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# Mercury in the Atmosphere, Snow and Melt Water Ponds in the North Atlantic Ocean during Arctic Summer

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Atmospheric mercury speciation measurements were
performed during a 10 week Arctic summer expedition in
the North Atlantic Ocean onboard the German research vessel
RV *Polarstern* between June 15 and August 29, 2004.
This expedition covered large areas of the North Atlantic
and Arctic Oceans between latitudes 54°N and 85°N
and longitudes 16°W and 16°E. Gaseous elemental mercury
(GEM), reactive gaseous mercury (RGM) and mercury
associated with particles (Hg−P) were measured during
this study. In addition, total mercury in surface snow and
meltwater ponds located on sea ice floes was measured.
GEM showed a homogeneous distribution over the
open North Atlantic Ocean (median $1.53 \pm 0.12$ ng/m³),
which is in contrast to the higher concentrations of GEM
observed over sea ice (median $1.82 \pm 0.24$ ng/m³). It is
hypothesized that this results from either (re-) emission of
mercury contained in snow and ice surfaces that was
previously deposited during atmospheric mercury depletion
events (AMDE) in the spring or evasion from the ocean
due to increased reduction potential at high latitudes during
Arctic summer. Measured concentrations of total mercury
in surface snow and meltwater ponds were low (all
samples <10 ng/L), indicating that marginal accumulation
of mercury occurs in these environmental compartments.
Results also reveal low concentrations of RGM and Hg−P
without a significant diurnal variability. These results
indicate that the production and deposition of these reactive
mercury species do not significantly contribute to the
atmospheric mercury cycle in the North Atlantic Ocean
during the Arctic summer.

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## Introduction

Compared to most heavy metals, mercury behaves excep-
tionally in the environment mainly due to its unusual physical
properties including a relatively high vapor pressure and a
low Henry's law constant (*1*). Mercury forms toxic methyl-
mercury compounds and can readily bio-accumulate in the
aquatic food chain, which targets this as an environmental
pollutant of global concern (*2*). The atmosphere is an
important medium for the transport of mercury from a local
to a global scale, which leads it to be found in remote areas
including Polar regions (*3*). Mercury in the atmosphere results
from numerous anthropogenic and natural processes (*4*).
During the last two decades, there has been growing interest
concerning the atmospheric transport, transformation, depo-
sition, and re-emission processes of mercury. Recent de-
velopment of commercially available continuous measure-
ment techniques has resulted in a better understanding of
mercury's complex cycling in the environment. However,
many questions still remain open (*2*, *5*). Atmospheric cycling
of mercury includes both oxidation and reduction in gaseous
and aqueous phases, deposition and re-emission to and from
natural and anthropogenic sources. Under normal atmo-
spheric conditions, gaseous elemental mercury (GEM) is the
most dominant species, with a northern hemispheric back-
ground concentration of 1.7 ng/m³ (*3*). Under these same
normal conditions, the so-called reactive mercury species,
such as the operationally defined reactive gaseous mercury
(RGM) and mercury associated to airborne particulate matter
(Hg−P), are found in much lower concentrations; often not
more than 1−5% of the total atmospheric mercury composi-
tion (*6*). Further, RGM and Hg−P are effectively removed
from the atmosphere by wet and dry deposition, which leads
to an atmospheric residence time of these species on the
scale of days (*7−8*).

Oxidation of gaseous mercury by $O_3$, OH radicals, $H_2O_2$,
and other photochemical oxidants is an important removal
process of $Hg^0$ to form $Hg^{II}$ that further deposits onto surfaces
(*9−11*). In the marine boundary layer (MBL), it is also shown
that heterogeneous reactions involving halogen-containing
aerosols continuously produce RGM to such an extent that
it is important for the overall deposition of mercury (*12*, *13*).
At temperate latitudes, braking waves and sea spray on the
ocean surface are the source of halogen containing sea salt
aerosols in the atmosphere (*14*).

Atmospheric mercury depletion events (AMDEs), dis-
covered at Alert, Canada (*15*), lead to an increased input of
oxidized mercury into Polar ecosystems (*16*, *17*) which may
explain the accumulation of mercury in Polar environments
and the enhanced levels of mercury found in the diet of
native populations (*18*). In Polar regions, AMDEs commonly
occur during the spring where concentrations of GEM
decrease rapidly transforming this mercury species to RGM
and Hg−P through a sequence of photochemically initiated
oxidation reactions involving marine halogens (*16*, *19−23*).
However, most of the reported observations are from coastal
sites and not directly over the Ocean. In Polar regions, halogen
enriched sea salt aerosols can be caused by frost flowers
growing on newly formed sea ice (*24*) and are most likely
involved in the coinciding rapid depletion of mercury and
tropospheric ozone (*25*, *26*).

At several Arctic coastal locations, such as Alert, Barrow,
and Amderma, elevated concentrations of GEM have been
observed after snowmelt and during the summer (*16*, *23*). As
stated by Steffen et al. (2005) (*23*), it is tempting to assign the
enhanced concentration of GEM in the summer to previously

**TABLE 1: Summary of Sample Collection Parameters and Selected Statistical Parameters for Measured Concentrations of the Atmospheric Mercury Species:  GEM, RGM, and Hg−P[a]**

|  | GEM Tekran #085 | GEM Tekran #008 | GEM Tekran #135 | RGM$_{auto}$ | RGM$_{man}$ | Hg−P$_{man}$ |
|---|---|---|---|---|---|---|
| no. of measurements | 976 | 958 | 201 | 288 | 74 | 74 |
| sample collection flow | 1.3 lpm | 1.0 lpm | 1.0 lpm | 8 lpm | 10 lpm | 10 lpm |
| sample collection time | 5 min | 5 min | 5 min | 2 hours | 2−12 hours | 2−12 hours |
| sample collection period | 16.06.04−29.08.04 | 16.06.04−29.08.04 | 17.07.04−29.08.04 | 16.06.04−29.08.04 | 17.07.04−29.08.04 | 17.07.04−29.08.04 |
| mean concentration | 1.56 ng/m$^3$ | 1.50 ng/m$^3$ | 1.49 ng/m$^3$ | 2.0 pg/m$^3$ | 2.3 pg/m$^3$ | 1.8 pg/m$^3$ |
| minimum concentration | 1.27 ng/m$^3$ | 1.15 ng/m$^3$ | 1.22 ng/m$^3$ | 2.0 pg/m$^3$ | 1.6 pg/m$^3$ | 1.6pg/m$^3$ |
| maximum concentration | 2.07 ng/m$^3$ | 1.94 ng/m$^3$ | 1.72 ng/m$^3$ | 22 pg/m$^3$ | 9.6 pg/m$^3$ | 6.3 pg/m$^3$ |
| median concentration | 1.56 ng/m$^3$ | 1.51 ng/m$^3$ | 1.51 ng/m$^3$ | 2.0 pg/m$^3$ | 1.6 pg/m$^3$ | 1.6 pg/m$^3$ |
| SD | 0.10 ng/m$^3$ | 0.13 ng/m$^3$ | 0.10 ng/m$^3$ | 1.8 pg/m$^3$ | 1.5 pg/m$^3$ | 0.79 pg/m$^3$ |
| MDL | 0.17 ng/m$^3$ | 0.17 ng/m$^3$ | 0.17 ng/m$^3$ | 4.0 pg/m$^3$ | 3.1 pg/m$^3$ | 3.0 pg/m$^3$ |
| % measurements < MDL |  |  |  | 90% | 33% | 50% |

[a] Data collected when RV *Polarstern* crossed the sea ice is not presented in the table.

deposited mercury during springtime AMDEs. However, they conclude that a more vigorous analysis is needed in order for this suggestion to be proved.

The ocean plays an important role in the global mercury cycle since it serves as both a source and a sink for atmospheric mercury through air-sea exchange (*8*). Deposition of atmospheric mercury is the most important input of mercury to remote water bodies (*4*, *27*). Additionally, the Arctic snowpack plays a key role in the mercury cycle. Studies have shown that during AMDEs, Hg$^{II}$ is deposited onto snow surfaces where it undergoes both reduction and oxidation processes in the snow and is partly re-emitted back to the atmosphere as Hg$^0$ (*28*, 29).

The purpose of this study was to investigate the spatial distribution of mercury species in the Polar summer atmosphere over the Arctic Ocean. Further, this study examines mercury in different environmental compartments and observes postdeposition mercury accumulation or (re-) emission as a result of AMDEs.

## Materials and Methods

**Sampling Location.** Measurements were carried out on board the German research vessel RV *Polarstern* during a 10 week summer expedition from Bremerhaven (Germany) to the Arctic Ocean in the North Atlantic between June 16 and August 29, 2004. The cruise was split into two legs called ARK-XX 1 and 2, according to the code of Alfred Wegener Institute. ARK-XX/1 occurred between June 16 and July 17 and ARK-XX/2 occurred between July 17 and August 29. The two legs traveled between latitudes 54°N to 85°N including two cross sections at 75°N from 16°E to 16°W (Greenland Sea) and at 78°N from 9°E to 11°W (Fram Strait).

RV *Polarstern* has, in the past, shown to be a suitable platform from which to make low level atmospheric measurements (*30*, *31*). However, some local pollution from the ship itself does occur including exhaust from helicopter take off and landings, on board waste incineration, and exhaust from the ships engines blown in the direction of sample inlets. To avoid these artifacts, GEM, RGM, and Hg−P results affected by contamination from the ship were removed from the dataset. For example, results obtained when the wind came from between 135 and 225 degrees (relative to the ship's front) and when wind speeds were below 5 m/s were filtered from the data set.

**Description of Methods and Quality Control.** During the entire expedition, a set of continuous and manual air measurements were performed to quantify concentrations

of mercury species in ambient air. Air samples were collected outside an air chemistry research container located at the upper front deck about 12 m above sea level. Analysis of the collected atmospheric mercury species took place inside the container. The measurement program included collecting concentration data for the atmospheric mercury species GEM, RGM, and Hg−P. A summary of sampled atmospheric mercury species with selected sampling parameters is given in Table 1. Throughout the cruise, GEM and RGM were measured semi-continuously using a prototype version of the automated Tekran speciation system that had been previously used in similar cruises in the Antarctic (*30*). Briefly, RGM was collected on a KCl coated and heated (~50 °C) annular denuder. GEM passed over the coating and was quantified by a Tekran mercury vapor analyzer (*32*), as described by Landis et al. (*33*). After collection of RGM, this component was thermally desorbed and quantified as GEM by the Tekran 2537A. During this time, measurements of GEM were interrupted. In addition, duplicate parallel sampling of manually collected RGM and Hg−P was performed during the second cruise leg, ARK-XX/2. RGM and Hg−P were manually collected from the same airflow on KCl coated and heated (~40 °C) annular denuder tubes and on quarts filters, respectively. Analysis included thermal reduction of RGM and thermal decomposition of Hg−P followed by quantification as Hg$^0$ by the Tekran 2537A, as generally described by Landis et al. (*33*) and Lu et al. (*34*).

The Tekran analyzers were calibrated approximately every 48 h using the provided internal calibration source (*32*). In addition, the accuracy of all analyzers was verified by manual injections of known amounts of Hg$^0$ before and after the cruise. No significant deviations (>5%) between the theoretical and measured values were found. Comparability and precision of GEM, RGM, and Hg−P measurements were evaluated by replicates.

Surface snow and water from meltwater ponds were collected from the sea ice. Meltwater ponds are small ponds of varying size (diameter typically in the range of 1−10 m and depth between 10 and 30 cm) that form on the sea ice during the Polar summer (Figure 1). As the aim was to investigate atmospheric deposition, samples were only collected from meltwater ponds that had not melted through to the seawater. To ensure this requirement, the pH and conductivity of the sample water was measured as well as an analysis of heavy metals and major cations and anions was conducted. Results of the chemical analysis showed values comparable to freshwater indicating that the sampled

**FIGURE 1.  Meltwater ponds formed on multi-year sea ice.**

meltwater ponds were all closed ponds. The sea ice was reached by helicopter landing on sea ice floes. Samples were collected upwind as far from the helicopter as possible in order to avoid pollution from the helicopter exhaust. Surface snow and water from the meltwater ponds were collected into ultra cleaned Teflon bottles and caps containing known amounts of supra pure HCl to preserve the Hg in the samples. Samples were kept frozen until controlled melting in a dark environment was possible. The melted snow samples were weighted and BrCl was added as a digesting agent for mercury. Total mercury was determined using cold vapor atomic fluorescence spectrometry after reduction by stannous chloride (35). The principle of this methodology is described elsewhere (36).

Method detection limit (MDL) was 0.17 ng/m$^3$ for GEM, based on a sampling volume of 7.5 l (5). For measurements of RGM, Hg−P and total Hg in snow and meltwater ponds,

MDL was calculated as t*SD. That resulted in MDL = 4.0 pg/m$^3$ for automated measurements of RGM (where $t = 1.650$, $P = 95\%$, SD = standard deviation of all concentration values of RGM collected above open water (37)), MDL = 3.1 pg/m$^3$ for manually measured RGM and 3.0 pg/m$^3$ for Hg−P ($t = 2.92$, $P = 95\%$, SD = standard deviation of field blanks, performed according to Landis et al. (33)) assuming sample collection time and flow as given in Table 1. MDL for snow and meltwater pond samples was 0.05 ng/l total Hg in solution.

**Ancillary Data.** Meteorological data were obtained from PODAS (Polarstern Data System) and back trajectories were calculated based on a global model from the German Weather Service. Ozone was measured using an API ozone monitor based on UV detection. Sea ice conditions were determined by visual observations on an hourly basis during the cruise from July 24 to August 17 2004 (38).

## Results and Discussion

**Increased Concentrations of GEM in the Polar Summer Atmosphere.** GEM concentrations measured during the entire cruise ranged between 0.94 and 2.72 ng/m$^3$. The results are summarized in Table 2 and shown as time series in Figure 2, panel A. The mean concentration values of GEM measured over open water was $1.53 \pm 0.12$ ng/m$^3$. This was comparable to simultaneous measurements at Ny-Ålesund, Svalbard (∼79°N). In Ny-Ålesund, the summertime average during the cruise was $1.53 \pm 0.17$ ng/m$^3$. The median for all data from all instruments measured over open water is the same as the arithmetic mean (1.53 ng/m$^3$), indicating that the data set was not significantly influenced by outliers caused by advection of air masses from the European or North American continents along the cruise track.

GEM was homogeneously distributed over the North Atlantic Ocean from 54°N to about 82°N, and hence, no concentration gradient was observed from south to north (Figure 3). However, it can be seen that there is a step function in the average concentration values of GEM measured north of 82°N, where the GEM concentration was significantly higher ($1.82 \pm 0.24$ ng/m$^3$) when compared to the lower latitudes. Back trajectory analysis showed that the elevated

**TABLE 2: Measured Concentrations of GEM, RGM, and Hg−P from the Work Presented Herein Compared with Other Recent Ship Based Studies[a]**

| Hg species | location | concentration[b] | | | diurnal variation | reference |
| | | mean ± SD | min | max | | |
|---|---|---|---|---|---|---|
| GEM | North Atlantic 54-85°N[c] | 1.53 ± 0.12 | 1.15 | 1.95 | no | this work |
| RGM | | 2.4 ± 2.0 | 0.0 | 22 | no | |
| Hg-P | | n/a | n/a | n/a | n/a | |
| GEM | North Atlantic 78-85°N[d] | 1.82 ± 0.24 | 1.17 | 2.72 | no | |
| RGM | | 2.6 ± 2.3 | 0.0 | 21 | no | |
| Hg-P | | 2.4 ± 1.1 | 0.2 | 6.3 | no | |
| GEM | Florida[e] ∼26°N | 1.6 ± 0.06 | n/a | 18 | n/a | Malcom et al. (47) |
| RGM | | 1.6 ± 1.4 | n/a | 6.9 | yes | |
| Hg-P | | 6.3 ± 4.4 | n/a | 11 | n/a | |
| GEM | North Pacific 22-48°N | 2.5 ± 0.5 | 1.6 | 4.7 | yes | Laurier et al. (12) |
| RGM | | 13.8 ± 13.1 | 2.8 | 92.4 | yes | |
| Hg-P | | n/a | n/a | n/a | n/a | |
| TGM | Mediterranean 30-40°N | 1.9 ± 1.0 | 0.4 | 11 | n/a | Sprovieri et al. (13) |
| RGM | | 8 ± 8 | 0.2 | 30 | yes | |
| Hg-P | | n/a | n/a | n/a | n/a | |
| GEM | North Atlantic ∼30°N | ∼2.0 | 1.3 | 2.5 | no | Mason et al. (45) |
| RGM[f] | | ∼540 | <14 | ∼1800 | no | |
| Hg-P | | <0.01pmol/m$^3$ | n/a | n/a | n/a | |
| TGM | South Atlantic 56-72°S | 1.1 ± 0.2 | 0.75 | 1.42? | no | Temme et al. (30, 31) |
| RGM | | 8 ± 6 | 1.0 | 30 | no | |
| Hg-P | | n/a | n/a | n/a | n/a | |

[a] Data not available. [b] Concentration units are ng/m$^3$ for GEM and TGM, and pg/m$^3$ for RGM and Hg−P. [c] Data obtained over open water. [d] Sea ice concentration more than 70%. [e] Land based measurements. [f] RGM in this paper assumed to be $HgCl_2$.
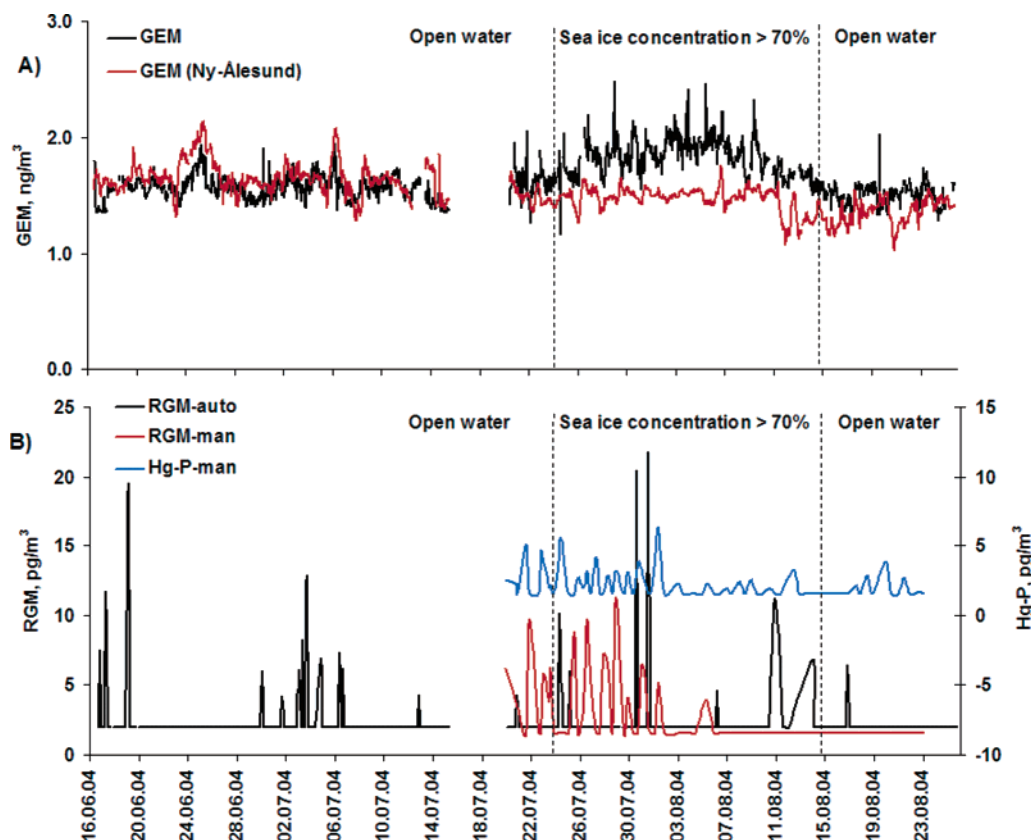
FIGURE 2. Time series of atmospheric mercury species concentrations along the entire cruise. Presence of sea ice is indicated in the figure by the dashed vertical lines. Panel (A) GEM concentrations measured onboard the *Polarstern*. GEM concentrations measured at Ny-Ålesund, Svalbard are added for comparison. Panel (B) Concentrations of automatically and manually collected RGM and manually collected Hg−P. Presence of sea ice is indicated in the figure by the dashed vertical line.
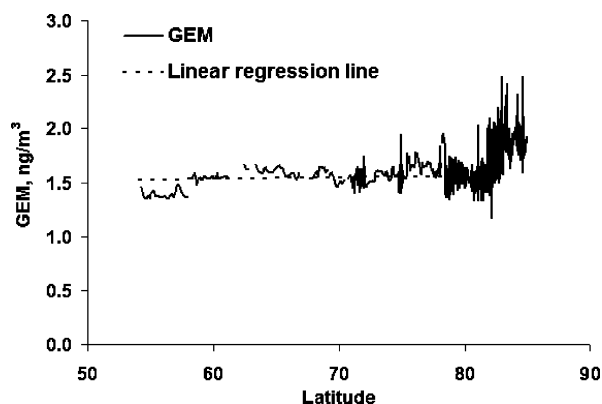


FIGURE 3. Measured GEM concentrations showed as function of latitude. The linear regression line indicates no GEM concentration gradient from 54°N to 82°N.

GEM concentrations were not caused by advection of polluted air masses from the European or North American continents. The higher GEM concentrations were observed when RV *Polarstern* was in an area where the ocean was covered with more than 70% sea ice (Figure 2, panel A).

Corresponding elevated concentrations of dissolved gaseous mercury (DGM) in seawater (*39*) were observed along with the high concentrations of GEM above 82°N. Higher DGM was likely due to higher reduction potential in the seawater at higher latitudes and/or the sea ice acting as a diffusion barrier for sea/air exchange of Hg[0]. This barrier of sea ice could result in a non-steady state for the partitioning of Hg[0] between surface ocean water and the overlying atmosphere. During the relatively short polar summer, primary production of microorganisms can control the

reduction rates of Hg in the ocean water (*40*). It is suggested that inorganic Hg reduction is biologically mediated in surface waters and that there is a positive correlation between Hg[0] production and primary production (measured as chlorophyll a concentrations). Biotic processes dominate over abiotic production of Hg[0] in open surface waters (*40*). Open leads in the sea ice can lead to higher fluxes of Hg[0] from the water to the air, acting as a potential source for Hg[0] in the atmosphere during Arctic summer.

A significant fraction of mercury species being deposited in the polar spring during AMDEs is retained on the snow surface and could potentially accumulate in polar ecosystems (*17, 21*). A substantial fraction is also re-emitted to the atmosphere as elemental mercury shortly after deposition (*28, 29, 41*). Lindberg et al., (*16*) have hypothesized that deposited mercury accumulates in the snow and is transported to underlying surfaces with snowmelt. As the surface snow on sea ice melts, to some extent, during the polar summer, it is likely that mercury follows the melting snow and accumulates in the meltwater ponds. To investigate the fate of deposited mercury during the polar spring, snow and meltwater pond samples were collected and analyzed for total mercury. Concentration of total mercury in surface snow and meltwater ponds ranged between 1.3 and 8.1 ng/L and below MDL up to 5.1 ng/L, respectively (Figure 4). The results are comparable with surface snow measurement at remote Arctic locations prior to Polar spring (*19, 35*). This reveals no elevated concentration of total mercury in either surface sea ice snow or meltwater ponds. Therefore, there appears to be no long-term accumulation of mercury in these compartments after springtime ADMEs. This indicates that *if* mercury was deposited on the snow and sea ice that were sampled, either mercury contamination of the Arctic environment caused by AMDEs is a short time phenomenon or the
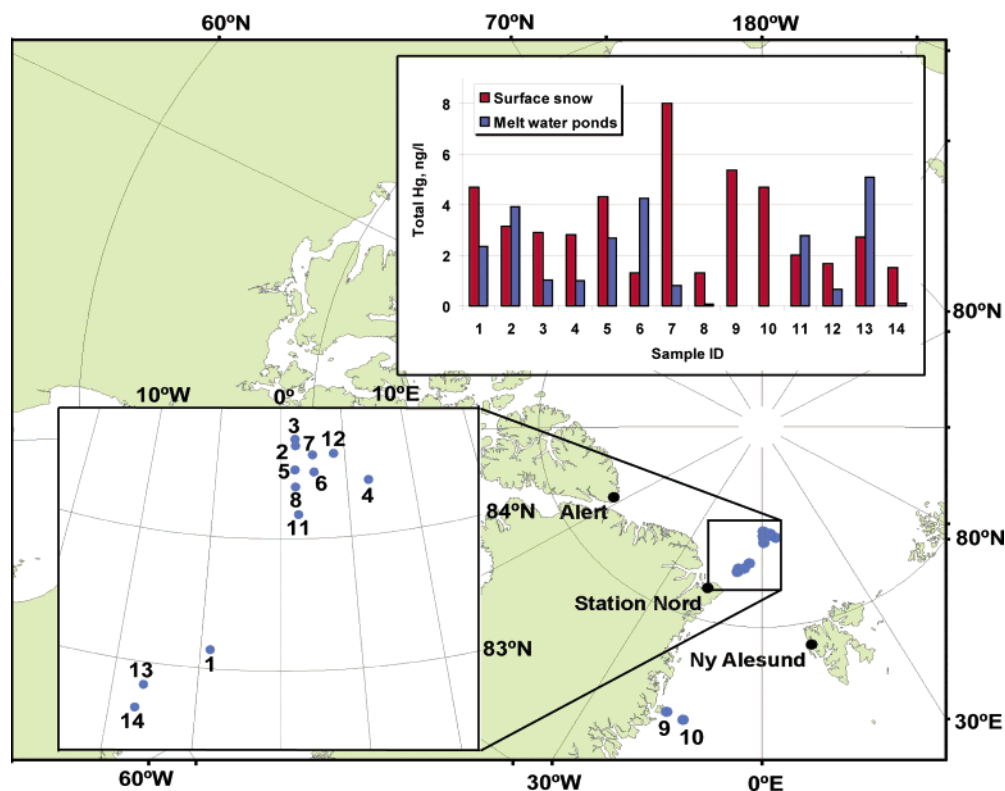
**FIGURE 4. Spatial distribution of summertime concentrations of total Hg in surface snow and meltwater pond samples from the Arctic Ocean. The square in the lower left corner shows an enlarged section of the sampled areas, and the numbers indicate the sample ID. The bars in the upper right corner shows the concentration of total Hg in surface snow and meltwater.**

deposited mercury was shifted from the sea ice to another compartment. The average summertime sea ice temperature is in the range of air temperature and seawater temperature ($\sim -2\ °C$), and thus much warmer than, for example, glacier ice. Even though multi-year sea ice is present, mercury has probably been re-emitted earlier in the season, due to both enhanced photochemical reduction potential during spring and summer (*28*, *42*) and the relatively warm sea ice. As we could not determine the age of the sampled surface snow and meltwater ponds, it is impossible to investigate whether chemistry had occurred before sampling.

We hypothesize that the higher GEM concentrations observed over sea ice were due to a combination of evasion from the ocean caused by increased possibility of reduction at high latitudes during Arctic summer and re-emission of previously deposited mercury during AMDEs in the spring season. Nevertheless, the increased concentrations of GEM cannot be traced back to previous deposited mercury during AMDEs by measurements.

**Oxidized Mercury Species.** Results indicate that concentration values of RGM and Hg−P were low during the whole cruise (Figure 2, panel B and Tables 1 and 2). RGM and Hg−P were measured in the range of below MDL up to 22 pg/m³ and below MDL up to 6.3 pg/m³, respectively. 74% (weighted average) of the reactive mercury species measurements were below MDL of the specific method. Therefore, for calculations involving reactive mercury species, concentration values being below the MDL are replaced by MDL/2. The relative average deviation between automated and manually sampled RGM was within 32%. Considering that ~70% of the recorded concentration values were below MDL, it was concluded that the automated and manual RGM systems compared well. For this study, the relative average deviation between replicates for manually measured RGM and Hg−P was 23 and 22%, respectively.

Global circulation models are an often-used tool to understand the cycling of mercury through different envi-

ronmental compartments (*43*). Global mercury models have identified wet and dry deposition of RGM and particles, in addition to evasion of dissolved gaseous mercury from the ocean and land, as key controls over mercury cycling and fate on the Earths surface (*44*). In contrast to GEM, there was no significant difference in the observed concentrations of RGM and Hg−P that were obtained over open water compared to over sea ice (Figure 2). The results of oxidized mercury species were, in general, lower compared to other recent ship-based measurements at temperate latitudes on the Northern Hemisphere (*12*, *13*, *45*) and model calculations for similar locations (*46*). However, the results were comparable to a land based study in Florida when clean marine air was measured (*47*) and measurements over the South Atlantic Ocean during Antarctic summer (*30*). Table 2 summarizes results from the previously mentioned field studies. Measured concentrations of RGM are generally a result of either in-situ production or atmospheric transport of previously emitted RGM from the source to the measurement location. Due to relatively short atmospheric lifetime, it is not likely that RGM observed over the North Atlantic Ocean is a result of long-range transport. It is generally recognized that the marine boundary layer (MBL) can be a source of RGM in the atmosphere when halide enriched sea-salt aerosols are present (*8*, *13*, *46*). RGM is then formed either by direct oxidation of Hg⁰ or outgassing of HgCl₂ from aerosol particles (*48-49*). Results from recently published global circulation models point out the importance of RGM formation over remote water bodies (*50*, *51*). Mason and Sheu (*8*) estimated that RGM contributes up to 35% of the total input of mercury to the oceans. However, the low results observed in this study indicate that the North Atlantic MBL during Arctic summer is not an important contributor to either dry or wet deposition of RGM to the ocean.

No diurnal variation was observed in the RGM concentrations in this study, which is in contrast to other Northern Hemisphere ship-based campaigns at temperate latitudes

(*12, 13*) as shown in Table 2. At temperate latitudes, meteorological conditions that favor formation of RGM are strong solar radiation that produces potential oxidants such as OH radicals or $O_3$ (*10, 46*). Additionally, low wind speed and low relative humidity is needed for enhanced concentration values of RGM to be observed because turbulent conditions and aerosols scavenge RGM from the atmosphere (*12, 13*). However, the Arctic summer is dominated by high relative humidity (>90%), low visibility, low ceiling, and fog patches. With the exception of a few days, the solar radiation did not increase above 200 W/m² during the cruise. For comparison, summer daytime radiation maximum in the Mediterranean Sea is measured between 600 and 700 W/m² (*13*). While OH radicals are efficient oxidants for $Hg^0$ (*11*), the concentration of OH in the Arctic MBL is lower than at temperate latitudes, and perhaps not high enough for efficient $Hg^0$ oxidation. North of the Arctic Circle (66°33′N), the relative humidity was high (>85%), with a few exceptions (July 3 and Aug 2). In addition, high humidity can readily scavenge RGM and thus RGM can be wet deposited on the snow and water surfaces, resulting in observations of low concentrations of RGM in the air.

## Acknowledgments

## Literature Cited

(1) Schroeder, W. H.; Munthe, J. Atmospheric mercury—an overview. *Atmos. Environ.* **1998**, *32*, 809–822.

(2) Schroeder, W. H.; Steffen, A.; Scott, K.; Bender, T.; Prestbo, E.; Ebinghaus, R.; Lu, J. Y.; Lindberg, E. Summary report: first international Arctic atmospheric mercury research workshop. *Atmos. Environ.* **2003**, *37*, 2551–2555.

(3) Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Temme, C.; Munthe, J.; Wangberg, I.; Schroeder, W.; Steffen, A.; Berg, T. Worldwide trend of atmospheric mercury since 1977. *Geophys. Res. Lett.* **2003**, *30*, Art. No. 1516.

(4) Nriagu, J. G.; Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. *Nature* **1988**, *333*, 134–139.

(5) Aspmo, K.; Guachard, 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.* **39**, 7607–7619.

(6) Ebinghaus, R.; Jennings, S. G.; Schroeder, W. H.; Berg, T.; Donaghy, T.; Guentzel, J.; Kenny, C.; Kock, H. H.; Kvietkus, K.; Landing, W.; Muhleck, T.; Munthe, J.; Prestbo, E. M.; Schneeberger, D.; Slemr, F.; Sommar, J.; Urba, A.; Wallschläger, D.; Xiao, Z. International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland. *Atmos. Environ.* **1999**, *33*, 3063–3073.

(7) Lindberg, S. E.; Stratton, W. J. Atmospheric mercury speciation: Concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **1998**, *32*, 49–57.

(8) Mason, R. P.; Sheu, G. R. Role of the ocean in the global mercury cycle. *Glob. Biogeochem. Cycles* **2002**, *16*, Art No 1093.

(9) Hall, B. The gas-phase oxidation of elemental mercury by ozone. *Water, Air, Soil Pollut.* **1995**, *80*, 301–315.

(10) Sheu, G.-R.; Mason, R. P. An examination of the oxidation of elemental mercury in the presence of halide surfaces. *J. Atmos. Chem.* **2004**, *48*, 107–130.

(11) Sommar, J.; Gårdfeldt, K.; Strømberg, D.; Feng, X. A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. *Atmos. Environ.* **2001**, *35*, 3049–3054.

(12) Laurier, F. J. G.; Mason, R. P.; Whalin, L. Reactive gaseous mercury formation in the North Pacific Ocean's marine bound-

(13) Sprovieri, F.; Pirrone, N.; Gårdfeldt, K.; Sommar, J. Mercury speciation in the marine boundary layer along a 6000 km cruise path around the Mediterranean Sea. *Atmos. Environ.* **2003**, *37*, Suppl 1, S63–S71.

(14) Sander, R.; Keene, W. C.; Pszenny, A. A. P.; Arimoto, R.; Ayers, G. P.; Baboukas, E.; Cainey, J. M.; Crutzen, P. J.; Duce, R. A.; Honninger, G.; Huebert, B. J.; Maenhaut, W.; Mihalopoulos, N.; Turekian, V. C.; Van Dingenen, R. Inorganic bromine in the marine boundary layer: a critical review. *Atmos. Chem. Phys.* **2003**, *3*, 1301–1336.

(15) Schroeder, W. H.; Anlauf, K.; Barrie, L. A.; Lu, J. Y.; Steffen, A.; Schneeberger, D. R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394*, 331–332.

(16) 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.

(17) Ariya, P. A.; Dastoor, A. P.; Amyot, M.; Schroeder, W. H.; Barrie, L.; Anlauf, K.; Raofie, F.; Ryzhkov, A.; Davignos, D.; Lalonde, J.; Steffen, A. The Arctic: a sink for mercury. *Tellus* **2004**, *56B*, 397–403.

(18) AMAP (Arctic Monitoring and Assessment Programme) *Arctic pollution 2002: Persistent organic pollutants, heavy metals, radioactivity, human health, changing pathways;* AMAP: Oslo, 2002.

(19) Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, A.; 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 tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28*, 3219–3222.

(20) Berg, T.; Bartnicki, J.; Munthe, J.; Lattila, H.; Hrehoruk, J.; Mazur, A. Atmospheric mercury species in the European Arctic: measurements and modelling. *Atmos. Environ.* **2001**, *35*, 2569–2582.

(21) Skov, H.; Christensen, J. H.; Goodsite, M. E.; Heidam, 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

(22) Ebinghaus, R.; Kock, H. H.; Temme, C.; Einax, J. W.; Lowe, A. G.; Richter, A.; Burrows, J. P.; Schroeder, W. H. Antarctic springtime depletion of atmospheric mercury. *Environ. Sci. Technol.* **2002**, *36*, 1238–1244

(23) Steffen, A.; Schroeder, W.; MacDonald, R.; Poissant, L.; Konoplev, A. Mercury in the Arctic atmosphere: An analysis of eight years of measurements of GEM at Alert (Canada) and a comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada). *Sci. Total Environ.* **2005**, *342*, 185–198.

(24) Kaleschke, L.; Richter, A.; Burrows, J.; Afe, O.; Heygster, G.; Notholt, J.; Rankin, A. M.; Roscoe, H. K.; Hollwedel, J.; Wagner, T.; Jacobi, H.-W. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. *Geophys. Res. Lett.* **2004**, *31*, L16114.

(25) Douglas, T. A.; Sturm, M.; Simpson, W. R.; Brooks, S.; Lindberg, S. E.; Perovich, D. K. Elevated mercury measured in snow and frost flowers near Arctic sea ice leads. *Geophys. Res. Lett.* **2005**, *32*, L04502.

(26) Gauchard, P. A.; Aspmo, K.; Temme, C.; Steffen, A.; Ferrari, C.; Berg, T.; Ström, J.; Kaleschke, L.; Dommergue, A.; Bahlmann, E.; Magand, O.; Planchon, F.; Ebinghaus, R.; Banic, C.; Nagorski, S.; Baussand, P.; Boutron, C. Study of the origin of atmospheric mercury depletion events recorded in Ny-Alesund, Svalbard, spring 2003. *Atmos. Environ.* **39**, 7620–7632.

(27) Mason, R. P.; Fitzgeral, W. F.; Morel, F. M. M. The biogeochemical cycling of elemental mercury—anthropogenic influences. *Geochim. Cosmochim. Acta.* **1994**, *58*, 3191–3198.

(28) 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.

(29) Ferrari, C. P.; Gauchard, P.-A.; Dommergue, A.; Magand, O.; Nagorski, S.; Temme, C.; Bahlmann, E.; Ebinghaus, R.; Steffen, A.; Banic, C.; Aspmo, K.; Berg, T.; Planchon, F.; Barbante, C.; Boutron, C. F. Snow-to-air exchanges of mercury in an Arctic seasonal snowpack in Ny Ålesund, Svalbard. *Atmos. Environ.* **39**, 7633–7645.

(30) Temme, C.; Einax, J.; Ebinghaus, R.; Schroeder, W. H. Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the south Atlantic Ocean during polar summer. *Environ. Sci. Technol.* **2003**, *27*, 22–31.

(31) Temme, C.; Slemr, F.; Ebinghaus, R.; Einax, J. Distribution of mercury over the Atlantic Ocean in 1996 and 1999−2001. *Atmos. Environ.* **2003**, *37*, 1889−1897.

(32) Tekran Inc., Model 2537A: Principles of operation; Tekran, Inc.: Toronto, 1998.

(33) Landis, M.; Stevens, R. K.; Schaedlich, F.; Prestbo, E. M. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* **2002**, *36*, 3000−3009.

(34) Lu, J. Y.; Schroeder, W. H.; Berg, T.; Munthe, J.; Schneeberger, D.; Schaedlich, F. A device for sampling and determination of total particulate mercury in ambient air. *Anal. Chem.* **1998**, *70*, 2403−2408.

(35) Berg, T.; Sekkesæter, S.; Steinnes, E.; Valdal, A. K.; Wibetoe, G. Springtime depletion of mercury in the European Arctic as observed at Svalbard. *Sci. Total Eviron.* **2003**, *304*, 43−51

(36) Bloom, N. S.; Crecelius, E. A. Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* **1983**, *14*, 49−59.

(37) U.S. EPA Definition and Procedure for the Determination of the Method Detection Limit, *Code of Federal Regulations,* part 136, appendix B, rev 1.11, title 40.

(38) Lieser, J. L. Sea ice conditions in northern North Atlantic in 2003 & 2004: Observations during RV POLARSTERN cruise ARKTIS XIX/1 a&b and ARKTIS XX/2. In *Reports on Polar and Marine Research, 504;* Alfred Wegener Institute for Polar and Marine Research: Bremerhaven, Germany, 2005.

(39) Temme, C.; Baukau, J.; Schneider, B.; Aspmo, K.; Fain, X.; Ferrari, C.; Gauchard, P.-A. *Air/water exchange of mercury in the North Atlantic Ocean during Arctic summer.* Proceedings of the XIII International Conference on Heavy Metals in the Environment, Rio de Janeiro, Brazil, June 5−9, 2005.

(40) Mason, R. P.; Rolfhus, K. R.; Fitzgerald, W. F. Mercury in the North Atlantic. *Mar. Chem.* **1998**, *61*, 37−53.

(41) 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.

(42) 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.

(43) Dastoor, A. P.; Larocque, Y. Global circulation of atmospheric mercury: a modelling study. *Atmos. Environ.* **2004**, *38*, 147−161.

(44) Shia, R.-L.; Seigneur, C.; Pai, P.; Ko, M.; Sze, N. D. Global simulation of atmospheric mercury concentrations and deposition fluxes. *J. Geophys. Res.* **1999**, *104*, 23747−23760.

(45) Mason, R. P.; Lawson, N. M.; Sheu, G.-R. Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters. *Deep-Sea Res. II.* **1998**, *48*, 2829−2853.

(46) Hedgecock, I. M.; Pirrone, N.; Sprovieri, F.; Pesenti, E. Reactive gaseous mercury in the marine boundary layer: modelling and experimental evidence of its formation in the Mediterranean region. *Atmos. Environ.* **2003**, *37*, Suppl 1, S41−S49.

(47) Malcolm, E. G.; Keeler, G. J.; Landis, M. S. The effects of the coastal environment on the atmospheric mercury cycle. *J. Geophys. Res.* **2003**, *108*, article no. 4357.

(48) Pirrone, N.; Costa, P.; Pacyna, J. M.; Ferrara, R. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmos. Environ.* **2001**, *35*, 2997−3006.

(49) Hedgecock, I. M.; Pirrone, N. Mercury and photochemistry in the marine boundary layer-modelling studies suggest the in situ production of reactive gas-phase mercury. *Atmos. Environ.* **2001**, *35*, 3055−3062.

(50) Bergan, T.; Rodhe, H. Oxidation of elemental mercury in the atmosphere; Constraints imposed by global scale modelling. *J. Atmos. Chem.* **2001**, *40*, 191−212.

(51) Seigneur, C.; Karamchandani, P.; Vijayaraghavan, K.; Lohman, K.; Shia, R.-L.; Levin, L. On the effect of spatial resolution on atmospheric mercury modelling. *Sci. Total Environ.* **2003**, *304*, 73