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Interactive comment on "Effect of sea-salt aerosol on tropospheric bromine chemistry" *by* L. Zhu et al.

Anonymous Referee #2

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In this work, Zhu and co-authors presented tropospheric bromine chemistry simulated using a global chemical transport model (GEOS-Chem), and the results are compared to sea salt bromide enrichment factor measurement compilation, GOME-2 tropospheric BrO column, as well as BrO measurements from recent aircraft campaigns. This paper is very interesting and scientifically sound to merit publication in Atmospheric Chemistry and Physics once the following concerns have been addressed.

The current form of the paper is very compact. However, I also feel that some essential information is missing. My major concerns are as follows:

1. The reactive uptake of HOBr onto bromide-containinng particles is critical, which is very sensitive to acidity. However, in the present form of the manuscript, neither sea salt aerosol acidity nor the titration (by HNO3, H2SO4, SO2, etc) is justified by

observations. This is the case for non-sea-salt aerosols and cloud droplets as well. Without proper justifications of modeled particle acidity and the acidic gases, such as HNO3, H2SO4, SO2, etc, I am not fully convinced that the modeled magnitude of sea salt debromination and bromide enrichment factors presented in the present form are necessarily for the right reason. I will get back to this later.

2. The oceanic emission of acetaldehyde (Millet et al 2010) rapidly removes Br atoms in the remote troposphere and essentially shuts off chain propagation. However, the oceanic fluxes of acetaldehyde and the modeled acetaldehyde distributions in the remote troposphere remain untested, partially due to the known measurement artifacts for acetaldehyde in clean air (please see discussions in Millet et al 2010). This weakens one major conclusion of this work, that ocean emissions of aldehyde (especially acetaldehyde) plays a key role in reconciling the large debromination source with the relatively low BrO observations in the marine boundary layer. How does the modeled acetaldehyde compare to recent observations in the remote atmosphere?

Specific comments:

3. This work does reproduce the mean bromide enrichment factors observed in ten surface sites around the globe, however the seasonality is only examined at one site. Any particular reason that the modeled seasonality is not examined against observations for the rest of the nine sites? Also, as shown in Figure 2, the modeled bromide enrichment factor shows almost the opposite annual trend, which appears to be inconsistent with the modeled alkalinity...? Anyway, this figure certainly deserves more in-depth discussions. And I would suggest adding similar plots for other sites too (depending on data availability of course).

4. The authors claim that two types of sea salt aerosols are emitted in the model: coarse and fine modes. The lifetime of sea salt aerosol depends on size. Is the modeled vertical distributions of fine and coarse sea salt aerosols supported by observations?

5. The author also mentioned that "Bry mobilized from coarse SSA to fine SSA as HBr", yet zero detail is given in the present form of the manuscript. Bry mobilizing from coarse SSA to fine SSA implies different enrichment factors between coarse and fine particles. Is this supported by observations? Come to think of it - is this "enrichment factor" being discussed throughout the paper weighted between coarse and fine particle?

6. The reported HOBr reactive uptake on tropospheric aerosols in the literature varies in magnitude. Roberts et al (2014) brought up a very interesting concern about the reactive uptake of HOBr on bromide-containing particles, that the widely used termolecular kinetic approach is strictly valid for a specific pH range, and the reactive uptake of HOBr on H2SO4-acidified particles may be substantially overestimated in current models. For the first time, Roberts et al (2014) reconciles the different reactive uptake coefficients reported from laboratory experiments. I understand that the evaluation of the new HOBr uptake framework (Roberts et al., 2014) in a global model may well be worth another paper. However, I feel this is not totally beyond the scope of the present work, given the profound impact of HOBr on the tropospheric bromine activation. Therefore I would strongly suggest at least a few sensitivity tests on different pH values for sea salt and non-sea-salt aerosols. This brings me back to my very first comment: What is the pH for fresh and aged sea salt aerosols? How much acidic gases (HNO3, H2SO4) does the model predict and are these predictions supported by observations? How about non-sea-salt aerosols and cloud droplets?

7. Page 7 Line 4-5: It seems to me that the model predicts lower BrO in the free troposphere in the western tropical Pacific, which happens to be a hot spot for deep convection. Liang et al (2014) demonstrated that varying model deep convection strength can introduce a significant change in inorganic Bry scavenging and eventually the bromine product gas injection at the tropopause. How does the model handle convective transport and how may this affect the BrO (and Bry) predictions in this region?

8. Page 7 Line 5: If "oneline aerosol pH" yields better pH, why don't you use it then? This is an issue throughout, that pH is so important yet virtually no detail is given in

the present form of the paper. How much acidic gases does the model predict in the marine boundary layer and the free troposphere? How big of a difference does this "online pH calculation" make and how does this translate into the modeled BrO? To fully justify the findings (which are very interesting) in this work, I strongly suggest that the authors should get to the bottom of this. I am sure the readers will appreciate it, as it makes the paper much stronger.

Technical comments:

9. Page 1 Line 21 and Page 2 Line 2: I myself don't think "deplete" is the proper verb for OH radicals. Bromine chemistry converts HO2 into OH but also destroys O3 which itself is an OH precursor.

10. Page 1 Line 24: define BrO.

11. Page 2 Line 26: I believe Millet et al (2010) only discussed acetaldehyde, not "oxygenated organics".

12. Page 4 Line 1: please define alkalinity and remind the readers how this is derived / calculated.

13. Page 5 Line 9-10: Does Bry also "mobilize" to non-sea-salt aerosols?

14. Page 5 Line 22 and Figure 3: please separate in-cloud processing from multiphase chemistry on sulfate aerosols.

15. Page 6 Line 10-12: Please elaborate how does chlorine chemistry reduce the bias, and by how much.

16. Page 7 Line 2-4: "The CONTRAST flight campaign took more readings over a region (near Guam) with higher SSA emission and load compared with CAST, resulting in higher level of BrO" this seems to be confusing to me. As described in the present form of the manuscript, it looks like CONTRAST and CAST were pretty much at the same time in the same region, i.e. they are sort of like different subsets of the same

dataset. If more reading in one campaign leads to higher or lower values than the other, are you implying sampling bias in either or both?

17. Page 7 Line 7-9: How much HOI and I2 does the model predict in this region? And how much BrO does the model predict without iodine chemistry at this site? This is quite interesting.

18. Figure 1: please add site names onto the map.

19. I would love to see a vertical distribution of the inorganic Bry speciation plot.

References

Roberts, T. J., Jourdain, L., Griffiths, P. T., and Pirre, M.: Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes, Atmos. Chem. Phys., 14, 11185-11199, https://doi.org/10.5194/acp-14-11185-2014, 2014.

Liang, Q., Atlas, E., Blake, D., Dorf, M., Pfeilsticker, K., and Schauffler, S.: Convective transport of very short lived bromocarbons to the stratosphere, Atmos. Chem. Phys., 14, 5781-5792, https://doi.org/10.5194/acp-14-5781-2014, 2014.

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Discussion paper