

Towards an advanced description and modelling of the multiphase DMS chemistry: CAPRAM DMS module 1.0

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Oceans cover approximately 70 % of earth's surface and are the general emitter of dimethyl sulphide (DMS), the major natural sulphur source (ANDREAE, 1990). The main DMS oxidation products are methyl sulfonic acid (MSA) and sulphate. Hence, DMS is of high importance for the formation of non-sea salt sulphate aerosol (nss-SO₄²⁻) and secondary particulate matter and thus very important for global climate. Despite many previous model studies of the DMS oxidation, there are still important knowledge gaps, especially in aqueous phase DMS chemistry, of its atmospheric fate (BARNES ET AL., 2006).

To close these gaps, a comprehensive multiphase DMS chemistry mechanism, the CAPRAM DMS module 1.0 (DM1.0), has been developed. The newly developed reaction module includes 103 gas phase reactions, 5 phase transfers and 54 aqueous phase reactions. The DM1.0 has been coupled with the multiphase chemistry mechanism MCMv3.2/CAPRAM4.0α+HM2.1 (BRÄUER ET AL., 2013; BRÄUER ET AL., 2015; RICKARD ET AL., 2015) to investigate the multiphase DMS oxidation in the marine boundary layer (MBL). Therefore, a pristine ocean scenario was simulated using the 0-D air parcel model SPACCIM (WOLKE ET AL., 2005). The scenario includes non-permanent clouds with 8 cloud passages of the air parcel - 4 at noon and 4 at midnight. The cloud passages allow the investigation of the influence of deliquesced particles and clouds on multiphase DMS chemistry during both daytime and nighttime conditions. Advantageously, even multiphase DMS chemistry under cloud formation and evaporation can be investigated. To test the influence of various subsystems on multiphase DMS chemistry different sensitivity runs have been performed. Investigations of multiphase chemistry of DMS and its important oxidation products are done using concentration-time profiles and detailed time-resolved reaction flux analyses. The flux analyses determine the most important chemical cycles and help to understand the time evolution of the concentration profiles. The model results are also compared to previous model studies and atmospheric measurements.

The model studies revealed the importance of aqueous phase chemistry for DMS and its oxidation products. Overall about 21.4 % of DMS is effectively oxidised by O₃ in the aqueous phase of clouds. Furthermore, modifications in multiphase DMS chemistry after cloud passages are noticeable. For different sensitivity runs the conversion efficiency of DMS to SO₂ in the gas phase was simulated between 0.30 and 0.6 for the pristine ocean scenario run and a simulation without treating aqueous phase chemistry of DMS, respectively. The studies indicate that the thermal decomposition of CH₃SO₃ is the main contributor to gas phase production of H₂SO₄ from DMS oxidation. Contrary to other studies, the DM1.0 contains aqueous phase production of MSA from reactions of methyl sulphinic acid (MSIA) with O₃. Therewith, the simulations were able for the first time to capture measured MSA aerosol concentration levels of about 0.22 to 0.26 µg m⁻³. The MSA yield for different sensitivity runs was simulated between 0.02 and 0.32, which is much higher compared to current implementations in higher scale models. The lowest yield is reached treating only gas phase chemistry of DMS. The simulations showed that in a pristine MBL only 2.3 % of the produced MSA is further oxidized. Furthermore, the simulation with the whole mechanism indicate that multiphase DMS oxidation produce as much MSA as sulphate leading to strong implications for nss-SO₄²⁻ formation, activation to cloud condensation nuclei and cloud albedo over oceans. Therefore, future modelling should consider those processes.

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