induced heterogeneous reactions with the marine halogens Br and Cl (21, 22). Regardless of the mechanism of deposition, there was a rapid decline in Hg concentrations in surface snow following both events (Figure 4), as observed at Alert (Figure 3).

On May 13, prior to the first Hg deposition event, concentrations of total gaseous Hg in the interstitial airspaces of all layers of the snowpack were approximately 1.5 ng/m³ (Figure 5), similar to background concentrations normally found in the High Arctic atmosphere prior to atmospheric Hg depletion events (Figure 5). However, when concentrations of THg in the surface snow increased on May 15, concentrations of total gaseous Hg in the surface layers of snow also began to increase. As concentrations of THg in the surface snow decreased from 12.6 to approximately 6.4 ng/L in the following 2 days (May 16 and 17), concentrations of total gaseous Hg in the interstitial air of the surface layer of the snowpack increased sharply to 7.2 ng/m³, whereas concentrations in the lower snowpack remained at 1.5 ng/m³. Concentrations of total gaseous Hg varied little in two snowpacks sampled 1.5 km apart on May 17 (Figure 5).

Because we withdrew ~30 L of air to make our measurements, high concentrations of total gaseous Hg in interstitial air spaces of surface snow were likely diluted with low concentrations drawn from lower layers of the snowpack and the atmosphere above. Regardless, our observations

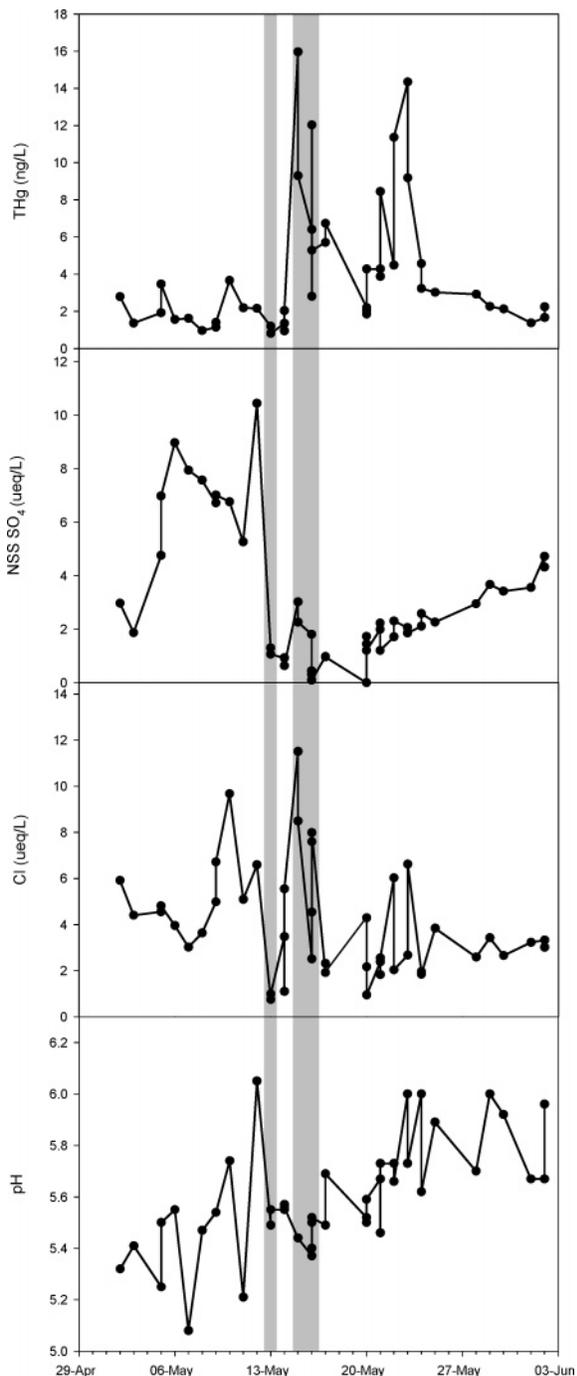


FIGURE 4. Concentrations of THg, NSS SO₄, and Cl and pH in surface snow collected on John Evans Glacier in 2002. Shaded vertical bars indicate periods of precipitation.

suggest two things: (1) there was a rapid photoreduction of Hg(II) in the surface snow to gaseous elemental Hg(0), and (2) because of the high concentrations of gaseous Hg(0) in the interstitial air spaces of the surface snow relative to presumed concentrations in the atmosphere of 1.5 ng/m³ or less, gaseous elemental Hg(0) diffused out of the snowpack. These results should not be surprising. Reduction of Hg(II) to gaseous elemental Hg(0) in snow has previously been well documented (36–39). In fact, Steffen et al. (35) found that during atmospheric Hg depletion events at Alert in 2000, concentrations of gaseous elemental Hg(0) in the interstitial air in snowpacks increased above ambient concentrations likely due to the photoreduction of Hg(II), resulting in a loss of some Hg from snowpacks back to the atmosphere. If Hg(II)

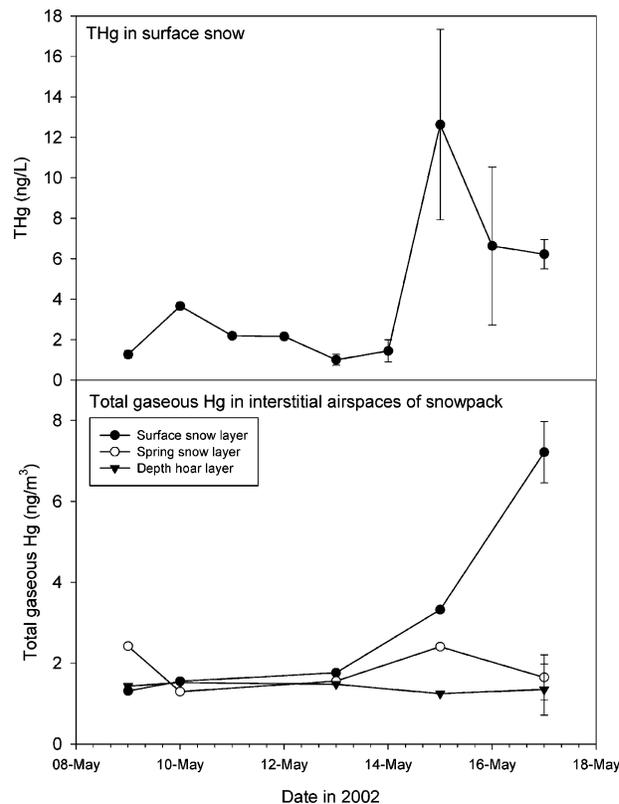


FIGURE 5. Concentrations of THg in surface snow collected on John Evans Glacier (top panel; also see Figure 4). Concentrations of total gaseous Hg (assumed to be primarily gaseous elemental Hg(0)) in the interstitial airspaces of the different layers of the snowpack (bottom panel).

reduction in the High Arctic is induced by light (particularly in the ultraviolet part of the spectrum) as found elsewhere, then reduction of Hg(II) throughout the upper layers of the snowpack should be accelerated by wind redistributing surface snow. This hypothesis is supported by our results from Alert in 2002, showing that the surface snow exposed to the sun following the second major depletion event had lower THg concentrations than the spring snow layer buried beneath it (Figure 5). As a result of photoreduction, at our specific sites on Ellesmere Island, it appears that most of the Hg(II) dry-deposited to snowpacks following atmospheric Hg depletion events remained in snowpacks for only a short period of time.

Net Deposition of THg and MMHg in Snow. Snow was collected for analyses of THg and MMHg from pits dug at Alert in 2001 and 2002, the Prince of Wales Icefield in 2001, and John Evans Glacier in 2002. Concentrations of THg in snowpacks ranged between 0.1 and 21.11 ng/L (Table 1). Concentrations of MMHg in the snowpack ranged between our detection limit of 0.020 ng/L and 0.281 ng/L (Table 1). Of the 84 snow samples analyzed for MMHg, 14.3% contained concentrations below our detection limit; 75% of these samples were from the depth hoar layer of the snowpack.

There was no relationship between concentrations of inorganic Hg (IHg; calculated as THg minus MMHg) and concentrations of MMHg in snowpacks (Figure 6). There was, however, a negative exponential relationship between THg and the percentage of the THg that was MMHg (Figure 6). More specifically, a large portion of the Hg in the snowpack was MMHg (up to 110%) at times when concentrations of MMHg were high and concentrations of IHg were very low and approaching our analytical limits of detection (Figure 6).

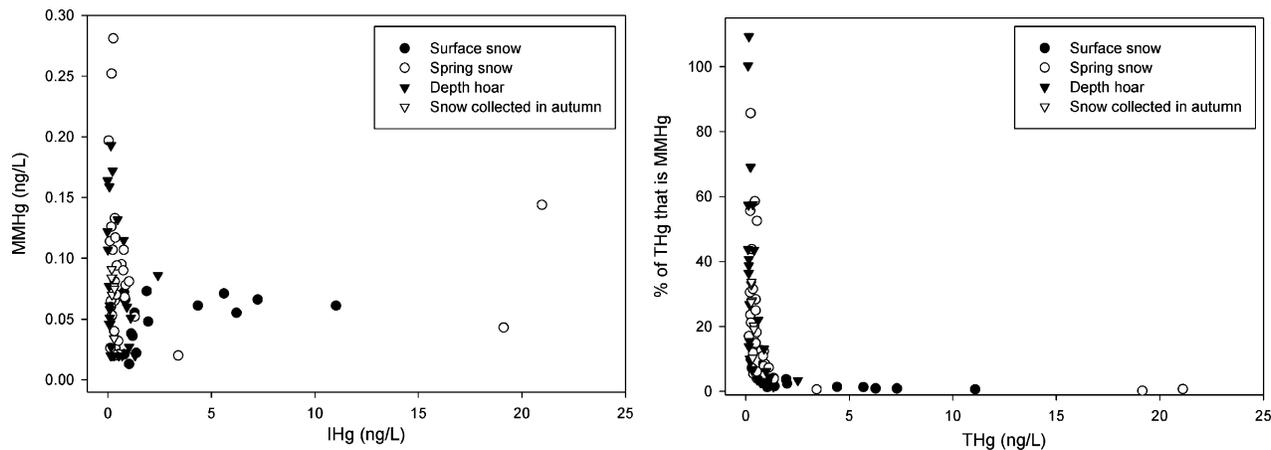


FIGURE 6. Relationship between inorganic Hg (IHg = THg minus MMHg) and MMHg, and percentage of the THg that is MMHg (%MMHg), in snowpack samples collected at Alert (on land and over the sea ice), Prince of Wales Icefield, and John Evans Glacier.

TABLE 2. Areal Quantities of THg and MMHg in Snow at Four Locations on Ellesmere Island

site	date	snow depth (mm water equivalents)	THg deposition (mg/ha)	MMHg deposition (mg/ha)
Alert over land	April 2001	154 ± 95 (4)	1.93 ± 2.51 (4)	0.10 ± 0.08 (4)
Alert over land	April 2002	139 ± 22 (4)	3.89 ± 4.98 (4)	0.03 ± 0.01 (4)
Alert over sea ice	April 2002	171 ± 48 (4)	5.92 ± 5.67 (4)	0.06 ± 0.03 (4)
Prince of Wales Icefield	May 2001	140 ± 41 (15)	0.39 ± 0.21 (15) ^a	0.12 ± 0.08 (15) ^a
John Evan's Glacier	May 2002	95 ± 10 (5)	0.46 ± 0.10 (5)	0.03 ± 0.01 (5)
Overall average		138 ± 49 (32)	1.72 ± 3.18 (32)	0.09 ± 0.07 (32)

^a Surface snow samples were not collected on the Prince of Wales Icefield, and as a result, deposition rates may be underestimated, especially for THg.

Concentrations of THg were on average highest in surface snow (3.2 ± 3.1 ng/L), and progressively lower in spring snow (1.8 ± 4.8 ng/L), depth hoar (0.52 ± 0.54 ng/L), and snow actually collected in the autumn prior to its transformation during winter into depth hoar (0.31 ± 0.06 ng/L) (Table 1). THg concentrations in snow from Alert were on average higher than concentrations in snow collected on the Prince of Wales Icefield and John Evans Glacier, primarily because the average concentrations calculated for Alert contained samples collected following atmospheric Hg depletion events (Figure 3).

Although average concentrations of THg decreased from the surface to the bottom of the snowpack, concentrations of MMHg were on average similar throughout (Table 1). As a result, the percentage of the THg that was MMHg increased from $2.9 \pm 2.3\%$ in surface snow to $21 \pm 20\%$ in the spring snow, and to $31 \pm 35\%$ in the depth hoar and $25 \pm 8.4\%$ in snow actually collected in the autumn.

Using the depth of the layered snowpack, water equivalent of the snow (eq 1), and measured THg and MMHg concentrations, we calculated *net* wet/dry areal deposition rates of Hg to the different areas we sampled. These calculated deposition rates were considered *net* instead of *gross* because of photoreduction of Hg(II) to Hg(0) in the snowpack following deposition of Hg(II) during atmospheric Hg depletion events. Although snowpacks were near their maximum annual depth at the time we sampled in April and May, and a large portion of springtime atmospheric Hg depletion events had already occurred in this region, these should also not be considered *net annual* deposition rates because a significant portion of annual precipitation on Ellesmere Island occurs during the Arctic summer. At the Alert and Eureka meteorological stations (Figure 1) operated by Environment Canada, for example, long-term (1971–2000) average annual precipitation rates were 154 mm and 76 mm, 60% and 52% of which fell as snow between September and May at these two

sites, respectively (40). The remaining precipitation fell between June and August, of which 26% and 70% was rain, not snow (40). Summer deposition may therefore provide a significant additional load of Hg to the High Arctic ecoregion.

On average, there was 1.7 ± 3.2 mg THg/ha in snowpacks sampled at all sites (Table 2). Net THg deposition to snowpacks was on average higher at Alert (1.9–5.9 mg/ha) than on the Prince of Wales Icefield and John Evans Glacier (0.4–0.5 mg/ha) (Table 2). The higher average net deposition rates calculated for Alert resulted from including in our calculations snowpacks with high concentrations of THg sampled following atmospheric Hg depletion events (Figure 3). For example, there was 11–14 mg THg/ha in the snowpack sampled near the Ice Camp and on the plateau near the Global Atmospheric Watch laboratory following the atmospheric Hg depletion event recorded at Alert on April 23–25 2002, but only 1.4–1.8 mg THg/ha at these sites on April 27–30.

Even during atmospheric Hg depletion events, combined *wet/dry* deposition rates at our sites on Ellesmere Island were lower than any *wet only* deposition rates measured in the United States and southern Canada (27–210 mg/ha) (41). Considering that dry deposition of Hg(II) in the United States, Canada and Scandinavia can be quite large relative to wet deposition (for example, throughfall and litterfall deposition can add 300–500% more THg to forested watersheds than wet deposition in the open (7)), even immediately following atmospheric Hg depletion events net deposition of THg to snowpacks at our sampling sites on Ellesmere Island appears to be very low.

There was on average 0.09 ± 0.08 mg MMHg/ha in the snowpacks. This compares to annual wet depositions rates of 0.8–4.1 mg MMHg/ha in Scandinavia, 0.9 mg MMHg/ha in Wisconsin, and 0.9 mg MMHg/ha at the Experimental Lakes Area in northwestern Ontario (summarized in 7 and 42). In forested watersheds, throughfall and litterfall deposi-

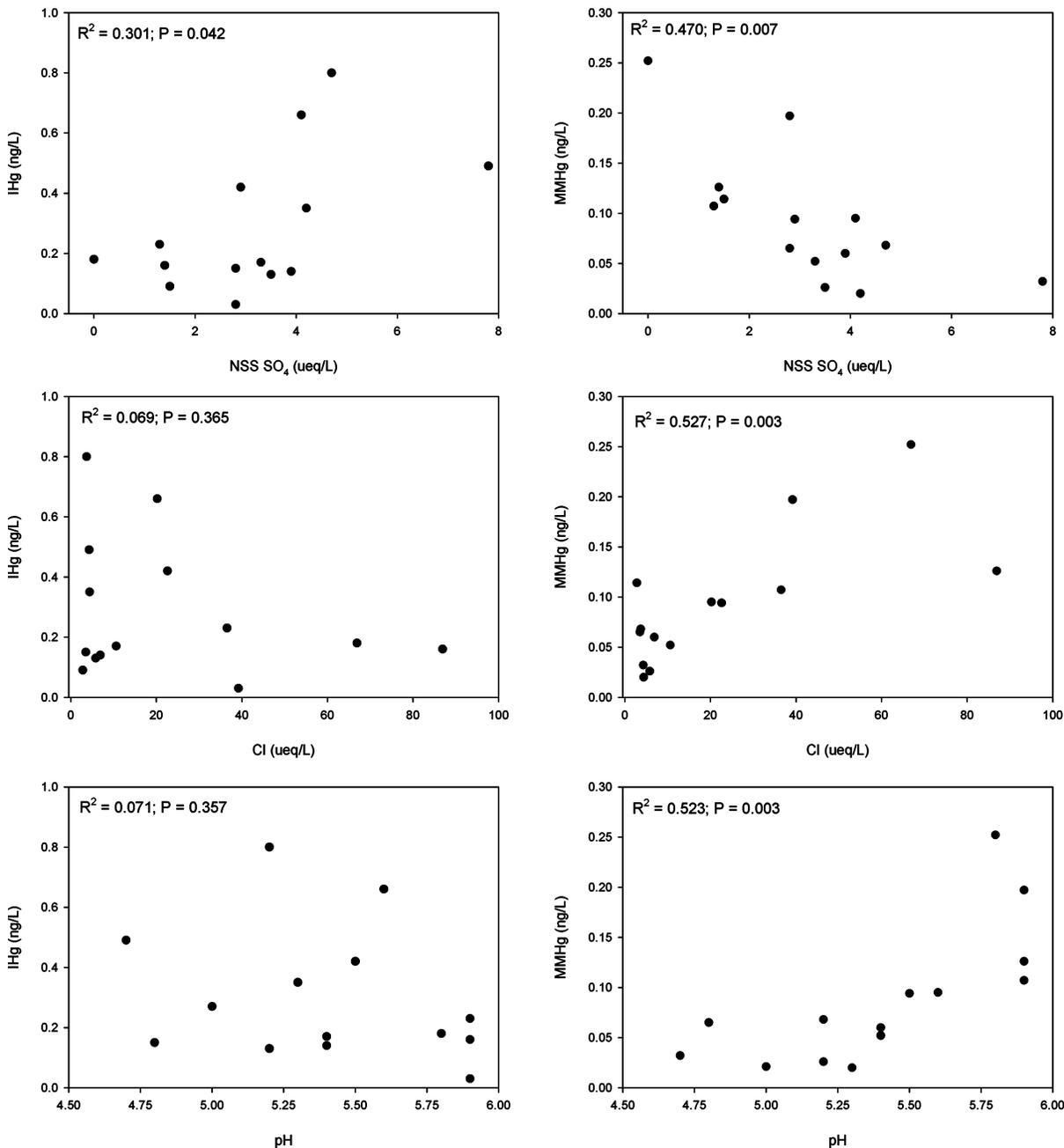


FIGURE 7. Relationship between concentrations of inorganic Hg (IHg = THg – MMHg) and MMHg in surface snow and concentrations of NSS SO₄ and Cl and snow pH.

tion can further enhance MMHg deposition by 200–600% relative to wet deposition in the open (7). As observed with THg, on average, MMHg deposition in the High Arctic appears to be very low. However, localized deposition of MMHg to snowpacks can be quite high as we describe below.

Relationship between Hg Concentrations in Snow and Snow Chemistry, and Sources of Hg to the Snowpack. We correlated Hg concentrations with concentrations of NSS SO₄ and Cl, as well as pH, in the snow collected on the Prince of Wales Icefield in May 2001 (Figure 7). Because a large portion of the THg in some samples was MMHg, we calculated concentrations of IHg in snow for statistical purposes.

In snow deposited in spring 2001 on the Prince of Wales Icefield, IHg was marginally correlated with NSS SO₄ (Figure 7), suggesting that there was a possible background anthropogenic source of IHg to the high Arctic. Up to 80% of the NSS SO₄ found in the surface of Arctic snowpacks has been shown to originate from industrial pollutant sources (SO₂)

(30, 31), and similar to Hg(II), deposition of NSS SO₄ is enhanced by photochemical reactions after polar sunrise (43). Concentrations of IHg in snow deposited in the spring were not correlated with concentrations of Cl or H⁺ (Figure 7).

MMHg concentrations in the spring snow were negatively correlated with NSS SO₄, but positively correlated with Cl and pH (Figure 7). The positive relationship between concentrations of MMHg and Cl and pH in snowpacks suggests a marine source of MMHg, because Cl in the snowpack most likely originated from sea salt aerosols, which also neutralize sulfuric acid aerosol (affecting pH). Methylated Hg species have been found in subthermocline North Atlantic waters, with dimethyl Hg (DMHg) typically being the most dominant (44). In regions of deep-water upwelling or deep winter thermocline mixing, DMHg can be brought to the surface and subsequently lost to the atmosphere by gas exchange. Atmospheric DMHg is likely rapidly photolyzed

to MMHg ($\text{Cl} + \text{CH}_3\text{HgCH}_3 \rightarrow \text{CH}_3\text{HgCl} + \text{CH}_3$) (45), making the ocean a potential source of atmospheric MMHg. Because 58% of the air masses arriving at the Prince of Wales Icefield between February and April in 2001 originated over Baffin Bay, whereas only 8% of them originated from the open water regions of the North Atlantic, we hypothesize that MMHg found in snowpacks on the Icefield originated from DMHg fluxing through leads in the sea ice and polynyas, in particular the large North Water Polynya located between southern Ellesmere Island and Greenland. Future climatic warming and ice melt in the far north may enhance the deposition of MMHg to snowpacks throughout the High Arctic if the MMHg in snowpacks originates from DMHg fluxing through open water regions in sea ice.

Two studies in polar regions have suggested a DMHg source of high concentrations of MMHg in snow (47, 48), whereas other studies have proposed that there are coastal sources of MMHg in precipitation in North America (42, 49, 50). Regardless of the source of MMHg in snowpacks, we hypothesize that MMHg-Cl (or MMHg bound to another marine halogen) is less prone to demethylation in snowpacks than Hg(II) is prone to photoreduction because of the negative exponential relationship we observed between IHg and MMHg in snow collected from our various sites on Ellesmere Island (Figure 6). In other words, once deposited into snowpacks, Hg(II) is removed through photoreduction to Hg(0), whereas MMHg remains largely unaltered.

Neither IHg nor MMHg concentrations were significantly correlated with solute concentrations in depth hoar collected on the Prince of Wales Icefield. However, snow chemistry likely changed during temperature gradient metamorphism during winter, masking any relationships between Hg concentrations and snow chemistry that might have existed when the snow was originally deposited in the fall. Furthermore, fall snow tends to have low solute concentrations because the High Arctic atmosphere is cleansed of aerosols by precipitation in the spring and summer.

In the High Arctic, some marine animals contain concentrations of MMHg high enough to cause exposure risks to northern peoples consuming them as traditional foods (e.g., 17). Concentrations of MMHg in snowpacks we sampled were as high as 0.26 ng/L (Figure 7). For comparison, concentrations of 0.08–0.25 ng/L have been observed in runoff from catchments containing wetlands in the boreal ecoregion, which are known to be important sites of MMHg production (12). In the High Arctic near open water leads and polynyas, there may be a pulse of MMHg into marine ecosystems each spring at snowmelt, which would be directly available for accumulation into the Arctic marine food web.

THg and MMHg in Snowmelt and Glacial Runoff. Average concentrations of THg in supraglacial runoff were very low in both 2001 and 2002 (0.72 ± 0.90 and 0.73 ± 0.17 ng/L, respectively) and tended to decline over time as snowmelt progressed (Table 3). In 2002, when snow was collected on John Evans Glacier in May prior to snowmelt, average concentrations of THg throughout the snowpack were 0.60 ng/L (Table 1, Figure 4), similar to concentrations found in supraglacial runoff (Table 3). Concentrations of THg in filtered supraglacial runoff water were on average only 0.54 ± 0.68 and 0.41 ± 0.14 ng/L in 2001 and 2002, respectively, suggesting that between 18 and 65% of the THg was bound to particles greater than $0.45 \mu\text{m}$ in size. In 2001 when samples were collected from supraglacial pools resulting from runoff, average concentrations of THg (0.52 ± 0.29 ng/L) were similar to concentrations found in supraglacial runoff (Table 3). As in supraglacial runoff, 30–64% of the THg in pools was bound to particles (Table 3).

Average concentrations of THg in unfiltered runoff water routed under John Evans Glacier were much higher (2.6 and 2.0 ng/L in 2001 and 2002, respectively) than those in

supraglacial runoff, but between 76 and 96% of the THg was bound to particulates greater than $0.45 \mu\text{m}$ because filtered water contained on average only 0.25 ng/L (Table 3).

Concentrations of MMHg in snowpacks sampled on John Evans Glacier in May 2002 prior to snowmelt ranged between 0.046 and 0.133 ng/L. However, concentrations of MMHg in the initial supraglacial runoff samples we collected prior to a rain event on July 14 and 15 reached 0.24 ng/L, constituting about 25% of all the Hg in the sample. Between 75 and 90% of the MMHg was bound to particles greater than $0.45 \mu\text{m}$ because filtered samples contained less than 0.06 ng/L MMHg (Table 3). Because concentrations of MMHg in initial snowmelt were on average more than double the average concentrations found in snowpacks prior to melt (Table 1), there appeared to be either sublimation of snow or preferential leaching of MMHg from snowpacks at the start of snowmelt (51), further accentuating the pulse of MMHg to downstream marine or freshwater ecosystems at the spring onset of biological activity. However, we cannot exclude the possibility that active microbial Hg(II) methylation may also be occurring on the surface of John Evans Glacier. Complex microbial ecosystems have been documented in individual cryoconites (depressions in the ice surface containing microbial mats) (52, 53).

From July 13 to 19, 2002, average concentrations of MMHg in unfiltered supraglacial runoff (0.13 ± 0.08 ng/L) were 2.5 times higher than those in unfiltered subglacial runoff (0.05 ± 0.01 ng/L) (Table 3). Although there was a large source of particle-bound THg in subglacial runoff, virtually none of it was MMHg. Much of the dissolved phase MMHg appeared to go from snowmelt through the subglacial system with little change because average concentrations of MMHg in filtered water were identical in supra and subglacial runoff. However, on average, 20% of the dissolved Hg exiting the bottom of the glacier was methylated compared with only 12% in supraglacial runoff (Table 3). It is likely that the percentage of the dissolved Hg that was methylated was higher in subglacial runoff than in snowmelt because Hg(II) was removed to particles in the subglacial environment while dissolved phase MMHg was not.

John Evans Glacier is underlain primarily by limestone and dolomite, with some anhydrite and gypsum, bedrock. Rock flour likely constituted the majority of particulate matter to which Hg was bound in our subglacial samples. High concentrations of NSS SO_4 in subglacial runoff (on average $2300 \mu\text{eq/L}$ in 2001 and 2002) originated from the dissolution of gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$) and anhydrite (CaSO_4) because concentrations of NSS SO_4 in snowmelt on the surface of the glacial were less than $20 \mu\text{eq/L}$. Although sulfate-reducing bacteria, known to actively methylate Hg(II) in the environment, have been found beneath John Evans Glacier (54), any subglacially produced MMHg would likely go undetected due to strong dilution by surface waters. We found that dissolved phase MMHg moved from snowmelt through the subglacial system with little change in concentration (Table 3).

Concentrations of THg and MMHg in Ponds and Lakes. Average concentrations of THg in small ponds less than 1 ha in surface area in Quttinirpaaq National Park on Ellesmere Island (2.66 ± 2.70 ng/L) were 2.5 times those found in the larger ponds and lakes (1.11 ± 0.48 ng/L) (Table 4). Average concentrations of MMHg in small ponds (0.63 ± 0.85 ng/L), though, were 16 times higher than those in the larger systems (0.04 ± 0.03 ng/L). As a result, the percentage of the THg that was MMHg was much higher in small ponds ($19.5 \pm 12.1\%$ MMHg) than in the larger ponds and lakes ($4.5 \pm 4.2\%$ MMHg) (Table 4).

Both high concentrations of MMHg and a high percentage of the THg methylated in aquatic ecosystems often indicate elevated rates of net methylation there (10, 55, 56). For

TABLE 3. Concentrations of THg and MMHg in Unfiltered and Filtered Runoff Water Samples Collected on John Evans Glacier in 2001 and 2002

site	date	THg unfiltered (ng/L)	THg filtered (ng/L)	MMHg unfiltered (ng/L)	MMHg filtered (ng/L)	%MMHg unfiltered	%MMHg filtered	NSS SO ₄ (μeq/L)	Cl (μeq/L)	pH
2001										
supraglacial runoff	Jun 20	1.76	1.32					14.6	21.5	7.65
supraglacial runoff	Jul 13	0.22	0.15					5.2	12.4	7.16
supraglacial runoff	Jul 30	0.17	0.14					17.6	12.8	8.13
overall average		0.72 ± 0.90	0.54 ± 0.68					12.5 ± 6.5	15.6 ± 5.1	7.65 ± 0.49
Nunatak Lake	Jun 23	0.52	0.30					0.25	0.11	7.34
Pond	Jul 18	0.23	0.16					22.8	8.3	9.02
Ridge Lake Moulin	Jul 28	0.80	0.29					6.3	11.3	7.19
overall average		0.52 ± 0.29	0.25 ± 0.08					9.8 ± 11.7	6.6 ± 5.8	7.85 ± 1.02
subglacial outburst	Jun 30	2.07	0.24					4150	103	8.74
subglacial outburst	Jun 30	1.39	0.17					3610	61.8	8.28
subglacial runoff	Jul 15	3.03	0.13					2140	4.5	6.90
subglacial runoff	Jul 29	4.06	0.39					583	14.8	7.40
overall average		2.64 ± 1.16	0.23 ± 0.11					2620 ± 1600	46.0 ± 45.4	7.83 ± 0.83
2002										
supraglacial runoff 1	Jun 28	0.93	0.60	0.235	0.057	25.3	9.5	3.1	9.8	7.25
supraglacial runoff 2	Jul 13	0.82	0.29	0.213	0.020	26.0	3.8	7.9	6.7	8.08
supraglacial runoff 3	Jul 18	0.60	0.42	0.086	0.075	14.3	17.9	1.1	4.4	
supraglacial runoff 1	Jul 18	0.58	0.33	0.080	0.051	13.8	15.5	4.4	7.4	6.60
overall average		0.73 ± 0.17	0.41 ± 0.14	0.154 ± 0.082	0.049 ± 0.027	19.9 ± 6.7	11.7 ± 6.3	4.1 ± 2.9	7.1 ± 2.2	7.31 ± 0.74
subglacial outburst	Jul 4	1.48		0.036		2.4		1580	18.6	7.43
subglacial runoff	Jul 12	2.35	0.57	0.064	0.054	2.7	9.5	2990	35.3	7.74
subglacial runoff	Jul 16	1.81	0.19	0.127	0.060	7.0	31.6	1990	7.5	7.88
subglacial runoff	Jul 19	1.52	0.17	0.034	0.041	2.2	24.1	2090	9.7	8.60
subglacial runoff	Jul 23	3.01	0.22	0.050	0.035	1.7	15.9	1530	7.1	8.80
overall average		2.03 ± 0.65	0.29 ± 0.19	0.062 ± 0.038	0.048 ± 0.012	3.2 ± 2.2	20.3 ± 9.6	2040 ± 587	15.6 ± 11.9	8.09 ± 0.58

TABLE 4. Concentrations of THg and MMHg in Unfiltered Water Collected from Ponds and Lakes on Ellesmere Island

site	surface area ^a (ha)	temp (°C)	latitude	longitude	THg (ng/L)	MMHg (ng/L)	%MeHg	pH	DOC (mg/L)
EP-14	0.01	19.0	81°49.236'N	71°32.279'W	3.03	1.296	42.8	8.9	31.8
EP-13	0.02	18.0	81°48.710'N	71°33.614'W	2.63	0.917	34.9	8.4	27.2
EP-10	0.05	14.5	81°48.965'N	71°24.995'W	1.00	0.181	18.1	8.5	8.1
EP-18	0.05	17.5	81°49.306'N	71°21.045'W	10.94	3.043	27.8	8.3	13.4
EP-4	0.06	18.0	81°50.721'N	71°23.928'W	2.02	0.526	26.0	8.9	31.1
EP-6	0.06	19.0	81°50.773'N	71°24.815'W	1.81	0.028	1.5	7.9	5.6
EP-20	0.09	18.5	81°49.533'N	71°19.999'W	2.02	0.458	22.7	8.0	21.6
EP-12	0.13	18.5	81°48.590'N	71°34.732'W	2.43	0.247	10.2	8.2	36.0
EP-15	0.14	15.0	81°49.899'N	71°31.629'W	1.32	0.230	17.4	8.5	9.2
EP-5	0.16	19.0	81°50.752'N	71°23.849'W	2.57	0.406	15.8	8.7	29.6
EP-AB	0.63	6.0	81°58.490'N	80°04.140'W	0.86	0.040	4.6	7.9	1.7
EP-11	0.76	11.0	81°48.650'N	71°26.922'W	1.27	0.160	12.6	8.9	9.1
average		16.2 ± 4.0			2.66 ± 2.70	0.628 ± 0.846	19.5 ± 12.1	8.4 ± 0.4	18.7 ± 12.1
EP-7	1.4	17.5	81°50.337'N	71°20.060'W	0.72	0.031	4.3	8.4	12.5
EP-22	1.6	8.5	81°49.260'N	71°45.040'W	0.67	0.133	19.9	8.5	3.9
EP-I	2.4	5.5	82°55.110'N	66°51.880'W	0.86	0.029	3.4	8.5	2.6
EP-24	2.8	5.0	81°49.041'N	71°46.886'W	1.01	0.020	2.0	7.5	0.7
EP-Z	4.1	14.0	81°00.500'N	78°13.030'W	0.60	0.020	3.4	8.5	2.3
EP-P	6.0	14.0	81°36.170'N	73°53.110'W	1.44	0.101	7.0	8.2	4.7
EP-O (Glacier Lake)	6.3	0.5	82°16.000'N	77°53.320'W	2.35	0.029	1.2	7.5	0.7
EP-V	6.7	12.5	81°13.150'N	72°19.460'W	1.14	0.055	4.8	8.8	5.0
EP-AA (Kettle Lake)	7.7	15.0	81°23.800'N	76°47.141'W	0.94	0.042	4.5	8.7	4.8
EP-C (Brainard Lake)	18	5.0	81°45.810'N	68°10.320'W	1.65	0.020	1.2	8.0	3.6
EP-J (Ward Hunt Island)	35	4.0	83°05.300'N	74°09.870'W	1.17	0.052	4.5	8.3	1.0
EP-L	99	5.5	82°58.600'N	75°24.700'W	1.67	0.061	3.7	8.3	1.4
EP-W	114	7.5	81°04.890'N	74°20.670'W	1.35	0.045	3.3	8.3	0.6
EP-F	125	2.5	82°25.200'N	68°12.770'W	1.56	0.020	1.3	8.1	1.5
EP-U (Lake Carolyne)	161	6.0	81°17.960'N	70°43.480'W	0.70	0.020	2.9	8.3	0.9
EP-N	165	4.5	82°49.590'N	77°56.240'W	1.07	0.038	3.6	7.7	2.4
EP-A (Craig Lake)	1455	12.5	81°50.340'N	68°51.130'W	0.67	0.046	6.9	8.5	3.1
EP-19 (Lake Hazen)	54,200	5.5	81°49.369'N	71°20.184'W	0.49	0.020	4.1	7.7	1.1
average		8.1 ± 4.9			1.11 ± 0.48	0.043 ± 0.030	4.5 ± 4.2	8.2 ± 0.4	2.9 ± 2.8

^a Ponds and lakes arranged in ascending order by surface area.

example, at the Experimental Lakes Area, the average percentage of THg that was methylated was approximately 1% in precipitation, and 3–15% in runoff from catchments containing wetlands (12). Some of the highest percentages of THg as MMHg ever recorded (averaging 30%, but reaching 70%) have been found in reservoirs, such as those created for hydroelectricity production, where decomposition of flooded organic matter fuels high rates of microbial Hg(II) methylation (57, 58).

Following partial drydown each summer, vegetation such as grasses (*Carex* spp.) and cottongrass (*Eriophorum* spp.) grow around the periphery of many of the small ponds that we sampled (Figure 8). When the vegetation in these shallow ponds is inundated the following year with snowmelt, it likely decomposes. Because these ponds are shallow with dark bottom sediments that attenuate solar heat flux, they warm faster and to a greater extent than the larger and deeper lakes. For example, the average surface temperature of the small ponds (16.2 ± 4.0 °C) was twice that of the larger ponds and lakes (8.1 ± 4.9 °C) (Table 4). The warm sediments likely influence the intensity of microbial activity, as has been observed in small ponds on the Hudson Bay lowlands (59). In fact, we found an exponential relationship between surface water temperatures and concentrations of DOC (Table 4, Figure 9), indicating active microbial decomposition of organic carbon in the warm ponds, and a significant correlation between concentrations of DOC and the percentage of the THg that was methylated (Figure 10). The microbial methylation of Hg(II) is likely linked to the decomposition of flooded organic matter, as was seen during the experimental flooding of a small wetland at the Experimental Lakes Area to create a reservoir (57, 58). There, microbial activity in the open water region increased 5–10 times after flooding, as evidenced by high concentrations of DOC and dissolved CO₂ and CH₄. In the first years of flooding,

average annual concentrations of MMHg in reservoir water increased 10-fold from 0.08 ng/L to 0.80 ng/L, reaching 3.0 ng/L in mid summer when water temperatures and microbial activity were at their highest. Concentrations of THg, however, remained relatively constant at ~2.5 ng/L regardless of flooding. Both MMHg and THg concentrations in the experimental reservoir were very similar to those seen in many of the warm, small ponds we sampled on Ellesmere Island.

These findings may help us understand MMHg contamination in some freshwater food webs in the High Arctic. However, these small ponds tend to be isolated on the landscape, and during the summer when Hg(II) methylation rates are at their highest, primarily support dense populations of zooplankton (not fish) and sometimes waterfowl as the top-level predators in the food web.

Overall Significance of our Findings. Our results from Ellesmere Island show that there is a low net accumulation of Hg(II) in winter snowpacks, even though there were atmospheric Hg depletion events which temporarily elevated concentrations of Hg(II) in the upper layers of snowpacks. Once deposited, the Hg(II) appeared to be quickly photoreduced to Hg(0), which then fluxed back to the atmosphere. More importantly, we found quite high concentrations of MMHg in snowpacks and initial snowmelt at some locations. Because Hg(II) requires methylation prior to accumulating through food webs, it is intriguing to discover that there is a pulse of already methylated Hg to Arctic ecosystems at spring melt. We hypothesize that at least some of the MMHg found in snowpacks had a marine origin, possibly as DMHg fluxing through open water regions in the sea ice. As a result, climate warming and the thinning and melting of sea ice may partially explain why concentrations of MMHg in certain marine mammals used as traditional food by aboriginal peoples of the north have increased over the past few decades



FIGURE 8. Lakes EP-I and EP-13 in Quttinirpaaq National Park. There was no vegetative growth near EP-I, whereas EP-13 inundated vegetation such as *Carex* spp. grasses and cottongrass. At the time of sampling, water temperatures in EP-I and EP-18 were 5.5 and 18 °C, respectively. The percentage of the THg that was methylated in EP-I (3.4%) was 10 times less than in EP-13 (35%) (Table 4). Photo credits: B. Keatley.

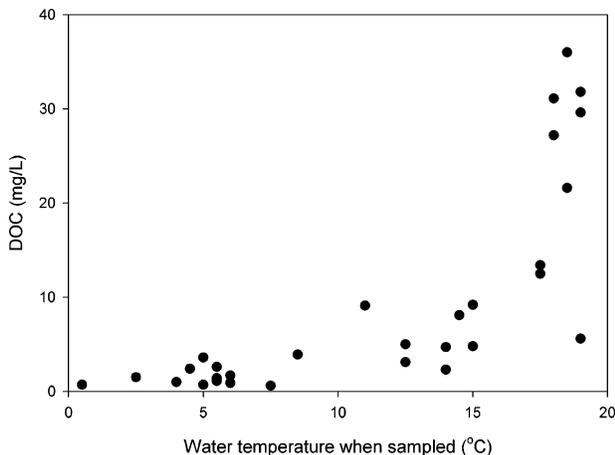


FIGURE 9. Relationship between surface water temperature and DOC concentrations in lakes and ponds in Quttinirpaaq National Park.

(17). However, active microbial Hg(II) methylation in the sediments of warm and shallow ponds also appears to be a source of MMHg to High Arctic freshwater systems that we studied.

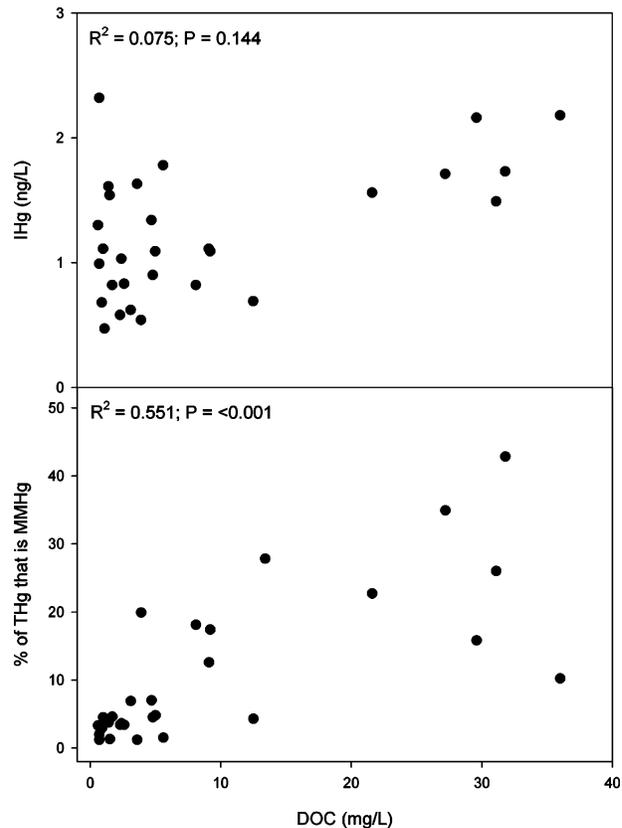


FIGURE 10. For lakes and ponds in Quttinirpaaq National Park, the relationship between DOC concentrations and inorganic Hg (IHg = THg minus MMHg) (top panel) and the percentage of the THg that is MMHg (bottom panel).

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