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Atmospheric
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Discussions

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

K. A. Read et al.

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The authors thank Referee 2 for his comments and have responded to them below.

1) Does 10e3 refer to a rate coefficient or a rate times an assumed concentration?

Response: The authors agree that the statement in item 2660, line 22 is clearly wrong whether you consider 10e3 as a rate coefficient or as a rate times an assumed concentration. Table 2 highlights the rate coefficients for both the OH and BrO with DMS reactions and the OH + DMS reaction is clearly faster by a factor of 4. If one assumes typical global concentrations of OH and BrO of 1x10e6 molecules cm-3 (Bloss et al, 2005) and 4.5x10e7 molecules cm-3 (1.5 pptv) (Von Glasow, 2004) respectively, the rate of oxidation of DMS is 10 times (not 10e3 times) faster by BrO rather than by its reaction with OH. Although Antarctic values for these species (lower [OH], higher [BrO]) may increase this by up to a factor of 30 to 300 times, the text value of 10e3 is still in major error. As this particular discussion is regarding laboratory experiments, the authors have replaced the sentence in error with the following:-

In recent years the rate of reaction of DMS + Br has been explored and found to be 60 percent faster than previously reported by Barnes et al (1991), leading to a rate which is less than one order of magnitude slower than that for DMS + OH (Ingham et al, 1999). Considering BrO is often present in significantly higher atmospheric concentrations than OH this has an important impact on the rate of production of DMSO and hence also of MSA via the DMS + BrO route.

2) In the corrected version an OH concentration of 1 x 10e5 rather than 3 x 10e5 is used, but is this assumed as an annual average? If so how is this applied to calculate DMSO/MSA production, because when OH is high, so is the DMS concentration, but under local winter condition both are low? Can a reasonable estimate of how [OH] varies with time be used to calculate DMSO/MSA production?

Response: The corrected OH value of 1 x 10e5 molecules cm-3 detailed in the authors response to M. Legrand was used only for the calculation of a DMS lifetime during winter (Section 4.1, last sentence), not for the calculations of DMSO and MSA production later in the paper. The authors calculate DMSO and MSA production for only the summer periods (December-March) for which a constant value of 3x10e5 molecules cm-3 was used for [OH] (measured 24hr average during January-February 2005, Bloss et al, 2007). As a constant value of BrO is also used in the calculations rather than a temporally varying one, the relative contributions to DMSO via each of the BrO and OH routes can be accurately compared without the need to use changing [OH]; particularly as the aim was not to recreate DMSO and MSA concentrations directly. The data in Figure 9 however is calculated using varying in situ measured [OH], [BrO] and [DMS], which although is only for summer 2005, does provide a more accurate picture of how the relative rate of production of DMSO would change with temporally changing oxidants.

3) What filter data is said to appear to correlate?

Response: Item 2676, line 3 has been rewritten to include additional detail of the filter data being discussed:-

The biweekly SO42-, MSA and derived nss-SO42- filter data appears to correlate with the DMS data in that they show maximum values in summer and minimum in winter but in reality the data show very low regression values with DMS due to the infrequency and differences in sampling rates of the filter data, in addition to the various complexities in the rate of oxidation to form these products.

References

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