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Atmospheric Chemistry and Physics Discussions

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.

X. Faïn et al.

xavier.fain@dri.edu

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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.

General:

This manuscript presents an interesting data set for speciated atmospheric mercury at a site in the Rocky Mountains. The authors state that previous research at the site suggests little influence from boundary layer air. I think the authors need to dig into the data deeper and demonstrate (or not) this point. I think, as stated in my specific

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comments, that there is reason to believe that the high RGM may be related to boundary layer air reaching up to the site. I think one way to resolve this would be to collect canister samples for analysis of biogenic hydrocarbons. This would clearly indicate the presence of boundary layer or free tropospheric air at the site. I am mystified as to how these elevated RGM events can persist for up to nearly one week in time. However, the scale on Figure 1 does not allow a detailed look as to the timing of the see-sawed shape of the RGM during the events. What does the time series of ozone and CO look like? This could offer some clues as to what is going on in this data set. The authors need to take a very careful look at the data, and sort it out instead of just plotting all the data together. Separation of the peaks and valley data might yield answers to what is driving the trends at the sampling site. What I am thinking here is what the authors labeled as individual events, may actually be a series of days where boundary layer air reaches up to the site causing multiple sharp peaks in RGM (see below). These aspects of the data set should be explored to try and gain a better understanding of the processes influencing the site.

Authors' Reply (AR). We considerably modified the manuscript to address the reviewer's concerns, and to demonstrate that high RGM events were not systematically related to pollution from boundary layer, although some contribution may exist. If high RGM levels were systematically due to anthropogenic pollution, we should have observed simultaneous increases in RGM and GEM, similar to such patterns reported from rural sites affected by close-by urban pollution (e.g., Yatavelli, et al., 2006). However, we reorganized our manuscript and included a new figure and a new section 3.2. Are RGM enhancements related to anthropogenic pollution?". In this section, we now discuss in details one specific event (new figure showing a specific enhancement event) which indicates both influences of boundary layer pollution and free tropospheric air. Including this new figure also should address the reviewer's concern about the scale of Figure 1. In our corrected manuscript, we now report and carefully discuss diel patterns for all available parameters (RGM, GEM, ozone, aerosols, carbon monoxide, water vapor mixing ratio, temperature, and relative humidity).

ACPD

9, C4921–C4931, 2009

There are papers documenting the extremely high levels of Hg(0) and RGM in the southwest that are related to mining operations (Gustin group papers). The mining operations could add some CO but little ozone. This elevated RGM might be carried in very dry air from the arid mining areas. Terrain-forced flows could potentially transport these emissions to the sampling site. I think this source must be considered. Again, the biogenic hydrocarbons might be key indicators in this analysis.

AR. Lyman and Gustin (2008) investigated GEM, RGM and HgP at two Mercury Deposition Network sites in Northern-east Nevada (sites NV02 and NV99). Potential sources of mercury to the atmosphere (e.g., historical mercury mines and enriched substrates) exist closely to these MDN sites. However, Lyman and Gustin (2008) do not report extremely high level of Hg(0) and RGM. Although Hg(0) levels may be enhanced during summer when warm conditions with frequent thunderstorms favored emissions from enriched substrates, RGM concentrations are within ranges reported for other rural sites as discussed in section 3.1 of our manuscript (i.e., RGM : 13$\pm$18 and 13$\pm$12 pg m-3, HgP: 9$\pm$7 and 7$\pm$8 pg m-3). So we do not consider that high RGM could be carried from arid mining area located in Nevada up to Strom Peak Laboratory, although we agree we may have influence of boundary layer air (as discussed before).

The word “height” is used in the text repeatedly, sometimes multiple times in one sentence. It would seem better to use “altitude” since your analysis concerns the middle and upper troposphere.

AR. We corrected the manuscript and use altitude instead, and made some text edits to avoid repetitions.

The times reported in this manuscript appear that they are local (not UTC), and as such this should be stated explicitly.

AR. The times reported in the manuscript are local (i.e., Mountain Time: UTC-7). The manuscript was corrected (e.g., see caption of Fig. 2).

ACPD

9, C4921–C4931, 2009

From p. 16651 onward, the text contains a lot of speculation, and much of the information might fit better in the Introduction section. The text goes on and on, but does not say much in explanation of the data set of interest. I think more detailed analysis and a re-working of the last few sections of the manuscript would improve it greatly. This is an interesting data set, but the authors have not conducted an in-depth analysis of it. I believe that there is much more to be learned from the data than the hand-waving explanations offered in the current version. I encourage the authors to do this.

AR. To address the reviewer's concern, we considerably shorten the paragraph describing potential processes involved in atmospheric RGM production and moved it to the introduction, removed all speculations related to heterogeneous processes form the manuscript, and moved some sections reporting previous results to the Introduction as suggested by the reviewer. However, it is important to note that lot of uncertainties remain about the mechanisms of RGM formation in the free troposphere - this applies to our study but also to all other studies since it is currently unclear what the main oxidants are for RGM production in the troposphere. A lack of correlation to any of our chemical tracers (ozone, aerosols, CO) does not help solving this issue. We strongly feel that our analysis is adequate given the data we have and the improvement in analysis we made in the new submission, and we mention possible mechanisms to discuss our observed patterns. More importantly, however, we feel that our study provides important evidence that high RGM are not limited to the very upper troposphere and that there is a strong link between RH and troposphere RGM, and we have put a focus on these important patterns. Notably, we expanded Figure 7 which now shows relationships between RGM and meteorological parameters, and in addition segregate data between nighttime and daytime.

Specific:

Abstract – The authors have used both CO and carbon monoxide in this section. Also, ozone is written out throughout the text, but the chemical symbol is used for CO and mercury. There should be consistency in the usage of these terms.

ACPD

9, C4921–C4931, 2009

AR. The abstract was corrected.

p. 15643, lines 1-4 – nobody really knows, in my opinion, if Hg-particulate is divalent or not.

AR. Particulate Hg is defined as the mercury content of atmospheric particles collected on quartz fiber filters, and is commonly considered as divalent mercury, although the forms of Particulate Hg are still uncertain (Landis, et al., 2002).

p. 15643, last few lines - In fact, there are two papers that discuss Hg-particulate measurements from aircraft.

Murphy, D. M., D. S. Thomson, and M. J. Mahoney (1998), In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, Science, 282, 1664– 1669.

Murphy, D. M., P. K. Hudson, D. S. Thomson, P. J. Sheridan, and J. C. Wilson (2006), Observations of mercury-containing aerosols, Environ. Sci. Technol., 40, 3163–3167. The PALMS instrument used by Murphy is an in situ measurement, so the text here and previously requires some re-wording.

AR. We already referred to Murphy et al. (2006) in the paragraph pointed out by the reviewer. To be more exact, we corrected our manuscript and mentioned that only "direct measurements of RGM" are not available.

p.15646, first sentence, last paragraph – did you re-calibrate the instrument every 26 hours, or just verify the overall calibration?

AR. The instrument was re-calibrated every 26 hours. The manuscript was corrected to better explain this procedure.

p. 15666, Figure 1 – It would be better if the relative humidity was converted to specific humidity. I believe you have all the meteorological data to do this. This would provide a real indication if the air with enhanced RGM consistently had the same characteristics

ACPD

9, C4921–C4931, 2009

and potential altitudinal source.

AR. Water vapor mixing ratios were originally reported in our initial manuscript, and they are very similar to specific humidity. Thus we still report mixing ratios in our corrected manuscript. We report on Figure 7 correlation plots of RGM and mixing ratios for the entire study and we present on Table 1 correlations between RGM and mixing ratios for all individual events. These correlations provide evidence that the free troposphere is a source of RGM at Strom Peak Laboratory. However, the free troposphere is likely not the unique source, and we also want to specifically highlight the strong link to relative humidity and troposphere RGM in our manuscript. Relative humidity was the dominant factor affecting RGM levels with high RGM levels always present whenever relative humidity was below 40 to 50%, this is an important result and is discussed in detail in this revised manuscript.

p. 15667, Figure 2 – I would advise that either symbols or colors be added to make it easier for the reader to distinguish between the variables plotted in this figure. The afternoon peak in aerosols suggests boundary layer air is reaching the site – 3000 cm-3 is a typical boundary layer number density, but only in pollution would it reach this high in the free troposphere. The close tracking of aerosols, RGM, and temperature suggest to me that this is indeed caused by boundary layer air reaching up to the sampling location during the day. Again, specific humidity would be the preferred over relative humidity here.

AR. Our corrected manuscript has now an updated Figure 2 with more parameters and clear color codes. Figure 2 now report diel patterns for RGM, GEM, ozone, aerosols, carbon monoxide, water vapor mixing ratio, temperature, and relative humidity. As mentioned above, boundary layer air masses may contribute to the high RGM levels observed at Storm Peak Laboratory, and we discuss this in detail in section 3.2 based on our Figure 2. However, boundary layer air is likely not the only source of RGM at the laboratory, as illustrated by on description of Event #5 (text on section 3.2, and new figure showing high temporal resolution data for RGM, GEM, ozone and carbon

ACPD

9, C4921–C4931, 2009

monoxide during this specific event).

p. 15668, Figure 3 – I'm a bit confused about ozone. In my initial screening of this paper ozone mixing ratios spanned up to about 250 ppbv. In this version it tops out at about 60 ppbv. There was no mention of this in the text. What's going on here? In my earlier interpretation I thought that there might have been an issue with the CO calibration. Now the ozone values look more like clean boundary layer mixing ratios. They seem low for free tropospheric air. In this version the ozone seems too low for the moderately high CO. The CO seems too high for free tropospheric air masses.

AR. Before publication online on ACPD, we had to provide a corrected manuscript and address comments from two reviewers. Notably, an important correction made during this process referred to the ozone data (Figure 3). Our previous figure showed erroneously high ozone levels due to a plotting error, and we were very grateful that reviewer #1 caught this error. We apologized for this oversight and have corrected figure 3 and text to correct this error. This was mentioned in our detailed response to the initial review process but unfortunately not communicated with the reviewer.

I would sort the data with elevated RGM and plot it versus ozone. I would do the same with CO. A little further analysis is warranted here in my opinion. There is obviously no correlation with aerosols, so I would omit this panel and just say so in the text. I would also plot elevated RGM versus specific humidity.

AR. We sorted the data with elevated RGM (i.e., data collected during the high RGM events) and plotted them versus ozone and CO. However, no relationship between RGM and ozone nor CO were observed for individual events, as reported in the first sentence of the section 3.2.

p. 15653, second paragraph – Why would you expect to find a correlation between RGM and ozone? This doesn't make any sense to me – omit?

AR. There are only two others high altitude locations where atmospheric mercury spe-

ACPD

9, C4921–C4931, 2009

ciation has been investigated to our knowledge: Mt Bachelor (Swartzendruber, et al., 2006) and Mt Lulin (Sheu, et al., 2009). At both Mt Bachelor and Mt Lulin, inverse correlation between RGM and ozone were observed. RGM would peak at night simultaneously to decrease in ozone levels, as a consequence of the presence of upper free tropospheric air masses. We did not observe such relationship between RGM and ozone atmospheric RGM at Storm Peak Laboratory, and we thus we concluded that RGM levels were mostly unrelated to the diurnal changes in air masses.

p. 15651, Section 3.2 – I honestly don't seem the point of the discussion in this section. In general, there has not been budget closure found in studies of Hg(0), RGM, and Hgparticulate. This area of mercury research needs significant work, and much of the text here seems superfluous.

AR. At Mt Bachelor, a slope near unity (i.e., -0.89) between RGM and GEM was observed during nighttime RGM enhancements, indicating a near mass balance closure between RGM and GEM (Swartzendruber, et al., 2006). It seems important to compare our different observations to this spectacular result.

p. 15652, Figure 5 – Just because these 10 day trajectories show the general flow was from the over the North Pacific, doesn't rule out very local terrain-forced flow in the mountains. This would never be picked up by the data used in the trajectory calculations.

AR. We agree with the reviewer that backtrajectories can not be used to address local transport of air masses, and consequently potential influence of boundary layer air at the Storm Peak Laboratory. Thus, we used other tracers to investigate local terrain-forced flow, as now discussed in details in section 3.2 of our manuscript.

p. 15652, Section 3.3 – Much of the information in this section is more suited for the Introduction as its general information rather than directly related to the data reported here.

ACPD

9, C4921–C4931, 2009

AR. We agree with the reviewer, and moved much of the general information of section 3.3 to the introduction. We shortened the description of chemical pathways for GEM oxidation.

p. 15654 – As I suggested in my initial screening of this manuscript, I think that the authors should look at the PV over the North Pacific in the vicinity of the trajectories. This will tell if stratospheric air possible influenced air masses advected to the sampling location. The authors need to explore all possible explanations for their data set.

AR. Since the ozone level did not exceed 65 ppb, there is no indication of stratospheric influence and thus we do not feel this analysis is needed. Furthermore, previous studies of stratospheric intrusions (Parrish, et al., 1998; Langford, et al., 2009) showed abrupt changes in ozone and high concentrations in Colorado than were seen in this study.

p. 15655, paragraph 2 – I doubt that halogens released from sea salt have an influence on air masses in the middle and upper troposphere (based on your trajectories). This discussion seems highly speculative. In the middle of the North Pacific boundary layer, the air masses are in general quite clean, indicating little heterogeneous chemistry and subsequent halogen release.

AR. We also shortened this discussion, because it is admittedly speculative, and we now make clear that it is a hypothesis that needs further testing. However, we feel that the backtrajectories indicate a possible link to Pacific air masses, in agreement with modeling studies. There are evidences that strong surface winds cause high sea salt production over the North Pacific during springtime with inorganic bromine species estimated around 8 pptv (e.g., Yang, et al., 2005). Consequently, heterogeneous chemistry leading to RGM production may occur. However, we agree that direct onboard measurements would be required to clearly address this comment. Yang et al. (2005) used a 3D tropospheric chemical transport model to investigate tropospheric bromine chemistry. Interestingly, these authors show that at mid-northern latitudes over the Pacific

ACPD

9, C4921–C4931, 2009

Ocean, similar levels of BrO can be expected from the surface to a 600 hPa altitude. Our back trajectories reports influence of air masses coming from different elevation with a large fraction between 1000 and 600 hPa above the North Pacific.

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ACPD

9, C4921–C4931, 2009

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