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Comment

## ***Interactive comment on “DMS and MSA measurements in the Antarctic boundary layer: impact of BrO on MSA production” by K. A. Read et al.***

**K. A. Read et al.**

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The authors thank Referee 1 for their comments and have responded to them point by point below.

### General Comments

Comment: A number of assumptions were made that cannot be easily justified particularly when using data from different years without considering interannual variability in these parameters where your own data shows that most if not all components do show a fair to strong interannual variability.

Response: To clarify, wherever possible actual measurements were used throughout

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the analysis of this paper and this holds for all DMS, MSA, and BrO calculations. OH had to be assumed for the first summer as did FT non-DMS sulphate concentrations for the whole period because there were no available measurements. Additional detail has now been included to clarify the assumptions that were made and justification in making those assumptions. See specific comments below regarding the FT non-DMS sulphate (from previous long-term measurements of 210Pb) and also regarding the OH.

Comment: Overall- regarding the importance of BrO chemistry you might want to add that satellite measurements clearly show that BrO is present in the Antarctic spring all around the Antarctic coastline and that ship-borne measurements in first year sea ice show BrO appearance about a month earlier than satellites, i.e. already in late winter (Wagner et al., ACP, 7, 3129-3142, 2007). Response: Done.

#### Specific comments

pptV "concentrations" have been replaced with "mixing ratios".

The abstract has been altered to include the implication of these findings for the interpretation of ice cores.

p.2658, l. 12: "Conflicting" has been replaced with "alternative".

p.2658. l. 25: "from....oceanic sources from dimethylsulphoniopropionate" has been replaced with "via DMS from the breakdown of dimethylsulphoniopropionate (DMSP) present in phytoplankton".

p.2658. l. 26: "small injections" has been replaced with "intermittent injections".

p.2659, l.1-6. This sentence was concerned with putting the measurements from this paper into context and so referred specifically to the region detailed within this manuscript. At high southern latitudes in the oceanic regions DMS is the main source for oxidised sulphur compounds in the atmosphere because anthropogenic sources of SO<sub>2</sub> are significantly lower (Gondwe et al., 2003). The sentence now includes the

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context and reads:-

"..dimethyl sulphide (DMS), mainly dominated by the smaller biogenic inputs (Liss et al., 1997), is the major source of oxidised sulphur compounds at high southern latitudes away from direct continental source emissions of SO<sub>2</sub> (Gondwe et al., 2003)."

p.2661, l.7: Done.

p.2663, l.6: molecules cm<sup>-3</sup> has been added.

p.2664, 2nd para: There are peaks of 75 pptV and 63 pptV on the 14th and 22nd of October respectively, and at the beginning of November mixing ratios begin to rise and there are also peaks of 175 pptV and 126 pptV in late November. Low temperatures (<260 K) coupled with higher wind speeds (16-20 m/s) around the continent at this time (Jones et al., 2007) ensure that in addition to having an extended atmospheric lifetime allowing transport from further north in a few days, the sea-air flux of DMS from the polynas is also likely to be enhanced as a result of the higher wind speeds (Berresheim et al, 1998b). The following text has been added: -

"Peaks in October and late November of up to 175 pptV are harder to attribute to exact sources, however at these times the wind speed around the continent reached 20 m/s (Jones et al., 2007), which is expected to enhance sea-air flux of this species from local areas of open water in addition to increasing the rate of transport from further north."

p. 2665, l. 12: "particles" has been replaced with "ions".

p.2666, l. 8: The bracketed section now reads "(R<sub>2</sub> = 0.039 and R<sub>2</sub> = 0.001 for MSA and derived nss-SO<sub>4</sub><sup>2-</sup> respectively)".

p. 2666, l. 20-22: The monthly variation between January and February is lower than the 1 sigma standard deviations on the actual measurements. The sentence has been rewritten to emphasise this:-

"Levels of oxidants such as OH and BrO measured at the site show little month to

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month variation with respect to the 1 sigma standard deviations on the average measurements (January, 0.018 +/- 0.013 pptV and 1.9 +/- 3.0 pptV respectively compared to February, 0.015 +/- 0.009 pptV and 2.7 +/- 2.2 pptV respectively), however these are local measurements and may not be representative of the oxidant levels along the back trajectory of the air mass."

p. 2666, l. 27: Reference was duplicated so has been removed.

p.2669, l.13-14: The sentence has been rewritten to account for the abstraction route of MSA formation but the second of these alternative routes (via the reaction of DMSO+OH) has been accounted for by the fact that we assume that only one third of DMSO becomes MSA later in the manuscript. The amended sentence now reads:-

"An alternative route for the production of MSA exists via the abstraction channel but it is a much more complex route involving NO<sub>2</sub> chemistry (Von Glasow et al., 2004). Considering that in the Antarctic environment NO<sub>2</sub> mixing ratios are typically < 15 pptV this alternative route is considered a negligible source of MSA."

p.2669, l. 15- p.2670 l. 5: The value for FT non-DMS sulphate for coastal Antarctica proposed by Minikin et al., (1998), was an average calculated using 210Pb data obtained over a number of years from Neumeyer (1983-1995), Dumont D'Urville (1991-1995), and Halley (1991-1992). It is nonetheless true that there must be interannual variability which therefore adds some uncertainty and errors of +/- 5 ng m<sup>-3</sup> and +/- 13 ng m<sup>-3</sup> for winter and summer respectively were used by Legrand and Pasteur, (1998) when they did the same calculation. We have also applied these uncertainties here and as a result have included them in both the main text and within error bars on Figure 6. This uncertainty could be substantial in winter but is unlikely to be so much in summer (compare +/- 13 ng m<sup>-3</sup> with values of nss-sulfate of around 200 ng m<sup>-3</sup>).

P.2670, l. 25: "although" replaced with "because".

p.2670, l. 29: Previous measurements of OH in Coastal Antarctica for February 1994

show mean 24hr values of  $1.1 \times 10^5$  molecules  $\text{cm}^{-3}$  (Jefferson et al., 1998) which agree within 43 percent of the measured OH here ( $2.6 \times 10^5$  molecules  $\text{cm}^{-3}$  for February). The typical maximum daily OH values were also similar with  $7 \times 10^5$  molecules  $\text{cm}^{-3}$  for the Palmer study comparing well with the maximum of  $7.9 \times 10^5$  molecules  $\text{cm}^{-3}$  observed in 2005 (Bloss et al, 2007). In addition, using a 24hr value for OH of  $1.1 \times 10^5$  molecules  $\text{cm}^{-3}$  rather than  $3.9 \times 10^5$  molecules  $\text{cm}^{-3}$  (Bloss et al, 2007) leads on average to an increase in our calculated MSA of 3 pptV which for the most part is not significant. The phrase "for consistency between the two summers" has been removed and the sentence now reads:-

"OH measurements only began in December 2004-February 2005 and so an average 24 hour value of  $3.9 \times 10^5$  molecules  $\text{cm}^{-3}$  (0.012 pptV) was used for the analysis of both summers. Previous measurements made eleven years earlier show values in good agreement for February (Jefferson et al., 1998)."

p.2671, Discussion of equation 3: Changing delta t only affects the actual MSA concentration not the relative impact of the two oxidants which is the important aspect of this study. The data used in the later Figure 9 is however calculated using varying in situ measured [OH], [BrO] and [DMS], and therefore has fewer assumptions. Although it is only for summer 2005, it does provide a very accurate picture of how the relative rate of production of DMSO (and therefore MSA) would change with temporally changing oxidants.

p.2672, l.2.: "[MSA]" added to end of sentence.

p.2672, l. 6: The authors agree that it is very easy to access data regarding the total sea ice cover variability between the two years however it would take a significant amount of work to discover whether the areas where there was no cover or gaps in the cover (e.g. polynas) correlate with the chlorophyll distribution and the trajectory that a specific air mass has taken. In fact the sea ice cover in 2005 (5.0 million sq km) was significantly less than in 2004 (5.8 million sq km) (Fetterer et al., 2002), which implies

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that this isn't the reason for the lower concentrations at the site. The difference in trajectories between the two years is the far more likely explanation for the interannual variability. Having said that, this section is referring to whether the site DMS mixing ratios were realistic numbers to use for the calculation of MSA at this time and so considering the trajectories the conclusion is that they are too low. DMS was likely to be higher at source and the reason for the lower values of DMS at the site is because over the continent there are fewer fresh emissions, the air becomes more aged and DMS reacts to make MSA. The sentence in question has therefore been removed because it was not relevant for the explanation and the previous sentence has been adjusted to clarify the effect of the contrasting trajectories: -

"The air mass trajectories show more air has travelled over the continent in 2005 rather than from the northern sea regions (Fig. 4b) implying that the site received more aged air and had fewer fresh emission injections compared to 2004; so the DMS mixing ratios measured at the site may not be representative of those at the source."

p.2672, l. 18/19: Done.

p.2672, l. 24-26: The reference has been changed from Von Glasow et al., (2002b) to Von Glasow et al., (2004). 2002b has been altered to 2002 throughout the paper.

p.2673, l. 2: The sentence now reads: - "Although this modelling study was fairly crude, higher measured ratios compared to model predictions such as these which neglect to include BrO, may also imply an influence from this source."

p.2673, l.17: "in situ" has been changed to "locally measured".

p.2673. l.24: "the measured MSA" has been added.

p.2674, l. 8: Typo, Figure 10 has been changed to Figure 9.

p.2673/2674: l. 23: "good" has been replaced with "better".

p.2674, l.19: Done.

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p.2674, l. 21: Done.

p. 2675, last para: This paper in effect goes some way to quantify, using measurements; some of the modelling work previously performed by Von Glasow et al, (2002), and (2004) and so have common implications. A reference to the work of Von Glasow, (2002) has however been included in this section.

p.2675, section 6.1: The suggestion of a relationship of BrO with sea ice comes mainly from the GOME data (Hollwedel et al., 2004), but also from studies using back trajectories at Neumeyer. A reference to the AICI review paper (Simpson et al., 2007), which contains both GOME maps and the Friess diagram has been added into the manuscript text at this point. The authors were aware that Cosme et al., (2005) did not include halogens, and this reference was there to refer to the modelling techniques rather than to their inclusion. The sentence has been rewritten however to clarify this:

"Modelling studies (Cosme et al., 2005) for S compounds have not yet included a realistic assessment of BrO, or its spatial and vertical distribution, which will be needed to determine whether BrO is really a major influence."

p.2675, l. 20. Done.

References: All required alterations made.

Tables 1: A depletion or excess of chloride can arise from the reaction of sea salt with acids (such as sulfuric acid), and as in previous studies (Wagenbach et al., 1998, Rankin and Wolff, 2003) in this study we observe a slight depletion of chloride in summer and an excess in winter. The higher Cl-/Na+ ratio seen here is most likely because a larger proportion of the sea salt in this study occurred in winter when compared to the 2001 study, which affects the average ratio.

2: "Reaction rates" has been changed to "reaction rate coefficients".

The quality of all figures has been improved.

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