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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement and modelling of reactive halogen species over the tropical Atlantic Ocean" *by* A. S. Mahajan et al.

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Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean

Mahajan et al.

Response to comments by anonymous referee #2

We thank the referee for the comments on our manuscript. Here we present detailed responses to the questions raised and have made the corresponding changes in the new draft of the manuscript.

This paper presents a dataset of measurements of iodine and bromine monoxides

taken at the Cape Verde islands over an eight months period. These data, and the modeling analysis, complement and expand over the recent reports of the impact of halogens on tropospheric ozone in this region. Therefore I recommend the manuscript is published in ACP, after the authors have addressed a few important points.

GENERAL COMMENTS

R2.1) A key aspect of the paper is the description of long-term measurements of IO and BrO at Cape Verde. These measurements are essential to understand the role played by these species in the tropical MBL. However, the data are shown only in aggregate form. It would be appropriate to show the time series as well, together with some examples of the fits (as mentioned on page 24286), and a discussion of the uncertainties and of the detection limits. Some or all of this information could be provided in the supplement, if not possible in the text.

RESPONSE: The data presented in the manuscript is over 8 months and hence showing the entire timescale, while being able to discern the individual days, is not feasible. The monthly averaged data shows the typical profiles, which were seen on most days and hence were chosen in Figure 1. A detailed discussion on the fitting procedure along with examples of fits and a discussion of the uncertainties and detection limits has already been published in earlier work (as referenced in the manuscript).

R2.2) A large part of the discussion is based upon the fact that the average profiles of IO and BrO show a "top hat" distribution. I am not sure "top hat" is the correct nomenclature (please check this and correct if necessary), but besides this, Figure 1 actually suggests that the profile is quite variable. Sometimes there are distinct peaks in the morning and late afternoon (eg, BrO in March) and it could even be argued that BrO increases throughout the morning and peaks in the afternoon (e.g, February, December). IO in January appears to be lower in the afternoon than in the morning. The error bars are quite large, so it is hard to say whether this is really true and statistically significant, especially since the individual measurements are not shown (see comment

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above). But the authors should clarify this point, because so much of the discussion relies on this particular distribution. I would also encourage the authors to add a similar plot with the medians (or maybe use a box-whiskers plot), because if there are many outliers in the original data the averages might be skewed and bias the analysis.

RESPONSE: We have modified the sentence to remove the words 'top hat' and explain what we mean in the manuscript. We agree that the BrO data is much more scattered in comparison to the IO data, however, on averaging for the whole year, the data shows that the mixing ratios of both BrO and IO do not increase substantially during the daytime from 0900 – 1700 GMT. Considering that the absolute levels of IO and BrO do not exhibit a pronounced change during the year, there is no reason to expect that the diurnal profile would be compromised as a result of averaging either. A higher temporal resolution would indeed be more useful to check if there is a strong variation between the months in the diurnal profile, and this should be the subject of a future study at Cape Verde. The error bars show the standard deviation of the data for each month and hence the extent of the scatter.

R2.3) The calculation about bromine in section 4.1 is not very clear. The authors say 10 ppt of gas-phase bromine to reproduce the observations, but based on the measurements of aerosol volume they estimate release of only 4 ppt? Does this means the aerosol volume should be larger? Is this still within the variability of the aerosol measurements at Cape Verde? And the 12 ppt of Br measured at Cape Verde were aerosol + gas phase or only gas phase? Please clarify.

RESPONSE: The estimate of 4 pptv of bromide available through emission from the aerosol phase is considering that the aerosols are not replenished. If the life time of gas-phase bromine is larger than the replenishment time of fresh sea salt aerosols, then more than 4 pptv of total bromine would be present in the gas phase. This is now made clear in the manuscript, where we explain that the total bromine measured at Cape Verde by Pszenny and Keene is in the gas phase.

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R2.4) The issue of the additional source of iodine is obviously critical to the discussion. The authors tested the model with a continuous and a daytime flux of I2: do they result in the same IO concentration or one is better than the other? Maybe the profile of IO obtained with the two different fluxes should be shown. Figure S4 show a very particular curve, which maybe requires some rationalization in the context of the proposed I2 formation mechanism. The authors claim that the continuos flux results in a post sunrise pulse, which is not really discernible in the model results shown in Fig 3. In addition to this, while it is true that laboratory experiments have suggested a mechanism to generate iodine upon ozone deposition, some of these experiments did not measure I2, but halocarbons and some were conducted in the dark, which is not consistent with the conclusion that a day-time flux gives better results (as claimed on page 24292, line 25). Would a continuous flux generate enough I2 to be detectable by DOAS at night? Please expand the discussion on these issues in section 4.2.

RESPONSE: Both a continuous flux of I2, and the flux used to produce the best fit to the diurnal IO profile (which is shown in the manuscript), can be adjusted to produce the same average daytime IO concentration. Hence, matching the daytime average IO concentration does not discern between them. A continuous emission of I2 causes a diurnal IO profile similar to that produced by the continuous iodocarbon flux (but with higher mixing ratios), except for the post sunrise pulse that is mentioned in the manuscript. We have not included this profile in Figure 3 to maintain its clarity. In contrast, a much better fit to the diurnal profile is achieved using a source flux that is active only during the day time (as mentioned in the manuscript). We are not aware of a laboratory study to examine the role of O3 deposition and photochemistry simultaneously in generating the emission of inorganic (or possibly organic) iodine compounds from sea water. This is certainly something that should be performed. The study by Reeser et al. [J. Phys. Chem. A. 113 8591-8595 (2009)] provides good evidence for the photosensitized release of halides from sea-water. In this paper we simply state what kind of a flux gives the best fit to the IO observations. A continuous flux would still not generate enough I2 during the night time to be observed by the DOAS, which has

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now been made clear in the discussion.

R2.5) The results -and hence the conclusions- seem to be very sensitive to the Kz profile (as stated on page 24292). The authors should comment whether it could be possibile or realistic to use the measured VOIC fluxes and a different Kz profile to explain the IO observations (that is, without invoking a new source of iodine).

RESPONSE: No. The IO concentrations cannot be generated using the measured iodocarbon fluxes without invoking a completely unrealistic diurnal variation in Kz profile. This was the main reasoning behind requiring an additional iodine source, and this is now mentioned in the manuscript.

R2.6) The discussion of IOP formation is well done, but it raises the question about the mechanism. It would appear that only the IO+OIO and OIO+OIO paths were in the model, but not the formation of I2O4 and I2O5 by reaction with ozone. Please clarify and if the mechanism by Saiz-Lopez et al. (2008) has been modified in this regard, please say so. The model predicts that particle formation would be a nighttime process (page 24296, line 8) but wasn't it observed in the afternoon, eg. at Mace Head (Saiz-Lopez et al., 2006) and in this case how would that be consistent with rapid OIO photolysis? This issue would not be relevant in Cape Verde if particle formation is unimportant there, but since it is discussed in the manuscript it should be clarified.

RESPONSE: The latest experiments at the University of Leeds demonstrate that oxidation of I2O3 and I2O4 by ozone is not required to generate IOPs (although these reactions may still occur). This is now made clearer in the text. Iodine particles have indeed been observed in coastal locations such as Mace Head and Brittany during the daytime. However, these observations coincide with low tide, when the huge emission of I2 from exposed macroalgae generates much higher IO mixing ratios than seen at Cape Verde, so that the polymerization of OIO with IO or itself competes effectively with OIO photolysis.

SPECIFIC and TECHNICAL COMMENTS

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R2.7) page 24283, line 9-10: please reword, it seems HOx is being defined as HO2/OH and NOx as NO2/NO

RESPONSE: Reworded.

R2.8) page 24287, line 1: "duration" not "length"

RESPONSE: Changed.

R2.9) page 24288, line 12: is the model referred to here the THAMO model?

RESPONSE: No. This calculation is using a simple box model.

R2.10) page 24289, line 21-22: this sentence is unclear in the context of the previous paragraph.

RESPONSE: Reworded

R2.11) page 24290, line 9-11: are these averages of the measurements at Cape Verde?

RESPONSE: These are typical measured values, i.e. average values after filtering the spikes in the data.

R2.12) page 24291, line 13-16: maybe move the discussion of ozone impact to next section?

RESPONSE: We feel that this sentence is also necessary for further explaining the need for an extra I source. However, the sentence has been elaborated on in the next section.

R2.13) page 24293, line 17-19: is this process included in the model?

RESPONSE: We do not treat horizontal mixing but consider that the air mass is horizontally advected, and hence the distance will be described by the time step.

R2.14) page 24293, line 22: add a reference to Fig. 3

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RESPONSE: Added.

R2.15) page 24293, line 27: figure 4 not 3

RESPONSE: Corrected.

R2.16) page 24294, line 1: "phenomenon"?

RESPONSE: Changed to 'prediction.'

R2.17) page 24291, line 9: does the DOAS and the LIF instrument sample at the same height? Whalley et al. 2009 say they sampled at 3.5 m

RESPONSE: The LIF measured at a height of 3.5 m above the ground, which was about 4-5 m above the ocean surface. Thus the heights are comparable.

R2.18) page 24294, line 12: "reproduce"?

RESPONSE: Yes, as OH is recycled, considering HO2 is mostly formed from the reaction of OH with CO.

R2.19) page 24294, line 21: "seen"?

RESPONSE: Removed.

R2.20) page 24295, line 4-6: please explain that the mechanism explained here refers to BrO and IO, not to OH and this is why they reduce the CCN formation potential.

RESPONSE: We have mentioned that this mechanism is for halogen oxides.

R2.21) page 24296, line 28: how is it determined that it "might" grow large enough and was the 20 nm threshold chosen arbitrarily?

RESPONSE: The reason we say 'might' is because the exact process of particle formation is still not known, as has been made clear in the manuscript. The probability of growth to 20 nm is determined by the rate of growth of the smaller particles relative to the rate of loss to background aerosols. A size of 20 nm was (arbitrarily) chosen for the

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purpose of demonstration, because beyond that size the loss to background aerosols does not compete with further condensational growth and hence the particles have a high probability of survival.

R2.22) page 24297, line 20: "particlescm-3", insert space

RESPONSE: Typesetting error.

R2.23) page 24297, line 26: "dependence of"?

RESPONSE: Corrected.

R2.24) page 24298, line 1: "both the"?

RESPONSE: Corrected.

R2.25) page 24298, line 3: "wider role" than what?

RESPONSE: Corrected.

R2.26) Figures: Fig 1c: please show the detection limits The average detection limits are mentioned in the caption. Fig 2: "between" ... "with", please correct Corrected. Fig 3: add "and IO mixing ratio" to caption Added. Fig 6: show the measurements or mention in the caption Mentioned. Fig 7: please add circle and square next to the color The legend contains the circle and square. Fig S1: the DOAS lightpath is not very visible, would be better in color We have made the figure clearer.

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