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Atmospheric Chemistry and Physics Discussions

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 the referee W. Simpson:

First of all we want to thank the referee W. Simpson 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.

General Comments:

This paper shows interesting data on the abundance of bromine monoxide (BrO) in the Antarctic lower troposphere. Important results include the identification of BrO during winter conditions, seasonally before satellite remote sensing had observed BrO, and the ubiquitous nature of the enhanced BrO at any time that the measurements

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were made in the first-year ice areas. The technical change of using MAXDOAS as compared to satellite-based DOAS is extensively explored and shows that MAXDOAS is much more sensitive to boundary layer BrO under these conditions, which helps to explain why satellite measurements did not observe BrO this early in the winter season. The paper is generally readable. The implications of BrO during winter are not very highly explored.

Author Reply: Many thanks for this positive assessment. We added more information on polar BrO chemistry (see point C above).

Specific Comments:

Point 1: The fact that BrO is observed under winter time conditions is exciting, but barely explored in the manuscript. During day, BrOx are generally partitioned by a balance of the reaction of Br with O3 and the photolysis of BrO (which is Ÿminute timescale for solar zenith angles (SZA) Ÿ80 degrees, corresponding to 10 degree elevation). Some of the data here are for large SZA (even for sun below the horizon). In these conditions, BrO photolysis would not repartition BrOx towards Br atoms, and BrO reactions (not Br reactions) would dominate its loss. Considering a few possible BrO reactions, there is the self reaction of BrO (which is quadratic in [BrO]), possible cross reactions with ClO and IO, the reaction of BrO with dimethyl sulphide (DMS), and the reaction with HO2. Many losses of BrOx actually occur via reactions of Br atoms (e.g. Br + hydrocarbons), and if BrOx spends little time as Br atoms, it might be more stable under these low-light conditions than would otherwise be expected. In the case that higher levels of BrO are present due to less chemistry, that would be interesting to consider. The levels shown, however, are near the threshold where BrO+BrO starts to become fast, and that reaction depletes ozone. What is the inferred loss rate of ozone from the measurements, and how does this compare to ozone measurements (which are not shown, but I'm sure exist in the Polarstern data set)? The manuscript nicely shows that BrO is absent over the unfrozen ocean. The ocean is likely a source of DMS, which reacts with BrO, and may thus provide a sink for BrO that is larger than

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over the ice. For these reasons, I would like the authors to consider discussing the implications of BrO during winter: Are they chemically important or more of a "reservoir" species?

Author Reply: We added more information on polar BrO chemistry (see point C above).

Point 2, particularly in the vicinity of page 1832, line 8 - 21 and also other locations. Various different profiles of BrO and clouds are being explored here to state the sensitivity of the satellite and ground-based techniques for BrO, and I think the statements made are a bit too strong based upon the few number of profiles used. The main issues is the last sentence of this paragraph. In figure 1e, they have explored the case of homogeneous aerosol layers with increasing optical depth and show that you can still see BrO via satellite in the case that the ground is of high albedo and the cloud is somewhat thin (AOD$<$20). However, I would imagine that a cloud like the simulation 1d would have different effects. In that case, a thick cloud that doesn't have BrO within it might shield the BrO from detection. My guess of the radiative transfer could be wrong, but my point is that they have not explored very many situations (particularly common Arctic cloud situations of layer clouds above clear air near the ground) and thus may be overstating the case for the ability to detect BrO via satellite-based measurement in the presence of clouds.

Author Reply: Although it is intuitively not easily understandable, we are convinced that satellite instruments can indeed partly look 'through' clouds, if the surface albedo is high. In addition to the presented case, we derived similar findings for many other cases with clouds above or at the same height as the BrO layer. The main reason for these relatively high AMFs is, that in cases of high ground albedo the probability of photons to be absorbed in the cloud or at the ground is rather low. Thus even photons which penetrated the cloud and have been reflected by the ground have a high chance to penetrate the cloud a second time (in contrast, for cases of low albedo, the number of these photons would be strongly reduced due to absorption at the surface). As stated by the referee in an additional comment, in many cases the surface albedo might be

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even larger than 80%. In such cases, the probability of the photons of penetrating the cloud and correspondingly the AMF for trace gases located below the cloud becomes even higher.

Point 3, page 1833, near line 16, and figures. The calculation shown here seems to imply that the visibility could allow the instrument to view on the order of 57 km, which is not possible, even for a particle-free atmosphere. The Rayleigh limit at 350 nm is around 10 km for a horizontal path at atmospheric pressure. It is clear that the authors know this fact, but the manuscript is not very clear on the point. One way to estimate the effective pathlength (the visibility in the UV) in their calculations is to consider the product of the delta AMF times the vertical path of the layer (when geometric effects do not take the view out of the layer). For the 1 degree elevation without any aerosols, delta AMF = 40, and the vertical path is 0.2km, leading to an effective path of 8km (Fig. 1a). Aerosols make this path shorter, as demonstrated by lower delta AMFs in those simulations. Therefore, to speak of 57 km doesn't make much sense. Another confusion on this point is the Polarstern visibility data. With what wavelength light were these data recorded? It appears that they are for some visible wavelength and the instrument seems to have a maximum of 10km. Please provide some details on the measurements and describe how to consider these data with respect to UV radiation.

Author Reply: Many thanks for this hint. We agree that even for a pure Rayleigh-scattering atmosphere the visibility in the UV would be shorter than 57km. We changed our statement into: 'for an elevation angle of 1° the geometrical light path between the telescope and the cloud base would be 1km / sin(1°) " 57km, which is much larger than the visibility at 350nm for a clear atmosphere'. We added also the following information to the manuscript: 'Please note that the visibility is measured from the backscattered light of a xenon flash light in the visible spectral range (Videograph III von Impulsphysik); also the sensed volume is restricted to a distance $<$13m from the instrument. In some cases the visibilities measured by this instrument might not be fully representative for those which control the MAX-DOAS observations. The MAX-DOAS

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observations typically sense a much larger volume, especially also higher altitudes. In addition, especially for fine aerosols, the wavelength dependence of aerosol scattering might lead to slightly shorter visibilities in the UV spectral range.'

Point 4, page 1835 bottom and 1836, bottom. It is argued that the conversion between deltaSCD and concentration is "not very sensitive to assumed altitude range". This argument is based upon believing BrO is present in box-profiles with constant concentrations from the surface to some maximal height. The vertical profile is very likely to be more complex than their assumed profiles due to stable stratification that is common in the boundary layer over ice during wintertime. If the vertical profile is more complex, then the conversions they present here are not correct. Additionally, the high degree of nonlinearity of ozone depletion chemistry induced by the quadratic pressure dependence of the BrO-BrO self reaction means that there is a high sensitivity to concentration in terms of the chemistry. Therefore, a change from 26 to 51 ppt of BrO (doubling the concentration) would cause a 4-fold increase in the rate of the BrO-BrO self reaction, which is clearly not trivial. The conversion from deltaSCD data to concentrations, possibly including "hotspots" in the vertical dimension is complex, and the MAXDOAS data should not be overinterpreted.

Author Reply: We agree and we performed the conversion for much more profiles. We summarised the results in a new table. Our main conclusion is that for typical profiles during the ship cruise (see points A and B above), the derived mixing ratios are indeed rather high. We added a detailed discussion in the new section 5.3 and in the conclusions.

Technical Corrections:

Page 1825, line 7, the acronym GOME appears to not be defined (if this is the first usage).

Author Reply: We added the full name here.

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Page 1825, line 14, it is stated "areas covered by so called frost flowers". The reference does not actually detect frost flowers, but instead a proxy called "potential frost flowers", which are "areas potentially covered by frost flowers". Add the word "potential" between "areas" and "covered" to be in agreement with the reference.

Author Reply: We added ‘potentially’ between ‘areas’ and ‘covered’

Page 1825, line 20, our group has recently published a paper indicating that potential frost flowers (PFF) are not a good indicator of BrO at Barrow, Alaska (Simpson et al., ACP 7, 621, 2007). This reference is relevant to the discussion of production of reactive halogen species from young sea ice. The current paper does not specifically state where the BrO came from; only that it is correlated with first year ice and likely new ice formation (e.g. nylas, leads, etc.). That choice to not identify a source is reasonable given that the current paper does not present a way to separate ice influences; however, it would be interesting to do a trajectory or other analysis of the BrO data presented here to see if PFF is a good indicator for these data or not. I would encourage the authors to do such analysis in a separate paper and simply note the relevant reference here. A good reference to mechanisms for salts getting into snow on sea ice is Domine et al., (2004). Additionally, in Antarctica, there is another mechanism of salt injection into snow on sea ice - the snow’s weight can "sink" the sea ice causing brine to percolate upwards through the brine channels. This apparently makes Antarctic sea ice and snow on that ice very saline.

Author Reply: We indeed performed some trajectory analyses (see new section 5.2 and new Fig. 7). However, we agree with the referee that a detailed study to investigate the specific type of source is beyond the scope of paper. From our simple trajectory study, it was possible to relate the magnitude of the observed BrO DSCDs to the duration of the contact of the air masses to the ice covered surface, and we find a positive correlation like in Simpson et al. [2007]. We agree that it would be interesting to investigate the relation of our observations to the details of the surface properties in a future study. We added the suggested references to our manuscript.

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Page 1826, line 14-19. Two cases related to spatial averaging in satellite data are discussed. I would also see the case of short length scale BrO variations not being well represented in satellite retrievals, although I think it is not clear if any short length scale BrO variations exist. Please reword or generalize to cover all possible cases.

Author Reply: We added the sentence: 'In general, it is not possible to directly retrieve information about spatial gradients on scales with smaller dimension than the ground pixel size of satellite observations.' We also changed the first sentence of this chapter to 'Another important question concerns the spatial homogeneity and extension of the air masses of enhanced BrO concentrations.'

Page 1826, lines 22-23. The word "clouds" is used in two senses here (and I think a couple other places). One meaning is water clouds, and the other is BrO "clouds". I think it this becomes confusing. Possibly eliminate "clouds of enhanced BrO" and replace with "regions of enhanced BrO". Then, clouds could be used for water clouds.

Author Reply: We replaced (BrO) 'clouds' by 'air masses'

Page 1826, line 26. The statement that BrO has only been observed "very close to" first year ice is not true. Hoenninger and Platt (2002) shows a high level of BrO at Alert, Canada, which is quite distant from young ice. Also, satellite images commonly show enhanced BrO over the land west of Hudson's bay, over the North Slope of Alaska, and over Russia. While I agree that most BrO is associated with newer ice, it certainly can transport over snow-covered land, multi-year ice, and possibly over ocean.

Author Reply: Many thanks for this hint. We changed 'only' to 'mainly'

page 1827, line 17. Replace "towards" with "to"

Author Reply: corrected

page 1827, line 22. I think that the main point of this sentence is not that you can unambiguously detect BL BrO over oceans with MAXDOAS, but more that you can detect its absence with MAXDOAS (while satellites are essentially insensitive).

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Author Reply: We changed the sentence into ‘Thus, in contrast to satellite observations, low BrO DSCDs measured by MAXDOAS unambiguously indicate low boundary layer BrO concentrations over the open ocean.’

page 1828, line 12. I think the fibers are quartz not glass.

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

page 1829, line 15. Was no warmer ozone spectrum used? Typically a warmer temperature of ozone spectrum is used to fit for tropospheric ozone. If no warmer spectrum was used, what allowed this simplification (spectral region, lack of variability from the Fraunhaufer reference spectrum)?

Author Reply: Typically for MAXDOAS retrievals, most of the stratospheric absorptions cancels out, because the stratospheric AMF is very similar for the different elevation angles. Thus any signal of O3 absorption can be either attributed to a) tropospheric ozone or b) remaining small differences in the stratospheric AMF. From our experience we found that the O3 absorptions detected in the MAXDOAS analyses were very small (typically below one permille). Especially for the O4 analysis we found no significant difference if we included a single O3 spectrum for different temperatures, or even two O3 spectra. This can mainly be related to the fact that we analysed each measurement with the zenith spectra of the same elevation sequence.

Page 1831, line 9, remove the word "on" at the end of the line"

Author Reply: Corrected

Page 1831, line 14. An albedo of 80% is used in the simulations. This is fine for this publication, but in the future, the authors should consider using 90% or even 95%. The UV albedo of snow is quite high (see Warren (1982) or many other spectral albedo references).

Author Reply: From our radiative transfer simulations for MAXDOAS observations we found that the dependence of the sensitivity on the surface albedo is very small. And

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even for satellite observations, the relative influence of variations in the surface albedo decreases for increasing albedo (meaning that an increase in surface albedo from 2% to 4% would have a much stronger effect on the sensitivity than an increase from 80% to 82%). Nevertheless, we agree that snow can have even higher albedo that 80%, and we are thankful for the hint. We included a statement on the albedo of snow and the reference in our manuscript.

Page 1831, lines 24-26. These two sentences are awkward. What does "slant" mean here? Please reword.

Author Reply: We reworded this part of the text and added more explanation.

Page 1834, top of page, and Fig. 3. Please color the data points by their elevation angles and disconnect the lines. These changes would make it easier to read the plots and remove spurious lines (like those at the beginning and end of days).

Author Reply: We changed the figure as suggested.

Page 1834, lines 20, 28, and maybe other places. Two styles of dates are used. On the mentioned lines, dates are listed like 17 June, while in other locations dates are listed as 17.06. Please make the date format clear and consistent throughout the text.

Author Reply: We made the date format consistent throughout the text. One remaining exception is Fig. 5 for which the software possibilities for changing the date format are unfortunately limited.

References

Domine, F., R. Sparapani, A. Ianniello, and H. J. Beine (2004), The origin of sea salt in snow on Arctic sea ice and in coastal regions, Atmos. Chem. Phys., 4, 2259-2271.

Author Reply: We added this reference to the manuscript.

Hoenninger, G., and U. Platt (2002), Observations of BrO and its vertical distribution during surface ozone depletion at Alert, Atmos. Env., 36, 2481-2490.

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Author Reply: corrected

Simpson, W. R., D. Carlson, G. Hoenninger, T. A. Douglas, M. Sturm, D. K. Perovich, and U. Platt (2007), First-year sea-ice contact predicts bromine monoxide (BrO) levels better than potential frost flower contact, Atmos. Chem. Phys., 7, 621 - 627.

Author Reply: We added this reference to the manuscript.

Warren, S. (1982), Optical properties of snow, Rev. Geophys. Space. Phy., 20, 67-89.

Author Reply: We added this reference to the manuscript.

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