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Atmospheric Chemistry and Physics Discussions

Interactive comment on "DMS and MSA measurements in the Antarctic boundary layer: impact ofBrO on MSA production" *by* K. A. Read et al.

Anonymous Referee #1

Received and published: 2 April 2008

Read et al. present very interesting measurements of dimethyl sulphide (DMS) and its particulate oxidation products MSA and nss-SO_4^{2-} from Halley Station, Antarctica, for the duration of the CHABLIS campaign. They find a lack of correlation between DMS and the oxidation products. They discuss the different oxidation routes and show estimates of the relative importance of the oxidation of DMS by BrO compared to OH, finding that BrO is a key oxidant under these conditions.

Overall I think that this is an important contribution to the field and should be published after minor modifications. The weakest point is probably the quantitative assessment because a number of assumptions were made that cannot easily be justified (I won't

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Interactive Discussion
Discussion Paper

comment on rate coefficients as this has been done in 2 previous interactive comments). This is esp. true 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. Overall - regarding the importance of BrO chemistry, which was questioned by one of the interactive comments - 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; see this paper for a number of refences to the satellite work). This information might also be useful to at least qualitatively discuss BrO levels during the transport to Halley.

Specific comments

The paper seems to be written somewhat hastily given the number of grammar mistakes, incomplete references and sentences. Please improve this for the final version. Some incidents are highlighted below.

Please note throughout the text, tables and figures that when you refer to "ppt" you are referring to mixing ratios and not to concentrations.

Abstract: Maybe you want to add that this might have implications for the interpretation of ice cores?

p. 2658, l. 12: "Conflicting" is probably not the right word here, rather "different".

p. 2658, l. 25: Please rephrase to avoid that the reader thinks that DMSP is a direct source for sulphur - DMSP breakdown in the ocean releases DMS which then degasses.

p. 2658, l. 26: Volcanic emissions are a very large and relevant source of SO_2, especially because most of it is emitted into the free troposphere where deposition rates are smaller than in the MBL.

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Interactive Comment

p. 2659, l. 1-6: In the absence of clouds the lifetime of SO_2 is longer than that of DMS. Anthropogenic SO_2 is the dominant source of oxidised sulphur to the atmosphere - please rephrase.

p. 2661, l. 7: Niemeyer → Neumayer

p. 2663, l. 6: Unit missing.

p. 2664, 2nd para: Are these sources sufficient to explain the DMS peaks in October and November?

p. 2665, l. 12: MSA and SO_4^{2-} are not particles, please rephrase.

p. 2666, l. 8: Please be specific what compounds you are referring to with the two correlation coefficients.

p. 2666, l. 20-22: Please be careful with the words "little" and "variation" - the variation (which is, I assume, what you are listing in brackets) is very large. Also the BrO mixing ratio in February is 70% higher than in January.

p. 2666, l. 27: Reference is not complete ("et al.").

p. 2669, l. 13-14: What do you base your assumptions on to ignore alternative oxidation routes?

p. 2669, l. 15 - p. 2670, l. 5: What about interannual variability? You can't just take measurements from a random year and assume that you can use these numbers for a quantitative analysis of a different year. Please add an explanation and some statements about this assumption and the consequences. The numbers resulting from these calculations should be treated with a lot of caution!

p. 2670, l. 25: "although" → "because"?

p. 2670, l. 29: Again you use data from different years for your quantitative analysis! Why is it "consistent" to use data from the wrong year in OH when your data show

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a fairly strong difference between the 2 years in all the other compounds that were measured?

p. 2671, Discussion of equation 3: Again you use numbers that are likely not appropriate for your case. However this time you state that this assumption introduces some error. In order to show the relevance of the different oxidation pathways you should probably do more of a sensitivity analysis with a range of numbers than trying to stick to exact measured values which are, however, not from the relevant time period.

p. 2672, l. 2, end of line: Word missing.

p. 2672, l. 6: It is very easy to find out what the sea ice cover in summer 2005 was, so please don't use expressions like "may" in this context.

p. 2672, l. 18/19: Grammar incorrect, please adjust plural/singular.

p. 2672, l. 24 - 26: Reference is not complete ("et al."), also why cite "2002b" when you only cite one paper from these authors from 2002? Also, in this paper no global estimates were made. This was done by Boucher et al., ACP, 2003 and von Glasow et al., ACP, 2004.

p. 2673, l. 2: Note that Gondwe et al. used a very simple oxidation scheme with fixed yields for the different oxidation products.

p. 2673, l. 17: The BrO values are not *in situ* but averaged over the length of the light path, however the second half of the sentence remains true.

p. 2673, l. 24: "overestimates" - what? Word missing.

p. 2674, l. 8: You probably refer to figure 9 here?

p. 2673/2674: I think, that you are a bit too positive when describing "agreement" of your calculations with the measurements. The agreement with the measured data is a lot better than without including BrO as oxidant but the absolute numbers are still quite different, esp. for 2005.

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p. 2674, l. 19: Delete first occurrence of "in".

p. 2674, l. 21: Delete "as".

p. 2675, last para: I agree that this is an important statement but I have seen this at least once before in a different paper, actually one that you cite: von Glasow et al. (2002), paragraph 28.

p. 2675, section 6.1: You seem to equate high BrO with large sea ice extent - what is this based on? Can you be more specific on lines 10 and 11? Why do you cite Cosme et al in this context? They explicitly say that their model does not include BrO chemistry. If this is what you want to point out here, please rephrase to make it more obvious.

p. 2675, l. 20: Please insert "aerosol" before "filter".

References:

Overall: please add the initials consistently according to the ACP style guide - you sometimes list them before sometimes after the last name.

Falbe Hansen: Please change NO3 to NO_3.

Frieß etal. : Please correct the spelling of the first author.

Ingham et al.: This paper was published 8 years earlier!

Legrand and Pasteur: "acide" → "acid"

Tables

Table 1: Do you have an explanation why Cl^- is so strongly enriched (looking at the Cl^-/Na^+ ratio) both with regard to the 2001 measurements and sea water?

Table 2: You are listing reaction rate coefficients not reaction rates. This term has also been used incorrectly in the text.

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Figures

The quality of all figures is fairly poor, please improve for the final version of the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2657, 2008.