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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.

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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 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.

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 ˜minute timescale for solar zenith angles (SZA) ˜80 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 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?



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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.

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.



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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.

Technical Corrections:

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

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.

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 reason-



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able 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.

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.

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.

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.

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

page 1827, line 22. I think that the main point of this sentence is not that you can unambigously 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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page 1828, line 12. I think the fibers are quartz not glass.

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)?

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

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).

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

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).

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.

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.

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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better than potential frost flower contact, Atmos. Chem. Phys., 7, 621 - 627.

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