Fast depletion of gaseous elemental mercury in the Kongsvegen Glacier snowpack in Svalbard

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Fast depletion of gaseous elemental mercury in the Kongsvegen Glacier snowpack in Svalbard

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[1]   Gaseous elemental mercury (GEM, Hg°) was measured in the snowpack interstitial air on the Kongsvegen Glacier (Svalbard) between the surface and 190 cm depth. A rapid depletion of GEM from $\sim$5 to 0.4 ng.m^{-3} in the snowpack air was measured in less than 8 hours at a calculated depletion rate of $\sim$0.5–0.7 ng.m^{-3}.h^{-1} while concentration of GEM above the snow stayed constant about 1.7 ng.m^{-3}. This depletion could only be explained by chemical processes and this study suggests that Br$^{\cdot}$ could be the most important reactant for the oxidation of GEM in the interstitial snow air. The lifetime of GEM was estimated to be $\sim$10 minutes with second order reaction rate constant between GEM and Br$^{\cdot}$ of about $\sim$2 $\times$ 10^{-11} cm^{-3}.molecule^{-1}.s^{-1}. These first experimental kinetic values for GEM oxidation in the snow air are in good agreement with both theoretical and modelling studies previously reported. **Citation:** Fain, X., C. P. Ferrari, P.-A. Gauchard, O. Magand, and C. Boutron (2006), Fast depletion of gaseous elemental mercury in the Kongsvegen Glacier snowpack in Svalbard, *Geophys. Res. Lett.*, *33*, L06826, doi:10.1029/2005GL025223.

1.   Introduction

[2]   Gaseous elemental mercury (GEM) is the predominant form of mercury in the atmosphere and it is emitted from both natural and anthropogenic sources. Polar environments could be of great importance in the global cycle of this metal. Atmospheric mercury depletion events (AMDEs) occur after polar sunrise in both the Arctic [*Schroeder et al.*, 1998] and Antarctic [*Ebinghaus et al.*, 2002] and lead to the rapid deposition of Hg onto snow surfaces [*Lindberg et al.*, 2002; *Sprovieri et al.*, 2005]. The fate of mercury species after deposition onto snow is still not clearly understood. The snowpack can act as a sink for GEM through homogenous and heterogeneous oxidation processes of GEM occurring in the interstitial snow air involving halogen compounds as Br$^{\cdot}$/ Br0$^{\cdot}$ radicals [*Ferrari et al.*, 2005]. Conversely, the snowpack can also be a source of GEM to the atmosphere through the reduction of mercury complexes by HO2$^{\cdot}$ and/or direct photodissociation of these complexes [*Dommergue et al.*, 2003b; *Ferrari et al.*, 2005]. The aims of this study were to document the processes of production and consumption of GEM on a high accumulation perennial snowpack which is not influenced by any permafrost effects and to investigate experimental kinetics of GEM oxidation in an Arctic snowpack. Here we report the first investigation about daily GEM evolution in a perennial snowpack, on the Kongsvegen Glacier, Svalbard.

2.   Experiment

[3]   Experiments were conducted on the Kongsvegen glacier the 20th of April, 2005. The front of this glacier is located 10 km south-east from Ny Ålesund, Svalbard (78°54′N, 11°53′E), an international Arctic scientific research station. The sampling area was chosen in an accumulation area at 600 meters a.s.l., 40 km far from Ny Ålesund.

[4]   Measurements of GEM in the SIA (snow interstitial air) were performed using GAMAS (gaseous mercury in interstitial air in snow), a device dedicated to sampling gaseous mercury and the temperature of air within a snowpack [*Dommergue et al.*, 2003a]. GAMAS probes were connected to a Tekran 2537A mercury vapour analyser. The detection limit of the 2537A Tekran analyser is about 0.1 ng.m^{-3}. Electricity was provide by a gas powered generator located 75 meters from the sampling site. Attention was paid about the wind direction, The generator location was chosen so as to avoid any contamination with wind from the exhaust plume. A closed and insulated box equipped with a temperature regulation system was designed to keep the analyser at 25°C during the entire experiment. Nine GAMAS probes were installed from the snow surface down to a 190 cm depth. The probes were connected successively to the mercury analyser with a 10 meter unheated clean Teflon line. A soda lime was used to pre-filter the air samples. The sample flow rate was 1.5 L/min for 5 minutes for a total volume of 7.5 L. One full profile of GEM concentrations in the snow air needs two continuous hours of sampling, as we measured at one meter above the snow surface and at the successive depths of 20, 40, 57, 97, 115, 137, 158, 180 and 190 cm. A synchronized two-port switch unit (Tekran model 1110) controlled alternating sampling between two PTFE lines. While one line was sampled SIA, the other line was hand moved from one probe to another, using PE gloves so as to avoid any contamination. The valve unit switched automatically every 10 minutes in order to collect duplicate measurements for each depth. No data are presented for the 80 cm depth as the probe was damaged during the study.

3.   Results

[5]   A pit was dug close to where the probes were installed to study snowpack stratigraphy. The yearly accu-

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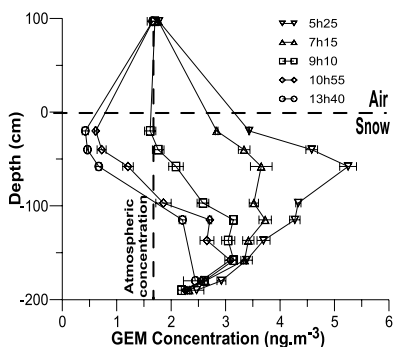
Figure 1. Monitoring of GEM in the lower atmosphere and the snowpack on Kongsvegen Glacier, Svalbard, the 20th of April 2005. Times reported here correspond to the first measurement of each profiles.

mulation thickness was estimated to be about 210 cm. Two ice layers were found between ~171 and 174 cm depth, and between ~184 and 186 cm depth (± 2 cm). The density of the snowpack increased slightly from ~0.28 g.cm^{-3} at 10 cm to ~0.50 g.cm^{-3} at 190 cm. Snow temperatures were stable at $-10 \pm 0.5°C$ and $-11.5 \pm 0°C$ from 40 cm to 140 cm, respectively. At 20 cm depth, the snow temperature decreased from $-8 \pm 0.5°C$ to $-9.5 \pm 0.5°C$ from 5:00 am to 3:00 pm.

[6] Net global radiation and atmospheric temperature were measured 300 meters from the sampling area at the NILU meteorological station (Tromso, Norway). The experiment started at 5:00 am, just after a very cloudy period (irradiation around 25 W.m^{-2} during six hours before the beginning of the experiment) We had clear skies for most of the experiment (irradiation increased to 200 W.m^{-2}). At 6:00 am, the air temperature was $-10 \pm 0.5°C$ and increased during the day to $-5.5 \pm 0.5°C$ in the afternoon.

[7] Results of GEM measurements in the SIA for the entire experimental period are shown in Figure 1. Depth uncertainty due to large volume of air sampled was estimated about ±15 cm, but is not represented on Figure 1 for clarity. GEM concentrations were constant throughout the experiment at approximately 1.75 ng.m^{-3} at one meter above the snow surface. Similar concentrations were measured at the Zeppelin Station (Ny-Ålesund), which is located approximately at the same altitude (i.e. 430 meters a.s.l.). No Atmospheric Mercury Depletion Events were observed on the 20th of April during this experiment. Rapid changes in GEM concentration in the snowpack were observed by the SIA between 5:00 am and 3:00 pm. The highest GEM concentrations were measured at 5:00 am, with a maximum of 5.3 ng.m^{-3} at a 60 cm depth. From 5:00 to 10:00 am, GEM concentrations decreased from the surface to 160 cm depth but stayed higher than atmospheric level. From 10:00 am to 3:00 pm, concentrations lower than atmospheric ones were observed in the first 120 cm depth of the snowpack. The lowest concentrations were observed very close to the surface (20 cm depth), with ~1.6 ng.m^{-3} at 9:30 am, ~0.8 ng.m^{-3} at 11:00 am and ~0.4 ng.m^{-3} at 1:30 pm. Concentration changes were measured between the surface and 160 cm depth, but no such variation was observed at 190 cm depth, where concentrations were stable around 2.3 ng.m^{-3}. *Albert and Perron* [2000] showed that

ice layers could considerably retard or obstruct gas transport. An icy layer was present around 170 cm depth so caution should be exercised when interpreting the GEM measurements at the 180 and 190 cm depths. Values at 20 cm depth could be influenced by some artifact measurements. *Albert et al.* [2002] found that when sampling a flow rate of 2 L/min on the seasonal snowpack at Alert, Canada a significant forced ventilation was induced. The flow rate used in this study was 1.5 L/min. Nevertheless, the air sampled at 20 cm depth could be mixed with ambient air and concentrations within the surface snowpack are probably higher or lower than that measured, depending if these concentrations are above or below atmospheric level.

4. Discussion

4.1. GEM Production in the Air of Snow

[8] It was assumed that GEM production in the snowpack occurred before measurements because concentrations were higher in the snowpack (5.3 ng.m^{-3} at 5:00 am) than one meter above it (1.7 ng.m^{-3}). Maximum concentrations were measured at 60 cm below the snow surface. Lower GEM concentrations at 20 and 40 cm snow layers could result from natural wind ventilation as well as experimental limits discussed before. GEM production in the snowpack has been observed at Station Nord (Greenland) during the night time shortly after polar sunrise [*Ferrari et al.*, 2004]. GEM production was first explained by direct photodissociation of mercury complexes such as HgCl$_n$ chlorocomplexes, as observed by *Lalonde et al.* [2003]. Mercury complexes are also reduced by photochemically initiated products such as hydroperoxyl radical (HO$_2$·) in the snow as suggested by *Dommergue et al.* [2003b]. HO$_2$· radicals, which are mainly produced by formaldehyde photolysis [*Sumner and Shepson*, 1999], are present at night in sufficient concentration to explain nighttimes production of GEM [*Ferrari et al.*, 2004]. In this study, we observed a production of GEM after a 6 hours cloudy period characterized by low irradiation between 20 and 30 W.m^{-2} and a solar zenith angle below 15°.

4.2. GEM Destruction in the Interstitial Snowpack Air

[9] While no depletion was recorded in the ambient air above the snowpack, a GEM depletion was observed between the surface to 160 cm depth between 5:00 am and 3:00 pm (Figure 1). Concentrations measured with the SIA decreased from 5.3 ng.m^{-3} to 0.4 ng.m^{-3} at 60 cm depth during this time period. This phenomenon has been observed in sub-Arctic (Kuujjuarapik, Quebec) and Arctic (Station Nord, Greenland; Ny Ålesund, Svalbard) locations, and cannot be explain by GEM adsorption on snow grains [*Bartels-Raush et al.*, 2002]. Studies have shown that Br· is the most efficient oxidant for GEM in the Arctic troposphere [*Ariya et al.*, 2004; *Skov et al.*, 2004]. *Goodsite et al.* [2004] proposed a mechanism for GEM oxidation in the troposphere based on a recombination of GEM with Br·, followed by the addition of a second radical (Br, OH or I) in competition with thermal dissociation. Fast recombination reaction rates between GEM and Br·, and the abundance of Br· in the marine boundary layer are sufficient to destroy GEM within a day [*Ariya et al.*, 2004]. Cl·, ClO· and BrO· do not play a significant role in GEM destruction because Cl· concentrations are insufficient (<10^4 cm^{-3}) in the

Table 1. Experimental GEM Lifetimes and Rate Constants in Kongsvegen Glacier Snowpack Measured on the 20th of April, 2005 Assuming a Second Order Reaction Between GEM and Br[·]

Depth, cm	τ,[a] min	k,[b] $cm^3 \cdot molecule^{-1} \cdot s^{-1}$
20	8.4 ± 0.5	2.00×10^{-11}
40	8.2 ± 0.1	2.03×10^{-11}
57	9.2 ± 0.2	1.81×10^{-11}

[a]Lifetime $\tau = (k\,[Br^·])^{-1}$, with k second order rate constant obtained using Figure 2.
[b]Constant reaction rate evaluated considering $[Br^·] = 1 \times 10^8$ molecule. cm^{-3}.

marine boundary layer [*McFiggans et al.*, 2002], and the reactions of BrO[·] and ClO[·] with GEM are likely endothermic [*Tossel*, 2003]. In the lower atmosphere, Br[·] radicals are formed by Br_2 photodissociation at wavelengths below 620 nm. At Alert, *King and Simpson* [2001] showed a decrease (factor 100) of spectral irradiance at 519 nm in the first 20 cm of the Arctic snowpack and *Foster et al.* [2001] showed that Br_2 levels in the SIA were twice those measured in the atmosphere ($\sim$25 ppt, or $\sim$1 $\times$ 10^8 molecule.cm^{-3}). Physical and chemical interactions occur in the snowpack and Br_2 is formed at the surface of the snow grains. Finally, we assume that heterogeneous reactions can produce Br[·] radicals by Br_2 photodissociation in the first 20 cm of the snowpack, as there is sufficient radiation and Br_2 concentrations to produce these Br[·] radicals. We suggest that Br[·] radicals could diffuse with depth and become available for GEM oxidation in the first 60 cm of the SIA of the snowpack. The decrease of GEM concentrations observed below 100 cm depth is likely due to diffusion of GEM from the bottom of the snowpack to the surface. Finally, mercury was accumulated in the Kongsvegen glacier snowpack in its oxidized form $HgBr_2$ from 5:00 am, when solar irradiation became strong enough to produce Br[·] radicals.

4.3. Kinetic Considerations

[10] GEM depletion rates in the snowpack at this site were estimated to be between $\sim$0.5 and $\sim$0.7 ng.m^{-3}.h^{-1}. These rates are higher than depletion rates calculated from measurements made at Station Nord ($\sim$0.3 ng.m^{-3}.h^{-1}) by *Ferrari et al.* [2004]. These values are also higher than AMDE rates of $\sim$0.05–0.2 ng.m^{-3}.h^{-1} measured during spring 2003 at Ny Ålesund (Svalbard) by *Gauchard et al.* [2005]. A decrease in depletion rates at 20 and 40 cm depth after 11:00 am was observed. Diffusion of GEM from the atmosphere to the snowpack could explain this apparent decrease in rate of reaction during the period where the snowpack exhibited lower GEM concentrations than the atmosphere. However, the rate of reaction from 5:00 to 11:00 am could have been overestimated since the GEM formed in the snowpack could diffuse immediately to the atmosphere. Neglecting ventilation of the snowpack by wind, the maximum emission flux for the 20 cm layer at 5:00 am was $\sim$0.38 ng.m^{-2}.h^{-1}, and an incorporation flux of $\sim$0.25 ng.m^{-2}.h^{-1} at 3:00 pm (see *Dommergue et al.* [2003b] for details). These weak fluxes confirm that the Kongsvegen snowpack is not a significant sink or source for the atmospheric GEM reservoir.

[11] Different theoretical studies [*Lindberg et al.*, 2002; *Goodsite et al.*, 2004; *Skov et al.*, 2004] and modelling investigations [*Ariya et al.*, 2004] described before involved Br[·] as the predominant oxidative agent to explain GEM oxidation in the Arctic troposphere, where Br_2 is rapidly photolysed to yield Br[·] atoms with a lifetime $\tau_{Br2} \approx$ 30s-1 min. Table 1 presents field evaluations of GEM lifetime in the SIA of Kongsvegen Glacier at depths where we assumed that GEM depletion could be due to oxidation mechanisms. These lifetimes were evaluated considering that the main GEM oxidation process was a second order reaction between GEM and Br[·] and using Br[·] concentrations of 1 $\times$ 10^8 molecule.cm^{-3} [*Foster et al.*, 2001]. *Ariya et al.* [2004] estimated the rate constants for GEM oxidation by modelling to be approximately $(3.2 \pm 0.4) \times 10^{-12}$ cm^3.molecule^{-1}.s^{-1}. *Skov et al.* [2004] gave an estimation of this rate about $\sim$1 $\times$ 10^{-12} cm^3. molecule^{-1}.s^{-1} using a correlation between GEM and ozone concentrations during an AMDE. *Goodsite et al.* [2004] presented a theoretical constant of 1.48×10^{-12} cm^3. molecule^{-1}.s^{-1} for the first step of their mechanism (described before) at 263 K. Reaction rate constants in the SIA calculated from field measurements on Kongsvegen glacier reported in Figure 2 (considering $[Br^·] = 1 \times 10^8$ molecule.cm^{-3}) are one order of magnitude higher than rate constants determined for the arctic troposphere. GEM Oxidation processes are faster in the SIA than in the lower atmosphere. The lifetime of GEM during an AMDE are estimated to be between 3 and 4 hours [*Skov et al.*, 2004; *Gauchard et al.*, 2005]. A lifetime of 8–9 minutes for GEM in the snowpack confirms the role that catalytic surfaces play in increasing kinetic constants. The snowpack offers a large internal surface which increases heterogeneous and photochemical reaction rates [*Dominé and Shepson*, 2002]. Diffusion with depth of bromine radicals that are photolysed close to the surface is likely and could explain GEM oxidation in the first 60 cm of the snowpack. In the second meter of the snowpack, GEM depletion is probably mostly due to diffusion processes from deep layers to the surface.

5. Summary and Conclusion

[12] Our studies of GEM distribution in the SIA in a glacier from a perennial snowpack in Svalbard have revealed active chemistry 40 km from the seashore. Production and rapid depletion of GEM in the snowpack have been shown. Depletion of GEM, probably linked to bromine radicals, was located within the first meter of the snowpack. Depletion rates for GEM on the Kongsvegen Glacier in the
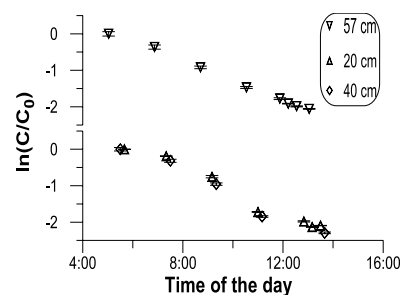

Figure 2. Decay of ln(C/C$_0$) in the snow pack from the surface to 60 cm depth with time on the 20th of April. C_0 represents GEM concentration when starting experiment (t = 0) and C represents GEM concentration at t time (from 5:00 am to 2:00 pm), at the depth considered.

snowpack were higher than AMDE depletion rates. We describe this event as an interstitial air mercury depletion event (IAMDE). Short lifetimes were evaluated for GEM in the Kongsvegen glacier snowpack to be approximately 8–9 minutes. This is in good agreement with previous atmospheric studies although slightly lower. The snowpack is a multiphase reactor where GEM could be oxidized at a faster rate because of surface catalysis. Higher bromine concentrations in the snow air than in the marine boundary layer could also facilitate GEM oxidation processes. Nevertheless, additional measurements are needed to better document the production event and complete the cycle. This will be an objective of future studies in different snowpacks.

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