Final Authors' responses to reviewer comments

Temperature and sunlight controls of mercury oxidation and deposition atop the Greenland ice sheet

S. Brooks, C. Moore, D. Lew, B. Lefer, G. Huey, and D. Tanner

Referee #1 comments in RED
Referee #2 comments in GREEN
Referee #3 comments in BLUE

Author responses are in Black and are often-repeated responses are numbered.

We appreciate the excellent reviews and the hard work of the reviewers. We are in agreement with all their general comments. Since this paper was submitted to Special Issue 107 of ACP the Liao et al. and Stutz et al. discussion papers have been added to the special issue. These papers discuss mercury chemistry and, air masses histories and BrO, respectively. We will be revising our paper to reference selected materials from the Liao et al. and Stutz et al. papers.

Our added references from the Summit group and Special issue are:

Updated references

Liao, J., Huey, L. G., Tanner, D. J., Brooks, S., 5 Dibb, J. E., Thomas, J. L., Stutz, J., Lefer, B., Haman, C., and Gorham, K.: Observations of hydroxyl and peroxy radicals and the impact of BrO at Summit, Greenland in 2007 and 2008, Atmos. Chem. Phys. Discuss., in preparation, 2011.

Stutz, J., Thomas, J. L., Hurlock, S. C., Schneider, M., von Glasow, R., Piot, M., Gorham, K., Burkhart, J. F., Ziemba, L., and Dibb, J.: Observations of BrO at Summit, Greenland, Atmos. Chem. Phys. Discuss., in preparation, 2010. 30931, 30939, 30949, 30950

Thomas, J. L., Stutz, J., Lefer, B., Huey, L. G., Toyota, K., Dibb, J. E., and von Glasow, R.: Modeling chemistry in and above snow at Summit, Greenland - Part 1: Model description and results, Atmos. Chem. Phys. Discuss., 10, 30927–30970, doi:10.5194/acpd-10-30927-2010, 2010.

Thomas, J. L., Stutz, J., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., and von Glasow, R.: Modeling halogen chemistry in and above snow at Summit, Greenland – Part 2: Radical chemistry and sensitivity studies, Atmos. Chem. Phys. Discuss., in preparation, 2011.

The comment most often repeated in all reviews was – Why did the authors just analyze two selective data periods in depth?

Response #1 We admit that we did a poor job explaining why we presented the two data periods in detail. Utilizing FLEXPART Stutz et al. (this issue) identified our first period in 2007 (14–19 May 2007) as the sole case in 2007 when the air mass recirculated over the Greenland ice sheet prior to our measurements. The air mass had remained fairly close to the surface of the Greenland ice sheet for the >2 days prior to reaching the station. Likewise in 2008 our June 7-13 period was the longest period in 2008 where, again, the air mass had remained fairly close to the surface of the Greenland ice sheet for the >2 days prior to reaching the station – this period was also selected for their sole analysis period by Thomas et al. (this issue). From Thomas et al. - "This focus period was chosen due to consistent meteorological conditions…In addition, FLEXPART emission sensitivity maps indicate that the air at Summit during this period had been cycling over the Greenland snowpack for at least three days prior to the focus period without influence of marine air (Stutz et al., 2010). Therefore, we anticipate that the composition of local air masses at Summit was strongly influenced by contact with the surface snowpack."

The two periods presented in detail in the paper were also the only multiday (> 48 hours) periods of consistent (lowest variation) and low wind speeds. Large variability in wind speeds have the confounding effect of rapidly changing the depth and volume of the mixing layer, entraining air from above when wind speeds increase, and leaving residual layers aloft when the wind speed drops. The winds are plotted in Liao et al. (this issue). The selected data periods best illustrate the solar and temperature controls without the confounding influences of rapidly varying winds and mixing layer depths, entrainment of air from aloft, or recent marine influences.

The remainder of the 2007 and 2008 data are fully consistent with our main results that sun angle > 5 degrees and air T < -15 C are necessary to produce RGM in the near surface air. We will add an RGM vs. Temperature scatter plot and an RGM Vs. solar elevation plot for the entire 2007 and 2008 periods – These are effective plots that shows significant RGM levels exist solely below -15C and solar angles >5 deg.

A second repeated comments was – "Since the authors have concurrent measurements of BrO, it is not clear why they used the indirect evidence from J(Br2)"

Response #2 - We used J(Br2) because we do not have continuous [BrO] concentrations for the selected time periods. During the 2007 the [BrO] measurements conducted by the Georgia Tech group using CIMS were not reported before 5/27 due to technical problems. Even after 5/27 the BrO data showed a great deal of noise until the dataset was restarted on 6/7. In Figure 9. We present this "restarted" [BrO] and RGM , and continued the graph until the [BrO] measurements ended on 6/11. Figure 9. shows the only available period of continuous "low noise" [BrO] concentrations from 2007. We did not graph RGM Vs. BrO for 2008 because the CIMS data was noisy until 6/12, discontinuous from 6/14 to 6/20 and generally showed very low concentrations (~ 1 ppt) afterwards. The Stutz et al. (this issue) DOAS BrO data set is discontinuous primarily due to morning fog.

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.

Response #3 The reviewer raises an important point. Reactive gaseous mercury (RGM) is operational defined and we have no information on the chemical composition, except that it is generally considered to be Hg(II). Liao et al. (this issue) presents our RGM dataset with comparisons to HO2 + RO2 and OH. In the revised paper we will add alternative oxidation mechanisms, and, where appropriate, reference the Liao et al. mercury analysis.

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

See Response #1 – We purposely selected our time periods for in-depth analysis specifically because in both cases the air mass had remained just over the ice sheet for an extended period of days, and because of the low wind speeds. This gives us our best defense that these mercury observations are not from the upper troposphere, entrainment, or marine (non ice sheet) influences.

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).

Response #4 – We will add a discussion of enhanced BrO/Br at the low sun angles and colder temperatures as potential other influences on RGM production.

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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.

Response #5 - The reviewer is quite correct. The emissions are suggested by the diurnal GEM peaks, but the actual flux magnitudes were not measured. We will change “the majority of the deposited RGM is readily photoreduced and re-emmitted to the air as GEM” to “The diurnal peaks in GEM following solar noon suggest photoreduction of deposited RGM, where a portion of the deposited mercury in the surface snow is re-emitted as GEM”.

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.

See Response #1

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 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.

Response #6 - We will change AMDE (Atmospheric Mercury Depletion Event) to “diurnal dip in [GEM]” throughout the text.

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.

We will fix the duplications in the revised paper

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

Coefficient of Variation – the ratio of the standard deviation to the mean of the variable - is now defined in the revised text

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.

Yes – We should have just referenced Goodsite et al. (2004) for this statement . This error is corrected in the revised text.

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."

Yes – we did not directly measure the fluxes – we will replace "The majority" with "A portion" .

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 does not reflect gross deposition

This was poorly worded on our part. We meant to indicate that mercury, as an element, is neither created nor destroyed. We will delete that portion of the text.

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.

The concentrations of RGM and FPM using the Tekran front end speciation unit are always determined by subtracting the mercury measured during the zero gas flush, just prior to thermally desorbing the denuder and particulate traps, from the heating cycles of the denuder and particulate traps. If one has a soda lime cartridge problem which affects the magnitude of the [GEM] concentration input to the Tekran 2537A, one can have confidence in the [RGM] and [FPM] values without having confidence in the [GEM] values. This is the case here where the contaminated soda lime trap caused an unacceptable signal to noise ratio for the [GEM] measurements, but we accept the [RGM] and [FPM] concentrations because these species were preconcentrated to levels where the resultant quantity of measured RGM and FPM were orders of magnitude greater, than the GEM contamination evident in the zero gas flush conducted just prior to denuder and particulate trap heatings.

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

see Response #1

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

“Decoupled from temperature” was a clear misstatement in the text. We meant to say that RGM in fig. 7 is correlated to both J(Br2) and Temperature.

don’t see how the authors can claim that RGM is correlated to one and decoupled from the other.

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?

We will add an RGM vs. Temperature scatter plot and an RGM Vs. solar elevation plot for the entire 2007 and 2008 periods – These are effective plots that shows significant RGM levels exist solely below -15C and solar angles >5 deg.

There is not any discussion of the uncertainty of measurements and of the assumptions of e.g. made in the paper. As a consequence the paper present _13 tons/year deposited as a final estimate of mercury accumulation to the Greenlandic ice sheet. It would be better make uncertainty budgets and then come with a range of deposition, re-emission and of the final net accumulation.

We will add a full uncertainties text to the discussion and will highlight the clear problems of extrapolating one point to the remainder of the vast Greenlandic ice sheet.

Page 3667 to 3669. A presentation of the uncertainties of the measurements is needed and has to be applied in the following interpretation of results.
page 3669. The lifetime of GEM is said to be _1 year (Schroeder and Munthe, 1995). This is a too old reference and the lifetime of GEM from the latest results is most likely shorter (only a few month). The term background concentration can also be disputed. Sorensen et al. 2010 EST, Vol. 44, 7425-7430 demonstrated that GEM has a strong seasonal behaviour in the marine boundary layer, which fit with a lifetime of a few month. The modelling results of Holmes et al. 2006 as you cite yourself also found lifetimes of GEM in the order month and that complies also well with the latest experimental data.

Yes – We agree that the GEM lifetime of ~1year with our reference to Schroeder and Munthe (1995) is too old and more recent work has refined the lifetime to a few months.

Line 15. e.g. HgCl2 is not extremely water soluble e.g. 0.0002 g/100 cc and HgBr2 is 0.61/100 cc. For comparison is Hg(NO3)2 is very soluble (Handbook in Chemistry and Physics, CRC press). Therefore delete extremely => RGM is water soluble.
page 3672 Use chemical equilibrium versed signs for Hg + Br ї́C
́C
HgBr

Done

Counted Line 12 from the top There is one study of the dry deposition of RGM to snow surfaces Skov et al. 2006, Atm. Env. 40, 5452-5463 where a Vd was found to be _1 cm/sec, therefore a ref. to this paper should be given (By the way Brooks is co-author on that paper?). This will also improve the confidence in the indicated Vd.

Yes – we will reference Skov et al. (2006) for the estimate of deposition velocity of RGM

Page 3673 The reference to the figures have to be corrected as there are some confusion
here. There is more reference to Figure 3 but in some cases it is Fig. 4. I cannot see the anti-correlation between RGM and T in Fig. 6 where T is not appearing? I cannot see such a connection in fig. 7 but maybe in fig. 8.......

We will add the temperatures to Figures 3, 5 and 6

Page 3675 3 line 3.0 g l-1 should be 3.0 ng l-1
In the discussion it is important as already mentioned that the range of the estimates are given e.g. the accumulation range _300 kh m-2 _ 200%?
The conclusion has to be updated according the changes in the presentation

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..?

See Responses #1. We will add a discussion of the remainder of the data, and plots of the diurnal averages of the data outside our two selected time periods.

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.

We will add the error bars on the GEM and RGM lines of figures 3, 5, and 6. We will add the r values on figures 7, 8 and 9

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.

See Response #3

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.

See Response #1

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).

This really doesn't work well – we tried it - because RGM is continually produced, and deposited, and GEM is continually consumed and re-emitted via Hg(II) photoreduction at the snow surface.

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.

The -15C criterion holds throughout the ~70 days of the 2007 and 2008 data collection. It is our best suggestion to explain the observations. We will clarify in the text that the sun angle and air temperature criteria hold for the entire 2007 and 2008 datasets. The temperature dependence of the HgBr dissociation is from Goodsite et al. (2004) and Holmes et al. (2006).

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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.

We agree - see Response #6

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.

We will include a discussion of Fain et al. (2008). The diurnal post solar-noon peaks in GEM are certainly surface re-emissions.

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).

We agree, and we will highlight the clear problem of extrapolating one point to the remainder of the vast Greenlandic ice sheet. However, we did go to the effort of collecting a clean core to a depth of 7.1m, representing a decade of accumulation. Below about 1.2m depth the mercury concentrations (collected every 30cms) were quite uniform at ~3.1 ng/l. We believe it is useful for the paper to present an estimate of modern sequestration, and we will caution the reader that this is based on a single 7.1m core.

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).

We will add the error bars on the GEM and RGM lines of figures 3, 5, and 6. We will add the r values on figures 7, 8 and 9

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.

See Response #2

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.

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

This is covered in the overview paper for this special issue - Dibb et al. (this issue). We will provide this reference for camp influences

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 !?

We have deleted references to AMDE’s and replaced these with “diurnal dip in GEM”

Section 3
The Jitaru et al. (Nature Geoscience) and Fain et al. (PNAS) papers should be discussed
here.

We will include a discussion of these papers

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.

This was poorly worded on our part. We meant to indicate that mercury, as an element, is neither created nor destroyed. We will delete that portion of the text.

Section 4
Blanks levels, and detection limits based on blanks are missing for the RGM and PM measurements.

We will add these

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.

The mass flow in the 2537a or b is based on a standard cubic meter. However for the denuder it is based on a flow time. The denuder is designed so that gases will diffuse to the collection surface in the 0.1 sec residency time but the particles will not. At altitude one needs to reduce the mass flow rate setting on the denuder module to maintain the 0.1 second design residency time for air inside the denuder.

How often did the authors change denuder and RPF?

We will add these

Mention if you always used soda lime.

As a rule we only use soda lime when there is evidence of trap passivity on the 2537 units.

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

We will reference the Stutz et al. (this issue) BrO paper

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): : :

We will expand this snow discussion and place the snow measurements in a separate section

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 - "_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.

Plotting RGM vs. GEM really doesn't work well – we tried it - because RGM is continually produced, and deposited, and GEM is continually consumed and re-emitted via Hg(II) photoreduction at the snow surface. As GEM production via photoreduction at the surface and RGM production via Br2 photolysis both depend on solar input, GEM and RGM can peak at nearly the same time.

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

We will clarify

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.

The concentrations of RGM and FPM using the Tekran front end speciation unit are determined by subtracting the elemental mercury measured during the zero gas flush, just prior to thermally desorbing the denuder and particulate traps, from the heating cycles of the denuder and particulate traps. If one has a soda lime cartridge problem which affects the magnitude of the [GEM] concentration input to the Tekran 2537A, one can have confidence in the [RGM] and [FPM] values without having confidence in the [GEM] values. This is the case here where the contaminated soda lime trap caused an unacceptable signal to noise ratio for the [GEM] measurements, but we accept the [RGM] and [FPM] concentrations because these species were preconcentrated to levels where the resultant quantity of measured RGM and FPM were orders of magnitude greater, than the GEM contamination evident in the zero gas flush conducted just prior to denuder and particulate trap heatings.

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

On average, from the results of DOAS and CIMS BrO – the BrO levels in 2007 was about half the levels observed in 2007 – this is covered in Stutz et al. (This issue).

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

We have deleted reference to AMDE’s

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 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.

The -15C criterion holds throughout the full ~70 days of the 2007 and 2008 data collection. It is our best suggestion to explain the observations. We will clarify in the text that the sun angle and air temperature criteria hold for the entire 2007 and 2008 datasets. Further, we will add an RGM vs. Temperature scatter plot and an RGM Vs. solar elevation plot for the entire 2007 and 2008 periods – These are effective plots that shows significant RGM levels exist solely below -15C and solar angles >5 deg.

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?

We will add more details on the snow core in a new section

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- 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.

We will add the error bars on the GEM and RGM lines of figures 3, 5, and 6. We will add the r values on figures 7, 8 and 9
We will add the temperatures to Figures 3, 5 and 6

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

That was a Typo – it should have been 5 deg.

Response to Comment submitted by Thorsten Bartels-Rausch

Did you find a correlation of GEM emission and temperature? Our results indicate that the emission decreases at colder temperatures. It‘s unlikely that this is due to adsorption of GEM on the snow surface, as this process is only occurring at much lower temperatures [2]. I was wondering if you see GEM emission at temperatures below -30 _C.

Response – This is difficult to discern from our dataset because midday (high solar elevation) temperatures were never below -30C. Nighttime (low solar elevation) temperatures were only below -30C for the first week of measurements in 2007. There are strong correlations between [GEM] and solar elevation, and [GEM] and temperature, but there is an equally strong correlation between solar elevation and temperature. The snow surface undergoes radiative cooling at night (low solar elevations) dropping the near surface temperatures, with the reverse at solar noon. It is generally thought that Hg(II) exists as a dissolved salt on the quasi-liquid surface of the snow crystals. And any increase in temperature expanded this quasi-liquid layer. The sunlight photoreduces this to GEM in the upper 5cm of the snow surface, with the two requirements being sunlight and liquid water (or a snow crystal surface with a quasi-liquid layer).

In Barrow in 2003 we used polycarbonate chambers on the snow surface with and without solar shielding and got mixed results, as the GEM emissions were much greater when the chambers were placed in the sunlight - but at the same time the temperatures in the chambers went up dramatically when in the sunlight. To attempt to discern the difference between temperature and sunlight we bought surface snow indoors under chambers where we had heating but no sunlight. The result was GEM emissions occurred with increasing temperature. It was not nearly as great as sunlight+temperature increase in GEM emissions, but there was a significant temperature correlation to GEM emissions in theabsence of sunlight. Our results were present a conferences, but were not published.