Modelling the Multiphase Formation of High H_2O_2 Concentrations Observed during Winter Haze Periods in the NCP

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Introduction

During winter, the North China Plain (NCP) is frequently characterized by severe haze conditions connected with extremely high $PM_{2.5}$ and NO_x concentrations, i.e. strong air pollution. 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 H_2O_2 concentrations of about 1 ppb suggesting H_2O_2 as a potential contributor to secondary $PM_{2.5}$ mass, e.g., due to sulphur(IV) oxidation in haze particles. However, the multiphase H_2O_2 formation under such NO_x concentrations is still unclear. Therefore, the present study aimed at the examination of potential multiphase H_2O_2 formation pathways, and the feedback on sulphur(IV) oxidation.

Methods

Multiphase chemistry simulations of the measurement campaign are performed with the box model framework SPACCIM. SPACCIM contains the gas-phase mechanism MCMv3.2 (Jenkin et al., 2003; Saunders et al., 2003) and the aqueous-phase mechanism CAPRAM4.0 (Bräuer 2015) together with both its aromatics module CAPRAM-AM1.0 (Hoffmann et al., 2018) and its halogen module CAPRAM-HM2.1 (Hoffmann et al., 2019). Furthermore, based on available literature data, the multiphase chemistry mechanism is extended considering an advanced HO_x mechanism scheme enabling higher in-situ H_2O_2 formations in haze particles. The simulations have been performed for three periods characterized by high H_2O_2 concentrations, high RH and $PM_{2.5}$ 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 H_2O_2 formation.

Conclusions

Simulations with the improved multiphase chemistry mechanism shows a good agreement of the modelled H_2O_2 concentrations with field data. The modelled H_2O_2 concentration shows a substantial dependency on the soluble TMI content. Higher soluble TMI contents result in higher H_2O_2 concentrations demonstrating the strong influence of TMI chemistry in haze particles on H_2O_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_2O_2 is produced in-situ within the haze particles and does not origin from the gas phase. Further chemical analyses show that the aqueous-phase reaction of H_2O_2 with sulphur(IV) contributes considerably to sulphur(VI) formation beside the HONO related formation of sulfuric acid by OH in the gas-phase. Therewith, the simulations demonstrate that an improved knowledge of chemical haze interactions is crucial to interpret the chemical gas and aqueous composition observed during highly polluted haze conditions.

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