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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temperature and sunlight controls of mercury oxidation and deposition atop the Greenland ice sheet" *by* S. Brooks et al.

Anonymous Referee #3

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This is an interesting and new study of gaseous Hg(II) at Summit, top of Greenland ice sheet. This study is in the scope of ACP, but would need major improvements. The authors have only given it a cursory examination. A much more in-depth analysis may yield more insight. The quality of the manuscript could also be improved by re-writing some sections, avoiding repetitions, and by a better organization of the different sections.

General comments:

The authors report a qualitative analysis of 2 selected periods (total: 10 days) when 2 months of data are available. A more in-depth analysis of their dataset would be

possible by investigating multiple-correlations. Which part of the RGM variability could actually be explained by environmental factors like irradiation, wind speed, temperature..? Can we isolate different correlation schemes for different time periods? Overall some statistics need to be included in the manuscript: they authors mention correlations, but never report r or p values.

The authors have chosen one possible pathway to explain RGM enhancement at Summit (GEM oxidation by Br radicals). They should explore other possibilities. Br radicals are not the only oxidant for GEM. Although we have evidences that Br radicals could be the most efficient oxidant, the discussion should be broaden to other oxidants (Cl radicals, OH. . .), eg comparing levels and kinetics rates.

Another mechanism potentially involved in the observed RGM patterns at Summit could be downwelling of free tropospheric air. Elevated levels of RGM have been observed before at high altitude laboratories (Swartzendruber et al. 2006; Fain et al. 2009), and during airborne campaign (eg Talbot et al., 2008). Ozone and water vapor have been used as tracers for free tropospheric air at Mt Bachelor (Swartzendruber et al. 2006): maybe it would be interesting to investigate the relations between these parameters and RGM at Summit? Overall, the eventual influence of free tropospheric RGM-rich air at Summit needs to be included in the study.

The authors could plot RGM vs GEM. If really the RGM pattern is fully explained by in situ oxidation of GEM at Summit, they should observed a -1 slope (or slightly closer of 0 as RGM deposition is fast).

The criteria of no RGM formation occurring above -15 degrees C is arbitrary and too speculative in my view. It is based on only 6 days of observations during July 2008 (Fig. 8). Such hypothesis would require modeling effort. Obrist et al. (2010) have reported atmospheric production of RGM at a temperate location (Dead Sea : 45 degrees C) for BrO levels as low as 4 pptv. The temperature dependence of the HgBr dissociation needs to be examined more carefully in this manuscript.

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Interactive Comment

The authors discuss AMDEs. However, a 0.1 depletion in GEM cannot be considered as an AMDE. I think that all the discussion related to AMDEs should be removed from the manuscript.

The authors mention RGM deposition, but never discuss in details air-snow exchanges of Hg species. A efficient cycling of Hg between snowpack and lower atmosphere is likely to happen. Some data have been reported before at Summit by Fain and coworkers and could help for the discussion. Could we explain the diurnal GEM cycle observed in 2007 by GEM emission from snow surface? This GEM diurnal pattern needs to be discussed in more details.

I am skeptical about the estimation of Hg sequestered by the Greenland ice sheet, and in my view this should also be removed from the manuscript. The authors extrapolate 21 Hg(II) analysis from a single core collected at Summit to all the Greenlandic ice sheet. They assume that the Hg chemistry would be the same everywhere above the ice cap. Air-snow exchanges processes could also vary with location (e.g. the snow ionic composition will change with the distance from coast).

Figures 5 and 6 (diurnal patterns) do not include any error estimate. Standard errors need to be calculated and shown. The reader does not know if the trends discussed in the paper are significant (e.g., page 3673 line 24, the bimodal trend discussed for GEM from Fig. 6).

All the discussion on RGM oxidation is based on J(Br2), i.e. irradiation. I would recommend that the authors use the available BrO data to investigate directly the link between RGM and Br. Again, statistical analysis would be warranted.

The authors may want to improve the outline of the paper. I would combine the sections 1, 2, 3 and 6 in the introduction.

Specific comments:

Section 1

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Page 3665, line 11- no pollution from the camp was detected. Please clarify how this was evaluated.

Section 2

As mentioned in my general comments, the discussion about AMDEs is not relevant. However, the comparison with Antarctic studies is interesting, but need to be clarified. The author refers to Brooks et al. (2008) and Dommergue et al. (2010), stating that these studies have reported AMDEs in the Antarctic polar plateau. This is not true when reading these papers. Interestingly, the Brooks et al. paper from 2008 (South Pole) did not report atmospheric GEM !?

Section 3

The Jitaru et al. (Nature Geoscience) and Fain et al. (PNAS) papers should be discussed here.

P 3667 line 4 - Hg is certainly not a stable element ! And the authors cannot claim that "While other compounds within ice cores may change over time, total mercury concentrations will remain forever unaltered." We have no evidence that Hg is so stable in the deep ice. This would need to be investigated carefully.

Section 4

Blanks levels, and detection limits based on blanks are missing for the RGM and PM measurements.

Page 3668 line 9 - the mass flow in the Tekran units should be the same at any elevations. Thus users of the Tekran units usually adjust the volumic flow. E.g., at higher altitude (lower pressure), the volumic flow should be increased. This need clarification, and the authors should report the flow values they used.

How often did the authors change denuder and RPF?

Mention if you always used soda lime.

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BrO method is not reported. The authors can also include DOAS specifications: how/where it was located on the field, detection limit. . . etc.

Section 5

More details are required about the method used for Hg(II) analysis in snow : references of the instruments, blanks levels, investigation of matrix effect (OPR). . .

Section 6

Overall, this section could be moved in the introduction. Additional references would be a good improvement for this section.

Page 3669, line 8 – I guess this number of 97% was suggested before evidence of high RGM in the upper troposphere.

Section 7

Page 3670, line 2 - "$\sim$1.5 ng/m3", be more specific using number reported in Table 1.

Page 3670, line 4 - A depletion of 0.1 ng/m3 is about the precision of the 2537 analyzer.

Page 3670 line 5 - a more quantitative discussion is needed. If GEM decreases when RGM increases, plot RGM vs GEM. On the other hand, Fig. 7 shows simultaneous increases in GEM and RGM. Please clarify.

Page 3670 line 5 - How did the authors calculate DL?

Page 3670 line 11 - It is not clear for me why the RGM and PM data are good and the GEM data wrong. If the authors had troubles with the soda lime, this could have impacted all analysis. Please clarify.

Page 3670 line 14 - "Br chemistry was lower ": what does this mean? Please clarify.

Page 3671 line 3 - "Obvious sign of AMDEs" : I do not see such obvious sign.

Section 8

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Page 3670 line 20 - Hg has been investigated at coastal locations in the Arctic, and I doubt that Summit is similar to these locations.

Page 3672 - "[RGM]=. . ." this is a nice equation, but it is not used further in the paper.

Page 3673 line 14 - "broad enhancement of PM" : this is not clear to see from Fig. 3. What do we learn from these PM patterns?

Page 3673 line 16 - "GEM ∼1.5 ng/m3", repetition from section 7. There are more repetition in the manuscript. I did not listed all of them.

Page 3673 line 27 - What does "consistent concentrations" mean? Please clarify.

Page 3673 line 28 - The authors claim they "calculate" that both solar elevation angle >5 degrees and air temperature < -15 degrees C are required for atmospheric RGM production. They need to provide details on these calculations. Reading the manuscript as it is, the reader have no evidence that these criteria are not fully speculative.

Page 3674 line 16 - The authors report concentrations for Br radicals, but what do we really learn from these calculations/results?

Page 3674 line 22 - "RGM is not formed above -15 degrees C. . ." : again this is speculative.

Page 3675 line 4 - what is the standard deviation of the Hg(II) concentration in the firn core?

Section 10

Page 3676 line 14 - The author have not demonstrated that HgBr is further oxidized to stable RGM. They assumed that this mechanism reported by Goodsite et al. (2004) occured at Summit.

Page 3676 line 20 - RGM means Reactive Gaseous Mercury. When deposited to the snow surface Hg(II) is not "gaseous" anymore. There is no discussion about snow-

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air Hg exchanges in the manuscript, and the authors conclude about the importance of such processes. I would recommend to discuss more in depth this point in the manuscript.

Table 1 is not referenced in the text. What is “Coeff. Of Variation”?

Figs. 6 and 7 do not report the same days of measurements.

Fig. 8 : If RGM and air temperature are “anti-correlated” (caption), report r and p values. Eventually, plot RGM vs Temperature.

Fig. 10: in the caption, the solar angle criterion is “exceeds 7deg”. It is discussed as larger than 5deg in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3663, 2011.