

Towards an operational CAPRAM multiphase halogen and DMS chemistry treatment in the chemistry transport model COSMO-MUSCAT

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Oceans are the general emitter of dimethyl sulfide (DMS), the major natural sulfur source, and halides and cover approximately 70 % of Earth's surface. The main DMS oxidation products are SO₂, H₂SO₄ and methyl sulfonic acid (MSA). Hence, DMS is very important for formation of non-sea salt sulfate (nss-SO₄²⁻) aerosols and secondary particulate matter and thus global climate. Reactive halogen compounds, activated by multiphase chemistry processes, are known to effectively deplete ozone, oxidise VOCs (especially DMS under marine conditions) and remove NO_x from the atmosphere by conversion into particulate nitrate. Despite many previous model studies, a detailed representation of the multiphase chemistry occurring in aqueous aerosols and cloud droplets in CTMs is still missing. To develop a detailed representation, a manual reduction of near-explicit multiphase chemistry mechanisms by means of detailed box model studies has been performed. The mechanism has been developed from the near-explicit DMS and halogen multiphase chemistry mechanism, CAPRAM DM1.0 and CAPRAM HM3. The reduced mechanism is evaluated by process model studies. Comparisons of simulations performed with the explicit and reduced mechanism reveals that the deviations are below 5 % for key inorganic and organic air pollutants and oxidants under pristine ocean and polluted coastal conditions, respectively.

Subsequently, the reduced mechanism has been implemented into the chemical transport model COSMO-MUSCAT and tested by 2D-simulations. Simulations are performed for two different meteorological scenarios mimicking unstable and stable weather conditions over the pristine ocean. The simulations demonstrate that the modelled concentrations of important halogen compounds such as HCl and BrO agree with ambient measurements demonstrating the applicability of the mechanism for tropospheric modelling investigations.

The 2D studies with the reduced mechanism are carried out to examine the oxidation pathways of DMS in a cloudy marine atmosphere in detail. They have shown that clouds have both a direct and an indirect photochemical effect on the multiphase processing of DMS and its oxidation products. The direct photochemical effect is related to in-cloud chemistry that leads to high DMSO oxidation rates and subsequently an enhanced formation of methane sulfonic acid compared to aerosol chemistry. The indirect photochemical effect is characterised by cloud shading, particularly in the case of stratiform clouds. The lower photolysis rates below the clouds affects strongly the activation of Br atoms and lowers the formation of BrO radicals. The corresponding DMS oxidation flux is particularly lowered under thick optical clouds. Besides, high updraft velocities lead to a strong vertical mixing of DMS into the free troposphere predominately under convective conditions. Furthermore, clouds reduce the photolysis of hypohalogeneous acids (HOX, X=Cl, Br, I) resulting in higher HOX-driven sulfite oxidation rates in aqueous aerosol particles below clouds.