

Final report for Project **1128**

Project title: **Investigation of the influence of air pollution on DMS and its role in the Earth's climate**

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The focus of this project was to investigate the importance of dimethyl sulfide (DMS) oxidation, the largest natural sulfur source into the atmosphere, but also on how oxidation of other chemical substances, i.e., isoprene, effect the atmospheric composition. Moreover, the effect of wildfire related intrusion of gases and particles into the atmosphere was simulated. To achieve the investigations simulations with the chemistry-climate model ECHAM6.3-HAM2.3-MOZ1.0 were performed. From the project results several publications at high-ranking journals were achieved. These are listed at the end. In the following the main results will be summarized.

The first chemical subsystem under investigation was the oxidation of DMS and how it is affected when the chemical mechanism is changed. Therefore, the DMS oxidation scheme in ECHAM-HAMMOZ, that lacked current advancements in DMS chemistry, was updated and extended to better describe the representation of the state-of-the-art. The first investigations focused on better description and representation of gas-phase MSA concentrations. For this purpose, the DMS oxidation has been updated to comprise an extension of the addition channel to yield the known stable oxidation products MSIA and DMSO₂, a simplification of the H-atom abstraction channel and a particle acidity dependent reactive uptake of MSIA on aerosol surfaces to be in line with the importance of multiphase chemistry on MSA formation. Afterwards, global simulations have been performed and compared with MSA gas-phase measurements at the Northern and Southern Hemisphere for the year 2017, to verify the simulations. In addition, sensitivity studies have been performed in which the made changes were successively incorporated to see the effect of different changes. In these sensitivity studies strong differences have been simulated regarding the yield of gas-phase MSA, SO₂ and H₂SO₄ and related formation of sulfate. Subsequently, effects on the radiative budget in the Arctic region have been simulated. It could be shown that the consideration of the reactive uptake of MSIA increased the performance to compare simulated with field measurements for gas-phase MSA. In a next step the developed DMS oxidation scheme for H-atom abstraction was enhanced to deal recent laboratory finding with regards to the formation of HPMTF and also the gas-phase oxidation of MSIA. An adjunct global simulation focused on the amount of H₂SO₃ formation by OH radical related MSIA oxidation in the gas phase, a compound that was believed it cannot be formed in the gas phase. A high amount of H₂SO₃ formation in the gas phase is modelled. Hence, the simulation indicates that the further chemical processing of H₂SO₃ and effects on the atmospheric formation and growth of particles has to be performed.

Another chemical subsystem under investigation was the oxidation scheme of isoprene. Laboratory and theoretical work showed the formation of hydrotrioxides (ROOOH) from the reaction of organic peroxy radicals with the OH radical. A reaction sequence of RO₂ radicals from isoprene oxidation by the OH radical to yield ROOOH and further oxidise these were included into the default HAMMOZ chemistry scheme. After the implementation global simulations were performed that focus on the importance of this reaction sequence on global scale. For this purpose, the new reaction sequence has been compared to the currently included RO₂ reactions of isoprene. The main focus of this study was to estimate the proportion of this channel in comparison to the classical RO₂ reactions and provide an annual production rate of ROOOH from isoprene oxidation. Globally, it is modelled that around 1% of formed RO₂ from isoprene reacts with OH radicals ending up into a formation of up to 10 million metric tons of the hydrotrioxide. Other simulations of isoprene oxidation by the OH radical focused on the formation of highly oxidised molecules (HOMs) under different NO_x conditions. The amount of formed HOMs from isoprene was calculated offline using the simulated loss rates of isoprene derived RO₂. Finally, these values were compared to the HOM yields from alpha-pinene oxidation by the OH radical as well as ozone.

To model wildfire related changes on the atmospheric composition, two fire episodes (i) California

wildfires in 2017 and (ii) Australian bushfires in 2019 were simulated. The focus was on the Australian bushfires and how these effected the evolution of the ozone hole. For the Australian bushfire simulation, a setup designed for ECHAM-HAM was already available and used. Five simulations were performed, divided into three simulations dealing sole aerosol particle emission from the wildfires and two simulations with aerosol particle, NO_x and VOC emission into the stratosphere. The simulations results were compared with the monthly averaged ozone column measurements provided at the NASA Ozone Watch website (<https://ozonewatch.gsfc.nasa.gov>, last access: 16 June 2023). The comparison with the measurements and the default simulation revealed that the strong ozone hole observed during September and October 2020 can be simulated, when aerosol particles are emitted into the stratosphere, solely. However, a simulation with deactivated radiative forcing through the emitted aerosol particles reveal also a shrinking of the ozone hole. Overall, the simulations revealed that it is import to dedicate the emission height of particles and VOCs by wildfires in global models, to accurately simulate changes in the atmosphere.