

## ***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 short comment by D. Pöhler.

We thank D. Pöhler for his comments on the manuscript. Presented here are detailed responses to the questions raised and changes are made accordingly to the manuscript.

I like to congratulate the authors to this manuscript which is a very useful supplement

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of the RHS observations at Cape Verde Island presented from Read et al. 2008. Not only the presentation of all measurement data, but also the extensive analysis and modelling, can enhance our understanding of the involved processes. I have a view minor comments (see below), which can hopefully improve the manuscript. I hope they can be involved in a revised version.

R3.1) p. 24283 l. 5 "...while over the last three decades bromine and iodine chemistry have been shown to cause O3 depletion events (ODEs) in the polar tropospheric boundary layer (BL) in the Arctic and Antarctic (e.g., Bottenheim et al., 1986; Barrie et al., 1988; Kreher et al., 1997; Tuckermann et al., 1997; Wessel et al., 1998; Frieß et al., 2004; Jones et al., 2006; Saiz-Lopez et al., 2007a)". Please separate BrO, IO and Arctic and Antarctic clearly, as until now no publication reliable demonstrate the observation of IO in the arctic!

RESPONSE: We have now separated the IO and BrO references as suggested. However, we do not agree that there are no 'reliable' publications on the presence of IO in the Arctic. IO has been positively detected in the Arctic troposphere (Wittrock et al., 2000). In addition, a recent study by Mahajan et al. (submitted to JGR, 2009), shows that IO is present intermittently in the Arctic boundary layer, although at comparatively low levels.

R3.2) 24284 l. 10 "In the mid-latitude MBL, BrO has been positively detected only at three coastal locations: Leser et al. (2003) observed variable levels around the Canary Islands peaking at 2.4 ppt, Saiz-Lopez et al. (2004) saw post sunrise peak levels of 6 ppt with an average of 2 ppt over the day at Mace Head, Ireland, while Mahajan et al. (2009a) reported elevated BrO mixing ratios peaking at 7.5 ppt in the semi-polluted coastal environment at Roscoff, France." & 24289 l. 15 ". . .no studies have been performed in the tropical remote MBL and to our knowledge these are the first measurements of reactive iodine species (RIS) over the tropical open ocean." Close to the Cape Verde measurement site, near the African upwelling region, MAX- DOAS BrO and IO observations were performed in 2007 (Martin et al. 2009). The highest

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observed concentration of 10.2 ppt BrO is reported, but no IO above the detection limit of 0.77ppt could be found!

RESPONSE: The measurements presented in this paper are from work done in 2006-2007 at the Cape Verde observatory. These observations were first published in Read et al. (2008) and this paper further expands on the measurements. Hence we still feel that these are indeed the first measurements of halogen oxides in the tropical open ocean environment. Martin et al. (2009) was accepted into ACP after our manuscript was submitted and was hence not included. We thank you for pointing out that Martin et al. (2009) is now published and we have included the citation in the revised manuscript.

R3.3) 24287 I. 21 "Figure 2 shows the variation of BrO and IO with wind speed." Why a correlation to wind speed is given, even if no correlation to the wind speed is expected from the explained processes, but no correlation to wind direction (or even back trajectory) is shown. Also if the author state that there is no dependency, this correlation plot would be more important to convince the reader.

RESPONSE: It has been suggested that BrO, if mainly emitted by sea salt, should show a wind speed dependence and hence we think that the lack of any such observation is indeed interesting. Additionally, although no wind direction dependence was observed, as mentioned in the manuscript, the back trajectories were mainly from the northeast and hence the wind direction plot, being not very informative, was omitted.

R3.4) 24287 I. 24 "In the case of BrO, all measurements were made when the wind happened to be from the prevailing north-easterly direction, and hence a correlation analysis cannot be made". Why do you not continuously measure all halogen trace gases? Note that also the maximum BrO values were observed for the same wind direction from Martin et al. 2009.

RESPONSE: As mentioned in the manuscript, and in Read et al. (2008), the wind direction was from the north east about 95% of the time. Hence it is not a case of a sparse dataset but rather the prevailing meteorological conditions. We cannot measure

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IO and BrO at the same time using the present DOAS setup due to the different retrieval windows and hence all the species were not measured continuously.

R3.5) 24288 I. 12 "Box model calculations for conditions seen at Cape Verde show that to sustain an average [BrO] of  $\sim 2.8$  ppt, there needs to be a total gas-phase bromine loading of  $\sim 10$  ppt." Can the authors please state on what these calculations are based?

RESPONSE: Box model calculations were done considering similar conditions to the 1-D model, and are described in the manuscript. The only exception is that the BrO observations were used as a constraint in the 1-D model but in the box model, the total Br loading was tuned to reproduce the observed average BrO value during daytime.

R3.6) 24289 I. 1 ". . . indicating that the observed BrO levels can satisfactorily be explained through emissions from sea-salt aerosol." From the authors' conclusion the BrO is emitted from sea salt aerosol, and should therefore be independent from the location in the marine boundary layer. Or at least no strong spatial variation should arise. How can the authors then explain, that on ship MAX-DOAS measurements (Martin et al. 2009, Leser et al. 2003), high local variations of BrO concentration is observed in this area?

RESPONSE: As mentioned in the manuscript, we do not mention that sea salt 'is the only source', but only indicate that it 'can' account for the BrO observations. We do not explore bromine chemistry in detail and do not reproduce the BrO observations in the 1-D model but use the observations as a constraint to reproduce the measured IO. Factors which can cause variability are that the wind-dependence of sea-salt aerosol production, and the role of atmospheric acidity in the release of halogens from sea-salt aerosol. The presence of high local variation is indeed interesting and should be explored in future studies.

R3.7) 24289 I. 21 "Hence, it is probable that these waters represent a large area of increased iodine release. A recent study by Martino et al. (2009) has suggested that

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deposition of O<sub>3</sub> on the ocean surface could lead to the emission of iodocarbons in the presence of dissolved organic matter, which on photolysis could contribute to RIS in the MBL. Fluxes of iodocarbons measured over the open ocean close to the measurement site, as a part of the RHaMBLe campaign, confirm their presence (Jones et al., 2009) and indicate that they could indeed act as a source of RIS in the remote MBL." How can the author explain that IO is only observed at Cape Verde Island with LP- DOAS and not over the ocean with MAX-DOAS (Martin et al. 2009 and other studies)? If the assumed process for Iodide release is based on sea water surface, it can not explain this difference!

RESPONSE: IO has been measured using the LP DOAS over Cape Verde (Read et al., 2008 and this study) and also over Tenerife (Allan et al., 2000), in the north Atlantic Ocean. Both studies observed comparable levels of IO. As shown by the modelling results, the vertical profile of IO should exhibit a strong gradient and hence the measurement technique needs to be highly sensitive to the lowermost region of the MBL. Unfortunately the full treatment of the MAX-DOAS IO data, which strongly depends on the radiative transfer calculations, is not shown in Martin et al. (2009) and hence we cannot draw any direct conclusions. Martin et al. (2009) also assume that the species are well mixed over a 1 km boundary layer and hence calculate an upper limit of 0.77 ppt. If converted into a vertical column, this is much higher than the model predictions (section 4.2). If the fluxes are similar to around Cape Verde, IO should indeed be discernible over the ocean surface in other places but with a strong vertical gradient. Future studies of halogen oxides and source fluxes are necessary to establish whether this is the case.

R3.8) 24293 "The total column abundance predicted by the model is  $9.7 \times 10^{11}$  molecules cm<sup>-2</sup>, which is below the upper limit of  $2 \times 10^{12}$  molecules cm<sup>-2</sup> for current satellite measurements (Schönhardt et al., 2007)." These values make the expression that satellite measurements can almost detect these concentrations. But in reality the satellite detection limit over the ocean is much worse, especially in the lowest layers

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due to: the low surface albedo over the ocean, typical cloud cover, no homogeneous distribution of trace gas over the measurement pixel, low temporal and spatial resolution!

RESPONSE: We agree that the detection limit of the satellites is not as low over the ocean surfaces. However, in Schönhardt et al. (2007) a full treatment of the Air Mass factor is provided with a value of  $\sim 1$  over the mid-latitudinal ocean surface, and the average detection limit over one year is stated in the manuscript. For a single pass, the satellite detection limit is indeed much higher.

New References: Martin, M., D. Pöhler, K. Seitz, R. Sinreich, and U. Platt; BrO measurements over the Eastern North-Atlantic; ACP 9, 9545–9554, 2009. Added

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

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