Modelling the non-ideal chemical processing in aqueous aerosol particles with SPACCIM-SpactMod

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Highly-polluted urban regions are often characterized by high aerosol particle loadings impacting atmospheric chemistry and, hence, air quality. Tropospheric deliquesced particles including haze particles are a complex multiphase and multi-component environment with simultaneously occurring multiphase chemical transformations. Such chemical processes are able to alter the chemical composition and the deduced physical aerosol properties. Deliquesced particles are characterised by concentrated non-ideal solutions ('aerosol liquid water' or ALW) that can affect the occurring multiphase chemical processing. The effects of such non-ideal solutions have generally not been adequately investigated by present complex multiphase chemistry models. Thus, the present study is aimed at accessing the impact of non-ideality on multiphase chemical processing. Therefore, simulations with a multiphase chemistry model (SPACCIM-SpactMod) including the CAPRAM chemical mechanism are performed for polluted and less polluted environmental conditions. The present study shows that activity coefficients of inorganic ions are often below unity under deliquesced aerosol conditions, and that most uncharged organic compounds exhibit activity coefficient values around or even above unity. The model studies demonstrated that the inclusion of non-ideality considerably affects the multiphase chemical processing of transition metal ions (TMIs), key oxidants, and related chemical subsystems, e.g. organic chemistry.

In detail, both the chemical formation and oxidation fluxes of Fe(II) are substantially lowered by a factor of 2.8 under polluted haze conditions compared to a case study without non-ideality treatment. The reduced Fe(II) processing in the polluted base case, including lowered chemical fluxes of the Fenton reaction (-70 %), results in a reduced processing of HO_x/HO_y. under deliquesced aerosol conditions. Therefore, higher multiphase H_2O_2 concentrations (by a factor of 3.1 larger) and lower aqueous-phase OH concentrations (by a factor of ≈ 4 lower) were modelled during aerosol conditions. For H_2O_2, the consideration of non-ideality increases S(VI) oxidation fluxes under aqueous aerosol conditions by 40 %. Moreover, the chemical fluxes of the OH radical are about 50 % lower in the non-ideal haze case. Accordingly, the consideration of non-ideality affects the chemical processing and the concentrations of organic compounds under deliquesced particle conditions in a compound-specific manner. For important organic carboxylic acids, e.g. glyoxylic acid and oxalic acid, the reduced radical oxidation budget under aqueous particle conditions leads to increased concentration levels. For oxalic acid, the present study demonstrates that the non-ideality treatment enables more realistic predictions of high oxalate concentrations observed under ambient highly polluted conditions. Furthermore, the simulations show that lower humidity conditions, i.e. more concentrated solutions, might promote higher oxalic acid concentration levels in aqueous aerosols due to differently affected formation and degradation processes. Overall, the performed studies demonstrate the important role of a detailed non-ideality treatment in multiphase models dealing with aqueous aerosol chemistry and the needs to further improve current model implementations.

Modelling the multiphase formation of high H_2O_2 concentrations 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 $PM_{2.5}$ and NO_x 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 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.
Multiphase chemistry simulations of a NCP measurement campaign are performed with the box model framework 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 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.
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, during the morning hours, the aqueous-phase reaction of H_2O_2 with S(IV) contributes considerably to S(VI) formation beside the HONO related formation of sulfuric acid by OH in the gas-phase. Therewith, the

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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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