Bioavailable Mercury in Arctic Snow Determined by a Light-Emitting \textit{mer-lux} Bioreporter

by Karen J. Scott

\textbf{INTRODUCTION}

\textbf{BIOAVAILABILITY OF INORGANIC MERCURY}

Mercury (Hg) is a heavy metal with unique chemical properties that make it an attractive resource in many industries. Hg is also a by-product of fossil fuel combustion and other industrial processes. It exists in the environment in many different forms: as a gas, a liquid, and a solid, and as both inorganic and organic compounds (Lindqvist and Rodhe, 1985). Some forms of Hg are relatively harmless to humans and wildlife, while others, such as methylmercury (MeHg), are extremely toxic. Levels of MeHg in fish, shellfish, and marine mammals often exceed the recommended consumption allowance of 0.5 \( \mu \)g/g (Welch et al., 1999), even in areas far from point source pollution.

The pervasive nature of Hg is due to its predominance (\( \geq 80\% \)) in the atmosphere as elemental Hg (Hg\textsubscript{0}), a very stable gas (Lindqvist and Rodhe, 1985). The residence time of Hg\textsubscript{0} in the atmosphere is estimated to be approximately one year (Lindqvist and Rodhe, 1985) because of its chemical stability and low water solubility (Schroeder and Munthe, 1998), thus permitting its dispersion in the atmosphere over long distances. Over time, atmospheric Hg\textsubscript{0} is oxidized to more water soluble forms, e.g., divalent inorganic Hg (Hg(II)), and scavenged from the atmosphere by wet and dry deposition (Brosset, 1981). It is predominantly these inorganic species of Hg that enter remote ecosystems via the atmosphere.

The Arctic, a repository for many chemicals that originate elsewhere and travel poleward, is especially vulnerable to incursions of air pollution (Brasseur et al., 1999). While there may be local sources, it seems probable that Hg in the Arctic comes from more distant fossil-fuel and industrial sources in North America, Siberia, China, and Europe. Several studies suggest not only that inputs of Hg to the Arctic have increased relative to pre-industrial levels, but that such increases have also been detected in Arctic marine mammals (Hermanson, 1993; Pacyna and Keeler, 1995; Lockhart et al., 1995; Braune, 1999). The consequences of this are serious, as marine mammals constitute a large part of the traditional diet of Native coastal communities (Kinloch et al., 1992).

In aquatic environments, Hg(II) is the substrate for two important microbial processes: the reduction of Hg(II) to Hg\textsubscript{0} and the methylation of Hg(II) to MeHg (Osborn et al., 1997). The genes specifying the various functions needed for reduction of Hg(II) are organized in what is known as the mercury resistance (\textit{mer}) operon. The \textit{mer} operon is the best understood genetic system for the detoxification of a heavy metal. For Hg(II) to become microbially transformed, however, it must first enter the bacterial cell or be "bioavailable." Distinguishing between bioavailable and unavailable forms of Hg(II) and understanding the factors that control the concentration of bioavailable Hg (bioHg) are critical in evaluating the potential of microorganisms to transform Hg(II) to Hg\textsubscript{0} and to MeHg in aquatic ecosystems.

The past fifteen years have brought many advances in measuring trace levels of Hg(II) in environmental samples using chemical methods (Bloom and Crecelius, 1983; Stratton and Lindberg, 1995). However, these methods do not provide information on the fraction of Hg(II) that is available to bacteria and therefore has the potential to be biotically methylated to MeHg or microbially reduced to Hg\textsubscript{0}. A new analytical method, using genetically engineered bacteria (Selifonova et al., 1993), has provided a way to gain insight into the fraction of Hg(II) that is available and into the factors that control its bioavailability. These genetically engineered bacteria, called \textit{mer-lux bioreporters}, produce light when Hg(II) enters the bacterial cell. They measure the amount of Hg(II) that is bioavailable, as opposed to the total amount, which chemical analytical methods measure. The \textit{mer-lux} bioreporter used in my research is \textit{Vibrio anguillarum} pRB28. Briefly, \textit{V. anguillarum} was transformed with the plasmid pRB28, which is composed of the regulatory region (\textit{merR}) of the \textit{mer} operon (but not \textit{merA}, the genes for Hg(II) reduction to Hg\textsubscript{0}) and of \textit{lux} genes coding for luciferase (\textit{luxAB}) and fatty acid reductase (\textit{luxCDE}), required for bacterial luminescence. Hg(II) entering cells containing this plasmid would not be reduced (as it would in nature if the cells contained the entire \textit{mer} operon), but will cause transcription of the \textit{lux} genes. The light produced by these bacteria,
The snow story continues with other interesting, and somewhat more groundbreaking, snow research being conducted in the Canadian Arctic (Alert, Nunavut, 82.5˚ N). In 1998, Dr. Bill Schroeder (Atmospheric Environment Services) and colleagues described seasonal Hg0 (or total gaseous Hg) depletion events in the Arctic troposphere that strongly resembled tropospheric ozone depletion (Schroeder et al., 1998). They found that before Polar sunrise, which occurs in March in Alert, total gaseous Hg concentrations in the atmosphere and ozone levels were moderately variable, but normal. At Polar sunrise, and for approximately three months following Polar sunrise, total gaseous Hg and ozone concentrations became erratic, with a pronounced tendency towards unusually low concentrations. These were described as “Hg depletion events.” Between 1 April and 15 June, during these Hg depletion events, the air column was “emptied” of its Hg content at least five times. Dr. Schroeder and colleagues concluded that gaseous Hg was being oxidized by an undefined, sunlight-induced chemical oxidation mechanism associated with ozone depletion in the lower troposphere and that the Hg species produced (unknown, but possibly particulate Hg or reactive gas mercury (RGM), or both) have a shorter residence time in the atmosphere. Essentially, they were describing a direct pathway for the introduction of Hg into the biosphere.

My research involves the development of this mer-lux bioreporter for use in field studies to further our understanding of environmental factors that affect the bioavailability of Hg(II) in aquatic environments. I am also quantifying the bioavailability of Hg(II) entering remote ecosystems via the atmosphere. One of my study sites is the Experimental Lakes Area (ELA) in northwestern Ontario, a federal government research station located in the boreal forest of the Canadian Shield. Consumption guidelines have been set for fish in many of the lakes of this area because of elevated levels of MeHg in their tissues. Some of my early findings at the ELA suggested that snow is an important source of bioHg input to the ELA. The second remote location included in my studies is Barrow, Alaska (79˚ N) in the Arctic.

THE SNOW STORY

The snow story begins at the ELA. The Hg input to the ELA, believed to be atmospheric in origin, is composed largely of Hg(II) species such as HgCl2. When it rains, or when snow melts, the precipitation can enter lakes directly from the atmosphere, via throughfall (rain that has passed through a canopy of trees), and as runoff (rain that has passed over terrestrial surfaces). Figure 1 shows concentrations of bioHg from each of these inputs. Surprisingly, there was a considerably larger percentage of bioHg in snow than in the other inputs from this location, suggesting that snow may be an important vector for bioHg entry to remote areas.

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So where was the Hg going? A group of researchers from the Department of Fisheries and Oceans at the Freshwater Institute (FWI) in Winnipeg, led by Drs. Lyle Lockhart and Harold Welch, had previously found elevated concentrations of Hg in snow meltwater collected near Arctic communities (Welch, 1998). These concentrations ranged between 2.1 ng/L (Baker Lake) and an alarming 237 ng/L (Cambridge Bay). Furthermore, the FWI group observed a seasonal increase in Hg concentrations in surface snow over the ice pack (Welch et al., 1999). Dr. Schroeder’s work, together with the FWI group’s snow data, strongly suggested that much of the atmospheric Hg in the Arctic is likely ending up in the snowpack during an intensive three-month period following Polar sunrise.

Examining the fate of Hg in the snowpack is crucial to our understanding of the biogeochemical cycle of Hg in Arctic ecosystems and to modeling these biogeochemical processes. If the majority of the Hg accumulated in the snowpack returns to the atmosphere through volatilization, then these Hg depletion events may have a limited impact on the Arctic ecosystem. However, if this Hg is bioavailable and gets flushed from the snowpack into the ecosystem during the spring melt, runoff could be a major mechanism for the transport of bioHg and would represent a disturbingly important input of Hg to Arctic ecosystems at a biologically active time of the year.

PROJECT DESCRIPTION AND RESULTS

The initial objective of this component of my research was to determine the bioavailability of Hg(II) in snow entering the Arctic via long-range atmospheric transport. In addition to samples for bioHg, snow samples were collected for total Hg, MeHg, and major cation chemistry. Polar sunrise at Barrow is in late January, and the melt period begins in June. Samples were therefore collected before Polar sunrise in January and after Polar sunrise in March, May, and June 2000.

BioHg was undetectable in Barrow snow in January, and total Hg concentrations were low. BioHg then increased from 0.22 ng/L (~1% of total Hg) in March to 8.8 ng/L (nearly 13% of the total Hg) in May (Fig. 2). (Rarely have environmental samples that I have analyzed exceeded 0.5 ng/L.) Our June snow sample was taken just before the intensive snowmelt period began, so the snow was slushy but not melted. BioHg had decreased to 2.9 ng/L, which is still very high for a remote area. Furthermore, this concentration represented over 50% of the total Hg in Barrow snow. Because Barrow has sunlight 24 hours a day during the melt period, melting occurs over a relatively short time. If these concentrations of bioHg are sustained during this period, a very large pulse must be entering the ecosystem in the spring. (We will be examining the melt period more intensively in 2001; see below.) An interesting and unexpected finding was that during Polar sunrise, MeHg also increased to concentrations commonly found in boreal wetlands, where it is biotically produced. The mechanism of MeHg formation in the Arctic atmosphere is as yet unknown; however, we hypothesize that it could involve the demethylation of dimethyl mercury (diMeHg) produced biogenically in the ocean.

These initial objectives could not have been accomplished without the collaboration of Dr. Steve Lindberg, Environmental Sciences Division (Oak Ridge National Laboratory), and Dr. Steve Brooks (Oak Ridge Associated Universities), who are examining the reaction mechanisms of Hg0 depletion events in Barrow, Alaska. They focused on the atmosphere, making the first simultaneous, continuous direct measurements of atmospheric RGM and Hg0 during Polar sunrise. Industrial sources are known to emit RGM species; however, their direct production in the atmosphere had never been demonstrated prior to this study. Drs. Lindberg and Brooks attributed this production of RGM during Hg depletion events to in situ oxidation of Hg0 by photochemically active bromine, the same species believed to be involved in surface ozone destruction. Furthermore, because RGM species have a much shorter atmospheric lifetime than Hg0 (Lindberg and Stratton, 1998), they probably comprise a significant proportion of the bioHg entering the snowpack from the atmosphere.

FUTURE PLANS

During the winter of 2001, we plan to confirm the trends observed during Polar sunrise in 2000. In addition, we will be sampling open leads in the sea ice for diMeHg to determine whether the concentrations are sufficient to produce the levels of MeHg observed in snow. Most exciting will be the intensive melt period in June, when I hope to be on site in Barrow to better quantify and characterize the meltwater in terms of the fate of bioHg, total Hg, and MeHg.

In the longer term (2002), I plan to focus on the Arctic as part of my post-doctoral research, continuing collaborations with the Oak Ridge National Lab group led by Dr. Lindberg. My fieldwork will probably include intensive analyses in one or two locations to identify some of the mechanisms involved in the production and fate of bioHg and MeHg in the Arctic. However, I would also like to include a more geographical perspective by conducting a survey of bioHg and MeHg throughout the circumpolar region in collaboration with other groups. If the oxidation phenomena first observed by Dr. Schroeder in the Canadian Arctic and later confirmed by Dr. Lindberg in the American Arctic exist throughout the circumpolar region, the Arctic could represent an important sink in the global cycle of Hg.

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REFERENCES


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