

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

Sander (Referee)

rolf.sander@mpic.de

Received and published: 4 December 2018

Zhu et al. investigate the effect of sea-salt aerosol on tropospheric bromine chemistry. The study is very interesting and I recommend publication in ACP after considering several changes as described below.

Specific comments

• Abstract: "We show, for the first time, observed levels of SSA debromination can be reproduced in a manner consistent with observed BrO concentrations."

A key argument of your study is that acetaldehyde is "critical in moderating tropo-

C1

spheric BrO levels". It should be noted, however, that this topic has already been studied in 2004 by Toyota et al. (doi 10.5194/ACP-4-1961-2004). They wrote: "Model calculations with the new chemical scheme reveal that the oceanic emissions of acetaldehyde (CH3CHO) and alkenes (especially C3H6) are important factors for regulating reactive halogen chemistry in the MBL by promoting the conversion of Br atoms into HBr..."

The reaction HOBr + S(IV) has also been included in previous halogen studies, e.g., Long et al. (doi 10.5194/ACP-14-3397-2014).

To support your statement about HOBr and acetaldehyde, it would be good to add a table showing the relative importance of all reactions that convert reactive bromine back to HBr in your model.

• Abstract: "Bromine radicals influence global tropospheric chemistry by depleting ozone and OH, and by oxidizing elemental mercury, sulfur species, and volatile organic compounds."

In the main ozone-depleting cycle (Br \rightarrow BrO \rightarrow HOBr \rightarrow Br), the OH radical is produced, not destroyed! If you see lower OH when you switch on Br chemistry in your model, this is more likely due to indirect effects. Maybe there is less OH production because of less ozone?

I don't think that VOCs are affected much by Br. The reactions with most VOCs (e.g. alkanes) are very slow. I agree that alkenes and aldehydes can be important for Br but this doesn't necessarily imply that Br is important for them. Can you tell us what the relative contributions of OH and Br to the oxidation of aldehydes are in your model?

• Page 5, lines 8-9: "Bry mobilized from coarse SSA is transferred to fine SSA as HBr. EF values drop further inland as Bry is remobilized from the fine SSA."

This is very interesting! However, so far you have only presented the overall EF.

Can you calculate the EF for fine and coarse SSA individually? Then you can check if your statement is supported by the model.

- Page 4, lines 2-3: "SSA alkalinity is depleted by uptake of HNO3 and SO2." The alkalinity is not depleted by SO₂. This happens only after it has been oxidized to S(VI).
- Page 6, lines 10-11: "The biases at high latitudes can be reduced by including a detail chlorine chemistry"

At high latitudes, tropospheric ozone depletion events occur which dominate the halogen chemistry in those regions. Unless your model includes a good description of these events, I would not attempt to compare the model results with measurements here.

Technical Comments

- Reactions occuring inside liquid aerosols should be called "multiphase", not "heterogeneous" (see e.g., Ravishankara, doi 10.1126/science.276.5315.1058).
- According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck "Units for use in atmospheric chemistry", Pure & Appl. Chem., 67(8/9), 1377-1406, 1995, https://www.iupac.org/publications/pac/pdf/1995/pdf/6708x1377.pdf) the usage of "ppb" and "ppt" is discouraged for several reasons. Instead, "nmol/mol" and "pmol/mol" should be used for gas-phase mole fractions. I suggest to replace the obsolete units.
- Page 2, line 17 and elsewhere: *"concentrations are typically of the order of 1 ppt"* The physical properties "mixing ratio" and "concentration" are used as if they were identical. This is not the case! (for details, see http://www.rolf-sander.net/

C3

res/vol1kg.pdf) Please check all occurrences of the word "concentration" in the main text and check if it should read "mixing ratio" instead.

• Data availability section: "Data are available upon request"

Obtaining data via personal request can be quite unsatisfactory, especially after a couple of years when it often becomes difficult to contact the authors. I suggest to present the most important data in the supplement to this article. This could include:

- The data files used to create the figures.
- The reaction mechanism (KPP equation file). Did you use Standard.eqn as supplied by GEOS-Chem 12.0.0, or did you modify the mechanism?

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1239, 2018.