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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.

H. Timonen et al.

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We want to thank reviewer #2 for constructive criticism. We have clarified our statements and removed any unclear statements.

Anonymous Referee #2

I was a bit confused by this manuscript. Anytime there are the right oxidants in the atmosphere, elemental mercury will be oxidized. I do not think that it is surprising at all that oxidation is occurring in anthropogenic pollution plumes. I always assumed that this would be the case.

Reply: There is quite a controversy over Hg oxidation mechanisms and rate constants. At present there is little observational evidence to indicate what the "right oxidants" are.

Models have used OH, O3 and Br, but the rate constants have large uncertainties. For Br, the atmospheric mixing ratios are very uncertain. While models can be used to speculate on the mechanisms, our manuscript provides direct observations of oxidized Hg, which will ultimately lead to improved understanding of the processes involved.

Reviewer: Apparently, the authors have not seen the recent paper by Dibble et al. (ACP, 2012). They should read it if they have not. It might change their box model calculations.

Reply: We thank the reviewer for bringing to our attention the recent paper by Dibble et al. (2012). We recognize that the results of Dibble et al. (2012), and the related results of Goodsite et al. (2012), which suggest lower stability for the HgBr radical than previously recognized, significantly influences our interpretation of RGM production via Br-initiated Hg0 oxidation. We admit that our box model calculations are highly speculative, until mechanisms can be spelled out by laboratory kinetics studies. Nonetheless, atmospheric observations of oxidized Hg are essential to understand the cycling and evaluate models. We have chosen to remove Chapter 3.4.1 from the paper. At this time, we feel that the discussion on Hg0 chemistry that we added to the main text of Chapter 3.4 is more useful than the box model.

Reviewer: I believe that the title and a few of the statements in the manuscript need to be edited. In particular, the last sentence of the abstract is off-base. To me this certainly did not change my conceptual understanding of the formation and distribution of oxidized mercury in the atmosphere. I have always assumed that it was going on throughout the troposphere; it is just very difficult to observe a slow process with such small mixing ratios.

Reply: The title was changed to be more descriptive: Oxidation of elemental Hg in Anthropogenic and Marine airmasses. The last sentence of the abstract "The identification of these processes changes our conceptual understanding of the formation and distribution of oxidized Hg in the global atmosphere" was deleted as unnecessary. To

repeat our response from above: There is quite a controversy over Hg oxidation mechanisms and rate constants. At present there is little observational evidence to indicate what the “right oxidants” are. Models have used OH, O3 and Br, but the rate constants have large uncertainties. For Br, the atmospheric mixing ratios are very uncertain. While models can be used to speculate on the mechanisms, our manuscript provides direct observations of oxidized Hg, which will ultimately lead to improved understanding of the processes involved.

Reviewer: Another sentence is in the Introduction section, lines 18-20. Again, this seems to be a startling statement. Whoever assumed that oxidation was only occurring in the stratosphere?

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 chapter was reformulated to say: “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: One other comment is that I think the authors should use mixing ratios in parts per quadrillion by volume (ppqv). If you talking trace gases why use mass concentrations?

Reply: For Hg, we have chosen to use the standard ng/standard m3 units. It is simple to convert between these and ppqv. Our reference temperature and pressure (273.15 K, 1.01 mbar) are given in the experimental section. We added a sentence to the manuscript: “The measured Hg concentrations are expressed as mass concentrations ng m^{-3} or pg m^{-3} at standard temperature and pressure (273,15K, 1.01 bar).”

Reviewer: In summary, I think that the authors should change the title to refer to oxidation of elemental mercury in anthropogenically influenced air mass. Then, they should reassess the overall content of the manuscript and focus on oxidation in anthropogenic air masses. In other words, drop the drama and focus on the science.

Reply: We have changed the title as suggested to: “Oxidation of elemental Hg in Anthropogenic and Marine air masses”. We have eliminated broad statements in the manuscript. We note that we have also made significant corrections to the manuscript to make our discussion of RGM sources and Hg0 oxidation more balanced. However, we feel it is important to keep our discussion of the marine events in the manuscript. Previous studies have only described the oxidation of GEM in MBL. We provide observational evidence for GEM oxidation in airmasses that are lofted from the MBL to FT, and subsequently transported in FT. Also, observed RGM concentrations in this study are substantially larger than concentrations previously measured in the MBL.

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