Atmos. Chem. Phys. Discuss., 8, S5867–S5877, 2008
www.atmos-chem-phys-discuss.net/8/S5867/2008/

Atmospheric
Chemistry
and Physics
Discussions

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

A. Kerkweg et al.

Received and published: 12 August 2008

We thank the anonymous referee #2 for the in depth review.

In general, we agree with the referee, that the impact of short-lived bromocarbons on the bromine budget and on ozone loss in the UTLS region is of great interest for a part of the ACP readership. But this is not only true for the UTLS, this study is also of interest for the troposphere where the degradation of the short-lived bromocarbons and the release of bromine from sea salt both contribute to ozone chemistry. As the bromine budget and its influence on ozone can only be discussed when both sources are analysed in detail, we decided to discuss this issue after the analysis of the bromine release from sea salt. The decision to split the analysis of all bromine sources into two parts was made for two reasons: First, the two processes (degradation of bromocarbons by photolysis and OH attack and release from sea salt) are completely different in their nature. We therefore have to prove (by comparison to observations) first, that our model is representing the different processes realistically. And second, we attempt to provide a detailed analysis of all contributing processes (which we think is a scientific contribution as such). To combine everything in one enforcedly long paper, is therefore not feasible.

The referee criticises that we use the emission scenario of Warwick et al. (2006) without performing further sensitivity studies. The focus of the study of Warwick et al. (2006) was the evaluation of diverse emission scenarios to give most reasonable results. Our study, in contrast, aims at describing the full bromine chemistry within one simulation and just wants to utilise an available emission scenario. We took the one which performed best in the study of Warwick et al. (2006), which was the best we could do in the framework of our study.

We agree further that the analysis about the lifetime of CH3Br appears problematic and we will drop it (see also reply to referee #3).

We admit that the evaluation is somewhat sketchy, but as you state yourself, this can hardly be changed due to the paucity of the data. The main differences of p-TOMCAT and ECHAM5/MESSy are: First, p-TOMCAT is a CTM (i.e., driven by 6 hourly meteorology) and ECHAM5/MESSy is a general circulation model (GCM) calculating its own meteorology in each time step. This inevitably influences the chemistry as cloud microphysics and circulations are much more variable in a GCM than in a CTM. Second, the top of the p-TOMCAT model is at 30 km height, whereas our model includes the middle atmosphere (up to 0.01 hPa, i.e., $\approx$ 80 km). As chemistry below 30 km is influenced by chemistry and transport above 30 km (and vice versa), the different vertical domains of the models can lead to differences in the simulated chemistry. This is already indicated in the introduction of the article.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The use of the ALE/GAGE/AGAGE ground-based observations might not be substantially new, but at least it shows how well this assumption to reproduce the stratospheric methyl bromide budget, is suited also for the troposphere. Nevertheless the –to our knowledge– only available emission flux data is that of Warwick et al. (2006). They performed a 6 year simulation. Hence, this emission flux was never applied for longterm simulations and tested to give reasonable results in the upper stratosphere. But this was done for the ALE/GAGE/AGAGE pseudo-emission approach. Thus we used the most consistent emission assumption available for our model setup.

As explained above, we have reasons to delay the discussion about reactive bromine to the next part in the paper series. We see that this is disappointing for the reader of this paper. Nevertheless, with splitting this discussion into two parts, we are then in the dilemma to conclude with some vague statements like “this might be a consequence of the bromine release from sea salt”, which does not improve the discussion.

We agree, that some more sensitivity studies would provide a better basis for the debate about the results of this single simulation. As explained in the paper, the simulation is very CPU-time (and real time) consuming. Thus it is not feasible to perform a lot of sensitivity studies. (They would require approximately 1 Mio. CPU hours, some 100’s of TByte data storage, and at least a 2 year contract.) Yet, this article does provide some more scientific findings. You state yourself, that the analysis of the less important bromocarbons was never performed in such detail before.

We will at least reduce the number of panels in the multi-panelled figures and in exchange, add a document in the supplement including all panels comparing the six bromocarbons with all available measurements from the three PEM campaigns. We refrain from merging this paper with the next paper for the reasons given above.

1. CHBr3
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 CHBr3 mixing ratios in the UTLS.
Most of the over-prediction is due to a typo in the reaction rate of $CHBr_3$ and OH. (See statement of referee #1.)

Previous models also had this problem and some detailed discussions were provided. See their interpretation of 2-D/3-D CHBr3 modeling results in Dvortsov et al. (1999), Nielsen and Douglass (2001), and Warwick et al. (2006), which all seem to have over-predicted CHBr3 in the UTLS.
Obviously, this depends on the viewpoint. At least, Dvortsov et al. (1999) and Nielsen and Douglass (2001) do not talk about an “over-prediction” but about a higher importance of bromoform for the UTLS and the TTL.

..it is stated that the applied CHBr3 emissions are most likely too high. But it appears to me that just scaling down the emissions globally would lead to under-predicted CHBr3 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 CHBr3 mixing ratio around Indonesia (Fig.3 - is it consistent with shipboard measurements by Yokouchi et al.?) is partly responsible for the over-predicted UTLS CHBr3 because deep convective activity should be quite strong around there.
After correcting the bromoform mixing ratios for the $CHBr_3$ + OH reaction rate, we agree with the referee, that the emissions are not in general too high and that some hot-spots due to the enhanced coastline emissions in the tropics might in conjunction with convective transport lead to the enhanced bromoform abundance in the TTL. The surface bromoform mixing ratio around Indonesia is approximately twice as high as those measured by Yokouchi et al. But most probably not only the maximum at Indonesia, but also overestimated sources in other tropical coastal areas might be responsible for the enhanced bromoform abundance.

I also wonder if the present model result indicates a possibility of some anti-correlation

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

between SSTs and CHBr3 emissions - which might lead to decreased CHBr3 transport via deep convection in the end. High chlorophyll concentrations in the equatorial ocean may be somehow linked to up-welling motion in water and therefore lower SSTs (e.g., Strutton et al., 2001). In addition, regional preference in coastal up-welling (therefore lower SSTs and higher biogenic activities) may also lead to regional difference in coastal CHBr3 emissions.
Interesting theory, but a systematic analysis of those patterns is beyond the scope of this study.

In the emission scenario used by Kerkweg et al. there are so many coastlines and therefore high CHBr3 emissions from Indonesia - but is this realistic?
As discussed above, the emissions added for the coastlines seem to be very high. The scenario we used is that of Warwick et al. (2006) and especially the additional coastline emissions did improve the results in their case.

If possible, the authors may also want to discuss if any difference can be identified against p-TOMCAT simulation of CHBr3 profile by Warwick et al.(2006) especially because the same CHBr3 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.
Some obvious differences exist. These are that p-TOMCAT is a CTM, whereas ECHAM5 is a GCM, i.e., one model calculates its own consistent meteorology, whereas the CTM is externally driven by 6-hourly meteorology. This must influence the dynamics. In addition, all processes associated with tracer transport, are most probably differently parameterise in both models: i.e., advection, convection, cloud parameterisations and so on.

2. CH2Br2
Yes, the model still over-predicts the abundance in the UTLS. But, if the over-predicted

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

mixing ratio of CHBr3 at the tropopause would have been caused by an overestimated convective flux CH2Br2 should show a similar C-shape, which is not the case. From this we conclude that the source of CH2Br2 is overestimated and not the convective flux.

3. CHClBr2, CHCl2Br and CH2ClBr

We will add the Class and Ballschmiter (1988) data to the comparison. Schall and Heumann (1993) was already included in the discussion paper. The other articles report measurements in the polar or at least high latitude regions. These measurements have mostly been performed to understand a typical tropospheric polar/high-latitude phenomenon i.e. the so called polar ozone depletion events. As these events are not yet fully understood and a reasonable parameterisation for a global model does not exist, we could not include this process into our simulation. Hence, the comparison of those measurements made in polar and high-latitude regions with our simulation is not feasible. We state this in the introduction to Section 3. We will add a remark at the beginning of Subsection 3.3 to remind the reader of the restriction of our comparison to the mid-latitudes and tropics.

4. CH3Br

I have some concerns about how TNUDGE can handle the ocean and soil uptake of CH3Br, which is known to be a substantial part of global CH3Br 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 CH3Br as is done now in the present paper. I suspect that the CH3Br lifetime is calculated to be longer partly because the surface CH3Br sink is underrepresented.

No, it cannot calculate emissions and depositions independently, because it prescribes observed mixing ratios in the lowest model layer by a Newtonian relaxation technique and diagnoses the additional tendency as a pseudo-emission flux. As explained in the model description section and in more detail in the cited Technical Note, TNUDGE is

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

used, when emission fluxes are highly unknown, in contrast to surface concentrations. Thus TNUDGE simply calculates a flux which adjusts the mixing ratio of a species present in the model to a prescribed climatological mixing ratio. The latter is derived from the ALE/GAGE/AGAGE stations. The loss of CH3Br is explicitly calculated using the MESSy submodel DRYDEP taking the underlying surface and the wind velocity into account. Thus we can interpret the TNUDGE flux as the emission flux of CH3Br minus the flux from loss processes not represented by dry deposition.

Ideally, the authors should dig into their CH3Br 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).
Due to the completely different methods of "constructing" the net emission flux by Warwick et al. (2006) and us, the only quantity that can be compared is the global total. Direct comparison of the emission patterns are not feasible for some reasons: the resolution of the input fields is different. Whereas Warwick et al. (2006) prescribe the emissions on a 5.6° grid with a latitudinal dependency, we use latitudinal averages due to the paucity of the data. Hence the distribution resulting from our distribution cannot show local effects as shown by Warwick et al. (2006). Furthermore, our diagnosed flux shows artificial maxima at each latitude where the prescribed mixing ratio changes. You may argue that our approach is very coarse. But at least, this one is tested to give reasonable amounts of methyl bromide in the upper stratosphere. This has not been tested for the Warwick et al. (2006) emission scenario, which may lead to some spurious effects in the upper atmospheric regions. Because of the computational expensiveness of our simulation (including aerosol chemistry) it was not feasible to perform long term simulations testing if the Warwick et al. (2006) scenario produces reasonable results in the upper stratosphere. The only comparable is the global total emission fluxes and these are very similar (131 Gg/yr vs. 130.6 Gg/yr).

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

The low mixing ratios are caused by high deposition velocities. These are high around China because of low soil pH and high leaf area index (LAI). (For details of the dry deposition parameterisation we refer to the Technical Note of Kerkweg et al., 2007.) Due to the high deposition the difference between the measured and the simulated mixing ratios are higher, causing the pseudo-emission flux to become higher as well. This might be unrealistic as TNUDGE compensates for high dry deposition. The compensation may be wrong, as no measurements over China are available.

Also, in Fig. 18, there is no negative value in the CH3Br flux. How do you get 46.1 Gg/yr of CH3Br dry deposition as shown in Table 2?
As explained above dry deposition is calculated by the submodel DRYDEP. The given dry deposition flux is the one determined by DRYDEP.

5. Dry deposition of bromocarbons

I presume that DRYDEP submodel is used except for CH3Br, but no specific detail is provided in the model description section.
No. As explained above, the dry deposition flux is calculated by DRYDEP for all six halocarbons.

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 CH3Br). Therefore the authors may also want to provide some rationale for including this process in the present model.
We have taken the dry deposition of the other bromocarbons into account in order to achieve a consistent budget.

6. Resultant Bry mixing ratios

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 (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.*

The tropospheric Bry mixing ratios will be evaluated in detail in the upcoming next part of this series. As release from sea salt is a major source of inorganic bromine in the troposphere the discussion has to be postponed to this article, as this source of gaseous bromine has to be evaluated first to allow a reasonable discussion.

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 reorganised, unless the issue is linked to longterm 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.

We will follow the suggestion of the referee and show one figure displaying the combined effects of reaction with OH and photolysis. Consequently Section 4 will partly rewritten and shortened.

Also, is there any implication from the present model results for the issue of repre-

senting total organic bromine (including halons) by CH3Br alone as done by some stratospheric models - such as the over-prediction of inorganic bromine in the tropical lower stratosphere?
Yes, we say on page 9493, line 23-26, that the use of CH3Br as the only bromocarbon is not in contradiction to our model results for the upper stratosphere. So far we did not refer to the halons. We will do so in the revised version. All halons cannot be substituted by CH3Br as they contribute bromine amounts that are in the same order of magnitude as CH3Br and have a different lifetime. In the UTLS CHBr3 can contribute substantial amounts of bromine. As bromoform photolysis is much more efficient in the UTLS compared to the CH3Br photolysis, it will not be possible to describe the effect of bromoform by lumping it to a pseudo-CH3Br species with CH3Br properties.

Minor comments
P9479, L19-21 This has been shown by **?** by analysing the O_3-budget and by comparison of simulated O_3 profiles with observations. The interested reader is referred to the analysis of the ozone profiles in this publication.
P9480, L4-7 We will add this information.
P9482, L13 ff. Methyl bromide was initialised from the ECHAM5/MESSy S1 simulation (Jöckel et al., 2006), which used the same pseudo-emission. We will add this information.
P9490, L20-25 The data used for TNUDGE is specific for each month and year. This is important because Montzka et al. (2003) show that there is a trend. We will add this information.
P9494, L25-26 We will add the calculated contribution of the halons to Table 3 and make a more precise statement here.

Technical corrections
All suggested technical corrections will be applied.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9477, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper