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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Enhanced tropospheric BrO concentrations over the Antarctic sea ice belt in mid winter observed from MAX-DOAS observations on board the research vessel Polarstern" *by* T. Wagner et al.

T. Wagner et al.

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Reply to the comments of anonymous Referee 4:

First of all we want to thank this referee for the positive assessment of our manuscript and the very helpful comments. We almost completely followed them as outlined in detail below. The questions and recommendations of this and a second referee led us to explore many aspects of our observations in much more detail and we added several new sections to our manuscript. Before we respond to the specific comments, we give a short overview on the major changes with respect to the original version of our manuscript.

A) We carried out a detailed inspection of the sequences of measured BrO DSCDs as function of elevation angle. We found that it is very unlikely that the major part of the boundary layer BrO concentrations is located close to the surface: for no single elevation sequence during the whole campaign, we found the strong increase of the BrO DSCD for decreasing elevation angle, which had to be expected for a BrO layer close to the ground (e.g. within the lowest 200m). Even for days with high visibility, high ceiling height (and also high O4 absorption), the increase of the BrO DSCD from 3° elevation to 1° elevation is similar or even smaller compared to the increase from 6° elevation to 3° elevation. For days with limited visibility, we could of course not completely rule out that the influence of aerosol scattering would mask the effect of a potential surface-near BrO layer. However, the fact that not for a single observation during clear skies the increase of the BrO DSCD from 3° elevation to 1° elevation was as high as to be expected for a surface-near BrO layer, indicates that this is a rather typical finding. One example for the sequence of the BrO DSCD as a function of elevation angle (for a clear day) is added to Fig. 2. The fact that similar findings were not derived from previous MAX-DOAS observations can be explained by the fact that they had not sufficient observations at low elevation angles. For example for the observations of Hönninger and Platt [2002] and Hönninger et al. [2004] the lowest elevation angle was 5°. Thus from their measurements, no fine details on the vertical distribution within the boundary layer could be derived. As suggested by the referee, we performed additional AMF calculations. In Figures 2 and 3 we added the AMFs and DAMFs for additional height profiles (200-400m and 800-1000m). Please note that the assumed (box) profiles might not be representative for the true BrO concentration profiles. Nevertheless, they can give an indication on the overall dependence of the sensitivity of MAXDOAS and satellite observations on the altitude of the BrO layer. We also added results for satellite AMFs for situations with clouds above the BrO layer.

B) We inspected the routine radio sonde observations of meteorological parameters made daily during the ship cruise (see upper air soundings, http://www.awi-bremerhaven.de/MET/Polarstern/raso.html). For many days, it was possible to esti-

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mate the upper edge of the boundary layer from the hieght of the temperature inversion. Especially during July, the boundary layer was often confined to altitudes below 500m. Note that similar low altitudes are typically also found for the ceiling height. Combining this finding with the fact that the maximum BrO concentration is not located close to the surface (as derived from the MAXDOAS observations, see point A), we can only conclude that the maximum of the BrO concentration is very probably located close to the upper edge of the boundary layer. Depending on the vertical thickness of the boundary layer, the layer with maximum BrO concentration might extend over several hundred meters. This finding is in good agreement with the results of the studies of von Glasow and Sander [2001] and von Glasow et al. [2002], who found decreasing pH and also increasing BrO concentrations with increasing altitude. An additional reason for the maximum BrO concentration around the upper edge of the boundary layer might be related to vertical transport processes: while on the one hand the temperature profiles of the radio sonde observations made at Polarstern typically indicate very stable inversion layers, it is on the other hand very probable that often rapid changes of these inversion layers might occur, e.g. when the variation between warm ocean and cold the sea ice surfaces lead to strong temperature gradients. Such convective vertical air motions might cause effective transport of ozone-rich air masses from the free troposphere into the boundary layer and transport of air masses with activated bromine compounds from the boundary layer into the free troposphere. Assuming such transport processes one could expect a maximum BrO concentration around the upper edge of the boundary layer. The existence of strong vertical gradients of BrO and O3 might also have an additional important implication: the observation of an almost continuously enhanced BrO DSCDs during the whole ship cruise within the sea ice would be difficult to explain under the assumption of a continuously stable inversion layer. In this case one would expect that after a few days all O3 should be destroyed and accordingly also no BrO could be formed any more. The observation of continuously enhanced BrO DSCDs indicates that vertical mixing processes and vertical gradients of O3 and BrO might play an important role. Unfortunately, during this ship cruise no ozone data from in-situ

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measurements or ozone sondes are available to compare with our BrO observations.

C) We added a new chapter and new figure (Fig. 1) on bromine chemistry with special emphasis on situations of low sun elevation. We agree with the referee that during low light conditions the balance between BrO and Br/Br2 is shifted towards BrO. This has important implications for the loss rate of BrOx and for the rate of ozone destruction. We also added Roland von Glasow to the authors list. He contributed significantly to the interpretation of our observations.

D) We calculated back trajectories using the HYSPLIT model (http://www.arl.noaa.gov/ready/hysplit4.html). For each day during the cruise we estimated the total time which the air masses had been in contact to the sea ice surface. The comparison to the measured BrO DSCDs with this duration shows a positive correlation similar to that found by Simpson et al. [2007] indicating that increasing contact time increases the amount of activation of bromine compounds.

According to this new findings, we applied also major changes to the abstract and the conclusions. We made some additional minor changes, which are not directly related to suggestions of the referees:

We changed the linear axes of the upper parts of Fig. 4 (Fig. 3 in the original manuscript) into logarithmic axes. This allows a better visibility of values at low altitudes.

We added a Table on the conversion of the BrO DSCDs into mixing ratios for different profile shapes.

This manuscript describes MAX-DOAS measurements of tropospheric BrO made during a cruise through first year sea ice during the Antarctic winter 2006. Enhanced tropospheric BrO was, apart from one exception, continuously observed for a two month period when the ship was within the sea ice area, while outside the sea ice belt mostly only low BrO concentrations were observed. The paper also includes a detailed discus-

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sion of modelled MAX-DOAS AMFs which are important for the proper interpretation of the observed slant columns. The authors put quite some emphasis on discussing the advantages of ground-based MAX-DOAS observations compared to satellite observations and point out why ground-based MAX-DOAS is an important tool for the observations of tropospheric bromine explosion events. The important findings of this study are in short: First, enhanced tropospheric BrO was observed one month earlier than had been previously observed by satellite; second, RT simulations indicate that MAX-DOAS observations are about an order of magnitude more sensitive compared to satellite observations; third, since the sensitivity of MAX-DOAS observations does hardly decrease with large SZA and low albedo, they are very well suited for observing enhanced BrO concentrations in the polar boundary layer. The paper is overall well written and presents some important new results.

Author Reply: Many thanks for this positive assessment.

Specific & technical comments:

Title: I am really struggling a bit with the title, specially the "..observed from MAX-DOAS observations .. "; how about a shorter approach such as: "Enhanced tropospheric BrO over Antarctic sea ice in mid winter observed by shipborne MAX-DOAS"

Author Reply: We changed the title to: ‘Enhanced tropospheric BrO over Antarctic sea ice in mid winter observed by MAX-DOAS on board the research vessel Polarstern’

Page 1824, lines 20-21, abstract: "Furthermore, combination of both techniques .. " This has not been investigated in the manuscript any further and could be part of the conclusions but shouldn’t be in the abstract.

Author Reply: We removed this statement from the abstract

Page 1825, lines 25-29: "remain" should come straight after "questions", not at the end of the sentence.

Author Reply: We changed the text as suggested

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Page 1828, line 12: "glass fibres", should be "quartz fibres" ??

Author Reply: We replaced ‘glass’ by ‘quartz’

Page 1834, line 5: additional space between O4 and deltaSCDs.

Author Reply: This seems to have happened during the copyediting process. In our original text there was no gap.

Page 1834, lines 3-10: Can you speculate why there are times when the near surface BrO is low? Backtrajectory calculations to determine the origin of the observed airmass should be a useful tool to help explain this further. These calculations would also be a very helpful addition for the interpretation of the data set in general and I recommend that the authors should at least look into the possibility to add this to the analysis to strengthen their interpretation of the results.

Author Reply: Many thanks for this important suggestion! We performed back trajectory calculations using the Hysplit model (http://www.arl.noaa.gov/ready/hysplit4.html). It turned out that the magnitude of the observed BrO DSCD was indeed correlated with the duration of contact of the air masses with the sea ice surface. We added a figure showing correlation analysis to the paper. (new Fig. 7) It should however be taken into account that part of the observed variation in the BrO DSCDs might also be caused by variations of the visibility and the profile shape. These dependencies could explain at least part of the scatter of the correlation analysis.

Page 1834, line 8: could remind the reader here what the dates are for the whole period (24 June to 15 August).

Author Reply: We added this information.

Page 1834, lines 16 & 20: dates should be used in a consistent way throughout the paper.

Author Reply: We made the date format consistent throughout the text. One remaining

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exception is Fig. 5 for which the software possibilities for changing the date format are unfortunately limited.

Page 1834, 1 para.: Based on Figure 4, only on 7 July was very low tropospheric BrO observed for the whole day. The authors state that "Days with such large errors include the 6, 7, 11, and 13 July, when the optical density of the residual was up to 3%". Could you put the 3% residual in perspective to the optical density of BrO measured on 7 July? Since this is the only day when low BrO was observed within the sea ice region, is the retrieval quality good enough that this value really holds up??

Author Reply: It is difficult to directly assess the detection limit from the analysis of the measured spectra. In the case of 07.07.2006, the optical depth of BrO is $<$0.02%. It is clear that from spectroscopy alone, no meaningful conclusion on the significance can be drawn. The only reason why we think the low BrO DSCDs on this day might be indeed an indication for low BrO concentrations comes from the comparison to the neighbouring days, for which similar high residuals, but enhanced BrO DSCDs were found. We added some more information on the limited significance of the observed low BrO DSCDs to the text.

Page 1836, 21-23: This statement in the conclusion and abstract is quite strong ("we find that MAX-DOAS observations.. ") while caption of Fig. 1 rather says "Our results indicate that.. ". Are you really sure that you can make the strong statement in the conclusion and abstract based only on this one case study (although admittedly a rather convincing one)?

Author Reply: The only situations, where the sensitivity of MAXDOAS observations is strongly reduced, are cases with limited visibility. Indeed, in such cases the sensitivity of MAXDOAS observations can become zero, while satellite instruments will still ‘see’ part of the BrO. We added the exception of cases with reduced visibility to our statement. To make our statements more consistent, we replaced ‘indicate’ by ‘show’ in the caption of Fig. 2 (Fig. 1 in the original version).

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Fig. 4d: The amount of BrO changes a lot during the two months period. It would be very interesting to see this further investigated. As mentioned above, a study where the observed airmass originates from and how long it has spent in close proximity to the sea ice should help to understand the fluctuations in BrO better. It would also be very interesting to look at in-situ ozone measurements to define if the large tropospheric BrO values coincide with ozone depletion events. If in-situ ozone data is available then this would be a great addition to the results presented here and should really be included in this paper.

Author Reply: Unfortunately no in-situ ozone observations were carried out during the cruise. Also no ozone sondes were launched. We agree that such observations would have made our study much more complete. Concerning the suggestion on trajectory analyses we agree and we used the Hysplit model to perform such studies. We found that the magnitude of the observed BrO DSCDs are indeed positively correlated to the duration of the contact of the air masses to the sea ice surface (see new Fig. 7).

Some of the labels/axis captions in Figures 1,2,3 are quite small; they are readable but if they could be enlarged somewhat that would improve the figures, especially Fig. 3.

Author Reply: We increased the labels and axis captions of figures 1-3. We also increased the sizes of the individual graphs in Fig. 3.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1823, 2007.