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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean" *by* L. J. Carpenter et al.

Anonymous Referee #1

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The paper "Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean" deals with the variability of oceanic emissions of two natural organo-bromine compounds which may have important impact on the atmospheric oxidant chemistry. This topic is of current global interest, since spatial and temporal emissions of the short-lived compounds are needed for atmospheric modeling and future ozone predictions The paper provides new data, and a comparison of published air-sea fluxes of two important compounds and it discusses their flux ratios. The analytical method and data in this paper are of sound quality and the paper is well written, clearly structured and precise. There are good ideas in data visualization to clarify the data and controlling factors. There are a few mistakes, which I discovered during reading and some assumptions and statements will need to be clarified, corrected and /or elabo-

rated not last to strengthen their implications, the conclusions and the key messages of the paper. The paper needs some revisions and I add my detailed comments below.

Few mistakes where found:

1) 18412/6: Nielsen instead of Nielson

2) 18412/27: pmol mol-1 instead of ppt

3) 18413/ 18: something is wrong here, probably: in document should become a parenthesis

4) 18414/13: pmol mol-1 instead of ppt

5) 18415/12: Table 1 instead of Table 2

6) 18416/9: 65°S instead of 65VS

7) 18418/24 and 25: fluxes are nmol m-2d-1, instead of nmol m2d-1

Some assumptions, statements and conclusions need to be clarified, respectively corrected and/or elaborated:

8) 18410/8-10: Coastal contributions to global fluxes have been published before. Thus the approach to calculate global coastal fluxes by the application of the authors' limited data is not appropriate, there are more coastal concentrations and fluxes in the literature, see comments 17-22, thus the authors are asked to put their applied data and calculations in a more detailed context to published values and revise this statement.

9) 18413/1-3: The uncertainty for the air-sea flux is not equal to the uncertainty of the water measurements of a supersaturated compound. The uncertainty of the air measurements and of the model kw (Schmidt-number) and applied model come into account as well and contribute. For a detailed error-propagation of oceanic emission estimates, see details e.g. in Bange et al. 2001, Nitrous oxide emissions from the Arabian Sea: A synthesis, Atmos. Chem. Phys. 1, 61-71, 2001. The authors should

ACPD

8, S8834–S8839, 2008

add some more sentences about the possible error and its magnitude in the air-sea flux calculation.

18413/11: between ˜20°W (30°W is too far)

10) 18414/8: The statement, whereas the Chl-a distribution was very patchy is not seen in the Figures 2 and 3, there the Chl-a distribution follows the low SSts.

11) 18414/10: (+ve CHBr3 - Chl-a correlation, r2=0.28): After asking several people, the meaning of +ve is not obvious, and r2=0.28 correlation is actually no correlation!? Please clarify both.

12) 18414/18: Since air masses are always (mainly) transported from NE over the upwelling, also during the elevated mixing ratio events in the mentioned publications, the authors should clarify this statement.

13) 18414/18-23: The statement: (Fig.4) all reveal rather higher concentrations in SACW, than in NACW should be underlined by the calculation and presentation of the means and ranges, since the statement is not completely obvious. Where all or only selected surface seawater concentrations taken?

14) 18417/23-26: For the unexpected selective surface water loss of CHBr3 compared to CH2Br2 from coastal regions to the open ocean, alternative explanations may be valid, see e.g. Quack, B., I. Peeken, G. Petrick, and K. Nachtigall (2007). Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling, J. Geophys. Res., 112, C10006, doi: 10.1029/2006JC003803. The ratio shift would include convection, deep mixing and entrainment of thermocline waters into the mixed layer, which the authors may want to consider as well.

15) 18417/27-18418/2: The ratio plot in Figure 8 shows sea water concentrations, which where transferred to emission ratios by correcting for slightly different transfer velocities. The authors should describe the assumptions for this method and their procedure in more detail. Additionally this method would only be valid, if the atmo-

ACPD

8, S8834–S8839, 2008

Interactive Comment

spheric concentrations were 0, otherwise the saturation anomalies (here used for the concentration gradient: sea water concentration - equilibrium concentration of water with overlying atmosphere) would serve as basis for this approach. I think, that their approach and additionally the numbers need to be corrected, starting from saturation anomalies and not concentrations in Fig 8. Additionally a hint for a possible flaw can be found in the discrepancy between the slopes in Figure 8 and the actual ratio from the number in line 18418/24 (mean fluxes of 41.2 and 13.3 nmol m-2 d-1 for CHBr3 and CH2Br2, respectively) is 0.32. Please clarify.

16) 18418/20: Please clarify what is meant here by coastal regions, since the upwelling is also in a coastal region, additionally not all coastal regions have been investigated-thus I think the authors refer to macro algal rich coasts, which they should add.

17) The global and regional flux extrapolations need some revision. The authors should refer their numbers and extrapolations to the published values, respectively include those in their calculations, thus should include a little more literature work. There have more concentrations been reported (especially for coastal regions) and more fluxes been calculated, which either underline or contradict the calculations in this paper, at least they open a range. The authors should include more flux-data (e.g. in Butler, Yokouchi, Chuck, Quack , Zhou,...) in order to put their own data and calculations in context. There are only few flux data from upwelling regions, but a number from coastal, covering the range from -1000 to 2500 nmol m-2 d -2, which needs to be considered. A table could be added, showing the range of the obtained global figures.

18) 18418/25: respectively) which is in accordance with earlier published fluxes (Quack, B., E. Atlas, G. Petrick, and D. W. R. Wallace (2007), Bromoform and dibromomethane above the Mauritanian upwelling: Atmospheric distributions and oceanic emissions, J. Geophys. Res., 112, D09312, doi:10.1029/2006JD007614.)

19) 18418/26: Chuck (2005) and Quack (2004) published fluxes for the equatorial upwelling which open a range

ACPD

8, S8834–S8839, 2008

This more even more true for the coastal regions:

20) 18419/21-27: Since more coastal sea water data are available, the authors should either calculate a range with the literature data or should underline by literature values, that their sea water concentration are representative. Again the method of the air-sea flux calculation from these data should be enlightened, including the applied atmospheric mixing ratios, which can't be neglected (see e.g. calculations in Butler, 2007)

21) 18420/2: It is obvious that all earlier, including the current, studies use different coastal areas and different sea water concentrations, different atmospheric mixing ratios and different environmental conditions. I feel that at this stage it would really help the paper and the community, if a table is added or at least for the coastal assumptions Table 2 is elaborated, including all parameters applied for the air-sea flux calculation in the literature, to show the variability of data, approaches and fluxes and discuss the range of possible flaws.

22) 18420/4-6: On which assumptions is it possible to reduce Butler's coastal emissions? I guess by area coverage (not 10%, but ?% coastal), which the authors should explain. And it is not clear, why the authors calculate a coastal % contribution there, and not for the other values

23) 18420/7: It is not clear, why this sentence starts with however. And despite this true statement, I feel that further sea water data are required because the coastal data and emissions are so variable, ranging from ?? to ??... and could make up globally ?? %. Please discuss.

24) 18420/15: Please add, what the controls in coastal regions are. Possibly a clear differentiation of the natural from other coastal sources is needed here.

25) 18420/18: Upwelling systems as hotspots for emissions have been suggested earlier elsewhere. Revision of the wording of this sentence would make the authors

ACPD

8, S8834–S8839, 2008

new suggestion clearer.

26) 18420/19: The entire concluding section can be strengthened, if the authors revise the forgoing section as suggested and include here a range of %, for the fluxes contributions from different regions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18409, 2008.

ACPD

8, S8834–S8839, 2008

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