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

M. Legrand

legrand@lgge.obs.ujf-grenoble.fr

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Minor comments:

Introduction: Line 30: your statement that DMS measurements at DDU are mainly focused on the summer period is incorrect (see Preunkert et al. [2007] in which winter values are shown over several entire winters). The variability of DMS levels was also shown to be strongly controlled by the state of the marine biota (see Preunkert et al. [2007]).

Experimental section: Are you sure that fluoride is a major anion in these regions ?

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Section 4.1: For Dumont d’Urville, you only refer to the DMS summer value in 1999 (290 pptv). However as discussed by Preunkert et al. [2007] this year was not typical and in fact summer DMS 1999-2003 values at Dumont d’Urville range from 60 pptv in 2003 to 244 pptv in 2002.

At the end of the section you discuss DMS winter levels: the mentioned value in 1999 at DDU was in fact not correct due to contamination by the pump membrane (see details in Preunkert et al. [2007]). Mean winter DMS levels (June-October) exhibit rather constant values at DDU (from 13 pptv in 2001 to 16 pptv in 2002).

Last sentence: From June to August the OH concentrations would be far lower than 3 105 molecule cm-3 and the DMS lifetime with respect to OH reactions far higher than 10 days. Note also that your 10 days value conflict the 23 days reported in Table 2 for summer (see my major comment below).

Major comments

I have a major problem with you kinetic calculations. The last update of kinetic can be found in Atkinson et al. [2006]:

K1 = 1.12 10-11 e-250/T K2 = (9.5 10-39 [O2] e5270/T)/(1+7.5 10-29 [O2] e5610/T)

So at 260 K, K1 is equal to 4.3 10-12 and K2 to 2 10-11. Therefore, your assumed OH concentration of 3 105 molecule cm-3 would lead to a lifetime of DMS with respect to OH (K2, addition pathway) of 2 days (the value of 23 days you reported in Table 2 seems to be calculated with K1 of the abstraction pathway). Therefore it is not correct to say that BrO controls the DMS lifetime.

In Figure 9, I think you also used incorrect kinetics: just comparing the two production terms in equation 4, if we assume an averaged OH concentrations of 3 105 and BrO concentrations of 7.5 107 (˜3 pptv), β1 k2 [OH] [DMS] = 4.8 10-6 [DMS] and β2 k5 [BrO] [DMS] = 2.4 10-6 [DMS]. That does not fit with your plots in Figure 9.

For K4 (heterogeneous reaction of DMSO), you have used a value empirically deduced from field observations by Legrand et al. [2001]. But this process has been later on quantified by kinetic studies [Bardouki et al., 2002]. The efficiency of this process is also discussed in Barnes et al. [2006]. I think you should try to use these approaches for your calculations.

In conclusion your paper is important since showing that at least at your site (well exposed to high brO levels) the role of BrO is significant with respect to OH. But the erroneous calculations of the present version tend to suggest that BrO almost totally control the DMSO production and this statement is clearly incorrect.

Bardouki, H., M. Barcellos da Rosa, N. Mihalopoulos, W.-U. Palm, and C. Zetzsch (2002), Kinetics and mechanism of the oxidation of dimethylsulfoxide (DMSO) and methanesulfinate (MSI-) by OH radicals in aqueous medium, Atmos. Envir., 36, 4627-4634.

Barnes, I., J. Hjorth, and N. Mihalopoulos (2006), Dimethyl sulphide and dimethyl sulfoxide and their oxidation in the atmosphere, Chem. Rev., 106, 940-975.

Atkinson, R., R. Cox, J. Crowley, R. Hampson Jr., and R. Hynes (2006), Summary of evaluated kinetic and photochemical data for atmospheric chemistry, section 1, Ox, HOx, NOx, and SOx reactions, http ://www.iupac-kinetic.ch.cam.ac.uk/.

Preunkert, S., M. Legrand, B. Jourdain, C. Moulin, S. Belviso, N. Kasamatsu, M. Fukuchi, and T. Hirawake, Interannual variability of dimethylsulfide in air and seawater and its atmospheric oxidation by-products (methanesulfonate and sulfate) at Dumont d’Urville (Coastal Antarctica) (1999-2003), J. Geophys. Res., 112, doi:10.1029/2006JD007585, 2007.

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