

THE BARROW ARCTIC MERCURY STUDY (BAMS): RECENT MEASUREMENTS OF THE PRODUCTION OF REACTIVE GASEOUS MERCURY DURING MERCURY DEPLETION EVENTS AT POINT BARROW, ALASKA

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ABSTRACT

We have sampled gaseous elemental mercury vapor (Hg^0) at the NOAA climate dynamics laboratory in Point Barrow, AK since September 1998 in an effort to determine the geographic extent and reaction mechanism of mercury depletion events. One year later, we began the first automated measurements of reactive gaseous mercury (RGM) ever attempted in the Arctic. During fall and early winter, Hg^0 and RGM exhibit minor variation, Hg^0 remaining within ~10% of global background (1.6-1.8 ng/m^3). Within days of Arctic sunrise in January, Hg^0 exhibits major variations from the mean, rapidly dropping to levels as low as 0.05 ng/m^3 and then cycling back to typical concentrations. These events continue throughout Arctic spring, then end abruptly following snowmelt in early June, when Hg^0 begins a gradual increase, to levels as high as 4 ng/m^3 . Prior to Arctic sunrise, RGM remains near detection (<2 pg/m^3), but after sunrise increases dramatically in synchrony with the “depletion” of Hg^0 . Both phenomena exhibit a strong diel cycle, in parallel with UV-B. We propose that MDE’s involve rapid in-air oxidation of Hg^0 to a species of RGM by photochemically-driven reactions, probably involving reactive bromine compounds.

INTRODUCTION

Mercury levels in Arctic wildlife are known to be elevated, often significantly above normal levels, and levels have been increasing over time (e.g. Wheatly and Wheatly 1988). However, there are no positively identified Arctic sources of reactive gaseous mercury (RGM), and long range transport of elemental Hg vapor (HgE) must be considered. The recent discovery of so-called mercury depletion events (MDE, characterized by extremely low levels of HgE , well below global background concentrations) at Alert in the Canadian high Arctic (Schroeder et. al. 1998) suggests a possible mechanism for Hg accumulation from the global background pool of elemental Hg. One hypothesis for MDEs is that HgE is transformed into a reactive gaseous mercury (RGM) species which then deposits locally. Although this reactive atmospheric species has not been measured in the Arctic, data collected in the southeastern U.S. with methods developed in our lab support the concept that RGM is highly soluble and rapidly removed by dry and wet deposition to surfaces (Lindberg and Stratton 1998). Elevated levels of particle-bound Hg have been reported during MDE periods (Schroeder and Lu, pers. comm.), but particle sampling methods may not quantitatively separate RGM from particles. Also, particles would be less likely to deposit quickly to the local snow surface than would RGM. Hence, it is crucial to quantify RGM in the Arctic since their positive identification is the key to

¹Research sponsored by the NOAA Arctic Program and the US EPA Office of International Programs. ORNL is managed by UT-Battelle for the U.S. Department of Energy.

understanding the chemistry of MDEs.

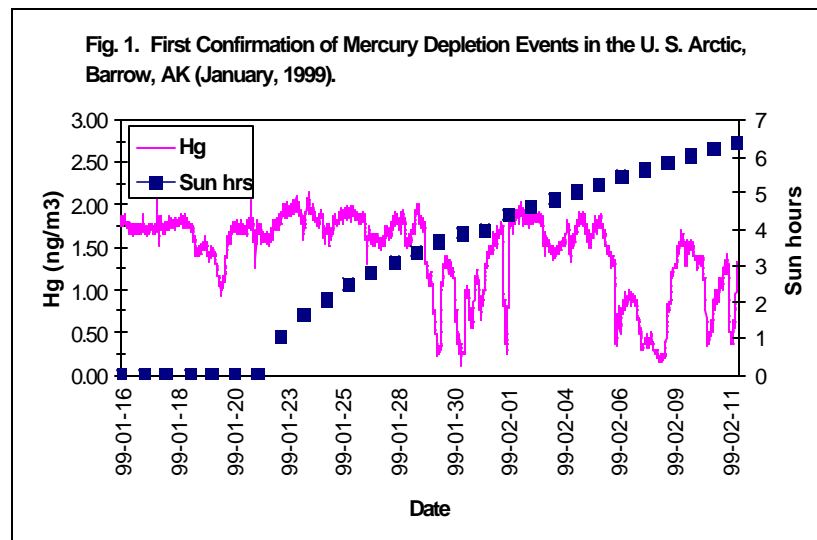
Prior to beginning speciation studies, MDE's must first be confirmed at other Arctic sites. This was the initial objective of the Barrow Arctic Mercury Study (BAMS), which has since expanded to include speciation, snow chemistry, and flux studies, with the objective of determining the fate of the "depleted" Hg. This paper will briefly describe the project and some initial Hg⁰ and RGM measurements from the winter/spring of 1999-2000 which strongly suggest that Hg⁰ is being oxidized in the air column below the boundary layer to RGM. More extensive data on Hg⁰/RGM interactions measured during BAMS-2000 will be presented at the conference.

METHODS AND SITE

We initiated routine measurements of gaseous Hg⁰ at Barrow, AK in September, 1998 with an automated Tekran 2537A analyzer. Descriptions of the Tekran and its operating parameters have been published (the device collects airborne Hg⁰ by gold amalgamation, then releases the trapped Hg by thermal desorption for quantification by CVAFS; e.g. see Lindberg et. al. 2000). Hg⁰ is sampled with a 5-min time resolution using a heated Teflon inlet line mounted ~5 m above the ground on a mast 2 m above the roof of the NOAA CMDL building. There are no Hg sources within the CMDL, no emission points on the roof, nor any known major Hg point sources in the town of Barrow, which is located ~10 km southwest of the CMDL. The CMDL is located near the peninsula at Point Barrow, ~2 km from the shoreline, ~9m above mean sea level, and is surrounded primarily by water to the N, E, and W. Prevailing winds are from the NE. Barrow is geographically the northern-most point in the U. S., located at 71° 19' N, 156° 37' W. In latitude, Barrow is ~1600 km south of Alert. We began sampling RGM at Barrow in September, 1999, and measured Hg⁰ and RGM simultaneously during the winter-spring of 2000. RGM is being sampled with a Tekran 1130 automated KCl-coated denuder using a method not yet published in the open literature (Stevens et. al. 1999). Ancillary data available at the CMDL include routine meteorological data and trace gases such as ozone (e.g. Oltmans et. al. 1989).

RESULTS AND DISCUSSION

The initial year's data provide the first confirmation of MDE's at this more southerly Arctic site (Fig. 1), and data from year 2 confirm that RGM is produced during MDEs. This is the first evidence that the MDE phenomenon could be a widespread characteristic of Arctic dawn, since Barrow is several thousand km from Alert. Depletion events begin within a few days of polar sunrise (Fig 1), and persist



until snowmelt (not shown). During this period, Hg° exhibits a strong correlation with ozone ($r^2 = 0.75$), as also seen at Alert (Schroeder et. al. 1998), suggesting a possible link with the chemical reactions which destroy tropospheric ozone. These reactions involve reactive bromine, perhaps both in the aerosol and in the gaseous phase (eg. Fan and Jacob, 1992), and are a common feature at Barrow (Oltmans et. al. 1989). In comparison, there is no correlation between O_3 and Hg° in the months before polar sunrise ($r^2 < 0.1$).

Other Arctic data provides clues of the causes of MDEs. Both gaseous and aerosol Br exhibit strong seasonal peaks at Barrow, peaking annually between February and June (from polar sunrise to snowmelt; Berg et. al. 1983). During this period, aerosol Br increases as much as 20-fold over typical concentrations (aerosol Br can exceed 100 ng/m^3). Hypotheses for the sources of this Br include aerosol enrichment by bubble bursting from the sea-surface microlayer, by gaseous reactions resulting from organic Br emissions from marine algae (eg. bromoform is thought to be emitted by ice algae), and/or by heterogeneous gas/solution reactions at the interface of hygroscopic sea salt aerosols (e.g. Oltmans et. al. 1989). Many of these reactions may be initiated in the surface microlayer of the snow-pack (Barrie and Platt 1997). Several reactive airborne Br species may result which have the potential to oxidize Hg° to *gaseous* Hg-II compounds (e.g. BrO, BrCl). Many of the compounds arising from reactive Br exhibit a strong diel pattern, indicating the importance of sunlight and photochemical reactions (Vogt et. al. 1996).

Our data from March 2000 strongly support the hypothesis that Hg° is being oxidized to RGM during depletion events, generating levels of RGM rarely seen even near major point sources (Fig. 2,

c.f. Lindberg and Stratton 1998). Our data also suggest that peak RGM production and Hg° depletion occur primarily at midday during maximum UV. To better understand the periodicity and magnitude of MDEs, one of us (S.B.) developed a simple predictive model using local meteorological data. This model closely simulates the patterns of Hg° depletion events during 1999, and suggest that sunlight, wind

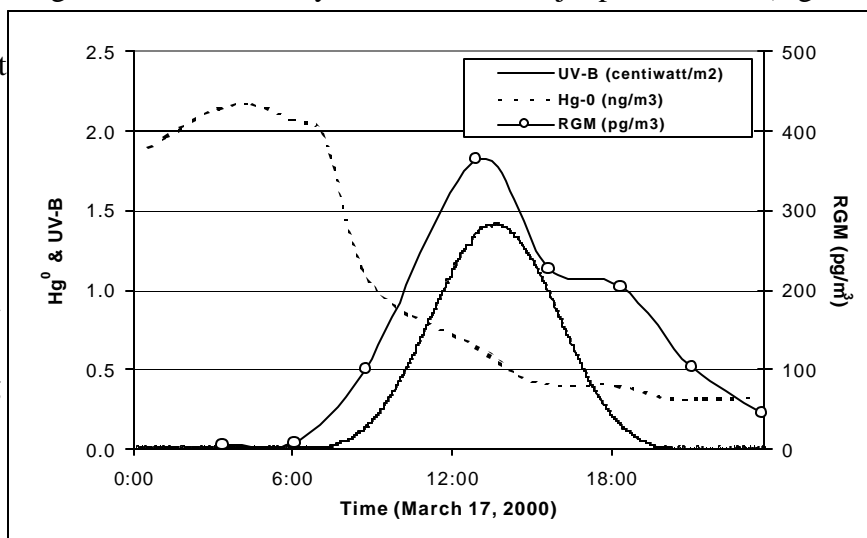


Fig. 2. Production of RGM during a mercury depletion event at Barrow.

speed, and temperature are important factors. This model can predict Hg deposition rates based on the assumption that the depleted Hg is accumulating locally by dry deposition. The model predicts short-term (~20 weeks) dry deposition fluxes of $\sim 40 \mu\text{g m}^{-2}$ at Barrow during February-May. This flux is much higher than annual wet deposition rates measured in the eastern U.S. ($\sim 10\text{-}20 \mu\text{g m}^{-2} \text{ y}^{-1}$, NADP/MDN, 1999). The model is being improved with more detailed meteorological data, especially high-resolution measurements of UV-B.

There are a number of potential reaction pathways between Hg° and Br which could explain the occurrence of depletion events by oxidation of HgE to some RGM compound such as HgO or a

Hg-halide compound (possible forms of RGM). Hence, it will be critical to continue to measure RGM in the Arctic during and after these events, and to confirm the predicted levels of accumulation of Hg in surface snow at Barrow (levels as high as 80 ng/L are predicted from the first generation model). Preliminary data on total Hg in snow from April 2000 support the elevated accumulation rates modeled above (Hg in one surface snow sample was as high as 70 ng/L).

Snowmelt brings an interesting twist to the Hg story at Barrow. Data from June 1999 suggest that some of the oxidized Hg accumulated in the snowpack may be reduced and evaded as HgE following snowmelt. This is manifested as an elevated and long-lived spike in ambient Hg^o following snowmelt (persisting from ~ mid-June to mid-August, see Table 1). To test our

Table 1. Statistics for Hg^o concentrations and related parameters at Barrow, AK (Br data derived from Berg et. al. 1983)

Day No.	Dates	Mean Hg ^o (ng/m ³)	StdDev Hg ^o	Mean Sun Hours	Mean Aerosol Br (ng/m ³)	Period
292 - 322	Oct 18 - Nov 19	1.76	0.07	4.5	6	Fall
365 - 20	Jan 1 - 20	1.71	0.29	0	12	Winter
30 - 146	Jan 30 - May 25	1.37	0.75	13	35	Arctic dawn
64 - 74	Mar 4 - 13	0.71	0.56	10.5	55	a single MDE
165 - 195	Jun 13 - Jly 13	2.30	0.39	24	4	post snowmelt

various hypotheses, we plan two major sampling campaigns in 2001: 1) to measure RGM, aerosol Hg, reactive Br, and Hg in snow prior to and following polar sunrise during the winter-spring period, and 2) to measure Hg speciation in snow and runoff and evasion of Hg^o over melting snow during the spring-summer period. BAMS-2001 will also include measurements of methyl- and bioavailable Hg in Arctic snow (measured with a bioreporter method, K. Scott and C. Kelly in prep.), and we hope to develop a near-real-time micrometeorological method to directly quantify Hg fluxes to the surface to confirm the mechanism of Hg accumulation in the snowpack (eg. Meyers et. al. 1996).

ACKNOWLEDGMENTS

We wish to thank the sponsors of this project for their continued support (the NOAA Office of Arctic Research, and the U. S. EPA Office of International Programs), Dan Endres and Malcolm Gaylord for local support at CMDL, F. Schaedlich for extended assistance with Tekran equipment, S. Oltmans for Barrow ozone data, Mary Anna Bogle for data plots, and R. Stevens and M. Landis for help with development and deployment of automated RGM denuder methods now in use at Barrow. This is publication No. _____, Environmental Sciences Division.

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