

## ***Interactive comment on “What do we learn on bromoform transport and chemistry in deep convection from fine scale modelling?” by V. Marécal et al.***

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### General comments

Referee#1 found the paper poorly written. The revised version has been corrected by a native English speaker. The abstract has been significantly modified for improvements. The Appendix has been shortened for clarity. The main corrections of the paper appear in red in the revised version.

p. 29565: The CATT-BRAMS model is described briefly in the revised version.

p. 29568, l.12: Chlorine gas phase chemistry has an impact on the lifetime of CHBr<sub>3</sub>

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and therefore the production of PGs. The rate constant of the reaction  $\text{Cl} + \text{CHBr}_3 \rightarrow \text{HCl} + \text{CBr}_3$  is approximately 1.5 times larger than the rate constant of the reaction  $\text{OH} + \text{CHBr}_3 \rightarrow \text{H}_2\text{O} + \text{CBr}_3$  in the lower atmosphere. Cl concentrations in the lower atmosphere are between 103 to 106 cm<sup>-3</sup> (Chang et al., 2004; Finlayson-Pitts, 1993) while OH concentrations are higher than 106 cm<sup>-3</sup>. For most cases the degradation of CHBr<sub>3</sub> by chlorine can be therefore neglected. In cases of large concentrations of the Cl radical, it is however comparable to the degradation by OH. Nevertheless, since in both cases the organic bromine product of the reactions is the same (CBr<sub>3</sub>), it is equivalent to take into account the degradation of CHBr<sub>3</sub> by Cl or to increase artificially the concentration of OH. The impact of chlorine gas phase chemistry on bromine atoms on the organic bromine chemistry is now discussed in section 2.2, page 7.

p 29568, l.14: The rate constants given in JPL are not useful for us since they concern sulphate aerosol at low temperature. We now give in section 3.2.2, pages 18-19, the values and the references of the needed rate constants for the reactions in the aqueous phase:  $\text{HOBr} + \text{Cl}^- + \text{H}^+ \rightarrow \text{BrCl}$  and  $\text{HOCl} + \text{Br}^- + \text{H}^+ \rightarrow \text{BrCl}$ . A long discussion and some sensitivity tests have been added in the text on the possible role of chlorine chemistry in the aqueous phase in a new section 3.2.2. pages 18-21. Compared to Fickert et al., we have lower Br<sup>-</sup> (from the VLSL degradation given by the simulation) and Cl<sup>-</sup> (taking measurements in raindrops, Graedel and Keene Global biogeochemical cycles, 1995) concentrations that may lead to different conclusions concerning the production of Br<sub>2</sub> with respect to BrCl. There is an uncertainty on the value of the rate constant of one of the key reactions ( $\text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2\text{Cl}^-$ ). With our Cl<sup>-</sup> and Br<sup>-</sup> concentrations, it is not possible to definitively conclude whether the dominant final product is Br<sub>2</sub> or BrCl. Sensitivity tests were performed with a rate constant corresponding to the production of BrCl. In this case, the impact of the chlorine chemistry in the aqueous phase on the transport of Br<sub>x</sub> to the upper troposphere and TTL is negligible. If Br<sub>2</sub> was to be formed (corresponding to a higher value of the rate constant), this would lead to a more efficient transport of Br<sub>x</sub> to the upper troposphere and TTL.

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p. 29572, l.26: We agree that it would have been better to make a spin-up before beginning the simulation. From the BG simulation we found that the equilibrium in the NO<sub>y</sub> family is rapidly reached (~1 day). A sensitivity test taking into account a spin-up period of 2 days has shown that the errors on OH averaged over the 10-day simulation lead mainly to errors on the mixing ratio of the less soluble organic PGs. This error is evaluated to be less than 5%. We think that it is small enough to justify not re-running the PERT simulations with a spin-up period.

p. 29573, l. 4: The 40 pptv initial value used for bromoform is very large but realistic since it was measured in the Eastern Pacific. It is only representative of locations close to strong bromoform sources. This is now mentioned in the revised version in section 2.3, page 11. We have also added some simulations with a an initial value of 1.6 pptv which corresponds to the mean value from measurements from WMO (2010). Results are given in section 3.2.3, page 21.

p. 29576, l. 10-20: Sunlight on the edges of the convective system leads to the so-called “bromine explosion”, since Br<sub>2</sub> is rapidly photolysed to give Br, BrO then HOBr which can react one more with HBr in the aqueous phase. This leads to a continuous loss of HBr in the cloud droplet and to a continuous production of Brx. This cannot take place in the middle of the cloud because of sunlight attenuation. We also mention in the revised version that less Br<sub>2</sub> is produced in the middle of the cloud because HBr and HOBr are rapidly washed out in this part of the cloud. Both processes (no bromine explosion and less production of Br<sub>2</sub>) lead to a smaller Brx mixing ratio compared with the cloud edge. The ascent velocity in the middle of the cloud is larger than at the edge. The consequence of the small production of Brx in the middle of the cloud is then a relatively low Brx mixing ratio transported at high altitude. We have improved the text to explain better these points in section 3.2.1, page 16.

p. 29577: We agree with your suggestion. Figures 11 are now replaced by figures 13.

p. 29578 l. 9: A new figure (Figure 12b) showing the horizontally averaged mixing

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ratio of HBr at the end of the convective event compared with Br + BrO and HOBr is included in the revised version. HBr mixing ratio is clearly lower than Brx. This is particularly true in the TTL. We explain in the conclusion why we did not take into account heterogeneous reactions on ice in this study. We are mainly interested in the rapid transport from the lower troposphere to the upper troposphere and TTL in the convective event. We also say that this process is likely important several hours after this event, in particular in the TTL.

Minor comments/corrections

All technical corrections have been taken into account.

For the figure labels, we have not changed them yet since the format of the figures in ACP is generally larger than in ACPD. We will check before the final edition of the paper that the labels are readable.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29561, 2011.

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