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Biogeosciences Discussions

Interactive comment on "Modelling the vertical distribution of bromoform in the upper water column of the tropical Atlantic Ocean" *by* I. Hense and B. Quack

I. Hense and B. Quack

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Authors' response to both reviewers:

We thank both reviewers for their constructive and helpful comments which led us to reconsider our findings and the way they are presented. In our revised version we have therefore introduced a section about model philosophy which will hopefully clarify our approach and goals and eliminate misunderstandings. We acknowledge the request for validation and have added observations to show that the coupled physical-biogeochemical model produces reasonable results. However, current measurements do not allow the validation of the seasonal variability of air-sea fluxes of bromoform. Flux measurements have been obtained during individual campaigns and show a large

variability of the air-sea fluxes on short time scales (shorter than one week) and there has been not attempt, yet, to remove these signals and systematically investigate the seasonal cycle.

Authors' response to the comments of Reviewer 1:

- *P 4921 L 27/8: The bacteria studied in Wahman et al. 2005 are Nitrosomonas europaea, a common model for a soil- and water-dwelling nitrifier. Please add the species name, as not all Nitrosomonas 1) may be able to co-metabolize bromoform or 2) occur in seawater.*

– we use the full species name in the revised version.

- *P4922 L2: I suggest you remove this footnote, as it doesn8217;t contribute much to the general context.*

– we removed the footnote.

- *P4923 L7: Please explain why you found no need to change the parameters. Have you checked chlorophyll-a concentrations? Verified that the biomass is within the observed range? As far as I know, there is quite a difference in the ecosystem composition to be expected between BATS and the Mauretanian upwelling area. Comparing e.g. community composition as described in Steinberg et al. 2001 for BATS with e.g Zubkov et al. 2000 for AMT, I see that both areas are dominated by Prochlorococcus and Synechococcus species, but there may be considerable differences in diatom/flagellate abundances (compare e.g. Tilstone et al. 2003 for the Northwest Iberian Upwelling). Hence, this choice should be better justified.*

– the original biogeochemical model by Schartau and Oschlies (2003) has not specifically been designed for BATS but uses an optimized parameter set tuned

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to several locations in the Atlantic Ocean. The model has been also successfully applied basinwide to the Atlantic Ocean (coupled to a 3-dimensional ocean-circulation model) including the North and Equatorial basin (the region of interest for our study). Model results have been validated with data from the Eastern North Atlantic. Hence, we do not see a reason why we should change the biogeochemical parameters for our process study. Nevetheless, we have added a small paragraph where we address this issue. As a final note we would like to point out that we are not considering the Mauritanian upwelling region which is north-east of the Cape Verde Islands.

- *P 4924 L 16-21: 8217;Supporting evidence..8217; This is no evidence, as the presence of the enzyme only does not tell you anything about if, how, when and where bromoform is produced. As an example from the marine sulfur cycle, the DMSP-cleaving enzyme DMSP-lyase has been identified in several plankton species, but their DMSP content of those species varies over orders of magnitude. And there are several DMSP producers that showed no DMSP-lyase activity at all in the laboratory. Furthermore, the second assumption is most likely wrong. I think it would be more realistic to say that, given that you have only one phytoplankton group, you can use only one value, and the aim was to use a value somehow related to observational estimates. Also, mention that the community you study is dominated by small picophytoplankton, some of which have been shown to express bromoperoxidase. Except for Nitzschia sp, the species you derive your values from are cold-water species. You should mention that this is a possible limitation of the applicability of the values you find.*

– we agree with the reviewer and changed this paragraph accordingly.

- *P 4925 L 8: In your conclusion you mention the production of dibromomethane from bromoform as a process described already in Quack et al. 2004. Why has this process not been considered here?*

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– we now mention the process of reductive debromination in the introduction section of our revised version. According to the current state of knowledge about the possibility of reductive debromination as an anoxic process in the oxygenated water column, it seems best to use remineralization as a proxy.

- *P 4925 L 22: Why have you chosen your parameters in such a way that the estimated half-life lies outside the measured range?*

– we refer to our newly added paragraph about model philosophy. The loss terms for bromoform for our numerical experiments have been adjusted in order to obtain the best fit for each experiment. Using our approach of bromoform production this rate for degradation (4.37 instead of minimum 5 years) gives the best result.

- *P 4926 L 9-18: I am not particularly happy with the parameterization used here: Shouldn8217;t nitrification also be controlled by 1) ammonia concentrations 2) oxygen abundances and 3) temperature? Why have you used light here? As oxygen is not modeled by your NPZD model, I understand that you couldn8217;t use this as a proxy, but you do have nitrogen concentrations and temperature? Please justify your approach.*

– we assume that nitrification (i.e. ammonium oxidation) is only limited by the presence of light, neither temperature nor oxygen. However, we have carried out an additional model run where we use the parameterisation for nitrification by coupling the loss to nitrogen concentrations as suggested by the reviewer. The results show that the vertical profile of bromoform is similar to the one we used originallly (coupled to light instead of nitrogen).

- *P 4927 L 17: Please justify why you think that Cape Verde is representative for the entire eastern tropical Atlantic.*

– we have conducted several additional model experiments at other locations further south (e.g. 11°N). Differences in the vertical mixing lead to small changes

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in the depth of the subsurface phytoplankton biomass and bromoform maximum. The profiles of the individual experiments are similar and conclusions remain valid. We have added this to our revised version.

- *P 4928 L 1-14: Here you definitely need to show some validation data. The reader cannot judge whether your model 8217;simulates temperature and salinity fields reasonably well8217;, if you don8217;t show the data. I suggest not showing annual means, but using some of your cruise data for an(some) individual month(s) instead. Furthermore, you should absolutely compare phytoplankton biomass to observations. You could e.g. estimate chlorophyll-a from N/C (Redfield) and C/Chl-a ratios of small phytoplankton (125 g C/g Chl-a) and compare to satellite or in situ data (as, e.g. ,visualized in Quack et al. 2004).*

– we restore our model towards climatological monthly values (derived from observations) but we understand that the reader would like to see how well our model simulates the temperature and salinity fields. We therefore added in the appendix summer and winter profiles of observed and simulated salinity and temperature. In order to show that the biogeochemical model is reasonable, we present profiles from simulated and observed nutrients and phytoplankton biomass (using a vertically dependent C:Chl-ratio).

- *P 4928 L 26: This could be formulated more precisely. The main point here is not that 8217;remineralization occurs above 200m8217; but that the strong temperature sensitivity of your remineralization (1.06622 = 3.6; 1.0668 = 1.67) leads to lower rates at low depths.*

– we agree and explicitly mention this in the revised version.

- *P4929 L 2: 8217;Escaping bromoform8217;: Is there any parameterization of particle sinking in your model (I don8217;t think so) or doesn8217;t bromoform*

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just simply accumulate at depth and experience some sort of advection and diffusion? Reformulate this sentence for increased clarity.

– we rephrased this sentence to reflect that bromoform is not transported by particles into the deeper layer but simply accumulates due to diffusion in the absence of sinks.

- *P 4929 L 9-10: 8217;Erodes the subsurface maximum..8217; Please reformulate, as we do not know in which way this should 8217;erode8217; the maximum.*

– we rephrased this sentence.

- *P 4929 L 12-15: Isn8217;t this due to your NPZD model being in steady-state, with an eternally reproducing seasonal cycle? I mean, don8217;t phytoplankton production and consumption processes need to be equal in the annual mean, so that you do no longer see a net change in concentration over the years? Then it would be obvious rather than 8217;disappointing8217; that you do not see differences in bromoform patterns for those 2 sources after 50 years, if bromoform is proportional to phytoplankton production/consumption. Again, here it could be interesting to look at monthly rather than annually averaged profiles, because I would think that Q1 and Q2 have different seasonality, as you briefly mention in footnote 3. Hence, I suggest including the statement in footnote 3 in the main text and elaborating a bit more on the mechanisms.*

– as the location of phytoplankton production and losses may not be similar in the water column, differences might also occur in vertical profiles of bromoform for the two experiments. This is irrespective of a steady state approach. We have moved footnote 3 into the main text and give fuller explainations about the differences in the seasonal cycle of the two experiments.

- *P 4930 L7-12: If bromoform is of phytoplanktonic origin and if bromoform dynamics and phytoplankton dynamics are tightly coupled in your model, this outcome*

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is hardly surprising. You could overlay both observed and simulated chlorophyll-a/biomass onto your plots and see whether they coincide. If so, bromoform could be described entirely using something like B = alpha(z,T) x P and you would be able to test whether the rather complicated source and sink terms you use are really needed.

– this simplification is not helpful or meaningful in our context. We assume that bromoform production and primary production are coupled but this does not imply that biomass and bromoform profiles are similar. The losses for bromoform and phytoplankton are completely different. The same is true for the boundary conditions: in contrast to bromoform there is no flux of phytoplankton between ocean and atmsophere. Hence, the vertical profiles of phytoplankton and bromoform differ as can be seen Figure 1 and 2. In addition, prescribing such a profile would eliminate the possibility to determine temporal changes as well as air-sea fluxes; nothing could be learned about the system (e.g. loss terms of bromoform).

• *P 4930 L 11-12: 8217;Given...8217; Please carefully revise this sentence. Which assumptions are supported by which feature of the model results? (see comment above)*

– we like to refer to our model philosophy and our response above. We keep our original text “Given the uncertainties of model parameters and forcing, the robustness of the results support the validity of our assumptions.”, because it is not a priori clear that e.g. the obtained ratio between primary production and bromoform production results in reasonable subsurface concentrations.

• *P4930 L 20: Please reformulate, as it seems confusing to talk about the 8217;thickness of a profile8217;. Suggestion 8217;width, half-width8217;, etc.*

– we do talk about thickness of a layer, i.e. subsurface maximum layer, not 8217;thickness of a profile8217;. This is an accepted and usual term and we

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feel that a replacement would add confusion rather than clarification.

- *P4930 L22: Please compare the width of the subsurface biomass maximum with experimental data to support this hypothesis (see comments above on model evaluation).*

– as mentioned in the manuscript, a high vertical resolution ($<$ 10 m, see Beckmann and Hense, 2007) in observations (and models) is necessary to resolve the subsurface maximum layer and determine its thickness. However, the resolution in the field measurements is rather 20m.

- *P 4931 L22: I suggest comparing the simulated seasonality of bromoform with the seasonality of biomass, MLD and solar radiation (and wind speed) in Figure 5/6 as these are the variables your model seems most sensitive to. Could you derive simple diagnostic dependencies between environmental/ecosystem variables?*

– please see our comment above. Phytoplankton biomass and bromoform are not tightly coupled, particularly not near the surface where photolysis and air-sea flux determine the bromoform concentrations. We therefore do not include an additional figure with phytoplankton biomass.

- *P 4932 L2: Please show biomass seasonality as predicted by your model in Figure 6. In addition, none of the subplots of Fig 6 are labeled a) - c).*

– please see our comment above. We labeled the subplots.

- *P 4932 L2f: Can the high seasonality in ChBr3 fluxes be supported by atmospheric data? Cape Verde Observatory? Cruises?*

– Bromoform measurements have been carried out mainly in October/November and hardly in any other season. The high seasonality is an outcome of the model and needs to be investigated in the field in future. However we would like to point

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out that atmospheric values obtained during individual cruises vary by at least an order of magnitude.

- *P4933 L13: 8217;in the presence of some nitrifiers8217;*

– we have changed the sentence accordingly.

- *P4933 L14-17: See remark above. Why don8217;t you mention this mechanism already in the introduction and explain why you chose not to model it?*

– the mechanism is mentioned in the introduction of the revised version; please see our response above.

- *P4933 L18: If the seasonality in ChBr3 is really high, wouldn8217;t you expect this to be reflected in BrO concentrations? However, BrO concentrations exhibit a much smaller seasonal cycle (max. factor 2, Read et al., 2008). Can you explain this? Can you show differences between summer/winter fluxes in ChBr3 from cruise/atmospheric data?*

– please see our response above. We acknowledge that the next step should be the development of a fully coupled ocean-atmosphere model for bromoform where also atmospheric sinks can be considered. The dynamics are complex (e.g. the lifetime of inorganic are shorter than of organic bromine species) and seasonality of bromoform and bromine oxides might not be necessarily similar. However, this is speculative and since the focus in this study are the sources/sinks in the ocean we do not discuss these issues.

- *Technical Comments*

– the technical issues are addressed in the revised version.

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Reviewer 2:

- *Ultimately, the importance of this work is to show how the outgassing of CHBr3 to the atmosphere is effected by various parameters. The work shows, unsurprisingly since it is the surface concentration of CHBr3 which controls the outgassing, that photolysis and volatilisation are the 2 most important factors in this regard. However, both of these are treated in a very crude way in this work. I strongly recommend that the authors improve the treatment of these factors (see specific comments below) before this manuscript is accepted for publication.*

– The goals/outcome of our study is not the attempt "to show how the outgassing of CHBr3 to the atmosphere is effected by various parameters". Instead, our goal is to investigate the source and sink terms for bromoform within the water column. This is reflected by the title, has been stated in the abstract and can be seen from the result section (which presents the outcome of numerical experiments with different sources and sinks of bromoform in the water column). We do not agree that our parameterisation of photolysis and fluxes is overly simplistic. We would also like to refer to our newly introduced section on model philosophy which hopefully eliminates misunderstandings.

- *One of the main conclusions is that winter time fluxes are an order of magnitude higher than summer time fluxes. This model result seems to be mainly driven by large seasonal changes in the wind field, although a complete treatment of photolysis and of volatilisation may well change this result significantly. Thus there needs to be some discussion of the wind field - comparison with observations - how localised is it to this area etc. Also, as far as I know, there is there no experimental evidence for large seasonal changes in CHBr3 fluxes - some discussion of measurements would be advantageous.*

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– The model is forced by wind fields, atmospheric temperatures, cloud cover, and precipitation from ECMWF reanalyses which rely on observations. Although these data are not perfect (as it is the case for all data products) we believe that the climatological seasonal cycle is reasonably well represented. We also like to refer to our comments about seasonality above.

• *P4920 L23. Implies that reactive bromine observed by Read et al. (2008) in MBL is due to CHBr3, which is unlikely to be the case (most reactive bromine in the MBL is believed to be from sea spray).*

– we have changed the paragraph to emphasize the role of the tropical Atlantic Ocean in releasing inorganic and organic bromine species into the marine boundary layer.

• *P4921 L10 "organic matter, i.e. phytoplankton" ambiguous sentence, needs rewriting..*

– we have modified the sentence.

• *P4921 final paragraph. The conversion of CHBr3 to CH2Br2 via reductive hydrogenolysis (Vogel et al., 1987) under anoxic conditions (as discussed in Quack et al. 2007) should surely be included in list of CHBr3 decay processes.*

– this has been added.

• *P4923 L2. A vertical resolution of 1 m is much too coarse in the upper layers to satisfactorily parameterise UV photolysis.*

– UV penetrates several meters in clear waters and as a parameterisaton (which addresses only main aspects of this process) we think our appoach is sufficient. To study the dynamics in the lower atmosphere – upper ocean, we agree that a higher resolution would be necessary, but this is not the topic of this paper.

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- *P4925 L 11-19. The photolysis parameterisation is extremely crude; it relies on an annual average irradiance and a very rough estimate by Carpenter and Liss (2000) of the photolysis turn over time. Given the importance and of seasonal changes in the computed CHBr3 sea-air fluxes, the authors should specifically include absorption cross sections and quantum yields for photolysis of CHBr3 in water (see I. Nicole, J. de Laat, M. Dore, J. P. Duguet, H. Suty, Environ. Technol. 12, (1991) 21-31 and W. M. Kwok, C. Zhao, Y.-L. Li, X. Guan, and D. L. Phillips, J. Am. Chem. Soc. 126 (2004) 3119-3132.) , plus monthly or seasonal average irradiances (rather than annual average).*

– We do not use an annual average irradiance for computing photolysis. Instead the monthly mean UV-irradiance is taken and the vertical decay rate is normalized using an annual average irradiance (see formula). We do not see this as overly simplistic.

- *P4925 L 23. The authors should fully justify their value for the half-life due to hydrolysis and halide substitution of 4.37 years - since this is outside the range of 5-74 years reported.*

– please see our comment to reviewer 1 on the same issue.

- *P4926 L 3. Similarly, where does the time scale for remineralisation of detritus come from? It needs fuller justification.*

– similar to Schartau and Oschlies 2003, where the remineralization rate is temperature dependent, we use a temperature dependent loss rate for the bromoform compartment, depending on the detritus concentrations. The decay rate for bromoform has been adjusted in order to obtain the best fit with observations (see our section about model philosophy).

- *P4926 L 14. Setting the atmospheric concentration of CHBr3 constant will affect the conclusions regarding seasonally variability of CHBr3 emissions. For self-*

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consistency, it would be much better to calculate the CHBr3 MBL atmospheric concentrations from the calculated sea-air emissions and a seasonally-changing prescribed (atmospheric) radiation field.

– In order to compute the air-sea fluxes which serve as the boundary condition for our ocean model, atmospheric concentrations have to be specified. Hence the calculated air-sea exchange of bromoform in the model cannot be used in turn to calculate the atmospheric concentrations. We acknowledge that the next step should be the development of a fully coupled ocean-atmosphere model for bromoform but the focus in this study are the sources/sinks in the ocean.

• *P4932 L 5-10, and Fig 6. The seasonal variation of wind speed seems quite extreme; and of course has a large bearing on the results of this work. Is this replicated by measurements or other models?*

– please see our comment to reviewer 1 on the same issue.

• *P4933 L 23. As stated in the General Comments, some discussion of what previous measurements reveal about seasonal changes is warranted, plus how the modelled fluxes agree with previous measurements.*

– please see our comment to reviewer 1.

Interactive comment on Biogeosciences Discuss., 5, 4919, 2008.