

Interactive comment on “Mercury in the snow and firn at Summit Station, Central Greenland, and implications for the study of past atmospheric mercury levels” by X. Faïn et al.

X. Faïn et al.

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We would like to thank the reviewer for his interesting comments and suggestions that enabled us to improve our manuscript. We will first discuss the specific comments and then the technical comments.

Answers to specific comments:

1. Both in Alert (Steffen et al., 2002) and during our study, analyzers Tekran 2537A were used to investigate Gaseous Elemental Mercury (GEM) concentrations in the atmosphere. These instruments use a precision mass flow meter to measure sample flow, and they provide volumes referenced to NTP (Normal Temperature and Pressure, i.e. 20 deg. C, 1 atm). Thus, data obtained at Summit do not need any pressure

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correction and could be compared with data from Alert. However, this comparison has to be considered with caution, as no inter-calibration of the instruments used at Alert and Summit has been performed (we mentioned it in the section 3.3). To clarify this point, the description of the 2537A analyzer was modified (section 2.2).

2. Two models were used to assess the influence of diffusion and sampler-induced advection on GEM concentrations in the snow interstitial air (SIA) at Summit. The use of the straightforward diffusion model demonstrated that diffusion processes during both summer and spring were too slow to explain the diel cycles of GEM concentrations observed in the SIA. The advection model demonstrated that our SIA-sampling could induce artifact in GEM measurements. The advection model could not be applied to the 2005-summer data, because the evolution of snow permeability with depth was lacking. Thus, in the paragraph starting "Snow permeability data was ..." (line 28, page 18236), we first mentioned that no advection model was used for the 2005-summer data. We then present results obtained with the diffusion model. This diffusion model has been previously described in the first paragraphs of the section 3.4.3. The section 3.4.3 needs some clarifications. We modified the manuscript to better present these results.

3. In the section 3.4.4, we discussed the evolution of GEM concentrations observed at different depths in the SIA at Summit during summer 2005 and spring 2006. We showed that both photolytic and dark mechanisms were involved in GEM destruction. In other words, our data demonstrated that GEM oxidation could happen in the sunlit snow (i.e. the first half meter of the snowpack, where light can penetrate) as well as deeper in the snowpack (where light is no longer available). In the section 3.4.5, we discussed some possible mechanisms for both photolytic and dark GEM oxidation. Many studies have investigated the photo-induced oxidation processes of GEM, and Br^* radicals are probably the most efficient oxidant for GEM. Existing kinetic results indicate that the direct Br^* reaction with GEM is more important than BrO^* (Goodsite et al., 2004). However, BrO^* radicals could also be formed in the SIA when ozone and Br^*

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radicals are available. Raofie and Ariya (2004) published the first experimental product study of BrO^* initiated oxidation of GEM, suggesting that BrO^* could be another potential oxidant for GEM in the sunlit zone of the snowpack. We corrected the manuscript to suggest that Br^* radicals are not the only potential oxidants for GEM in the SIA.

On the other hand, to our knowledge only one study has reported dark oxidation of GEM in an Arctic snowpack (Dommergue et al., 2003b). However, these authors have not proposed a chemical mechanism to explain their observations. The main goal of our discussion in section 3.4.5 was to discuss how GEM could be oxidized without light. We proposed a chemical mechanism to describe dark oxidation of GEM in the SIA at Summit using both kinetic and thermodynamic studies (Tossel et al., 2003; Goodsite et al., 2004) and previous observations in the Alert snowpack (Foster et al., 2001). We agree with the reviewer that this section is long. However, our hypothesis is new and has to be discussed. We suggest that GEM could be oxidized in the dark by Br_2 . We first compared the kinetic of this process with the photo-induced oxidation of GEM by Br^* radical, as proposed by Goodsite et al. (2004). We then discussed the dark production of Br_2 in the SIA. Finally, we compare our assumption with the ozone data available at Summit.

Answers to technical comments:

1. Dekabon lines are polyethylene lines with an external aluminum protection. Thus the gas sampled is only in contact with polyethylene. We did not quantify loss of GEM in our Dekabon lines, because polyethylene and teflon exhibit very similar permeability for CO_2 , H_2 , O_2 , as well as N_2 (data easily available, for example in Cole Parmer catalog). We have additional evidence that no GEM was lost in Dekabon lines: a. If we consider GEM lost by diffusion through polyethylene during sampling, we should also consider diffusion of atmospheric air to the inside line during blank measurements (when air zero is flushed through the line). However, our blanks were excellent. b. If we consider an uptake of GEM on the lines, the addition of air zero and the gradient of concentrations induced should cause a GEM reemission during blank tests. Again, our

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blanks were excellent. Finally, our good blanks with zero air likely show that no GEM was absorbed on the polyethylene inside the lines.

2. The acronym SIA (snow interstitial air) is first defined in the section 3.4.1 (line 18).

3. We admit that the manuscript does not clearly explain why the Chemical Zone (CZ) goes to 2.7 meters. In the section 3.4.4, we described the chemical mechanisms involving GEM in the snow interstitial air. We observed at Summit photo-induced processes close to the snow/atmosphere interface (i.e. in the sunlit zone, the first ~60 cm of the snowpack). But we also measured deeper in the snowpack during spring 2006 null and constant concentrations of GEM from 200 to 270 cm depth. There is evidence that chemical processes involving GEM in the SIA occurred from the surface to 270 cm depth. Below 270cm depth in spring 2006, we observed GEM concentrations increasing again. This phenomenon could only be explained by a slowdown or a stop of GEM oxidation combined with diffusion from deeper snow layers. There is clearly an evolution in the nature of the chemical processes involving GEM below 270 cm depth. The definition of the Chemical Zone is based on these considerations: we assumed that no chemical processes involving GEM were occurring below 270 cm depth. Results shown in Figure 11 (and described in section 3.5.4) validate a posteriori this hypothesis. The section 3.5.2 was modified to better explain these arguments.

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