Operational CAPRAM multiphase halogen and DMS chemistry in the CTM COSMO-MUSCAT

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Oceans cover approximately 70 % of Earth's surface and are the general emitter of dimethyl sulfide (DMS), the major natural sulfur source, and halides. The oxidation of DMS by multiphase chemistry processes is very important for formation of non-sea salt sulfate (nss-SO_4^{2-}) aerosols (von Glasow und Crutzen, 2004) 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 (Saiz-Lopez und von Glasow, 2012; Schmidt et al., 2016). Despite many previous model studies, a detailed representation of the multiphase chemistry occurring in aqueous aerosols and cloud droplets in CTMs is still missing.

Here, we present the development of a comprehensive multiphase chemistry mechanism that deals the multiphase chemistry of DMS and reactive halogen compounds. This mechanism was developed based on a manual reduction of near-explicit multiphase chemistry mechanisms by means of detailed box model studies. The mechanism has been developed from the near-explicit DMS and halogen multiphase chemistry mechanism, CAPRAM DM1.0 (Hoffmann et al., 2016) and CAPRAM HM3 (Hoffmann et al., 2019). The reduced mechanism has been validated by comparing simulations performed with the explicit and reduced mechanism. The comparison reveals that the deviations are below 5% for key inorganic and organic air pollutants and oxidants under both pristine ocean and polluted coastal conditions, respectively.

Afterwards, 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 convective and stable weather conditions over the pristine ocean. The simulations show 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 are further used to examine the oxidation pathways of DMS in a cloudy marine atmosphere in detail. The simulations imply 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 dimethyl sulfoxide (DMSO) oxidation rates and subsequently to an enhanced formation of methane sulfonic acid (MSA) 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 Cl/Br atoms and lowers the formation of BrO radicals. The corresponding DMS oxidation flux is particularly lowered under thick optical clouds. Furthermore, high updraft velocities lead to a strong vertical mixing of DMS into the free troposphere predominately under convective conditions.

E. H. Hoffmann, A. Tilgner, R. Schrödner, P. Bräuer, R. Wolke und H. Herrmann (2016) *Proc. Natl. Acad. Sci. USA*, **113**, 11776-11781.

E. H. Hoffmann, A. Tilgner, U. Vogelsberg, R. Wolke und H. Herrmann (2019) *ACS Earth Space Chem.*, **3**, 2452-2471.

A. Saiz-Lopez und R. von Glasow (2012) *Chem. Soc. Rev.*, **41**, 6448-6472.

J. Schmidt, D. Jacob, H. Horowitz, L. Hu, T. Sherwen, M. Evans, Q. Liang, R. Suleiman, D. Oram, M. Le Breton, C. Percival, S. Wang, B. Dix und R. Volkamer (2016) **121**, 11819-11835.

R. von Glasow und P. J. Crutzen (2004) *Atmos Chem Phys*, **4**, 589-608.