

***Interactive comment on* “Consistent simulation of  
bromine chemistry from the marine boundary  
layer to the stratosphere – Part 2: Bromocarbons”  
by A. Kerkweg et al.**

**Anonymous Referee #2**

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[General Comments]

This paper by Kerkweg et al. describes a part of their work of simulating the sources and fate of reactive bromine from the atmospheric boundary layer up to the mesosphere by the ECHAM5/MESSy model. The work is perhaps presented in two or more separate manuscripts. The present paper comprises Part II of the work and is about the bromine source from short-lived C1-bromocarbons ( $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{ClBr}$ ,  $\text{CHClBr}_2$ ,  $\text{CHCl}_2\text{Br}$  and  $\text{CHBr}_3$ ) as well as  $\text{CH}_3\text{Br}$ . Other part(s) of their work (Part I and possibly Part III etc.) are perhaps supposed to address bromine release from sea salt in the end, but at the present time only the simulation of sea salt pH has been published

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as "Part I" in ACPD. The impact of short-lived bromocarbons on bromine budget and ozone loss in the UTLS is of great interest for ACP readership. Also, I can see a great deal of work carried out by the authors for evaluating model results. But, even though this paper is a part of the ambitious attempt for an unprecedented approach to simulate bromine chemistry from the troposphere to the stratosphere, I consider that the paper as it stands belongs more to a technical note rather than a scientific paper. In addition, one of the major scientific points raised by the authors about the lifetime of CH<sub>3</sub>Br appears problematic and should be dropped or revised substantially before the paper can be published in ACP.

The present paper starts from somewhat sketchy evaluation of the simulated bromo-carbon mixing ratios based on published emission fields of bromocarbons by Warwick et al. (2006) except for that of CH<sub>3</sub>Br. I understand that this sketchiness is rather inevitable considering the paucity of observational data. Therefore the observational data from different years had to be compared with model results representing the year 2000 meteorology in this study by Kerkweg et al. Indeed, previous model studies also suffered from the same kind of problem. But the present model simulation is performed based on a single emission scenario taken from the work of Warwick et al. without any sensitivity tests for reconciling it. This model evaluation must be a necessary step to the end of tropospheric and stratospheric bromine chemistry simulation, but I do not see a substantial scientific value by itself especially because presented findings do not provide substantial new insights. The authors seem to place a major value of their present work on potential difference in dynamics and transport between ECHAM5/MESy and p-TOMCAT models (the latter was used by Warwick et al.), but after all this issue is not discussed in the paper. On the other hand, the Warwick et al. paper lacked in the evaluation of simulated mixing ratios of CH<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>ClBr, CHClBr<sub>2</sub> and CHCl<sub>2</sub>Br, which are of less importance for the atmospheric bromine budget than CH<sub>3</sub>Br and CHBr<sub>3</sub>. Therefore we can place some value of the paper on this part of model evaluation.

For the simulation of CH<sub>3</sub>Br, the surface mixing ratio climatology (as function of latitude

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and season) from AGAGE ground-based observation network is used for constraining the model. This approach may be reasonable considering the long atmospheric lifetime of CH<sub>3</sub>Br and large uncertainty in CH<sub>3</sub>Br emission estimates. The model evaluation for CH<sub>3</sub>Br mixing ratios highlights the issue of the present approach, which is likely to overlook the hot spots of CH<sub>3</sub>Br emissions such as from biomass burning and tropical rainforest. This information is useful from a technical point view to see how well the simplistic approach taken by the authors can work for simulating CH<sub>3</sub>Br mixing ratios in various parts of the atmosphere. But again I do not see a substantial scientific value by itself.

These evaluations of simulated bromocarbon mixing ratios are followed by the analysis of simulated source strength of reactive bromine from each bromocarbon's photodecomposition below and above the tropopause, but I consider that the presented findings are not substantially new. I am a bit disappointed to see that an important question, the issue of short-lived bromocarbons contribution to stratospheric bromine loading, is not addressed in the present work; we would rather like to know the resultant mixing ratios of reactive (inorganic) bromine in each part of the atmosphere than the source strength from bromocarbon photodecomposition. But I have some suggestion to the authors in my specific comments below as regards what to discuss from the present model result.

I appreciate it very much that the authors have added some statement about the characteristics of model transport etc. in this published version of ACPD paper. But I am still inclined to feel that, in order for the present work to qualify enough as a scientific paper by itself, it should have elaborated some sensitivity model runs with rectified surface emissions, etc. to reduce and/or explain discrepancies between observed and simulated bromocarbon mixing ratios. Otherwise the volume of the paper (especially the number of plots) could be reduced and then merged to other part(s) of their paper series - which I suppose should contain substantial new findings considering their ambitious modeling approach.

[Specific comments]

## 1. CHBr<sub>3</sub>

This species is believed to be among the most important short-lived bromocarbons for UTLS bromine chemistry. It was clearly identified by the authors that their model over-predicts CHBr<sub>3</sub> mixing ratios in the UTLS. Previous models also had this problem and some detailed discussions were provided. See their interpretation of 2-D/3-D CHBr<sub>3</sub> modeling results in Dvortsov et al. (1999), Nielsen and Douglass (2001), and Warwick et al. (2006), which all seem to have overpredicted CHBr<sub>3</sub> in the UTLS.

According to statement in the present paper by Kerkweg et al., the ECHAM5/MESSy model is rather unlikely to overpredict deep convective transport itself but still the over-predicted CHBr<sub>3</sub> mixing ratios are likely to be associated with air detrained from deep convective activities. Then, at the end of Sect.3.1, it is stated that the applied CHBr<sub>3</sub> emissions are most likely too high. But it appears to me that just scaling down the emissions globally would lead to underpredicted CHBr<sub>3</sub> mixing ratios in the lower to mid troposphere, as model-observation agreement looks relatively good in this altitude range. I am tempted to feel that regional maximum in simulated surface air CHBr<sub>3</sub> mixing ratio around Indonesia (Fig.3 - is it consistent with shipboard measurements by Yokouchi et al.?) is partly responsible for the overpredicted UTLS CHBr<sub>3</sub> because deep convective activity should be quite strong around there. I also wonder if the present model result indicates a possibility of some anti-correlation between SSTs and CHBr<sub>3</sub> emissions - which might lead to decreased CHBr<sub>3</sub> transport via deep convection in the end. High chlorophyll concentrations in the equatorial ocean may be somehow linked to upwelling motion in water and therefore lower SSTs (e.g., Strutton et al., 2001). In addition, regional preference in coastal upwelling (therefore lower SSTs and higher biogenic activities) may also lead to regional difference in coastal CHBr<sub>3</sub> emissions. In the emission scenario used by Kerkweg et al. there are so many coastlines and therefore high CHBr<sub>3</sub> emissions from Indonesia - but is this realistic?

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Also, if large-scale upward motion in the TTL is overpredicted, it could also lead to overpredicted CHBr<sub>3</sub> in the lower stratosphere.

If possible, the authors may also want to discuss if any difference can be identified against p-TOMCAT simulation of CHBr<sub>3</sub> profile by Warwick et al. (2006) especially because the same CHBr<sub>3</sub> emission field is used whereas some difference might exist between p-TOMCAT and ECHAM5/MESSy for tropical convective transport as well as large-scale TTL uplifting.

## 2. CH<sub>2</sub>Br<sub>2</sub>

This species may be the second most important among short-lived bromocarbons but the evaluation of simulated mixing ratios have not been performed as detailed as it is done in the present work. So this contribution is quite welcome. It appears that the model again overpredicts CH<sub>2</sub>Br<sub>2</sub> in the UTLS. This could have resulted from transport biases etc. similar to CHBr<sub>3</sub>.

## 3. CHClBr<sub>2</sub>, CHCl<sub>2</sub>Br and CH<sub>2</sub>ClBr

These species are not very important as reactive bromine source, yet not negligible. Also the model evaluation suffers from the data paucity. But obviously the model-observation discrepancy in the mid-latitude is something unique that is not seen for CHBr<sub>3</sub> etc.

Unlike what the authors mention, atmospheric surface measurements of CHCl<sub>2</sub>Br & CH<sub>2</sub>ClBr exist (Class and Ballschmitter, 1988; Schall and Heumann, 1993; Yokouchi et al., 1996; and also firm data by Sturges et al., 2001) so that the authors can perform some model evaluation for seasonal variations in their surface mixing ratios at high latitudes including Spitsbergen. Possibly more data can be found by starting from these papers. Actually the Schall and Heumann paper is already cited by the authors for CHClBr<sub>2</sub> validation. Also have a look at Rolf Sander's supplement to Simpson et al. (2007), ACP, 7, 4375-4418.

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#### 4. CH<sub>3</sub>Br

I have some concerns about how TNUDGE can handle the ocean and soil uptake of CH<sub>3</sub>Br, which is known to be a substantial part of global CH<sub>3</sub>Br sink. Can TNUDGE calculate surface emission and surface deposition separately rather than net flux (i.e. emission minus deposition) at each grid point? If not, it is almost impossible to discuss the lifetime of CH<sub>3</sub>Br as is done now in the present paper. I suspect that the CH<sub>3</sub>Br lifetime is calculated to be longer partly because the surface CH<sub>3</sub>Br sink is underrepresented.

Ideally, the authors should dig into their CH<sub>3</sub>Br pseudo-emission flux shown in Fig. 18 especially in terms of consistency and discrepancy with previous emission flux estimates such as Warwick et al. (2006).

What is the cause of low mixing ratios (Fig.17) and high pseudo-emissions (Fig.18) from around southern China?

Also, in Fig. 18, there is no negative value in the CH<sub>3</sub>Br flux. How do you get 46.1 Gg/yr of CH<sub>3</sub>Br dry deposition as shown in Table 2?

#### 5. Dry deposition of bromocarbons

It appears that dry deposition of bromocarbons is calculated somehow in the present model run and comprises a significant part of their budgets. I presume that DRYDEP submodel is used except for CH<sub>3</sub>Br, but no specific detail is provided in the model description section. I don't think that the dry deposition of bromocarbons has been taken into account in previous model studies (except for the soil and ocean uptake of CH<sub>3</sub>Br). Therefore the authors may also want to provide some rationale for including this process in the present model.

#### 6. Resultant Bry mixing ratios - unaddressed issue in the present work

One of the major reasons why we are interested in the budget of short-lived bromocarbons is that they are likely to influence ozone loss in the lowermost stratosphere

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(Salawitch et al., 2005) and even in the troposphere (Yang et al., 2005). It appears that all the previous effort of modeling the stratospheric influence of bromoform assumed the uniform lifetime of 10 days for inorganic bromine (Bry) against rainout/washout in the troposphere. If ECHAM5/MESSy can handle this issue in a more vigorous manner with some rationale then it should be really interesting to dig into. Also note, Sinnhuber and Folkins (2006) argued that Bry removal in the TTL would be a key to determining the influence of short-lived bromocarbons on the lowermost stratospheric loading of inorganic bromine.

At this point the authors are just showing the source strength of Bry from photodecomposition of each bromocarbon. It may serve as some background information for understanding resultant Bry mixing ratios simulated by the model, but it does not provide substantial novel findings.

In Sect.4 the authors dig into the relative contributions of OH-attack and photolysis to the photodecomposition of each bromocarbon. But do we really need to be so specific about OH-attack vs photolysis? This is what we already knew crudely. I suggest that this discussion should be shortened and reorganized, unless the issue is linked to long-term trends in OH abundance and UV levels in the troposphere and the stratosphere. Also, Fig. 25 appears unnecessary to me. I suggest that Fig. 24 is modified to show Br radical production from each bromocarbon via OH-attack and photolysis (combined rate rather than that for photolysis alone), which might give a clue to speculate the role of each bromocarbon in the production of inorganic bromine from the troposphere to the stratosphere and thus better fits to the overall goal of the study.

Also, is there any implication from the present model results for the issue of representing total organic bromine (including halons) by CH<sub>3</sub>Br alone as done by some stratospheric models - such as the overprediction of inorganic bromine in the tropical lower stratosphere?

[Minor Comments]

P9479, L19-21:

"... realistically simulates the exchange between stratosphere and troposphere (STE) in the applied vertical resolution."

How realistic is it? Can you be more specific? Is this statement related to large-scale uplifting rate in UTLS?

P9480, L4-7:

Might be useful if campaign periods are mentioned explicitly here. PEM-West B Feb-Mar 1994, PEM-Tropics A Aug-Oct 1996, PEM-Tropics B Mar-Apr 1999, GABRIEL Oct 2005, etc.

P9482, L13-:

Initial condition for CH<sub>3</sub>Br mixing ratios? Or is it not important at all?

P9490, L20-25:

The issue of CH<sub>3</sub>Br trends - what years does the AGAGE CH<sub>3</sub>Br database represent?

P9494, L25-26:

"In the stratosphere the photolysis of halons contributes substantially to the Br production."

This statement is rather out of the blue. Perhaps some numbers can be added to Table 3 for halons.

[Technical Suggestions]

P9481, L27: "calculate" -> "calculated"

P9483, L9: "and one from ..." -> "and the other one from ..."

P9485, L11: "to much" -> "too much"

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P9485, L13: "by the fact, that ..." -> "by a fact that ..."

P9489, L10: "campaign" -> "campaigns"

P9489, L23: "so far" -> "so far"

P9495, L22-23: "most probably" -> "most likely"

P9502, L13: Perhaps remove ", ed."; also which chapter?

P9505, table caption: "g/sin" -> "g(Br)/s"

P9506, figure caption: Remove "Simulated"

P9522, figure caption: Remove "(a)"

P9527: Add "pmol/mol" to the y-axis of each plot

P9530: Color bar scales should be consistent between photolysis (left) and OH-attack (middle) plots. Also, perhaps "0.0003" should be changed "0.0005" for the photolysis plot.

[References not cited in the Kerkweg et al. paper but cited above]

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