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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites" *by* P. Weiss-Penzias et al.

Anonymous Referee #1

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The authors analyse free tropospheric elemental and reactive mercury data from five altitude sites and they compare their seasonal patterns with simulations using GEOS-Chem model. The simulations were made using two different oxidation schemes: Br and O3/OH. One of the aims of the study was to find which of the oxidation schemes can better explain the observed patterns. The authors find that the observed reactive mercury (RM) is mostly negatively correlated with gaseous elemental mercury (GEM) and water vapour mixing ratios (WV) and positively with O3, in qualitative agreement with the Br chemistry model. O3/OH reaction scheme provided GEM and RM concentrations closer to observations than the Br reaction scheme but a clear cut hint for one

of the schemes was not found.

The paper is difficult to read, especially for people who are interested in the cycle of atmospheric mercury but are not familiar with the detailed discussion of oxidation mechanisms. A brief presentation of the two oxidation mechanisms and their deficiencies at the outset would help. From such presentation the authors could derive criteria or relationships which could distinguish between the schemes. The search for such criteria or relationships would then provide a backbone for the paper and make it more readable. I still think that the investigations in the paper are valuable and should be published in a final version when the authors improve the readability and take into consideration the following comments and suggestions:

The accuracy of RM measurements is adequately discussed in Section 2.2. But how comparable are the GEM measurements? The RAMIX intercomparison showed that the GEM measurements might not be always comparable. The accuracy of GEM measurements is also needed for the comparison of model data with observations.

The given observed and modelled concentrations probably refer to m3 at 273.14 K and 1013 hPa? This has to be stated in Sections 2.2 and 2.3.

The WV criterion works probably well for the mountain top stations but I wonder about its efficiency at DRI and NV02 which are both in desert valleys, with DRI being in the vicinity of substantial anthropogenic emissions of all sorts of pollutants. One would thus expect larger differences between the WV filtered and unfiltered GEM and RM concentrations than those shown in Fig. 1. Could the authors demonstrate the WV criterion efficiency using other pollutants such as CO, NOy, or concentrations of condensation nuclei? The somewhat higher average GEM concentration in the unfiltered than in WV filtered data at DRI and NV02 alone does not prove that the WV filtered data are free from local influence.

Lyman and Jaffe (2011) reported RM/GEM slope in FT air being close to -1 opposite to some -0.5 in the lower stratosphere. Here both the modelled and even more

ACPD
14, C7469–C7472, 2014

the observed slopes are in absolute terms much smaller and the observed ones are sometimes even positive. These deviations from the intuitive slope of -1, both of the model and the observations deserve a more extended discussion, not only in Section 3.3.

Page 2274, line 6: "..RM reached 260, 250, and 100 pg m-3 .." is probably correct.

Section 3.3, page 2274, line 20: Are 23 ppb of O3 the seasonal mean or the unusually low concentration? Please clarify. The O3 minimum of 23 ppb coinciding with a GEM minimum and RM maximum at MBO shown in Fig. 4 is a clear sign of transport from marine boundary layer which is not captured by the models. Of course such event has nothing to do with FT and has to be excluded from the FT chemistry discussion. What would be the RM/GEM slope without this event? Another problem with the interpretation of MBO observations is that the observed O3 is substantially lower than the modelled one, opposite to DRI and NV02 sites where they roughly agree. In summary, the discussion in the section 3.3 is not quite correct and has to be fixed.

Section 3.4: In the last paragraph the authors claim that ".. this suggests that OH as an oxidant via the HgBr + OH could be more important in summer at the desert sites. . .". This would, in the first approximation, require higher OH concentrations at desert sites than at MBO. In view of comparable O3 mixing ratios but substantially lower WV concentrations at the desert sites than at MBO this seems unlikely. Another more general problem is that the HgBr + OH reaction appears from nowhere. A reader unfamiliar with the detailed reaction mechanisms would appreciate some beforehand information about this reaction. He would also appreciate some explanation why this reaction was singled out from the dozens of other reactions.

Page 22776, line 1: "Thus we run GEOS-Chem with the OH + O3 kinetics to see where the Br mechanism might be deficient." This would work only if the OH + O3 mechanism were without any deficiencies. Since the OH/O3 mechanism has its own deficiencies (some of them are mentioned in the introduction), the authors check the deficiencies

ACPD
14, C7469–C7472, 2014

of one reaction scheme using another deficient reaction scheme. I think that this is the general problem of this and similar studies. An unbiased wording is needed.

Page 22776, line 28: “on average 2.8 $\pm$ 2.6 than the mean observed RM/GEM ratio” – average and standard deviation should always be accompanied by number of observations. No statistical tests for the significance of differences to zero or collection inefficiency estimate by Gustin et al. (2013) can be made when one of the three numbers (average, standard deviation, number of observations) is missing. This applies even more to the data in Table S1.

In Section 4 the authors conclude that ”this indicates that OH as an oxidant via the HgBr + OH pathway could be more important. . .”. Does this reaction belong to the Br or OH/O3 reaction scheme?

Table S2: The units of RM/GEM, RM/O3, and RM/WV slopes and intercepts should be given.

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