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Manuscript for Atmospheric Chemistry and Physics Discussions (MS No.: acp-2019-819)
“Treatment of non-ideality in the multiphase model SPACCIM-Part2: Impacts on the multiphase chemical processing in deliquesced aerosol particles” by Ahmad Jhony Rusumdar, Andreas Tilgner, Ralf Wolke, and Hartmut Herrmann

Dear Christian,

please find attached our response to the reviewer comments for the manuscript mentioned above together with its revised versions of the manuscript and supplement. We would like to thank both reviewers for all of their valuable comments to improve the manuscript. We have carefully considered all the reviewer comments and revised the manuscript accordingly. Below, we provide responses to the comments in blue, with changes made in the manuscript.

Yours sincerely,



Prof. Dr. Hartmut Herrmann
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Anonymous Referee #1

We thank reviewer 1 for the constructive comments to improve the manuscript. The comments of the reviewer are addressed point by point in the sections below. The answers to the reviewer comments are marked as blue text. Furthermore, all changes made in the manuscript are marked in the version with tracked changes. In order to provide a more conceive manuscript and for the sake of clarity, the subsection on the C₃ chemistry has been moved to the supplement.

The study presented in this paper aims to quantify the activity coefficients of species dissolved in deliquescent atmospheric particles. The approach is based on the modeling of two continental scenarios (urban, remote) simulating the chemical evolution in various phases (gas - particle - cloud droplets). The study examines the activity coefficients of inorganic (HOx, SOx, H₂O₂, metals) and organic (C1-C3) species. The effect of the non-ideal behavior of the species on the dynamic evolution of the system is evaluated by comparing the results obtained when the ideal behavior in the aqueous phase is imposed or not. For the scenarios tested, the budget of key species (S(VI), H₂O₂, organic acids ...) is substantially modified when the non-ideal behavior of the solution is considered. The results presented are relevant to this journal. The paper is well organized but the writing could likely be more concise.

I have a few comments (see below) that the authors might consider for submitting a revised article to ACP.

1. The description of the two scenarios considered in this study is inadequate. The authors refer to an article by Ervens et al. (2003) (page 7, line 24), but I did not find more detailed information in the article cited. Additional information is necessary to characterize the simulations carried out with the box model (initial conditions, emissions, speciation of organic species, deposition, NO_x regime, NH₃ level, etc.) and to weigh the simulated behavior of the species (e.g. the accumulation of S(VI) presented in fig.3, page 16 and reaching 90 µg/m³). The details of the simulation conditions could for example be added to the additional material.

Answer to the reviewer comment:

We thank the reviewer for this comment. Unfortunately, the link provided in Ervens et al. (2003) is not up-to-date anymore. Therefore, we have added a link to the CAPRAM webpage, in addition to Ervens et al. (2003). There, initial gas phase conditions, emissions and deposition are provided.

2. The paper examines the effect of the non-ideality of the solution on the condensed phase reactivity but does not discuss its effect on the gas/particle partitioning, as suggested for example page 12, line 4. No result of the non-ideal behavior is presented on the simulated aerosol mass concentrations, their compositions (e.g. inorganic vs organic), their liquid water content... . Adding a section presenting the effects on the overall aerosol properties (mass concentration, composition, water content in particular) would be useful to evaluate the sensitivity of this non-ideal behavior in models dealing with aerosols formation.

Answer to the reviewer comment:

The applied model calculates both the phase partitioning and the occurring multiphase chemistry simultaneously. The latter can substantially affect the budgets of the compounds. Hence, the predicted concentrations in either phase are a result of both the phase partitioning and the multiphase chemistry. Therefore, it is difficult here to discuss the effects of the non-ideality on the gas/particle partitioning and the applied multiphase chemical reactions individually. Due to the focus of the present study on the occurring multiphase chemistry we have not focused on the phase partitioning topic alone and have only cited literature (Cappa et al. (2008)) addressing this issue in more detail.

According to the reviewer comment, we have added a section to the SI presenting additional model results, e.g. total and organic aerosol mass for different model runs/scenarios.

3. The iron activity decreases notably when the non-ideal behavior of the species is considered. The authors show that this decrease in activity is one of the main causes explaining the simulated effects. However, the authors state that the model ignores the "middle range interaction" for Fe and Mg ions, leading to uncertainties about the activity coefficients calculated for these species. This limitation is reminded very regularly in the paper, including in the conclusion of the article (e.g. line 15, page 34). Although clearly mentioned, this uncertainty considerably weakens the conclusions of this study. I think that a test would be necessary to examine the sensitivity of the simulations to uncertainties about the activity of iron. An educated guess could perhaps be made to estimate the effect of the middle range interactions, e.g. using another TMI as a proxy.

Answer to the reviewer comment:

The authors fully agree with the reviewer that the missing middle range interaction parameters for Fe and Mg ions might weaken the conclusions of this study. The authors already thought about this issue quite a bit during the analysis of the modelled data. An educated guess to estimate those middle range interaction parameters was already discussed. For this reason, we have already compared available middle range interaction parameters of different metals. This comparison showed that also similar metals, for example Mg^{2+} and Ca^{2+} (same charge and main group in the periodic table), can be characterized by rather different middle range interaction parameters. Moreover, the use of the Cu^{2+} interactions parameters for Fe and Mn ions can be also difficult as the chemistry of copper is known to be different from those of Fe and Mn. Nevertheless, according to the reviewer comment, we have included a new section in the SI comparing the base model runs with runs where the parameters for Cu^{2+} have been applied for Fe^{2+} and Mn^{2+} . A link to the sensitivity studies in the supplement is now included into the revised manuscript (see Sect. 3.4).

4. Minor comments: The term "flux" is used systematically by the authors to define the rate of processes. I think that using "flux" is inappropriate here and should be replaced by "rate" everywhere in the text and in figures 5, 8, 10 and 12.

Answer to the reviewer comment:

The term "flux(es)" has been replaced by "rate(s)" in the revised manuscript.

5. The writing of the chemical formula are often difficult to read for organic molecules. For example in Table 4, $\text{OH}_2\text{CHCH}_2\text{OH}$ would be more easy to read as $\text{CH}(\text{OH})_2\text{CH}_2\text{OH}$ to represent hydrated glycolaldehyde. Similarly, $\text{C}_2\text{H}_4\text{COOH}_2$ would be more easy to read as $\text{C}(\text{O})\text{OHCH}_2\text{CH}_2\text{C}(\text{O})\text{OH}$ to represent succinic acid, etc . . . Furthermore, the writing is sometime misleading, like in figure 8 for OHCCHCHCHO (which I guess is for butenedial $\text{CHOCH}=\text{CHCHO}$) or, in figure 10, $\text{C}(\text{OH})_2\text{O}_2\text{COOH}$ which I cannot identify (a typo?) but

understand to be glyoxylic acid from the text. I suggest to use only “conventional” formula in the text, figures and tables.

Answer to the reviewer comment:

The writing of the chemical formulas has been revised.

Page 2, line 20: the word "including" in the context of the sentence is unclear. Change to "leading to"?

Answer to the reviewer comment:

"including" was replaced by "leading to".

Page 3, line 16: the paper use both ALWC and ALW. Duplication of 2 similar acronyms could be avoided (ALWC is used only 2 times in paper).

Answer to the reviewer comment:

The ALWC is not used anymore in the revised manuscript.

Page 10, line 26-27: One of the 2 "finally" should be removed.

Answer to the reviewer comment:

One "finally" has been removed.

Page 11, line 22: pyruvic acid is not a simple carboxylic acid (i.e. without another functional group), as suggested in the context of the sentence.

Answer to the reviewer comment:

The sentence has been rephrased and reads now as follows:

“Only carboxylic acids with further substituents and a longer non-polar carbon chain (e.g. pyruvic and butyric acid) show higher activity coefficients, particularly with decreasing RH.”

Page 12, line 18-20. The sentence seems useless in the context of the paragraph and could be removed.

Answer to the reviewer comment:

The sentence has been removed.

Page 13, line 8. I don't understand the meaning of the word "obstruct" in the context of the sentence.

Answer to the reviewer comment:

The sentence has been rephrased and reads now as follows.

“Mainly, microphysical parameters such as the ALW content pattern pH and ionic strength.”

Page 14, line 5-6: the sentence is obvious in the context of the paragraph and could be removed.

Answer to the reviewer comment:

The sentence has been removed.

Page 15, line 14-16: The sentence is obvious in the context of the paragraph and could be removed.

Answer to the reviewer comment:

The sentence has been removed.

Page 19, line 1: the second processing in "processing of Fe(II) processing aqueous" could be removed.

Answer to the reviewer comment:

The second processing as been removed. The sentence reads now as follows:

“To summarise, the model simulations implicate that the multiphase processing of Fe(II) in aqueous particles is significantly affected by the treatment of non-ideality and the effect depends strongly on the ALW conditions.”

Page 19, line 17-31: The reading of this paragraph is tedious. A figure similar to 5, 8, 10 or 12 could be useful.

Answer to the reviewer comment:

For the sake of clarity, we have not included such a Fig. here, but according to the reviewer comment, we have added a similar Fig. for H₂O₂ in the SI (see Fig. S6).

Page 21, line 7: units are missing for OH concentration. Number of significant figures should be consistent for the 2 numbers.

Answer to the reviewer comment:

The unit has been added and the numbers were unified.

Page 24, line 25: I don't understand "formation-substituted" in the sentence.

Answer to the reviewer comment:

The sentence has been rephrased as follows:

“...in-cloud oxidations of C₂ carbonyl compounds such as glycolaldehyde and glyoxal lead to the formation of substituted organic acids (e.g. glyoxylic and glycolic acid),...”

Page 26, line 10-32: The reading of this paragraph is tedious. A figure similar to 5, 8, 10 or 12 could be useful.

For the sake of clarity, we have not included such a Fig. here, but according to the reviewer comment, we have added similar Fig.s for glycolic and glyoxalic acid in the SI (see Fig. S7-8).

Page 31, line 8: Typo in "sSect."

Answer to the reviewer comment:

The typo was corrected.

Page 31, line 14: it is stated that keto malonic acid is the final C₃ oxidation product. Figure 12 (page 32) show however a loss process which is not discussed in the text (and not "explained" from the legend in the figure).

Answer to the reviewer comment:

The comment is difficult to understand. Keto malonic acid is the C₃ oxidation product of this reaction chain, subsequent products only include 2 carbon atoms. According to the reviewer comment, the word has been removed from the sentence.

Page 32, figure 12: Only the first 3 processes (dark blue, light blue and pink) can be discerned in the figure. The other processes could be merged in either the "other source" or "other sinks" boxes.

Answer to the reviewer comment:

The Figure has been revised.

Anonymous Referee #2

The authors present a sensitivity study of the impact of considering non-ideal solution effects on predictions of aqueous aerosol chemistry using the SPACCIM-SpactMod model. The study is well-conceived, and the results highlight the potential significance of non-ideal solution effects in multiphase atmospheric chemistry, something that is generally ignored in atmospheric models due in part to computational expense but also because of a lack of data. I think the manuscript will be suitable for publication in ACP after a few clarifications.

The authors thank reviewer 2 for the positive and thoughtful comments to improve the manuscript. The comments of the reviewer are carefully addressed point by point in the section below. The answers to the reviewer comments are marked as blue text. Moreover, all changes made in the manuscript are marked in the version with tracked changes.

- The aqueous chemical kinetic data in CAPRAM, which the multiphase chemical kinetic simulations in this study were based on, for the most part was not originally measured/reported as a function of activity but rather of concentration. The measurements that form the basis of that data were also mostly performed under much more dilute and closer to ideal conditions than the aqueous aerosol conditions considered here. How accurate is it to use those rate laws but plug in the activities calculated here - which are in many cases very different from the activities where the rates were originally measured both because of the high concentrations of atmospheric aerosols but also because of the non-ideality? Is it even possible to evaluate this?

Answer to the reviewer comment:

The reviewer is right that most of the kinetic reaction parameters are determined in the laboratory under much more dilute and closer to ideal conditions than aqueous aerosol conditions. Thus, effects of important parameters such as the ionic strength are not investigated by such studies and are therefore not considered in the current version of CAPRAM. However, the ionic strength is a main parameter in the calculation of the activity coefficients and consequently also in the calculation of the reactive fluxes.

Ionic strength effects are believed to be an important parameter of particle chemical reactions such as S(IV) oxidation (Martin and Hill, 1987; Lagrange et al., 1993; Lagrange et al., 1994; Maaß et al., 1999; Ali et al., 2014; Cheng et al., 2016), although experimental data at the extremely high ionic strengths typical of atmospheric aerosols are limited. Studies available studying the ionic strength effects (see e.g. Weller et al. (2010) and Herrmann et al. (2015) and references therein), however, often only quantify the overall effect of both ionic strength and the activity coefficients. To provide ionic-strength dependent reaction rate constants, the activity coefficients of the educts need to be considered to finally derive the single effect of the ionic strength. Such combined laboratory studies and model calculations would be a way to come up with datasets that can overcome the current model implementation limitation.

The current limitation in the applied mechanism is now briefly addressed in the revised manuscript in Sect.2.2. and reads as follows:

“Overall, it is worth to be noted that most of the kinetic reaction parameters considered in CAPRAM are determined in the laboratory under dilute and closer to ideal conditions rather than concentrated aqueous aerosol conditions. Thus, effects of important concentrated solution parameters such as ionic strength have not been investigated by such studies and are therefore not considered in the current version of CAPRAM. Once more ionic-strength

dependent reaction rate constants become available, they have to be considered in future mechanisms.”

- I agree with the other referee’s comment that the uncertainty in the MR parameterizations for Fe and Mn are a significant weakness, especially given the likely importance of those two ions in multiphase atmospheric chemistry. Could the authors estimate those parameters, perhaps from available lab data, to at least constrain the effect?

Answer to the reviewer comment:

The authors fully agree with the reviewer that the missing middle range interaction parameters for Fe and Mg ions might weaken the conclusions of this study. The authors already thought about this issue quite a bit during the analysis of the modelled data. An educated guess to estimate those middle range interaction parameters was already discussed. For this reason, we have already compared available middle range interaction parameters of different metals. This comparison showed that also similar metals, for example Mg^{2+} and Ca^{2+} (same charge and main group in the periodic table), can be characterized by rather different middle range interaction parameters. Moreover, the use of the Cu^{2+} interactions parameters for Fe and Mn ions can be also difficult as the chemistry of copper is known to be different from those of Fe and Mn. Nevertheless, according to the reviewer comment, we have included a new section in the SI comparing the base model runs with runs where the parameters for Cu^{2+} have been applied for Fe^{2+} and Mn^{2+} . A link to the sensitivity studies in the supplement is now included into the revised manuscript (see Sect. 3.4).

- Considerable uncertainty exists in the measured and reported rate data for much TMI chemistry, especially when it comes to ionic strength and pH dependence. Can the authors comment on the relative significance of these uncertainties to the non-ideal solution effects calculated here?

Answer to the reviewer comment:

The reviewer is certainly right that there are considerable uncertainties in available reaction rate data of the TMI chemistry and potential gaps exist in the scientific knowledge about their speciation, reactivity and complex interactions. The uncertainties and knowledge gaps are surely related to the complex dependencies of the TMI chemistry on the acidity and ionic strength (see Deguillaume et al. (2005) and references therein) and are able to affect different key chemical subsystems such as the HOx, organic and sulfur chemistry. CAPRAM contains already a rather complex TMI chemistry implementation which is far from being complete due to many gaps in the scientific knowledge. When better measured chemical rate constants of TMI reactions become available they definitely need to be integrated into upcoming CAPRAM mechanism versions.

Regarding the relative significance of the uncertainties compared to the non-ideal solution effects, the authors think that a more advanced TMI chemistry knowledge would be surely needed but effects of non-ideality will be definitely also play a key role due to the potential impact of activity coefficients on the reaction rates and speciation constants. Thus, laboratory future studies need to investigate important parameters such as the “middle range interaction” parameters of different TMI compounds as they can impact the overall rates by about 2 orders of magnitude depending on the non-ideality of the solution.

- How often in the simulation are the activity coefficients recalculated, i.e. as concentrations change in the aqueous phase? Does it happen at every timestep?

Answer to the reviewer comment:

In simulation, activity coefficients are calculated at each timestep. Further details about the implemented procedure is given in Rusumdar et al. (2016). According to the reviewer comment, we have slightly updated SPACCIM-SpactMod description in Sect. 2.1 and address this issue now in the revised manuscript.

- Since much depends in this study on the model chosen for activity coefficients, it would have been nice to see a sensitivity study of other popular approaches that could have been used instead. This is done somewhat in Table 3 and page, last paragraph. Given the sharp criticism presented, the discussion of Mao et al (2013) in this paragraph needs more elaboration (how do you know the implementation was 'incorrect'?), perhaps in the SI.

Answer to the reviewer comment:

1. A sensitivity study using other popular activity coefficient approaches (EAIM, ...) that could have been applied instead of AIOMFAC is an excellent idea but beyond the scope of the present study. A comprehensive sensitivity study using other popular activity coefficient approaches will be definitely a gainful task for the future.
2. Unfortunately, most multiphase chemistry studies do not apply activity coefficients in their models or, if activity coefficients are considered, studies do often not provide the calculated activity coefficients in the publications. We did again a literature survey and have extended Table 3 with available data found and updated the discussion in Sect. 3.1.1. Nevertheless, presently no comprehensive comparison is possible.
3. In the study of Mao et al. (2013), an activity coefficient γ of 0.01 was applied for Fe^{3+} based on the lowest estimate from Millero and Woosley (2009). However, the lowest estimate in Millero and Woosley (2009) is $\ln(\gamma)=-2$, i.e. γ should be 0.135. Thus, the decadic logarithm was used by Mao et al. (2013) instead of the natural logarithm. This issue is now outlined in the remarks of Table 3.

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Treatment of non-ideality in the multiphase model SPACCIM-Part2: Impacts on the multiphase chemical processing in deliquesced aerosol particles

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Abstract

Tropospheric deliquesced particles are characterised by concentrated non-ideal solutions ('aerosol liquid water' or ALW) that can affect the occurring multiphase chemistry. However, such non-ideal solution effects have generally not yet been considered in and investigated by current complex multiphase chemistry models in an adequate way. Therefore, the present study aims at accessing the impact of non-ideality on multiphase chemical processing in concentrated aqueous aerosols. Simulations with the multiphase chemistry model (SPACCIM-SpactMod) are performed in different environmental and microphysical conditions with and without a treatment of non-ideal solutions in order to assess its impact on aqueous-phase chemical processing.

The present study shows that activity coefficients of inorganic ions are often below unity under 90 % RH-deliquesced aerosol conditions, and that most uncharged organic compounds exhibit activity coefficient values of around or even above unity. Due to this behaviour, model studies have revealed that the inclusion of non-ideality considerably affects the multiphase chemical processing of transition metal ions (TMIs), oxidants, and related chemical subsystems such as organic chemistry. In detail, both the chemical formation and oxidation [rates](#) of Fe(II) are substantially lowered by a factor of 2.8 in the non-ideal base case compared to the ideal case. The reduced Fe(II) processing in the non-ideal base case, including lowered chemical [rates](#) of the Fenton reaction (~70 %), leads to a reduced processing of HO_x/HO_y under deliquesced aerosol conditions. Consequently, higher multiphase H₂O₂ concentrations (larger by a factor of 3.1) and lower aqueous-phase OH concentrations (lower by a factor of ≈ 4) are modelled during non-cloud periods. For H₂O₂, a comparison of the chemical reaction [rates](#) reveals that the most important sink, the reaction with HSO₃⁻, contributes with a 40 % higher [rate](#) in the non-ideal base case than in the ideal case, leading to more efficient sulfate formation. On the other hand, the chemical [formation rates](#) of the OH radical are about 50 % lower in the non-ideal base case than in the ideal case [leading to](#) lower degradation [rates](#) of organic aerosol components. Thus, considering non-ideality influences the chemical processing and the concentrations of organic compounds under deliquesced particle conditions in a compound-specific manner. For example, the reduced oxidation budget under deliquesced particle conditions leads to both increased and decreased concentration levels, e.g. of important C₂/C₃ carboxylic acids. For oxalic acid, the present study demonstrates that the non-ideality treatment enables more realistic predictions of high oxalate concentrations than observed under ambient highly polluted conditions. Furthermore, the simulations implicate 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.

1 Introduction

Aerosol particles represent a more or less omnipresent multiphase compartment within the troposphere, which generally comprises complex mixtures containing different organic and inorganic compounds including water (see e.g. Saxena and Hildemann (1996); Pöschl (2005); Hallquist et al. (2009); and references therein). Aerosol properties and their impacts largely depend on chemical composition, size, and phase. Due to the various important impacts of aerosols on atmospheric chemistry (Andreae and Crutzen, 1997; Ravishankara, 1997), air pollution (Akimoto, 2003; von Schneidemesser et al., 2015), biosphere (Adriano and Johnson, 1989), climate (Charlson et al., 1992; Lohmann and Feichter, 2005; Boucher et al., 2013; Myhre et al., 2013), and public health (Holgate, 1999; Brunekreef and Holgate, 2002; Lelieveld et al., 2015), it is a key challenge to understand how aerosol particles are physically and particularly chemically processed in the tropospheric multiphase system in order to finally clarify their global importance and impacts.

Tropospheric aerosol particles are a complex multiphase and multi-component environment, in which a variety of physical and chemical processes can alter the physical and chemical composition of the troposphere, potentially on a global scale. With regard to aerosol particles, chemical reactions can occur heterogeneously at the surface and homogeneously in a bulk of organic and aqueous aerosol particles (Ravishankara, 1997; George et al., 2015; Herrmann et al., 2015). Through interaction with ambient water vapour, aerosol particles can be deliquesced, forming an aqueous-aerosol phase characterised by highly concentrated solutions with rather low ALW contents, between $3 \cdot 10^{-7}$ and $1 \cdot 10^{-3} \text{ g m}^{-3}$ (Herrmann et al., 2015). Chemical bulk processes in the deliquesced aerosol phase are expected to be of importance (Ervens et al., 2011; Tilgner et al., 2013; Herrmann et al., 2015). Aqueous-phase processes are known to be very efficient in occurring on short timescales and in producing secondary compounds, i.e. contributing to secondary aerosol mass, e.g. aqSOA (Tilgner and Herrmann, 2010; Ervens et al., 2011; McNeill et al., 2012a; Tilgner et al., 2013; Ervens, 2015; Herrmann et al., 2015). Additionally, chemical processes in aqueous aerosols can alter the composition of the surrounding gas phase (Tilgner et al., 2013). However, compared to processes in well-diluted environments such as the tropospheric gas and cloud phase, chemical processes in highly concentrated non-ideal solutions of deliquesced aerosol particles are much less investigated.

To assess the role of multiphase chemical processes related to aerosol particles and cloud droplets, a variety of complex multiphase chemistry mechanisms and multiphase models were developed and applied in the past (see e.g. (Sander and Crutzen, 1996); Vogt et al. (1996); Vogt et al. (1999); von Glasow et al. (2002a, 2002b); Deguillaume et al. (2004); Ervens et al. (2004); Lim et al. (2005); Barth (2006); Pechtl et al. (2007); Tilgner and Herrmann (2010); Ervens et al. (2011); Ervens (2015); Hoffmann et al. (2016); Mouchel-Vallon et al. (2017); Hoffmann et al. (2018); Rose et al. (2018)). Many studies focused on the role of chemical aqueous-phase processes mainly involving cloud droplets and partly deliquesced particles. Model studies dealing with chemical processes in deliquesced particles were often focused on marine particles (see e.g., Vogt et al. (1996); Vogt et al. (1999); von Glasow and Sander (2001); von Glasow et al. (2002a, 2002b); von Glasow et al. (2004); Pechtl et al. (2007); Brüer et al. (2013); Hoffmann et al. (2016)) and to a minor fraction on continental particles (Tilgner and Herrmann, 2010; McNeill et al., 2012b; Tilgner et al., 2013; Guo et al., 2014). Such studies often revealed the potential role

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of deliquesced particles to act as a reactive aqueous chemical environment in the troposphere (see e.g., Tilgner et al. (2013)). However, the treatment of particle-phase chemistry in complex chemistry box models is mostly approximated by dilute electrolyte solution, neglecting non-ideal solution effects. However, because of [their](#) very low ALW [contents](#), deliquesced aerosol solutions are often characterised by quite high ionic strengths of 2 - 45 mol L⁻¹ (see [for example](#), Herrmann et al. (2015) and references therein). Therefore, highly concentrated solutions of typical deliquesced particles cannot be treated as ideal solutions anymore, where intermolecular interaction forces between the non-solvent molecules are almost unimportant. Laboratory experiments (see e.g., Cappa et al. (2008)) have also confirmed that mixtures of aerosol components which are solids as pure substances become liquid-like and exhibit non-ideal behaviour.

In highly concentrated solutions, dissolved electrolytes and polar non-electrolytes are located very close to each other, causing electrostatic forces or other physical interactions. These intermolecular forces are able to influence both the phase transfer processes of a compound and its affinity to undergo chemical reactions. Hence, an adequate treatment of non-ideality is definitely needed for simulating chemical processes in deliquesced particles. Thermodynamic non-ideality in a specific multicomponent mixture, caused by all-molecular interactions, can be represented by activity coefficients of the different components. Consequently, suitable chemistry models have to apply activities instead of concentrations in multiphase chemistry models. For the sake of completeness, it is noted that besides the thermodynamic non-ideality, ionic strength effects of reactions also play a role in highly concentrated solutions (see Herrmann et al. (2015) for further details).

In the past, several approaches have been developed for the computation of required activity coefficients (see e.g. Pitzer (1991); Li et al. (1994); Prausnitz et al. (1998); Yan et al. (1999); Ming and Russell (2002); Raatikainen and Laaksonen (2005); Zaveri et al. (2005a); Zaveri et al. (2005b); Erdakos et al. (2006a); Erdakos et al. (2006b); Clegg et al. (2008); Zuend et al. (2008); Zuend et al. (2011)). At the same time, several authors attempted to develop these activity coefficient models to simulate aerosol thermodynamic equilibrium at variable complexity (e.g., AIM (Clegg et al., 1998a, b), GFEMIN (Ansari and Pandis, 1999), ISORROPIA and ISORROPIA II (Nenes et al., 1998; Fountoukis and Nenes, 2007), EQUISOLV II (Jacobson et al., 1996; Jacobson, 1997); MESA (Zaveri et al., 2005a); UHAERO (Amundson et al., 2006; Amundson et al., 2007)). However, complex multiphase chemistry models dealing with deliquesced particles usually neglect or only roughly estimate the effect of solution non-ideality on chemical processing (see e.g., Vogt et al. (1999); von Glasow et al. (2002a, 2002b); Tilgner and Herrmann (2010); Brüuer et al. (2013); Mao et al. (2013); Tilgner et al. (2013); Guo et al. (2014)). Therefore, detailed studies characterising the effect of non-ideal solutions on multiphase chemistry, e.g. in tropospheric deliquesced particles, are still lacking. For this reason, during the last years considerable effort has been devoted to developing kinetic model frameworks for the modelling of processes in multicomponent atmospheric particles, which include both a detailed description of organic and inorganic multiphase chemistry as well as detailed thermodynamic comprehensions of its non-ideal behaviour (see Shrivastava et al. (2011); Rusanmaki et al. (2016)).

In this context, the SPACCIM model framework (Wolke et al., 2005) was advanced by implementing a complex activity coefficient calculation module. The extended model approach of SPACCIM, including the treatment of non-ideality, is

described in the companion paper (see Rusumdar et al. (2016)). In the past, SPACCIM has been successfully applied in several chemical process model studies using the complex multiphase mechanism CAPRAM (Herrmann et al., 2005; Tilgner and Herrmann, 2010; Bräuer et al., 2013; Tilgner et al., 2013), focusing on both chemical and microphysical processes in cloud droplets and deliquesced particles, assuming ideal solution conditions. In the companion paper, the considered module SpactMod (Rusumdar et al., 2016) was tested against other activity coefficient modules and compared to the measurement data as well as showed its applicability within the model framework. Consequently, the present follow-up study aims at investigating and, finally, assessing the impact of non-ideality on aqueous-phase chemical processing in tropospheric deliquesced particles. Overall, the treatment described in Rusumdar et al. (2016) and applied here [allows the application of CAPRAM for aerosol liquid water \(ALW\) chemistry with its full scope of detailed chemistry](#).

This paper is split into four sections. Sect. 2 outlines the multiphase model framework SPACCIM-SpactMod and the applied multiphase chemical mechanism along with performed simulations. In Sect. 3, the modelled activity coefficients of inorganic and organic compounds under different environmental conditions are discussed separately. Subsequently, the modelled results are described and discussed, including the differences between the simulations, considering multiphase chemistry as ideal and non-ideal solutions for key chemical organic and inorganic subsystems. Finally, the main findings of the study are summarised in Sect. 4 and an outlook on future model developments and investigations is given.

2 Model and mechanism description

2.1 Multiphase chemistry model SPACCIM-SpactMod

In the present study, the extended version of the multiphase chemistry model SPACCIM (Wolke et al., 2005), including the considered activity coefficient module (SpactMod, Rusumdar et al. (2016)) entitled as SPACCIM-SpactMod in the following, has been applied to investigate the influence of the treatment of non-ideality on multiphase chemistry.

To put it briefly, SPACCIM is an air parcel model combining a complex size-resolved multiphase chemistry model and a cloud microphysical model. The interaction between both models is implemented by a coupling scheme, enabling both models to run separately as far as possible. Changes of the chemical aerosol composition due to gas scavenging and chemical reactions have a feedback on the microphysical processes and properties. The multiphase chemical model uses a high-order implicit time integration scheme, which exploits the special sparse structure of the model equations (Wolke and Knöth, 2002). The microphysical model applied in the SPACCIM model framework is based on the work of (Simmel and Wurzer, 2006) and Simmel et al. (2005). In the microphysical model, the growth and shrinking processes of aerosols by water vapour diffusion as well as nucleation and growth/evaporation of cloud droplets and other microphysical processes, such as impaction of aerosol particles and collision/coalescence of droplets, are described explicitly. Based on the Köhler theory (Köhler, 1936), the dynamic growth rate in the condensation/evaporation process and the droplet activation is implemented. Moreover, cloud droplet formation, evolution, and evaporation are implemented using one-dimensional sectional microphysics, considering

deliquesced particles and droplets, respectively. Due to the focus of present model studies on the effects of non-ideality on multiphase chemistry, microphysical processes, such as impaction of aerosol particles, collision/coalescence of droplets and precipitation, are not covered in the model of the present study. Overall, the complex model framework enables detailed investigations of multiphase chemical processing of gases, deliquesced particles, and cloud droplets. Further details about the SPACCIM model are given elsewhere in the literature (see Sehili et al. (2005); Wolke et al. (2005) and references therein).

In its latest version, SPACCIM-SpactMod additionally considers the treatment of non-ideality. In the incorporated activity coefficient module SpactMod (Rusumdar et al., 2016), non-ideality is treated with the approach by Zuend et al. (2008)/(Zuend et al., 2011) applied in the AIOMFAC model (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients, <http://www.aiomfac.caltech.edu/index.html>). This model is a thermodynamic group-contribution model specifically developed to describe typical tropospheric aerosol compositions. The group-contribution concept treats organic molecules as structures composed of different functional groups. This approach allows for the representation of thousands of different organic compounds using a relatively small number of functional groups. The module SpactMod is based on AIOMFAC and combines a Pitzer-like model approach with a UNIFAC model to predict activity coefficients of mixed organic-inorganic systems. The activity coefficient model approach considers both ion interactions and interactions of organic compounds.

The non-ideality of a thermodynamic system is characterised by excess Gibbs energy, which is expressed as the sum of long-range (LR), middle-range (MR), and short-range (SR) contributions. The LR interactions are described by an extended Debye–Hückel term. The MR part represents the effects of interactions involving ions and permanent or induced dipoles, and it contains most of the adjustable parameters to describe concentrated aqueous electrolyte solutions and organic–inorganic mixtures. The SR term is calculated through a modified UNIFAC approach (Fredenslund et al., 1975) using the revised parameter set of Hansen et al. (1991). Modifications of the UNIFAC model part within SpactMod further the introduction of inorganic ions in order to account for their effects on the entropy and enthalpy of mixing apart from their charge-related interactions. The original SpactMod (Rusumdar et al., 2016) mainly applies the interaction parameter data set of Zuend et al. (2008). In order to treat various aerosol constituents, additional parameters were included from the modified LIFAC approach by Kiepe et al. (2006), which can be rewritten in the AIOMFAC formalism. For the present study, the module has been updated and extended based on Zuend et al. (2011).

Overall, SpactMod ensures a reliable calculation of activity coefficients for organic-electrolyte mixtures from diluted aqueous solutions to mixtures of high ionic strength composed of various ions and organic compounds with several functional groups at each time step. A detailed description of SpactMod and its integration into SPACCIM is given in a companion paper (Rusumdar et al., 2016). Lastly, it has to be noted that the current version of SpactMod does not consider the latest development stage of the AIOMFAC model (Ganbavale et al., 2015; Gervasi et al., 2019). Nevertheless, it has also been observed that SPACCIM-SpactMod allows for model simulations with and without consideration of non-ideality by treating molarities as concentrations and activities, respectively. Therefore, the present implementation of the SPACCIM-SpactMod allows for

detailed studies investigating the importance of non-ideality effects on the multiphase chemistry in deliquesced particles for the first time.

2.2 Multiphase chemistry mechanism

For current model applications, the existing aqueous-phase mechanism CAPRAM 3.0i (Herrmann et al., 2005; Tilgner and Herrmann, 2010; Tilgner et al., 2013) and the latest CAPRAM4.0 (Bräuer et al., 2019) were rather complex. Hence, a condensed chemical mechanism that still reflects the main chemical processes in tropospheric cloud droplets and deliquesced particles was extracted from the CAPRAM3.0i mechanism. The current employed mechanism consists of the inorganic core of the CAPRAM3.0i (Ervens et al., 2003; Herrmann et al., 2005; Tilgner et al., 2013) combined with the organic extension of the CAPRAM 3.0red (Deguillaume et al., 2009) along with a condensed oxidation scheme of malonic acid and succinic acid based on the CAPRAM 3.0red (Deguillaume et al., 2009). Overall, it is worth to be noted that most of the kinetic reaction parameters considered in CAPRAM are determined in the laboratory under dilute and closer to ideal conditions rather than concentrated aqueous aerosol conditions. Thus, effects of important concentrated solution parameters such as ionic strength have not been investigated by such studies and are therefore not considered in the current version of CAPRAM. Once more ionic-strength dependent reaction rate constants become available, they have to be considered in future mechanisms.

A schematic illustration of current multiphase mechanisms used in this model study and the number of considered processes can be found in Fig. S3. Briefly, the applied aqueous-phase mechanism with 395 reactions is coupled with the RACM-MIM2ext gas-phase mechanism (see Tilgner and Herrmann (2010) for further details) with about 277 reactions. The uptake processes of 42 soluble species are included in the mechanism specified according to the Schwartz approach (Schwartz, 1986) considering Henry's law solubility, gas phase diffusion, and mass accommodation coefficient.

2.3 Model simulations

A meteorological scenario has been created for the present simulations, in which an air parcel moves along a predefined trajectory including four cloud passages (two daytime (noon) and two nighttime (midnight) clouds) of about 2 hours within 58 hours of modelling time and a non-cloud deliquesced aerosol period at 90 % relative humidity (RH) in the base case. The applied meteorological scenario is depicted schematically in Fig. 1. Additionally, a sensitivity run considering a lower RH level has been performed at 70 % RH after the second cloud passage to investigate non-ideality effects under lower aerosol liquid water (ALW) conditions. To access the role of a non-ideality treatment for modelling multiphase chemistry in concentrated aqueous aerosols, simulations have been performed both with and without a treatment of non-ideality. Moreover, model simulations were carried out for two different environmental scenarios (urban: anthropogenic polluted case, remote: continental background case) considering summer conditions beginning at 0:00 on the 19th of June (45°N). The two scenarios use different initial gas compositions based on Ervens et al. (2003) ([see https://capram.tropos.de/capram24.pdf for details](https://capram.tropos.de/capram24.pdf)). Applied physical and chemical aerosol initialisation data of the two environmental scenarios are provided in the supplement

(see Table S1/S2). For the simulations, a mono-disperse particle population is assumed, with a dry radius of 0.2 μm . For the sake of clarity, the acronyms "NIDU/NIDR" (Non-Ideal-Urban/Remote) are used for simulations considering the treatment of non-ideality for urban (remote) environmental scenarios and the acronym "IDU/IDR" (Ideal-Urban/Remote) for the ideal solutions for urban (remote) environmental scenarios. An overview on the performed model runs including the acronyms used in this study can be found in Table 1.

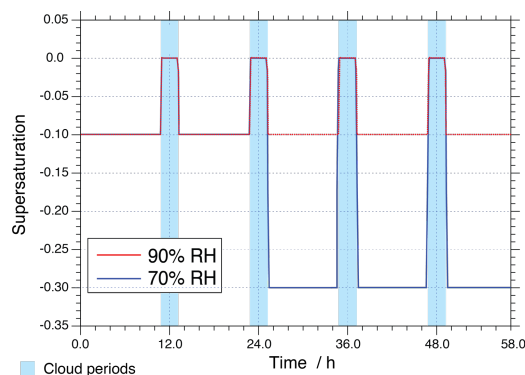


Figure 1 Depiction of the supersaturation along the trajectories of the two different model scenarios with non-cloud periods at 90 % and 70 % relative humidity.

3 Model results and discussions

In this section, SPACCIM-SpactMod simulation results are presented, focusing on (i) the modelled activity coefficients of key compounds under different microphysical conditions, (ii) the impact of a non-ideality treatment on particle acidity and ionic strength, and (iii) the non-ideality impacts on the multiphase processing of key inorganic and organic compounds.

3.1 Modelled activity coefficients

According to the treatment of activities instead of concentrations in the NID runs, the chemical **rates** calculated by the model are affected by the predicted activity coefficients. A comprehensive knowledge of the predicted activity coefficients is, therefore, indispensable in order to understand potential differences between model runs with and without a non-ideality treatment. Thus, the predicted activity coefficients are discussed in the beginning for the most important inorganic and organic compounds, and later subsections focus on the non-ideal solution effects on multiphase chemical processing.

First model test applications using SPACCIM-SpactMod in the companion publication (see Rusumdar et al. (2016)) have already briefly addressed the modelled activity coefficients of a few selected compounds. However, the current paper aims at a more comprehensive investigation of the predicted activity coefficients. Moreover, for the sake of clarity, predicted activity coefficients of key inorganic ions and organic compounds are presented separately in the next two subsections.

3.1.1 Inorganic ions

The predicted activity coefficients of key inorganic ions and water under deliquesced particle conditions (at 29 hours of modelling time) are tabulated in Table 2 for urban and remote environmental conditions for the two different RH cases of 70 % and 90 % (70 %-NIDU/90 %-NIDR), respectively (see Fig. 1 for details). Additionally, the respective ionic strength and the water activity of the highly concentrated solutions are given. As enumerated in Table 2, the predicted activity coefficients are presented separately for inorganic anions and cations. Table 2 shows that activity coefficients of inorganic ions are often less than unity mainly due to long-range electrostatic forces in highly concentrated solutions. However, in some cases, activity coefficients of inorganic ions exceed unity, particularly under lower humidity conditions. Furthermore, Table 2 shows that the 70 %-NIDU/70 %-NIDR cases are characterised by higher ionic strengths ($21.5 \text{ M}^{-1}/25.8 \text{ M}^{-1}$) compared to the 90 %-NIDU/90 %-NIDR cases ($5.2 \text{ M}^{-1}/8.5 \text{ M}^{-1}$).

In detail, singly charged anions show activity coefficients within the range of 0.43-1.03 (0.29–0.66), whereas for the double anion SO_4^{2-} a substantially lower value of 0.02 (0.02) is predicted in the base case (90 %-NIDU (90 %-NIDR)). A similar behaviour including a strong deviation of the predicted activity coefficients from the ion charge state is also observed for cations. For singly charged cations, the predicted activity coefficients are in the range of 0.25-0.38 (0.13-0.30), whereas for doubly and triply charged cations substantially lower values are calculated, with 0.07-0.19 (0.02-0.21) and 0.001 (0.001) under urban (remote) conditions (90 %-NIDU/90 %-NIDR case), respectively.

A comparison of the predicted ion activity coefficients with a small number of values applied in former chemical model studies (Sander and Crutzen, 1996; Mao et al., 2013; Guo et al., 2014) shows reasonable agreements for singly charged anions and cations, but larger differences for doubly and triply charged cations (see Table 3). The above-mentioned studies have considered constant activity coefficients for some aerosol constituents or have applied an activity coefficient of a representative compound, i.e. calculated activity coefficients of a selected ion assuming specific ionic strength, aerosol liquid water (i.e., RH) etc. conditions. Thus, the studies applied one single time-constant activity coefficient representative for singly, doubly, and triply charged anions and cations, ignoring individual ion interaction properties of single ions and RH dependencies. Table 3 shows that the considered activity coefficients in former model studies lie in the range of the coefficients predicted in the present work. For doubly and triply charged ions, larger deviations are obtainable. Nevertheless, it can be observed that the activity coefficients span a range of values, and an approximation with a single representative value can introduce errors into models. The low value of 0.01 for triply charged ions applied by Mao et al. (2013) is caused by an incorrect implementation of the lower limit estimate by Millero and Woosley (2009) ([see remarks in Table 3 for details](#)). The correct value should be

0.13, which is also much higher than the value predicted in the present study. This deviation is caused by the missing middle-range interaction parameters of iron and manganese in the current model implementation. In contrast to these two transition metal ions, the Cu^{2+} cation shows a more complex behaviour when lowering RH and increasing ionic strength. The predicted Cu^{2+} cation activity coefficient at 90 % RH is about 0.19 (0.21) in the urban (remote) case, which is similar to the activity coefficient of Fe^{2+} and Mn^{2+} . However, at lower RH conditions, the predicted Cu^{2+} cation activity coefficient increases to about 3.7 and 1.75 under urban and remote conditions, respectively. This increase cannot be observed for Fe^{2+} and Mn^{2+} . The behaviour of activity coefficients of metal ions to be lower than unity with increasing ionic strength down to a certain minimum followed by an increase to values partly above unity with further increasing ionic strength is known for many metal ions (see Millero and Woosley (2009) for details). However, due to the missing middle-range interaction parameters of iron and manganese ions in the current model, only the ion-ion interactions are considered, leading to an activity coefficient below unity only. The known behaviour with further increasing ionic strength can only be obtained for Cu^{2+} and Mg^{2+} . This limitation needs to be kept in mind because of the potential impacts on the multiphase chemistry discussed later in Sect. 3.3 and 3.4.

The comparison of the two sensitivity cases (70 %-NIDU/NIDR) reveals that the predicted activity coefficients show a considerable variation between the different RH cases (see Table 2). The predicted activity coefficients do not show a linear dependency on relative humidity (RH) and water activity coefficient/ionic strength. The water activity coefficient increases by about 0.04 under urban conditions, and decreases by about 0.01 while decreasing RH under remote conditions. In contrast, it can be seen that the activity coefficients of both anions and cations are often lowered while decreasing RH (see Table 2). The highest percentage decreases can be observed for the triply charged ions Fe^{3+} and Mn^{3+} , which are lowered by a factor of about 3/2 in the 70 %-NIDU/NIDR cases compared to the base cases (90 %-NIDU/NIDR). However, absolute differences are very low for both of these triply charged ions under urban (remote) conditions. Still, it has to be kept in mind that, due to the missing middle-range interaction parameters of iron and manganese ions in the current model, only the ion-ion interactions are considered, which leads to an overestimation of this effect. Interestingly, the smallest percentage decrease/increase in the activity coefficients of the considered singly charged ions has been found for OH^- and H^+ , showing changes of only 12 % (8 %) and 7 % (13 %) between the 70 %-NIDU(NIDR) and 90 %-NIDU(NIDR) runs. Furthermore, a comparison of these model runs shows that the activity coefficients of singly charged halogen ions (except I⁻) are higher at lower RH conditions.

In total, activity coefficients of inorganic ions are often considerably lower than unity and notable differences exist between urban and remote aerosols. Thus, it can be expected that the multiphase processing of inorganic ions is mostly decreased in comparison to model runs assuming ideal conditions. However, for some ions, the activity coefficients tend to increase again under more concentrated conditions (lower RH conditions). Consequently, a RH decrease leads to both lowered and increased activity coefficients, implying an even more reduced or partly increased chemical processing where inorganic ions are involved. The obtained differences in water activity will subsequently affect microphysical parameters, i.e. radius and saturation ratio. Finally, it needs to be mentioned that due to the missing salt formation processes in the present chemical mechanism, the observed values, in particular those for lower RH conditions, might be slightly biased. Consequently, the

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present studies have not treated aerosol conditions below 70 %, where insoluble salt and complex formation processes will play an increasing role.

3.1.2 Organic compounds

Similar to inorganic ions, the predicted activity coefficient values of key organic compounds are tabulated in Table 4 under deliquesced particle conditions (at 29 hours of modelling time) for both urban and remote environmental conditions and the two different RH cases. As can be seen, the predicted activity coefficients of organic compounds show a quite uneven pattern overall with values both below and above unity, depending on the functional subgroups of the corresponding compound and the modelled environmental as well as RH conditions. The predicted activity coefficients were observed to be quite variable even though they are chemically very similar and differ only within the functional subgroups (e.g., CH₂, OH, and/or C(O)OH).

For organic compounds with one or more alcohol functionalities (i.e. without other functionalities), the calculated activity coefficients are usually larger than unity under remote conditions. Exceptions are methanol and hydrated formaldehyde, which partly shows values slightly below unity. Organic compounds such as hydrated glycolaldehyde and glyoxal, including more than three OH functionalities, show activity coefficients of about 1.1-3.1 and 1.1-2.9, respectively, in the two RH cases (90 %-NIDU/70 %-NIDU). The higher activity coefficients are calculated in the 70 % RH runs. Table 4 shows that activity coefficients for mono alcohols and gem-diols are mostly lower under urban conditions than under remote conditions. Moreover, activity coefficients for mono alcohols and gem-diols generally increase while decreasing RH under urban and remote conditions, respectively.

For carbonyl compounds, the behaviour of the activity coefficients of the different compounds is more even. For aldehydes (without other substituents, except HCHO) and substituted carbonyl compounds (see Table 4), activity coefficients are modelled above unity, whereas activity coefficients increase with an increasing carbon chain length. Similar to alcohols, activity coefficients modelled for aldehydes increase with a decreasing RH.

Activity coefficients of monocarboxylic acids, which are often present in deliquesced particles, are less than unity for dissociated acid anions and in most cases around unity for undissociated acids. Only carboxylic acids with further substituents and a longer non-polar carbon chain (e.g. pyruvic and butyric acid) show higher activity coefficients, particularly with decreasing RH. Non-unity activity coefficients for aerosol components have previously been inferred from other measurements (Jang et al., 1997; Mukherji et al., 1997). Interestingly, the predicted activity coefficients of smaller protonated and deprotonated mono acids are partly quite close. The activity coefficients of dissociated acids are expectedly lower but not significantly so. In Table 4, it can further be seen that the predicted activity coefficients of organic acid anions are largely in the same range as those of inorganic anions. A similar behaviour can be observed for dicarboxylic acids anions and their corresponding iron complexes (see Table 3). Mono anions are characterised by higher activity coefficients than dianions, whereas undissociated diacids show activity coefficients partly above unity, particularly when they do not contain many additional substituents. The values of predicted activity coefficients (see Table 3) that are less than unity are somehow

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unexpected, especially because this will lead to an increased partitioning of these compounds in the particle phase. As argued by Cappa et al. (2008), the vapour pressures of individual components show strong, identity-dependent deviations from ideality (i.e., Raoult's Law), with the vapour pressures of the smaller, more volatile compounds decreasing significantly in the mixtures. In addition, in their experimental investigations, they found that the activity coefficients for some of the organic compounds are also less than unity, as the present model results show. Furthermore, based on the obtained numerical values, it can be expected that the non-ideal behaviour of these compounds can modify their gas-particle partitioning.

Overall, the present study shows that activity coefficients of organic compounds are quite variable and compound-specific. Thus, a quite uneven pattern is predicted, with values both below and above unity, leading to both increased and decreased multiphase processing and partitioning of organic compounds due to the treatment of non-ideal conditions. Resulting chemical effects of a non-ideal treatment on key organic subsystems are discussed in detail in the following section.

3.1.3 Other compounds

For the sake of completeness, it should be noted that the non-ideality of some non-electrolyte compounds, including key tropospheric oxidants such as OH, NO₃, O₃ and H₂O₂, are not yet considered in SPACCIM-SpactMod (see Rasmusdal et al. (2016) for details). They are considered with a constant activity coefficient equal to unity. This is a slight limitation of the current implementation which needs to be addressed in the future. For highly concentrated salt solutions, it is known that non-electrolyte compounds can also influence the thermodynamic equilibrium, although the corresponding interactions will generally be much weaker than charge interactions. Accordingly, inorganic non-electrolytes can be treated in principle in the same way as organic non-electrolytes in the current SPACCIM-SpactMod implementation (Walther, 1997; Rasmusdal et al., 2016). However, this approach requires specific short-range interaction parameters. When such parameters are available, the SPACCIM-SpactMod implementation will be improved. However, for many of the considered non-electrolyte compounds, e.g. radical compounds; such short-range interaction parameter are not available yet. Thus, other simpler estimation methods need to be applied. From the literature (see Marini (2007) and references therein), it is well-known that logarithm of the activity coefficient of neutral solutes is a linear function of the effective ionic strength and the Setchenow (also: Setschenow, Sechenov) coefficient (Setchenow, 1892). This relation is typically applied to calculate the activity coefficients of neutral solutes and determine their salting-in/-out behaviour when Setchenow coefficient and effective ionic strength is known (Oelkers and Helgeson, 1991). Unfortunately, Setchenow parameters are unknown for many chemical compounds. In this case, available empirical or theoretical prediction methods should be applied to calculate the Setchenow parameters (see Johnson (2010); Yu and Yu (2013) and references therein).

Moreover, it should be mentioned that also radical anions such as SO₄⁻ and Cl₂⁻ are not yet treated by the current SPACCIM-SpactMod and so their activity coefficients are set to unity. In the future, radical anions such as SO₄⁻ might be treated similarly to their comparable non-radical mono anion (HSO₄⁻) in case of missing interaction parameters. Finally, all of the above-mentioned model improvements will be part of upcoming SPACCIM-SpactMod studies.

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3.2 Particle acidity and ionic strength (I)

3.2.1 Particle acidity

Particle acidity and ionic strength (I) are important factors for physico-chemical multiphase chemistry. Thus, the evolution of acidity and ionic strength throughout the simulation was investigated for cloud and deliquesced particle conditions. The H^+ activity was initialised by means of a charge balance in SPACCIM. Afterwards, the time evolution of pH is computed dynamically throughout the simulation time (see Sehili et al. (2005) for details). Both particle acidity and ionic strength can be affected by changes in chemical processing and microphysical conditions. Mainly, microphysical parameters such as the ALW content pattern pH and ionic strength. The modelled evolution of pH and ionic strength of the 90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU model run throughout the whole simulation time is shown in Fig. 2. The corresponding remote plot is given in the supplement (see Fig. S9).

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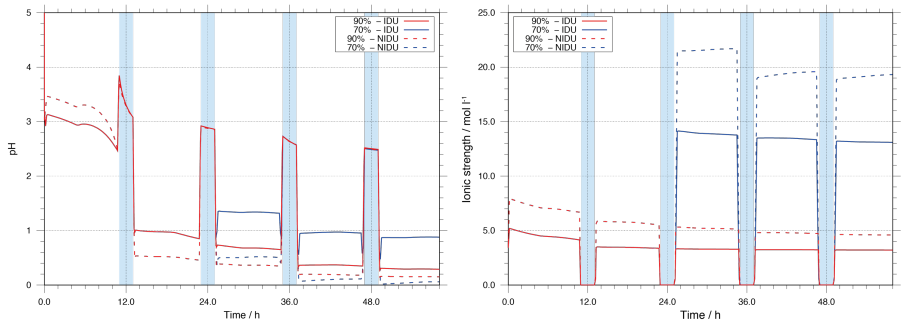


Figure 2 Modelled pH value (left) and ionic strength (I, right) as a function of simulation time for the urban scenario for the different simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

As shown in Fig. 2, the predicted pH value is initially at around 3 in the performed base case simulations (90 %-IDU/NIDU). During the first cloud formation period (daytime cloud), the pH increases from about 2.5 under deliquesced particle conditions (at 90 % RH) up to 3.8 under in-cloud conditions (≈ 100 % RH), i.e. the solution becomes less acidic under diluted cloud conditions. During the first daytime cloud, the aqueous-phase oxidation of acid precursors such as SO_2 leads to an acidification of the cloud solution and a pH value of about 3.1 at the end of the first daytime cloud. Together with cloud evaporation and the substantial decrease of the ALW, the aerosol pH of the processed aerosol drops down to about 1.0/0.5 (90 %-IDU/NIDU), which is about 1.5/2.0 lower than the value before cloud processing. Subsequently, the pH slightly decreases further in both cases (90 %-IDU/90 %-NIDU), and the solution becomes more acidic during the aqueous deliquesced particle periods on the first day. Afterwards, the value of pH slightly decreases during the following cloud and deliquesced periods. The simulation

results show substantially lower pH values for the NIDU cases. The predicted pH at the end of the urban case simulation is about 0.15 and 0.3 for the 90 %-NIDU and 90 %-IDU model runs, respectively.

A comparison of the two different RH cases (see Fig. 2) shows larger differences in the predicted pH between the ideal and non-ideal model run for the lower RH case. The predicted pHs at the end of the 70 %-NIDU and 70 %-IDU model runs are about 0.05 and 0.9, respectively. This tendency of increasing deviations from the ideal solution with decreasing relative humidity has been also observed in experimental and model studies, e.g. Chameides and Stelson (1992); Fridlind and Jacobson (2000); von Glasow and Sander (2001). Nevertheless, experimental investigation of pH in particles is rather difficult, since the ALW contents are usually too small for direct pH measurements (Craig et al., 2018). However, model studies that varied relative humidity were performed mainly for marine environmental conditions (see Fridlind and Jacobson (2000)). Similar studies for remote and urban environmental conditions to compare the present results to are still scarce. Chameides and Stelson (1992) observed a decrease in sea salt aerosol pH when decreasing relative humidity in box model simulations. von Glasow and Sander (2001) argued that the results and the explanation given by Chameides and Stelson (1992) were shown to be insufficient by means of effects of activity coefficients, since microphysical variables also have a certain influence on particle acidity (see von Glasow and Sander (2001)). Moreover, Fridlind and Jacobson (2000) applied the equilibrium model EQUISOLV II in order to analyse the pH of sea salt aerosol for the data obtained through the Aerosol Characterisation Experiment (ACE1) campaign. Their results show that the aqueous-phase aerosol particle pH is less acidic in decreasing relative humidity. Although these results explained the behaviour of the particle pH of marine aerosol particles, similar results were achieved in the sensitivity studies for all the simulations on urban environmental conditions using SPACCIM-SpactMod. During the last simulation period, the 70 %-NIDU case shows slightly lower pH values than the 90 %-NIDU case. In the review of Herrmann et al. (2015), the compiled pH data for measured urban aerosols shows values between -2 and 4. Thus, the predicted pH values of urban conditions of the present study fit into this data range. From the examination of the impact of the non-ideality treatment on pH, it can finally be concluded that the resulting effects on occurring multiphase chemistry (e.g. due to the impact on dissociation equilibria) should be higher with decreasing relative humidity and, vice versa, that the non-ideality treatment leads to differences in multiphase chemistry, which has feedbacks on acidity.

3.2.2 Ionic strength

Besides particle acidity, ionic strength (I) is a key parameter in influencing multiphase chemistry in highly concentrated aqueous solutions. In Fig. 2, the evolution of ionic strength is illustrated for the simulations 90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU, respectively, throughout the whole simulation time. The corresponding plot for the remote simulations is given in the supplement (see Fig. S9). Figure 2 depicts that the ionic strength predicted for the 90 %-IDU case is rather stable, with values from 5 at the beginning to around 3 mol l^{-1} throughout the simulation time during deliquesced aerosol periods. Just during the well-diluted cloud periods, ionic strength drops down to about $2 \cdot 10^{-3} - 8 \cdot 10^{-3} \text{ mol l}^{-1}$. Due to secondary aerosol mass formation (e.g. via in-cloud sulfur(VI) production), the ionic strength of the in-cloud solution decreases slightly from cloud to

Gelöscht: Therefore, the difference of the predicted pHs in the ideal and non-ideal cases is about 0.85 higher between the 70 % RH cases.

cloud. Interestingly, the ionic strength of the aerosol solution stays rather constant throughout the simulation. This behaviour can be explained by two issues. Firstly, connected to the formed soluble secondary aerosol mass, the predicted ALW increase, i.e. the water fraction stays almost constant throughout the simulation time. This compensation mechanism leads to less increased molarities of important ions such as sulfate. Secondly, ionic strength is buffered in aerosol solutions by the acidity effect. The acidification, due to chemical processing (e.g. in-cloud sulfur(VI) formation), affects the dissociations of acids and, thus, the ratio between singly and doubly charged forms. In the case of sulfur(VI), a shift towards the mono anion form (HSO_4^-) is found throughout the modelling time. This shift lowers ionic strength because of the reduced charge number. Overall, both issues buffer an ionic strength increase under deliquesced aerosol conditions. Compared to the ideal base case (90%-IDU), the 90 %-NIDU case shows slightly higher ionic strength levels (approximately 2-3 mol l⁻¹ higher during the non-cloud periods). The higher ionic strength values result partly from higher sulfur(VI) concentrations formed in the 90 %-NIDU case compared to the 90 %-IDU case.

In contrast, for the 70 %-IDU/70 %-NIDU cases, the ionic strength increases to about 14/22 mol l⁻¹ after the second cloud passage when the air parcel is under lower relative humidity conditions (70 % RH). The ideal case (70 %-IDU) always shows somewhat lower ionic strength values than the 70 %-NIDU one. From the present simulations, it can be determined that the ambient RH conditions and the ALW are most likely key impact factors for the ionic strength of the aerosol solution. Finally, the predicted ionic strengths for urban aerosols are in agreement with the data range of literature values (7-45 mol l⁻¹) compiled in the review of Herrmann et al. (2015).

3.3 Multiphase processing of key inorganic compounds

In this section, the impact of a non-ideality treatment on key inorganic compounds is discussed. As key inorganic chemical compounds, such as sulfur(VI) and transition metals, are present in ionic form, their chemistry can be strongly affected by non-ideal solution effects. Furthermore, this leads to affected oxidant levels that are discussed secondly in this section.

3.3.1 Sulfur chemistry

Since S(VI) is one of the main aerosol components substantially formed in the atmospheric aqueous phase, the effects of the non-ideality treatment on S(VI) formation has to be investigated. S(VI) is formed through aqueous-phase oxidation of sulfur dioxide (SO_2) through several oxidants (see Tilgner et al. (2013) for details). Figure 3 shows the modelled aqueous-phase S(VI) concentration in $\mu\text{g m}^{-3}_{(\text{air})}$ as a function of the modelling time for the urban scenario with and without consideration of non-ideality. As shown in Fig. 3, S(VI) is mainly effectively produced in cloud droplets. Furthermore, the production is higher in daytime clouds compared to nighttime clouds. Additionally, it can be seen that there is a small difference in the formed S(VI) of the ideal and non-ideal simulations (90 %-IDU/90 %-NIDU). At the end of the simulation, the concentration in the 90 %-NIDU case is about 12 $\mu\text{g m}^{-3}_{(\text{air})}$ higher than in the 90 %-IDU case (approximately 20 % more S(VI) production). This result reveals that the treatment of non-ideality plays a minor role in predicting the multiphase processing of S(VI) under

Gelöscht: Whereas just a small difference in ionic strength is observed for two simulations at 90 % RH, a more distinct difference of about 6-8 mol l⁻¹ is observed between the 70 %-IDU and 70 %-NIDU cases.

cloudy conditions, but might be important under hazy conditions. The observed findings can be explained by a stronger SO_2 oxidation in the NIDU cases, where higher H_2O_2 concentrations are modelled, leading to higher S(IV) oxidations in daytime aerosol conditions. However, it should be mentioned that the number of available aerosol particles under real haze conditions in strongly polluted areas can be much higher than in the present model study and, thus, the available uptake interface cloud could be larger there. Consequently, S(VI) formation would be less restricted by the uptake of SO_2 into the acidic aerosol phase. Due to quite acidic aerosol solution conditions (see Sect. 3.2.1) and a low aerosol surface/ALW volume, the uptake of the weak acid SO_2 is limited. Therefore, the aqueous-phase formation of S(VI) is more restricted compared to cloud droplets in the present simulations, but would be higher under hazy conditions (higher aerosol loadings and ALWs). From the present study, it can be concluded that for simulating S(VI) formation in polluted continental regions, the cloud phase still represents the most important formation medium. However, considering non-ideal solution effects in the chemistry model, higher S(VI) formation rates under deliquesced aerosol conditions are modelled. This finding implicates the possibility of a stronger contribution under strongly polluted hazy conditions, which should be investigated in upcoming studies.

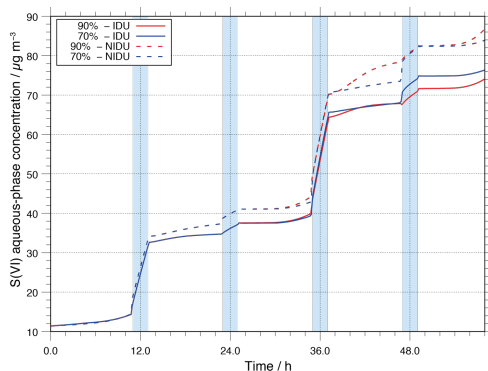


Figure 3 Modelled sulfur(VI) aqueous-phase concentration in $\mu\text{g m}^{-3}$ throughout the modelling time for the different urban simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

3.3.2 Processing of Fe(II)

The time-dependent chemical processing of iron in clouds and deliquesced particles under non-ideal conditions is a quite important process, because iron speciation and redox-cycling is responsible for several chemical interactions (Deguillaume et al., 2005; Tilgner et al., 2013). Deguillaume et al. (2005) argued in their review that there is still a large uncertainty of aqueous-phase TMI (transition metal ion) chemistry, since iron speciation is an indicator for atmospheric oxidation and reduction as well as reactivity of aqueous-phase radical chemistry. However, uncertainty remains mainly because of the restricted

knowledge about the aqueous particle phase processing of TMIs, such as iron. Tilgner et al. (2013) have shown that the chemical processing of iron in deliquesced particles strongly affects other important chemical subsystems, such as HOx chemistry. Therefore, the present study is aimed at reducing the uncertainties of multiphase processing of Fe(II) by treating aqueous-phase aerosol chemistry as non-ideal. In the following, only modelled results were presented for the urban environmental scenario (IDU/NIDU) due to the higher concentration levels and influence of iron under these conditions.

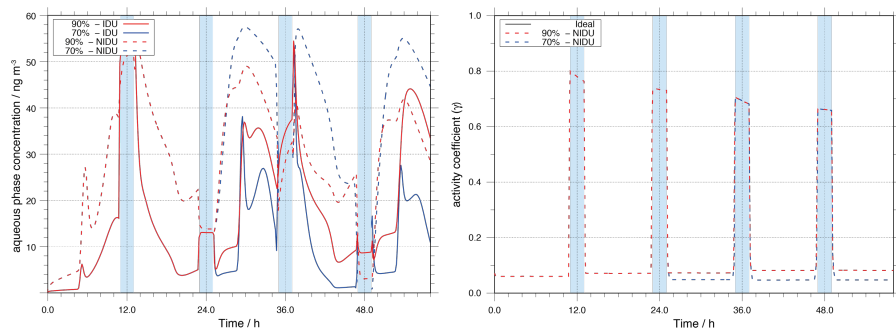


Figure 4 Modelled Fe(II) aqueous-phase concentration in ng m^{-3} throughout the modelling time (left) and corresponding time evolution of activity coefficient (right) for the different urban simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

Figure 4 illustrates the aqueous-phase concentration of Fe(II) throughout the simulation time along with the temporal evolution of corresponding predicted activity coefficients in the different urban simulations. As can be seen in Fig. 4, the aqueous-phase concentration is on average a factor of 2.9 higher throughout the whole simulation time for the 90 %-NIDU simulation compared to the 90 %-IDU model run. Especially under deliquesced particle phase conditions, the concentrations of Fe(II) are substantially higher, indicating a lower oxidation of Fe(II) to Fe(III) in the non-ideal case. The activity coefficient values are less than unity for the whole modelling time (below 0.1 in non-cloud periods), so the non-ideality treatment leads to a reduced multiphase processing of Fe(II). Moreover, Fig. 4 shows that the activity coefficient values tend to have slightly lower values and higher aerosol concentrations of Fe(II) in the 70 %-NIDU case.

A comparison of the modelled total chemical sink and source rates of both urban base case model runs (90 %-IDU/90 %-NIDU) are presented in Fig. 5. There, the modelled chemical sink and source rates of Fe(II) in the aqueous phase plotted for the second model of the 90 %-IDU vs. 90 %-NIDU case can be seen. The corresponding plot for the remote cases is presented in the supplement (see Fig. S10). Figure 5 shows a characteristic daytime profile of the redox-cycling rates, which is interrupted by cloud periods. The comparison reveals both reduced formation and oxidation rates for the 90 %-NIDU case compared to the 90 %-IDU simulation. This finding shows that the Fe(II) oxidation is less efficient when considering non-ideality. Whereas the chemical rates are quite similar under cloud conditions of the 90 %-IDU/90 %-NIDU cases, the chemical

rates under deliquesced aerosol conditions are substantially lowered. Throughout the simulation time, the rates of the 90 %-NIDU case are approximately a factor of 2.8 lower compared to the 90 %-IDU case. Figure 5 reveals that Fe^{2+} interacts mainly with other ions of the aerosol solution. The reaction of Fe^{3+} and Cu^+ is, for example, the main source of Fe^{2+} under deliquesced aerosol conditions. Due to the calculated activity coefficient of ions (see Table 1), which are predicted as less than unity, the calculated reaction rates are lowered under consideration of non-ideality. Hence, the contribution of this reaction during the overall processing of Fe^{2+} is decreased in aqueous particles. As a result, reduced formation rates, including the rates of the most important sink processes, such as the Fenton reaction of Fe^{2+} and H_2O_2 , are modelled. This leads to a reduced processing of HO_2/HO_2 (see the following two subsections for further details).

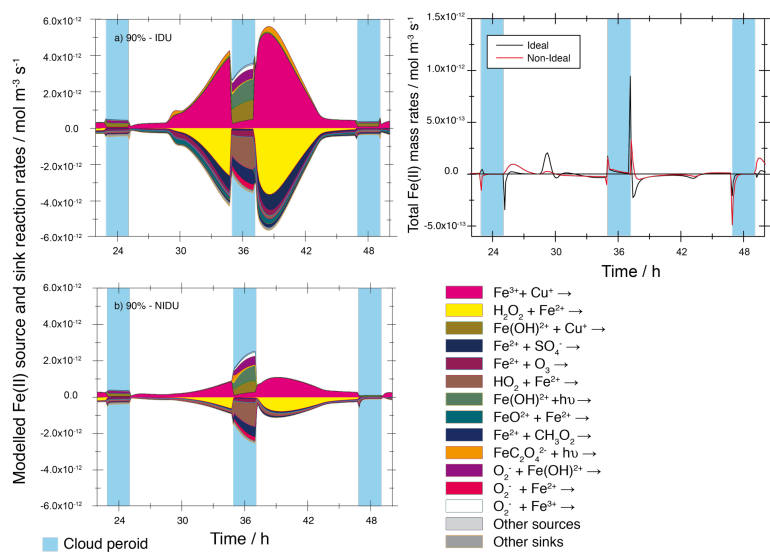


Figure 5 Modelled chemical sink and source mass rates of Fe(II) in the aqueous phase in $\text{mol m}^{-3} \text{s}^{-1}$ for the second day of the urban cases (90 %-IDU/90 %-NIDU). a) ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), c) corresponding total rates (sum of source and sink rates). Only sinks and sources with a contribution larger than $\pm 3\%$ are shown.

To summarise, the model simulations implicate that the multiphase processing of Fe(II) in aqueous particles is significantly affected by the treatment of non-ideality and the effect depends strongly on the ALW conditions. By treating aqueous-phase chemistry as non-ideal solutions, considerably smaller reaction rates of Fe(II) have been observed in deliquesced particles

Gelöscht: processing

compared to ideal solution runs. The impact of this lowered processing on other chemical subsystems, e.g. the changed H_2O_2 processing in the aerosol phase, is discussed in the following sections.

3.3.3 Non-ideality effect on the H_2O_2 budget

Because of the substantially reduced Fe(II) cycling, the resulting effects on the H_2O_2 budget have been studied. The time concentration profiles of gaseous and aqueous H_2O_2 are plotted in Fig. 6 for both the 90 %-IDU/90 %-NIDU and the 70 %-IDU/70 %-NIDU cases. Figure 6 reveals that due to the consideration of a non-ideality, the predicted H_2O_2 concentrations are significantly affected. Figure 6 shows that the predicted gaseous and aqueous concentrations of H_2O_2 are higher for the NIDU simulation cases. The comparison of the two base cases (90 %-IDU/90 %-NIDU) shows that the modelled aqueous concentrations of H_2O_2 are on average a factor of 3.1 larger during the non-cloud periods in the 90 %-NIDU case. A similar pattern can be observed for the gas-phase concentrations of H_2O_2 . This finding is interesting because it demonstrates that the treatment of non-ideality has a potential impact on the multiphase (gas and aqueous phase) budget of H_2O_2 . Using an ideal solution treatment, the gaseous budget of H_2O_2 would be underpredicted and less H_2O_2 would be available for other processes such as aqueous-phase S(VI) oxidation. The higher H_2O_2 concentrations can be explained by chemical [rates](#) (see Fig. S6 in the [supplement](#)).

The analysis of the chemical sink and source mass [rates](#) of aqueous H_2O_2 reveals higher aqueous-phase formation [rates](#) (without considering phase-transfer as a source) during the non-cloud periods in the 90 %-NIDU case. The uptake of H_2O_2 from the gas phase is an important source of aqueous H_2O_2 in the 90 %-IDU case with a contribution of about 48 %. However, the overall uptake [rate](#) of H_2O_2 from the gas phase is about 22 % lower in the non-ideal simulation (90 %-NIDU). This fact is consistent with the 23 % larger aqueous-phase formation [rates](#) in the 90 %-NIDU simulation. Besides the lower uptake [rate](#) from the gas phase, [rate](#) analysis shows an increased contribution of the reaction of HO_2 with Cu^+ to aqueous H_2O_2 formation. The formation [rate](#) of H_2O_2 by reaction of HO_2 with Cu^+ is about 32 % larger in the 90 %-NIDU case than in the ideal simulation, and is the most important source with about 53 %. Moreover, the analysis of the chemical sink [rates](#) of aqueous-phase H_2O_2 shows that the most important H_2O_2 sink, the reaction with HSO_3^- , contributes more in the 90 %-NIDU case (40 % higher [rates](#)). That is the reason for the higher sulfate formation in the non-ideal case. On the other hand, the overall [rate](#) of the other key sinks of H_2O_2 , the Fenton reaction with Fe^{2+} , is about 70 % lower in the 90 %-NIDU case than in the 90 %-IDU one. The reaction [rate](#) analysis implies that the contribution of reaction pathways containing doubly or triply charged ions (e.g. the Fenton reaction of Fe^{2+}) is reduced and, in contrast, the contribution of reaction pathways containing singly charged ions (e.g. the reaction of HO_2 with Cu^+ and HSO_3^- oxidation) increases when non-ideality is considered in the simulation. Overall, it can be concluded that the treatment of non-ideality generally leads to higher multiphase H_2O_2 concentrations and to changes in the [rates](#) of different reaction pathways. Finally, similar results are modelled for the remote cases (see Fig. S11 in the [supplement](#)) but with smaller differences than in the urban case.

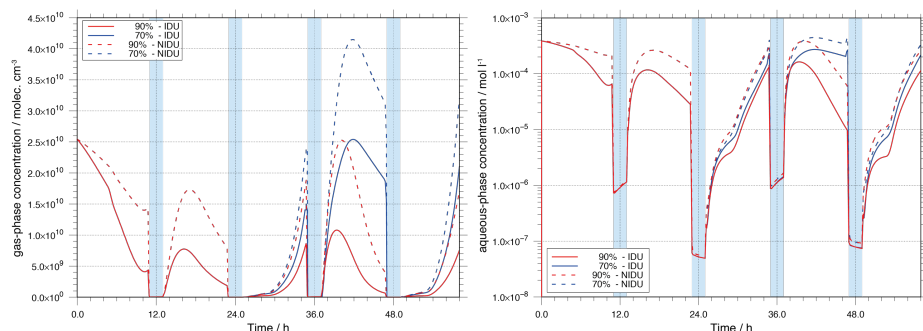


Figure 6 Modelled gas- and aqueous-phase concentrations of H_2O_2 throughout the simulation time for the different urban simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

3.4 Aqueous-phase processing of OH radicals

5 Aqueous-phase OH concentrations

In Fig. 7, the aqueous-phase concentrations of OH in mol l^{-1} are plotted for the urban simulations at 90 % RH (90 %-IDU/90 %-NIDU) and 70 % RH (70 %-IDU/70 %-NIDU). The corresponding plots for the remote scenario are presented in the supplement (see Fig. S12). Due to the strong dependency on both microphysical conditions (e.g. aerosol/cloud water content) and different chemical sink/source [rates](#), the aqueous-phase OH radical concentrations show a diurnal profile interrupted by cloud periods. The modelled OH concentrations in the deliquesced particles are higher than the concentrations under in-cloud conditions. Comparing the concentration levels in the deliquesced particles before and after a cloud passage, Fig. 7 shows a reduction after cloud evaporation. This reflects effective in-cloud oxidations, which affects OH formation pathways after cloud passages. The reduction after cloud evaporation is more distinct in the non-ideal cases.

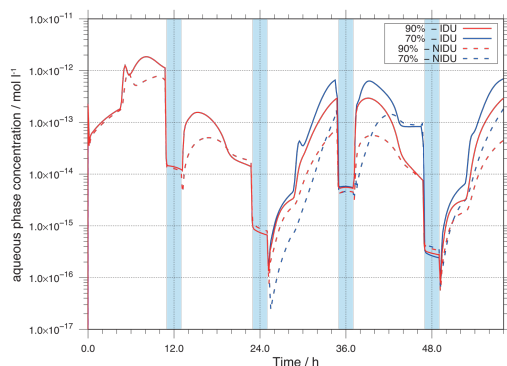


Figure 7 Modelled OH aqueous-phase concentrations in mol l^{-1} throughout the simulation time for the different urban simulation cases (90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU).

A comparison of the ideal and non-ideal base case simulations (90 %-IDU/90 %-NIDU) shows substantially higher OH concentrations for the ideal case (90 %-IDU). The ideal base model run (90 %-IDU) is characterised by higher concentrations, on average a factor of 4 higher, than the concentrations in the 90 %-NIDU case under non-cloud conditions. At the end of the 90 %-IDU/90 %-NIDU simulations, deliquesced particle-phase concentrations of about $3.0 \cdot 10^{-13}/4.5 \cdot 10^{-14} \text{ mol l}^{-1}$ are modelled, showing a factor of about 7 higher OH levels under aerosol conditions. On the other hand, the cloud concentrations in both cases are almost similar. This behaviour can be explained by the importance of different sources under deliquesced aerosol and cloud conditions. The in-situ sources are strongly affected by the non-ideality treatment under non-cloud conditions, whereas its impact under cloud conditions is minor.

Interestingly, OH concentrations of the 70 %-NIDU simulation are partly higher than the ones modelled in the 90 %-NIDU case. This change in the concentration pattern can be explained by changes in the reaction [rates](#) (see below). Moreover, the 70 %-NIDU case also shows higher concentrations during the first half of the second night period than the 90 %-NIDU case. The modelled concentration is almost one order of magnitude higher in the 70 %-NIDU case before the second nighttime cloud ($\approx 47 \text{ h}$), indicating higher OH formation [rates](#) in this model case. This also enables higher OH oxidations during this night period (see below for details). At the end of the simulation, the daytime aerosol concentrations of the 70 %-NIDU case are about a factor of 4 higher than in the 90 %-NIDU case, but still lower than in the two ideal simulations.

Aqueous-phase OH formation and oxidation [rates](#)

The significant differences obtained in the ideal and non-ideal concentration patterns suggest that the activity coefficients of the reaction partners of OH have a strong influence on the modelled chemical sinks and sources and, finally, the aqueous-

phase concentrations of OH. Even though the activity coefficients for neutral radicals such as OH are considered as unity in the present model, the influence of non-ideality has been considered for the computation of reaction rates, when the radicals react with other organic/inorganic compounds. As tabulated in Table 2 and Table 4, the activity coefficients of key inorganic and organic OH reaction partners strongly vary. Subsequently, the chemical mass rates of sink and source reactions for the OH radical can be increased or decreased depending on individual activity coefficients. The differences in the aqueous-phase reaction rates are depicted in Fig. 8.

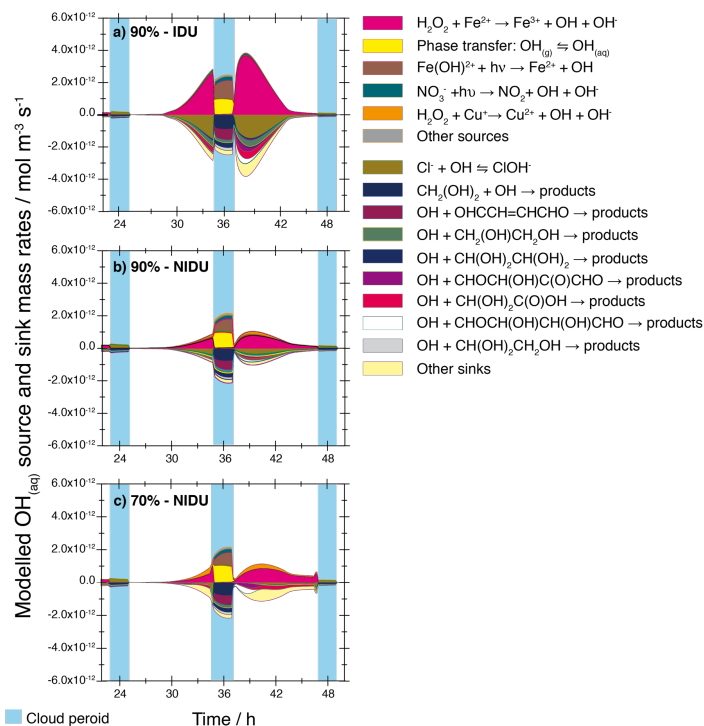


Figure 8 Modelled chemical sink and source mass rates of OH in the aqueous phase in mol m⁻³ s⁻¹ for the second day of modelling time for the urban scenario for the simulations 90 %-IDU vs. 90 %-NIDU vs. 70 %-NIDU. a) ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), and c) non-ideal solutions (70 %-NIDU).

In detail, Fig. 8 shows the chemical mass **rates** of different OH reaction pathways (sinks/sources) for the simulations 90 %-IDU, 90 %-NIDU, and 70 %-NIDU for the urban scenario throughout the second model day. Figure 8 shows only minor differences in the chemical **rates** under cloud conditions where non-ideality effects are minor and are therefore not further discussed. Larger differences can be obtained during the deliquesced aerosol periods. As illustrated in Fig. 8, both the total source and sink **rates** are lowered in the deliquesced particle phase when non-ideality is considered. Further, the peak in the source and sink **rates** is slightly delayed towards the later afternoon for the 70/90 %-NIDU simulations compared to the 90 %-IDU one. Due to the treatment of non-ideality, the total OH formation **rate** of the 90 %-NIDU case is reduced by about 52 % throughout the whole simulation time compared to the 90 %-IDU case, and by a factor of ≈ 4 in the afternoon peak on the second day (see Fig. 8). Interestingly, a **rate** comparison of the 70 %-NIDU and 90 %-NIDU simulations reveals a slightly higher afternoon peak on the second day and markedly higher **rates** in the first half of the second nighttime period in the 70 %-NIDU case. This finding implies higher OH oxidation **rates** in aqueous aerosols at nighttime in the more concentrated case (70 %-NIDU). Overall, the total OH **rate** in the deliquesced particle periods of the 70 %-NIDU case is about 8 % higher than in the 90 %-NIDU one. This finding implies that the chemical processing in deliquesced particles might be more favourable under more concentrated solutions rather than higher humidity aerosol conditions.

A more detailed look at the specific reaction **rates** reveals that, in all simulation cases, the OH production under aqueous particle conditions is strongly related to the Fenton reaction of Fe^{2+} . This means that in-situ OH production strongly depends on both Fe^{2+} and H_2O_2 concentrations. This finding is in agreement with former CAPRAM mechanism studies (see Tilgner et al. (2013)). Additionally, a comparison of the formation **rate** pattern of the two non-ideal cases reveals that the Fenton-like reaction of copper contributes noticeably more to the aqueous-phase formation of OH in deliquesced particles. This additional source leads to the slightly higher OH formation **rates** in the 70 %-NIDU case than in the 90 %-NIDU one. The stronger contribution of this OH source can be explained by both the substantially higher activity coefficient of Cu^+ under 70 % RH conditions (see Table 2), leading to higher chemical **rates**, and the larger H_2O_2 budget in the 70 %-NIDU case. The latter additionally causes higher formation **rates** in the 70 %-NIDU case until the second nighttime cloud. After its evaporation, the formation **rates** are lowered as a consequence of the substantially lowered H_2O_2 budget due to efficient in-cloud sulfur oxidation.

As shown in Fig. 8, the OH sinks are also affected in the deliquesced particle periods due to the treatment of non-ideality. Figure 8 shows a change in the sink **rate** pattern between the 90 %-IDU and 70/90 %-NIDU cases, respectively. In aqueous particles, the relative OH radical loss by reactions with organic compounds and the gaseous OH uptake is increased and, on the other hand, the fraction of Cl^- interaction with OH is lowered under 90 %-NIDU conditions compared to the ideal base case. Throughout the whole simulation, the Cl^- interactions with OH contribute about 36 %, 26 %, and 14 % to the OH sink **rates** during the non-cloud periods in the 90 %-IDU, 90 %-NIDU, and 70 %-NIDU cases, respectively. Accordingly, the relative contributions of OH oxidation reactions of organic compounds, particularly substituted carbonyl compounds and undissociated organic acids, often increase in the non-ideal cases. Moreover, a comparison of the two non-ideal simulations,

90 %-NIDU and 70 %-NIDU, shows differences (see Fig. 8) in the sink reactions under deliquesced particle conditions. In the 70 %-NIDU case, OH reactions of substituted carbonyl compounds and undissociated organic acids are more important than in the 90 %-NIDU one. For example, the contribution of the OH oxidation of pyruvic acid/glycolic acid (undissociated) to the total sink rates (over 58 h) is increased from 0.7 %/2.8 %, 0.8 %/3.6 % to 2.6 %/4.7 % in the 90 %-IDU, 90 %-NIDU, and 70 %-NIDU cases, respectively. The raised contribution of substituted organic compounds can be partly explained by the higher activity coefficients of such compounds under more concentrated conditions (see Table 4 and Sect. 3.1.2). The raised degradations of some organic undissociated acids and other substituted organic compounds leads to an affected concentration pattern of those compounds (see the following subsection for details).

Overall, the present model investigations reveal that the processing of OH radicals (formation and loss processes) in aqueous particles is reduced, considering the treatment of non-ideality of concentrated solutions, mainly because of the lowered in-situ formation of OH. Furthermore, the treatment of non-ideality leads to differences in the chemical sink and source contributions of different chemical pathways. However, the results here strongly depend on the non-ideality effects of transition metal ions and microphysical conditions (ALW conditions). As discussed above, missing middle-range interaction parameters of iron and manganese ions in the current model lead to activity coefficients below unity only for iron and manganese ions. This limitation may lead to a strong under-prediction of the Fenton reaction rates and thus to undervalued OH formations and aqueous-phase oxidation rates. Additionally, performed sensitivity studies, which have applied the MR interaction parameters of Cu²⁺ for Fe²⁺/Mn²⁺ (see supplement for further details), shows a more active TMI-HOx cycling (see Fig. S15-S17) under deliquesced aerosol conditions and clearly demonstrate that MR interaction parameters of key TMIs represents crucial parameter that need to be determined in future laboratory experiments to improve current model implementations.

3.5 Multiphase processing of organic compounds

The aqueous-phase chemical processing of organic compounds is expected to not only be limited to in-cloud conditions but also to proceed in aqueous particles with significant chemical rates (Tilgner and Herrmann, 2010; Tilgner et al., 2013). In contrast to former studies that assumed aqueous-phase chemistry as ideal solutions, the present SPACCIM-SpactMod study is aimed at investigating the effects of a non-ideality treatment on the organic processing of important organic C₂ and C₃ oxidation pathways. The results of the C₂ chemistry are presented in the following and the C₃ chemistry results are presented in the supplement for the sake of clarity.

As shown in many former model studies (Ervens et al., 2003; Herrmann et al., 2005; Tilgner and Herrmann, 2010; Ervens et al., 2011), in-cloud oxidations of C₂ carbonyl compounds such as glycolaldehyde and glyoxal lead to the formation of substituted organic acids (e.g. glyoxylic and glycolic acid), which can be further oxidised into oxalic acid, contributing to aqSOA under both cloud and aerosol conditions. However, available studies within the literature have not yet considered the effects of non-ideality and therefore have to be deemed incomplete.

Gelöscht: <#>C₂ organic chemistry

Figure 9 shows the modelled aqueous-phase mass concentrations of oxalic acid and its precursors, glyoxylic and glycolic acid, along with corresponding activity coefficients vs. simulated time under urban environmental conditions for the 90 %-IDU/90 %-NIDU and 70 %-IDU/70 %-NIDU simulations, respectively. For the sake of clarity, the sums of dissociated and undissociated aqueous-phase concentrations of the carboxylic acids are plotted in Fig. 9.

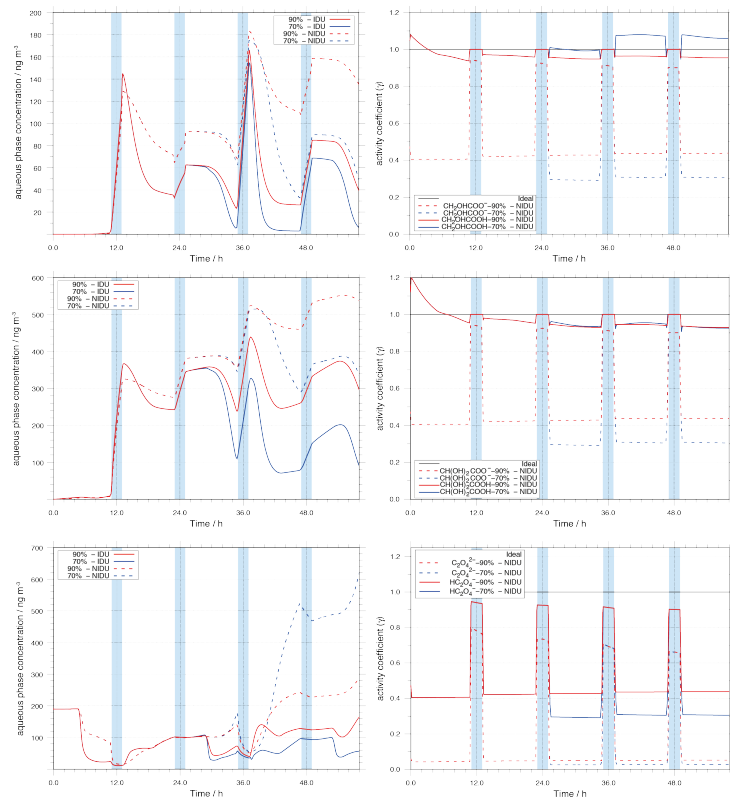


Figure 9 Modelled aqueous-phase concentrations in $\text{ng m}^{-3}(\text{air})$ and corresponding activity coefficients for the important C_2 oxidation products, (i) glycolic acid (top), (ii) glyoxylic acid (centre), and (iii) oxalic acid (down). The plotted concentrations represent the sum of the dissociated and undissociated forms of the acids.

As shown in Table 4 and Fig. 9, the activity coefficients of dissociated and undissociated forms of the above-mentioned acids are different. The predicted activity coefficients of the undissociated acids are substantially higher than those of the dissociated forms. These differences in the activity coefficients of dissociated and undissociated forms of the organic acids, together with the different oxidant budget, affect the chemical processing of those acids in deliquesced particles along with the molarity of the compound under different RH conditions.

The predicted concentration-time profiles presented in Fig. 9 show that the oxalic acid precursors, glyoxylic and glycolic acid, are effectively produced under cloud conditions. Furthermore, it can be seen that their degradation proceeds almost in deliquesced particles. Both findings are in agreement with former studies (see e.g., Tilgner et al. (2013)).

Glycolic and glyoxylic acid

For glycolic and glyoxylic acid, the modelled in-cloud productions in the 90 %-NIDU and 90 %-IDU cases are similar (see Fig. S7 and S8 in the supplement). However, due to the incorporation of activity coefficients, lower degradations in the 90 %-NIDU than in the 90 %-IDU case are modelled in aqueous aerosols. Furthermore, the production in the aqueous particle phase is also not similar. Throughout the whole simulation period, the deviation increases with the simulation time for 90 %-IDU and 90 %-NIDU.

The modelled concentrations of glycolic acid in the 90 %-NIDU case are substantially higher at about 135 ng m⁻³ at the end of the simulation time compared to the 90 %-IDU case at about 40 ng m⁻³. A comparison of the two non-ideal cases (90 %-NIDU/70 %-NIDU) reveals a faster and longer ongoing degradation of glycolic acid in the deliquesced particle phase under the lower humidity conditions of the 70 %-NIDU case. At the end of the simulation, the modelled glycolic acid is, surprisingly, closer to the modelled 90 %-IDU case than to the 90 %-NIDU one at about 50 ng m⁻³. The modelled glycolic acid concentration pattern reveals substantially higher degradation levels in the afternoon of the second day and the first half of the second night period (37 h–47 h) until nighttime cloud formation. Therefore, the final glycolic acid concentration is much lower in the 70 %-NIDU case than in the 90 %-NIDU one. Due to the considered non-ideality treatment, both formation and degradation rates are decreased in the non-ideal 90 %-NIDU case. The formation and degradation rates of glycolic acid in the ideal case are 28 % and 74 % larger, respectively, throughout the whole simulation time. Moreover, the comparison of the time-resolved overall sink rates shows 13 % and 71 % higher formation rates in the 90 %-IDU case under in-cloud and aqueous aerosol conditions, respectively. Furthermore, the sink rates under aerosol conditions are about 2 times larger than in the non-ideal base case. Consequently, the larger sink rates in the ideal case (90 %-IDU) reflect that the resulting glycolic acid concentrations are higher in the 90 %-NIDU case than in the 90 %-IDU one. The lower oxidation of glycolic acid in the 90 %-NIDU case, particularly in the afternoon, also leads to a shift in the contributions of oxidants to the overall oxidation rate.

Whereas the overall oxidation rate of glycolic acid via OH is lowered by 50 % due to the strongly lowered OH budget, the NO₃ oxidation rate of glycolic acid is increased instead, particularly during the nighttime cloud phase. During that phase, glycolic acid is more present in its dissociated form, electron transfer reactions are favoured more, and the concentration budget is higher because of the lowered daytime decay. A similar picture can be seen for glyoxylic acid. The modelled urban

concentration profiles of glyoxylic acid show the same trend as glycolic acid. Thus, a discussion of the glyoxylic acid concentration pattern and [rates](#) is omitted in the present study for the sake of clarity.

Oxalic acid

Besides glyoxylic acid and glycolic acid, Fig. 9 also depicts the concentrations of its key oxidation product, oxalic acid.

5 From the reduced degradation [rate](#) of the substituted mono carboxylic acids, one could expect lower oxalic acid concentrations under non-ideal conditions (90 %-NIDU). However, the lowered formation [rates](#) of oxalic acid do not lead directly to lower predicted concentrations of oxalic acid. The treatment of non-ideality significantly affects the chemical sinks of oxalic acid and the predicted degradation [rates](#) are lower in cases treating non-ideality effects. Thus, the resulting oxalic acid levels at the end of the simulation are substantially higher in the 90 %-NIDU and particularly in the 70 %-NIDU case. In the 90 %-NIDU
10 case, the final concentration is a factor of about 1.8 higher than in the 90 %-IDU case. The difference in the predicted oxalic acid mass is even higher in the 70 % cases (70 %-NIDU/70 %-IDU). There, the predicted oxalic acid concentration at the end of the simulation is a factor of 10 higher compared to the model without non-ideality treatment (70 %-IDU). A similar tendency with higher predicted oxalic acid concentrations in the non-ideal cases is also observed in the remote simulations, but at lower concentration levels (see Fig. [S13](#) in the supplement).

15 The higher Fe(II) concentrations, the reduced chemical processing of iron, and the modelled activity coefficients of the different oxalic acid anions and iron-oxalate complex ions in the simulations with non-ideality treatment leads to a smaller complexation of the diacid. This results in substantially lower [rates](#) of the photochemical decompositions of the iron-oxalate complexes and thus to higher oxalic acid concentrations in both the 90 %-NIDU and 70 %-NIDU cases. A comparison of the modelled reaction [rates](#) (90 %-IDU/90 %-NIDU, see Fig. 10) shows, firstly, a distinct reduction of the formation [rates](#) and,
20 secondly, a drastic change in the decomposition [rate](#) pattern.

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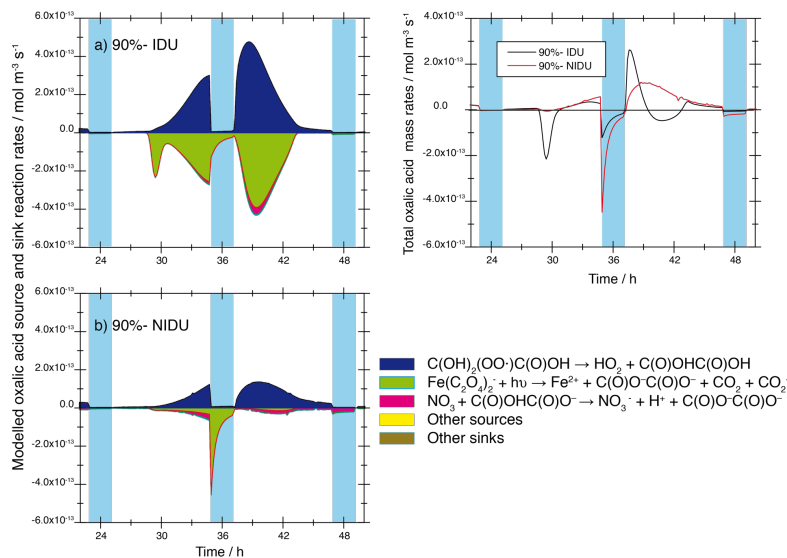


Figure 10 Modelled chemical sink and source mass rates of oxalic acid/oxalate in the aqueous phase in $\text{mol m}^{-3} \text{s}^{-1}$ for the second day of modelling time for the urban scenario for the simulations 90 %-IDU vs. 90 %-NIDU. a) Ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), c) corresponding total rates. Only sinks and sources with a contribution larger than ± 3 % are presented.

- 5 As discussed in Tilgner and Herrmann (2010), the formation of oxalic acid mostly takes place in the aqueous phase of deliquesced particles. As shown in Fig. 10, oxalic acid is effectively produced by the oxidation of glyoxylic acid, predominantly during the day, especially in deliquesced particles. On the other hand, oxalic acid is also substantially decomposed via the fast photo-catalytic decay of iron-oxalate complexes. Consequently, quite low oxalic acid concentrations are predicted in the ideal base case (90 %-IDU). A comparison of the modelled rate pattern (90 %-IDU/90 %-NIDU) in Fig. 10
- 10 reveals that the computed overall formation and degradation reaction mass rates were decreased by factor of 2.5 and 2.9, respectively, for the 90 %-NIDU simulation compared to the 90 %-IDU one. This stronger reduction leads to higher oxalic acid concentrations. Moreover, the sink rate pattern shows high values during cloud periods in the non-ideal case (90 %-NIDU) and only small photolytic decay rates during non-cloud periods. This change in sink pattern is caused by the non-ideality treatment that lowers the formation of iron-oxalate-complexes. The interaction of the doubly charged oxalate and the triply charged Fe^{3+} ion is reduced due to the modelled activity coefficients of such ions that strongly depend on the charge number.
- 15 Due to the high charge numbers of the complexing agents (high LR interactions), the iron complex formation is less efficient

than in the ideal case. Consequently, efficient photolysis is hampered and less oxalate is decomposed. In total, the present studies demonstrate that the treatment of non-ideality can significantly affect multiphase oxidation and the resulting concentration budget of important C₂ carboxylic acids. The non-ideality treatment also enables more realistic predictions of high oxalate concentrations as observed in field campaigns under highly polluted conditions (van Pinxteren et al., 2014; Kawamura and Bikkina, 2016; Zhu et al., 2018).

Overall, the present investigations of organic chemistry have demonstrated that the processing of organic compounds and, subsequently, their concentrations in aqueous particles can be affected substantially by considering the treatment of non-ideality of concentrated solutions. The effects are mainly caused by the changed oxidants budget and the different activity behaviours of the different organic compounds. Moreover, the non-ideality treatment leads to substantial changes in the chemical sink and source pattern compared to the ideal simulations.

4 Conclusions

For the first time, detailed simulations with the advanced parcel model SPACCIM-SpactMod have been carried out for the different microphysical conditions with and without a treatment of non-ideality for aqueous-phase aerosol chemistry. Special emphasis was put on the different chemical subsystems, including key inorganic compounds, radical and non-radical oxidants, and organic compounds, in order to examine the effects of a non-ideality solution treatment. The simulation results highlight that a treatment of activities instead of concentrations strongly affects the chemical multiphase processing in deliquesced particles.

The investigations of the predicted activity coefficients have revealed substantial differences between different charged and uncharged aerosol compounds. For inorganic ions, activity coefficients are often considerably lower than unity under 90 % RH conditions and strongly decrease with the increasing charge state of the respective ion because of the impact of long-range electrostatic forces in highly concentrated solutions. In detail, the predicted activity coefficients of singly, doubly, and triply charged inorganic ions are in the range of 0.25-1.03 (0.13-0.66), 0.02-0.19 (0.02-0.21), and 0.001 (0.001), respectively, under urban(remote) 90 % RH conditions. Interestingly however, the activity coefficients of some inorganic ions exceed unity, particularly under lower humidity conditions when the aerosol solution is even more concentrated. Consequently, an RH decrease can cause both lowered and raised activity coefficients, leading to more reduced or increased chemical processing for pathways involving inorganic ions. However, once more, increasing activity coefficients with values larger than unity under lower humidity conditions have only been modelled for some metal ions, such as Cu²⁺ and Mg²⁺. Unfortunately, the current model cannot model such an increase for other chemically important transition metal ions, e.g. Fe²⁺ and Mn²⁺. The behaviour of the activity coefficients of metal ions to be lower than unity with increasing ionic strength down to a certain minimum, followed by an increase to values partly above unity with further increasing non-ideality is strongly related to the MR interaction forces. However, due to missing MR interaction parameters in the current model, e.g. of iron and manganese ions, only ion-ion interactions are considered, leading to activity coefficients below unity only. As demonstrated by additional sensitivity studies, this limitation have potential impacts on the multiphase chemistry in the current model, leading to an

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As presented in former CAPRAM studies (e.g. Tilgner and Herrmann (2010)), methylglyoxal is effectively oxidised under cloud conditions, leading to the formation of substituted C₃ carboxylic acids, which are expected to be further oxidised in aqueous aerosols. In Fig. 11, the aqueous-phase concentrations of the main C₃ oxidation products, such as pyruvic acid, 3-oxo pyruvic acid, and finally keto malonic acid, along with corresponding activity coefficients are plotted throughout the simulation time for all urban scenarios. The corresponding plots for the remote scenario are presented in the supplement (see Fig. S7).

Figure 11 shows that the first stage oxidation product, pyruvic acid, is effectively produced under both day- and nighttime cloud conditions. Noticeably, urban nighttime clouds reveal a higher production of pyruvic acid than corresponding daytime clouds. This finding is in agreement with former studies (Tilgner and Herrmann, 2010; Tilgner et al., 2013), showing that in-cloud NO₃ radical oxidation represents an important sink for methylglyoxal and, consequently, a source for pyruvic acid under urban conditions.

Figure 11 illustrates that the activity coefficients of formed oxidation products are below unity for their dissociated forms in the 90 %-NIDU and 70 %-NIDU simulations under deliquesced aerosol conditions. However, their undissociated forms partly show activity coefficients above unity. Consequently, the non-ideality treatment can affect their further chemical processing differently in addition to the affected oxidant budget. In detail, undissociated pyruvic acid is characterised by activity coefficients above unity (about 1.5 in the 90 %-NIDU case) and its dissociated form by values of about 0.4 (90 %-NIDU case). Thus, non-ideality effects can increase the chemical processing of pyruvic acid and decrease the chemical processing of pyruvate. Under 70 %-NIDU conditions, pyruvic acid and pyruvate are characterised by even more different activity coefficients of about 3.0 and 0.3, respectively. Therefore, even higher differences between the ideal and the non-ideal treatment can occur.

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underestimation of certain chemical processes under lower RH conditions. Therefore, the present model studies implicate that there is a demand for further improvements of the current model implementation by MR interaction parameters from future laboratory studies.

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The predicted activity coefficients of organic acid anions are in the same range of those of inorganic anions. However, the behaviour of the activity coefficients of uncharged organic compounds is partly different because of their dependence on the nature of intermolecular interaction forces. Thus, the predicted activity coefficients of organic compounds are quite variable and compound-specific. This uneven pattern of organic compounds with values of predicted activity coefficients of both below and above unity implies an increased or decreased aqueous phase processing due to the treatment of solution non-ideality. In general, the activity coefficients for alcohols, gem-diols, aldehydes, dialdehydes, as well as undissociated mono and dicarboxylic acids with longer carbon chains are observed as larger than unity, whereas smaller carboxylic acids and particularly carboxylate ions are observed as below unity. The activity coefficients strongly depend on functional and CH_x groups contained in organic molecules. Moreover, the present study demonstrates that activity coefficients of many uncharged organic compounds, generally strongly increase while decreasing the RH under both urban and remote conditions.

As a consequence of the non-ideal solution treatment, the present model investigations show that the chemical multiphase processing of inorganic compounds is often strongly affected. The model simulations reveal that the multiphase processing of Fe(II) in aqueous particles is significantly reduced by the treatment of non-ideality and the effect depends strongly on the ALW conditions. The decreased Fe(II) processing has a substantial effect on other chemical subsystems leading to, for example, changed H₂O₂ and OH processing in aqueous aerosols.

In the case of H₂O₂, the model simulations illustrated that due to the consideration of a non-ideality treatment, the predicted H₂O₂ concentrations are significantly higher in both the gas and the aqueous phase. This effect is caused by the significantly lowered degradation rate of H₂O₂, mainly the Fenton reaction, and increased formation rates, e.g. via the reaction of HO₂ with Cu⁺. On the other hand, higher chemical rates of the sulfur oxidation, H₂O₂ reaction with HSO₅⁻, have been modelled. Thus, this study implicates that the treatment of non-ideality has a potential impact on H₂O₂, resulting in higher multiphase concentrations of this oxidant. This higher oxidant level is, consequently, available for other processes, such as a more aqueous-phase S(VI) oxidation leading to a higher aerosol mass. The present study has shown approximately 20 % more S(VI) production compared to an ideal urban model run.

The smaller importance of the Fenton reaction under aqueous aerosol conditions is shown to also affect other oxidants besides H₂O₂. The present model investigations reveal that the processing of OH radicals (formation and loss processes) in aqueous particles is substantially lowered considering the treatment of non-ideality of concentrated solutions, mainly as a consequence of the reduced in-situ formation of OH by the Fenton reaction. Additionally, the non-ideality treatment produces chemical differences in the sink and source patterns of different chemical pathways. However, this finding strongly depends on the non-ideality effects of transition metal ions and the microphysical conditions (ALW). Therefore, the missing MR interaction parameters of, for example, iron and manganese ions introduce uncertainties in the current model. This may cause a too strong

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underprediction of the Fenton reaction and may thus lead to an undervalued OH formation and OH-initiated aqueous-phase oxidation [rates](#). Thus, this issue needs further investigations in upcoming model studies.

Due to the affected concentration budget and the rates of oxidants, significant effects on multiphase oxidations and the resulting concentrations of important organic aerosol components have been observed by comparing ideal and non-ideal solution simulations. Interestingly, the reduced aqueous-phase OH oxidation budget leads to lowered oxidations in deliquesced particles and thus to higher concentration levels of oxidised compounds mainly produced in the cloud phase. On the other hand, the present simulations have demonstrated that production and degradation pathways can be asymmetrically influenced, resulting, for example, in higher oxalate concentrations. Although the oxalate precursors are less further oxidised in deliquesced aerosols and the oxalate formation [rates](#) are therefore reduced, the simulations with a non-ideality treatment revealed higher oxalate concentrations because of the even stronger reduced photolytic decays of iron-oxalate complexes. Thus, non-ideal simulations enable more realistic predictions of high oxalate concentrations as observed in field campaigns under highly polluted conditions. Moreover, this also makes artificial disregards of the photolytic decays of iron-oxalate complexes in some other multiphase chemical mechanisms (e.g. Ervens et al. (2004)) unnecessary. Furthermore, the present study implicates that lower humidity conditions, characterised by more concentrated solutions, might promote the formation of higher oxalic acid concentration levels in aqueous aerosols. In conclusion, the present investigations of organic chemistry have shown that the processing of organic compounds and subsequently their concentrations in aqueous particles can be affected substantially by considering the treatment of non-ideality of concentrated solutions. The effects are mainly caused by the changed oxidants budget and the different activity coefficient behaviour of the different organic compounds. Moreover, the non-ideality treatment leads to substantial changes in the chemical sink and source pattern compared to the ideal simulations. Nevertheless, it should be kept in mind that the present results are strongly related to the non-ideality effects of transition metal ions, oxidants, and ALW (microphysical) conditions. Therefore, the present results have to be considered as an initial step for further studies with more advanced model versions in the future.

Overall, the model studies have implicated the importance of the consideration of the treatment of non-ideality for tropospheric aerosol constituents for the first time, especially in the deliquesced particle phase. From the current SPACCIM-SpactMod model studies along with detailed reaction [rate](#) investigations, it can be concluded that the treatment of non-ideality is highly necessary in multiphase models to gain an understanding of physico-chemical multiphase processing in aqueous aerosols. Likewise, the current model studies reveal the need for further detailed analysis in order to understand the effect of non-ideality and unsolved issues of multiphase processing of aqueous aerosol particles by adopting more complex chemistry with a high number of organic compounds. Further studies also need to be performed for different meteorological conditions, i.e. marine environmental conditions. Additionally, adequate consideration of liquid-liquid separations as well as salt formation (crystallization) in deliquesced aerosol particles is also necessary, which can potentially alter the ionic strength and acidity, and thus influence non-ideality. Moreover, model advancements are necessary by extending the database with new organic and inorganic AIOMFAC interaction parameters (Ganbavale et al., 2015; Gervasi et al., 2019).

Data availability. The model initialisation data are provided in the Appendix. Further SPACCIM-SpactMod datasets and model simulation data of this study can be accessed by contacting the corresponding authors (H. Herrmann: herrmann@tropos.de / R. Wolke: wolke@tropos.de).

Supplement. The supplement related to this article is available online at:

- 5 *Author contributions.* AJR, AT, and RW have designed and performed the SPACCIM-SpactMod model simulations. AJR, AT, RW and HH have analysed model results. AT, RW, AJR and HH have written the paper.

Competing interests. The authors declare no conflicts of interest.

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Review statement.

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Tables

Table 1. List of the microphysical model scenarios and their acronyms used in this study.

Case	Chemistry treatment	Environmental 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

Table 2. Predicted activity coefficients of selected ions and water, as well as the ionic strength in deliquesced particles for the 90 %/70 %-NIDR and 90 %/70 %-NIDU simulations at 29 hours. $\Delta\gamma$ represents the ratio of the predicted activity coefficients of the 90 % case and the 70 % case, respectively.

Compound	Urban			Remote		
	90 %	70%	$\Delta\gamma$	90 %	70%	$\Delta\gamma$
<u>Inorganic anions</u>						
SO ₄ ²⁻	0.02	0.02	1.02	0.02	0.02	1.01
HSO ₄ ⁻	1.03	0.93	1.11	0.64	0.72	0.89
NO ₃ ⁻	0.44	0.23	1.95	0.29	0.18	1.58
OH ⁻	0.53	0.60	0.88	0.54	0.59	0.92
F ⁻	0.59	0.78	0.76	0.66	0.93	0.71
Cl ⁻	0.75	0.87	0.87	0.58	0.67	0.86
Br ⁻	0.85	1.07	0.80	0.63	0.79	0.80
I ⁻	0.43	0.32	1.35	0.40	0.30	1.34
<u>Inorganic cations</u>						
H ⁺	0.38	0.35	1.07	0.13	0.12	1.13
NH ₄ ⁺	0.26	0.18	1.43	0.25	0.18	1.37
Na ⁺	0.37	0.31	1.20	0.30	0.25	1.17
K ⁺	0.25	0.16	1.54	0.26	0.20	1.29
Mg ²⁺	0.08	0.30	0.26	0.02	0.08	0.24
Fe ²⁺	0.07	0.05	1.49	0.06	0.05	1.25
Mn ²⁺	0.07	0.05	1.49	0.06	0.05	1.25
Cu ²⁺	0.19	3.70	0.05	0.21	1.75	0.12
Fe ³⁺	1.3·10 ⁻³	4.6·10 ⁻⁴	2.94	9.1·10 ⁻⁴	4.3·10 ⁻⁴	2.14
Mn ³⁺	1.3·10 ⁻³	4.6·10 ⁻⁴	2.94	9.1·10 ⁻⁴	4.3·10 ⁻⁴	2.14
Water activity coefficient	1.02	1.06	0.97	1.05	1.04	1.00
Water activity	0.90	0.70	1.29	0.90	0.70	1.29
Ionic strength	5.21	21.53	0.24	8.46	25.77	0.33

Table 3: Comparison of activity coefficients applied in multiphase aerosol chemistry models. The data of the present study is based on Table 1.

Cations / Anions	Mao et al. (2013)	Guo et al. (2014)	Sander and Crutzen (1996)	Present study
X ⁺	0.6	0.8 (based on Na ⁺)	0.74/4.3 (NH ₄ ⁺ /H ⁺)	0.29-1.03
Y ⁻	0.6	0.6 (based on HSO ₄ ²⁻)	0.46-1.9 [#]	0.13-0.38
X ²⁺	≈ 0.067 (based on Cu ²⁺)	0.45 (based on Fe ²⁺)	=	0.02-0.21
Y ²⁻	—	0.02 (based on SO ₄ ²⁻)	0.05 (SO ₄ ²⁻)	0.02
X ³⁺	0.01*	0.3 (based on Fe ³⁺)	=	0.001

Remark: * In the study of Mao et al. (2013), an activity coefficient γ of 0.01 was applied for Fe³⁺ based on the lowest estimate from Millero and Woosley (2009). However, the lowest estimate in Millero and Woosley (2009) is $\ln(\gamma)=-2$, i.e. the γ should be 0.135. The decadic logarithm was used by Mao et al. (2013) instead of the natural logarithm.

[#] Other singly charged ions not listed in the paper are estimated by an activity coefficient of $\gamma = 0.44$ obtained from Debye-Hückel theory.

Table 4. Predicted activity coefficients of selected organic compounds in deliquesced particles for the 90 %/70 %-NIDR and 90 %/7 0%-NIDU simulations at 29 hours. $\Delta\gamma$ represents the ratio of the predicted activity coefficients of the 90 % case and the 70 % case, respectively.

Species	Urban			Remote		
	90 %	70%	$\Delta\gamma$	90 %	70%	$\Delta\gamma$
<i>Alcohols</i>						
Methanol (CH ₃ OH)	0.88	1.08	0.82	0.94	1.20	0.78
Ethanol (CH ₃ CH ₂ OH)	1.17	3.47	0.34	1.26	3.43	0.37
<i>Aldehydes</i>						
<i>Formaldehyde</i>						
CH ₂ (OH) ₂ (hydrated)	0.87	1.02	0.85	1.06	1.48	0.71
HCHO	0.87	0.99	0.88	0.85	1.00	0.84
<i>Acetaldehyde</i>						
CH ₃ CHO	1.23	3.78	0.33	1.36	3.54	0.38
CH ₃ CH(OH) ₂ (hydrated)	1.29	4.42	0.29	1.42	4.41	0.32
<i>Propionaldehyde</i> (CH ₃ CH ₂ CHO)	1.62	12.12	0.13	1.83	10.14	0.18
<i>Butyraldehyde</i> (CH ₃ CH ₂ CH ₂ CHO)	2.14	38.90	0.06	2.45	29.04	0.08
<i>Glycolaldehyde</i>						
CHOC ₂ H ₄ OH	1.21	3.57	0.34	1.54	4.39	0.35
CH(OH) ₂ CH ₂ OH (hydrated)	1.13	3.10	0.36	1.61	5.28	0.30
<i>Glyoxal</i>						
CH(OH) ₂ CH(OH) ₂ (hydrated)	1.11	2.93	0.38	1.82	6.56	0.28
CHOC ₂ H ₄ CHO	1.27	3.89	0.33	1.67	4.54	0.37
<i>Methylglyoxal</i>						
CH ₃ C(O)CH(OH) ₂ (hydrated)	1.75	9.39	0.19	2.60	18.00	0.14
<i>Monocarboxylic acids</i>						
<i>Formic acid</i>						
HC(O)OH	0.85	0.47	1.8	0.75	0.39	1.92
HC(O)O ⁻	0.43	0.29	1.50	0.41	0.29	1.40
<i>Acetic acid</i>						
CH ₃ C(O)OH	0.97	1.06	0.92	0.84	0.70	1.20
CH ₃ C(O)O ⁻	0.43	0.29	1.46	0.40	0.29	1.36
CH ₃ CH ₂ C(O)OH	1.28	3.39	0.38	1.13	2.00	0.56
CH ₃ CH ₂ CH ₂ C(O)OH	1.69	10.89	0.16	1.51	5.73	0.26
<i>Glycolic acid</i>						
CH ₂ (OH)C(O)OH	0.95	1.00	0.95	0.95	0.87	1.10
CH ₂ (OH)C(O)O ⁻	0.43	0.29	1.46	0.40	0.29	1.36
<i>Glyoxylic acid</i>						
CH(OH) ₂ C(O)OH	0.94	0.94	0.99	1.08	1.08	1.00
CH(OH) ₂ C(O)O ⁻	0.43	0.29	1.46	0.40	0.29	1.36
<i>Pyruvic acid</i>						
CH ₃ C(O)C(O)OH	1.48	3.03	0.49	1.54	2.96	0.52
CH ₃ C(O)C(O)O ⁻	0.43	0.29	1.46	0.40	0.29	1.36
<i>Dicarboxylic acids</i>						
<i>Oxalic acid</i>						
C(O)OHC(O)OH	0.79	0.30	2.59	0.64	0.18	3.61

Formatiert: Nicht Hochgestellt/ Tiefgestellt

Gelöscht: OHCCH₂OH

Gelöscht: OH₂CH

Gelöscht: C

Gelöscht: HOH₂CHOH₂

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: O

Gelöscht: H₂C₂O₄

Species	Urban			Remote		
	90 %	70%	$\Delta\gamma$	90 %	70%	$\Delta\gamma$
$\text{C}(\text{O})\text{O}_2\text{C}(\text{O})\text{O}^-$	0.05	0.03	1.89	0.04	0.03	1.61
$\text{C}(\text{O})\text{OHC}(\text{O})\text{O}^-$	0.43	0.29	1.46	0.40	0.29	1.36
$[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$	0.43	0.29	1.46	0.40	0.29	1.36
$[\text{Fe}(\text{C}_2\text{O}_4)]^+$	0.43	0.29	1.46	0.40	0.29	1.36
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	$1.3 \cdot 10^{-3}$	$4.6 \cdot 10^{-4}$	2.94	$9.1 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	2.14
<i>Malonic acid</i>						
$\text{C}(\text{O})\text{OHCH}_2\text{C}(\text{O})\text{OH}$	1.04	0.98	1.07	0.86	0.51	1.69
$\text{C}(\text{O})\text{OHCH}_2\text{COO}^-$	0.43	0.29	1.47	0.41	0.29	1.39
$\text{C}(\text{O})\text{O}_2\text{CH}_2\text{C}(\text{O})\text{O}^-$	0.05	0.03	1.89	0.04	0.03	1.61
<i>Succinic acid</i>						
$\text{C}(\text{O})\text{OHCH}_2\text{CH}_2\text{C}(\text{O})\text{OH}$	1.38	3.13	0.44	1.15	1.45	0.79
$\text{C}(\text{O})\text{OHCH}_2\text{CH}_2\text{C}(\text{O})\text{O}^-$	0.39	0.23	1.70	0.36	0.23	1.54
$\text{C}(\text{O})\text{O}^- \text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}^-$	0.05	0.03	1.89	0.04	0.03	1.61
<i>Keto malonic acid</i>						
$\text{C}(\text{O})\text{OHC}(\text{O})\text{C}(\text{O})\text{OH}$	0.88	0.66	1.33	0.86	0.67	1.28
$\text{C}(\text{O})\text{OHC}(\text{O})\text{C}(\text{O})\text{O}^-$	0.43	0.29	1.46	0.40	0.29	1.36
$\text{C}(\text{O})\text{O}_2\text{C}(\text{O})\text{C}(\text{O})\text{O}^-$	0.05	0.03	1.89	0.04	0.03	1.61
<i>Malic acid</i>						
$\text{C}(\text{O})\text{OHCH}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{OH}$	1.39	4.08	0.34	1.45	3.20	0.45
$\text{C}(\text{O})\text{OHCH}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{O}^-$	0.43	0.29	1.46	0.40	0.29	1.36
$\text{C}(\text{O})\text{O}_2\text{CH}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{O}^-$	0.05	0.03	1.89	0.04	0.03	1.61

- Gelöscht: C2042-
- Formatiert: Hochgestellt
- Gelöscht:
- Formatiert: Hochgestellt
- Formatiert: Nicht Hochgestellt/ Tiefgestellt
- Gelöscht: HC_2O_4^-
- Gelöscht: HOOC
- Gelöscht: COOH
- Gelöscht: HOOC
- Gelöscht: COO
- Gelöscht:
- Gelöscht: OOC
- Gelöscht: COO
- Gelöscht: 2
- Gelöscht: 4
- Formatiert: Nicht Hochgestellt/ Tiefgestellt
- Gelöscht: COOH_2
- Gelöscht: $\text{HOOCCH}_2\text{H}_4\text{CO}$
- Gelöscht: $^-$
- Gelöscht: $\text{OOCCH}_2\text{CH}_2\text{CO}$
- Gelöscht: HOOC
- Gelöscht: COOH
- Gelöscht: HOOC
- Gelöscht: COO
- Gelöscht: OOC
- Gelöscht: COO
- Gelöscht: HOOC
- Gelöscht: COOH
- Gelöscht: HOOC
- Gelöscht: COO
- Gelöscht: OOC
- Gelöscht: COO

Supplement of

**Treatment of non-ideality in the multiphase model SPACCIM-Part2:
Impacts on the multiphase chemical processing in deliquesced aerosol
particles**

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Appendix A: Additional material to section 3.5

C₃ organic chemistry results

As presented in former CAPRAM studies (e.g. Tilgner and Herrmann (2010)), methylglyoxal is effectively oxidised under cloud conditions, leading to the formation of substituted C₃ carboxylic acids, which are expected to be further oxidised in aqueous aerosols. In Fig. S1, the aqueous-phase concentrations of the main C₃ oxidation products, such as pyruvic acid, 3-oxo pyruvic acid, and finally keto malonic acid, along with corresponding activity coefficients are plotted throughout the simulation time for all urban scenarios. The corresponding plots for the remote scenario are presented in Fig. S14.

Figure S1 shows that the first stage oxidation product, pyruvic acid, is effectively produced under both day- and nighttime cloud conditions. Noticeably, urban nighttime clouds reveal a higher production of pyruvic acid than corresponding daytime clouds. This finding is in agreement with former studies (Tilgner and Herrmann, 2010; Tilgner et al., 2013), showing that in-cloud NO₃ radical oxidation represents an important sink for methylglyoxal and, consequently, a source for pyruvic acid under urban conditions.

Figure S1 illustrates that the activity coefficients of formed oxidation products are below unity for their dissociated forms in the 90 %-NIDU and 70 %-NIDU simulations under deliquesced aerosol conditions. However, their undissociated forms partly show activity coefficients above unity. Consequently, the non-ideality treatment can affect their further chemical processing differently in addition to the affected oxidant budget. In detail, undissociated pyruvic acid is characterised by activity coefficients above unity (about 1.5 in the 90 %-NIDU case) and its dissociated form by values of about 0.4 (90 %-NIDU case). Thus, non-ideality effects can increase the chemical processing of pyruvic acid and decrease the chemical processing of pyruvate. Under 70 %-NIDU conditions, pyruvic acid and pyruvate are characterised by even more different activity coefficients of about 3.0 and 0.3, respectively. Therefore, even higher differences between the ideal and the non-ideal treatment can occur.

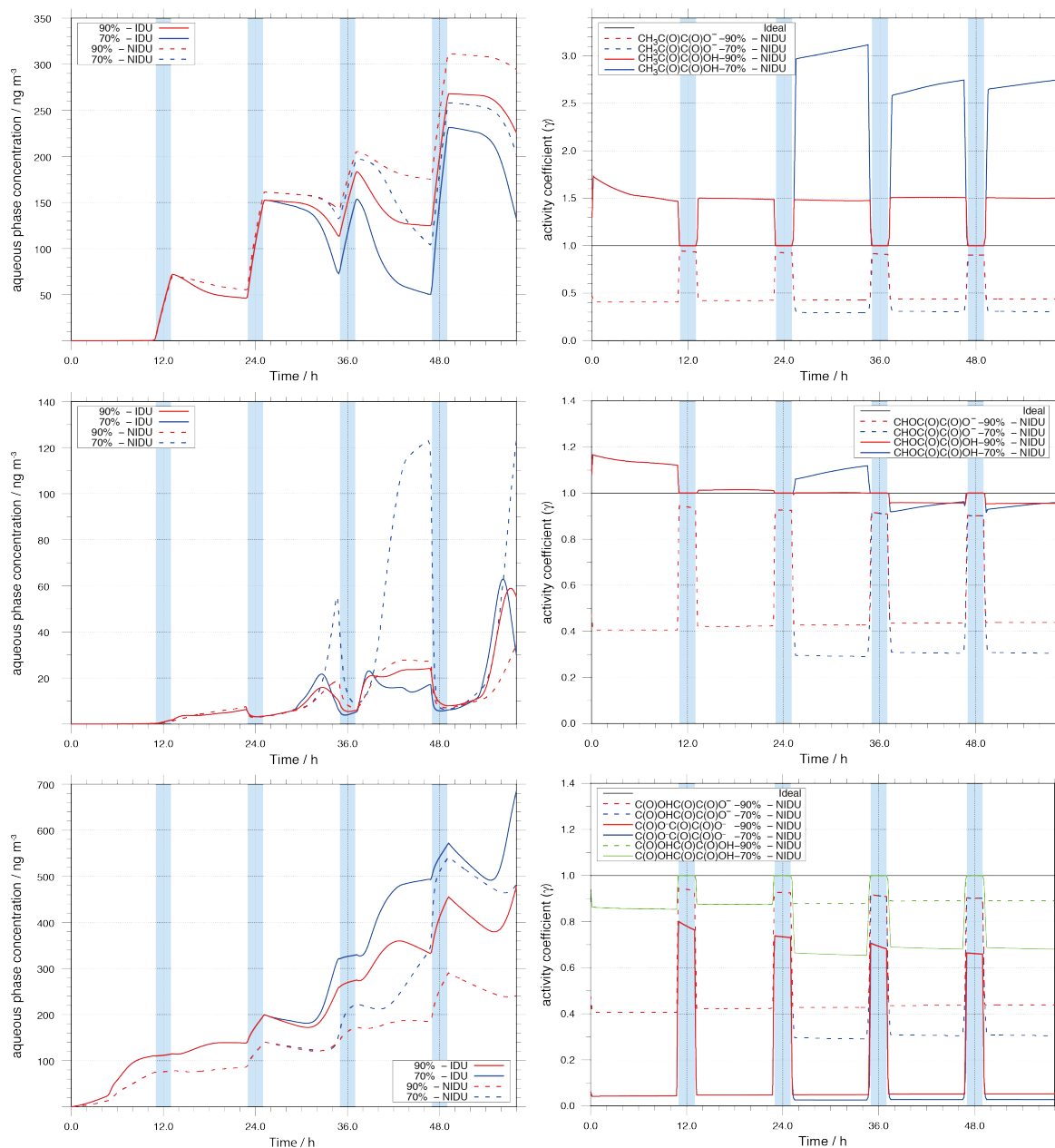


Figure S1 Modelled aqueous-phase concentrations in $\text{ng m}^{-3}_{(\text{air})}$ and corresponding activity coefficients for the important C_3 oxidation products, (i) pyruvic acid (top), (ii) 3-oxo-pyruvic acid (centre), and (iii) keto malonic acid (down). The plotted concentrations represent the sum of dissociated and undissociated forms of the carboxylic acids.

5 Figure S1 shows that the in-cloud formations of pyruvic acid and keto malonic acid are similar in the 90 %-NIDU and 90 %-IDU cases. Differences between predicted concentration curves arise mainly during deliquesced aerosol periods. For pyruvic

acid, the ideal simulation is characterised by a faster degradation during aqueous aerosol conditions. In contrast, the 90 %-NIDU case shows a much lower decrease. This lower oxidation rate leads to the higher concentrations of pyruvic acid in the 90 %-NIDU case than in the 90 %-IDU case. Interestingly, Fig. S1 illustrates that the decrease is lower in the 90 %-NIDU case but higher under 70 %-NIDU conditions. A comparison of the 90 %-NIDU vs. 70 %-NIDU concentration profiles shows a stronger oxidation in the more concentrated solution case in the afternoon and evening of the second model day. Therefore, lower pyruvic acid concentrations and, consequently, higher 3-oxo pyruvic acid concentrations can be found in the 70 %-NIDU simulation during this period. The reasons for these higher oxidation levels in the aerosol phase of the 70 %-NIDU case are (i) the higher OH budget in the 70 %-NIDU case (see Sect. 3.3) and (ii) the substantially higher activity coefficients of pyruvic acid under 70 % RH conditions, which leads to faster degradation. A reaction rate investigation of OH radicals has already revealed the higher degradation rates of pyruvic acid under lower humidity conditions (see Sect. 3.3). An analysis of the reaction rates of pyruvic acid reveals degradation rates that are a factor of 2.7 higher in the 70 %-NIDU than in the 90 %-NIDU case during the aerosol period of 37-47 h.

Subsequently, further oxidation of 3-oxo pyruvic acid mainly occurs during cloud periods and leads to the formation of keto malonic acid (see Fig. S2). Keto malonic acid is the C₃ oxidation product of this oxidation chain, which is formed particularly under cloud and daytime deliquesced particle conditions. Due to the non-ideality treatment, the predicted concentrations of keto malonic acid are lower when compared to the ideal cases. The predicted concentration of keto malonic acid at the end of the 90 %-NIDU simulation is a factor of 2 lower.

From Fig. S2, it can be seen that the generally lowered oxidation of the precursors leads to a smaller production of keto malonic acid. On the other hand, the lowered oxidation of keto malonic acid compensates for the lowered formation rates. In detail, both the total keto malonic acid formation and sink rates are approximately 50 % lower in the 90 %-NIDU compared to the 90 %-IDU case throughout the whole simulation time. This interplay causes the relatively small differences in the predicted concentrations modelled between the ideal and non-ideal cases. Furthermore, Fig. S2 shows that both the formation patterns change in a way that makes keto malonic acid show less chemical aerosol phase rates and more distinct in-cloud rates. This means that the non-ideality treatment could both decrease (e.g. in 90 %-NIDU) and increase (e.g. in 70 %-NIDU) the chemical turnovers in the aerosol phase.

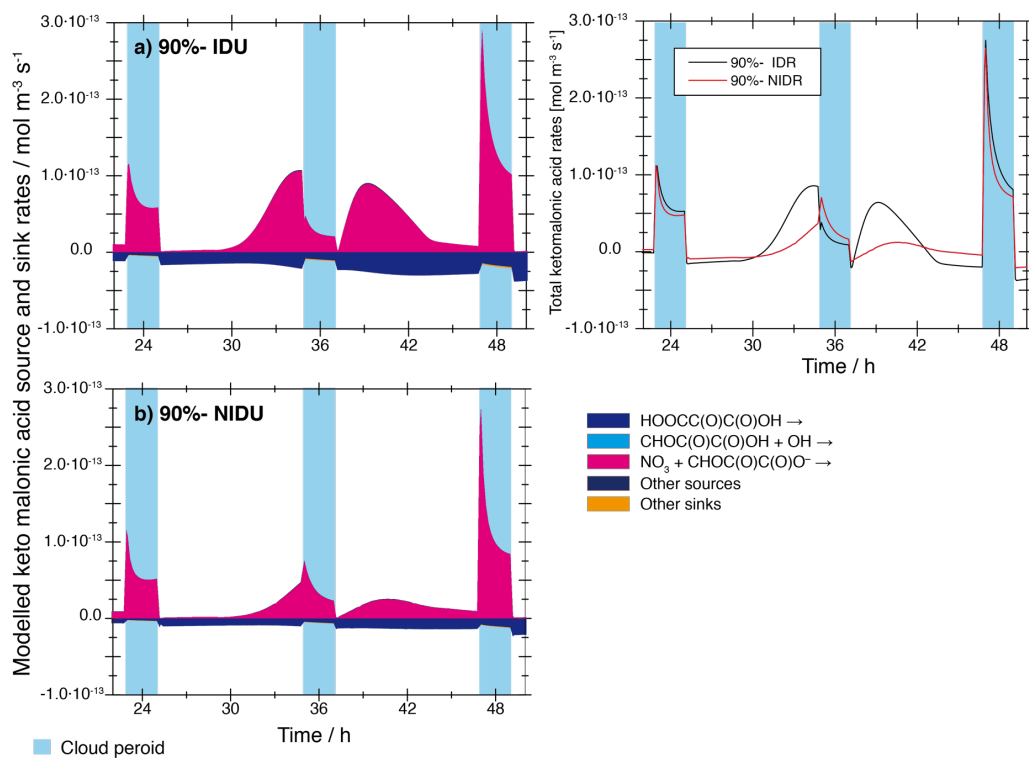


Figure S2 Modelled chemical sink and source mass rates of keto malonic acid in the aqueous phase in mol m⁻³ s⁻¹ for the second day of modelling time for the urban scenarios, 90 %-IDU vs. 90 %-NIDU. a) Ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU).

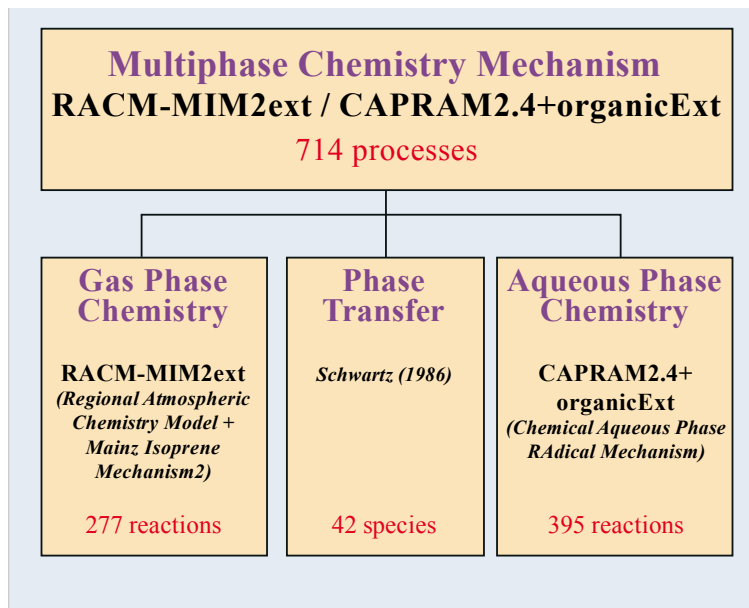


Figure S3. Schematic of multiphase mechanism employed in this study, including the number of processes, reactions, and phase transfer processes (modified from Deguillaume et al. (2009); Tilgner and Herrmann (2010)).

Additional model results of the remote and urban simulation cases

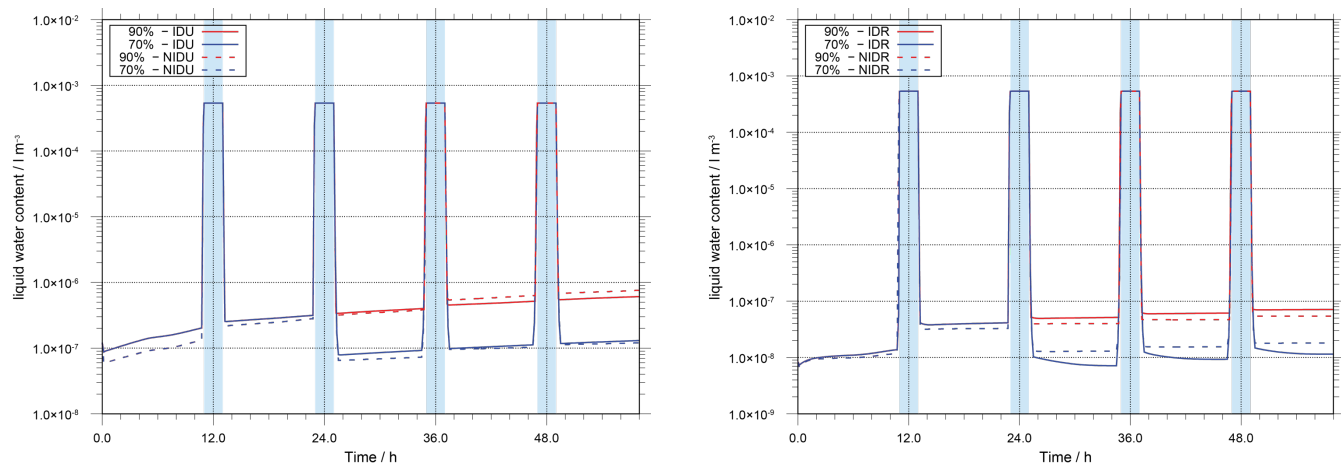


Figure S4. Modelled Liquid Water Content in $l_{(water)} m^{-3}_{(air)}$ throughout the simulation time for the different urban (left) and remote (right) simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

5

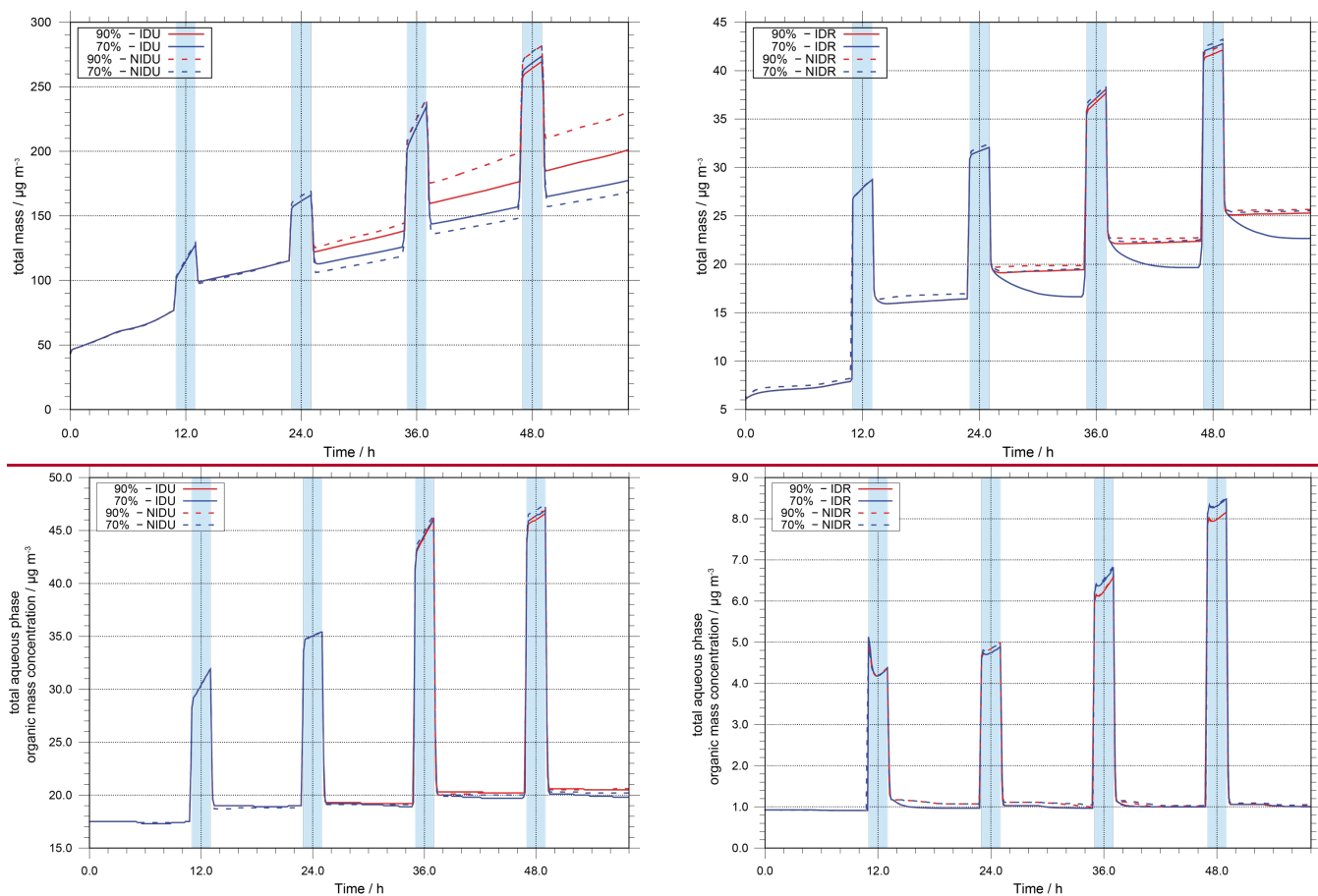


Figure S5. Modelled concentrations in $\mu g m^{-3}_{(air)}$ of the total (top), and organic (bottom) aerosol mass throughout the simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

Additional reaction rate analyses plots

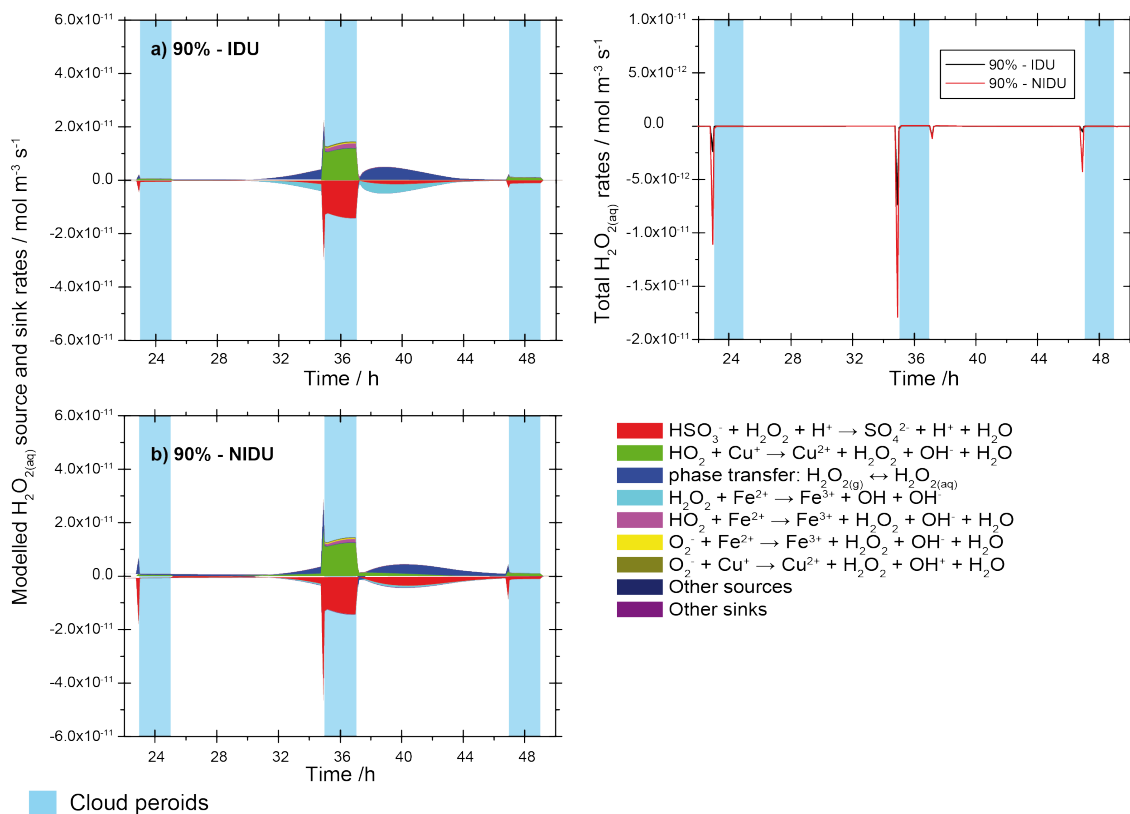


Figure S6 Modelled chemical sink and source mass rates of H_2O_2 in the aqueous phase in $\text{mol m}^{-3} \text{s}^{-1}$ for the second day of modelling time for the urban scenario for the simulations 90 %-IDU vs. 90 %-NIDU. a) Ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), c) corresponding total rates.

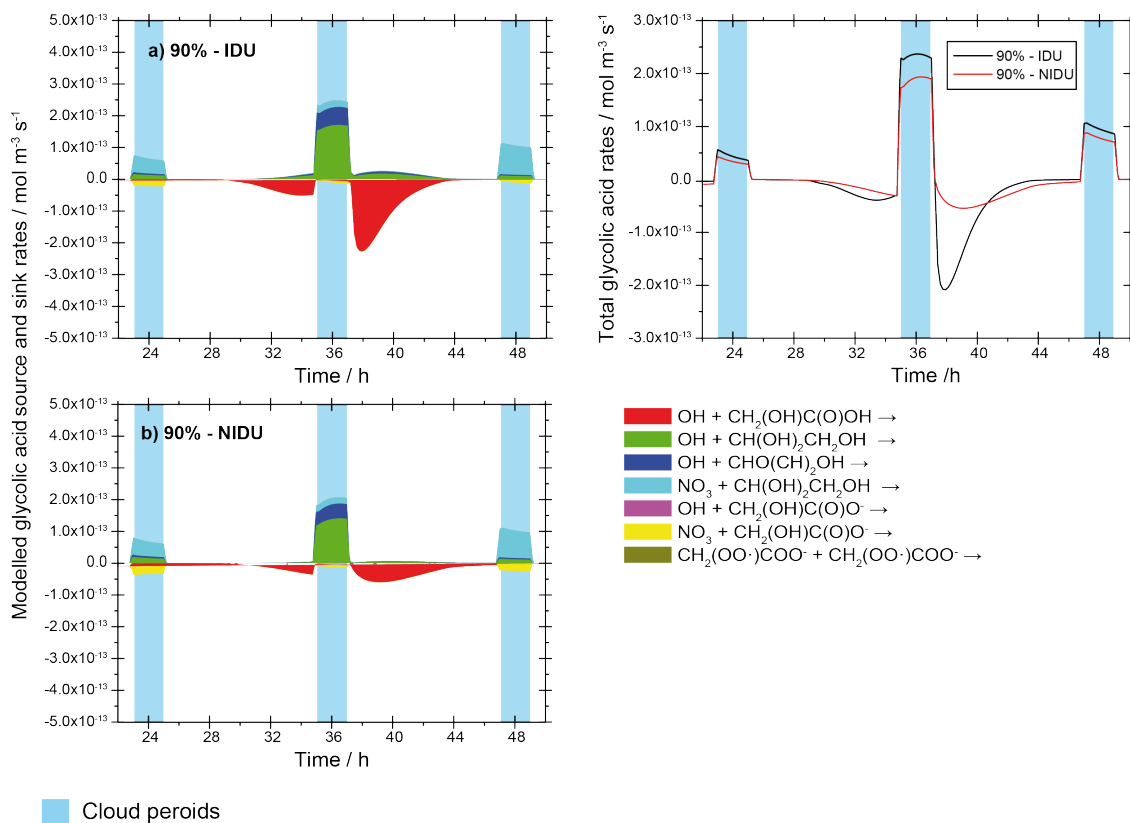


Figure S7 Modelled chemical sink and source mass rates of glycolic acid in the aqueous phase in $\text{mol m}^{-3} \text{s}^{-1}$ for the second day of modelling time for the urban scenario for the simulations 90 %-IDU vs. 90 %-NIDU. a) Ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), c) corresponding total rates.

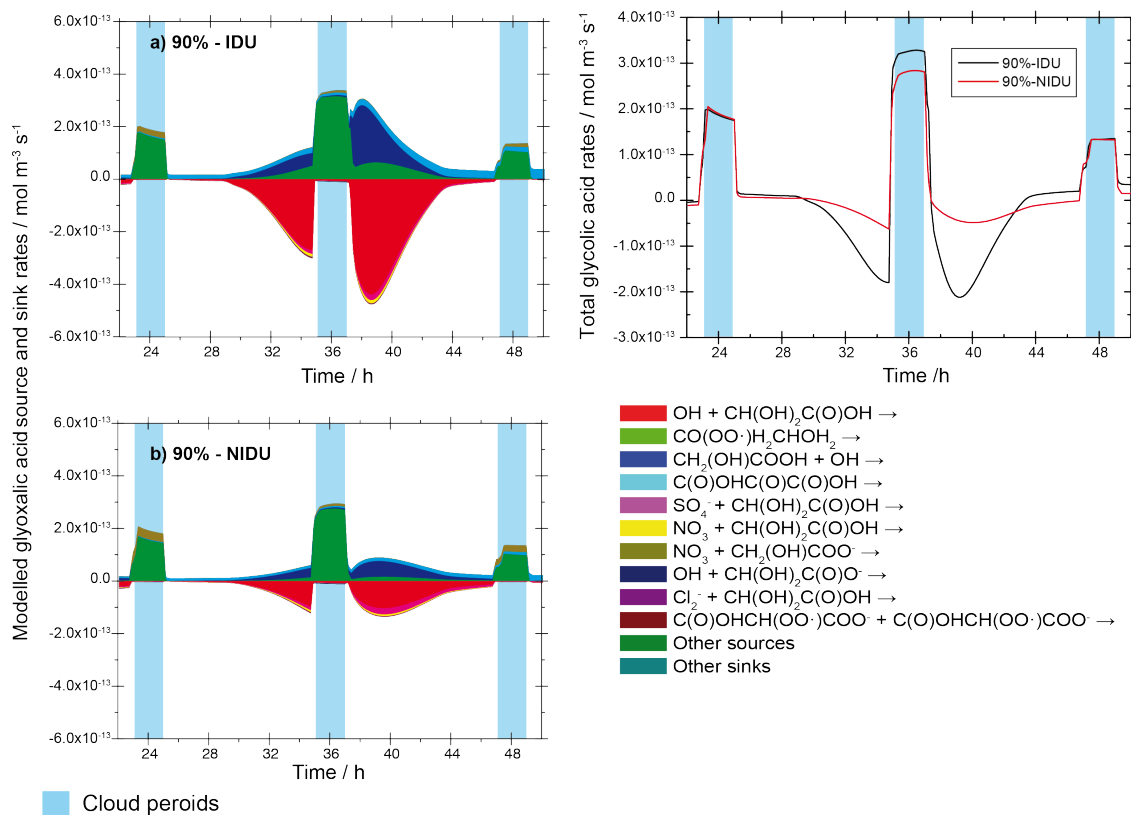


Figure S8 Modelled chemical sink and source mass rates of glyoxylic acid in the aqueous phase in $\text{mol m}^{-3} \text{s}^{-1}$ for the second day of modelling time for the urban scenario for the simulations 90 %-IDU vs. 90 %-NIDU. a) Ideal solutions (90 %-IDU), b) non-ideal solutions (90 %-NIDU), c) corresponding total rates.

Model results of the remote simulation cases

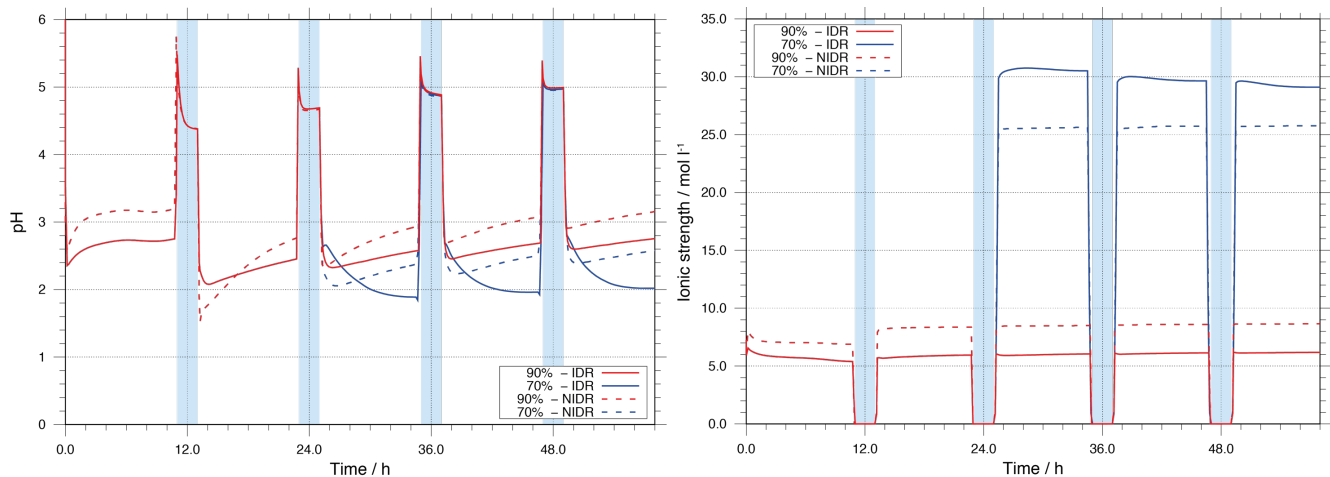


Figure S9. Modelled pH value (left) and ionic strength (I, right) as a function of simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

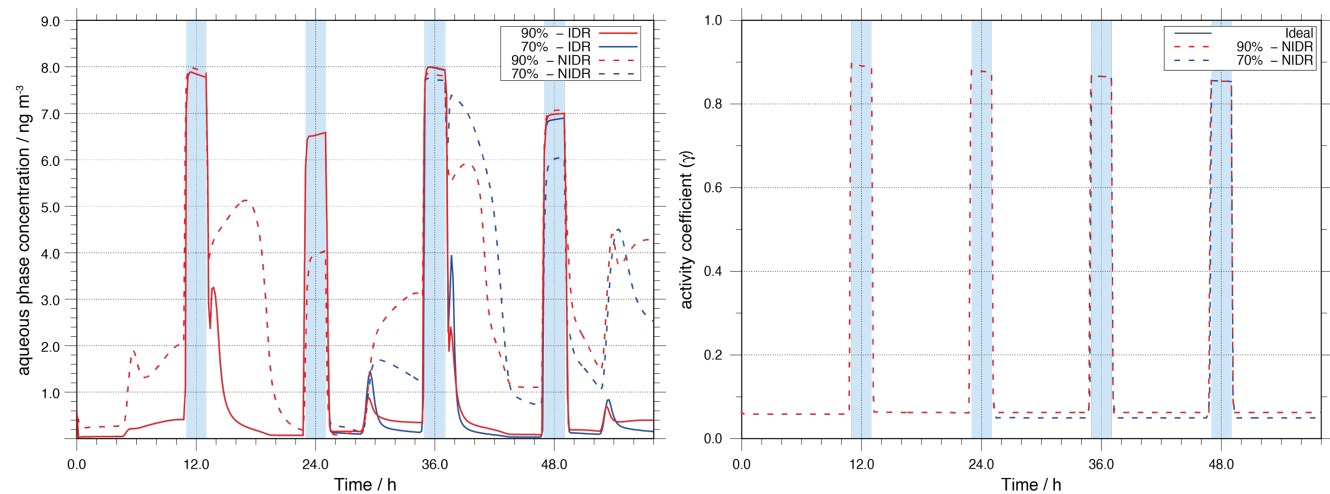


Figure S10. Modelled Fe(II) aqueous-phase concentration in ng m⁻³ throughout the modelling time (left) and corresponding time evolution of activity coefficients (right) for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

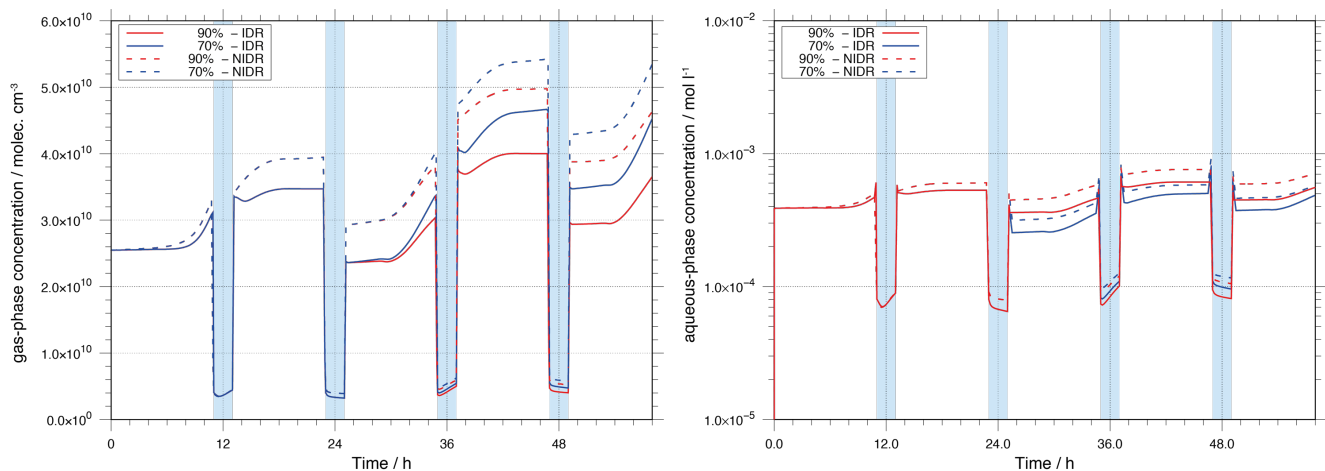


Figure S11. Modelled gas- and aqueous-phase concentration of H_2O_2 throughout the simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

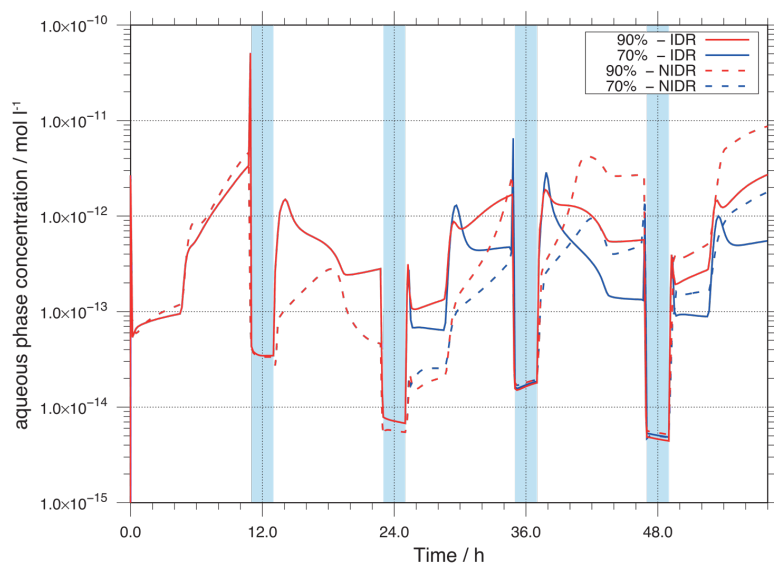


Figure S12. Modelled aqueous-phase OH concentration in mol l^{-1} throughout the simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR).

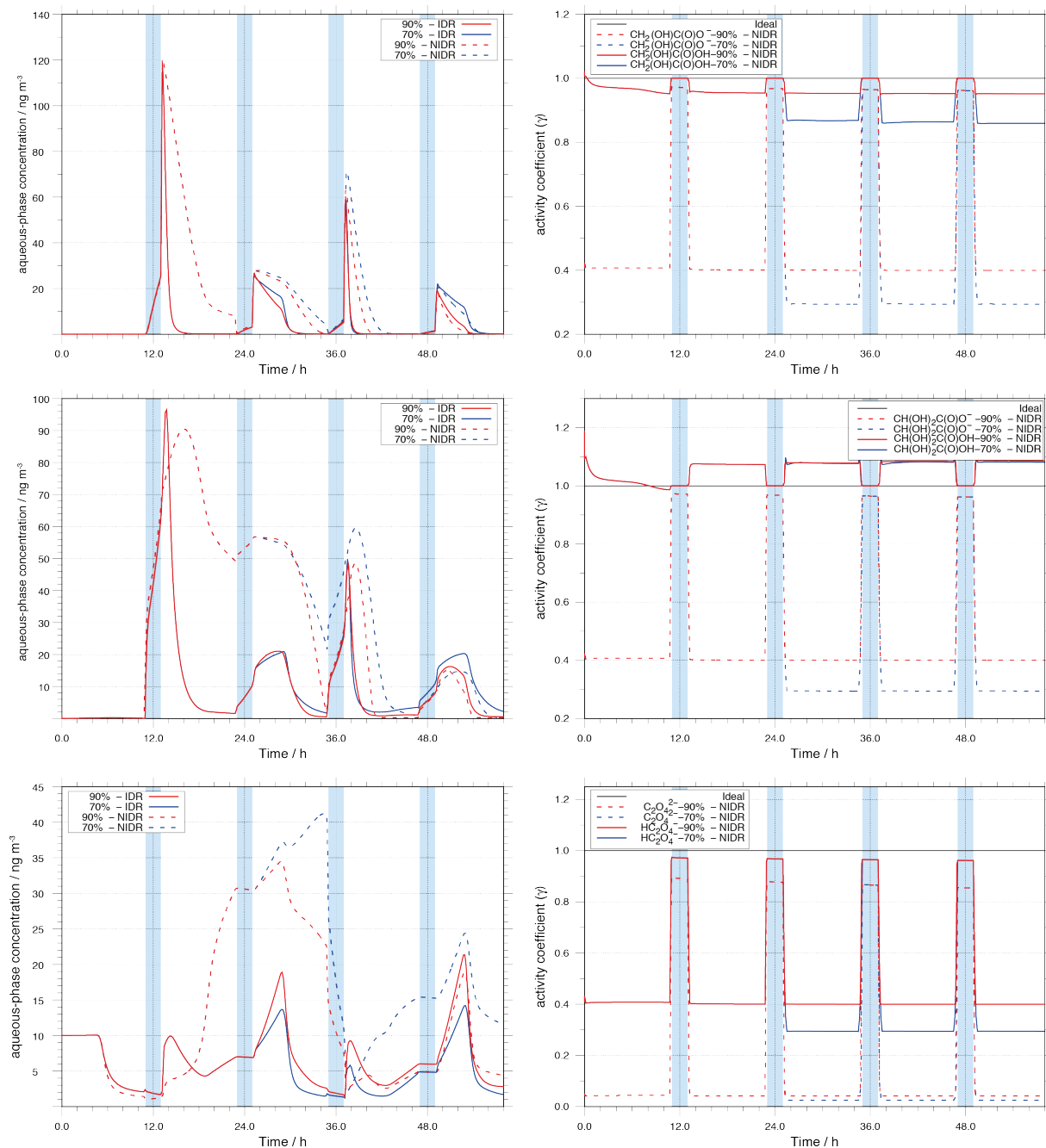


Figure S13. Modelled aqueous-phase concentrations in $ng\ m^{-3}(\text{air})$ and corresponding activity coefficients for important C_2 oxidation products, (i) glycolic acid (top), (ii) glyoxylic acid (centre), and (iii) oxalic acid (down) throughout the simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR). The plotted concentrations represent the sum of dissociated and undissociated forms of the carboxylic acids.

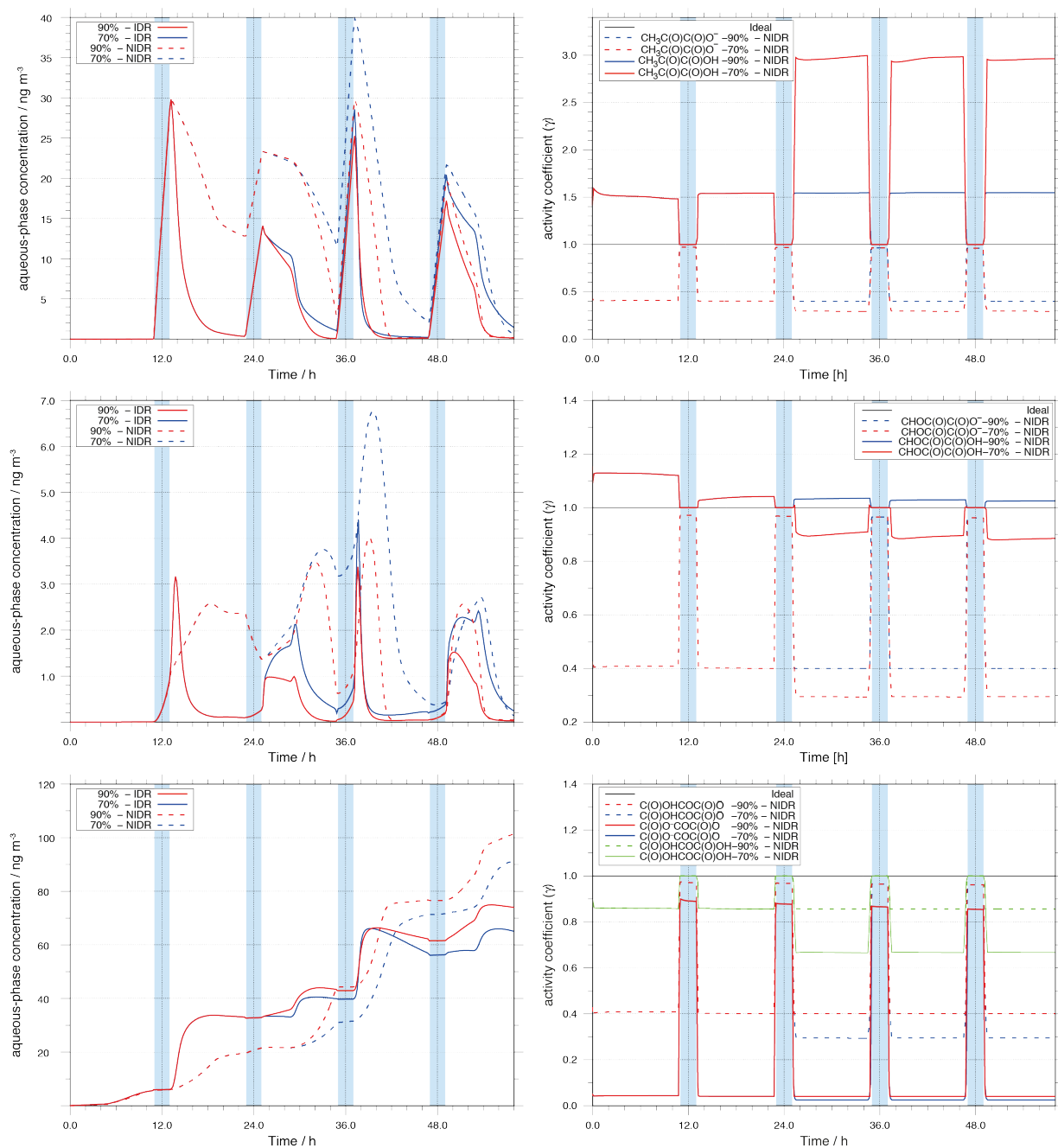


Figure S14. Modelled aqueous-phase concentrations in $\text{ng m}^{-3}_{(\text{air})}$ and corresponding activity coefficients for important C_3 oxidation products, (i) pyruvic acid (top), (ii) 3-oxo-pyruvic acid (centre), and (iii) keto malonic acid (down) throughout the simulation time for the different remote simulation cases (90 %-IDR/90 %-NIDR and 70 %-IDR/70 %-NIDR). The plotted concentrations represent the sum of dissociated and undissociated forms of the carboxylic acids.

Appendix C: Additional sensitivity runs

In order to study, the sensitivity of the model with regards to missing middle-range (MR) interaction parameters, additional sensitivity simulations have been performed (acronyms: 90/70% NIDU/NIDR (MR)). For the sensitivity simulations, the MR interaction parameters of Cu^{2+} has been applied for $\text{Fe}^{2+}/\text{Mn}^{2+}$. As there are no MR interaction parameters for triply charged transition metal ions available, no MR values are applied for those transition metal ions. However, since particularly Fe^{2+} is the key transition metal ion for the overall TMI processing, the performed sensitivity studies reveal the potential effects of an improved description of the MR interaction parameters.

In Fig. S13 and S14, simulation results of non-ideal runs with and without considered MR interaction parameters are shown for key chemical substances that are sensitive to a non-ideal treatment under remote and urban conditions. The consideration of MR interaction parameters for $\text{Fe}^{2+}/\text{Mn}^{2+}$ leads to similar activity coefficient pattern for Cu^{2+} and $\text{Fe}^{2+}/\text{Mn}^{2+}$ (cp. Fig. S15). In comparison to base run without the MR parameters, the activity coefficient values of $\text{Fe}^{2+}/\text{Mn}^{2+}$ significantly higher and even above 1 under 70% RH conditions as observed for Cu^{2+} . Particularly, the higher activity coefficient values of Fe^{2+} in the MR-cases significantly affects key chemical subsystems (cp. Fig. S16 and S17). For H_2O_2 , the model results show that the consideration of MR parameters leads to lower concentrations levels due to more effective loss processes such as the Fenton chemistry. As a consequence, the aqueous OH concentrations are significantly raised and slightly higher oxalic acid concentrations are modelled indicating a more effective organic acid formation as a result of the higher OH levels. On the other hand, the effects on the S(VI) formations are relatively small and only present in the urban simulations.

Because of the higher activity coefficient under consideration of MR parameters, the model results shift at least to a certain part towards the simulations without non-ideal chemistry treatment with a more active TMI-HOx cycling under deliquesced aerosol conditions. Overall, the sensitivity studies clearly show that middle-range (MR) interaction parameters of key TMIs represents crucial parameter that need to be determined in future laboratory experiments to improve current model implementations.

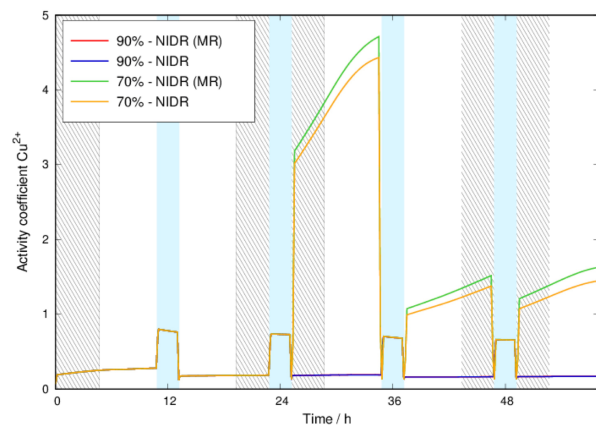
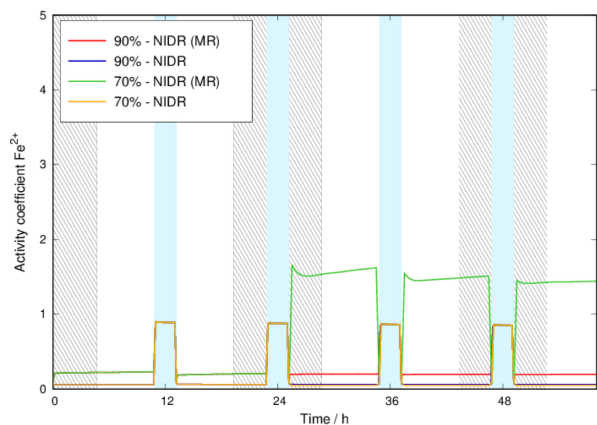
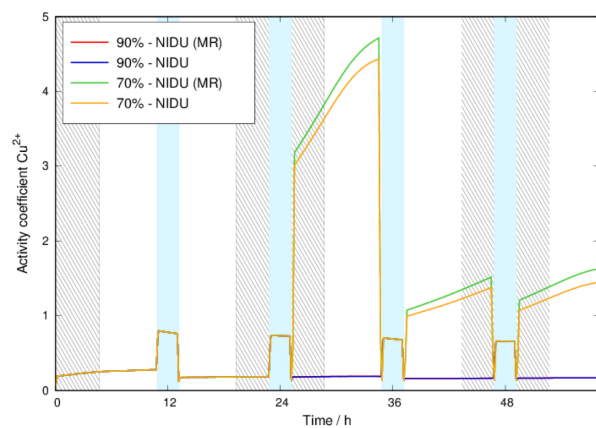
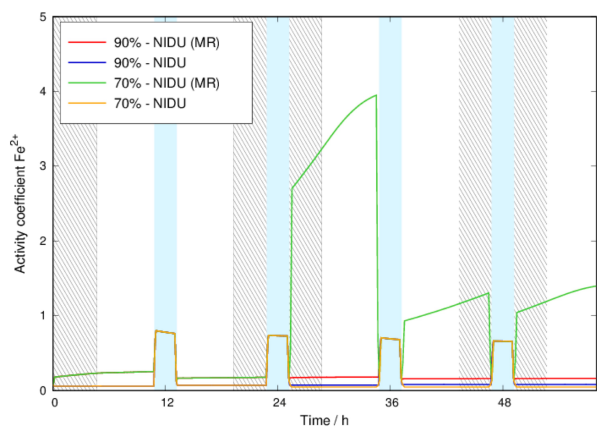


Figure S15. Modelled activity coefficients of Fe^{2+} (left) and Cu^{2+} (right) with and without considered MR parameters for the different non-ideal urban (top) and remote (bottom) model cases.

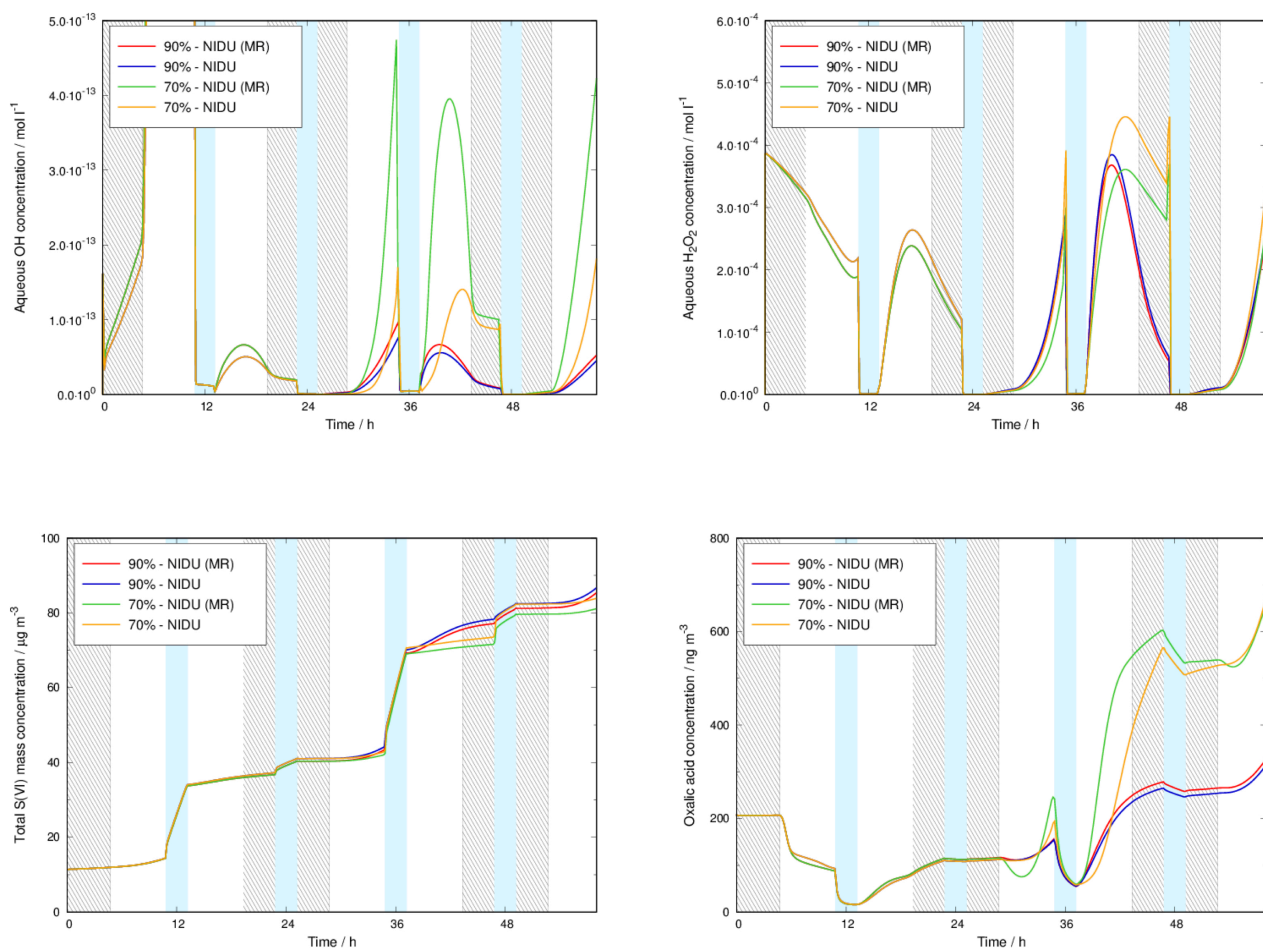


Figure S16. Modelled aqueous-phase concentrations of aqueous OH radical (top left), H₂O₂ (top right), sulfur(VI) (bottom left) and oxalic acid (bottom right) with and without considered MR parameters for the different non-ideal urban model cases.

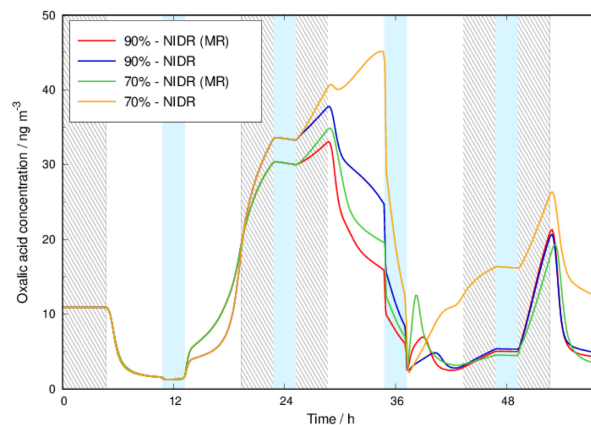
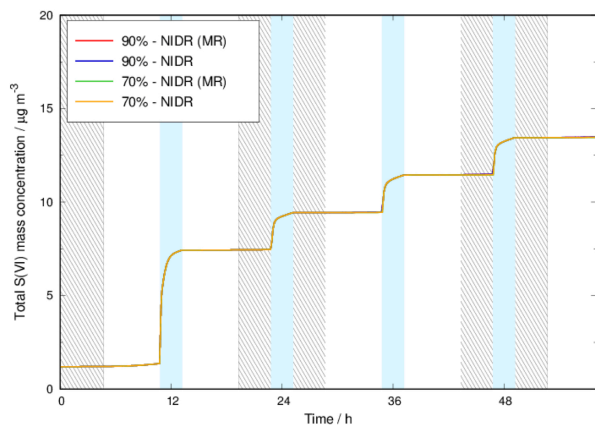
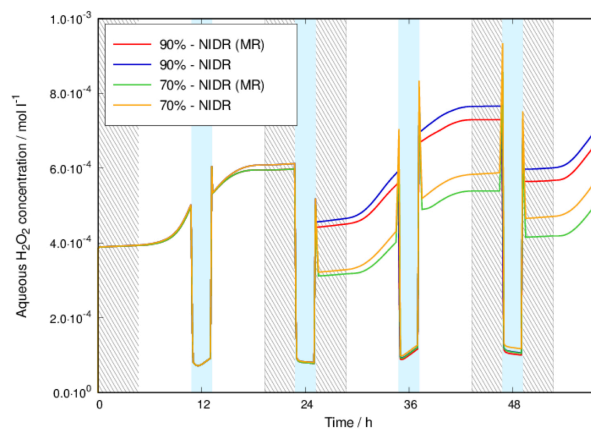
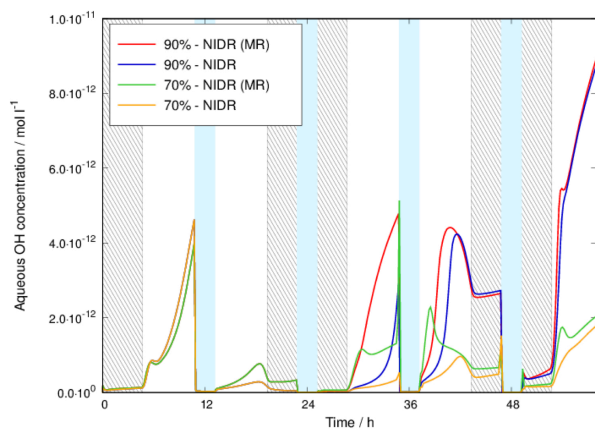


Figure S17. Modelled aqueous-phase concentrations of aqueous OH radical (top left), H_2O_2 (top right), sulfur(VI) (bottom left) and oxalic acid (bottom right) with and without considered MR parameters for the different non-ideal remote model cases.

Appendix D: Tables

Table S1. Initial chemical aerosol particle composition (relative contributions to the total particulate non-water mass) for the urban and remote environmental model scenarios.

Compound	Urban	Remote
NH ₄ ⁺	1.00E-01	9.80E-02
NO ₃ ⁻	2.49E-02	9.27E-02
SO ₄ ²⁻	2.61E-01	1.91E-01
Cl ⁻	1.92E-02	9.70E-05
Br ⁻	6.53E-04	1.77E-04
I ⁻	1.23E-04	1.52E-07
Mn ³⁺	1.54E-04	1.15E-04
Fe ³⁺	1.46E-03	1.42E-03
Cu ²⁺	1.53E-04	1.08E-04
<i>WSOM</i>	1.51E-01	5.57E-02
HC ₂ O ₄ ⁻	4.38E-03	1.62E-03
HOOCCH ₂ COO ⁻	2.79E-03	1.03E-03
HOOCCH ₂ H ₄ COO ⁻	1.59E-03	5.89E-04
<i>WISOM</i>	2.39E-01	8.83E-02
<i>EC</i>	1.56E-02	1.67E-01
<i>Other anions</i>	7.96E-05	1.89E-04
<i>Cations (+)</i>	3.26E-02	1.53E-02
<i>Cations (2+)</i>	1.49E-02	1.85E-02
<i>Other metals</i>	3.25E-02	4.05E-02
<i>SiO₂</i>	9.53E-02	2.27E-01
<i>P</i>	2.87E-03	2.73E-04

Remarks: Single species and compound groups marked in italics are treated in SPACCIM as non-reactive species. The respective ions are just considered for the charge balance.

5 Table S2. Parameters (N: Number, ρ: Density, r: Radius) of the mono-disperse aerosol particle initialisation for the urban and remote environmental model scenarios.

Parameter	Urban	Remote
N (#/cm ³)	7.0E+08	1.0E+08
ρ (kg/m ³)	1770	1770
r (m)	2.0E+07	2.0E+07

References

10 Deguillaume, L., Tilgner, A., Schrödner, R., Wolke, R., Chaumerliac, N., and Herrmann, H.: Towards an operational aqueous phase chemistry mechanism for regional chemistry-transport models: CAPRAM-RED and its application to the COSMO-MUSCAT model, J. Atmos. Chem., 64, 1-35, doi:10.1007/s10874-010-9168-8, 2009.

Tilgner, A., and Herrmann, H.: Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM, Atmos. Environ., 44, 5415-5422, doi:10.1016/j.atmosenv.2010.07.050, 2010.