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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 #3 for comments, which helped as to improve the manuscript.

Reviewer #3

This study identified the possible sources of the air masses during high RGM episodes at MBO. Reviewer: I agree with the other two reviewers that the authors should stick to this point and avoid sweeping, unfounded, sometimes false, statements.

Reply: We have made our best effort to remove sweeping statements, and to concentrate on the science. We have also made significant corrections to the manuscript to make our discussion of RGM sources and Hg0 oxidation more balanced.

Reviewer: The title is misleading. Previous studies from these authors' group suggested that the upper troposphere, Asia and MBL could be the source regions of the air masses arriving at MBO. What this paper did was quantify Hg levels in two of those three air mass types, which were not looked into in their previous work. It can be a valid study if the authors come up with a more appropriate title and rewrite the paper focusing on the science. However, not in the least the findings from this study would change "our conceptual understanding of the formation and distribution of oxidized Hg in the global atmosphere".

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. 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.

Reviewer: Oxidation processes are known to take place in anthropogenic plumes and marine airmasses, and GEM oxidation has been observed to occur in marine air masses (e.g., Obrist et al., 2010, Nature Geosci.). Given the right oxidants, why should not GEM oxidation occur in anthropogenic plumes? I think the value of their study is to provide quantitative information of such oxidation processes in the two air mass types.

Reply: The Obrist et al. paper is an important step forward, but I would not call the Dead Sea characteristic of the "normal" marine atmosphere. Our observations are relevant to understanding Hg oxidation in the bulk of the global atmosphere. We note that previous studies have only described the oxidation of GEM in the MBL. We provide observational evidence for GEM oxidation in air masses that are lofted from the MBL to the FT, and subsequently transported in the FT. Also, observed RGM concentrations in this study are substantially larger than concentrations previously observed in the MBL.

Reviewer: An important question is whether and how the potential oxidation mechanisms would be different in the Asian plumes and marine air. Yet the authors' box model

deployed the same Br-initiated reactions and the reaction of HgBr+OH. I suppose the different levels of Br, OH were used to represent different air masses. But can they really serve the purpose? In addition, what does their box model include? Only those four gas-phase reactions, no equilibrium and aqueous phase reactions? Didn't they speculate that surface and heterogeneous reactions might have played major roles in the observed high RGM levels? In my opinion, this kind of exercise cannot really add much at all. One more problem is the reaction rate constants of Hg+Br –> HgBr and HgBr –> Hg + Br used in the box model, which were from Goodsite et al. (2004). The authors should have used the constants from Goodsite et al. (2012, ES&T). By using the updated constants, the lifetime of GEM against oxidation by Br forming HgBr2 would be increased from 35-60 h to 61-257 h.

Reply: We fully agree with the reviewer that understanding the potential differences between oxidation mechanisms in the Asian plumes and marine air masses is important, and we did not adequately address this issue. In our box model we only considered the marine events and therefore only attempted to simulate conditions relevant to the marine air masses. Our goal in applying the box model was to determine if we could reproduce the measured RGM concentrations on the basis of current understanding of gas-phase Hg0 oxidation chemistry. However, as discussed in our responses to Reviewer 1, we acknowledge that we placed too much emphasis on the potential role of gas-phase bromine atom chemistry, and therefore did not provide a balanced discussion of other possible reaction pathways. We do speculate that heterogeneous chemistry might contribute to observed RGM enhancements; however, developing a model that incorporates heterogeneous and aqueous-phase chemistry is beyond the scope of our study. We thank the reviewer for brining to our attention the paper by Goodsite et al. (2012). We recognize that the results of Goodsite et al. (2012), and the related results of Dibble et al. (2012), which suggest lower stability for the HgBr radical than previously considered, significantly influences our interpretation of RGM production via Br-initiated Hg0 oxidation. On the basis of the reviewer's comments we have chosen to remove Chapter 3.4.1 from the manuscript. At this time, we feel that

the discussion on Hg0 chemistry that we added to Chapter 3.4 is more useful than the box model.

References:

Weiss-Penzias, P., Jaffe, D., Swartzendruber, P., Hafner, W., Chand, D. and Prestbo, E.: Quantifying Asian and biomass burning sources of mercury using the Hg/CO ratio in pollution plumes observed at the Mount Bachelor observatory, Atmos. Environ., 41, 4366–4379, 2007.

Dibble, T. S., Zelie, M. J., Mao, H: Thermodynamics of reactions of ClHg and BrHg radicals with atmospherically abundant free radicals, Atmos. Chem. Phys., 12, 10271–10279; doi:10.5194/acp-12-10271-2012, 2012.

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