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DMS and MSA measurements in the Antarctic Boundary Layer: impact of BrO on MSA production

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Abstract. In situ measurements of dimethyl sulphide (DMS) and methane sulphonic acid (MSA) were made at Halley Station, Antarctica (75°35' S, 26° 19' W) during February 2004–February 2005 as part of the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) project. DMS was present in the atmosphere at Halley all year (average 38.1±43 pptV) with a maximum monthly average value of 113.6±52 pptV in February 2004 coinciding temporally with a minimum in sea extent. Whilst seasonal variability and interannual variability can be attributed to a number of factors, short term variability appeared strongly dependent on air mass origin and trajectory pressure height. The MSA and derived non-sea salt sulphate (nss-SO_4^{2-}) measurements showed no correlation with those of DMS (regression R^2=0.039, and R^2=0.001 respectively) in-line with the complexity of DMS fluxes, alternative oxidation routes, transport of air masses and variable spatial coverage of both sea-ice and phytoplankton. MSA was generally low throughout the year, with an annual average of 42 ng m^{-3} (9.8±13.2 pptV), however MSA: nss-SO_4^{2-} ratios were high implying a dominance of the addition oxidation route for DMS. Including BrO measurements into MSA production calculations demonstrated the significance of BrO on DMS oxidation within this region of the atmosphere in austral summer. Assuming an 80% yield of DMSO from the reaction of DMS+BrO, an atmospheric concentration of BrO equal to 3 pptV increased the calculated MSA production from DMS by a factor of 9 above that obtained when considering only reaction with the hydroxyl radical. These findings have significant atmospheric implications, but may also impact on the interpretation of ice cores which previously relied on the understanding of MSA and nss-SO_4^{2-} chemistry to provide information on environmental conditions such as sea ice extent and the origins of sulphur within the ice.

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