

Rapid Reduction and Reemission of Mercury Deposited into Snowpacks during Atmospheric Mercury Depletion Events at Churchill, Manitoba, Canada

JANE L. KIRK,^{*,†}
VINCENT L. ST. LOUIS,[†] AND
MARTIN J. SHARP[‡]

Department of Biological Sciences, and Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3

Mercury (Hg) in some Arctic marine mammals has increased to levels that may be toxic to Northern peoples consuming them as traditional food. It has been suggested that sunlight-induced atmospheric reactions called springtime atmospheric Hg depletion events (AMDEs) result in the loading of ~150–300 tons of Hg to the Canadian Arctic archipelago each spring and that AMDEs are the ultimate source of Hg to Arctic foodwebs. AMDEs result from the oxidation of gaseous elemental Hg⁰ (GEM) in Arctic atmospheres to reactive gaseous Hg (RGM) and particulate Hg (pHg), both of which fall out of the atmosphere to snowpacks. We studied the springtime cycling of Hg between air and snowpacks near Churchill, Manitoba, for 2 years to determine the net input of Hg to Hudson Bay from AMDEs. In 2004, we monitored atmospheric concentrations of GEM, pHg, and RGM while simultaneously measuring concentrations of total Hg (THg) in surface snow collected over the sea ice on Hudson Bay. During numerous springtime AMDEs, concentrations of THg in surface snow increased, often to over 60 ng/L, demonstrating that AMDEs resulted in deposition of oxidized Hg (Hg(II)) to snowpacks. However, immediately following AMDEs, average concentrations of THg in snow declined drastically from between 67.8 ± 97.7 ng/L during AMDEs to only 4.25 ± 1.85 ng/L four or more days following them. In 2003, we measured THg in surface snow collected daily over the sea ice and total gaseous Hg (TGM) concentrations in the interstitial airspaces of snowpacks. When concentrations of THg in the surface snow decreased, concentrations of TGM in interstitial airspaces of the snowpack increased sharply from between ~1.4–3.4 ng/m³ to between ~20–150 ng/m³, suggesting that there was a reduction of deposited Hg(II) to GEM, which then diffused out of snowpacks. At snowmelt in both 2003 and 2004, average concentrations of THg in meltwater collected over Hudson Bay were only 4.04 ± 2.01 ng/L. Using concentrations of THg in meltwater and snow water equivalent, we estimated a *net* springtime loading of only 2.1 ± 1.7 mg/ha of Hg to Hudson Bay from AMDEs, indicating that only a small portion of the

Hg(II) deposited during AMDEs enters Hudson Bay each spring.

Introduction

Monomethyl mercury (MMHg) is a vertebrate neurotoxin present in some Canadian Arctic marine mammals and fishes at concentrations higher than Canadian marketing guidelines of 0.5 µg/g (1, 2). In western Hudson Bay, for example, Hg concentrations in the livers of beluga whales and ring seals are some of the highest in the Canadian north and have increased up to 10-fold over the past 15–20 years (1). Some Northern peoples subsisting mostly on traditional diets of fish and/or marine mammals were found to have blood MMHg concentrations that put them at risk of neurological damage (3). Peoples of some northern communities are continually monitored for Hg exposure, yet the origin of MMHg contamination in the Arctic is not known.

Recently it has been argued that springtime “atmospheric Hg depletion events” (AMDEs), are to blame for high concentrations of MMHg in Arctic foodwebs (4–7). Gaseous elemental Hg⁰ (GEM) concentrations in the Arctic atmosphere are typically ~1.7 ng/m³ (4, 8). However, during AMDEs, which begin at polar sunrise and end when air temperatures approach 0 °C, concentrations of GEM frequently drop well below 1 ng/m³ (4, 7). There is now mounting evidence that GEM is oxidized to particulate Hg (pHg) and reactive gaseous mercury (RGM) by sunlight-induced reactions with halogen oxide radicals or halogen atoms (particularly BrO and Br) present over sea ice (7, 9–12). Both RGM and pHg have higher dry deposition velocities than GEM and can quickly fall out of the atmosphere.

Since their discovery in 1995 at Alert in Nunavut, Canada (4), AMDEs have been observed in many polar regions (e.g., refs 7, 12–14), as well as in the sub-Arctic at Kuujjuarapik/Whapmagoostui on the eastern coast of Hudson Bay in Quebec, Canada (15), and have been implicated as the source of elevated concentrations of total Hg (THg) found in surface snow in the Canadian Arctic and Hudson Bay region (6, 7, 16). With the use of atmospheric concentrations of pHg and RGM measured during AMDEs, it has been estimated that ~150–300 tons of Hg(II) is deposited onto the Canadian Arctic archipelago each spring (7, 17). Furthermore, it has been suggested that a portion of the oxidized Hg (Hg(II)) is methylated to MMHg in the marine environment, then taken up by organisms and bioaccumulated through northern foodwebs (4, 6, 17). It has been hypothesized that AMDEs are recent phenomena resulting from Arctic climate change, particularly temperature warming and increased atmospheric circulation, which increase production and transport of chemicals involved in AMDEs (7).

Although AMDEs have been studied in detail (4–7, 9–15, 17, 18), the long-term fate of the Hg(II) deposited to snowpacks during AMDEs has not been examined. This is somewhat surprising since the exchange of Hg between snowpacks and the atmosphere is known to be extremely dynamic (16, 19–25) and Hg(II) in snowpacks can be reduced by UV-B-initiated reactions to GEM then reemitted to the atmosphere (19, 20, 22, 23).

We monitored AMDEs and Hg deposition to snow over the sea ice of western Hudson Bay continuously to quantify the *net* springtime loading of Hg(II) to a marine ecosystem. Our results suggest that, in polar regions, Hg(II) in snowpacks is (photo)reduced to GEM and emitted to the atmosphere resulting in little of the Hg(II) deposited during AMDEs

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

[†] Department of Biological Sciences.

[‡] Department of Earth and Atmospheric Sciences.

entering the marine ecosystem at snowmelt. As a result of these findings, we have begun exploring other potential sources of MMHg to Arctic marine environments (24, 26).

Methods

Study Site. All samples were collected at or near the Churchill Northern Studies Center (CNSC), located on the western coast of Hudson Bay ~23 km east of Churchill, Manitoba, Canada (Figure S1 in the Supporting Information). The CNSC is situated in the Hudson Plains Ecozone at ~4 m above sea level and ~4 km south of the Hudson Bay shoreline among wetlands, tundra, and stunted boreal forest. Annual average temperature and precipitation (1971–2000) at the Churchill Environment Canada meteorological station are -6.9 ± 1.3 °C and 430 ± 83 mm, respectively (27).

Sampling. *Detection of AMDEs.* In 2004, Tekran analyzers (model 2537A total Hg vapor analyzer, model 1130 RGM speciation unit, and a model 1135 pHg analyzer speciation unit) were used to quantify atmospheric concentrations of GEM, RGM, and pHg. The RGM and pHg collection modules were mounted on a platform on the edge of the CNSC roof from March 22 to June 4. The inlet was ~10 m above ground and far from sources of potential Hg contamination from building emissions. In June, the Tekrans were moved to the roof of a nearby smaller building due to increased use of the CNSC.

The Tekrans and their operation are described fully in the Supporting Information as well as in ref 7. Automated calibrations were performed every 28 h using an internal permeation source. Just prior to departure for the field, manual calibrations were carried out in the laboratory by injecting a known quantity of GEM into the 2537A Tekran. Automated and manual calibrations were within 5% of each other. Unfortunately, calibration standards for RGM and pHg are not available. Therefore, RGM and pHg are operationally defined, and the concentrations discussed throughout the paper should not be considered absolute. Method detection limits (MDL) for measuring GEM, RGM, and pHg using Tekrans have been determined previously by Aspmo et al. (28) and are 0.17 ng/m³, 16 pg/m³, and 7 pg/m³, respectively.

Deposition of Oxidized Hg to Snowpacks during AMDEs. To determine deposition patterns of Hg oxidized during AMDEs in 2004, we sampled surface snow for analysis of THg (which includes both Hg(II) and MMHg) and MMHg from a site 1 km off shore on the Hudson Bay sea ice (Figure S1). Surface snow samples were collected into 250 mL wide mouth Teflon bottles with a Teflon scoop. Teflonware was acid-washed prior to use in the field, and the standard two person “clean hands, dirty hands” Hg sampling protocol was used for sample collection to minimize potential contamination (29). Snow samples for THg analysis were collected almost every day, whereas samples for MMHg analysis were acquired every 2–3 days.

Snow samples were stored frozen until analysis at the University of Alberta Low-Level Hg Analytical Laboratory. Snow for THg analyses was melted in the dark and preserved with concentrated trace metal grade HCl equal to 0.2% of the sample volume. THg concentrations were determined using cold vapor atomic fluorescence spectrophotometry (CVAFS, Tekran model 2500), as described in ref 30, and Star Chromatography Workstation software (Varian Inc., Mississauga, ON) for peak area integration. Snow for MMHg analyses was melted in the dark just prior to analysis. Because snow samples contained low concentrations of organic matter, they were added directly to bubblers for ethylation in the aqueous phase followed by sparging onto carbo traps. Ethylated Hg species were separated by GC, pyrolyzed to GEM at 800 °C, and detected by CVAFS as in refs 31 and 32.

MDLs for THg and MMHg analyses were 0.05 and 0.015 ng/L at blank levels of 0.04–0.07 and 0.015 ng/L, respectively.

Samples in which MMHg concentrations were below the MDL were assigned a concentration of 0.015 ng/L. Approximately 20% of THg and MMHg samples were analyzed in duplicate and were within 10% and 20% of each other, respectively. Spike recoveries for THg and MMHg were generally >90% and >80%, respectively. Concentrations of THg and MMHg in snow samples that were split and analyzed in both the Low-Level Hg Analytical Laboratory and at Flett Research Ltd. (Winnipeg, Manitoba) agreed to within 5% of each other.

To observe the spatial and long-term deposition patterns of Hg(II) on Hudson Bay, we sampled snow from different depths in the snowpack at three sites on the sea ice (~2.5, 5, and 7 km from the shoreline) three times during the spring. The spring snowpack in northern regions generally consists of three distinct layers (33). The surface layer, comprised 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. The middle layer of the snowpack usually consists of snow deposited during the spring. The bottom layer consists of coarse granular depth hoar (snow that was deposited during the previous fall and subjected to temperature gradient metamorphism in winter). Pits were dug to the bottom of level snowpacks, and one side was cleaned using Teflon scrapers. Snow from each snowpack layer was collected by pushing acid-washed 2 L Teflon jars into the cleaned face of the pit. Snow pit samples were stored, processed, and analyzed for THg as described above.

Fate of Hg Deposited during AMDEs. From April 15 to May 15 2003, prior to owning the Tekran analyzers, we sampled surface snow daily ~1.5 km off shore on the Hudson Bay sea ice (Figure S1) while simultaneously monitoring concentrations of total gaseous Hg (TGM) in interstitial airspaces of snowpacks. Assuming that the majority of measured TGM was GEM, this sampling allowed us to determine whether Hg(II) deposited into snowpacks was (photo)reduced as has been demonstrated at more southerly latitudes and in the Arctic (19, 20, 22–24).

We collected TGM samples from ~10 cm above the snowpack surface and from the interstitial airspaces of the three snowpack layers. TGM samples were collected onto pre-cleaned gold traps using a Hg sniffer as described in ref 24, except that the sniffer probe was not made from glass but from 6.3 mm Teflon tubing that was sealed and perforated with tiny holes at one end. Air was vacuumed from the interstitial airspaces of the snowpack at ~1 L/min for 30 min. Upon return to the University of Alberta laboratory, Hg was thermally desorbed from the gold traps at 400 °C using a stream of UHP argon and detected by CVAFS on a Tekran 2500. Unused gold traps shipped to the field site and back (travel blanks) revealed that there was zero contamination of gold traps during storage.

Concentrations of TGM in interstitial airspaces of snowpacks were calculated by dividing the total quantity of Hg (ng) on the gold traps by the volume of air (L) that passed through the gold traps during sampling. Because we sampled a large volume of air (30 L), we likely obtained TGM originating in the air both above and below the level of our inserted probe. Samples from the upper snowpack layer, for example, likely underestimate the quantity of TGM present there because they contained some TGM from the above atmospheric air, as well as from the interstitial airspaces of the spring snow layer below.

Net Deposition of Oxidized Hg. Since it is snowmelt that actually enters marine ecosystems in the spring, we used the average concentrations of THg in meltwater and snow water equivalent (SWE) of snowpacks prior to snowmelt to approximate the net November–May/June (freeze-up to thaw) loadings of Hg(II) to Hudson Bay. On the morning of May

11, 2003, snow on Hudson Bay was slushy in spots, and by May 12, small ponds of snowmelt had formed on the sea ice. On May 12 and 14 water from these ponds was collected into Teflon bottles. In 2004, snowmelt began much later during the first week of June. Water from ponds on the sea ice was collected from June 3 to 6.

In 2004, an Adirondack corer was used to collect snow cores every 10 m along a 500 m transect near our daily snow-sampling site (Figure S1). Each core was weighed and SWE was determined as follows, assuming that the density of water is 1000 kg/m³:

$$\text{SWE (kg/m}^2\text{)} = \frac{\text{core weight (kg)}}{\pi(\text{corer radius (m)})^2} \quad (1)$$

Because the snowpack over Hudson Bay is extremely variable, we were unable to accurately approximate the average snowpack depth. Instead, the range of snowpack depths and SWEs along our 500 m transect were used to determine the variation in springtime Hg(II) loadings to Hudson Bay. With the use of the SWE for each snow depth along our 500 m transect, aerial water volumes (L/ha) were calculated as follows

$$\text{Aerial water volume (L/ha)} = \frac{\text{SWE (kg/m}^2\text{)}}{\text{density water (kg/m}^3\text{)}} \times 10^3 \text{ L/m}^3 \times 10^4 \text{ m}^2/\text{ha} \quad (2)$$

then multiplied by average concentrations of THg in meltwater (mg/L) to determine net loadings of THg (mg/ha).

Results and Discussion

Detection of AMDEs. We detected numerous AMDEs between March 19 and June 3, 2004 (Figure 1). Concentrations of GEM dropped below 1 ng/m³ every 1–5 days during this period, and on a few occasions, below the MDL. The frequency of AMDEs, and concentrations of GEM during them, were similar to those observed in the Canadian Arctic at Alert (4, 18), at Barrow, Alaska (7), Svalbard, Norway (12), Antarctica (13), and Greenland (14). When GEM concentrations fell below 1 ng/m³, concentrations of pHg and/or RGM dramatically increased. Concentrations of pHg and RGM were frequently higher than 500 pg/m³ (Figure 1b) with pHg peaking at ~2350 pg/m³ on April 14 and RGM reaching its highest concentration of ~1260 pg/m³ on May 8. Concentrations of pHg and RGM together often accounted for all of the GEM depleted from the atmosphere and were higher than those generally observed at other sites. For example, maximum RGM concentrations of ~950 pg/m³ were recorded at Barrow, Alaska in spring 2001 (7); however, virtually no pHg was observed during AMDEs there. On the east coast of Hudson Bay at Kuujjuarapik/Whapmagoostui, AMDEs were monitored from April 15 to May 8, 2001 and pHg and RGM concentrations did not rise above ~600 and 190 pg/m³, respectively (34).

Concentrations of pHg were much higher at the end of March and throughout most of April than later in the season, whereas the opposite was true of RGM (Figure 1b). In fact, pHg concentrations did not increase above 730 pg/m³ after April 25, whereas RGM did not increase above 400 pg/m³ prior to April 22. This late April “switch” from pHg to RGM as the dominant species produced during AMDEs has also been observed at Alert, where the mechanisms driving Hg speciation during AMDEs are being examined (A. Steffen, Environment Canada, personal communication, 2006). AMDEs ended at our site when air temperatures increased to 0 °C at the end of May (27) (Figure 1e). From June 20 to 28, average GEM concentrations increased to 1.94 ± 0.16 ng/m³ before dropping to 1.81 ± 0.20 ng/m³ for the remainder

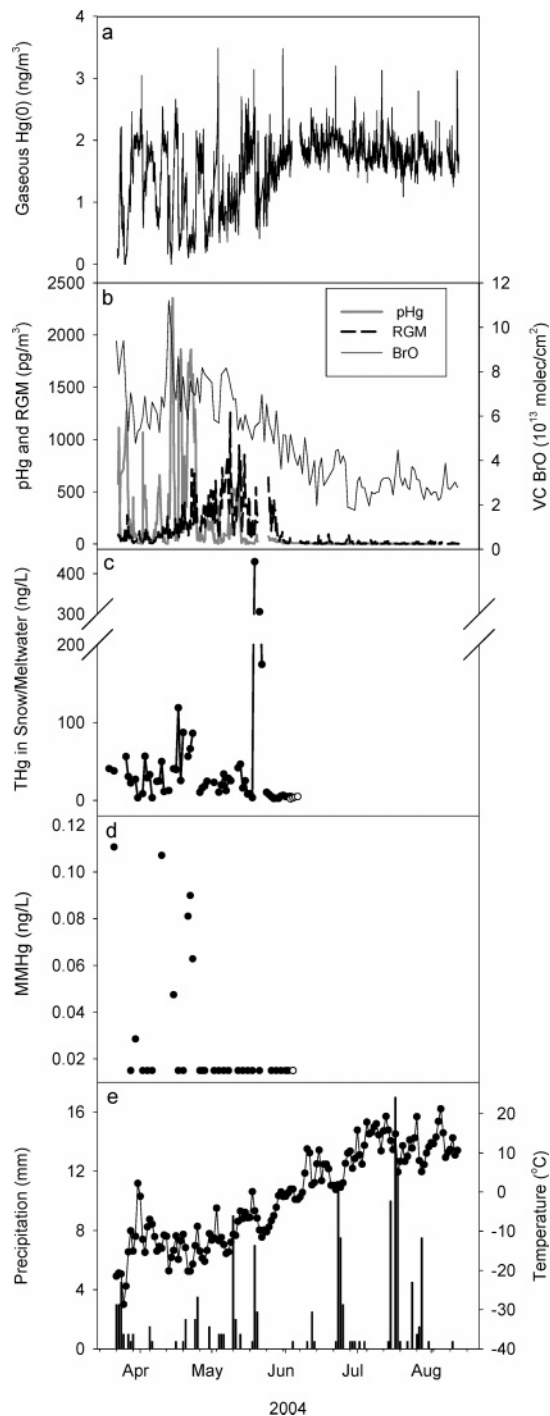


FIGURE 1. Atmospheric concentrations of gaseous elemental Hg⁰ (GEM) (a), particulate Hg (pHg) and reactive gaseous Hg (RGM) measured at the Churchill Northern Studies Center as well as BrO generated by the Belgian Institute for Space and Aeronomy (IASB/BIRA) (b); concentrations of THg (c) and MMHg (d) in surface snow (closed circles) and meltwater (open circles) collected on the sea ice over Hudson Bay throughout the spring. Samples in which concentrations of MMHg were below analytical detection limit were assigned a detection limit concentration (0.015 ng/L). Daily precipitation and temperature measured by Environment Canada at the Churchill airport (58°, 44' N, 94°, 3' W) (ref 27) (e).

of the summer (Figure 1a), although this is likely not a significant difference.

There is mounting evidence that AMDEs occur when Br and BrO radicals are produced over sea ice in the spring, possibly from catalytic reactions of sea salt halides (7, 9–12).

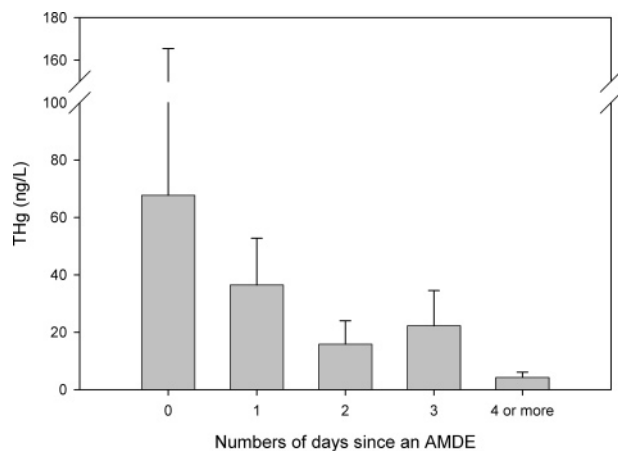


FIGURE 2. Average concentrations of THg in surface snow collected on Hudson Bay in 2004 during AMDEs, and 1, 2, 3, and 4 or more days following the end of individual AMDEs if subsequent AMDEs did not occur.

Br and BrO then react with GEM in the atmosphere to form oxidized species such as HgO, HgBrO or HgOBr, HgBr₂, and HgBr (9, 35), some of which may sorb to aerosols to form pHg (7). BrO data, generated using the SCIAMACHY differential optical absorption spectroscopy (DOAS) instrument aboard the European Space Agency satellite ERS-2 (36), were obtained from the Belgian Institute for Space and Aeronomy (37). BrO enhancements in the stratosphere and troposphere over Churchill coincided with elevated concentrations of pHg and RGM in the lower troposphere (Figure 1b), suggesting that BrO may have been involved in the AMDEs we observed. Vertical column densities (VCD) of BrO were $\sim 5 \times 10^{13}$ to 9×10^{13} molec/cm² from March 22 to the beginning of June, which is comparable to those observed at Barrow, Alaska (7) and at Neumayer station in Antarctica during springtime AMDEs (13). At snowmelt, when AMDEs ended, BrO VCD dropped off and remained between $\sim 2 \times 10^{13}$ to 5×10^{13} molec/cm² over the summer (Figure 1b).

Deposition of Oxidized Hg to Snowpacks during AMDEs.

Concentrations of THg in surface snow were higher during AMDEs than between them, demonstrating that AMDEs resulted in deposition of atmospheric Hg(II) to snowpacks (Figure 1a–c). During AMDEs, concentrations of THg in snow averaged 67.7 ± 97.7 ng/L, ranging between 8.25 and 429 ng/L (Figure 2), which is comparable to springtime concentrations observed in other Canadian Arctic regions (6, 7). Concentrations of THg in snow at the upper end of this range are the highest recorded in the sub-Arctic and were often observed during intense AMDEs that lasted for multiple days. For example, average THg concentrations in snow from April 16 to 23 were 68.3 ± 31.7 ng/L, coincident with an 8 day AMDE (between April 16 and April 24, average concentrations of pHg and RGM in the atmosphere were 952 ± 622 pg/m³ and 250 ± 158 pg/m³, respectively). THg concentrations at the lower end of the range were usually observed during AMDEs that lasted 2 days or less, or during periods when atmospheric pHg and RGM concentrations did not increase dramatically. For example, on the afternoon of April 27, an AMDE was just beginning, pHg and RGM concentrations were fairly low (averaging 44.9 ± 25.8 pg/m³ and 263 ± 72.6 pg/m³ throughout the day, respectively), and the concentration of THg in snow was only slightly elevated at 15.5 ng/L. Conversely, on May 19, the snow sample with the highest concentration of THg seen all spring was collected (~ 429 ng/L), but concentrations of RGM and pHg were quite low, averaging 29.6 ± 33.7 and 239 ± 164 pg/m³, respectively. Likely, an intense AMDE occurred on May 18 but was not recorded by the Tekrans because winds were from the south

off land for almost the entire day (average wind direction $\sim 177^\circ$; see below). On April 2, atmospheric concentrations of pHg and RGM were extremely high, averaging 588 ± 312 and 78.8 ± 54.1 pg/m³, respectively, but hardly any Hg(II) deposition was observed (the concentration of THg in snow was only 8.25 ng/L). These results indicate that many factors, such as proximity of snow-sampling sites to locations of actual pHg and RGM production and horizontal transport of snow by winds, affect surface snow concentrations of THg measured during AMDEs. Therefore, single location atmospheric measurements of GEM, pHg, and RGM may not be a good proxy of oxidized Hg deposition into snowpacks. However, we did frequently observe increases in snowpack THg concentrations during AMDEs.

Following the end of each AMDE, deposited Hg(II) was rapidly lost from snowpacks (Figure 1c and 2). Average concentrations of THg in surface snow declined dramatically, ranging from 67.8 ± 97.7 ng/L during AMDEs to only 4.25 ± 1.85 ng/L four or more days following them. Loss of deposited Hg from snowpacks has been observed in the high Arctic on John Evans Glacier, Ellesmere Island (24), in Sainte-Foy, Northern Quebec (20), at the Experimental Lakes Area in Northwestern Ontario (22), and following AMDEs at Barrow, Alaska (7). The loss of deposited Hg from snowpacks at our site is discussed further below.

Although AMDEs resulted in deposition of Hg(II) into the upper layers of the snowpack (Figure 1c), they did not alter MMHg concentrations in snow as GEM is not oxidized directly to MMHg (Figure 1d). In fact, MMHg concentrations in snow were often below our MDL of 0.015 ng/L. However, on several days following snowfall events at the end of March and throughout April, MMHg concentrations in surface snow were elevated to between ~ 0.06 – 0.11 ng/L. At the Experimental Lakes Area, a relatively pristine Boreal area, concentrations of MMHg in precipitation were similar, varying between 0.02 and 0.33 ng/L (38).

Concentrations of THg in samples from different layers of snowpacks at sites located 2.5, 5, and 7 km from the shoreline on March 31, April 16, and May 22–23 2004 were spatially and temporally variable (Figure S2 in the Supporting Information). Surface snow samples often contained the highest concentrations of THg (average 21.4 ± 27.2 ng/L). As in our daily surface snow samples, changes in THg concentrations in surface snow collected from snow pits reflected occurrences of AMDEs. For example, on March 31 the Tekrans indicated that an AMDE had not occurred since March 27 and concentrations of THg in surface snow at all three sites were low (on average 4.29 ± 2.56 ng/L). On April 16, an AMDE was occurring and concentrations of THg in surface snow samples were similar at the 2.5 and 5 km sites (38.0 and 31.4 ng/L, respectively) but were lower 7 km over the sea ice (12.8 ng/L). Differences in concentrations of THg in surface snow between sites on the same day are likely due to many factors, as discussed above, and reflect the site-specific deposition of Hg(II) during AMDEs.

Concentrations of THg in the deeper snowpack layers were also quite variable (15.2 ± 13.8 ng/L and 10.6 ± 9.63 ng/L in the middle and bottom layers, respectively) (Figure S2). High concentrations of THg in samples from lower snowpack layers are probably due to Hg(II) deposited during AMDEs penetrating snowpacks, as has been demonstrated by St. Louis et al. (24) by comparing concentrations of THg in snow samples collected on a Teflon-coated “snow table” with those collected in nearby snowpacks. Winds, which sometimes reached 90 km/h over Hudson Bay during our sampling period, may also have caused wind pumping in snowpacks, which likely enhanced transfer of RGM and pHg into the deeper parts of snowpacks.

Fate of Hg Deposited during AMDEs. Concentrations of THg in surface snow samples collected daily in spring 2003

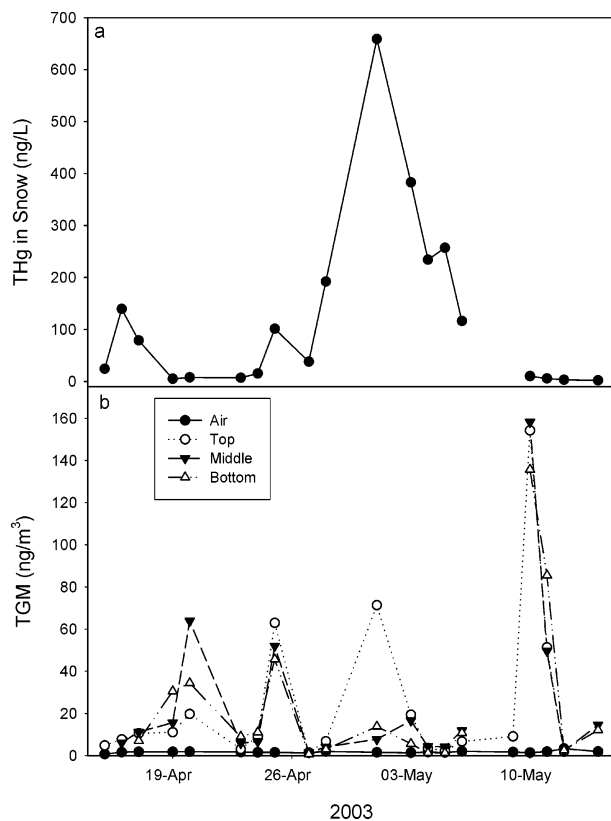


FIGURE 3. Concentrations of THg in surface snow collected on Hudson Bay in 2003 (a), and concentrations of total gaseous Hg (assumed to be primarily gaseous elemental Hg) in interstitial airspaces of the surface, middle, and bottom layers of snowpacks (b).

increased to between 101 and 659 ng/L on four occasions, then decreased to ~ 5 ng/L a few days later, indicating that there were periods of Hg(II) deposition followed directly by loss of this Hg from snowpacks (Figure 3).

As concentrations of THg in the surface snow decreased, concentrations of TGM in interstitial airspaces of the upper layers of snowpacks increased sharply from between 1.4 and 3.4 ng/m³ to between ~ 20 –150 ng/m³ (Figure 3). These observations suggest that Hg(II) was rapidly (photo)reduced to GEM in the upper snowpack layers and that the GEM then diffused to the atmosphere. (Photo)reduction of oxidized Hg in snow has been demonstrated in other studies using laboratory and field snow incubation experiments (19, 20, 22, 23) and sampling of TGM from interstitial airspaces of snowpacks at different depths (21, 25). During AMDEs at Alert in 2000, Steffen et al. (18) also observed GEM concentrations in the interstitial air of a snowpack elevated above those in ambient air, probably due to (photo)reduction of deposited Hg(II). However, (photo)reduction and reemission rates may vary among sites depending on such factors as speciation of deposited Hg, presence of other chemicals in snowpacks, solar radiation, snowpack temperature, and presence of water (23, 25).

Unexpectedly, concentrations of TGM in interstitial airspaces of the middle and bottom snowpack layers also increased to between ~ 8 –160 ng/m³ following Hg(II) deposition into snowpacks, although we hypothesized that (photo)reduction occurs primarily in the upper snowpack layer where sunlight penetrates. High concentrations of TGM in the lower levels of snowpacks probably resulted from diffusion and/or wind pumping of TGM from the upper snowpack layers. Extremely high concentrations of TGM in interstitial air of all three snowpack layers on May 10 and 11

(~ 150 , 160, and 140 ng/m³ on May 10, and ~ 51 , 50, and 85 ng/m³ on May 11 in the top, middle, and bottom layers, respectively) may be related to rain on May 8–9. The rain likely produced liquid layers in snowpacks, which Ferrari et al. (25) have suggested can enhance reduction of Hg(II) to GEM. Furthermore, following the rain, a thick ice layer formed on snowpacks and likely prevented TGM from fluxing to the atmosphere. Once temperatures increased above 0 °C and the ice melted on May 12, concentrations of TGM in air of the bottom layer of the snowpack decreased to 2.5 ng/m³.

If most of the Hg(II) deposited to snowpacks during AMDEs was subsequently (photo)reduced and lost back to the atmosphere as GEM, reemission following each AMDE should have been detected by the Tekrans as spikes in GEM well above global background concentrations of ~ 1.7 ng/m³ (8). In addition, these reemission spikes of GEM should be equal in magnitude to the dips recorded during AMDEs, and springtime GEM concentrations should average out to ~ 1.7 ng/m³. However, the average GEM concentration from March 22 to June 3 was only ~ 1.28 ng/m³. We hypothesize that changing wind directions prevented us from measuring reemission of GEM to the atmosphere.

Approximately 90% of combined springtime pHg and RGM concentrations over 300 pg/m³ were detected at our site when the wind originated from the north off Hudson Bay, where AMDEs take place (Figure 4). When northerly winds continued to blow after the end of AMDEs (for example, on April 10 and 15, May 3, 13, and 15), reemission was recorded as spikes in GEM concentrations between ~ 2.5 –3 ng/m³ (Figure 1a). However, when the wind was blowing off land from the south (Figure 4), reemission was not detected by the Tekrans because deposition of Hg(II) during AMDEs likely does not extend very far inland. For example, on April 2, there was a north wind (average wind direction 37.9°) and GEM concentrations were under 1 ng/m³ for much of the day (Figure 1a). On April 3, GEM concentrations climbed from ~ 1.3 to 2 ng/m³, suggesting reemission of GEM from snowpacks on the sea ice. However, when the wind direction changed to a more southerly direction in the evening of April 3 (average wind direction between the evenings of April 3–5 was 237°) reemission from snowpacks on the sea ice could not be recorded and average GEM concentrations were 1.76 ± 0.098 ng/m³. In addition, AMDEs occurred frequently during the spring at our site, and it is plausible that reemission of deposited Hg(II) occurred simultaneously with the next AMDE, “muddying” reemission signals.

As described above, following the end of AMDEs in June 2004, atmospheric concentrations of GEM were above average summertime concentrations of 1.81 ± 0.20 ng/m³ for ~ 1 week (1.94 ± 0.164 ng/m³ for June 20–28). A post-AMDE “hump” in atmospheric GEM concentrations has been observed by others and has been attributed to the reemission of a portion of the Hg(II) deposited throughout the winter during AMDEs (7). However, our results indicate that deposited Hg(II) is (photo)reduced following each AMDE, and at snowmelt, there is little Hg(II) remaining to be (photo)reduced (see below). The elevated concentrations of GEM at the end of June correspond to the approximate timing of ice out on the area of Hudson Bay near Churchill. In addition, concentrations of GEM in seawater collected under the sea ice near Churchill in May 2004 were 87.3 ± 13.4 pg/L (J. L. Kirk, unpublished data), which is much higher than the atmospheric concentrations of GEM measured simultaneously. These results suggest that the post-AMDE hump in atmospheric GEM results from the degassing of GEM that has built up in seawater under the ice during winter.

Net Deposition of Oxidized Hg. Snowmelt began in the second week of May in 2003, and concentrations of THg in meltwater collected on May 12 and 14 were only 7.54 and 3.49 ng/L, respectively. In 2004 snowmelt did not begin until

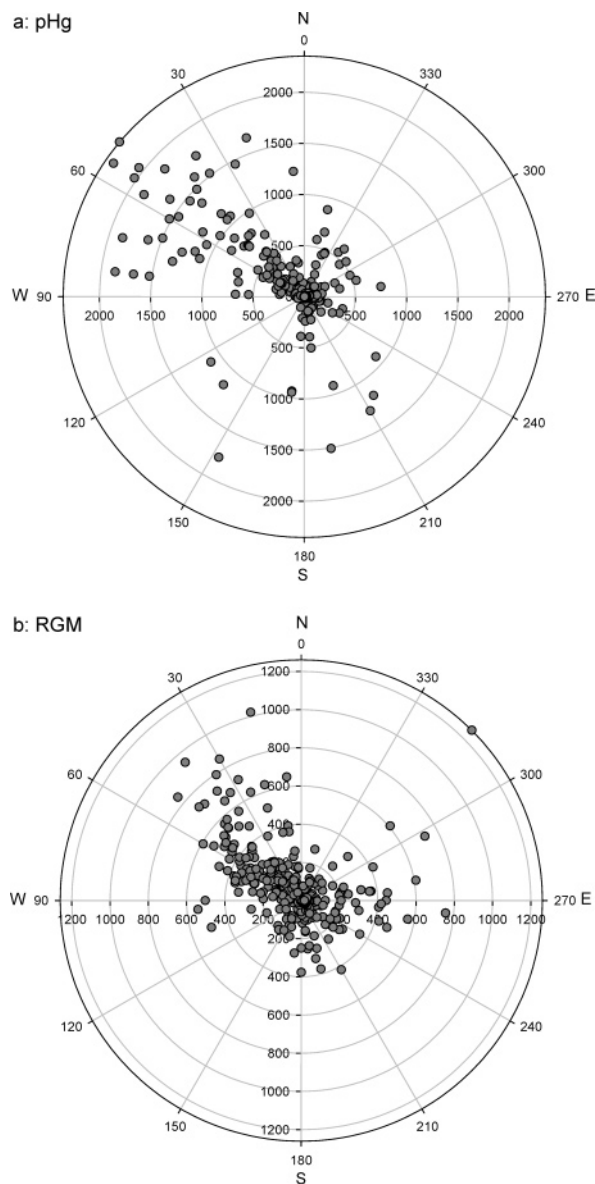


FIGURE 4. Relationship between wind direction and concentrations of atmospheric pHg (a) and RGM (b), measured from March 22 to June 20, 2004 at the Churchill Northern Studies Center. The radial axes represent concentrations of pHg or RGM in pg/m^3 .

the first week of June; however, average THg concentrations in meltwater of $3.31 \pm 1.35 \text{ ng}/\text{L}$ (Figure 1c) were similar to those observed the previous year. These concentrations are similar to those documented in meltwater on the eastern side of Hudson Bay at Kuujuarapik/Whapmagoostui (15) and northeast of Station Nord, Greenland on the Arctic Ocean (39), as well as in surface snow collected at snowmelt on the Northern Beaufort Sea (6), suggesting that only a small fraction of the Hg(II) deposited during AMDEs enters marine ecosystems at snowmelt. Snow depths and SWE measured every 10 m along our 500 m snow core transect ranged from 0 to 0.685 m and 0–188 kg/m^2 , respectively. By multiplying average meltwater THg concentrations in 2004 by aerial water volumes (in L/ha) derived from SWE, we calculated combined net wet and dry springtime THg loadings ranging between 0, where there was no snow cover, to $6.24 \pm 2.54 \text{ mg}/\text{ha}$ at maximum snow depths of 0.685 m (Figure S3 in the Supporting Information). Even at maximum snow depths, THg loadings were extremely low compared to annual wet-only loading rates of 30–210 mg/ha in lower North America (40). By multiplying the average of our calculated net THg

loadings ($2.10 \pm 1.66 \text{ mg}/\text{ha}$) by the $1.23 \times 10^8 \text{ ha}$ surface area of Hudson Bay, we estimate that only $\sim 260 \pm 200 \text{ kg}$ THg enters Hudson Bay each spring.

Acknowledgments

We thank the following for providing funds to conduct our research: Manitoba Hydro, NSERC Collaborative Research and Development Program, the Canadian Circumpolar Institute Circumpolar/Boreal Alberta Research (C/BAR) and Northern Scientific Training (NSTP) grant programs, and the Churchill Northern Studies Center (CNSC). We thank Alexandra Steffen for training us to operate the Tekran analyzers. Jen McColloch and Carley Basler of the CNSC operated the Tekrans from June 6 to August 12, 2004 and helped collect snow samples. Dave Wright, Cliff Paddock, Leeanne Fishback, Michael Goodyear, and Paul Venturelli helped collect snow samples, and Cindy Kao and Allison Kirk helped with mercury analysis and field preparations. Finally, we thank Charlene Neilsen for preparing Figure S1.

Supporting Information Available

Analytical details and figures of a study site map (Figure S1), THg concentrations in snowpits collected on Hudson Bay in spring 2004, ~ 2.5 , 5, and 7 km from the shoreline (Figure S2), and the range of springtime net combined dry and wet THg loadings to Hudson Bay (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Indian and Northern Affairs Canada. *Canadian Arctic Contaminants Assessment Report II; Highlights*; Minister of Indian and Northern Development: Ottawa, Canada, 2003.
- (2) AMAP. *Arctic Pollution 2002 (Persistent Organic Pollutants, Heavy Metals, Radioactivity, Human Health, Changing Pathways)*. Arctic Monitoring and Assessment Programme (AMAP): Oslo, Norway, 2002; xii + 112 pp.
- (3) Wheatley, B.; Wheatley, M. A. Methylmercury and the health of indigenous peoples: a risk management challenge for physical and social sciences and for public health policy. *Sci. Total Environ.* **2000**, *259*, 23–29.
- (4) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. A.; Lu, J. Y.; Steffen, A.; Schneeberger, D. R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394*, 331–332.
- (5) Lindberg, S. E.; Brooks, S. B.; Landis, M.; Stevens, R. Comments on “Atmospheric mercury species in the European Arctic: measurements and modeling” by Berg et al. *Atmospheric Environment* 14 (2001), 2569–2582. *Atmos. Environ.* **2001**, *35*, 5377–5378.
- (6) Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, S.; Welch, H. E.; Martin, K.; Lockhart, L.; Hunt, R. V.; Boila, G.; Richter, A. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to troposphere ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28*, 3219–3222.
- (7) Lindberg, S. E.; Brooks, S.; Lin, C. J.; Scott, K. J.; Landis, M. S.; Stevens, R. K.; Goodsite, M.; Richter, A. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **2002**, *36*, 1245–1256.
- (8) Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Temme, C.; Munthe, J.; Wängberg, I.; Schroeder, W.; Steffen, A.; Berg, T. Worldwide trend in atmospheric mercury since 1977. *Geophys. Res. Lett.* **2003**, *30*, 1516.
- (9) Ariya, P. A.; Khalizov, A.; Gidas, A. Reactions of gaseous mercury with atomic and molecular halogens: kinetics, product studies, and atmospheric implications. *J. Phys. Chem. A* **2002**, *106*, 7310–7320.
- (10) Clavert, J. G.; Lindberg, S. E. A modeling study of the mechanism of the halogen–ozone–mercury homogenous reactions in the troposphere during the polar spring. *Atmos. Environ.* **2003**, *37*, 4467–4481.
- (11) Brooks, S. B.; Saiz-Lopez, A.; Skov, H.; Lindberg, S. E. The mass balance of mercury in the springtime arctic environment. *Geophys. Res. Lett.* **2006**, *33*, L13812.
- (12) Skov, H.; Christensen, J. H.; Goodsite, M. E.; Heidem, N. Z.; Jensen, B.; Wahlin, P.; Geernaert, G. Fate of elemental mercury in the Arctic during atmospheric mercury depletion episodes

- and the load of atmospheric mercury to the Arctic. *Environ. Sci. Technol.* **2004**, *38*, 2373–2382.
- (13) Ebinghaus, R.; Kock, H. H.; Temme, C.; Einax, J. W.; Löwe, A. G.; Richter, A.; Burrows, J. P.; Schroeder, W. H. Antarctic springtime depletion of atmospheric mercury. *Environ. Sci. Technol.* **2002**, *36*, 1238–1244.
 - (14) Berg, T.; Sekkasaeter, S.; Steignes, E.; Valdal, A. K.; Wibetoe, G. Springtime depletion of mercury in the European Arctic as observed at Svalbard. *Sci. Total Environ.* **2003**, *304*, 43–51.
 - (15) Gauchard, P. A.; Ferrari, C. P.; Dommergue, A.; Poissant, L.; Pilote, M.; Guehenneuz, G.; Boutron, C. F.; Baussand, P. Atmospheric particle evolution during a nighttime atmospheric mercury depletion even in the sub-Arctic at Kuujjuarapik/Whapmagoostui, Quebec, Canada. *Sci. Total Environ.* **2005**, *336*, 215–224.
 - (16) Dommergue, A.; Ferrari, C. P.; Gauchard, P. A.; Boutron, C. F.; Poissant, L.; Pilote, M.; Jitaru, P.; Adams, F. C. The fate of mercury species in a sub-Arctic snowpack during snowmelt. *Geophys. Res. Lett.* **2003**, *30*, 1621, doi:10.1029/2003GL017308.
 - (17) Ariya, P. A.; Dastoor, A. P.; Amyot, M.; Schroeder, W. H.; Barrie, L.; Anlauf, K.; Raofie, F.; Ryzhkov, A.; Davidgnon, D.; Lalonde, J.; Steffan, A. The Arctic: a sink of mercury. *Tellus* **2004**, *56B*, 397–403.
 - (18) Steffen, A.; Schroeder, W.; Bottenheim, J.; Narayan, J.; Fuentes, J. D. Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the Canadian Arctic during Alert 2000. *Atmos. Environ.* **2002**, *36*, 2653–2661.
 - (19) Amyot, M.; Lalonde, J. D.; Ariya, P. A.; Dastoor, A. Behavior of mercury in snow from different latitudes. *J. Phys. IV (France)* **2003**, *107*, 45–48.
 - (20) Lalonde, J. D.; Poulain, A. J.; Amyot, M. The role of mercury redox reactions in snow on snow-to-air mercury transfer. *Environ. Sci. Technol.* **2002**, *36*, 174–178.
 - (21) Dommergue, A.; Ferrari, C. P.; Poissant, L.; Gauchard, P. A.; Boutron, C. F. Diurnal cycles of gaseous mercury within the snowpack at Kuujjuarapik/Whapmagoostui, Quebec, Canada. *Environ. Sci. Technol.* **2003**, *37*, 3289–3297.
 - (22) Lalonde, J. D.; Amyot, M.; Doyon, M. R.; Auclair, J. C. Photo-induced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada). *J. Geophys. Res.* **2003**, *108*, No. D6, 4200, doi: 10.1029/2001JD001534.
 - (23) Poulain, A. J.; Lalonde, J. D.; Amyot, M.; Shead, J. A.; Raofie, F.; Ariya, P. A. Redox transformations of mercury in an Arctic snowpack at springtime. *Atmos. Environ.* **2004**, *38*, 6763–6774.
 - (24) St. Louis, V. L.; Sharp, M. J.; Steffen, A.; May, A.; Barker, J.; Kirk, J. L.; Kelly, D. J. A.; Arnott, S. E.; Keatley, B.; Smol, J. P. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere Island in the Canadian high Arctic. *Environ. Sci. Technol.* **2005**, *39*, 2686–2701.
 - (25) Ferrari, C. P.; Gauchard, P. A.; Aspino, K.; Dommergue, A.; Magand, O.; Bahlmann, E.; Nagorski, S.; Temme, C.; Ebinghaus, R.; Steffan, A.; Banic, C.; Berg, T.; Planchon, F.; Barbante, C.; Cescon, P.; Boutron, C. F. Snow-to-air exchanges of mercury in an Arctic seasonal snow pack in Ny-Alesund, Svalbard. *Atmos. Environ.* **2005**, *39*, 7633–7645.
 - (26) Kirk, J. L. Potential sources of monomethyl mercury in Arctic and Subarctic seawater. *Arctic* **2006**, *59*, 108–111.
 - (27) Environment Canada. Canadian Climate Normals or Averages 1971–2000. http://climate.weatheroffice.ec.gc.ca/climate_normals/ (accessed Jan 17, 2005).
 - (28) Aspino, K.; Gauchard, P. A.; Steffen, A.; Temme, C.; Berg, T.; Bahlmann, E.; Banic, C.; Dommergue, A.; Ebinghaus, R.; Ferrari, C.; Pirrone, N.; Sprovieri, F.; Wibetoe, G. Measurements of atmospheric mercury species during an international study of mercury depletion events at Ny-Alesund, Svalbard, spring 2003. How reproducible are our present methods? *Atmos. Environ.* **2005**, *39*, 7607–7619.
 - (29) St. Louis, V. L.; Rudd, J. W. M.; Kelly, C. A.; Beaty, K. G.; Bloom, N. S.; Flett, R. J. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can. J. Fish. Aquat. Sci.* **1994**, *51*, 1065–1076.
 - (30) Bloom, N. S.; Creclius, E. A. Determination of mercury in seawater at subnanogram per liter levels. *Mar. Chem.* **1983**, *14*, 49–59.
 - (31) Bloom, N. S. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can. J. Fish. Aquat. Sci.* **1989**, *46*, 1131–1140.
 - (32) Horvat, M.; Bloom, N. S.; Liang, L. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II. Water. *Anal. Chim. Acta.* **1993**, *282*, 153–168.
 - (33) Sharp, M.; Skidmore, M.; Nienow, P. Seasonal and spatial variations in the chemistry of a high Arctic supraglacial snowcover. *J. Glaciol.* **2002**, *48*, 149–158.
 - (34) Poissant, L.; Hoenninger, G. Atmospheric mercury and ozone depletion events observed at the Hudson Bay in northern Quebec along with BrO (DOAS) measurements. *RMZ-Mater. Geoenviron.* **2004**, *51*, 1722–1724.
 - (35) Raofie, F.; Ariya, P. Product study of the gas-phase BrO-initiated oxidation of Hg⁰: evidence for stable Hg¹⁺ compounds. *Environ. Sci. Technol.* **2004**, *38*, 4319–4326.
 - (36) Van Roozendaal, M. C.; Fayt, C.; Lambert, J. C.; Pundt, I.; Wagner, T.; Richter, A.; Chance, K. Development of a bromine oxide product from GOME. *Eur. Symp. Atmos. Meas. Space* **1999**, *161*, 543–546.
 - (37) Belgian Institute of Space Astronomy. BrO Product. <http://www.oma.be/BIRA-IASB/Molecules/BrO/level3.php> (accessed Feb 8, 2005).
 - (38) Hall, B. D.; Manolopoulos, H.; Hurley, J. P.; Schauer, J. J.; St. Louis, V. L.; Kenski, D.; Graydon, J.; Babiarz, C. L.; Cleckner, L. B.; Keeler, G. J. Methyl and total mercury in precipitation in the Great Lakes region. *Atmos. Environ.* **2005**, *39*, 7557–7569.
 - (39) Aspino, K.; Temme, C.; Berg, T.; Ferrari, C.; Gauchard, P. A.; Fain, X.; Wibetoe, G. Mercury in the atmosphere, snow and melt water ponds in the North Atlantic ocean during Arctic summer. *Environ. Sci. Technol.* **2006**, *40*, 4083–4089.
 - (40) National Atmospheric Deposition Network. Mercury Deposition Network: a NADP Network. <http://nadp.sws.uiuc.edu/mdn/> (accessed Feb 20, 2006).

Received for review May 30, 2006. Revised manuscript received September 6, 2006. Accepted September 27, 2006.

ES061299+