Modelling the photochemical formation of high \( \text{H}_2\text{O}_2 \) concentrations and secondary sulfate observed during winter haze periods in the NCP

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During winter, the North China Plain (NCP) is frequently characterized by severe haze conditions connected with extremely high PM2.5 and NOx concentrations, i.e. strong air pollution. The NCP is one of the most populated regions worldwide where haze periods have direct health effects. Tropospheric haze particles are a complex multiphase and multi-component environment, in which multiphase chemical processes are able to alter the chemical aerosol composition and deduced physical aerosol properties and can strongly contribute to air pollution. Despite many past investigations, the chemical haze processing is still uncertain and represents a challenge to atmospheric chemistry research. Recent NCP studies during autumn/winter 2017 haze periods have revealed unexpected high \( \text{H}_2\text{O}_2 \) concentrations of about 1 ppb suggesting \( \text{H}_2\text{O}_2 \) as a potential contributor to secondary PM2.5 mass, e.g., due to sulfur(IV) oxidation. However, the multiphase \( \text{H}_2\text{O}_2 \) formation under such NOx concentrations is still unclear. Therefore, the present study aimed at the examination of potential multiphase \( \text{H}_2\text{O}_2 \) formation pathways, and the feedback on sulfur oxidation.

Multiphase chemistry simulations of a measurement campaign in the NCP are performed with the box model SPACCIM. The multiphase chemistry model within SPACCIM contains the gas-phase mechanism MCMv3.2 and the aqueous-phase mechanism CAPRAM4.0 together with both its aromatics module CAPRAM-AM1.0 and its halogen module CAPRAM-HM2.1. Furthermore, based on available literature data, the multiphase chemistry mechanism is extended considering further multiphase formation pathways of HONO and an advanced HOx mechanism scheme enabling higher in-situ \( \text{H}_2\text{O}_2 \) formations in haze particles. The simulations have been performed for three periods characterized by high \( \text{H}_2\text{O}_2 \) concentrations, high RH and PM2.5 conditions and high measurement data availability. Several sensitivity runs have been performed examining the impact of the soluble transition metal ion (TMI) content on the predicted \( \text{H}_2\text{O}_2 \) formation.

Simulations with the improved multiphase chemistry mechanism show a good agreement of the modelled \( \text{H}_2\text{O}_2 \) concentrations with field data. The modelled \( \text{H}_2\text{O}_2 \) concentration shows a
substantial dependency on the soluble TMI content. Higher soluble TMI contents result in higher H$_2$O$_2$ concentrations demonstrating the strong influence of TMI chemistry in haze particles on H$_2$O$_2$ formation. The analysis of the chemical production and sink fluxes reveals that a huge fraction of the multiphase HO$_2$ radicals and nearly all of the subsequently formed reaction product H$_2$O$_2$ is produced in-situ within the haze particles and does not origin from the gas phase. Further chemical analyses show that, during the morning hours, the aqueous-phase reaction of H$_2$O$_2$ with S(IV) contributes considerably to S(VI) formation beside the HONO related formation of sulfuric acid by OH in the gas-phase.

Finally, a parameterization was developed to study the particle-phase H$_2$O$_2$ formations as potential source with the global model ECHAM-HAMMOZ. The performed global modelling identifies an increase of gas-phase H$_2$O$_2$ by a factor of 2.8 through the newly identified particle chemistry. Overall, the study demonstrated that photochemical reactions of HULIS and TMIs in particles are an important H$_2$O$_2$ source leading to increased particle sulfate formation.