

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 #2

Received and published: 5 October 2014

The authors extracted a subset of high elevation GEM and RM data of free tropospheric origin using water vapor mixing ratios. They then compared these data with GEOS-Chem simulated GEM and RM concentrations that used Br and OH-O₃ oxidation mechanisms. Examining high elevation data is interesting. However, I am afraid that the approach is problematic. Why should these two mechanisms exclude each other? They may very well work together in atmosphere Hg cycling. Several studies suggested that GEM+O₃/OH reactions are not realistic in gas-phase and lab studies suggested that they occurred in solid phase. In the atmosphere these reactions may still occur, but just not necessarily in gas phase; possibly they are in liquid and solid

C7722

phase. However, the O₃/OH oxidation scheme in Selin et al. (2007) did not include heterogeneous chemistry, and those reactions are all gas-phase, which is apparently a seriously deficient mechanism. Holmes et al. (2010) published their work at the time to underscore the potential importance of GEM oxidation by Br; I doubt their intention was that Br was the only oxidant for GEM. In that scheme, my impression is that oxidation by O₃ and OH was not included. Their Br concentrations in the troposphere, excluding the marine boundary layer, were archived monthly averaged data, while in the MBL a value of 1 pptv was uniformly applied for BrO concentrations. The authors showed that RM/GEM ratios using the Br-oxidation scheme fall into two patterns, with a higher slope for the desert sites, and a lower slope for MBO and SPL, the mountain top sites, while the RM/GEM ratios using the OH-O₃-oxidation scheme from all sites generally fall along one line. To understand why the Br-mechanism caused that pattern, one might want to examine the distribution of Br concentrations for the desert sites vs. MBO and SPL, whereas O₃ and OH concentrations are orders of magnitude larger than GEM and hence the heterogeneous distributions of O₃ and OH may not affect RM/GEM ratios more than the inherent deficiency in the chemistry of the oxidation mechanism did. It is not clear to me how the authors arrived at the speculation, from that comparison, that “OH as an oxidant via the HgBr+OH pathway could be more important in the summer at desert sites”. In short, the authors were using one deficient mechanism to prove the other deficient one incapable of doing a good job.

I wouldn't be surprised to see better correlation between modeled and measured RM concentrations using the OH-O₃ oxidation mechanism than that using the Br oxidation mechanism, because at least the chemistry was consistently produced in one model using the former mechanism, whereas the latter was apparently not, considering it used archived Br data from a different model. In another word, the better correlation possibly reflected the dependence of Hg cycling and OH/O₃ chemistry on solar radiation more so than the model's capability of simulating the chemistry that produces RM.

What were the authors suggesting by stating "Modeled RM/GEM using either oxidation

C7723

scheme was on average 2.8 ± 2.6 higher than the mean observed RM/GEM, a factor roughly in line with the estimate of collection inefficiency of the KCl-denuder"? Does this collection inefficiency indicate measured GOM concentrations bias low? If that's the case, how should these data be used for model-measurement comparison?

Also, I am not sure that using the 75th percentile water vapor mixing ratios as criteria to extract the FT data works for the two desert sites, because it is already very dry at those two locations.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 22763, 2014.

C7724