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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Two new sources of reactive gaseous mercury in the free troposphere" *by* H. Timonen et al.

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We want to thank reviewer #1 for taking time to thoroughly read the manuscript and for your positive and constructive comments. We feel that these comments have helped us improve the quality of the manuscript.

Anonymous Reviewer #1

The authors present an analysis of long range transport events: 3 events with anthropogenic plumes and 4 events with transport of clean air originating from Pacific marine boundary layer. They found enhanced RGM concentrations in the anthropogenic plumes (type 2 events) and claim that they originate from in-situ formation during the transport. Very high RGM concentrations in clean air masses originating from Pacific

marine boundary layer (MBL, type 3 events) are attributed to chemistry within BL and possible evaporation of reactive mercury from particles during the long range transport to Mt. Bachelor.

Reviewer: The paper is well organized and lucidly written. But the authors tend to sweeping statements which are not borne by their data in several instances detailed below. I believe that they have a good case for the type 3 events (transport from MBL) but the presentation of the type 2 events would perhaps become more convincing if the contradictions in the data were addressed.

Reply: Thank you for the positive comments. We have done our best to remove any broad generalities in the manuscript. For specific changes in other aspects see below.

Reviewer: Page 29205, line 18: "Oxidation of GEM in the stratosphere (: : :) is the only known source of RGM above BL." This statement would imply that reactions producing RGM in the stratosphere do not occur in the troposphere. Obviously this cannot be true since all the suspected oxidants (O3, OH, Br, Cl, etc) also exist in the troposphere above the BL. Please reword. Dtto page 29208, line 17.

Reply: We agree that the statement about sources of RGM is incorrect. Oxidation likely occurs in the BL and troposphere, as well as in the stratosphere. What we meant to say is that oxidation of GEM in the troposphere is not well understood. The sentence was reformulated to be:" Oxidation of GEM in the FT is not well understood. Previous studies have shown that oxidation of GEM in the stratosphere (coupled with stratosphere to troposphere transport) is one source of RGM above the BL (Murphy et al., 2006; Swartzendruber et al., 2006; Lyman and Jaffe, 2011). However, based on previous studies and calculations this source accounts for only a small fraction of tropospheric RGM (Lyman and Jaffe, 2011)."

Reviewer: Page 29209, line 21: "We present three clear ALRT events (Fig. 2, Table 1).." but in Fig. 2 only one event is shown. Similarly for type 3 events on page 29211, line 5.

Reply: You are correct. The text is rewritten to say for type 2 : “Here we present as an example one clear ALRT event (Fig. 2) with total Hg (THg = GEM + RGM + PBM) and RGM concentrations substantially elevated above typical background FT levels. Atmospheric concentrations of Hg species and trace gases, aerosol scattering values, and correlations between main components are shown for each event in Table 1.” And for type 3: “Here we present as an example one clear MBL event (Fig. 7). During MBL events a simultaneous increase in RGM and decrease in CO, aerosol scattering, and O3 was observed (table 1).”

Reviewer: Page 29209, last paragraph and Fig.4: Based on the combination of data from 3 events in Fig.4 the authors claim here that the overall THg/CO slope is consistent with Asian plumes. However, when looking at individual events this statement appears too sweeping as e.g. the slope for the event in April 2008 is probably only half of the “on average” slope. What do the authors mean with “on average”: average of three slopes or a slope of all points in Fig.4? The latter is of course no average slope whatsoever.

Reply: You are correct, the term average slope is wrong. Due to there being a small number of data points during each event, we calculated one slope for all points. We have changed “on average slope” to “composite slope” (i.e., the slope calculated for all measurements during the three ALRT episodes) and we included values for the slopes we calculated for each individual episode. The THg/CO slopes for individual events (values between 0.0051 and 0.0081) are close to the composite slope and also typical for ALRT. The manuscript text was reformulated to say: “In addition, the THg/CO correlation slopes (with values between 0.0051 and 0.0081 ng $m-3$ $ppbv-1$; Fig. 4) were consistent with the ratios measured previously in Asian plumes (Jaffe et al., 2005; Weiss-Penzias et al., 2007). The THg/CO correlation slopes measured for North American pollution are typically significantly smaller than for Asian LRT. Weiss-Penzias et al., (2007) reported an average THg/CO slope of 0.0011 ng $m-3$ $ppbv-1$ for North American pollution.”

Reviewer: Page 29210, lines 8-9: Does the negative RGM/CO correlation for the April

2008 event really imply a “common origin”? In addition, Table 1 shows also that the correlations RGM vs GEM for May 2006, _sp vs RGM for April 2007, RGM vs CO for April 2008 and May 2006, and _sp vs CO for April 2008 and May 2006, are not significant, i.e. 6 of 12 correlations.

Reply: The value for the RGM/CO correlation during the April 2008 event is misleading and should not be included in the table. Unfortunately, we do not have CO data for the entire period bracketing the April 2008 Asian LRT event. Figure 2 shows a time series of CO, scattering and RGM. During the episode CO and scattering seem to correlate well. However, right after the episode, an increase in CO concentrations was observed. Based on high relative humidity and lack of correlation between scattering and CO, it is likely that this CO enhancement was not part of the Asian LRT episode, but instead originated in boundary layer. When we decrease the time period over which the correlations were calculated, so as to include only the Asian LRT episode, the number of data points for CO is too small, and thus we have not included this correlation for CO to the table. The sentence in question was reformulated to be:” During ALRT events RGM was correlated with the anthropogenic pollution tracers (CO or ïĄşsp and O3; Table 1). Yes, you are right, not all correlations are significant. The largest problem in this case is low time resolution of the RGM measurements (3 hours) and short duration of Asian LRT episodes (typically lasting only 12 to 48 hours), which means the size of datasets for each individual event is small. Also, in some cases, like April 2008, some CO data are missing due to instrument failure, making the correlations worse. However, we feel that the correlations are only one part of the evidences. Based on trajectories, low relative humidity and THg/CO –ratios during episodes, we know that these air masses originate from Asia. In addition, during these episodes, as the amount of anthropogenic pollution increases (CO and σsp), we see a clear increase in RGM and a simultaneous decrease in GEM concentrations, further pointing out that they RGM, CO, and ïĄşsp are associated with same air masses. In addition, we show that a correlation between at least one of the anthropogenic tracers and RGM is observed as well as anti-correlation between RGM and GEM.

Reviewer: Page 29213, line 18-19: Holmes et al. (2010) makes a good case for Br chemistry but conclude that the comparison of model data with measurements is inconclusive, i.e. does not preclude the possibility of O3/OH chemistry. This should be mentioned also at the end of the chapter 3.4.1.

Reply: We agree with the reviewer that we placed too much emphasis on Br· chemistry as being the dominant pathway for atmospheric Hg0 oxidation and that we did not properly summarize existing uncertainties in atmospheric Hg0 oxidation mechanisms or the potential significance of oxidants other than Br·, such as OH and O3. Accordingly, we have made major revisions to Chapter 3.4, "Oxidation mechanisms", to provide a better overview of uncertainties associated with atmospheric Hg0 oxidation. We feel our revised discussion provides a better balance of findings from previous work and better reflects the fact that oxidants other than Br· may be important.

Reviewer: Page 29213, paragraph starting at line 20: See the above comment about page 29210.

Reply: During ALRT events we have shown that the air masses originate from Asia (trajectories, THg/CO –ratio, high CO and PM concentrations). We also observe a simultaneous increase in RGM and decrease in GEM. Due to the low time resolution in the RGM measurements, and some missing data (April 2008 CO), unfortunately all the correlations are not as good as we would hope them to be. The sentence in question was reformulated to be: "During the ALRT events (type 2) the occurrence of simultaneous increases in RGM and tracers of anthropogenic pollution (CO or σsp) suggests that the oxidant responsible for RGM production might also be associated with anthropogenic pollution, although the mechanisms are unclear.

Reviewer: Page 29214, 1st paragraph: The authors discuss only the O3 and Br mechanisms, neglecting the possibility of OH mechanism. Fig. 3 in Holmes et al. (2010) shows high oxidation rates by O3/OH chemistry in latitudinal band between 30oS and 30oN, i.e. in region where most of the backward trajectories in Fig. 6 of this paper

originate.

Reply: The reviewer makes a very good point. We had indeed neglected the possibility that OH is an important oxidant during the MBL events. We now recognize the potential significance of the overlap between the trajectories we computed for the MBL events and the region where, on the basis of the results of Holmes et al. (2010), O3/OH-initiated Hg0 oxidation is expected to be most significant. Accordingly, we made substantial changes to our discussion in the last paragraph of Chapter 3.4. Our discussion now emphasizes the points made by the reviewer.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 29203, 2012.