Atmos. Chem. Phys. Discuss., 9, C10630–C10635, 2010
www.atmos-chem-phys-discuss.net/9/C10630/2010/

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.

**A. S. Mahajan et al.**

anoop.mahajan@ciac.jccm-csic.es

Received and published: 8 February 2010

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

Response to comments by referee R. Sander

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

Mahajan et al. present interesting measurements and model results of tropospheric halogen chemistry at Cape Verde. I recommend publication of the manuscript in ACP after making some changes as described below.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Major comments

R1.1) I only have one point of scientific criticism: I don't find the explanation very convincing that the missing source of iodine is I2 resulting from ozone deposition. Can you please address my concerns regarding your hypothesis?

– How can you exclude that iodocarbons which were not measured contribute significantly to the iodine source? As far as I understand, several individual iodocarbons were measured but not the sum of organic iodine.

RESPONSE: The fluxes of the major photolabile iodocarbons (CH2I2, CH2ICl and CH2IBr) that can contribute to boundary layer iodine chemistry were measured, and hence we can be reasonably confident that iodocarbons are not a sufficient source for the IO measured at Cape Verde. If there are other iodocarbons that can photolyse within the timescale of boundary layer chemistry, they have not been measured in the atmosphere. This could be due to very short lifetimes, and can thus be treated similar to I2.

– Ozone deposition does not require sun light, thus I cannot see why it should show a strong diurnal cycle.

RESPONSE: Ozone deposition on seawater has been shown to lead to the emission of iodocarbons and possibly I2 (Martino et al., 2009). This process would occur continuously and should not show much of a diurnal cycle. However, there is evidence from the study by Reeser et al. [J. Phys. Chem. A. 113 8591-8595 (2009)] for the photosensitized production of volatile halogen species at the sea surface. If this source dominated (or worked in conjunction with) O3 deposition, this would account for a significant diurnal source of iodine. However, we do not wish to speculate further - we are simply stating in the paper that the diurnal variation of IO seems to require a source that is mostly active during daylight.

– You suggest photochemical production of I2. However, the photolysis of I2 is very

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

fast. Thus I expect photochemical destruction during the day rather than photochemical production.

RESPONSE: This is correct. In fact, the iodine atoms which are produced by organic photochemistry in the sea surface microlayer may be injected directly to the gas-phase even before they recombine to make I2. So the "I2 source" which we have in the model is really a measure of the total flux of I from the surface. More speculation is not warranted until this process has been studied in detail.

Minor comments

R1.2) Title and first line of abstract: I suggest to replace "reactive halogen species" by "reactive tropospheric halogen species". Otherwise, this might also be a paper about stratospheric halogen chemistry.

RESPONSE: Changed accordingly.

R1.3) According to the IUPAC Recommendations (Schwartz & Warneck "Units for use in atmospheric chemistry", Pure & Appl. Chem., 67(8/9), 1377-1406, 1995), the usage of "ppb" and "ppt" is discouraged for several reasons. Instead, "nmol/mol" and "pmol/mol" should be used for gas-phase mole fractions. I suggest to replace the obsolete units.

RESPONSE: Changed accordingly.

R1.4) Abstract and elsewhere in the text: The phrase "total ozone depletion" usually refers to polar ozone depletion events. I think what you are referring to here could be better described as the "sum of all ozone sinks".

RESPONSE: Reworded.

R1.5) Page 24284, line 22: Change "IO was first detected at Mace Head" to "Atmospheric IO was first detected at Mace Head".

RESPONSE: Changed.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

R1.6) Page 24286: Out of curiousity, why do you use NO2 spectra from two different references for retrieving IO and BrO?

RESPONSE: Neither of the the two references covers both the spectral windows needed to retrieve IO and BrO. However, it should be noted that NO2 was under the DOAS detection limit throughout the campaign and would not make a large difference to the retrieval of IO and BrO.

R1.7) The physical properties “mixing ratio” and “concentration” are sometimes used as if they were identical. This is not the case! (for details, see http://www. mpch-mainz.mpg.de/∼sander/res/vol1kg.pdf) Please check all occurences of the word “concentration” in the text and check if it should be “mixing ratio” instead.

RESPONSE: Corrected.

R1.8) Page 24288: As a non-native speaker, I am not entirely sure what you mean by “top-hat variation”. Since you explan that it “is due to the removal of BrO via the reaction with HO2”, I assume that a diurnal variation with a top-hat shape automatically implies a local minimum at noon. Is that correct?

RESPONSE: By ‘top hat’ we meant that the species mixing ratios roughly represented a plateau, with neither increase nor decrease during the daytime. This has now been made clear in the new manuscript.

R1.9) Regarding the model studies that you cite here: Although the results of Vogt et al. and Yang et al. show similar diurnal cycles of BrO, I think that von Glasow et al. 2002a (which you already cite elsewhere) were the first to explain this shape.

RESPONSE: The above mentioned reference is now added.

R1.10) It is difficult to fully understand the model study without knowing the reaction mechanism. I suggest to show the complete reaction mechanism with all rate coefficients in the electronic supplement.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

RESPONSE: The reaction mechanism for the gas phase chemistry has been published in earlier work and has not been changed for the model study presented here. The references to the work are provided in the manuscript.

R1.11) The observatory is at 25âŮę W, thus local time is different from GMT. Could you indicate in the figures that use GMT where the local noon is?

RESPONSE: Added.

R1.12) Page 24293: The sentence "If the observed levels of halogens are now included in the model (1.5 ppt IO and 2.5 ppt BrO)" suggests that IO is prescribed in the model run. Can you please clarify if this is the case? Or is the model producing mixing ratios around this value based on the emissions of iodine?

RESPONSE: The model produces these values based on the emissions of iodine. This has now been made clear.

R1.13) Section 4.6: Several reactions of I2O3, I2O4, and I2O5 are mentioned here briefly. Iodine chemistry is quite complex and not very well-established. Thus, again, it would be good to show the complete iodine reaction mechanism in the supplement.

RESPONSE: The gas phase reaction scheme used is not different from earlier work and is referenced in the manuscript. The particle phase scheme used is still not well known as pointed out. However, we do not use a new scheme here – the proposed mechanism has been recently published and is referenced in the manuscript.

R1.14) Section 4.6: The discussion of the iodine oxide particle (IOP) formation is very interesting but I am missing one aspect of it: When you switch on IOP formation in the model (but leave the iodine emissions unchanged), how does this affect the concentration of IO and thus ozone? I think it would be very interesting to mention this.

RESPONSE: At the levels of IO observed in Cape Verde, there is little change due to the particle formation routine on the predicted IO mixing ratios because most of the higher oxides are lost to uptake on background aerosol. At higher levels of IO, there

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

would be a significant difference to the flux of iodine necessary to sustain IO if particle formation is switched off. This is now mentioned in the manuscript.

R1.15) Page 24297: I suggest to change “The figure shows rather graphically...” to simply “The figure shows...”. How else can a figure show something, if not graphically?

RESPONSE: Corrected.

R1.16) Page 24303, line 6: Add the Umlaut dots to the author “Hönninger”.

RESPONSE: Corrected

R1.17) Table 1: The rate coefficients for the reactions DMS + XO (X=Br,I) have been measured by different groups with different results. Which rate coefficients have you used to obtain the data presented in Tab. 1?

RESPONSE: The references are now mentioned in the table caption.

R1.18) Figure 2: I think the slopes are quite meaningless at these low correlation coefficients. I suggest to remove their values from the caption and only show R2.

RESPONSE: Changed.

---

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

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper