Atmos. Chem. Phys. Discuss., 15, C8679–C8682, 2015
www.atmos-chem-phys-discuss.net/15/C8679/2015/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Origin of oxidized mercury in the summertime free troposphere over the southeastern US" *by* V. Shah et al.

Anonymous Referee #1

Received and published: 29 October 2015

General Comments:

This manuscript describes a very large collection of work that includes airborne measurement and numerical modeling of atmospheric mercury. Having worked on the development of atmospheric mercury modeling myself until a few years ago, I was interested to see if necessary advances had been made in understanding the sources, transport, transformation and deposition of atmospheric mercury.

I was disheartened (but not surprised) to find that the chemical forms of atmospheric Hg(II) have still not been identified, as the authors state in the Introduction. Having not been directly involved in atmospheric mercury research for a while, I do not feel qualified to judge the merits of the newer measurement technologies used here. But I

will say that no modeling assessment should be taken with confidence until we know what materials we are dealing with. The authors note that the emission and deposition of mercury were not investigated as a part of this study. I think it is fair to say that both processes remain uncertain and must be better understood before any confident assessment can be made of the origins of mercury found at any particular location or within any particular region.

Nonetheless, coordinated measurement and modeling campaigns like this one are exactly what is required to direct future research towards the most critical unanswered questions. My only criticism regarding the model sensitivity studies performed here is that bromine was the only reactant considered for adjustment. Oxidation by OH/O3 and BrO was also considered, but only at one set of highly uncertain rates. Even if one was to find a perfect balance of bromine concentration and/or reaction rate that made the simulated mercury concentrations match observations, mercury is in a constant cycle through water, air, soil and vegetation. Any adjustment to the way mercury is added to the cycle or the way it partitions between air and the other media can ruin that balance. I understand why the authors decided not to consider adjustments to sources and deposition. The complexity of the problem becomes overwhelming with all of the possible combinations. But do we really know that bromine is the only important reactant we are uncertain about? I suspect not.

The conclusions of this study rightly point to the need for improved measurement methods. Until we truly know the chemical forms of atmospheric Hg(II), simulation of the entire mercury cycle will remain highly speculative. But at this point we still must speculate and the type of modeling performed here is a necessary part of the overall atmospheric mercury research endeavor.

Regardless of its limitations, this study provides results that are insightful and the conclusions drawn are all within the bounds of reason. I see no reason to withhold publication and would only recommend a few clarifications and that additional possibilities be mentioned where certain conclusions are drawn.

Specific comments:

Section 2.2 – Apparently the UW-DOHGS instrument can use either quartz wool or a cation exchange membrane to intercept Hg(II). Does the choice here affect the detection limit (DL) for Hg(II)? Given the problem with quartz wool releasing Hg(II) in humid conditions, it would seem that the DL would be affected. It is certainly unfortunate that 87% of the 532 observations within the boundary layer were below to DL. This is the part of atmosphere that loses Hg(II) to the surface immediately below and quantification of Hg(II) at various heights within the boundary layer would aid in our understanding of its deposition processes. Also, for the entire NOMADSS campaign, only 35% of the Hg(II) measurements were above the instruments DL. I don't recall such a problem with the DL for the older Tekran instruments. Did the discovery of the Tekran's problem with O3 interference raise the DL for that instrument? I think a lot could have been learned if the Tekran instruments had also been used.

Section 2.3.4 – Regarding application of the GEOS-Chem model in a nested global-to-regional configuration, it is good that the same model was applied for both domains. There was strong evidence from the North American Mercury Model Intercomparison Study (Bullock et al., 2008, 2009) that different treatments of physics and chemistry between the global and regional models led to artifacts at the regional boundaries. Also, in this section you state that two additional sensitivity simulations were performed related to Br concentration and reaction rate. But later in section 5, two more simulations are described where Hg oxidation by OH/O3 and BrO are included. To avoid confusion, it would be good to summarize in one location all of the simulations performed.

Section 9 – In the conclusions, the sensitivity simulations dealing with Br radical concentration and reaction rate are discussed. However, there is no mention of the tests with OH/O3 and BrO oxidation added. I guess I'm just uncomfortable with the focus on bromine as if it were known to be the only reactant. To put the conclusions in proper context, I think it is necessary to mention that we still don't know what the true forms of atmospheric Hg(II) are, and that additional reactions could prove to be important. As

a model developer, I have probably not done my career any favors by highlighting the inadequacies of the measurements on which we base our modeling. But it sure would be nice to know what we are really trying to simulate.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 26839, 2015.