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

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Motivation

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/haze particles are characterized by concentrated non-ideal solutions 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.

Multiphase Modelling

Multiphase chemistry simulations are carried out with the SPACCIM-SpactMod model framework [1,2] including an extended CAPRAM2.4 chemical mechanism [1,3,4]. This kinetic model framework incorporates an activity coefficient module based on the AIOMFAC approach [5,6] and additional interaction parameters from literature for mixed organic-inorganic systems (see [1] for details). Simulations are performed for both urban and remote environmental conditions using a non-permanent cloud scenario (only pollution haze cases presented here). In this meteorological scenario, an air parcel is moved along a predefined trajectory. Four cloud passages (two at daytime (noon) and two at night-time (midnight) clouds) of about 2 hours within a modelling time of 58 hours are included, as well as a non-cloud deliquesced aerosol period with 90% relative humidity (RH) in the base case. A scheme of the applied meteorological scenario is displayed in Figure 1. Additionally, a sensitivity run considering a lower RH level (70 % RH, after the second cloud passage) is performed to investigate the non-ideality effects under lower aerosol liquid water (ALW) conditions. Simulations are performed with and without treatment of non-ideality (ideal/non-ideal, see Table 1) examining the effects of non-ideality on the multiphase chemical processing.

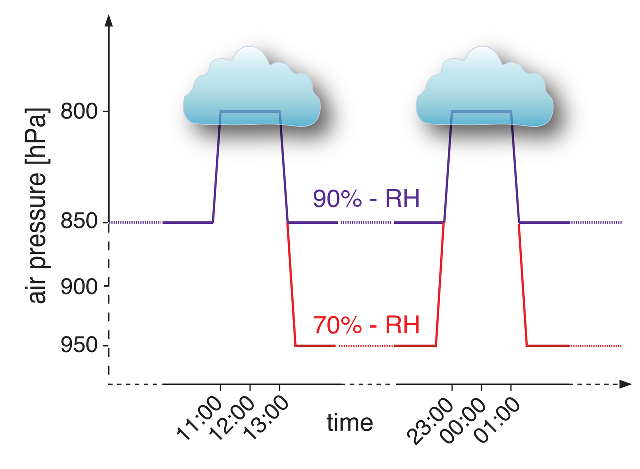


Fig.1: Scheme of the meteorological scenario.

Table1. Perfomed model simulations.

Case	Chemistry treatment	Environ. conditions	Acronym
Base case (90 % RH)	Ideal	Remote	90 %-IDR
		Urban	90 %-IDU
	Non-Ideal	Remote	90 %-NIDR
		Urban	90 %-NIDU
70 % RH	Ideal	Remote	70 %-IDR
		Urban	70 %-IDU
	Non-Ideal	Remote	70 %-NIDR
		Urban	70 %-NIDU

Model Results & Discussion

■ Modelled acidity and ionic strength

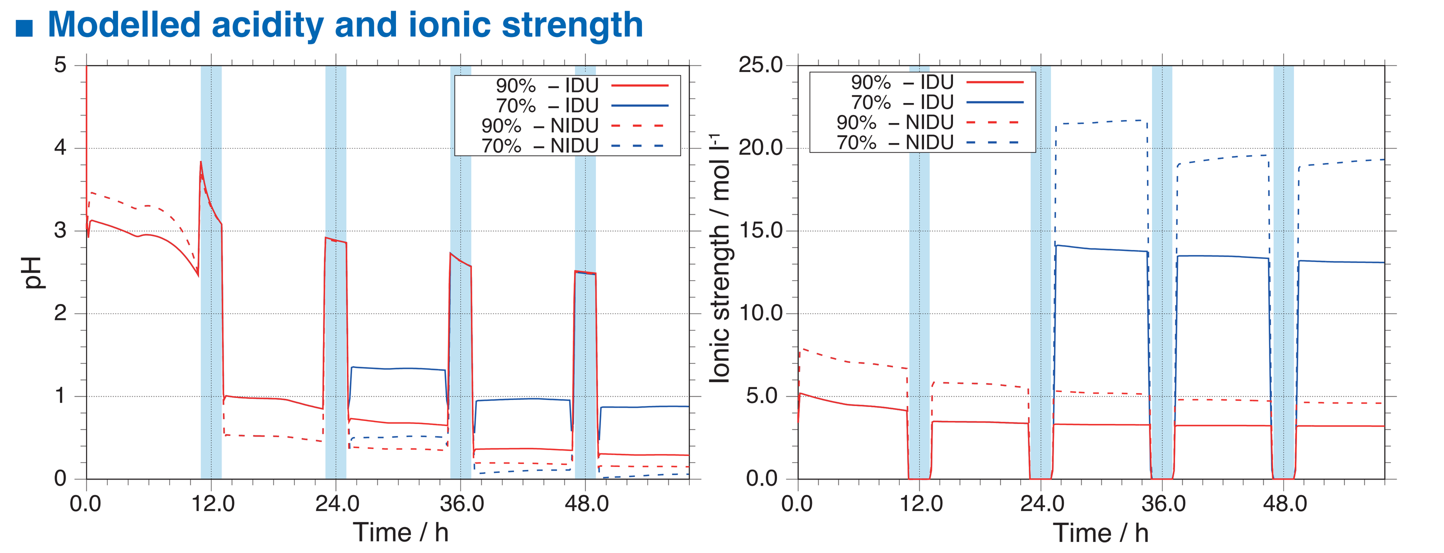


Fig.2: Modelled pH value (left) and ionic strength (I, right) as functions of the simulation time of the different urban simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

■ Modelled Fe(II) processing

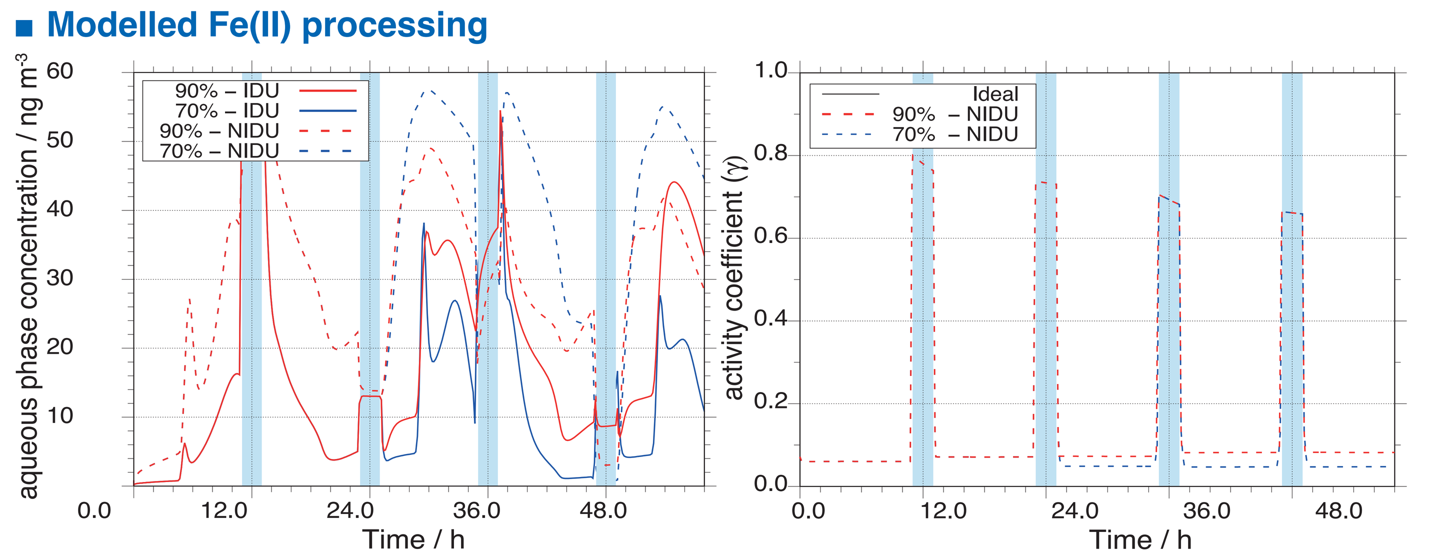


Fig.3: Modelled Fe(II) aqueous-phase concentration in ng m^{-3} for the different urban simulation cases throughout the modelling time (left) and corresponding time evolution of activity coefficients (right).

■ Modelled multiphase H_2O_2

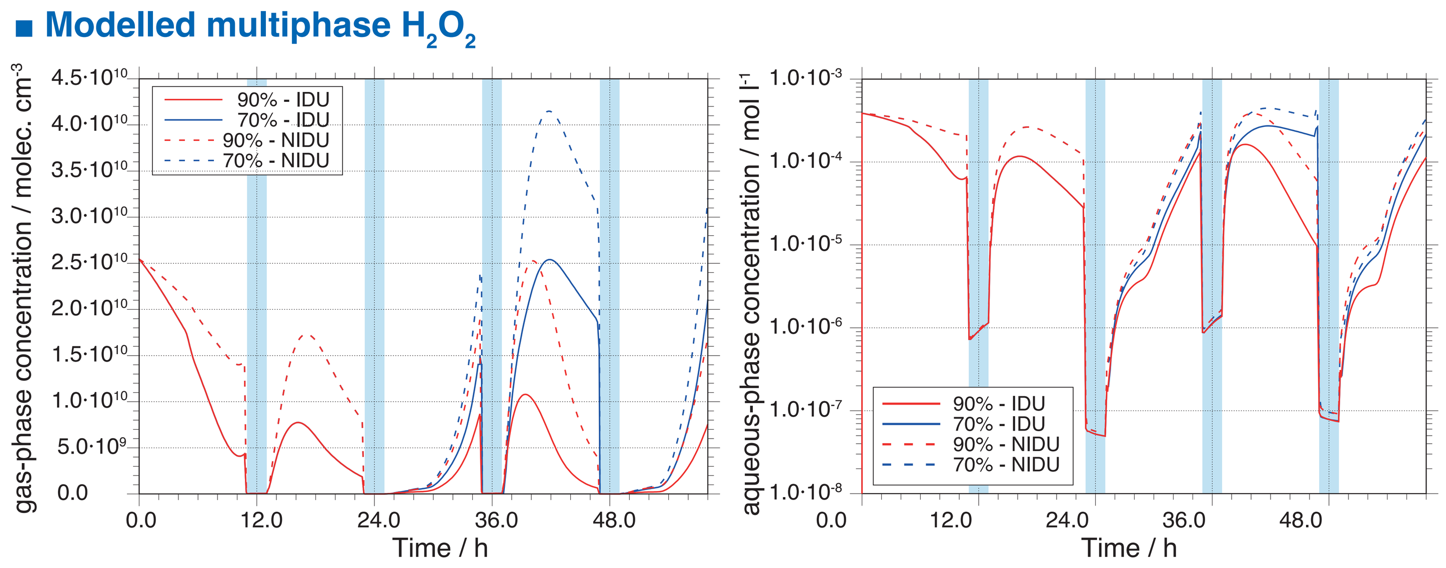


Fig.4: Modelled gas- and aqueous-phase concentrations of H_2O_2 in the different urban simulation cases (90%-IDU/90%-NIDU and 70%-IDU/70%-NIDU) throughout the simulation time.

■ Modelled S(VI) formation

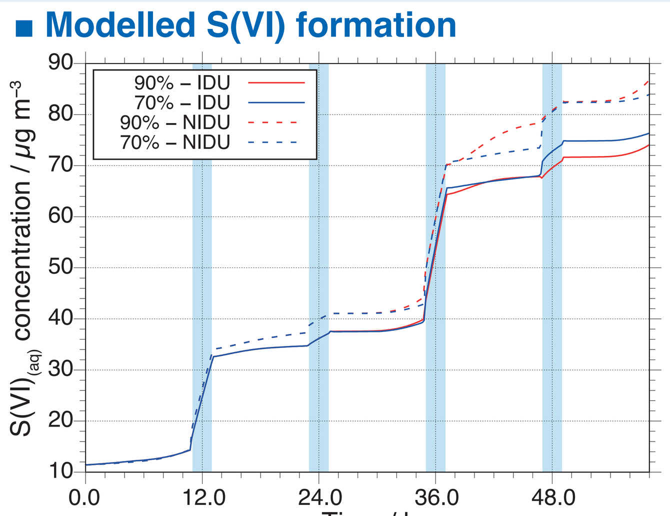
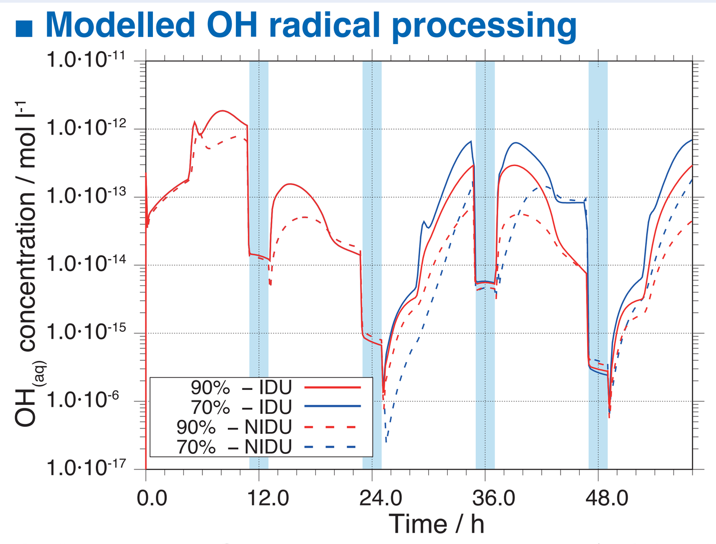


Fig.5: Modelled $S(VI)_{(aq)}$ concentrations in μg m^{-3} for the different urban simulation cases.

■ Modelled OH radical processing



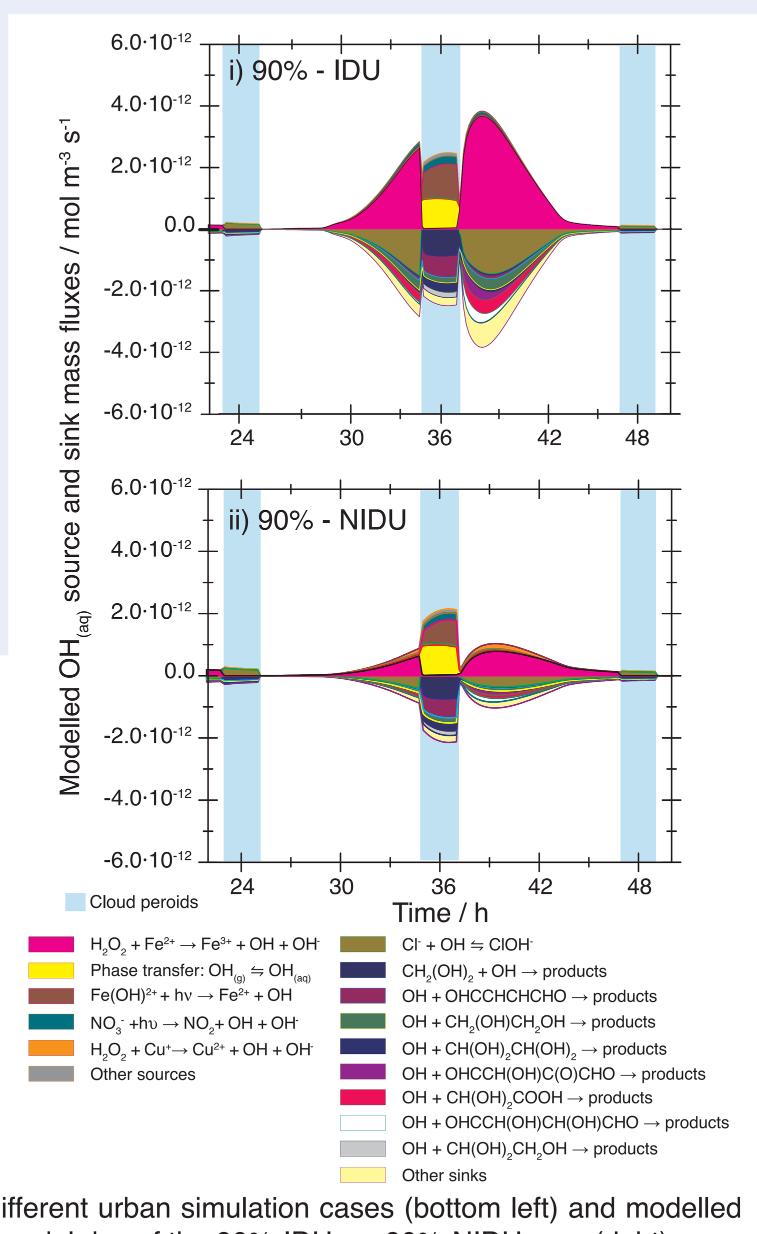


Fig.6: Modelled $OH_{(aq)}$ concentrations in mol l^{-1} of the different urban simulation cases (bottom left) and modelled chemical sink/source rates in mol m^{-3} s^{-1} on the second model day of the 90%-IDU vs. 90%-NIDU runs (right).

- Treatment of non-ideality leads to higher Fe^{2+} conc.s (Fig.3) and reaction rate analysis reveals a factor of 2.8 lower Fe(II) cycling

⇨ **Impact on HO_x/HO_y budget**

- Factor of 3.1 larger aqueous conc.s of H_2O_2 on average during the non-cloud periods (Fig.4); Fenton reaction with Fe^{2+} about 70 % lower (90%-NIDU case)
- Substantially lower OH conc.s in the non-ideal case under aerosol conditions and reaction flux analysis shows decreased OH rates (Fig.6)
- Glycolic and glyoxylic acid show decreased aerosol degradations due to the reduction of OH radical budget; Activity coefficients of dissociated and undissociated forms are less than 1 leading to lowered decays, too
- Non-ideality significantly affects the chemical fluxes of oxalic acid as a consequence of a reduced chemical processing of iron and the activity coefficients of the different oxalic acid anions and Fe-oxalate complex ions (Fig.7)
- Flux analysis of oxalic acid revealed both substantially lowered productions (factor 2.5 lower) and particularly decays (factor 2.9 lower) in the 90%-NIDU case
- Reduced decay leads to higher oxalic acid conc.s

⇨ **Non-ideality treatment enables more realistic predictions of high oxalate conc.s under high pollution conditions**

■ Modelled aqueous-phase C_2 chemistry

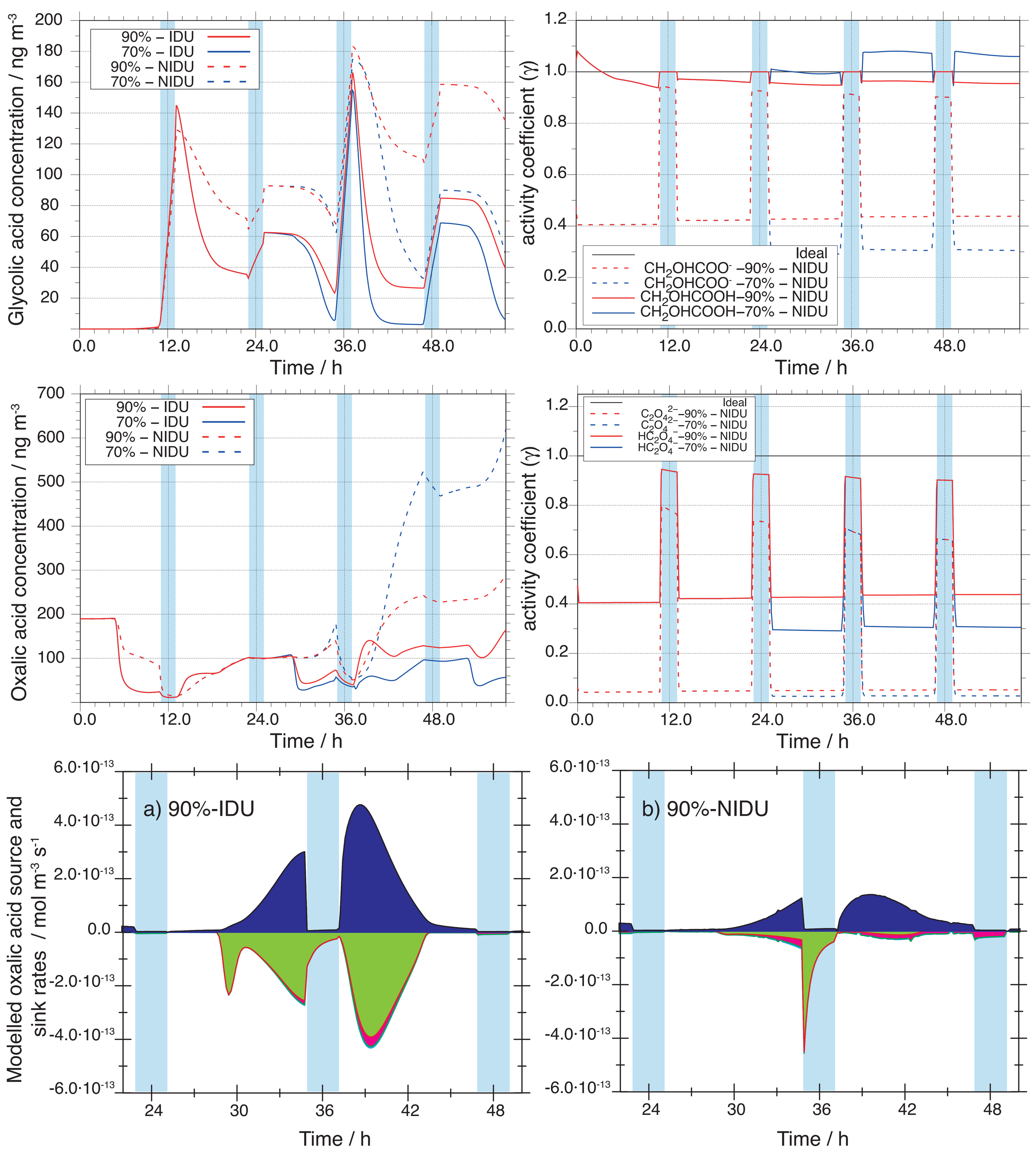


Fig.7: Modelled aqueous-phase concentrations in ng m$^{-3}_{(air)}$ and corresponding activity coefficients of the important C_2 oxidation products, (i) glycolic acid (top) and (ii) oxalic acid (centre). Modelled chemical sink and source mass fluxes of oxalic acid in the aqueous phase in mol m^{-3} s^{-1} for the 2nd model day 90%-IDU and 90%-NIDU.

Summary and Outlook

In order to examine the effects of non-ideal solutions on the occurring multiphase chemistry, simulations with SPACCIM-SpactMod are performed [7]. The present study shows that activity coefficients of inorganic ions are often below unity, and that most uncharged organic compounds exhibit activity coefficient values around or even above unity under deliquesced aerosol conditions. The model studies demonstrate 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 lower chemical fluxes of the Fenton reaction (-70 %), results in a reduced processing of HO_x/HO_y. Therefore, higher multiphase H_2O_2 concentrations (~ factor of 3.1 larger) and lower aqueous-phase OH concentrations (~ factor of 4 lower) are 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 urban haze case. Accordingly, the consideration of non-ideality affects the chemical processing and the concentrations of organic compounds 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 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 model studies demonstrate the important role of a detailed non-ideality treatment in multiphase models dealing with aqueous aerosol chemistry, and the needs to improve current model implementations.

References

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