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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 #1

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Review of "Temperature and sunlight controls of mercury oxidation and deposition atop the Greenland ice sheet," by S. Brooks et al.

Overall:

The authors have collected valuable and unique measurements of mercury, trace gases, and meteorology at Summit, Greenland. The paper interprets these measurements as evidence for oxidation of elemental mercury initiated by atomic bromine, which addresses one of the major outstanding issues in mercury research. They also derive temperature and insolation conditions required to support oxidation. In separate measurements, the authors measured total mercury in firn and extrapolated to total

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mercury deposition on the Greenland ice sheet.

This work is clearly within the scope of ACP and potentially a valuable contribution to the mercury research community. However parts of the manuscript currently lacks enough detail to support some conclusions. As written, the reader may wonder if the authors' have selectively analyzed favorable data, although I do not claim that they have. Possible alternative explanations of the mercury data are not adequately discussed. As a result, some claims in the abstract and conclusions are not sufficiently supported by the main text. I hope this will eventually be published, but it first requires major changes to the text.

I have organized this review into general issues, which concern multiple parts of the manuscript, and specific issues, which identify the passages described in the general issues as well as other lesser concerns.

General issues:

The authors' major conclusion is that oxidation of elemental mercury by atomic bromine is the best explanation for their observtions. This conclusion requires citing specific observations that the alternative mechanisms cannot explain. However, they provide no discussion of alternative oxidation mechanisms, which are chiefly thought to include oxidation by OH or O3. The authors' evidence for mercury oxidation by Br comes from correlations of the diurnal cycle with J(Br2). Since the authors have concurrent measurements of BrO, it is not clear why they use the indirect evidence from J-values rather than the more direct measurement of reactive species itself.

Much of the authors' evidence for in situ oxidation of GEM comes from interpreting diurnal cycles of GEM and RGM. Since entrainment of these species from above the boundary can vary on diurnal timescales, this must be explicitly discussed. If entrainment is not an important influence on the Summit data, then the authors must explain why. There is extensive evidence for elevated RGM and reduced GEM in the free troposphere relative to the low-altitude boundary layer (e.g. Talbot et al. 2008; Swartzen-

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druber et al. 2006;2008). At 3200 m, Summit could plausibly sample free-tropospheric air in which mercury was oxidized before reaching the measurement site.

Another major claim in this work is that thermal stability of HgBr at cold temperatures causes the peak of RGM and FPM at low solar elevation angles seen during 7-13 June 2008. This is possible, but other alternatives are also consistent with the data shown. The concentrations of Br and BrO may increase at low solar elevation, when the HOx sinks are smallest, which would increase GEM oxidation (Von Glasow et al. 2002; Hedgecock et al. 2004). Cold temperatures, which occur at low solar elevations, also favor Br production from aerosols, via the solubility of HOBr, which would also tend to favor GEM oxidation (Vogt et al. 1999).

The abstract and conclusions both claim that "the majority of the deposited RGM is readily photoreduced and re-emitted to the air as GEM." This is problematic because the analysis has not quantified either the deposition or emission fluxes. The data and main text suggest that *some* RGM is photoreduced and reemitted as GEM, but the it is unclear from this work whether the re-emissions are a large or small fraction of the deposition.

Data selection criteria. The authors have collected over 2 months of observations in Greenland in 2007 and 2008. Yet the analysis and discussion focuses only on 5 days from 2007 and 6 days from 2008. The reasons for discussing only those 11 days are unclear to the reader. Objective criteria for discarding the remainder must be clearly stated, otherwise the reader might suspect the authors have selectively presented data that supports their desired conclusions. Preferably, the authors would expand the analysis and discussion to describe the behavior of mercury species and relationship between mercury and meteorology outside of those 11 days.

AMDE terminology. The term "atmospheric mercury depletion event" (AMDE) is typically used in the literature to describe dramatic depletions of elemental mercury when concentrations fall 30%, or more, below their background concentrations, often below

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detection limit, and persist at low levels for hours or days. The Greenland observations in this work show midday declines of 0.1 ng/m3, or 7%, at most. It is misleading to call these AMDEs and it would be better for the authors to describe them as a diurnal dip in GEM.

The paper currently contains large duplications of material in different sections. These must be eliminated. I have pointed out the most obvious duplications in the specific issues.

Table 1 is never referred to in the text. It contains useful information, although one column "coeff. of variation" is nowhere defined.

Specific issues:

Page 3664 line 5. The abstract says, "Significant levels of BrO in the near surface air were often accompanied by depletions of gaseous elemental mercury below background levels." The paper does not support this statement because the authors have not compared BrO and GEM in the main text. The most relevant passage seems to be, "High correlations between RGM and BrO, for any extended period of time, were rare at Summit," which would not support the statement in the abstract. In addition, referring to noontime GEM dips of 0.1 ng/m3, or 7%, as "depletions" is misleading because the mercury literature usually refers to depletions as longer events with nearly total loss of GEM.

line 10. The abstract says, "we have conclusively detected bromine and mercury chemistry in the near surface air." I do not think the evidence is "conclusive," since the authors have not discussed why alternatives explanations fail.

line 11. "We suggest that the fate of the formed mercury-bromine radical is further oxidation to stable RGM or thermal decomposition." Goodsite et al. (2004) claimed this, so it is not a new conclusion by the authors. Also see comment in conclusions.

line 14. "verses" should be "versus."

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line 15 also P3676 line 17. "The availability of Br appears to be controlled by J(Br2)." This claim is not found anywhere in the paper, so it should not be in the abstract or conclusions.

line 16. "The majority of the deposited RGM is readily photoreduced and re-emitted to the air as GEM." Neither deposition nor emission fluxes have been quantified in this work, so the abstract should not compare their magnitudes, even qualitatively, as in "the majority of deposited RGM."

line 24. Please specify the longitude of Summit.

Page 3665 line 10. "Summit is a remote camp hundreds of kilometers from any ... infrastructure." The camp surely has infrastructure. Perhaps "industry" would be more accurate.

line 11. "Mercury emissions from the camp itself were not detected." Please explain how this was determined.

line 27. Sprovieri et al. (2002) and Temme et al. (2003) also report report polar AMDEs in Antarctica.

Page 3666 line 1. Brooks et al. (2008) and Dommergue et al. (2010) suggest that subsidence can explain their data, so these should not be called AMDEs.

line 4 "GEM/halogen chemistry" It is not clear what the authors mean by the slash "/" here and elsewhere throughout the paper. These should be replaced with plain language.

line 18. Holmes et al. (2010) provide a smaller estimate of deposition to the Arctic than the cited result from Ariya et al. (2004). Both should be mentioned.

Page 3667 line 6. "While other compounds within ice cores may change over time, total mercury concentrations will remain forever unaltered." This may be misleading because reemission from ice reduces the net deposition. i.e. the ice accumulation

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does not reflect gross deposition.

line 23. "swas"

Page 3668 line 8. "hot/cold zones and mercury absoprtion/desorption." The slash is vague and the order is reversed between the pairs.

section 6. This entire section should be cut or moved to the introduction. There is no information specific to the authors' measurements, only background. Terms GEM, RGM, FPM, which have already been defined, are redefined here using nomenclature that is inconsistent with that above.

page 3670 line 3. "$\sim$1.5 ng/m3" Please use exact numbers from the data. Mean GEM measurements were 1.31 and 1.45 ng/m3 for 2007 and 2008, according to table 1, which is an important difference from 1.5 ng/m3.

lines 5-6 Please give the mean or median for RGM and FPM.

line 12. "RGM and FPM are reported for this period because, unlike GEM, these measurements are based on a difference method." A difference method is not the standard way to analyze these species with a Tekran instrument, so this must be defined in section 4. It is not clear if RGM and FPM were always measured with a difference method or only when there was a problem with the soda-lime trap.

line 16. "...chemistry [was] significantly lower..." Chemistry cannot be lower.

line 19. "Total mercury in snow was slightly less in 2008 than in 2007..." The numerical amounts should be specified here or in a table.

line 20. "significantly less." It is not clear if the authors mean significantly in the sense of statistical likelihood or in a colloquial sense. If meant in the statistical sense, then method of determining significance should be specified, here and elsewhere.

line 25. "Both of our selected periods ... were characterized by light winds, and were bounded by higher wind speeds." Why were these criteria chosen? What happens in

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other conditions? See general comment above about selective data analysis.

Page 3671 line 3. "obvious signs of typical daily AMDEs" The authors have not described what is "typical" and I do not think this feature of the GEM diurnal cycle agrees with the conventional use of "AMDE" in the literature. See general comment above.

line 8. "FPM peaked at night ... due to colder temperatures favoring RGM absorption onto particles." This hypothesis is unproven and the text should reflect that. See extended comments in my general issues.

line 17. "peaking at night" Perhaps the authors mean "peaking at low solar elevation angles" since the sun was still above the horizon.

last equation. BrO self reaction is not thought to be important for most tropospheric ozone depletion, except under extremely high BrO concentrations. Rather, most BrO is lost through photolysis and reactions with HOx and NOx, or possibly IO (e.g. Platt and Honninger 2003).

Page 3672 equation beginning "Summation [RGM]". It is not clear what the left side of this equation means. The right side is the sum of HgBr losses, which has no clear relevance to the discussion.

Page 3673 line 6. "7-13 May" I think the dates should be 14-19 May.

lines 4-9. This paragraph mainly repeats material from paragraphs 3-4 of section 7.

line 13. "RGM was strongly correlated to J(Br2) and decoupled from temperature." Figure 7 shows that temperature and J(Br2) have nearly identical diurnal cycles. I don't see how the authors can claim that RGM is correlated to one and decoupled from the other.

line 15-18. Comparison of GEM to hemispheric background has already been discussed.

line 20. "thermal dissociation of HgBr dominated over the formation of HgBrX" This is a

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reasonable hypothesis to explain the observations, but there is no direct evidence, so it should be phrased as a hypothesis. Alternative explanations also deserve discussion. The concentration of Br and BrO may increase at low solar elevation angles, when the HOx sinks are smallest, which would increase GEM oxidation (Hedgecock et al. 2004). Cold temperatures also favor Br production from aerosols, via the solubility of HOBr, which would also tend to favor GEM oxidation (Vogt et al. 1999).

line 29. "We calculate that GEM oxidation... requires solar elevation angles > 5 degrees and air temperatures < -15 C." It is not clear how the authors derived these criteria. Is it based on some model calculation? Or are these the observed conditions under which the GEM diurnal cycle has a dip at midday and accompanying peak in RGM?

Page 3674 line 12. The equation is correct only in the limit that HgBr thermal dissociation is slow compared to oxidation of HgBr to Hg(II). When thermal dissociation is fast, [GEM]*k overestimates the RGM production so the required Br concentrations are higher. These caveats should be stated clearly.

Page 3675 line 1. This paragraph on snow does not belong in this section titled "Bromine/Mercury chemistry." Perhaps all of the snow measurements and analysis could be gathered into their own section rather than spread out.

Page 3676 line 11. "Halogen chemistry is normally associated with marine boundary layers..." Since halogen chemistry is also important in the stratosphere, this should be qualified as "Tropospheric halogen chemistry is normally..." or otherwise modified.

line 13. "We conclude that the fate of the mercury-bromine radical is further oxidation to stable RGM or thermal decomposition." Goodsite et al. (2004) claimed this, so it is not a new conclusion by the authors.

line 17. "verses" should be "versus"

line 20. "At Summit most of the deposited RGM is readily photoreduced and re-emitted to the air as GEM." This is a new claim which is not made or supported in the rest

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of the text. Neither the RGM deposition to snow nor the GEM emissions have been quantified in this work. This should not be in the conclusions.

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