Final Draft
of the original manuscript:

Ebinghaus, R.; Temme, C.; Lindberg, S.; Scott, K.:
Springtime Accumulation of Atmospheric Mercury in Polar Ecosystems
In: Journal de Physique 4 (2004) EDP Sciences

DOI: 10.1051/jp4:2004121013
SPRINGTIME ACCUMULATION OF ATMOSPHERIC MERCURY IN POLAR ECOSYSTEMS

Ralf Ebinghaus¹, Christian Temme¹ Steven E. Lindberg², and Karen J. Scott³

¹GKSS Research Centre Geesthacht, Institute for Coastal Research, Max-Planck-Str. 1, D-21502 Geesthacht, GERMANY

²Oak Ridge National Laboratory ORNL, Environmental Science Division, Oak Ridge, TN, USA

³Photuris, 720 Ingersoll Street, Winnipeg, MB, R3G 2J6, Canada. (Formerly at Department of Microbiology, University of Manitoba, Winnipeg, MB)

corresponding author phone: +49-4152-87-2354, fax: +49-4152-87-2332, e-mail: ralf.ebinghaus@gkss.de

Abstract. Mercury and many of its compounds behave exceptionally in the environment due to their volatility, capability for methylation, and subsequent biomagnification in contrast with most of the other heavy metals. Long-range atmospheric transport of elemental mercury, its transformation to more toxic methylmercury compounds, the ability to undergo photochemical reactions and their bioaccumulation in the aquatic food chain have made it a subject of global research activities. Atmospheric Mercury Depletion Events (AMDEs) during polar springtime have been experimentally observed in the Arctic and in the Antarctic. During these events Hg⁰ and ozone concentrations are significantly depleted and well correlated, whereas concentrations of reactive gaseous mercury species (RGM) simultaneously increase. The main reaction mechanism and corresponding chemical and physical properties of involved species in polar regions are summarized in this work. Hg⁰ is removed from the atmosphere and deposited onto the underlying surface snow. This paper focused on the fast, photochemically driven, oxidation of boundary-layer Hg⁰, the influence of reactive halogen chemistry, and the resultant net input of mercury into the polar ecosystem during and after polar springtime. Several estimates of the size of the Arctic sink for newly deposited Hg range from ≈ 100 – 300 T/y, while estimates of the Antarctic sink are far more uncertain. The role of re-emission of elemental mercury from the snow surface is critically discussed.

1. INTRODUCTION

Mercury (Hg) is outstanding among the global environmental pollutants of continuing concern. Especially in the last decade of the 20th century, environmental scientists, legislators, politicians and the public have become aware of Hg pollution in the global environment. It has often been suggested that anthropogenic emissions are leading to a general increase in Hg on local, regional and global scales. Hg is emitted into the atmosphere from a number of natural as well as anthropogenic sources. There is a growing body of evidence suggesting that presently Hg emissions from anthropogenic sources are at least as great as those from natural sources [1,2]. In contrast with most of the other heavy metals, Hg behaves exceptionally in the environment due to its dynamic speciation. Long-range atmospheric transport of Hg, its transformation to more toxic methylmercuric (MeHg) compounds, and their biomagnification in the aquatic foodchain have motivated intensive research on Hg as a pollutant of global concern. Hg takes part in a number of complex environmental cycles, and special interest is focused on the aquatic-biological and the atmospheric cycles.
Environmental cycling of Hg can be described as a series of chemical, biological and physical transformations which govern the distribution of Hg in and between different compartments of the environment. Hg can exist in a number of different chemical forms, which have a wide range of physical, chemical, and ecotoxicological properties and consequently are of fundamental importance for its environmental behaviour. The three most important chemical forms known to occur in the environment are:

- elemental Hg \([\text{Hg}^0]\), which has a high vapor pressure and a relatively low solubility in water;
- divalent inorganic \([\text{Hg}^{2+} \text{or Hg(II)}]\), which can be far more soluble and has a strong affinity for many inorganic and organic ligands, especially those containing sulphur;
- methylmercury \([\text{CH}_3\text{Hg}^+ \text{or MeHg}]\), which is strongly accumulated by living organisms.

Conversions between these different forms provide the basis of Hg's complex distribution pattern on local, regional, and global scales.

### 1.1 Global Transport of Anthropogenic Contaminants to Polar Regions and Ecosystems

The polar ecosystems are generally considered to be the last pristine regions of the earth. The Arctic, for example, is populated by few people, has minimal commercial fishing, little industrial activity, and is therefore perceived to be relatively unaffected by human activity. These generalizations hold true for most of the Arctic except for highly industrialized regions of the Russian Arctic including the Kola Peninsula, Pechora and Ob/Yenisey river basins [3]. In comparison with the Arctic, Antarctica is considered to be much less affected by any kind of anthropogenic influences resulting in even more pronounced pristine characteristics.

Growing evidence indicates, however, that there has been long-distance atmospheric transport of anthropogenic contaminants from mid- and low latitude sources to the polar regions ([3] and references therein). Three major pollutant groups are of growing concern:

- acidifying gases (SO\(_x\)) from Eurasian smelters and industry [4],
- heavy metals from fossil fuel combustion and mining [5], and
- persistent organic pollutants (POPs) including pesticides used in agriculture and polychlorinated biphenyls leached from electronic transformers [6].

Long-range transport of atmospheric pollution has led to bioaccumulation of these compounds by plankton [7]. Some contaminants biomagnify through the marine food chain to levels in top predators, including humans, which may have adverse physiological effects [8,9].

Generally, air pollution is not confined to local areas and can be atmospherically transported tens of thousands of kilometers to remote regions such as the polar ecosystems. The winter phenomenon of "ice crystal haze" observed by K.R. Greenaway during 1940s surveillance flights and later coined "Arctic haze" [10] was discovered not to be wind-blown dust, but air pollution from the mid-latitudes [11,12]. Arctic haze is a mixture of aerosols containing acidifying SO\(_x\) and NO\(_x\), coarse particles of soot, heavy metals, polycyclic aromatic hydrocarbons (PAH), and polychlorinated biphenyls (PCB) [13-15].

Arctic haze is concentrated in the lower troposphere (up to 3 km altitude) and is most pronounced during the coldest months of the year from December to April [16]. The seasonal cycle of anthropogenic emissions (e.g. April - June agricultural pesticide application) cannot adequately explain the distinct annual cycle of Arctic air pollution. Iversen and Joranger [13] proposed that a quasi-stationary, large-scale, meteorological phenomenon known as "blocking" is responsible for the seasonality of the pole-ward transport of pollutants. Episodically, mid-latitude source areas undergo periods of atmospheric stagnation due to the
blocking of the westerlies by anticyclones [17]. The resultant stagnant weather conditions reduce contaminant scavenging potential and thus permit accumulation of pollutants over the source areas. If a cyclonic system approaches the blocking high, a strong pressure gradient builds and forces northward transport of contaminated air. The transport path may persist long enough to permit the pollutants to be swept into the Arctic troposphere [18]. By using tracer aerosols it was demonstrated that particles could be transported from the source to the pole within 7 to 10 days [19]. Other studies have demonstrated that polluted air masses can reach the Arctic within 48 to 72 hours [20].

The occurrence of blocking highs corresponds well to observed seasonal variations of Arctic air pollution [13]. Rapid changes in circulating systems are responsible for the episodic nature of Arctic aerosol pollution [21]. The geographic position of blocking highs seasonally favors different sources. Eurasian sources, which are more available to the Arctic than North American emission sources, account for more than 50% of Arctic air pollution [22]. During winter, the strong Siberian anticyclone drives air from central Eurasia into the Arctic which then moves either over North America or into major anti-cyclonic regions in the Aleutians and near southern Greenland [23]. During the spring, the Siberian high-pressure cell dissipates and western Eurasia makes the greatest contaminant contribution to the Arctic. During summer, there is a weak north to south transport alternating with input from the north Pacific and the north Atlantic [23].

Volatile contaminants from mid- and low-latitudes reach the Arctic through a process known as "global distillation" [24]. Many of the developing countries which still use environmentally persistent pesticides, for example, are located in the tropics. This region is characterized by elevated temperatures and heavy rainfall which promotes the rapid dissipation of contaminants through air and water [25]. Contaminants evaporate from soils of these warm regions and become available for poleward atmospheric transport where they condense out in the colder air known as the "cold finger" [26] or "cold condensation" effect [27]. The sorption of high molecular weight organic vapors to atmospheric particulate matter is enhanced by low temperatures [7]. The theory of "global fractionation" describes how the most volatile contaminants, such as PCB and HCH, travel to the highest latitudes, while less volatile compounds, such as DDT, are less readily distilled and tend to remain near their source region [28]. Thus the volatile contaminants are apt to condense in the coldest Northern and Southern regions and, since these areas are a comparably small proportion of the Earth's surface, contaminants can concentrate to surprisingly high levels in the polar ecosystems.

Contaminants can be transported by one-hop or multi-hop pathways. One-hop describes the transport of a contaminant which enters the atmosphere in the source region, is directly transported to the polar regions and is deposited to the Earth's surface without returning to the atmosphere. Contaminants transported by one-hop pathways include non-volatile organochlorines, e.g. DDT, less volatile PAHs, e.g. benzo[a]pyrene, acids, and heavy metals with the exception of Hg [29]. In contrast, multi-hop contaminants undertake multiple atmospheric hops. Such chemicals include Hg and the more volatile organochlorines and PAHs [29].

Once contaminants reach the polar regions, their lifetime in the troposphere depends on local removal processes. Pollutant removal processes are inefficient in those regions especially during the winter due to low temperature, low solar radiation input, and low precipitation, thus low scavenging by wet deposition [18,22]. As a result, compounds which would be photodegraded in warmer climates may persist in the polar regions. Eventually, aerosol pollutants enter the terrestrial, aquatic and marine environments by gas-exchange across the air-seawater interface or deposition of particles with adsorbed pollutants. Detection of tropical pesticides and other contaminants in remote Canadian and Alaskan freshwater lakes and aquatic animals supports the atmospheric transport theory [30,31].
1.2 Phenomenon of Atmospheric Mercury Depletion Events (AMDEs) during Polar Springtime

The long average lifetime of Hg$^0$ in the atmosphere of about one year would allow homogenous mixing at least within one hemisphere; however, complete global mixing would need longer time scales. Since anthropogenic sources of Hg emissions into the atmosphere are mainly located in the northern hemisphere, a concentration gradient between the two hemispheres should be expected, provided that the lifetime estimate is correct.

The background concentration of gaseous elemental mercury (GEM) in the lower troposphere of the northern hemisphere is generally around 1.8 ng/m$^3$ and 1.3 ng/m$^3$ in the southern hemisphere respectively [32,33]. Long-term studies, such as the measurements at Mace Head [34] show only very few and short periods with concentrations below these background values.

However, highly time-resolved GEM measurements in the Arctic have shown that GEM concentrations in the lower troposphere are significantly depleted for several weeks at the time after polar sunrise. This phenomenon is generally referred to as Atmospheric Mercury Depletion Events (AMDEs) [35]. A possible explanation may involve chemical or photochemical oxidation of Hg$^0$ to Hg(II) (resulting either in particle-associated Hg [Hg$_{\text{part}}$] and/or reactive gaseous Hg [RGM] species, [36] and significantly enhanced deposition fluxes of Hg) leading to an unequivocal increased input of atmospheric Hg into the Arctic ecosystem [35,37].

AMDEs were later observed at a coastal site in Antarctica [38], and recently at the South Pole Station [39] giving evidence that both polar ecosystems are impacted by atmospheric Hg deposition especially during polar springtime.

Figure 1 shows the annual time series of GEM and ground level ozone at Neumayer Station, Antarctica

Figure 1. Annual time series of 1-hour averaged GEM and surface-level ozone concentrations at Neumayer, January 2000 – February 2001 and their weekly mean correlation coefficients r. The GEM concentrations were obtained from two separate Hg analysers and mean values were used if both analysers were operating in parallel.
Polar AMDEs are strongly correlated with ground-level ozone concentrations, as depicted in Fig. 1. These tropospheric ozone loss events in the Arctic are associated with enhanced bromine monoxide concentrations in the free troposphere [40]. It is hypothesized that Br atoms and/or BrO radicals are involved in a chemical reaction which destroys ozone [41] and that the depletion of surface-level atmospheric boundary layer Hg (at times up to an altitude of ≈ 1 km) is due to a reaction between Hg⁰ and BrO free radicals [42]. Recent modelling using newly available kinetics data suggests that reactive bromine can readily oxidize Hg⁰ to Hg²⁺ [43]. Figure 2 shows the proposed reaction scheme for the decomposition of ozone and the subsequent transformation of GEM into inorganic species that will deposit more rapidly onto terrestrial and/or marine surfaces.

**Figure 2.** Conceptual diagram of proposed Hg⁰ oxidation reaction sequences during polar springtime, subsequent to surface layer ozone depletion (originally by “Spektrum der Wissenschaften”).

### 1.3 Bromine explosions during polar spring as a prerequisite for ozone and mercury depletions

Since the 1980’s, sudden tropospheric ozone depletions have been reported for different Arctic research stations. Ground level ozone concentrations dropped within a few hours from around 40 ppb to levels close to the limit of determination of about 2 ppb. Barrie and co-workers [44] have found increased Br levels on filter packs during these ozone depletions leading to the hypothesis that reactive Br species are involved in ozone decomposition. It was assumed that atomic bromine decomposes ozone according to reaction (1). Resulting BrO-radicals can recombine to Br atoms and/or Br₂ molecules (2), (3), the latter can be photolytically decomposed according to (4):

\[
\begin{align*}
\text{Br + O}_3 & \rightarrow \text{BrO}^* + \text{O}_2 \quad (1) \\
\text{BrO}^* + \text{BrO}^* & \rightarrow \text{Br} + \text{Br} + \text{O}_2 \quad (2) \\
\text{Br} + \text{Br} + \text{O} & \rightarrow \text{Br}_2 + \text{O}_2 \quad (3) \\
\text{Br}_2 + \text{hv} & \rightarrow 2 \text{Br} \quad (4)
\end{align*}
\]
Tropospheric halogen chemistry seems to play a dominant role for polar ozone and subsequent Hg depletions, with bromine and iodine more likely to be important than chlorine [43,45]. The source of these halogens is thought to be sea-salt aerosols generated from open water such as leads and polynyas (open water in an actively upwelling region). These dynamic open water areas are important sources of sea-salt aerosols, water vapor, and heat from the comparatively warm ocean waters. The sudden increase of ground level BrO concentrations in polar regions is thought to be initiated by an auto-catalytic release of bromine via heterogeneous reactions on sea-salt aerosols according to the following reaction cascade [46-48]:

\[
\begin{align*}
\text{HOBr}_g & \rightarrow \text{HOBr}_{aq} \quad (5) \\
\text{HOBr}_{aq} + \text{Cl}^-_{aq} + \text{H}^+_{aq} & \rightarrow \text{BrCl}_{aq} + \text{H}_2\text{O} \quad (6) \\
\text{BrCl}_{aq} + \text{Br}^-_{aq} & \rightarrow \text{Br}_2\text{Cl}^-_{aq} \quad (7) \\
\text{Br}_2\text{Cl}^-_{aq} & \rightarrow \text{Br}_2(g) \quad (8) \\
\text{Br}_2 + \text{h\nu} & \rightarrow 2 \text{Br} \quad (9) \\
2 \text{Br} + 2\text{O}_3 & \rightarrow 2 \text{BrO}^* + 2 \text{O}_2 \quad (10) \\
2 \text{BrO}^* + 2 \text{HO}_2 & \rightarrow 2 \text{HOBr} + 2 \text{O}_2 \\
\end{align*}
\]

The resulting net-reaction is generally referred to as „bromine explosions“:

\[
\text{HOBr} + \text{Br}^-_{aq} + \text{H}^+_{aq} + 2 \text{HO}_2 + 2 \text{O}_3 \stackrel{\text{h\nu}}{\rightarrow} 2 \text{HOBr} + \text{H}_2\text{O} + 4 \text{O}_2
\]

The reaction cascade is terminated by the formation of HBr, as shown by reactions (13) and (14), which has a strong tendency to adsorb onto aerosol surfaces.

\[
\begin{align*}
\text{Br} + \text{HO}_2 & \rightarrow \text{HBr} + \text{O}_2 \quad (13) \\
\text{Br} + \text{HCHO} & \rightarrow \text{HBr} + \text{CHO} \quad (14)
\end{align*}
\]

Several boundary conditions are necessary prerequisites for bromine explosions, such as slightly acidic sea-salt aerosol surfaces (pH< 6.5), stable planetary boundary layer which is isolated from the free troposphere, the availability of sea-ice surfaces and sufficient UV-irradiation. The necessary combination of these prerequisites is only fulfilled during polar springtime. The suspected reaction leading to AMDEs is (15):

\[
\text{Hg}^0 + \text{BrO}^* \rightarrow \text{HgO} + \text{Br} \quad (15)
\]

1.4 Surface-snow accumulation of mercury during AMDEs

According to the observed AMDEs in the lower Arctic and Antarctic troposphere it can be assumed that GEM is removed from the atmosphere and deposited onto the underlying surface snow. Speciation measurements have shown that GEM is transformed into more reactive ionic species, commonly referred to as RGM [36] and/or Hg_{part} species [49]. Both chemical forms would have a much higher deposition velocity compared with GEM. The exact speciation of these compounds is not clear; however, it can be assumed that bromides, chlorides and oxides of Hg^{2+} would play some role [36], and recent models suggest that bromine compounds predominate [43,50].
To establish the link between observed AMDEs and Hg accumulation in the underlying surfaces it is necessary to investigate temporal and spatial trends of Hg in surface snow during and after polar springtime. Limited reference data on background Hg concentrations have been published and are summarized in Table 1:

<table>
<thead>
<tr>
<th>Hg in snow</th>
<th>Greenland</th>
<th>Canadian Arctic</th>
<th>Antarctica</th>
<th>High Alps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.05-0.2 ng/L</td>
<td>3-20 ng/L</td>
<td>0.19-2.21 ng/L</td>
<td>13-130 ng/L</td>
</tr>
<tr>
<td>Literature</td>
<td>[51]</td>
<td>[52]</td>
<td>[53]</td>
<td>[54]</td>
</tr>
</tbody>
</table>

From Table 1 it can be seen that in remote polar ecosystems, especially Greenland and the Antarctic, surface snow concentrations are significantly below 5 ng/L, whereas snow samples from areas more strongly influenced by human activity, such as the Alps, can have higher concentrations.

Seasonal variations in Hg concentrations in surface snow were first published by Welch et al. [55] and later by Lu and co-workers [37] during a 500 km drift experiment of a Canadian ice breaker (SHEBA). During the drift towards the south-west, fresh surface snow samples were collected over a time period of about 1 year. It was shown that during Arctic winter, the average concentrations were below 8 ng/L; however, they significantly increased during springtime to values around 34 ng/L [37]. A similar trend in Hg in snow was reported at Barrow, Alaska, with concentrations increasing from 1 ng/L in January to 70 ng/L in April [56,57]. In addition, spatial differences in surface snow concentrations have been investigated by Lu et al. [37] who collected snow samples in Greenland, the Eastern Canadian Arctic and the Hudson Bay region, and by Welch et al. [58] in the Canadian Arctic. Scott et al. [59] measured a notable trend in MeHg in snow from Barrow, Alaska. Concentrations gradually increased from 0.01 ng/L, prior to sunrise in January, to 0.6 ng/L prior to snowmelt in May; a remarkably high concentration not to mention an intriguing temporal trend. Other very recent reports of elevated concentrations of MeHg in fresh snow (e.g.[39]) poses an interesting question regarding its source, since methylation in the atmosphere or snowpack seems unlikely. One proposed source of MeHg in air and precipitation is evasion of diMeHg from the sea surface [60], again pointing to the importance of leads and other areas of open water during Polar springtime.

Highly elevated levels of total Hg in surface snow of around 160 ng/L in the North-Canadian Archipelago and the eastern Hudson Bay, and low Hg concentrations on the east coast of Greenland were qualitatively in good agreement with BrO maps obtained by satellite borne spectrometers ([37]; http://www.iup.physik.uni-bremen.de/gomenrt/).

More detailed atmospheric studies were later carried out by Lindberg and co-workers [36,39], measuring GEM and RGM fractions simultaneously at Barrow, a coastal site in Alaska. Although normally occurring in very low concentrations, RGM species play a dominant role for the deposition behaviour of this element due to their high dry and wet deposition potential. At Barrow, which is directly located at the polar Ocean shoreline, high RGM concentrations of up to 1000 pg/m$^3$ have been detected and are significantly elevated compared with the few reported data from Europe and North America (around 10 pg/m$^3$). Lindberg et al. [36] also showed that the enhanced RGM concentrations were correlated with increasing UV-B irradiation during polar spring and that increasing surface snow-concentrations were detected at the same time, as shown in Figure 3:
Based on deposition rate estimates, Lindberg et al. [36] suggested that between 100 to 300 tons of atmospheric Hg will be deposited into the Arctic during polar spring, estimates for the Antarctic are lower, between 50 to 100 tons. A recent Danish model run with and without AMDE chemistry suggests that for the area north of the Polar Circle, Hg deposition increases from 89 T/y for calculations without AMDEs to 208 T/y with the AMDEs [61], and new findings of enriched snow at the South Pole station [39] would lead to increased estimates of Hg deposition across the Antarctic continent greater than 100 T/y [62].

### 1.5 Bioavailability of deposited mercury

An important factor in terms of understanding the fate of deposited Hg in the Arctic is its bioavailability and if a significant fraction is available for uptake by microorganisms. Bacteria in particular play a critical role in the transformation of Hg and ultimately in the cycling of Hg in the environment.

Scott [57,63] used a highly sensitive and specific mer-lux bioreporter, *Vibrio anguillarum* pRB28, to assess the bioavailable fraction of Hg in snow collected in Barrow, Alaska in 2000 and 2001. The mer-lux bioreporter is a genetically engineered bacterium that produces light when Hg(II) enters the cell [64], thereby distinguishing so-called “bioavailable Hg(II)” from biologically inert Hg(II) species that are unable to enter the bacterial cell (Figure 4).
Figure 4. Schematic diagram of the mer-lux bioreporter, *Vibrio anguillarum* pRB28. Light production is due to plasmid RB28, which is composed of the regulatory region (merR) of the mer operon and lux genes coding for luciferase (luxAB) and fatty acid reductase (luxCDE). Hg(II) entering cells containing this plasmid causes transcription of the lux genes; light production is proportional to the amount of Hg entering the cells.

The behaviour of bioavailable Hg(II) in snow was consistent during the 2000 and 2001 field seasons. In January, prior to polar sunrise, bioavailable Hg(II) was not detectable in snow. As sunrise progressed, concentrations increased to 8.8 ng/L (2000) and nearly 23 ng/L (2001); considered extremely high inputs. Prior to this study, bioavailable Hg(II) had never been measured in the arctic. However, concentrations in snow and precipitation at a remote Boreal site in Canada were on average <0.5 ng/L [63].

During the early snowmelt period in late May/early June, the concentrations of both total and bioavailable Hg(II) in melting surface snow decreased considerably. However, because total Hg decreased to a greater extent over the same period, the fraction of the total Hg pool that was bioavailable increased to 56% (2000) and nearly 80% (2001). This likely reflects important differences in the photoreduction potentials of Hg(II) species. HgCl₂, for example, is not appreciably photoreduced [65], and could represent a refractory and highly bioavailable fraction of the total Hg pool that is able to persist during the melt period. Subsequent Hg(II) speciation changes involving both organic and inorganic ligands in tundra soils, meltwater ponds, and the ocean likely occur after snow melt is complete. Factors controlling the bioavailability of Hg(II) in those compartments of the arctic environment have yet to be explored.

1.6 Re-emissions of mercury from surface snow

The possibility of re-emission of Hg from snow surfaces by photoreduction and former conversion to Hg⁰ is not well understood.

It can be assumed that the most dominating fraction of deposited Hg is in the divalent form. Therefore reduction to Hg⁰ has to take place before re-emission of previously deposited Hg. First results obtained from lake water experiments have shown that a possible reduction can be induced by sunlight [66]. Dissolved organic carbon (DOC), e.g. in form of humic acids, can play a major role in this reaction mechanism.

On closer examination of a typical annual time series of atmospheric Hg concentrations in the Arctic and Antarctic (see Figure 1), slightly elevated average GEM concentrations could be seen in the period after springtime, when AMDEs have stopped. This could be a
seasonal effect, related to higher temperatures during summer. An alternative possibility for higher GEM concentrations in the boundary layer could be a re-emission of Hg from the snow surface. Lindberg et al. [36] observed significant increases in GEM just as snowmelt was initiated, as shown in Figure 5. The upward spike in GEM was transient, lasting until the snow was completely melted.

![Figure 5](image_url)  
Figure 5. The influence of snowmelt on Hg concentrations at Barrow, Alaska (originally published in [36]).

Steffen and co-workers [67] showed that during dark and 24-hour daylight conditions preceding AMDEs, no vertical gradient of GEM concentrations could be found; GEM concentrations close to the snow surface and \( \approx 2 \) m above showed no significant differences. Otherwise, during time periods when AMDEs took place in polar regions, highly elevated GEM concentrations were observed directly above the snow surface. Concurrent ozone profiles exhibited a sharp decrease at the surface level. These data suggest that the snow pack during and after springtime AMDEs can be a source of GEM and a sink for ozone. Hg\(_0\) behaves in a manner that is different from ozone as the two substances approach and interact with the frozen surface. This thesis is supported by observations which have revealed higher concentrations of GEM in the interstitial air of the snow than directly above the snow surface. Steffen et al. [67] concluded that GEM is produced by sunlight induced reduction in the first centimetres of the snow. Afterwards, Hg is outgassed from the snow to the atmosphere if the temperature increases during the day.

Some of these suppositions were experimentally confirmed by further investigations carried out by Christophe Ferrari’s group (Laboratoire de Glaciology et Géophysique der L’Environnement, Grenoble) in Greenland and at the Hudson Bay [52,68-69]. However, results were inconsistent concerning the re-emission of GEM from the snow pack.

Ferrari and co-workers have developed a Teflon probe, which measures temperature and GEM concentrations simultaneously in the interstitial air of snow samples. As an example,
the results will be explained on a snow pack with 120 cm depth; the average snow pack which accumulates at Station Nord, Greenland during the winter and usually melts completely by July. The air temperature during February was around -35°C. Snow temperatures at depths of 20 cm, 60 cm and 120 cm (directly above the soil surface) were around -30°C, -20°C, and -13°C, respectively. Hg concentrations decreased with increasing depth; at 20 cm depth, GEM concentrations were 1.2 ng/m³ (close to ambient concentrations of 1.5 ng/m³) and at 120 cm GEM concentrations were 0.1 ng/m³. A higher variability of the GEM concentrations in the upper layer of the snow pack was also found, which could be explained by interaction between the snow pack and the air immediately above it leading to Hg⁰ evasion from the snow pack. Ferrari and co-workers believe that a higher adsorption of gaseous Hg on snow particles with increasing depth is not plausible because temperature is increasing in deeper layers of the snow pack. He suggests an increasing oxidation rate removing Hg⁰ from the interstitial air of snow. The temperature in the deeper layers of the snow pack is higher and the residence time of gaseous compounds is much longer leading to more effective oxidation processes. Thus, similar to the depletions of atmospheric Hg and ozone in polar regions during springtime, Hg⁰ depletion in the interstitial air of the snow could be the result of fast oxidation processes involving halogenated radicals.

In addition, strong diurnal variations of GEM concentrations in the upper layer of the snow packs were observed. During the day, under sunlight conditions with solar irradiation strong enough to produce Br-radicals, Hg, in its oxidized form Hg(II), accumulated in the snow pack. Thus, oxidation was more active than reduction. After sunset, with solar radiation weaker, oxidation was less active and reduction predominated.

Even if these observations indicate that GEM is emitted from the snow surface during single events, Ferrari and co-workers conclude that deposition is the major process over a longer time period. Re-emission by outgassing of Hg⁰ from the snow surface plays only a minor role.

Further information about the air/snow exchange of Hg was gained by Brooks and co-workers [39] who used so-called dynamic flux chambers during their field experiments in Alaska to calculate the in-situ fluxes of snow-pack Hg to air and snow. The flux chamber is made of ultra-clean polycarbonate and covers the area being investigated so that the air in the chamber interacts with the snow surface. Ambient air is pulled through the chamber with a constant velocity, creating a dynamic equilibrium between air and snow cover in the chamber. GEM concentrations in ambient air and in the air of the chamber are measured simultaneously. Higher concentrations in the flux chamber compared with ambient air means an emission flux from the snow to the air. This flux can be calculated by determining the difference of these two concentrations, the air exchange rate of the chamber and the area covered by the flux chamber. Although the dynamic flux chamber has many advantages (easy handling, high sensitivity, high reproducibility), there are some disadvantages too; only small areas can be investigated, i.e. the transferability to larger areas has to be demonstrated by numerous replicates; important parameters like wind or advection are minimized by the presence of the flux chamber. Since these processes are of particular importance at the surface of fresh snow, quantitative information about the emission of chemical substances from large areas should be treated carefully. A better approach would be to use continuous micrometeorological methods, such as the modified Bowen ratio/gradient method for Hg⁰ (e.g. [70]), and these are now underway at Barrow.

In the chamber studies, Brooks and Lindberg observed that Hg was readily emitted from the snow pack in the Arctic with average fluxes of less than 10 ng/(m² h) and maximum values of up to 500 ng/(m² h). Fluxes over non-contaminated soils are in the range of 1 to 5 ng/(m² h). They also showed that the highest Hg⁰ fluxes from the snow to the atmosphere were correlated with solar irradiation and melting snow, and reconfirmed the results from Steffen and Ferrari. Based on these data, Brooks and Lindberg estimated that up to ≈ 25% of
previously deposited Hg (during AMDEs) can be re-emitted from the snow, primarily during snowmelt. The remaining Hg is potentially delivered to the Arctic tundra and surrounding ocean in snowmelt runoff.

2. SUMMARY AND CONCLUSIONS

Gaseous elemental mercury (Hg\textsuperscript{0}) is a globally distributed air toxin with a long atmospheric residence time. Significant quantities of Hg\textsuperscript{0} are transported to both poles, and the phenomenon of “Arctic haze” (consisting polluted air masses transported from the middle latitudes) is widely studied in northern systems. Although Hg\textsuperscript{0} is relatively inert, any process which reduces the atmospheric lifetime of Hg\textsuperscript{0} increases its potential for accumulation in the biosphere. New data from both Arctic and Antarctic research sites show that fast, photochemically driven, oxidation of boundary-layer Hg\textsuperscript{0} after Polar sunrise creates a rapidly depositing species of oxidized gaseous Hg in the remote polar troposphere which can reach highly elevated concentrations. The oxidation reactions involve naturally occurring halogens, and are most likely initiated by an auto-catalytic release of bromine via heterogeneous reactions on sea-salt aerosols as part of a reaction cascade involving ozone, bromine, and chlorine. Reactive halogen chemistry influences both polar ozone destruction and the subsequent Hg depletions, with bromine and iodine compounds having a greater potential to oxidize Hg\textsuperscript{0} than chlorine compounds. The sudden increase of ground level BrO concentrations in polar regions when ozone is destroyed is followed by rapid depletion of Hg\textsuperscript{0} and production of oxidized forms of Hg, including reactive gaseous Hg and aerosol Hg(II).

This Hg is deposited and accumulates in the snowpack during Polar spring at an accelerated rate and in a form which is highly bioavailable to bacteria. The fraction of deposited Hg that is not re-evaded back to the atmosphere likely remains in the biosphere. Several estimates of the size of the Arctic sink for newly deposited Hg range from \( \approx 100 – 300 \text{T/y} \), while estimates of the Antarctic sink are far more uncertain. Recent reports of MeHg in fresh snow and runoff suggests that some of the deposited Hg is already methylated and potentially available for uptake by biota [39]. The source of this methylated Hg remains an open question. Several lines of evidence suggest that AMDEs are a recent phenomenon which could accelerate as a result of continued climate change in the Arctic.

REFERENCES


[63] Scott K.J., Ph.D. Thesis – Development and use of a mer-lux bioreporter for the measurement and characterization of bioavailable Hg(II) in defined media and aquatic environmental samples (2003), Department of Microbiology, University of Manitoba, Winnipeg, Manitoba.


