

Interactive comment on “Bromocarbons in the tropical marine boundary layer at the Cape Verde Observatory – measurements and modelling” by L. M. O’Brien et al.

L. M. O’Brien et al.

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Thanks to all referees for reading the preliminary version of our paper and for making very useful and helpful comments. We have tried to take all of these comments into account. We have corrected any errors and omissions pointed out. We have changed the structure in order to improve the readability of our paper.

RESPONSES TO REVIEWER COMMENTS: ANONYMOUS REF 1

GENERAL COMMENTS

We spent some time before submission agonising about the structure/order of the paper. We acknowledge that we did not get it right and have modified the structure of the

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paper accordingly. We have tried to improve the introduction to make the subsequent sections more understandable. The order of the results section is changed: i) basic measurements, ii) correlations and modelling to understand emissions, iii) significance for oxidizing capacity. We have tried to consolidate discussion about specific points only at one point in the paper to avoid unnecessary repetition. We think this works better (thanks) and hope the referee agrees!

SPECIFIC COMMENTS

P4336 L10-13: The content of the sentences could be clarified, to that it has been own model runs, and it is not obvious from citing a paper, what is meant with this hint. It should rather be named than cited in the abstract.

Reply: Point noted and changed in the abstract to 'Our chemical transport model studies presented here with published bromocarbon emission rates do not reproduce the observations'.

P4338 L13: Major natural contributor of bromine is not quite right. Since it's the oceanic aerosol that contributes most. Please revise this sentence.

Reply: This sentence has now been revised to the following:

'Bromine is the major natural contributor of organic bromine to the atmosphere...'

P4338 L16: Cited as Butler is arbitrary, there was no identification of the source in his paper. In addition it seems that more papers in this section are arbitrarily cited (e.g. Goodwin et al., 1997 is not an original paper in that sense).

Reply: Point noted that more precise citations and references are needed. These have been changed in the text to the following:

Goodwin reference removed. We have added Carpenter and Liss, 2000.

Butler reference removed. We have added Tokarczyk and Moore, 1994.

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P4339 L3-4: Citing of a modelling paper for sea salt as an important source seems again not appropriate. Please refer to data papers.

Reply: Replaced by Sander et al., 2003.

P4339 L10-13: There has been work done on the phytoplankton source of CH₃I- please cite.

Reply: The work of Moore and Tokarczyk, 1993 and Moore et al., 1996 has now been cited as an example.

P4340 L2: Please specify the concentrations measured from Carpenter et al., 2008 as oceanic or atmospheric.

Reply: The concentrations we were referring to were the atmospheric ones; this has been specified in the text.

P4340 L7-9: This sentence seems senseless here. Please remove or specify.

Reply: This sentence has now been removed.

P4340 L 17: In the 2007 paper of Quack et al. that has been cited here, different oceanic sources of the compounds are suggested. Possibly the authors mean the other Quack et al. 2007 paper, where indeed an atmospheric correlation is described (please cite and/or remove citation).

Reply: We now reference both Quack et al. 2007 papers. Here we refer to the atmospheric measurements (Quack et al., 2007b)

P4344 L22-28: Could you estimate from the above information how the relative intensities would be, since I tried to follow this, but it is not obvious how you would calculate the absolute response of a compound from the effusive information you provided, thus I would prefer to see the last step here as well.

Reply: We have now rewritten this paragraph completely.

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P4345 L1-3: Since the authors described their method in detail and the interferences should indeed be small, I agree that it is possible to do so. However there are more compounds in the atmosphere, also in this retention range of the chromatogram. The air in tropical regions contains a lot of alkyl nitrates, which make strong ECD signals (e.g. see Atlas papers) and can be seen in the ECD-chromatogram of an air sample in Quack and Suess (1999) Volatile halogenated hydrocarbons over the western Pacific between 43° and 4°N, which the authors should consider for future work.

Reply: Noted. We will take this point into consideration for future work.

P4345, L25: There is no Scenario B in Warwick et al., (2006), thus please correct and add the amount of emitted compounds used for modelling.

Reply: Scenario B is described in Section 5.1 and Table 3 of Warwick et al. (2006). We have now specified the total flux of Br from organic compounds, and the flux from bromoform, in a new table describing the model scenarios (see below).

P4346 L12-P4347 L2: It is not clear why the authors describe the pressure situation in such a detail, because the entire section could perfectly do without these lines, and still contains all the important information for the data interpretation, thus I would strongly recommend to remove these lines.

Reply: We have reduced the length of the paragraph.

P4348 L22: please exchange...is also thought to be ... with... has been identified as ...

Reply: This sentence has now been revised as suggested.

P4348 L23 -P4349 L7: Since it has been shown in the cited papers, that air coming from the Mauritanian upwelling contain elevated amounts of bromoform, it is misleading to construct an argumentation chain, relating the elevated CHBr₃ concentrations in the air to the primary productivity, since both of the cited pa-

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pers show in detail that there are likely continental or coastal sources contributing to the high bromoform concentrations. Thus the lines should be removed and it is recommended to provide more information on the prevailing back trajectories during the elevated period, and a qualitative statement about the likely coincidence of elevated CHBr₃ encountered in air masses from northwest Africa. This is in better agreement with the recent scientific findings, than a relation to primary productivity which might not be the main source for the elevated CHBr₃, and is thus misleading.

Reply: We have changed the discussion about this point. In particular we discuss both the upwelling and possible West African sources (and refer again to the comments in the Quack et al, 2007b paper), in the context of the trajectories. In particular, we see no evidence for air crossing the continent, except on June 15, the last day of measurements.

P4349 L11-L13: Please suggest an explanation for the elevation of CHBr₃ and the decline in the anthropogenic compounds, otherwise remove this sentence, since this has already been described above.

Reply: We have retained this text. We are trying to emphasise the anti-correlation between anthropogenic and biogenic compounds.

P4349 L17: Here it would also be nice to learn about the obvious diurnal cycle in the data- have the authors suggestions of interpretations for their findings, could the shift in wind direction transport local air from coastal Santo Antao, with macroalgal compounds be the source for the elevation. Are there macro algal beds on the Cape Verde coastlines?

Reply: We have modified the discussion about the diurnal variation (and tried to de-emphasise this to some extent). We believe that diurnal emissions could be important (but have seen no correlation with tidal height). Lucy Carpenter's comments about the diurnal variation in CO point to variations in the boundary layer height playing an

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important role, which we now mention, too. All this discussion now occurs at the end of Section 4.2.2.

P4350, L13, P4351, L5: The authors should provide a table with the varying conditions and emissions and the gridding used for their model runs.

Reply: A table has now been included:

Emission Scenario	Br flux from halocarbons	Br flux from sea salt
MON	Warwick et al. (2006), Scenario B (with a total of 808 Gg Br/yr, of which 564 Gg Br/yr is from CHBr ₃)	Monahan et al. (1986)
NoBr	Zero	Zero
HiBr	As MON, but with elevated CHBr ₃ and CH ₂ Br ₂ emissions from 10-20°N and 20-30°W (see text)	Monahan et al. (1986)
Org	As HiBr	Zero
HiSALT	As HiBr	As MON, but using a higher flux from 10-20°N and 20-30°W, corresponding to a high windspeed of 13ms ⁻¹ (see text)

Table 2. A description of bromine emissions from halocarbons and sea salt aerosol used in the 5 model scenarios.

P 4350 L23 P4351 L 1: It is not completely clear, if the authors always refer to their own modelling work or to the model of Warwick. It should be termed more specific if the authors relate to a specific run or to another model. Please revise the section.

Reply: We have rewritten this section in an attempt to make this clearer.

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P4351 L1-5: These sentences should be merged, because the first one seems not to reflect an applied situation.

Reply: We have clarified the question of diurnal variations.

P 4351 L5; The emissions increased compared to what? Please clarify.

Reply: The emissions increased compared to the MON scenario. We have now clarified this in the text.

P 4351 L11-12: This global emission estimate should be removed in view of the only regional extension of the emissions.

Reply: This global emission estimate has been changed (and the discussion about global emission has been consolidated into Section 5)

P4351 L12-L14: Why should the emission of CH₃I resemble the emission of CHBr₃? Is there any evidence for this, since both compounds have fairly different sources?

Reply: Of course, there is no reason why the emission of CH₃I should resemble that of CHBr₃. The emissions profiles selected for use in the model were simply chosen arbitrarily. We have therefore rewritten this sentence, removing any suggested comparison between the two emission profiles.

P4351 L20-23: Please relate this sentence somehow to the foregoing and remove the relation to a biological source (since there might be no causal relation)- but since the sentence doesn't help the foregoing it can also be removed.

Reply: This whole section has been reworked, following the referee's suggestion to restructure.

P4352 L 4-7: Please put this in the table with model runs and move the sentence upward.

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Reply: We have now added a new table (Table 2), as previously mentioned.

P4352 L15-16: Please specify what you are relating to or remove.

Reply: We have now removed this sentence.

P4353 L14: Here you could include a new paragraph.

Reply: We have rewritten/reordered Sections 4 and 5 in an attempt to improve the readability of the paper.

P4354 L 2: ...is the explanation seems to teleological in this regard... thus please use...could be a likely explanation... or similar wording.

Reply: We have now changed the wording in this sentence to that suggested.

P4355 L6-17: The authors should look at the cause for the minimum ratios, which is the high elevation of CHBr₃, even slightly higher than the emission ratio of 10, which is a ratio found generally at coastlines with macro algal sources...in addition with the published literature this view could help to identify the sources.

Reply: Rather than looking for a specific cause (i.e. source) for the minimum ratio measurements, we have expanded the discussion about Figure 7 and have focused on the underlying assumptions and the inferences that can be drawn from the measurements we have made. The discussion of possible source regions is better kept in Section 4.1 (now revised).

P4356 L3 -8: Here the authors should refer to the literature. Since it is likely not plausible to extend the coastal emission ratio to the global ocean. Or the authors should argue why it should be applicable to do so. Please revise.

Reply: The discussion on emissions is now consolidated in Section 5. We make clear the difficulty of extrapolation but feel that it is still useful to see the differences between bottom-up and top-down approaches.

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P4356 L9 -17: This section does not seem to belong here; it rather belongs to the descriptive paragraph about the Cape Verde observations. There correlations with CHBr_3 have been described, why are now correlations with the longer-lived CH_2Br_2 applied. Please clarify your intention and please reorder the structure.

Reply: We have moved this section as suggested. All the basic correlations are now presented in the same section.

P4356 L12-14: Please clarify, what is meant by this sentence, considering the different sources.

Reply: We have removed this sentence.

P4356 L18: This section is a mix of discussion and conclusion and summary and should be named and ordered accordingly.

Reply: We have now rewritten and reordered Sections 4 and 5 as previously mentioned.

P4357 L7-23: This section would perfectly match behind P4356 L8. And I think it will increase the readability and comprehension of the paper to put it there.

Reply: We have moved this section into the Introduction. It provides a motivation for the use of correlations and we feel is best placed in Section 1.

P4357 L26: Here is an example for the improvement of the papers structure: This argument should have been mentioned much further above, to make the reader aware of the value of the used correlation approach.

Reply: This remains in Section 5, but is consolidated with discussion brought forward (i.e. removed from) from the earlier sections.

P4357 L24 - L6: This would belong into a conclusion section.

Reply: This has been done.

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P4358 L7-L18: Part of this has already been discussed in the results section, thus I would again recommend to combine results and discussion section and only present conclusions and summary at the end of the paper, which would condense the amount of information at the end and have the important discussion parts in the paragraphs, where they have partly been mentioned already.

Reply: This has been done.

RESPONSES TO REVIEWER COMMENTS: ANONYMOUS REF 2

Question a:

Note that the CHBr_3 flux used in the HiBr case should be 173 nmol/d/m^2 but not the number 80 given in the previous manuscript (which was wrongly converted!). The flux of CHBr_3 in the base run MON is 17 nmol/d/m^2 , which is nearly half of the observed value from Quack et al. and Carpenter. We performed an extra model run by using an upper level of CHBr_3 flux of 40 nmol/d/m^2 over the upwelling region (16-20W, 14-20N) and found that this emission only slightly affects the concentrations at Cape Verde, and cannot reproduce the observed high mixing ratios. We have put these experimental results in the paper.

We have also made clear that one aim of our experiments is to see what bromocarbon emission is required to match our observations.

Question b:

We also performed another experiment by using a CHBr_3 flux of 40 nmol/day/m^2 over West Africa coastal regions and found that during that period, the coastal emissions make almost no contribution to the Cape Verde CHBr_3 (as the air parcels reaching Cape Verde actually did not pass very close to the coasts).

Question c:

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We did see seaweed beds at Cape Verde region (this was a purely non-systematic observation). There is also some published evidence (Seaweeds: Their Environment, Biogeography and Ecophysiology by Klaus Lüning, Charles Yarish and Hugh Kirkman; Wiley-Interscience, 1990 (revised ed.), ISBN 0471624349, 9780471624349). A systematic study, in the context of possible emitters, is required. With specific reference to the diurnal variations, see the comments from Lucy Carpenter. We agree that transport could be an important part of this story.

Question d:

The date of the certification of the NOAA standard (December 2005) is now included in section 2.2.

Question 2:

Of course, there are big differences between a 1D model (e.g. the von Glasow et al., 2002) and our 3D model in terms of representation of key processes. In terms of bromine chemistry, one significant difference is likely to lie in the treatment of bromine cycling from source to sink. For example, our 3D model contains very effective wet removal, as both HBr and HOBr are very soluble (an 'effective' Henry's law constant rather than physical constant for HBr is used (Yang et al., 2005), which means there is a strong sink of total inorganic bromine in the 3D model. Certainly, another larger difference between the two models in dealing with sea salt bromine release (under the same wind speed). Our 3D model uses fixed size-dependent bromine depletion factors for sea salt bromine release (Yang et al., 2008a) which are based on global mean observations. This mean depletion factor (DF) implies that only 20-30% of the bromide ion in the sea salt can be released as a bromine source. In the 1D model, the bromine release depends on chemical processes (acid supply or pH), so the bromine deficit in sea salt could be more than 70%. This means, under a similar sea salt loading (or similar surface wind speeds), the Br flux from sea salt in our 3D model is only 1/3 or 1/4 of the Br in the 1D model. We conducted a further model test by assuming that all

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of the Br in the sea salt could be released and found that the simulated daily mean BrO near Cape Verde in June is ~ 1.3 ppt, which reduces the gap between the two models to some extent. Of course, further observations of the sea salt bromine depletion (or deficit) factor and/or pH of particles near Cape Verde are needed in order to get more certainty into the Br flux from sea salt.

RESPONSES TO REVIEWER COMMENTS: LUCY CARPENTER

Question 1:

Thanks for this. We have checked our model CO and find we do catch the significant diurnal variation over Cape Verde during that period, which corresponds well to variations in the local winds. So, we agree that transport is at least part of the answer.

Question 2:

We have changed the text when describing the model used by Read et.al. 2008. As you may see from the reply to referee #2's comment (question 2), the significant difference between our 3D model and a box model (e.g. as used in Read et al) in terms of Br-induced ozone loss is likely due to different Br₂ fluxes in the two models. Our 3D model contains very effective wet removal of inorganic bromine species, while we believe the box model only includes dry deposition. This means that a much stronger Br₂ flux is needed in the 3D than in the box model in order to sustain a similar BrO level, and as a result more ozone loss is simulated (certainly corresponding to a higher Br atom concentration and Br/BrO ratio).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4335, 2009.

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