

## Potential Sources of Monomethyl Mercury in Arctic and Subarctic Seawater

by J.L. Kirk

### INTRODUCTION

**M**ERCURY (Hg) IS A HEAVY METAL that exists in many different forms in the environment. One of these forms, monomethyl mercury (MMHg), is a strong vertebrate neurotoxin that bioaccumulates through food webs. In some Canadian Arctic marine mammals, MMHg has increased to levels that may be toxic to northern peoples who consume these species as traditional foods (INAC, 2003). Unfortunately, it is difficult to determine the sources of Hg contamination in northern food webs because the cycling of Hg is complex and not well characterized in Arctic marine ecosystems.

Mercury may enter the Arctic via a number of pathways (see general schematic). For example, gaseous Hg(0) released by industrial processes such as coal combustion and waste incineration is relatively stable in the atmosphere and can be transported to the Arctic on air currents (Shroeder and Munthe, 1998). Gaseous Hg(0) can flux into or out of waterbodies, such as lakes and oceans, depending on where concentrations of Hg(0) are higher. Inorganic Hg(II) and MMHg may also enter Arctic marine ecosystems in precipitation, river inflow, and glacial melt, as well as via ocean currents.

Mercury can change from one form to another within Arctic ecosystems (see general schematic). In the sediments of lakes and wetlands in more southern latitudes, sulphate-reducing bacteria are thought to methylate inorganic Hg(II) to MMHg, which can then be taken up by organisms and bioaccumulated through food webs (Compeau and Bartha, 1985; Gilmour et al., 1992; Hurley et al., 1995; Rudd, 1995). It is not known, however, how Hg(II) methylation occurs in polar oceans. MMHg can also be photodegraded by solar radiation, probably to Hg(II) or Hg(0), or both, in the surface waters of lakes and possibly oceans (Gardfelt et al., 2001; Chen et al., 2003). In the Arctic and Subarctic, Hg(II) species are formed from atmospheric gaseous Hg(0) during reactions called "springtime atmospheric Hg depletion events." Concentrations of gaseous Hg(0) in the Arctic atmosphere are typically  $\sim 1.7 \text{ ng m}^{-3}$  (Shroeder et al., 1998). However, from polar sunrise until snowmelt, atmospheric Hg(0) levels frequently drop below  $1 \text{ ng m}^{-3}$  (Shroeder et al., 1998). It is hypothesized that Hg(0) is oxidized to reactive gaseous Hg (RGM) and particulate Hg (pHg) by sunlight-induced reactions with marine halogens bromine (Br) and chlorine (Cl) (Lindberg et al., 2002; Clavert and Lindberg, 2003). Both of these oxidized forms of Hg have deposition velocities greater than that of gaseous Hg(0) and thus fall into snowpacks over the sea ice. It is thought that much of the deposited Hg enters marine environments at ice-out, and it has been estimated,

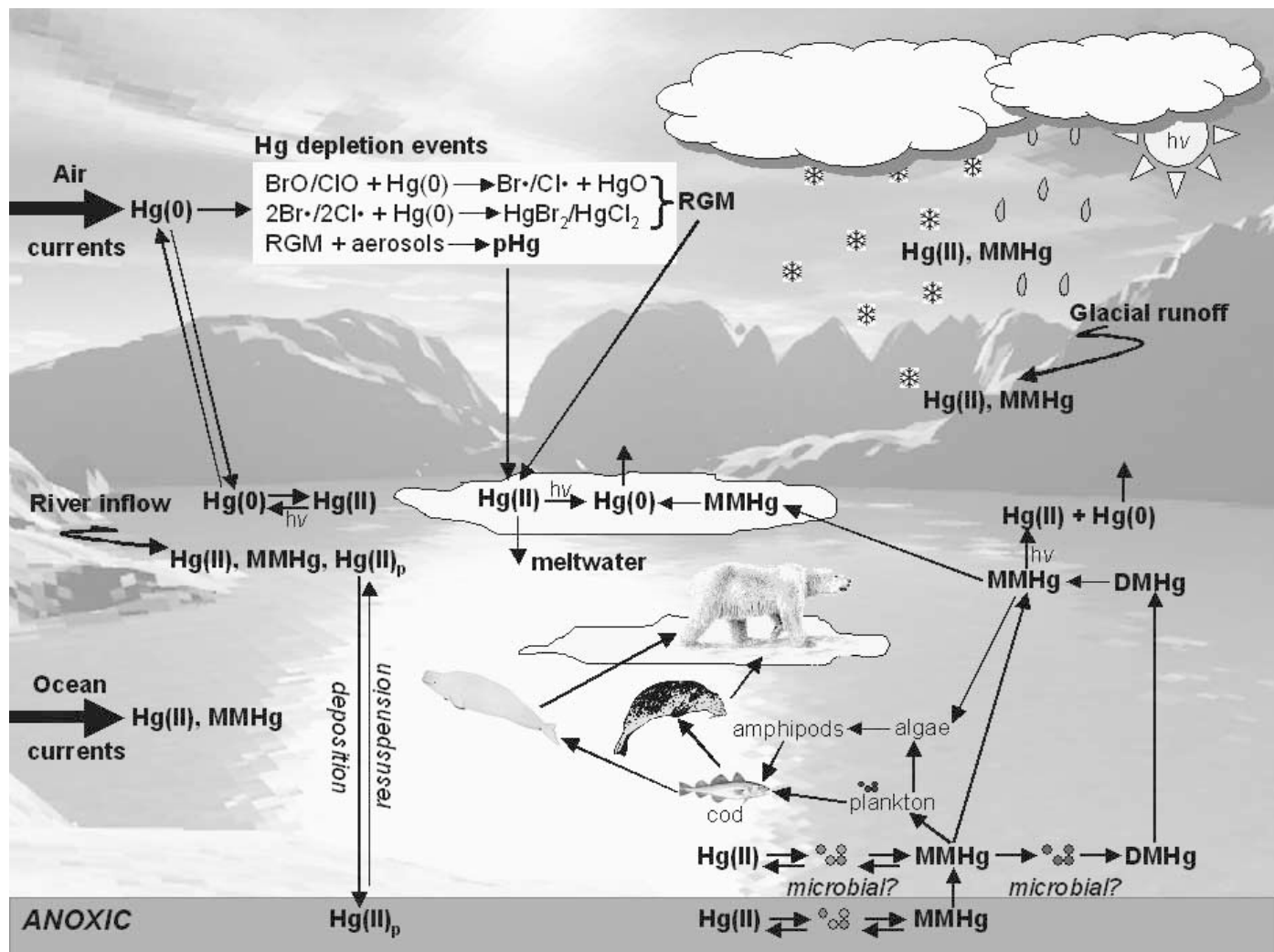
from atmospheric concentrations of RGM and pHg measured during Hg depletion events, that 150–300 T of Hg is loaded into the Canadian archipelago each spring (Lindberg et al., 2002; Ariya et al., 2004).

We studied atmospheric Hg depletion events over western Hudson Bay in spring 2004 by continuously monitoring atmospheric concentrations of gaseous Hg(0), RGM, and pHg while simultaneously measuring the deposition of Hg(II) into snowpacks. The results of this study, which are currently being prepared for publication, indicated that although a large amount of Hg was deposited into snowpacks during Hg depletion events, most of it was photo-reduced to gaseous Hg(0) and remitted to the atmosphere soon after depletion events ceased, and well before snowmelt entered the marine ecosystem at ice-out. We therefore hypothesize that the Hg transmitted to Arctic marine food webs must have other sources, and we have started to examine Hg cycling in polar oceans themselves.

St. Louis et al. (2005) recently found high concentrations of MMHg in surface snow collected on the Prince of Wales icefield (east coast of Ellesmere Island) along a transect west of the North Water polynya. Concentrations of MMHg in spring snow reached over  $0.28 \text{ ng/L}$  and were positively correlated with concentrations of Cl. These high concentrations are equivalent to those seen in runoff from Boreal ecoregion wetlands, which are very important natural sites of Hg methylation (St. Louis et al., 1994). These results strongly suggest a marine source (in this case, the North Water polynya) for the MMHg in Arctic snowpacks.

Methylated Hg species, including MMHg and dimethyl Hg (DMHg), have been found in sub-thermocline North Atlantic waters, where they are probably produced by marine bacteria (Mason et al., 1998). In regions of deepwater upwelling or winter thermocline mixing, DMHg can be brought to the surface and subsequently lost to the atmosphere by gas exchange. It is likely that atmospheric DMHg is rapidly photolyzed to MMHg ( $\text{Cl} + \text{CH}_3\text{HgCH}_3 \rightarrow \text{CH}_3\text{HgCl} + \text{CH}_3$ ) (Niki et al., 1983), making the ocean a potential source of atmospheric MMHg. We hypothesize that MMHg found in Arctic snowpacks originates from DMHg fluxing through polynyas and leads in the sea ice during the winter. Furthermore, we hypothesize that active methylation of Hg(II) in polar oceans produces not only DMHg, but also large quantities of MMHg.

I began testing these hypotheses from August to October 2005, while on board the icebreaker CCGS *Amundsen* as part of ArcticNet, a Network of Centres of Excellence of Canada developed to study the impact of climate change on Canadian Arctic coastal areas. Seawater was sampled at many sites in the High Arctic and Hudson Bay for



General schematic of Hg cycling in the Arctic and Subarctic, outlining potential sources of monomethyl Hg (MMHg) found in northern food webs. Marine mammals such as beluga whales, seals, and polar bears are used for food by northern peoples. The mechanisms behind many of the processes outlined here are still unclear. For example, it is suspected, but not known, that dimethyl mercury (DMHg) is produced by bacteria in deep regions of marine water columns. We hypothesize that monomethyl mercury (MMHg) is produced deep in water columns and in ocean sediments; however, we do not know the relative importance of these two sources to the concentrations of MMHg observed in ocean waters. The photodegradation of MMHg in surface waters to Hg(II) or gaseous Hg(0), or both, is also not fully understood.

concentrations of DMHg and MMHg, as well as for total Hg (THg; or all forms of Hg in a sample), and dissolved gaseous Hg(0). To delineate regions of production or loss (or both) of different Hg species within the water column, seawater was sampled from different ocean depths (surface, middle, and bottom). In collaboration with Igor Lehnerr, another PhD graduate student at the University of Alberta, I also performed experiments using state-of-the-art Hg stable-isotope techniques to determine if Hg(II) is being methylated to MMHg in the deep regions of oceans. This sampling design allows us to examine the spatial distribution of the four species of Hg in Arctic and Subarctic seawaters and to gain an understanding of the biogeochemical cycling of Hg at these sites.

## METHODS

### Sample Collection and Analyses

Seawater samples were collected in three acid-cleaned 12 L Teflon®-lined Niskin® bottles, which were installed on the CCGS *Amundsen's* water sampler, a SeaBird® Carousel rosette system. At each site, the rosette was lowered into the water by winch and the Niskin bottles were closed at various depths by Seabird 911+ controller. Seawater samples were collected from the Niskin bottles immediately after the rosette was brought back up to the surface, using “clean hands-dirty hands” standard Hg sampling protocol (St. Louis et al., 1994).



Jane Kirk with dimethyl Hg sparger. Photo: V.L. St. Louis.

### *Dimethyl Hg and Dissolved Gaseous Hg(0) Samples*

Water samples for DMHg and dissolved gaseous Hg(0) analyses were collected into acid-washed glass bottles, 2 L for DMHg and 1 L glass for Hg(0) samples. The glass bottles were covered with dark bags so that the samples would not be affected by light (e.g., photoreduction processes). DMHg and Hg(0) were obtained from the water samples immediately after sampling, using purge and trap techniques. DMHg and Hg(0) were stripped onto Carbo® traps and gold traps, respectively, by bubbling the samples with ultra-high purity (UHP) nitrogen passed through glass sparge heads.

Immediately after sparging, Carbo traps were capped, sealed with Teflon tape, individually bagged, and stored in air-tight, acid-washed canning jars purged with UHP nitrogen. Carbo traps were then sent to Dr. Holger Hintlemann at the Department of Chemistry, Trent University, for analyses of DMHg on an Inductively Coupled Plasma Mass Spectrophotometer (ICPMS). DMHg concentrations were calculated by dividing the number of picograms of DMHg on each trap by the volume of water sampled, then blank correcting (subtracting the residual Hg level determined by sparging Hg-free water).

Gold traps were analyzed for Hg(0) on board the ship immediately after sparging. Hg(0) was thermally desorbed

from the gold traps at 400°C and carried to a Tekran® Model 2500 cold vapor atomic fluorescence spectrophotometer (CVAFS) in a stream of UHP argon. Star Chromatography Workstation software (Varian Inc., Mississauga, ON) was used for integration of peak areas. Final Hg(0) concentrations will be calculated as described above for DMHg.

### *THg and MMHg Samples*

Water samples for MMHg and THg analyses were collected into acid-washed Teflon bottles (250 mL and 125 mL, respectively). Samples for THg analyses were immediately acidified to 0.2% HCl, whereas those for MMHg analyses were acidified to 0.4% H<sub>2</sub>SO<sub>4</sub> for preservation. All THg and MMHg analyses will be conducted at the University of Alberta Low-Level Mercury Analytical Laboratory, using standard protocols and CVAFS (Bloom, 1989; Horvat et al., 1993).

### *Isotope Incubation Experiments*

Seawater samples for Hg isotope incubation experiments were collected into acid-washed 500 mL amber glass bottles (Boston round) at five sites: Cambridge Bay, Peel Sound, the top of Hudson Bay, and two sites within Hudson Bay. At each site, six bottles of seawater were obtained (three from the surface and three from the bottom) and <sup>198</sup>Hg(II) and MM<sup>199</sup>Hg were added to all six samples. By adding both Hg(II) and MMHg isotopes, we will be able to determine whether methylation, demethylation, or both are occurring in the water column of oceans by examining both the production of MM<sup>198</sup>Hg from <sup>198</sup>Hg(II), and the loss of MM<sup>199</sup>Hg. One surface and one bottom sample were used as time-zero controls, and were therefore acidified to 0.4% H<sub>2</sub>SO<sub>4</sub> immediately after isotope addition to prevent methylation and demethylation reactions. The other samples were incubated for 12 or 24 hours before acidification. These samples will be analyzed at the University of Alberta for <sup>198</sup>Hg(II), using a Tekran model 2600 interfaced with a PerkinElmer® Elan ICPMS, and for MM<sup>198</sup>Hg and MM<sup>199</sup>Hg, by aqueous phase ethylation, GC separation, and quantification on the ICPMS.

## PRELIMINARY RESULTS

At present, I have only preliminary DMHg results from the CCGS *Amundsen* icebreaker cruise, as the other samples are currently being analyzed. Seawater samples collected at numerous sites in the North Water polynya, Northwest Passage, and Hudson Bay had very high concentrations of DMHg. Concentrations were the highest (often 100–200 pg L<sup>-1</sup>) in samples collected at bottom depths (below ~ 100 m), indicating that DMHg is being produced in deep Arctic seawaters. These results suggest that active methylation of Hg(II) occurs in polar waters,

and we therefore expect to see high concentrations of MMHg in many of the samples collected on the cruise. In surface water samples at all sites, concentrations of DMHg were low (often just above detection limits), likely because DMHg is photodegraded to MMHg by solar radiation. Using our measured concentrations of DMHg and piston velocities supplied by others on the CCGS *Amundsen* cruise, we will calculate surface fluxes of DMHg to determine how much atmospheric MMHg is potentially produced in oceans. We will then be able to determine the relative importance of MMHg originating from DMHg and MMHg directly produced in the water column or sediments of polar oceans. We will also calculate gaseous Hg(0) fluxes to determine whether polar oceans are sinks or sources of atmospheric gaseous Hg(0). We hope that the research described here, in addition to providing new information about the biogeochemical cycling of Hg in the Arctic, will help us to understand the sources of MMHg found in marine mammals that northern people use for food.

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#### REFERENCES

- ARIYA, P.A., DASTOOR, A.P., AMYOT, M., SCHROEDER, W.H., BARRIE, L., ANLAUF, K., RAOFFIE, F., RYZHKOV, A., DAVIDGNON, D., LALONDE, J., and STEFFAN, A. 2004. The Arctic: A sink of mercury. *Tellus* 56B:397–403.
- BLOOM, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Canadian Journal of Fisheries and Aquatic Sciences* 46:1131–1140.
- CHEN, J., PEHKONEN, S.O., and LIN, C.J. 2003. Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. *Water Research* 37:2496–2504.
- CLAVERT, J.G., and LINDBERG, S.E. 2003. A modeling study of the mechanism of the halogen-ozone-mercury homogenous reactions in the troposphere during the polar spring. *Atmospheric Environment* 37:4467–4481.
- COMPEAU, G.C., and BARTHA, R. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediments. *Applied and Environmental Microbiology* 50: 498–502.
- GARDFELDT, K., SOMMAR, J., STROMBERG, D., and FENG, X. 2001. Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase. *Atmospheric Environment* 35:3039–3047.
- GILMOUR, C.C., HENRY, E.A., and MITCHELL, R. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Science Technology* 26:2281–2287.
- HORVAT, M., BLOOM, N.S., and LIANG, L. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. 2. Water. *Analytica Chimica Acta* 281:135–152.
- HURLEY, J.P., BENOIT, J.M., BABIARZ, C.L., ANDREN, A.W., and SULLIVAN, J.R. 1995. Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environmental Science and Technology* 29:1867–1875.
- INAC (INDIAN AND NORTHERN AFFAIRS CANADA). 2003. Canadian Arctic Contaminants Assessment Report II: Highlights. Ottawa: INAC.
- LINDBERG, S.E., BROOKS, S., LIN, C.J., SCOTT, K.J., LANDIS, M.S., STEVENS, R.K., GOODSITE, M., and RICHTER, A. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environmental Science and Technology* 36:1245–1256.
- MASON, R.P., ROLFHUS, K.R., and FITZGERALD, W.F. 1998. Mercury in the North Atlantic. *Marine Chemistry* 61:37–53.
- NIKI, H., MAKER, P.S., SAVAGE, C.M., and BREITENBACH, L.P. 1983. A Fourier transform infrared study of the kinetics and mechanism for the reaction  $\text{Cl} + \text{CH}_3\text{HgCH}_3$ . *Journal of Physical Chemistry* 87:3722–3724.
- RUDD, J.W.M. 1995. Sources of methylmercury to freshwater ecosystems: A review. *Water, Air, and Soil Pollution* 80: 697–713.
- SCHROEDER, W.H., and MUNTHER, J. 1998. Atmospheric mercury: An overview. *Atmospheric Environment* 32:809–822.
- SCHROEDER, W.H., ANLAUF, K.G., BARRIE, L.A., LU, J.Y., STEFFEN, A., SCHNEEBERGER, D.R., and BERG, T. 1998. Arctic springtime depletion of mercury. *Nature* 394:331–332.
- ST. LOUIS, V.L., RUDD, J.W.M., KELLY, C.A., BEATY, K.G., BLOOM, N.S., and FLETT, R.J. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences* 51: 1065–1076.
- ST. LOUIS, V.L., SHARP, M.J., STEFFAN, A., MAY, A., BARKER, J., KIRK, J.L., KELLY, D.J.A., ARNOTT, S.E., KEATLEY, B., and SMOL, J.P. 2005. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere Island in the Canadian High Arctic. *Environmental Science and Technology* 39(8):2686–2701.

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