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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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1 General Comments

The manuscript presents a detailed modelling study of the chemistry of bromine VSLS and its inorganic and organic product gases (PG) in a convective event. The study models in much detail the physico-chemical gas- as well as liquid-phase processes involved in the decomposition of bromoform and the fate of the resulting inorganic and organic PGs. Up-to-date models are used and with few exceptions a representation of all the gas phase as well as heterogeneous processes is included (even where parametrisations are quite uncertain). In order to achieve a realistic simulation of the convective event the model is initialized and triggered employing model as well as experimental

data. Only few published modelling studies on VSLS transport and evolution have gone into similar detail. Most of the published studies have used global CTMs - often with crude process parametrizations - in order to provide total Br_y input from VSLS into the stratosphere. However, the study fails to put the results for the simulated isolated convective event into a global perspective, which admittedly isn't easy to do.

As the major result the authors present the fact that Br_2 production from heterogeneous processes enhances the supply of inorganic product gases to the TTL in the convective event due to the effect that it is not soluble and consequently is not washed out. This is a very interesting process, however, its significance depends critically on parameters that are not well known. Since the potential errors of these parameters are not discussed in detail and no sensitivity study is carried out the significance is not unambiguously shown in the current version of the manuscript. Extension of the study by a sensitivity study to the relevant heterogeneous parameters in question could isolate the ones that are most critical for the process of Br_2 formation and which need to be corroborated and improved by new laboratory studies in order to find better parameterizations for the atmospheric processes. This would make this study much more valuable scientifically.

The discussion goes into quite some detail on the relative horizontal bromine partitioning into $CHBr_3$ and organic and inorganic PGs but does not state clearly how much total bromine is finally introduced into the TTL for the different simulated scenarios in relation to the initialized boundary layer amounts. Also, no adequate intercomparison of the results with those of published studies is attempted. Since this study treats an isolated convective event comparison is not straight forward as stated above. However, it seems to me that the results are in contrast to the results of Aschmann et al., 2011, which seem to find much higher PG input also from mainly convective activity. The isolation of the causes of these discrepancies (if they exist) will be most important in order to advance our understanding also of the global significance of convection for stratospheric bromine input from VSLS.

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In summary the subject of the presented study is of relevance for the understanding of the global ozone budget under changing atmospheric conditions. Therefore it is very well suited for ACP. Scientifically the paper also has a good potential, however the authors should coment and/or improve on the points raised and listed below in detail before final publication. Extension of the study by a sensitivity study and some upscaling in order to put the study into perspective with previous studies would be very worthwhile and would add to the scientific relevance of the paper.

2 Detailed Major Comments

p.29565, l.17: The major characteristics of the CATT-BRAMS should be briefly presented here so the reader is aware of the basic principles driving the model dynamics without referring to Freitas et al. (2009).

p.29568, l.12: Chlorine gas phase chemistry is not modelled since Cl_y in the tropical region at these altitudes is relatively low (probably on the order of Br_y released from VSLS). However, since the reaction of Cl atoms with $CHBr_3$ is even somewhat faster than the appropriate reaction of OH, this might lead to an overestimation of the $CHBr_3$ lifetime. This should be briefly discussed and ruled out.

p.29568, l.14: From the comments in the JPL recommendation (2006) the relative yields of the heterogeneous reactions between HBr and HOCl and HBr and HOBr (NOT HOCl, as stated in the sentence) do not seem to be so dramatically different. The study by Fickert et al. focuses on chemistry of the maritime boundary layer with relatively high liquid concentrations of Cl^- and Br^- as compared to the trace amounts to be available in cloud or rain droplets. From this study the production of Br_2 seems to be highly favoured compared to BrCl production. The applicability of the Fickert et al. results (p.29571, l.9) should be discussed. Also, in light of the highly uncertain parameters involved in these calculations some

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sensitivity studies seem warranted employing realistic error ranges for the uptake coefficients. Additionally the authors should consider inclusion of Cl chemistry (although this may not be the driving uncertainty here and would in fact add some more uncertainties ...).

p.29572, l.26: Is there any spin-up time for the model to distribute NOy over the other family species, especially NOx? Otherwise this may affect (OH) chemistry dramatically during "spin-up". Would'nt it be better to start with a NOy partitioning as modelled after 1 or 2 days of simulation?

p.29573, l.4: The representativeness of the Yokouchi et al. data should be briefly discussed.

p.29576, l.10-20: Two types of explanations are given for the distribution of Br_x in the convective cloud. I do not understand why sunlight would have an effect on Br_x since it is the sum of Br_2, HOBr, BrO, ... which should be independent of photolysis in the first place. Also, why is Br_x sensitive to the ascent velocity? This should be explained in more detail.

p.29577: The discussion of Fig. 11 should be completely reworked since it is very hard to follow in the way presented. Wouldn't it be more obvious to simply plot horizontally averaged mixing ratios of the product gases and additionally CH_3Br as a function of altitude?

p.29578, l.9: From the plots it seems that Br_x is lifted to the TTL in comparable amounts to HBr. On the other hand it is stated that HBr transported to the TTL is so low that ice surface heterogeneous chemistry processes can be neglected. This should be clearly brought into perspective.

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3 Minor Comments/Corrections

Abstract, l.2: Bromoform is one of the most abundant halogenated ... (It is NOT a source of VSLS but a source of strat. inorganic bromine!)

Abstract, l.2: Use VSL Substances throughout!

Abstract, l.28: We also show ... (why use past here?)

p.29564, l.19: ... off-line output fluxes ...

p.29566, l.28: The term "prognostic turbulent kinetic energy" is not commonly known. Therefore it should be briefly explained when used.

p.29568, l.1: ... (resp. P.. term) ...

p.29568, l.20: ... in THE gas pahse ...

p.29568, l.23: ... using THE Fast-TUV ...

p.29568, l.26: Proper citations should be given for JPL and IUPAC recommendations (Sander et al. 2006/9, Crowley et al. 2010).

p.29570, l.22: Which species are meant here? The functional groups R and R' should be detailed or it should be mentioned that averaged values are used from different aldehydes and ketones.

p.29571, l.3: ... for cloudS is typically ...

p.29572, l.25: ... most abundant NOy species, it is ...

p.29573, l.18: The sentence is hard to understand and should be rephrased

p.29574, l.13: ... ... of simulation THE HBr mixing ratio ...

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Fig.4: The size of the axis labels may be rather small in this and the following figures (except Fig.5 and 7).

p.29577, l.8: In THE 0-5km layer ...

p.29577, l.23: ... lead to a stronger decrease ...

p.29578, l.12: Bromoform is not a source of VSLS (see comment above). Also, do not use "VSLSs"

p.29578, l.16: ... degradation of bromoform and ... (delete "the")

p.29578, l.23: ... in a future study.

p.29582, l.13: The proper terms "cloud and rain droplets" should be used throughout. Just using cloud and rain may be misleading.

p.29582, l.15: Instead of "which are relative to ..." use "which apply to rain droplets" etc.

p.29582, l.16: Same for cloud droplets.

p.29583, l.1: ... much larger ...

p.29583, l.2: ... in THE aqueous phase.

p.29583, l.2: Instead of "relative to ..." use "applying to rain droplets".

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