

Interactive comment on “High levels of reactive gaseous mercury observed at a high elevation research laboratory in the Rocky Mountains” by X. Faïn et al.

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We thank the anonymous referee for his/her attention and thoughtful comments which we addressed in our revised manuscript and which certainly improved our paper. The reviewer comments are answered in details below.

1. The abstract/conclusion does say why these observations are different from the other high altitude stations for enhanced RGM concentrations. In 1 sentence, add in why these observations are different from others reported.

Authors' Reply (AR). To our knowledge, there is only one published paper describing high altitude observations of atmospheric mercury speciation at Mt Bachelor

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(Swartzendruber, et al., 2006). Thus, the comparison between our observations and previous studies is limited. At Mt Bachelor RGM enhancement were limited to relatively short nighttime spikes only. We corrected the abstract where we mention now that RGM enhancements observed at Storm Peak Laboratory lasted for long time periods of 2 to 6 days and showed both enriched level during daytime and nighttime when other tracers (e.g., aerosols) showed different contribution of boundary layer air and free tropospheric air. Thus, we clearly make the point that our observation are different that the ones reported at Mt Bachelor.

2. No clear picture of the major oxidant that transforms GEM is given yet it is concluded that the high RGM levels are a result of oxidation of tropospheric GEM. Please address

AR. As mentioned in our answer to the first review, the challenge in discussing our results are a general absence of correlation to observed chemical tracers which make explanations of RGM production pathways somewhat speculative. However, we believe that we show key and interesting evidence for RGM levels in the troposphere. We present possible explanations for these patterns, and point out where our explanations are hypothetical. Nobody currently really knows that drives RGM production in the troposphere, and that's why we feel communicating these important experimental observations will be of great value to modelers and atmospheric chemists.

3. Introduction a. Maybe add in what the quartz filter cuts off in terms of size of the particles and that not all PHg is trapped.

AR. 0.1 μm filters were used to collect HgP in the 1135 Tekran unit. Section 2.2 was corrected to mention it.

b. At times in Polar Regions GEM is not 95% of the total atmospheric mercury. Maybe include this comment into the text.

AR. We understand that GEM depletion in the lower troposphere may occur under specific condition in Polar Areas, Marine Boundary Layer, or salt-rich water bodies (e.g.,

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the Dead Sea). However, and we prefer not directly focus our introduction on these situations. Note that we used “generally” when mentioning that GEM could represent over 95% of the total atmospheric mercury in the lower atmosphere.

c. Identify which global chemical models show divalent Hg species can dominate GEM in the upper troposphere.

AR. Global chemical models are Geos-CHEM model (Selin and Jacob, 2008) and CMAQ model (Sillman, et al., 2007). The manuscript was corrected.

d. The point about “in situ” oxidation needs to be really clarified. My understanding of in situ is that it means “in the place” and thus when one refers to in situ reactions happening it means that they are occurring where the measurements are being collected. That is not the case in this paper and you are referring to the reactions occurring elsewhere and being transported to the site. Thus, this is not in situ. Please clarify in the text what you mean by in situ as you refer to this throughout the paper and it’s confusing to the reader.

AR. We agree with the reviewer, and we corrected our manuscript to removed sentences where “in situ” was used.

e. Perhaps you should mention that shortcomings of this type of measurements in the paper somewhere. I know that you say that RGM is operationally defined as what we trap on KCl denuders but maybe you should go a bit further to say (at some point) that we have no standards for RGM and thus we cannot expect that $RGM+PHg = GEM$ because the instruments are not calibrated necessarily to give us that information accurately.

AR. We corrected section 2.2, notably to mention that no calibration procedures are currently available for the 1130 and 1135 speciation units.

4. Mercury measurements: a. Describe the inlet system. The reader may not know that the 1130/35 is a front end to the 2537 and that you are not collecting the species

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separately.

AR. The manuscript was corrected to better describe the integration of the 1130 and 1135 units with the 2537A analyzer.

b. Why is the flow of the 2537A set to 0.8 lpm as opposed to 1 as usually used? Is this because the pump can't pull 1 lpm? If so, please mention why this differs than what is commonly used. Because there are no calibration systems then all differences should be addressed.

AR. The internal pump of the 2537A analyzer did not allow for sampling flow larger than 0.8 lpm. The manuscript was corrected to mention this.

c. Did you use soda lime?

AR. Yes. The manuscript was corrected.

5. Meteorological and chemical measurements: a. Why did you average the data on 2 hours and not 1 hour? You are only sampling Hg for 1 hour and then analysing for 1 hour. . .would it not make more sense to have the met data match the sampling period and not the sampling and analysis period?

AR. We agree with the reviewer that it would make more sense to average the met data as well as the chemical data over 1-hour period, to match with the Hg sampling period. We have re-processed all met and chemical data, and we provide new figures 3 and 7. However, the 1-hour averaged data only slightly differ from the 2-hour averaged data (previously reported), and this improvement of our paper does not affect our discussion and conclusions.

6. Results and Discussion: a. Page 8 – Figure 2 does not show ozone as well as CO.

AR. Ozone and CO diel patterns are now reported on Figure 2.

b. Page 8 – if the number of aerosols increased can you comment on why the PHg concentrations did not?

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AR. Such comment is difficult to address as we did not characterize the chemical properties of aerosols during our study.

c. Figure 2 shows the RGM peaking in the afternoon – is that peak statistically significant?

AR. Yes, the RGM peak is significant, because it is larger than the standard errors (also reported on Fig. 2). This peak is now discussed in more details in section 3.2.

d. Figure 3 – Is there any relationship between PHg and aerosols and PHg and CO?

AR. We did not find any relationship between PHg and aerosol during our entire study (including when data were sorted for high RGM events). A unique significant correlation was found between PHg and carbon monoxide during event #7 ($r = 0.49$). However, event #7 is the only event where RGM did not correlate with GEM. We did not learn from this lack of relationship between PHg and aerosol and carbon monoxide respectively, thus we did not discuss this point in our manuscript

e. Page 9 – Discussion here about the in situ measurements imply that the reactions are occurring at the Storm Peak Laboratory. Are your observations from in situ reactions or transported from other areas?

AR. The significant inverse correlation observed between RGM and GEM during our study yields to an average slope of -0.10. We actually attributed such lack of mass closure between RGM and GEM to deposition and scavenging of reactive mercury prior to reaching the Storm Peak Laboratory. As discussed in the answer to comment 3.b., we corrected our manuscript to not use anymore the term “in situ”.

f. Page 11 – because there is no correlation between RGM and ozone then this is indicative that it is not the same mechanism as what occurs in Polar Regions because that correlation is well defined.

AR. In polar areas, during the Atmospheric Mercury Depletion Events, fast GEM oxidation likely involves halogens compounds (e.g., Br radicals). We are not fully clear on

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origins and reaction pathways of observed tropospheric RGM at Storm Peak Laboratory. Although halogen compounds may be involved, RGM production may occur far from the laboratory (as suggested by an obvious lack of mass closure between RGM and GEM) and potential correlation between RGM and ozone may be lost.

g. Page 11 – GEM depletions were not observed by Banic et al above 8km. . .I think.

AR. The reviewer is right that Banic et al. (2003) did not observe GEM depletion in the upper troposphere/lower stratosphere. There is still a lack of GEM observation at high altitude, and not all study report GEM depletions. So we corrected our manuscript to use more caution in our phrasing: “GEM oxidation [. . .] may lead to high RGM levels in the dry, upper troposphere and lower stratosphere.”

h. Page 11 – you suggest here that the GEOS-Chem model shows that RGM/PHg can dominate GEM but this is not shown at all in the data. The relationship between this comment and the data is unclear.

AR. The reviewer is right that the GEOS-Chem model does not shows that RGM/PHg dominating GEM in the upper troposphere and lower stratosphere (Selin and Jacob, 2008). We corrected the manuscript.

i. Figure 5 – the plots are really small and challenging to read

AR. We provided a high quality figure 5. We agree that figure 5 was difficult to read on the printed version but the reader should be able to get all details with the final, electronic version.

j. Page 12 - the BrO measurements measured by satellite are the whole column and do not show enrichment in the troposphere? I do not believe that they can distinguish.

AR. We agree with the reviewer, and thus we referred in our manuscript to a modeling study that addresses the altitudinal gradient of atmospheric BrO above the North Pacific (Yang, et al., 2005).

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k. Page 12 – most data show that BrO oxidation of GEM occurs near the surface

AR. We considerably shortened our discussion about possible reaction pathways, and we do not refer anymore to BrO oxidation of GEM in our discussion. However, a recent modeling study from Seigneur and Lohman (2008) investigated the effect of bromine chemistry on the mercury global cycle using a three-dimensional chemical transport model, and suggested that BrO oxidation of GEM not only occur near the surface.

l. Page 12 - you mention that most of the enhanced RGM is deposited prior to arrival at the Storm Peak Laboratory – have you done a quick calculation of the deposition velocity of RGM (specifically HgCl₂) and the distance the air mass has travelled to see if the concentration measured at the site is logical? That would be a good exercise.

AR. In our view, estimation of such rates would be problematic since we are not fully clear on origins, reaction pathways, chemistry, nor sinks of observed RGM in the troposphere.

m. Page 13 – you discuss the possibility of heterogeneous oxidation of GEM involving water droplets or snow crystals. Would you not see an increase in the PHg concentrations if there were some aerosols involved in this reaction?

AR. Our discussion about heterogeneous oxidation of GEM was speculative, and we removed it from the manuscript.

Language: 1. The “Rockies” is slang for the Rocky Mountains. One does not say Rockies Mountains

AR. The manuscript was corrected.

2. Page 2 – first sentence has mercury too many times and is a run on sentence.

AR. The sentence was rephrased.

3. Page 3 – sentence that starts “At a high elevation” must be rephrased.

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AR. The sentence was rephrased.

4. Page 3 - Dearth should be changed to “lack of”. Keep language simple.

AR. The manuscript was corrected.

5. Page 8 – sentence that starts with “At Storm Peak Laboratory” must be rephrased.

AR. The sentence was rephrased.

Reference:

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