Atmos. Chem. Phys. Discuss., 9, C8949–C8953, 2009
www.atmos-chem-phys-discuss.net/9/C8949/2009/

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.

Anonymous Referee #2

Received and published: 23 December 2009

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 modelling 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

- 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 possibile in the text.

- 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 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.

- 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.

- 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.

- 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).

- 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.

SPECIFIC and TECHNICAL COMMENTS

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

page 24287, line 1: "duration" not "length"

page 24288, line 12: is the model referred to here the THAMO model?

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

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

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

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

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

page 24293, line 27: figure 4 not 3

page 24294, line 1: "phenomenon"?

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

page 24294, line 12: "reproduce"?

page 24294, line 21: "seen"?

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 redice the CCN formation potential.

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

page 24297, line 20: "particlescm-3", insert space

page 24297, line 26: "dependence of"?

page 24298, line 1: "both the"?

page 24298, line 3: "wider role" than what?

Fig 1c: please show the detection limits

Fig 2: "between" ... "with", please correct

Fig 3: add "and IO mixing ratio" to caption

Fig 6: show the measurements or mention in the caption

Fig 7: please add circle and square next to the color

Fig S1: the DOAS lightpath is not very visible, would be better in color

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24281, 2009.