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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements and modelling of I_2, IO, OIO, BrO and NO_3 in the mid-latitude marine boundary layer" *by* A. Saiz-Lopez et al.

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General comments:

This paper presents measurements by long-path and zenith-sky DOAS instruments of the halogen compounds IO, OIO, I_2, and BrO as well as NO_3. The main findings are that IO has been observed at day and night, OIO at night only, constrained modeling showed that this could be explained by the reaction of I_2 with NO_3. NO_3 was shown to be depleted during some days in the lowest 2 km of the atmosphere, possibly caused by the reaction of DMS. I_2 was measured at night with mixing ratios up to 93 pmol

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mol^{-1}. Previously reported measurements of BrO have been compared with a constrained box model. Not surprisingly, the observed morning peak could be reproduced with a prescribed initial concentration of Br_2; several open questions regarding this modeling remain, as detailed below.

Specific comments:

p. 9732, l. 13 - 15: Please be more precise here. Your modeling didn't show that these amounts of bromine have been released from the sea salt, they have been prescribed and your parameterization of the recycling in the aerosols only showed that it can be kept in the gas phase for one day.

p. 9733, l. 11/12: It might be more helpful to cite the review paper of Sander et al., ACP, 2003, 3, 1301-1336) here or at least mention some of the early papers on this topic, because these depletions have been measured for decades already.

p. 9733, l. 25: It would be appropriate to list Vogt et al. (1999) here as well.

p. 9733, l. 26/27: The rate coefficient of IO with DMS has again been shown to not be fast enough to make this reaction an important sink for DMS (Gravestock et al., 2005, PCCP, 7, 2173 - 2181). To my knowledge, Toumi (1994, GRL, 21, 117 - 120) was the first (based on the data from Barnes et al., 1991) to highlight the importance of BrO + DMS for the budget of DMS.

p. 9738, l. 16-18: To support this statement please report DMS concentrations, so that it can be checked if the magnitude of this process is sufficient to explain the NO_3 decrease.

p. 9738, l. 26/27: See comments below regarding figure 5. Also, please show the actual and not average detection limits as these can differ significantly and for the measurements around detection limits they are necessary to interpret these data points. Do days without measurement symbols on figure 5 imply that the instrument was off or was there really no IO/OIO/I_2 present? On several occasions negative mixing ratios

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seem to have been cut off from the plot without

an explanation, please show the complete data set and explain the negative numbers.

p. 9739, l. 9/10: The time resolution of the data in figure 5 is not good enough to show this. Neither individual data points nor even day-night differences can be seen, please improve. The time resolution for the I_2 measurements is reported to be 30 min, how can you then conclude that the duration of the sharp peaks is 30-45min and not possibly significantly shorter?

p. 9739, l. 25-27: If I_2 were indeed coming from the open ocean, this would be very important information. How much I_2 was present under these conditions? Did you calculate back trajectories to exclude that you have been measuring re-circulated air masses that originated at the coast during low tide?

p. 9740, last paragraph: It would be appropriate to mention the work of Ingham et al, 2000 here, as they could not detect photolysis products in their earlier experiments, suggesting already then a small upper limit for the quantum yield of this reaction.

p. 9742, l. 13: The timing of the iodine species cannot be seen from the figures. According to p. 9735 the iodine species are measured every 30 min; is the delayed increase of OIO a consistent feature of the data set? If so, how long is the delay, the delay of the occurence of OIO in the model run including reaction (1) seems to be shorter than 30min, so do you really reproduce the timing with this additional reaction? Also, please report the I_2 source strength used for the modeling.

p. 9747 and Figure 9: It would be more helpful to show the evolution with time of BrO on all 3 days when BrO was measured to be able to better understand the chemistry. Also, error bars should be shown to confirm that the sunrise peak in BrO is really significant, as it consists only of two data points. In Saiz-Lopez et al. (2004) the whole dataset was published and from that it appears that the strong early morning peak mainly stems from 04. Aug. On 03. Aug a peak was observed only later but not at

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sunrise. An average of 3 significantly varying days is not a good indication that this peak is really consistent. What is the detection limit for BrO?

It is not surprising that prescribing the mentioned Br_2 and BrCl mixing ratios leads to the morning peak in BrO. What would be more interesting is, if it is possible for Mace Head conditions to produce these amounts of Br_2 and BrCl from sea salt aerosol. This is, however, not possible with a constrained model without aqueous phase chemistry.

Why is the decrease of $BrNO_3$ after sunset so slow, even making it the major bromine species at night? According to this, it is a major fraction of NO_y. This might be an indication that constraining NO_x concentrations fixed is not appropriate for this kind of investigation.

According to p. 9747, l. 5, the model is initialized with 10.5 ppt of photolyzable bromine (in form of Br_2 and BrCl), however, the plotted species in Figure 9 only add up to less than 5 ppt at 06:00 but increasing later. What compounds is the remaining bromine in? After the initial photolysis of Br_2 the sum of Br_x seems to decrease - why is that happening?

Overall, the bromine modeling seems to be too much constrained and, in my opinion, does not add much to our knowledge of bromine chemistry in coastal regions.

p. 9748, l. 2: Please note, that Wachsmuth et al. (2002, ACP, 2, 121 - 131) have measured the alpha of HOBr.

p. 9748, l. 7-11: If the acidification of the particles is not taken into account, it would be more appropriate to use teh pH of aged particles, around or lower than pH=5 (see measurements of Bill Keene and Alex Pszenny).

p. 9748, l. 14: How much is that in terms of gas phase bromine mixing ratio? Is it enough to explain the 10.5 ppt Br_2 and BrCl?

Figures:

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On the figures with time series (Figs 1, 5) the conclusions drawn in the text cannot be seen due to the size of the figures. This should be improved.

Fig. 1: The width of the figure should be increased, as it is not possible to really see the evolution with time. Was the instrument switched off at 27./28.8. or was really no NO_3 present?

Fig. 2 and 3.: I would prefer not to overlay the NO_3 measurements with the back trajectories as, esp. in Fig. 3, these graphs overlap.

Fig. 5: The width of the figure should be increased, as it is not possible to tell the evolution with time and not even if the data are day or night time numbers

Fig. 9: See text: please show error bars and detection limit and show the three days of data separately.

References:

Hönninger: use the o-umlaut in text and reference

Truesdale et al: correct "Canosamas" to "Canosa-Mas"

"Glasow, V." vs. "von Glasow": please use "von Glasow" consistently

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9731, 2005.