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Atmospheric Chemistry and Physics Discussions

Interactive comment on "BrO measurements over the Eastern North-Atlantic" *by* M. Martin et al.

M. Martin et al.

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First of all, we would like to thank the Referee for the comments. However, as we disagree in several of the main points the referee made, we want to give in the following some arguments for our standpoint to the reader.
The referee mentions the point, that we present only one vertical column density (VCD), for the time period with the highest BrO slant column densities (SCDs) on February, 18th. We have chosen this special day, as it seemed to us -due to the high slant column densities- the most interesting and reliable one in terms of VCD and concentration calculations. Furthermore, this decision was made based on the following reasons. First, calculations of VCD make only sense if the detected SCD is significantly above the detection limit and also a significant difference in SCD is measured for different elevation angles. Otherwise, the additional error from the modelling will give no reliable VCD. As for the presented time period only the BrO event at February 18th fullfills these criteria sufficiently, only this period was used

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to retrieve VCDs. For all other time periods quantitative discussions could only be made with SCD concentrations. Second, calculating reasonable air mass factors and with them VCDs is a very time-consuming process, which is not always possible to carry out in a given time span. The reviewer mentioned typical retrieved profiles from Max-DOAS measurements. These can only be retrieved with a reliable result, if the absorption signal is much stronger than that of the here presented BrO, or if other measurement setups are chosen (e.g. airborn measurements).

The referee further criticises missing information of dSCD sensitivity compared to VCD. As a basic Max-DOAS setup was used, the highest sensitivity of it is close to the ground (Sinreich et al. (2005)). Measurements were performed down to elevation angles of 1 degree. The results can therefore be compared to measurements at the ground (close above the ocean).

The undertaken IO measurements were not considered insignificant, but below the detection limit and were therefore not further discussed in the paper.

The referee also mentions the point, that we did not compare our measurements to other in situ measurements. This was not possible for us as BrO cannot be measured in situ in the needed accuracy at the detected concentrations. The values we saw can also not be detected by satellites, which will be shown in detail below, a comparison is therefore not possible. Unfortunately no other measurements of halogen species could be carried out during the cruise, as the research vessel Poseidon is limited in scientific equipment. Also no in situ atmospheric ozon measurements were performed, but the expected ozone destruction is below the accuracy of ozone in situ instruments for the measured short BrO event. However, comparison to other measurements is not absolutely necessary, as DOAS remote sensing is less affected to measurement and calibration errors. Furthermore, measurements give reliable values of absorption of trace gases. Additonally, enhanced BrO concentrations were already shown by Leser et al. (2003) and Ibrahim (personal communication) in this region, but the here presented SCD and VCD are much higher and give also additional information on the spatial distribution.

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As BrO measurements are not easy to carry out, scarce in general and especially in this remote region, where nevertheless BrO might play an important role in tropospheric chemistry, we think that the presented work is very interesting for the scientific community. It points out that BrO is an important indicator for very active halogen chemistry in this area, which should be further investigated and also considered for studies of chemical processes. It could also help to improve the knowledge about BrO chemistry in the atmosphere, which still holds several open questions.

Detailed answers to the points mentioned by the referee are given below.

1. Why was this time of year chosen for the cruise, is it a particularly active or inactive phytoplanktion/upwelling time of the year for this region, does this time of year represent stable weather conditions? Is there a reference for SOPRAN, where the aims of the campaign are outlined? Were any supporting in situ bromine measurements also made during this time? It would be useful if how these MAX-DOAS measurements of BrO support the aims of this campaign were given.These measurements do not represent a time of year or location that is known for being extremely convectively active (thus having stratospheric implications for these high BrO values).

Reply: This time of year was chosen as it is the time of peak plankton bloom in this area. It is expected that high plankton plume is correlated to high umpwelling activity and thus to higher halogen activity. As we were investigating tropospheric BrO, which need not have a direct influence on stratospheric BrO, with possible sources in the ocean or coming from the African mainland (as explained in detail in the introduction), this time period was a very interesting one for the undertaken measurements. Max-DOAS is one of the most sensitive and most accurate measurement techniques for BrO, and therefore comparing it to in situ measurements, which have much lower sensitivities, would not give new insights. As during this cruise no other BrO measurements could be performed, no correlation is possible. But it is known that

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in this upwelling region BrO is present. Also measurements at the Cape Verdy Islands proof that (Read et al. (2008)).

2.While meteorological data is referred to a number of times, and some dust measurements are mentioned as a personal communication, no other auxiliary observations were discussed. Supporting satellite observations of BrO at this time and location would strengthen (or not) the case for transport from distant bromine source regions that the authors postulate. It would be appropriate for the authors to support their claim with a back-trajectory study.

Reply: Satellite sensitivity is much lower than that of MAX-DOAS instruments. Assuming the optimum measurement conditions for satellites by making the following assumptions: a)Gome Satellite with best BrO detection limit (personal communication T. Wagner) b) averaging the data over three days (our event is only two hours) with several overflights the best detection limit (2σ) would be $2 \cdot 10^{13} molec/cm^2$ (Richter et al. (1998)) (which does not include less spectra close to the equator). Furthermore assuming c) no clouds and d) a homogenious distribution of BrO over the full measurement pixel (this is very optimistic, as it is a short BrO event and therefore unlikely homogenious distributed over tenth of kilometers) and e) an air mass factor over the ocean of 0.5 (the AMF ranges from 0.2 to 0.5, Wagner et al. (2001), Wagner et al. (2007)) the resulting VCD detection limit would be $4 \cdot 10^{13} molec/cm^2$, and thus above the measured VCD. But one has to keep in mind that we chose the optimum conditions for the satellite, which are not necessarilymet. Therefore, the satellite sensitivity is too low for the detected concentration. This demonstrates that even the observed maximum VCD of $3.6 \cdot 10^{13} molec/cm^2$ is at optimum satellite measurement conditions below the detection limit for satellite measurements. Also we have to consider that a satellite does not overfly the area of interest several times a day, but typically less than once a day. Several typical factors like clouds make the satellite detection limit much worse. (Clouds are considered in the ground AMF calculation, as are inhomogenious

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distribution of BrO, low surface reflection, and more.) Comparison with satellite data are for such an event therefore not possible.
We agree with the referee, that a back-trajectory study would be helpful for the reader. However, it will not give new informations, as a performed back trajectory study gave the same conclusions on the sources as made with the wind directions and therefore was not included in the paper. We will include this study if it improves the manuscript. As the comparison with dust measurements did not give any correlation to the observed BrO values they were not included in the manuscript. They do not give additional information on the source or other to BrO related procceses and can therefore not improve any conclusions from the presented data.

3.The authors outline how the vertical column can be derived from the slant column measurements using the Monte-Carlo derived McArtim air mass factors. However, only differential slant column measurements are presented in the figures.

Reply: As already explained in the general section, we did not derive vertical columns for the whole measurement period, as only for the selected period a reliable VCD could be calculated. However, calculating VCDs with AMFs derived for each period is theoretically possible, but is a very time consuming work and will not give reliable results. Furthermore, although the differential SCDs can not be seen as absoulte quantitative measurements, they still are a qualitative measure of the BrO concentration and therefore of the BrO distribution.

4.Only the VCD for the 18th of February is presented, (because this was the largest) considering this value is central to the conclusions of this paper (the high BrO vmr is quoted in the abstract and conclusion). I believe would be a figure (or two) with the VCDs over the entire cruise period, in both absolute concentration and volume mixing ratio units (with the layer thickness assumptions, this could be achieved with multiple y-axes representing different layer thicknesses).

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Reply: We refer to the Reply to the remark above this one.

Page 9303, line 20. A reference for the 108 value of HO_2 would be good here. Was ozone also detected on board? What do your O_3 slant columns show? Is there evidence to support the halving of the O_3 lifetime along the coastal region?

Reply: No O_3 measurements in the atmosphere were performed during the cruise. But also the expected loss in O_3 would be difficult to see below the general fluctuations and the accuracy of O_3 instruments. Unfortunately,the O_3 SCD can not be used, as the stratospheric signal dominates the SCD (much stronger than for BrO) so that tropospheric concentrations are impossible to retrieve with the required accuracy.

Furthermore, we would like to thank the referee to mention some logical faults to us which shall be corrected.

Leser, H., Hönninger, G., and Platt, U.: MAX-DOAS measurements of BrO and NO2 in the marine boundary layer., Geophys. Res. Lett., 30(10), 1537, doi:10.1029/2002GL015811, 2003. 9292, 9294, 9302

Read, K., Mahajan, A. S., Carpenter, L., Evans, M., Faria, B., Heard, D., Hopkins, J., Lee, J., Moller, S., 5 Lewis, A., Mendes, L., andH. Oetjen, J. M., Saiz-Lopez, A., Pilling, M., and Plane,J.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature, 453, 12328211;1235, 2008. 9294

Richter, A., Wittrock, F., Eisinger, M., and Burrows, J.P.: GOME Observations of Tropospheric BrO in Northern Hemispheric Spring and Summer 1997, Geophys. Res. Lett. 25(14), 26838211;2686, 1998

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9, S2388–S2394, 2009

Sinreich, R., Frieß, U., Wagner, T., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS) of gas and aerosol distributions, Faraday Discuss., 130, 1538211;164, 20 2005. 9299

Wagner, T., Leue, C., Wenig, M., Pfeilsticker, K., and Platt, U.: Spatial and temporal distribution of enhanced boandary layer BrO concentrations measured by the GOME instrument aboard ERS-2, J. Geophys. Res. 106(24), 242258211;24235, 2001

Wagner, T., Ibrahim, O., Sinreich, R., Frieß, U., von Glasow, R., and Platt, U.: Enhanced tropospheric BrO over Antarctic sea ice in mid winter observed by MAX-DOAS on board the research vessel Polarstern, Atmos. Chem. Phys. 7, 31298211;3142, 2007

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9291, 2009.