

Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry

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Abstract. Mercury - in the chemical/physical forms present in the biosphere - is a persistent, toxic, bioaccumulative pollutant that is dispersed throughout the environment on a global scale, mainly via the atmosphere. It is among the "heavy metals" for which the natural biogeochemical cycle has been perturbed by a wide range of human activities, including fossil-fuel combustion and waste incineration. Results of our recent measurements of gaseous elemental mercury (GEM), as well as total particulate-phase mercury (TPM) concentrations in Arctic air, 'total Hg' concentrations in Arctic snow, and tropospheric BrO concentrations from an earth-orbiting-satellite platform are presented and discussed. Findings of our research, and the conclusions derived therefrom, are important for environmental protection as well as the health and well-being of aboriginal people in Arctic circumpolar nations.

Introduction

Atmospheric mercury (Hg) has anthropogenic as well as natural sources. There is a growing body of evidence suggesting that, at the end of the 2nd Millennium, Hg emissions from anthropogenic sources rival or exceed those from natural sources. Once released into the atmosphere, mercury (mainly as Hg⁰ vapor) can undergo long-range atmospheric transport on continental and global scales [Petersen *et al.*, 1995; Schroeder and Munthe, 1998]. Air currents are a major pathway for entry of Hg (and other persistent toxic chemicals) into the Arctic environment [Boutron *et al.*, 1998; Cheng and Schroeder, 2000]. Recent scientific studies have

uncovered: (i) a marked increase in Hg deposition to Arctic lake sediments [Lockhart *et al.*, 1998]; (ii) rapid oxidation of Hg⁰ vapor to Hg(II) [operationally determined as total particulate-phase mercury, TPM, or reactive gaseous mercury, RGM] in Arctic surface-level air during and after polar sunrise at Alert, Nunavut Territory, Canada [Schroeder *et al.*, 1998] and more recently at Pt. Barrow, AK, U.S.A. [Lindberg *et al.*, 2001]; for locations see Plate 1. This conversion of GEM to (one or more) oxidized Hg species, results in greatly enhanced atmospheric mercury deposition to frozen surfaces in the Arctic; (iii) Hg levels in Arctic food supplies are high [Lockhart *et al.*, 1998] and are increasing [Wagemann *et al.*, 1996] and; (iv) Hg levels are elevated in native people of circumpolar countries [AMAP, 1997].

After polar sunrise, at Alert (82.5°N, 62.3°W), episodic depletions of GEM are frequently observed [Schroeder *et al.*, 1998]. During such mercury depletion events (MDEs) - which occur in the 3-month period following polar sunrise (mid-March to mid-June at Alert) and last from a few hours to several days - concentrations of GEM can drop from around 1.8 ng m⁻³ to undetectable levels (<0.1 ng m⁻³) and are strongly correlated with surface ozone (O₃) depletion [Schroeder *et al.*, 1998]. Polar tropospheric O₃ depletion is caused by photochemically-initiated autocatalytic reactions involving halogens (especially reactive halogen species such as Br and BrO) derived from sea-salt aerosols previously deposited on frozen ocean, aquatic and terrestrial surfaces [Barrie and Platt, 1997]. We have proposed [Schroeder *et al.*, 1999a] that BrO is a key oxidant converting Hg⁰ to Hg(II).

Results and Discussion

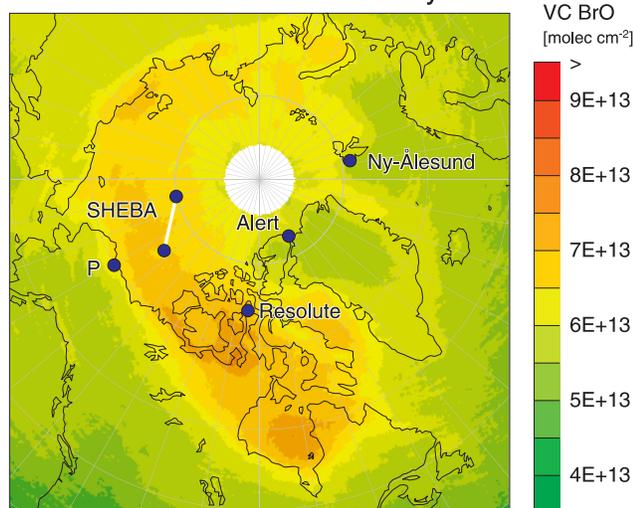
The AESminiSamplR[®] [Lu *et al.*, 1998] developed in our laboratory, is a new device for sampling and analysis of TPM (Hg associated with particulate matter/atmospheric aerosols). It was applied to examine the transformation and fate of GEM in Arctic air after polar sunrise. In the spring of 1998, concentrations of TPM determined concurrently at Alert and Ny-Ålesund, Spitsbergen (see Plate 1 for locations) ranged from 0.002 to 0.45 ng m⁻³ and 0.002

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A: GOME BrO 1 March - 31 May 1997



B: GOME BrO 1 March - 31 May 1998

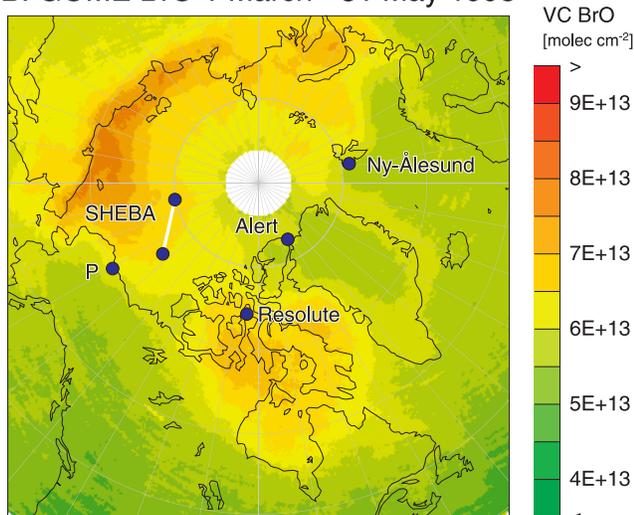


Plate 1. Mercury sampling locations, and the spatial distribution during March - May 1997 (a); and March - May 1998 (b); of the mean vertical column (VC) burden of BrO (molec cm^{-2}) derived from GOME satellite measurements.

to 0.16 ng m^{-3} , respectively. These TPM levels were often appreciably higher than those ($< 0.002 - 0.1 \text{ ng m}^{-3}$) measured in Toronto [Lu *et al.*, 1998] and in the Great Lakes region [Keeler, 1996].

During April and May 1998, concurrent TPM and GEM determinations were made daily at the Alert Global Atmosphere Watch (GAW) Laboratory and were found to be anti-correlated (Fig. 1). Ambient air TPM concentrations increased when GEM (and surface-level O_3) concentrations decreased, suggesting that GEM is converted to TPM (and to reactive gaseous mercury, RGM). By analogy with spring-time tropospheric O_3 depletion chemistry - which occurs over the Arctic Ocean where there is a virtually unlimited supply of the halide ion precursors leading to the formation of extremely reactive free-radical species responsible for destroying ozone - we believe that most, if not all, of the oxidation of Hg^0 to $\text{Hg}(\text{II})$ takes place there as well. Thus,

elevated Hg levels should exist in snow/snowpack on the Arctic Ocean and adjacent terrain.

The first observations of the seasonal variation of Hg content in snow on the Arctic Ocean are reported here (Fig. 2a). Samples were taken in conjunction with the "Surface Heat and Energy Budget in the Arctic" (SHEBA) study [Levi, 1998] deployed from a Canadian icebreaker adrift with the packice for a year (see Plate 1 for locations). Enhanced Hg levels in snow are clearly reflected in the 4-fold increase from the dark winter months (Nov. 1997 to Jan. 1998: 7.8 ng L^{-1}) to the sunlit spring months (Feb. to May, 1998: 34 ng L^{-1}). The dramatic plunge in Hg concentrations in June may be due to: (i) melting of surface snow and formation of meltwater pools; (ii) volatilization/co-distillation of Hg^0 [from reduction of $\text{Hg}(\text{II})$] along with water vapor released from snow/snowpack as air and snow temperatures rise to $\geq 0^\circ\text{C}$ (Plate 2b); (iii) meltwater leaching of easily soluble $\text{Hg}(\text{II})$ species in snow/snowpack at the onset of summer.

In addition to determining the seasonal variation of Hg levels in Arctic surface snow, we conducted comprehensive surveys in 1997 and 1998 of the spatial distribution of mercury in the spring snowpack of the Eastern Canadian Arctic, Hudson Bay, and Greenland (Plate 2). In the Canadian Island Archipelago, and at coastal sites on Hudson Bay, concentrations were generally much higher ($25 - 160 \text{ ng L}^{-1}$) than those at: (a) a western site near Tuktoyaktuk (site #30, 2.2 ng L^{-1}); (b) a sampling site on the eastern shore of Greenland at Scoresbysund (site #12, $< 2 \text{ ng L}^{-1}$); and (c) on the south shore of Lake Winnipeg (site #18; 5 samples in spring 1996 averaged 1.8 ng L^{-1}). Sites revisited in spring 1998 yielded results similar to those obtained in 1997. These snow data are consistent with observed tropospheric O_3 and GEM depletion events, and satellite observations of atmospheric BrO concentrations in the northern hemisphere [Richter *et al.*, 1998]. At Resolute on the coast of Cornwallis Island, snowpack showed a marked increase in Hg levels from 30 to 156 ng L^{-1} between March and May 1997, consistent with the seasonal variation observed at the SHEBA site. Collectively, these observations constitute direct evidence of

Site	Number
North of Alert	1
Alert	2
Arctic Bay	3
Anivat	4
Cambridge Bay	5
Cape Dorset	6
Chesterfield Inlet	7
Churchill	8
Clyde River	9
Eureka	10
Gjoa Haven	11
Greenland (East)	12
Hall Beach	13
Iqoalik	14
Iquluit	15
Kimminit	16
Kugluktuk	17
Lake Winnipeg	18
Mould Bay-buoy	19
Mould Bay	20
Pangnirtung	21
Pelly Bay	22
Pond Inlet	23
Quaqtaq	24
Repulse Bay	25
Resolute	26
Sachs Harbour	27
Sankiluaq	28
Taloyoak	29
Tuktoyaktuk	30
Whale Cove	31

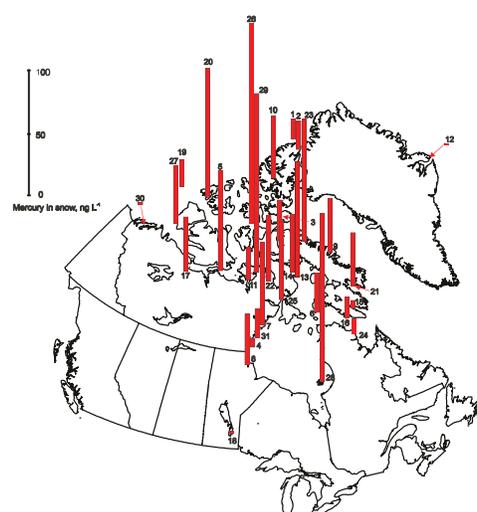


Plate 2. 1997 spatial distribution of mean Hg levels (ng L^{-1}) in snowpack of the eastern Canadian Arctic and the Hudson Bay region (mid-April to mid-May, before any melting occurred).

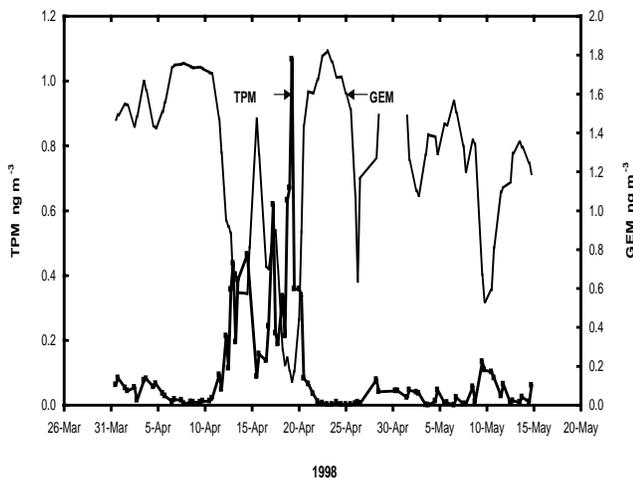


Figure 1. Daily mean concentrations of gaseous elemental mercury (GEM) and total particulate-phase mercury (TPM) in surface air at Alert during April/May, 1998.

a link between sunlight-assisted Hg^0 oxidation, greatly enhanced atmospheric $\text{Hg}(\text{II})$ wet &/or dry deposition, and elevated mercury concentrations in Arctic snow and snowpack in spring.

Estimates of the annual atmospheric loading of Hg to snowpack of Arctic seas and on Hudson Bay (Table 1) yield a total of about 50 tonnes. This number agrees very well with estimates from springtime GEM depletion episodes: 50 and 64 tonnes for 1995 and 1996, respectively [Schroeder *et al.*, 1999b]; lake sediment cores: $23\text{--}46 \text{ t y}^{-1}$ [Lockhart *et al.*, 1998] based on a net flux of $2\text{--}4 \mu\text{g m}^{-2} \text{ y}^{-1}$; and model calculations: $60\text{--}80 \text{ t y}^{-1}$ [Pacyna and Keeler, 1995]. These results indicate that: (1) the springtime (dry) deposition

Table 1. Estimates of the Total Amount of Mercury Deposited Annually on Northern Waters

	Area $\text{m}^2 \times 10^{12}$	[Hg] ng L^{-1}	Depth cm	Density g cm^{-3}	Snowpack t Hg
High Arc. Oc.	7.08	21 ^a	30	0.4	17
Hudson Bay/ Baffin Bay/ Davis Str	1.16	55 ^b	30	0.4	8
Labrador Sea	2.75	38 ^b	50	0.4	21
Cdn Archip.	0.71	45 ^b	30	0.4	4
	$\Sigma = 11.7$				$\Sigma = 50$

^aave [Hg] in surface snowpack at SHEBA site: Nov/97 to Jun/98 (Fig. 2a)

^bave [Hg] in surface snowpack in spring 1997 (Plate 2)

flux of mercury in the Arctic: $5.6\text{--}7.8 \mu\text{g m}^{-2} \text{ y}^{-1}$ for 1995 and 1996 [Schroeder *et al.*, 1998] is at least comparable to or greater than that observed at other N. Hemisphere locations: $0.1\text{--}4.7 \mu\text{g m}^{-2} \text{ y}^{-1}$ [Schroeder, 1996]; (2) > 90% of the total annual amount of Hg deposition occurs in a period of ~ 3 months each year (at Alert from mid-March to mid-June; earlier at lower latitudes), and even more importantly; (3) $\text{Hg}(\text{II})$ is released/flushed from the snowpack into receiving ecosystems, in a period of $\sim 2\text{--}4$ weeks during spring/summer melt, resulting in a mean flux of $\sim 300 \text{ ng m}^{-2} \text{ day}^{-1}$, which is 50 times higher than the mean winter accumulation rate. All this takes place at a time of the year when the Arctic biosphere is especially vulnerable to the intrusion of toxic, bioaccumulating pollutants such as mercury.

To understand the environmental cycling of Hg and the form(s) of mercury deposited to Arctic ecosystems, we need to consider the mechanism of the springtime GEM depletion phenomenon. For GEM, the principal component of total gaseous mercury (TGM) at remote continental and marine locations, the removal by physical sorption/condensation onto airborne aerosols (e.g., soot, dust, sea-salt particles, acid droplets), surface snow, snow flakes, or ice-fog crystals can be ruled out as cause of its depletion and concurrent TPM enhancement, because: (a) no significant depletion occurs during the dark winter months, before polar sunrise in the Arctic, even though concentrations of airborne soot, and particulate matter (conductive to ‘sorption’ of Hg^0), are at their highest and; (b) generally higher surface-air temperatures (Fig. 2b) in spring compared to winter should result in decreased (not increased) gas-to-particle transfer of Hg in springtime. Sunlight-induced chemical chain reactions are likely processes triggering the springtime ‘loss’ of atmospheric GEM through the formation and efficient deposition of TPM and/or RGM. This scenario explains the magnification of Hg levels in Arctic snow during spring.

Summary

Each spring at high latitudes, oxidation of atmospheric Hg^0 vapor occurs in concert with polar tropospheric O_3 depletion events, greatly enhancing the wet and dry deposition flux of this toxic heavy metal to the fragile biosphere. This oxidative transformation process (also observed in Antarctica for the first time last year: Personal Communications, Ebinghaus, 2000) converts Hg^0 vapor into one or more much-less-volatile $\text{Hg}(\text{II})$ species which deposit(s) to frozen sur-

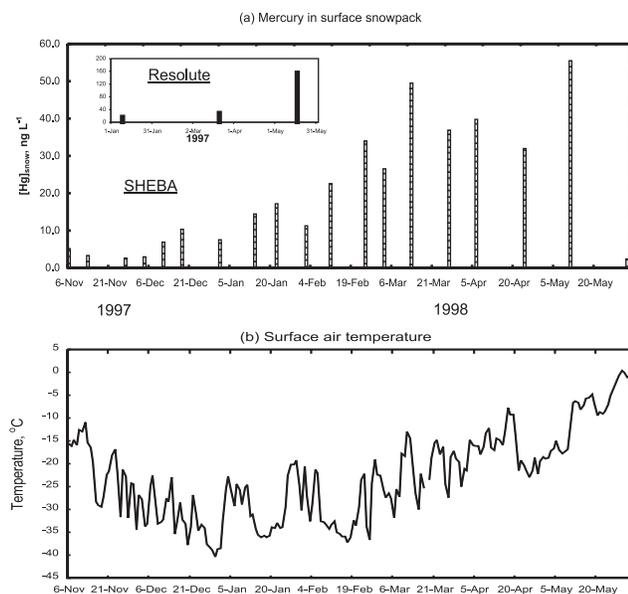


Figure 2. SHEBA ship time series (see locations in Plate 1) of (a) concentrations of total Hg (ng L^{-1}) in the snowpack column and (b) daily mean surface air temperature in 1997/98. The insert in (a) is the 1997 snowpack Hg concentration at Resolute, NWT (see Plate 1).

faces more rapidly than the precursor, and is/are much more water-soluble (significantly lower Henry's Law coefficient) than the original substance. Furthermore, oxidized inorganic Hg(II) species can be readily assimilated by polar ecosystems, thus transferring potentially toxic Hg to flora and fauna just as they commence replenishing energy reserves depleted during the long dark polar night. We believe that this perennial springtime (autumn in the S. Hemisphere) phenomenon exists wherever and whenever surface ozone depletion occurs, as reflected in the GOME satellite maps of BrO (Plate 1). Based on our research so far, environmental conditions favoring MDEs (at high latitudes) i.e., conversion of Hg⁰ to Hg(II) are: (1) marine/maritime location (source of sea-salt halides); (2) calm weather, low wind speeds, non-turbulent air flow; (3) the existence of a temperature inversion; (4) the presence of sunlight, and; (5) sub-zero temperatures (favoring heterogeneous surface chemistry by which sea-salt halides are converted to photolysable halogen species during and after polar sunrise). Strategic laboratory and field studies are needed to elucidate the exact mechanism(s) of tropospheric GEM depletion and greatly enhanced mercury deposition to polar ecosystems.

Conclusions

Our comprehensive Arctic measurements of gaseous Hg⁰, total particulate-phase Hg in air, and total Hg concentrations in snow, when combined with tropospheric BrO data from GOME, have revealed that: (1) each spring, upon polar sunrise, long-lived GEM is transformed to TPM &/or RGM; (2) this photochemically-initiated oxidation of GEM is highly correlated with 'low-ozone episodes' in the Arctic MBL; (3) physical/ chemical transformation(s) enhance the annual accumulation rate of Hg in snow/snowpack > four fold; (4) during the brief, but intense polar-spring-melt period, the rapid melting of snow/ice, as well as 'snowpack leaching' of the water-soluble, oxidized Hg compounds accumulated during the previous 6 months, results in massive pulsed inputs of Hg to the biosphere; (5) in polar regions (and under certain environmental conditions, perhaps, also in the marine boundary layer at lower latitudes) rapid transformation of Hg⁰ to Hg(II) is intricately inter-linked with sunlight-mediated, heterogeneous chemical processes generating extremely reactive halogen species (e.g., Cl, Br, ClO, BrO) from the copious amounts of sea-salt-derived halide ions present in snow/snowpack or associated with airborne (re)suspended aerosols. Undoubtedly, other substances capable of entering into 'redox' reactions with Hg⁰/Hg(II) are also present.

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