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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sensitivity of tropospheric chemical composition to halogen-radical chemistry using a fully coupled size-resolved multiphase chemistry/global climate system – Part 1: Halogen distributions, aerosol composition, and sensitivity of climate-relevant gases" *by* M. S. Long et al.

Anonymous Referee #1

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Review of "Sensitivity of tropospheric chemical composition to halogen-radical chemistry using a fully coupled size-resolved multiphase chemistry/global climate system – Part 1: Halogen distributions, aerosol composition, and sensitivity of climate-relevant gases"

By Long et al.

This paper presents a model study on the sensitivity of tropospheric chemical species to marine aerosol-derived inorganic chlorine and bromine. The simulated levels of some reactive halogen species are compared to selected observations and their associated impact, mainly driven by bromine, upon the oxidizing capacity in the troposphere is assessed. The simulated results presented here overestimate bromine levels by far over most of the global troposphere when compared with observations, and hence the suggested influence on O3, HOx, NOx and DMS is almost certainly unrealistic. The authors need to re-evaluate their computed bromine levels so that these are not a factor 2-6 higher than available observations, as reported here. Therefore, I cannot recommend this paper for publication.

A list of comments follows:

- Simulated bromine concentrations in the lower troposphere:

Table 2 shows a comparison of measured vs modeled total volatile Br. Except in the NE Atlantic the simulations presented here overestimate bromine loadings by a factor that ranges from 2.4 to 6.1 times the reported observations.

Table 3 compared measured and simulated BrO mixing ratios. Given the photochemical nature of the radical, reported BrO measurements would be representative of daytime levels. Overall, the simulations overestimate the measurements. This is particularly certain for the only long timeseries of boundary layer BrO in the tropics, at Cape Verde Islands (Read et al., Nature, 2008), where the observed daytime BrO levels are overestimated by a factor of 2.3.

Figure 5 shows the annual mean of PBL BrO mixing ratios. The annual BrO means range from 1 to 4 pmol mol-1 within the tropics. Assuming BrO remains close to zero at night, the approximate simulated daytime tropical annual BrO average (i.e. not peak daytime values) ranges from 2 to 8 pmol mol-1. If a 1 km boundary layer height is assumed, with no BrO in the free troposphere, this converts into a vertical column of approximately 2 x 1013 molecules cm-2. Satellite-derived tropospheric vertical columns

(i.e PBL and FT) in the tropics report levels below 2 x 1013 molecules cm-2 (Theys et al., ACP, 2011).

Overall, the computed high reactive bromine levels, without including bromocarbons, reported here are not supported by available observations.

- Influence on ozone depletion in the troposphere:

Previous modeling studies using different well-established global halogen models have reported much lower ozone loss percentages due to bromine chemistry. von Glasow et al., ACP (2004) reported 12-18% of tropospheric ozone loss due to bromine chemistry. The global study of Yang et al., JGR (2005) reported 4-6% bromine-driven ozone reduction in the tropical troposphere. Saiz-Lopez et al., ACP (2012), which concerned only with the tropics, reported 6-20% ozone reduction in the tropical troposphere due to combined bromine and iodine chemistry. Recently, Parrella et al., ACP (2012) have reported a global 6.5% global reduction in tropospheric ozone. The simulations in this paper report reductions global tropospheric ozone of 65%, being around 40-60% in the tropics. Furthermore, this is achieved here without including in the model the bromine loading that would arise in the upper troposphere when considering the photochemical breakdown of short-lived bromocarbons.

Figure 9 shows two runs with vertical profiles of mean O3 compared to boundary layer measurements. Although the agreement with observations is good, this may well be not for the right reasons: halogens destroy 20 ppbv of O3 in this simulation. This is an order of magnitude larger O3 destruction (i.e. approx. 2 ppbv) than what was measured at Cape Verde Islands when combining bromine with iodine chemistry (Read et al., Nature, 2008).

In Fig 7, the annual mean of PBL ozone reduction from 40S to 90S ranges from 80 to 100% in the Hal simulation. What are the simulated levels of PBL ozone in this area when including halogens? They must be very close to zero all year long.

- Influence on DMS:

This study reports a reduction of DMS of a factor of 5 when including halogens. Would this agree with DMS observations?. A recent report by Breider et al., GRL (2010) have suggested an annual decrease of 16% in the DMS levels.

In this reviewer′s view, the overestimation of bromine in the model is most likely due to an over efficient halogen-marine aerosol recycling mechanism. This in turn has inevitably led to the abovementioned unrealistic overestimations in the impact of this chemistry on the oxidizing capacity of the troposphere.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 6067, 2013.