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Tilgner, A., Bräuer, P. orcid.org/0000-0002-3815-7631, Wolke, R. et al. (1 more author) (2013) Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i. Journal of Atmospheric Chemistry. pp. 221-256. ISSN: 0167-7764

https://doi.org/10.1007/s10874-013-9267-4

J Atmos Chem (2013) 70:221–256
DOI 10.1007/s10874-013-9267-4

Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i

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Received: 12 December 2012 / Accepted: 5 August 2013 /

Abstract Modelling studies were performed with the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i to investigate the tropospheric multiphase chemistry in deliquesced particles and non-precipitating clouds using the SPACCIM model framework. Simulations using a non-permanent cloud scenario were carried out for two different environmental conditions focusing on the multiphase chemistry of oxidants and other linked chemical subsystems. Model results were analysed by time-resolved reaction flux analyses allowing advanced interpretations. The model shows significant effects of multiphase chemical interactions on the tropospheric budget of gas-phase oxidants and organic compounds. In-cloud gas-phase OH radical concentration reductions of about 90 % and 75 % were modelled for urban and remote conditions, respectively. The reduced in-cloud gas-phase oxidation budget increases the tropospheric residence time of organic trace gases by up to about 30 %. Aqueous-phase oxidations of methylglyoxal and 1,4-butenedial were identified as important OH radical sinks under polluted conditions. The model revealed that the organic C_3 and C_4 chemistry contributes with about 38 %/48 % and 8 %/9 % considerably to the urban and remote cloud / aqueous particle OH sinks. Furthermore, the simulations clearly implicate the potential role of deliquescent particles to operate as a reactive chemical medium due to an efficient TMI/$HO_{x,y}$ chemical processing including e.g. an effective in-situ formation of OH radicals. Considerable chemical differences between deliquescent particles and cloud droplets, e.g. a circa 2 times more efficient daytime iron processing in the urban deliquescent particles, were identified. The in-cloud oxidation of methylglyoxal and its oxidation products is identified as efficient sink for NO_3 radicals in the aqueous phase.

Keywords CAPRAM · Multiphase chemistry · Cloud processing · Multiphase oxidants · Deliquescent particles

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Electronic supplementary material The online version of this article (doi:10.1007/s10874-013-9267-4) contains supplementary material, which is available to authorized users.

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1 Introduction

Tropospheric clouds and aerosol particles have global and regional impact e.g. on weather (Rosenfeld 1999, 2000), climate (Charlson et al. 1992; Lohmann and Feichter 2005), ecosystems (Adriano and Johnson 1989), air pollution (Gong et al. 2006) and human health (Holgate 1999; Brunekreef and Holgate 2002). Tropospheric clouds are a complex multiphase and multi-component environment, in which a variety of physical and chemical processes take place. They can potentially alter the physical and chemical composition of the troposphere on a global scale (Ravishankara 1997). Moreover, so-called “twilight zones” (see Koren et al. 2007) might also provide appropriate conditions for aqueous chemical aerosol processing.

Contrary to the quite established microphysical in-cloud processes and gas-phase chemistry (Finlayson-Pitts and Pitts 2000), multiphase chemical interactions of tropospheric aqueous aerosols, including both cloud droplets and deliquescent particles, are still poorly understood. Their investigation is challenging because of the complexity of the interacting physical and chemical processes as well as the variety of chemical compounds and their interactions. Gas-phase photochemistry is directly and indirectly affected by physico-chemical processes involving cloud droplets and deliquescent particles. Clouds and deliquescent particles play an important role in controlling the tropospheric gas-phase chemistry by changing photolysis rates (Madronich and Flocke 1999; Tie et al. 2003) and by influencing the atmospheric gas-phase composition e.g. though the uptake of soluble gases (see e.g. Saxena and Hildemann 1996), deposition (sedimentation) of dissolved gases and microphysical redistribution (Grègoire and Chaumerliac 1994) and aqueous-phase chemical reactions (see e.g. Ervens et al. 2003).

While aqueous-phase chemistry of main inorganic species such as sulphur (Warneck 1999) have long been recognized as important, the role of clouds and especially deliquescent particles for the multiphase budget of radical and non-radical oxidants, the aqueous redox-cycling of transition metal ions (TMIs) and also for the oxidation of organic constituents were investigated to a much smaller extend. Hence, there are still numerous issues, which require further detailed investigations, which, therefore, are in the focus of the current study:

(1) What effects do chemical interactions in clouds and in aqueous particles have on the budget of multiphase oxidants and organic trace gases? (2) How important are chemical radical processes in aqueous particles compared to cloud droplets? (3) Which role do TMIs play for the chemical processing of oxidants and the organic chemistry under both aqueous particle and cloud conditions? (4) For which chemical key subsystems is the treatment of a complex organic chemistry required because of their close chemical interactions? (5) Do complex multiphase chemistry models applying a non-permanent cloud scenario provide similar model results than former model studies using unrealistic permanent cloud conditions?

In the following the state of the art related to the above-mentioned issues is briefly outlined. Over the last two decades, aqueous-phase interactions of both tropospheric radical and non-radical oxidants have been shown to be quite important for atmospheric chemistry. Whereas, several investigations have been mainly focused on cloud effects on the tropospheric ozone (e.g. Acker et al. 1995; Liang and Jacob 1997; Walcek et al. 1997), only few field experiments (e.g. Mauldin et al. 1997; Commane et al. 2010) and modelling studies (e.g. Jacob 1986; Frost et al. 1999; Jacob 2000; Ervens et al. 2003; Tilgner et al. 2005) were performed to elucidate the effect of multiphase cloud interactions on important radical oxidants such as OH and HO_2. Modelling studies (see e.g. Kreidenweis et al. 2003; Tilgner et al. 2005) pointed out that chemical aqueous-phase processes in clouds can influence radical concentrations. Recently, scientific questions concerning the importance of its heterogeneous and multiphase chemistry removal pathways of HO_2 by aerosol particles have been addressed (see e.g. Jacob 2000; Morita et al. 2004; Thornton et al. 2008; Taketani et al. 2008; Mao et al. 2013). Model studies with simple parameterisations have revealed the potential relevance of these removal processes to significantly affect the HO_x budget. However, there are still many uncertainties in the findings of such studies (see Thornton et al. 2008), i.e. with regard to the importance of particulate organics for the HO_2 budget. Compared to clouds, the multiphase chemical processing of oxidants in deliquescent particles has been investigated to a much smaller extent. Chemical processes in deliquescent particles have mostly been investigated in the context of the tropospheric halogen chemistry (von Glasow and Crutzen 2007; Bräuer et al. 2013) but less for continental aerosols, where organic compounds and transition metal ions (TMIs) play a more crucial role.

So far, only few studies (see e.g. Herrmann et al. 2000; Williams et al. 2002; Ervens et al. 2003; Herrmann et al. 2005) attempted to characterise higher organic oxidations in the tropospheric aqueous systems and their close interaction with other chemical subsystems such as the HO_x and TMI chemistry. The latter has found to affect the oxidising capacity (see Deguillaume et al. 2005 and references therein). The aqueous redox-cycling of TMIs is supposed to be responsible for many chemical interactions such as the HO_x/HO_y processing and the organic chemistry by OH. But, large uncertainties about TMI chemistry in clouds still exist (Deguillaume et al. 2005) and their processing in deliquescent particles is unknown.

Advanced chemical mechanisms, with a comprehensive description of both gas-and aqueous-phase chemistry, and sophisticated box models have shown to be a convenient means to gain better insight into remaining issues of chemical aerosol-cloud interactions. Model studies considering a complex multiphase chemistry have been carried out in the past mainly by using permanent cloud conditions, which are expedient to investigate in-cloud modifications only (e.g. Herrmann et al. 2000, 2005; Leriche et al. 2000). Investigations on multiphase chemical aerosol-cloud interactions are not feasible with such cloud chemistry models. Most past model studies of chemical aerosol-cloud interactions only considered simplified inorganic aqueous-phase chemistry representations (see Herrmann 2003), which partly neglect important interactions between different chemical subsystems (see Lelieveld and Crutzen 1991; Kreidenweis et al. 2003; Barth 2006). Just a few model studies were performed in the past emphasising both microphysics and multiphase organic and inorganic chemistry with the same complexity in order to comprehensively study multiphase aerosol-cloud interactions (see e.g. Tilgner et al. 2005; Leriche et al. 2007). However, such model studies were applied for single cloud events and have not addressed the chemistry of deliquescent particles. For the sake of completeness, it is noted that recently also higher scale models are reported in the literature treating aqueous phase chemical processes in clouds in somewhat more detail (see e.g. Myriokefalitakis et al. 2011).

The present model study aims at the investigation of the multiphase chemistry of important oxidants and related chemical key subsystems under deliquescent particle and warm cloud conditions by means of the complex multiphase chemistry model SPACCIM (SPectral Aerosol Cloud Chemistry Interaction Model, Wolke et al. 2005) using a non-permanent cloud model scenario. The model investigations intend to clarify complex chemical interactions by means of comprehensive time-resolved reactions flux analyses. Additionally, differences between the former permanent and the present non-permanent cloud model studies are clarified. It should be noted that model results outlined in Tilgner and Herrmann (2010), which primarily focus on the aqueous-phase carbonyl-to-acid conversion and organic acid degradation are not treated again in the present study.

2 Model and multiphase chemistry mechanism description

2.1 SPACCIM

The adiabatic air parcel model SPACCIM combines a complex size-resolved multiphase chemistry model and a model with a description of cloud microphysics. The SPACCIM model treats the aqueous phase chemistry in both deliquesced particles and cloud droplets, which can alter the chemical aerosol composition throughout the simulation time. The microphysical model applied in SPACCIM model framework is mainly based on Simmel and Wurzler (2006) and Simmel et al. (2005). The cloud droplet formation, evolution and evaporation are implemented using a one-dimensional sectional microphysics considering deliquesced particles and droplets, respectively. All microphysical parameters required by the multiphase chemistry model are transferred from the microphysical model after a coupling time step of 10 s model-time. In the present model studies, a moving bin version of SPACCIM was used. In the model, the growth and shrinking of aerosol particles by water vapour diffusion as well as nucleation and growth/evaporation of cloud droplets is considered. The dynamic growth rate in the condensation/evaporation process as well as the droplet activation is based on Köhler theory. Because of the focus of the present model studies on the complex multiphase chemistry, other microphysical processes such as impaction of aerosol particles and collision/coalescence of droplets and thus precipitation have not been taken into account. Furthermore, it should be noted that such an air parcel model is not able to assess the complexity of tropospheric mixing processes. The complex model framework enables detailed investigations of the multiphase chemical processing of gases, deliquescent particles and cloud droplets. Further details about the SPACCIM model are given elsewhere in the literature (see Wolke et al. 2005; Sehili et al. 2005; Tilgner and Herrmann 2010 and references therein).

2.2 Non-permanent cloud simulations with SPACCIM

The SPACCIM model simulation was performed analogous to previous model applications (see Tilgner and Herrmann 2010 for details). Briefly, simulations have been carried out using a meteorological scenario, which is based on the global cloud calculations of Pruppacher and Jaenicke (1995). In the base case scenarios, an air parcel moves along a predefined trajectory passing eight cloud events (4 times at noon and 4 times at midnight) for about two hours each. The in-cloud residence time of the modelled air parcel of about 15 % reflects the global average of the volume filled by clouds in the lower half of the troposphere (Pruppacher and Jaenicke 1995). For non-cloud periods, an intermediate aqueous aerosol state was considered at 90 % RH. A schematic representation of the applied model scenario including modelled meteorological conditions along the trajectory is given in Fig. S1 in the Electronic Supplementary Material (ESM) of the present paper. Additionally, a brief description and depiction of the liquid water content conditions along the model trajectory is given in the ESM (Fig. S2).

Simulations were done for the two different environmental scenarios (urban/remote) under summer conditions beginning at 0:00 on the 19th of June (45°N). It should be noted that the chosen summertime conditions with the highest photochemical activity will exhibit maximal effects, which can be smaller during winter with lower actinic fluxes, temperatures etc.. The two environmental scenarios are characterised by different initial gas and particle compositions, particle number distributions and emission fluxes given in Tilgner and Herrmann (2010). Additionally, a model run was performed without aqueous-phase chemistry (acronym: woAqChem) for comparison with the base case (acronym: AqChem) and to better reveal the effects of multiphase aerosol-cloud-chemistry interactions. The radiative conditions in both the AqChem and the woAqChem case are the same to allow a comparability of the model results. Moreover, the non-ideal behaviour of concentrated aqueous solutions was ignored in the present model calculations (AqChem) but will be considered in a forthcoming treatment. The SPACCIM model assumes deliquesced particles and well-diluted droplets with water as solvent. Activity coefficient models (see e.g., Zaveri et al. 2005; Clegg and Seinfeld 2006; Zuend et al. 2008), which provide the means for a more accurate description of the non-ideal behaviour of high concentrated solutions, were not applied in the present study. However, the present model runs have been only performed for relative humidity larger than 90 %, where deliquesced particles with a substantial amount of water can be assumed. Accordingly, the aqueous phase concentration of the non-volatile water-soluble particle phase compounds is determined by the modelled amount of aerosol water and the chemical particle composition. Aqueous concentrations of highly water-soluble compounds are additionally influenced by their phase transfer.

2.3 Multiphase chemistry mechanism: RACM-MIM2ext/CAPRAM3.0i

In the SPACCIM model framework, the complex multiphase chemistry mechanism RACM-MIM2ext (revised and extended Regional Atmospheric Chemistry Model + Mainz Isoprene Mechanism 2)/CAPRAM 3.0i (Chemical Aqueous Phase RAdical Mechanism) was used as in the former modelling studies by Tilgner and Herrmann (2010). With a total of 777 reactions, CAPRAM 3.0i contains a complex implementation of both aqueous-phase inorganic chemistry and a detailed reaction mechanism for atmospherically relevant organic compounds with up to mainly four carbon atoms. The radical-driven aqueous-phase chemistry of organic compounds in CAPRAM 3.0i is described in detail with more than 400 reactions (Herrmann et al. 2005; Tilgner and Herrmann 2010). In the multiphase chemistry mechanism, the phase transfer of 52 soluble gas phase species is described using the resistance model of Schwartz (1986). All required and used values for the description of the phase transfer of soluble compounds including mass accommodation coefficients, gas phase diffusion coefficients and Henry’s law constants are available online on the corresponding CAPRAM website (http://projects.tropos.de/capram/). Due to the assumption of deliquesced particles, the phase transfer is treated in the same manner for both cloud droplets and aqueous particles. The applied Henry’s law constants were not corrected by activity coefficients. Moreover, no salt formation processes and no organic accretion reactions are considered in the current mechanism. Thus, potentially increased effective Henry’s law constants of organics in concentrated solutions (see e.g. Healy et al. 2008) are not considered.

Despite the mentioned restrictions, non-permanent cloud modelling including both a more realistic in-cloud residence time and an up-to-date multiphase chemistry mechanism enables advanced investigations of aerosol cloud interaction compared to former cloud model studies. Throughout the present study, time-resolved reaction flux analysis was applied allowing improved interpretations of the obtained model results. Further details on the model setup, the chemical mechanism used and the model initialisation are given in Tilgner and Herrmann (2010) and can be found at the CAPRAM webpage (http://projects.tropos.de/capram/).

3 Results and discussion

3.1 Modelled pH conditions

Since acidity is both an important sum parameter as well as a determining factor for many multiphase chemical processes, the temporal and spectral evolution of the pH throughout the simulation time was investigated. The H^+ concentration is initialised in SPACCIM based on the charge balance and afterwards dynamically calculated throughout the simulation time. Figure S3 in the ESM shows the spectral evolution of the pH value as a function of the simulation time for remote and urban environmental conditions (AqChem). Significant temporal and spectral variations of the acidity become apparent from the 2-D plot. Both remote and urban conditions are characterised by a noticeable change of the colours during the cloud processing reflecting the successive acidification of the cloud condensation nuclei predominantly during cloud episodes and polluted conditions. Under remote and urban conditions, total pH values of about 4.8 and 2.9 have been modelled after 72 h of modelling time reflecting typical measured cloud water pH values in those environments (see e.g. Herrmann 2003 and references therein). Apparently, smaller processed particles tend to be more acidic than the larger ones, which is agreement with cloud measurements findings of more acidic smaller particles (see Collett et al. 1994; Moore et al. 2004).

For polluted conditions, a more significant acidification is observed even though with much smaller spectral differences in the acidity as there are enough acid precursors available for transfer into particles of all size classes. The modelled mean pH values of the deliquescent CCNs are around 2.3 and 1.3 in the remote and urban case, respectively, which is significantly lower than their in-cloud pendants. The tendency to lower pH values implies that other chemical processes in deliquescent particles may probably be more important in this medium than in cloud droplets. Measurements of aerosol particle pH values in urban air masses (see e.g. Li et al. 1997) show an average of pH=−1.2, which is even lower than the present results. However, the measurements have been performed mostly below 90 % relative humidity so that the deviations are presumably related to this difference. Size-resolved aerosol pH measurements have been performed in the past predominantly in maritime environments (see Keene et al. 2004; Pszenny et al. 2004; Yao et al. 2007) and only few data are available for continental aerosol particles (e.g. Stelson and Seinfeld 1981; Li et al. 1997). Therefore, further comparisons between modelled and measured pH size distributions have not been examined in this study. Moreover, for future investigations of particle acidity and its comparison with available field data, it is foreseen that the SPACCIM model should include a description of the non-ideal behaviour of concentrated solutions.

3.2 Multiphase chemistry of radical oxidants

3.2.1 Hydroxyl radical (OH)

This subsection is focused on (i) the effect of clouds and deliquescent particles on the OH gas phase radical concentrations, (ii) the chemical aqueous phase processing of OH radicals under deliquescent particle conditions and (iii) under cloud droplet conditions. For the sake of clarity and completeness, the discussion of the modelled aqueous phase OH concentration-time profiles is presented in the ESM.

(i) OH gas-phase concentration-time profiles and their interpretation

According to the importance of the photochemistry for the OH radical, the concentration profiles show a diurnal profile, which is significantly broken by the cloud periods (marked in blue in Fig. 1). Under daytime cloud conditions (2. day cloud event), the gas-phase concentration of OH (AqChem) is decreased by about 90 % and 75 % in the urban and remote scenario, respectively. Somewhat smaller in-cloud reductions of the OH gas-phase concentrations of about 25–73 % have been already modelled by other more simple models (Lelieveld and Crutzen 1990 and 1991; Jacob 1986; Monod and Carlier 1999; Frost et al. 1999). Furthermore, field measurements have shown reductions of the OH gas-phase budget

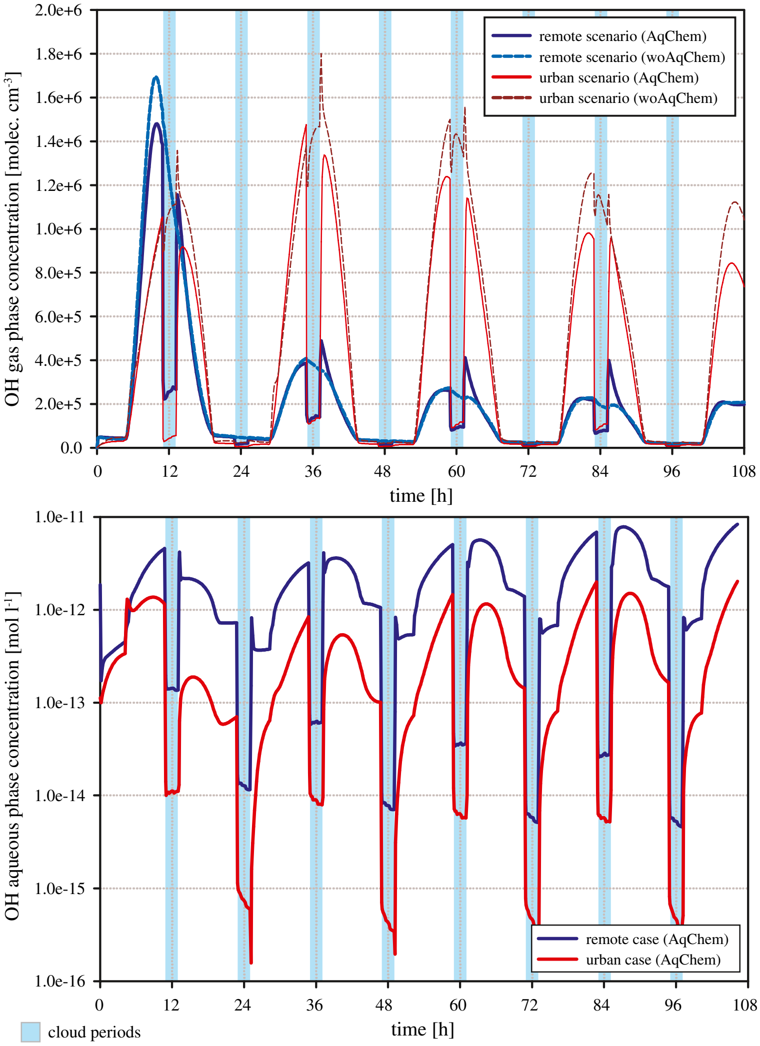

Fig. 1 Modelled gas-phase (*top*) and aqueous-phase (*down*) concentrations of the OH radical vs. modelling time for the urban and remote scenario with (AqChem) and without (woAqChem) aqueous-phase chemistry interaction

by a factor of 2-3 (see e.g. Mauldin et al. 1997; Frost et al. 1999). Within the limits of the present simulations, the modelled magnitude of the OH gas-phase decreases agrees with the few available observations.

The modelled OH reduction is mainly caused by the uptake of very soluble HO_2 and not primarily by the direct OH phase transfer into the droplets. The efficient uptake of the gaseous HO_2 radical causes an OH precursor separation between the two phases and a remarkable decrease in the formation flux (Fig. S4 in the ESM) up to about 90 % in the urban scenario in line with early model findings by Lelieveld and Crutzen (1991). In contrast to the remote case, in the urban case OH is mainly formed by the reaction pathway of HO_2 and NO. Therefore, the decrease is most clearly identified in the urban case. It should be noted that the regenerated NO_2 can form O_3, which can subsequently be photolysed leading to the OH formation via $O(^1D)$. Contrary to the urban scenario, the photolytic OH formation via the reaction of $O(^1D)$ with water acts as an important OH source under remote conditions besides the above-mentioned NO_x based formation pathway (see Fig. S4 in the ESM). Hence, the reduction of the gas-phase OH concentration is smaller in the remote scenario due to the smaller importance of the precursor separation effect.

Particularly under urban conditions, additional differences between the AqChem and the woAqChem case are recognisable during the non-cloud periods. The lowered concentration there is caused mainly by the chemical interaction of the OH precursor HO_2 with the deliquescent particles. The decreased HO_2 gas-phase concentration budget leads to lower OH concentration levels compared to the woAqChem case. It is noted, that the multiphase chemical interaction of the HO_2 radical is outlined in more detail in section 3.2.5. Due to the reduced gas-phase OH budget under cloud conditions, the oxidation of important organic trace gases is noticeably decreased under both urban and remote conditions. The OH oxidation reaction fluxes in the interstitial gas phase are much lower compared to non-cloud conditions. Thus, the tropospheric lifetimes of important organic trace gases are noticeably affected. This indirect chemical OH effect on organic trace gases is discussed in more detail in section 3.3.

Moreover, Fig. 1 shows increased gas-phase OH concentrations (AqChem case) after the evaporation of remote daytime clouds. This modelled effect is related to higher OH production fluxes after the cloud evaporation caused by increased fluxes of NO with HO_2 and organic peroxyl radicals (e.g. ISOP and MO_2), which are less soluble than HO_2. During the cloud periods, the reaction of NO and HO_2 is not acting as a source for OH (phase separation of the reacting educts). On the other hand, the reaction of ISOP with NO acts still as a source for the OH precursor HO_2 in the gas phase. The applied continuous emission scheme leads to an increasing gas-phase NO concentration. In total, the NO_x/HO_x budget is affected right after the daytime cloud evaporation. As a consequence of the recovery of the HO_2 gas-phase concentration and the increased NO budget after the cloud evaporation, e.g. during the descent period of the air parcel trajectory, the OH production and subsequently the OH concentration is raised for a short-time of about 1–2 hours. The reaction flux analysis shows an approximately two times higher gas-phase OH production flux in comparison to the fluxes before the cloud.

(ii) High aqueous-phase OH turnovers in the deliquescent particles: Chemical OH radical sources and sinks

In Fig. 2, the total sinks and sources of OH are plotted for a selected time interval of the modelling time (4. day) for urban conditions. The corresponding plot for the remote case is available in the ESM (see Fig. S5). The total OH fluxes show also a characteristic daytime-profile as modelled for the gas phase. The colour changes in the reaction flux plots show considerable differences in the sinks and sources between deliquescent aerosol conditions (non-cloud) and cloud conditions. In the deliquescent particles, OH formation is dominated by the Fenton reaction of Fe(II) with H_2O_2. Interestingly, the total source fluxes in the particles are fully comparable with the ones in cloud droplets under urban conditions. This means that the in-situ formation of OH is more efficient in the aqueous particles leading to similar chemical turnovers as under cloud conditions. The model results imply that the in-situ OH production under deliquescent particle conditions strongly depends on the TMI concentration and especially on the H_2O_2 concentration. Contrary to the urban case, the remote case shows mostly somewhat smaller OH formations under particle conditions (see Fig. S5 in the ESM). Figure S5 shows that the iron Fenton reaction is substantially increased

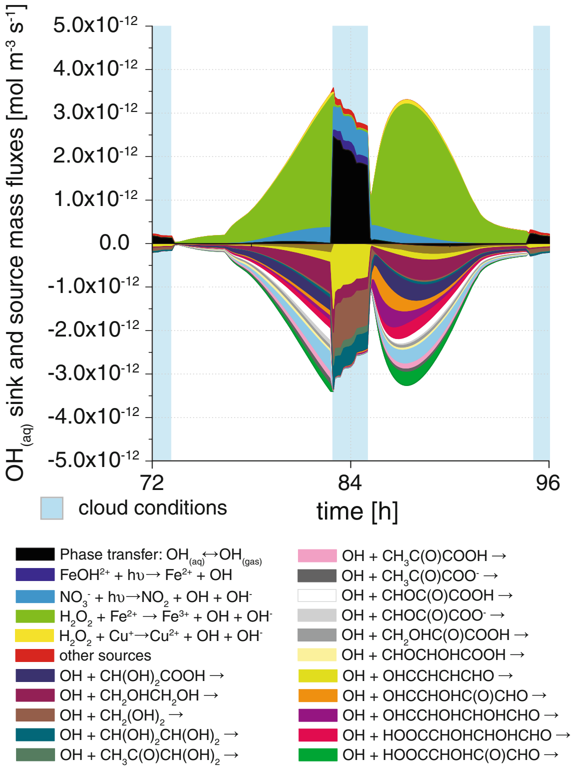

Fig. 2 Modelled chemical sink and source mass fluxes of OH in aqueous phase (mol $m^{-3}_{(air)}$ s^{-1}) for the fourth day of modelling time for the urban scenario

after the evaporation of the daytime cloud, so that OH production fluxes are reached similar those under cloud conditions (see Fig. S5 in the ESM). The observed increase is mainly caused by the production of H_2O_2 in the remote daytime clouds (see section 3.3 for further details).

The above-mentioned results are in good agreement with measurements of Arakaki et al. (2006), who investigated aqueous extracts of aerosol particles with regard to the photochemical formation of OH in deliquescent particles. They found a direct correlation between the OH formation and the dissolved iron concentration. However, more experimental work has to be done to point out the importance of the different formation pathways including the Fenton reaction to act as potential OH in-situ source in the particle phase. Additionally, the OH formation rates, as reported by Shen and Anastasio (2011), show a similar tendency that more aqueous OH is formed in urban aerosols than in aerosols from a rural site. However, the provided OH formation rates of about 1-3 10^{-13} mol m^{-3} s^{-1} in fine urban particle samples are approximately 1 order of magnitude smaller than the model source fluxes in the present study.

In contrast to cloud conditions, where the reactions of highly water-soluble organic compounds taken up from the gas phase, e.g. glyoxal, methylglyoxal, formaldehyde, or 1,4-butenedial, represents the main OH sinks, reactions of their various less volatile oxidation products such as pyruvic acid (6 %) and glyoxylic acid (12 %) act as sinks for OH in the urban scenario in the deliquescent particles (Fig. 2). The reactions of these species are less important under cloud conditions due to the competitive reactants, which are effectively taken up into the cloud droplets such as formaldehyde. The integrated percentage contributions of the most important OH sources and sinks are presented for the urban and remote scenario in Table S1 and S2 in the ESM.

In the remote case, the reactions with the less volatile oxidation products such as glyoxylic acid (8 %), glycolic acid (2 %) and pyruvic acid (8 %), act as sinks for OH in the deliquescent particles predominantly after the cloud evaporation (see Fig. S5 in the ESM). However, it can be seen from the plot and Table S5, that the organic chemistry is much more important in the urban case compared to the remote case. The inorganic chemistry involving, e.g. Cl^-, Br^- and Fe^{2+} and HSO_4^-, accounts on average for more than half of the OH sinks under remote deliquescent particle conditions (cp. Table S1 and S2 in the ESM).

Finally, it has to be noted, that all results mentioned in the last 2 paragraphs above imply the relevance of deliquescent particles to act as a reactive medium within the tropospheric multiphase system. Radical conversions appear to be driven by OH very efficiently produced from the Fenton reaction. The availability of such OH radical source in deliquescent particles may also be important for the formation of atmospheric secondary organic matter. Particularly, the entrainment and detrainment areas of tropospheric clouds may be also quite reactive media for the chemical aerosol processing. Apparently, the abundance of liquid water in aerosol particles will enable a complex chemistry, which in some parts resemble the dilute aqueous solution chemistry as encountered in cloud droplets, but which might be considerable different with regard to other aspects.

(iii) Processing of OH radicals in cloud droplets: Chemical sources and sinks

As above-mentioned, the reaction flux plots reveal considerable changes in their colour patterns indicating huge differences in the sinks and sources fluxes under deliquescent particle (non-cloud) and cloud conditions. These differences are mainly caused by the increased phase transfer flux of soluble compounds into the droplets, which can act there as additional considerable sinks and sources in the cloud droplets.

Integrated over all cloud periods, the most important source of OH in the aqueous phase is the direct transfer from the gas phase with about 73 % in the urban case (64 % in the remote case). In addition, the aqueous-phase nitrate (NO_3^-) photolysis, $FeOH^{2+}$ photolysis and the HO_3 decomposition contribute with about 7 %, 14 % and 4 %, respectively, to the OH formation in the aqueous phase under urban cloud conditions. In the remote case, mainly the Fenton type reactions of Cu(I) and Fe(II), the HO_3 decomposition as well as the photolytic decay of H_2O_2 and $FeOH^{2+}$ contribute with about 3 %, 16 %, 7 %, 7 % and 2 %, respectively, to the in-cloud sources of the OH radical besides the direct uptake from the gas phase. Former permanent cloud model studies using CAPRAM (Ervens et al. 2003; Herrmann et al. 2005) have revealed the same OH radical sources as important. However, their relative contribution to the OH sources fluxes differs from the obtained results here. This results mainly from the different meteorological scenarios using permanent and non-permanent cloud conditions, respectively. The permanent cloud modelling tend to underestimate the direct transfer from the gas phase.

Finally, the added formation fluxes over the whole simulation time and the separation according to cloud droplet and deliquesced particle conditions reveal that the total turnovers under both conditions are comparable under remote conditions with relative contributions of 48 % and 52 %, respectively. However under the urban conditions, the total turnovers in cloud droplets (23 %) and deliquescent particles (77 %) show with a ratio of approximately 1:3 a much higher contribution of the aqueous particle phase. But, it is noted that, the contributions of the aqueous particle phase are strongly related to the atmospheric conditions, e.g. the relative humidity, and the chemical composition of the gas and aqueous phase. Thus, the above-mentioned contributions can be quite different under different environmental conditions.

Compared to the reaction flux pattern of the OH sources, a much more complex pattern can be obtained for the OH sinks. The most important sinks under cloud conditions (urban case) are the reaction with hydrated glyoxal (13 %), methylglyoxal (5 %), formaldehyde (29 %), ethylene glycol (11 %), and 1,4-butenedial (31 %). In comparison to the urban case, the most important OH sinks under remote in-cloud conditions represents the reactions with formate, hydrated formaldehyde, glycolaldehyde and methylglyoxal with about 42 %, 37 %, 2 % and 7 %, respectively. The modelled contributions of the different OH sinks under remote cloud conditions are in a good agreement with the former permanent cloud model studies of Herrmann et al. (2005), where similar values were obtained. In comparison to former CAPRAM studies (Herrmann et al. 2000; Ervens et al. 2003), which have revealed hydrated formaldehyde and formic acid as major sinks under both urban and remote conditions, the present study shows that also higher functionalised organic compounds can be considerable OH sinks in the urban case. However, it is noted that currently OH oxidations of other potential reactants particularly higher organic compounds are neglected in the present multiphase chemistry mechanism due to restricted knowledge. Finally, it is noted that a detailed description of the modelled aqueous phase OH radical concentration-time profiles is given in the ESM

3.2.2 Nitrate radical (NO_3)

The modelled gas-and aqueous phase concentrations of NO_3 are presented in Fig. 3 for the urban and remote scenario simulations. Due to the fact that the NO_3 radical is only of minor importance under remote conditions, the present section focuses mainly on the model results of the urban scenario. Figure 3 reveals significantly reduced NO_3 gas phase concentrations under polluted conditions (AqChem case) compared to the woAqChem case. This is caused mainly by the effective aqueous-phase uptake and conversion of the NO_3 reservoir species N_2O_5. A negative correlation of measured NO_3 radical concentrations with the relative humidity, due to the indirect removal of the reservoir species N_2O_5 on aqueous particles, has been also observed in field studies (see e.g. Vrekoussis et al. 2007; Geyer et al. 2001). The modelled urban concentration profile (red line in Fig. 3) displays also distinctive decreases in the gaseous NO_3 concentration level after the cloud evaporation. The lowered concentration levels compared to the levels before the cloud formation indicate effective in-cloud oxidations.

The aqueous NO_3 radical concentrations (AqChem case) show also differences between the two scenarios (see Fig. 3). Interestingly, the aqueous-phase concentration profiles do not reflect the distinctive night-time concentration cycles of the gas phase. The aqueous-phase NO_3 concentrations are additionally affected by their sinks and sources in the aqueous phase (see discussion below). The modelled urban concentrations show just a small variability because of the significant continuous uptake flux into the droplets particularly during the night-time clouds. The urban night-time in-cloud concentrations of NO_3 are with $2.0\ 10^{-13}$ mol L^{-1} approximately 1 order of magnitude higher than the corresponding daytime in-cloud OH concentration. Simulated aqueous NO_3 radical concentrations are similar to those obtained in Ervens et al. (2003).

The urban NO_3 radical concentrations in the deliquescent particles are about one order of magnitude lower than that of the daytime OH. This is caused by the different chemical sink and source characteristics between the two radicals. In contrast to the OH radical, the phase transfer from the gas phase is almost the only source for the aqueous phase NO_3 radical in the urban case

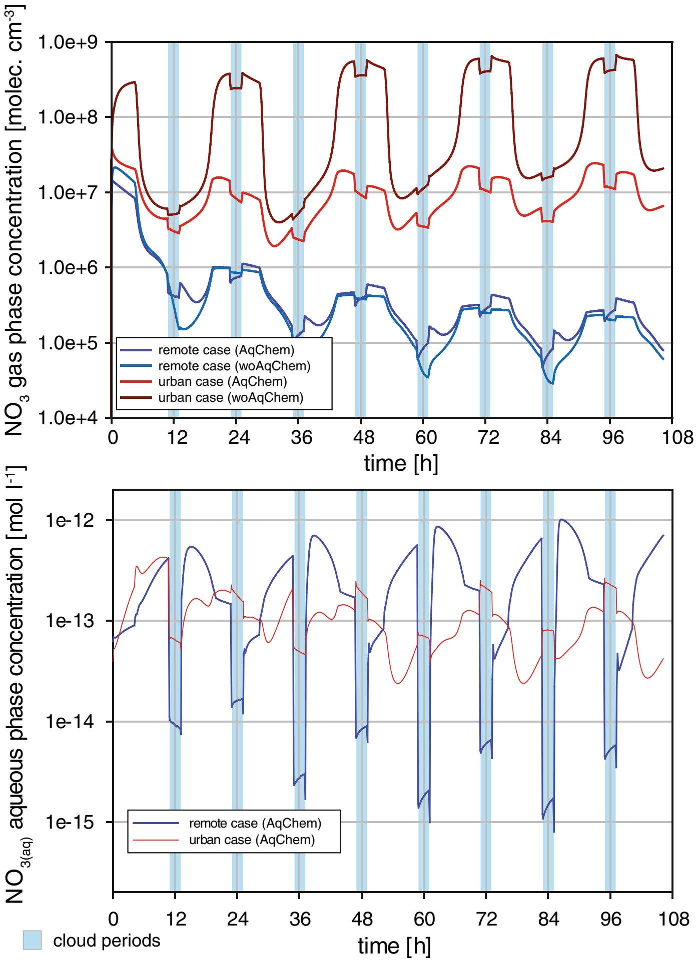

Fig. 3 Modelled gas-phase (*top*) and aqueous-phase (*down*) concentrations of the NO_3 radical for the urban and remote scenario with (AqChem) and without (woAqChem) aqueous-phase chemistry interaction

(see Fig. 4), which agrees with findings of former studies (Herrmann et al. 2000; Ervens et al. 2003). In-situ sources, i.e. internal aqueous-phase productions pathways, are just of minor importance apart from the first day of the simulation, where they act as both considerable sinks and sources for NO_3 radical in the deliquescent particles. Particularly, the radical inter-conversion reactions with chloride and bromide leading to the formation of Cl and Br atoms and radical anions act as important NO_3 sink as well as source in the deliquescent particles. The radical inter-conversion reaction between the NO_3^- and Cl/Br radicals act as source for NO_3 during daytime conditions.

The total in-cloud oxidation fluxes of the two main radical oxidants OH and NO_3 (max. day and night-time flux, respectively) are with about $(2\text{-}3)\times10^{-12}$ mol m^{-3} s^{-1} the same order of magnitude under polluted conditions. Furthermore, Fig. 4 shows that the in-cloud oxidation of methylglyoxal and its oxidation products such as pyruvic acid seems to be an efficient sinks for the NO_3 radical in the aqueous phase particularly under urban conditions. Comparable results are also obtained for remote conditions. The most important urban NO_3 sinks and sources

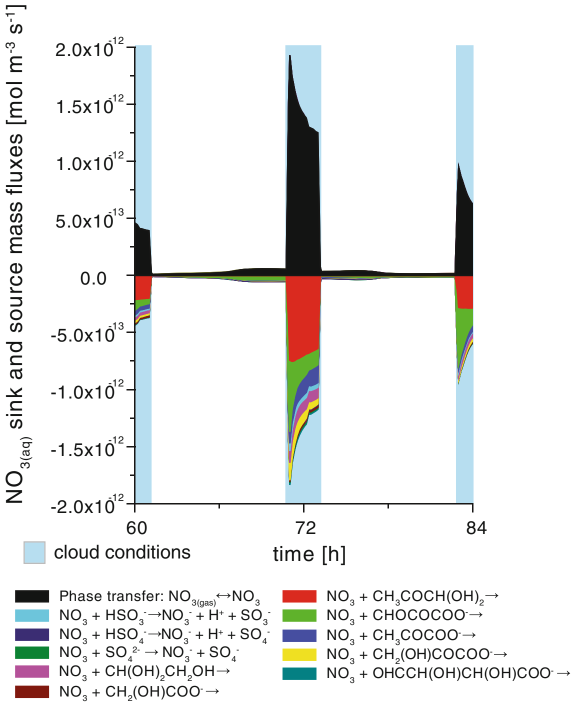

Fig. 4 Modelled chemical sink and source mass fluxes of the NO_3 radical in aqueous-phase (mol $m^{-3}{}_{(air)}$ s^{-1}) for a selected period of the modelling time under urban conditions (only sinks and sources with a contribution larger than ±1 % presented)

including their relative contributions are summarised in Table S3 in the ESM. In contrast to the OH radical budget, which is significantly influenced by C_1-C_4 organic compounds, the NO_3 budget is almost exclusively affected by C_3 organic species due to their considerable reactivity with the NO_3 radical compared to OH (see also Fig. 5). Moreover, the reaction mass fluxes in the deliquescent aerosol particles are mostly more than 1 order of magnitude smaller for the NO_3 due to the less efficient in-situ sources. Different from the OH radical, the NO_3 radical budget is determined by its gas-phase budget at least under highly polluted conditions and NO_3 reactions appear to be therefore only of less importance in the deliquescent particles.

A comparison of the NO_3 radical importance for oxidations of organic compounds among the performed non-permanent and the former permanent cloud chemistry model studies (e.g. Ervens et al. 2003; Herrmann et al. 2005) reveals considerable differences. The relevance of the NO_3 radical for tropospheric oxidations in the aqueous phase appears to be substantially under-determined using permanent cloud chemistry model conditions. Due to the almost permanent transfer of gas-phase NO_y species into the aqueous phase under cloud conditions, the gas-phase NO_x/NO_y budget becomes artificially decreased. This effect clearly increases with the simulation time and then leads to low NO_x as well as low NO_3 radical gas-phase conditions. Since the phase transfer of gas-phase NO_3 radical is the main source for the aqueous-phase budget, even the non-permanent cloud studies performed in this study might probably still underestimate the NO_3 radical importance due to the selected microphysical scenario and the long lifetime of the droplets. Substantial deviations between the estimated CAPRAM values and the recently measured constants (see Herrmann et al. 2010 and references therein) can be obtained only for the rate constants of organic acid anions such

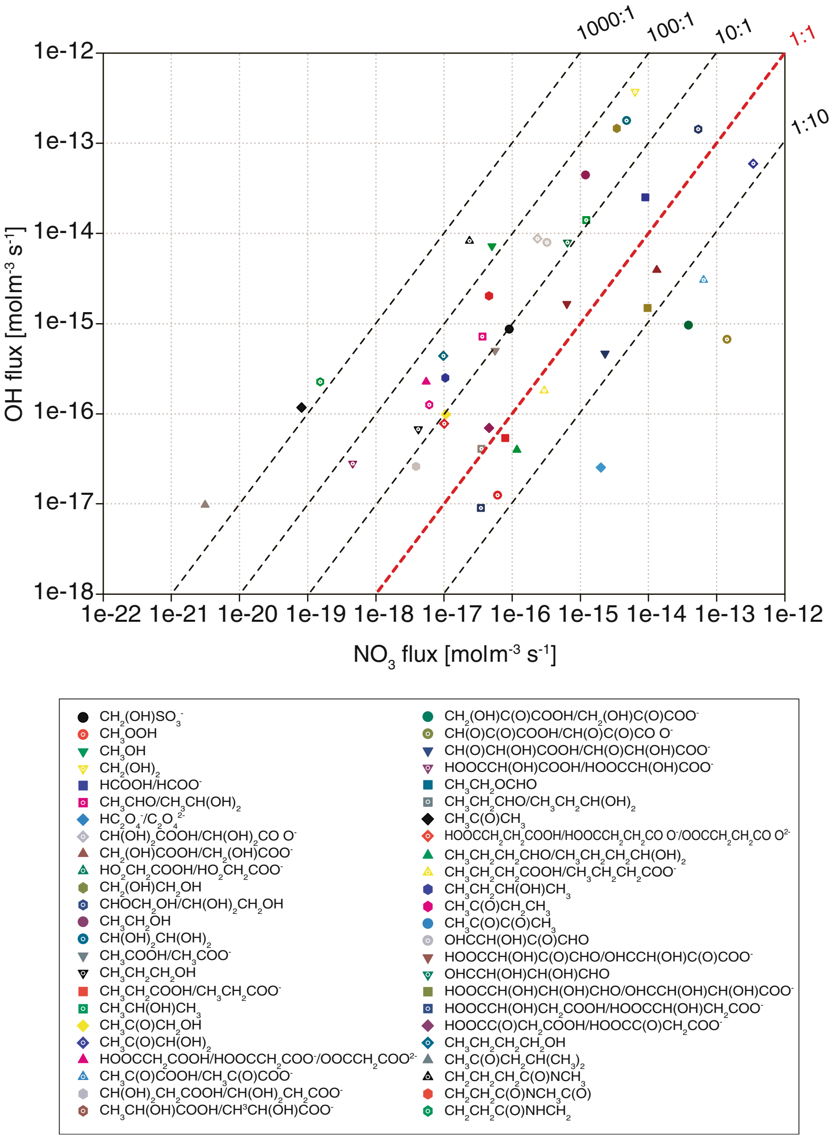

Fig. 5 Comparison of the modelled mean in-cloud NO_3 and OH degradation fluxes of organics compounds under urban conditions

as lactate. Thus, future mechanism developments should consider these measured data and, when needed, evaluated reaction rate prediction methods derived from them (see Herrmann et al. 2010 for further details).

3.2.3 Comparison of organic oxidation turnovers of OH and NO_3

The previous subsections have shown that organic compounds represent a crucial sink for aqueous-phase radical oxidants such as OH and NO_3. However, the previous sections have not compared the in-cloud turnovers of the different radicals for the oxidation of various dissolved organic compounds. A comprehensive comparison of the organic oxidation turnovers of OH and NO_3 radicals have been also not yet done in other available model studies.

For the comparison, the aqueous-phase OH and NO_3 organic oxidation fluxes were analysed for the cloud and non-cloud periods of the simulation. In Fig. 5, a comparison of the averaged reaction fluxes caused by the two radicals is presented for the in-cloud degradation of organic compounds under polluted cloud conditions. The calculated average reaction fluxes consider all data during both day- and night-time cloud periods in order to reflect the different diurnal relevance of the two radical oxidants. The plot shows that for a number of organic compounds the NO_3 radical oxidation flux can be equivalent with or even more important than the corresponding OH reaction pendant. Nevertheless, for the majority of the organic compounds, the major aqueous-phase radical oxidant is OH despite the high NO_x concentrations under polluted conditions. In addition, Fig. 5 indicates that the in-cloud degradation of methylglyoxal and its oxidation products like pyruvic acid might be an efficient aqueous-phase sink for NO_3 particularly under urban, but also under remote conditions. Similar comparisons considering the non-cloud periods only (fluxes in the deliquescent particles) reveal that NO_3 radical plays a crucial role only for cloud conditions, whereas OH chemistry clearly dominates under deliquescent particle conditions due to the effective in-situ sources of the OH radical, see section 3.2.1.

Based on those findings, the results of the CAPRAM runs were scanned through coherences between the NO_3 importance and the number of carbon atoms (C_x with x=1, 2, 3, 4), the functional group (aldehydes, diacids, dialdehydes, etc.) and the oxidation degree of the respective organic compounds (represented by the O/C atom ratio). The results are given in the ESM. In summary, the study showed no direct coherences between the OH/NO_3 flux ratio and the number of carbon atoms and the functional group, respectively. However, the study showed that the NO_3/OH flux ratio tends to increase with the polarity of the organic species.

Overall, the results of the present study indicate that necessarily more NO_3 radical oxidations of oxidised organic aerosol components should be investigated in the laboratory and afterwards considered in upcoming aqueous mechanisms due to the potential importance of NO_3 oxidation for such compounds. Additionally, the present model studies indicate that other mechanisms (e.g. Ervens et al. 2008) might underestimate the degradation of certain organic compounds in polluted environments by ignoring aqueous-phase NO_3 radical oxidations.

3.2.4 Sulphur containing radicals (SO_x^-)

Besides OH and NO_3, CAPRAM 3.0 contains also organic reactions ($C_1 – C_2$ chemistry) of other radicals and radical anions (see Herrmann et al. 2005; Ervens et al. 2003), which were found to be only of minor importance in former permanent cloud model studies. The present study shows that primarily the sulphate radical anion (SO_4^-) and the peroxymonosulphate radical anion (SO_5^-) can contribute to the in-cloud oxidation of organic compounds. The relative contributions of the SO_4^- and the SO_5^- radical anion for the oxidation of $C_1 – C_2$ organic compounds under remote and urban cloud conditions in comparison to the OH radical are summarised in Table 1. It should be noted that the NO_3 radical contributions is not given in Table 1, because the NO_3 represents not a significant sink for the investigated organic compounds (see Fig. 5 in the previous subsection).

Table 1 Relative contributions of the SO_4^- and the SO_5^- radical anion to the oxidation of C_1 - C_2 organic compounds under remote and urban cloud conditions in comparison to the OH radical

Organic reactant	Remote scenario			Urban scenario		
	SO_4^-	SO_5^-	OH	SO_4^-	SO_5^-	OH
$CH(OH)_2CH(OH)_2$ (hydrated glyoxal)	1 %	44 %	55 %	5 %	35 %	59 %
CH_3OH (methanol)	0 %	–	100 %	3 %	–	97 %
CH_3CH_2OH (ethanol)	1 %	–	99 %	6 %	–	85 %
$CH_2(OH)_2$ (hydrated formaldehyde)	1 %	–	99 %	5 %	–	93 %
CH_3CHO / $CH_3CH(OH)_2$ (acetaldehyde)	1 %	–	99 %	2 %	–	97 %
HCOOH /$HCOO^-$ (formic acid/ formate)	1 %	–	97 %	1 %	–	26 %
CH_3COOH / CH_3COO^- (acetic acid/ acetate)	24 %	–	76 %	20 %	–	72 %
$CH(OH)_2COOH$ / $CH(OH)_2COO^-$ (hydrated glyoxalic acid / glyoxalate)	0 %	–	100 %	6 %	–	92 %

The relative contributions represent an average over all day-and night-time clouds during the model simulation. Therefore, also even higher contributions of the SO_4^- and the SO_5^- radical anion are feasible during the simulation time (e.g. the SO_4^- radical anion contributes with about 32 % to the degradation of glyoxalic acid in the remote night-time clouds)

The sulphate radical contributions are in the range of few percent of the total degradation flux with somewhat higher values in the polluted case. The only exception is acetic acid with modelled contribution ratios up to 24 %. Moreover, the reaction flux analysis (see in Fig. 6) reveals that oxidations of organic compounds represent a significant chemical in-cloud sink for the SO_4^- radical. Particularly, the reactions with hydrated formaldehyde and glyoxal contributing with more than 50 % significantly to the total in-cloud SO_4^- degradation fluxes (see Fig. 6). The SO_4^- radical sink and source fluxes show a similar diurnal pattern as obtained for the OH radical. Figure 6 reveals, a cycling of the SO_4^- radical in the deliquescent particles including the SO_4^- formation via S(VI) reactions with OH and NO_3 as well as the SO_4^- consumption in the reaction of SO_4^- with Fe^{2+}.

The CAPRAM mechanism contains also oxidation reactions of glyoxal and oxalate with the SO_5^- radical. For glyoxal, the modelled oxidation fluxes of the SO_5^- radical are almost comparable to that of OH (see Table 1). Contrary to the SO_4^-, the SO_5^- radical reveals a characteristic cloud profile only (Fig. 6). This behaviour can be explained by the inefficient uptake of S(IV) into the acidic aqueous particles and the hence restricted aqueous source for SO_X^- radicals. Figure 6 shows that organic oxidations might also be considerable sinks for SO_5^- radicals besides the known inorganic pathways. The obtained results are consistent with model results obtained in the real cloud passage modelling (see Tilgner et al. 2005), where the importance of the SO_5^- radical for the in-cloud oxidation of glyoxal has already been pointed out for low OH radical conditions. However, it is noted that the relevance of the SO_5^- for the glyoxal oxidation is probably overestimated by the present model due to the largely missing SO_5^- kinetic constants for other organic compounds (see review by Herrmann 2003). For that reason, further laboratory studies and the subsequent development of reactivity estimations are needed to develop improved mechanisms and to assure the present findings of the SO_5^- radical importance. Finally, it should be noted that due to the mitigation of the anthropogenic SO_2 emissions in many parts of the world, the importance of the chemistry of sulphur containing radicals might decrease.

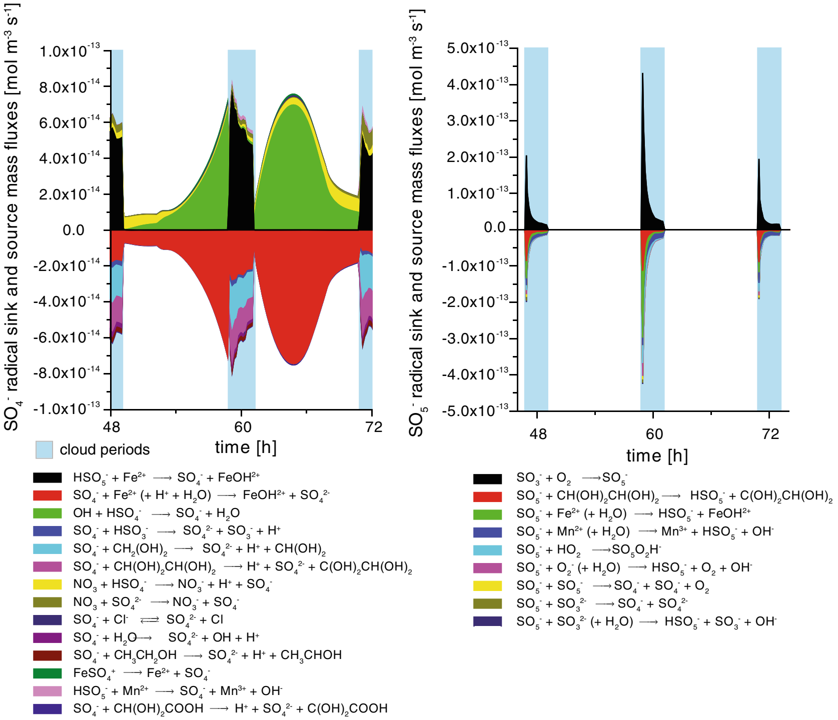

Fig. 6 Modelled aqueous chemical sink and source mass fluxes (mol m^{-3}$_{(air)}$ s^{-1}) of the SO_4^- radical (urban case, *left*) and SO_5^- radical (remote case, *right*) for a selected period of the modelling time

3.2.5 Hydroperoxyl radical/superoxide anion (HO_2/O_2^-)

As proposed by several model studies (e.g. Lelieveld and Crutzen 1991; Tilgner et al. 2005; Thornton et al. 2008) and shown in recent aircraft measurements (Commane et al. 2010), the aqueous phase can act as considerable sink for the gaseous hydroperoxyl radical HO_2. In-cloud reductions of the gas-phase HO_2 concentration are also simulated by the present simulations (AqChem cases). Figure 7 reveals that the HO_2 gas-phase concentration is drastically decreased under cloud conditions and often by more than one order of magnitude. These results agree with simulations of Lelieveld and Crutzen (1991), which showed similar reductions. The present model results reveal that reductions are more substantial particularly during the daytime cloud conditions. Observations of Commane et al. (2010) above the humid forest of West Africa have shown in-cloud reductions in the gaseous HO_2 concentration down to approximately one third of the non-cloud value. As the LWC of the modelled clouds is slightly higher than the LWC during the aircraft measurements of Commane et al. (2010) and due to the specific environment, the more significant reductions in the present study might presumably relate to these facts.

In contrast to the OH and NO_3 radical, the aqueous HO_2/O_2^- concentrations reveal just small variations throughout the simulation time. The concentration level in the deliquescent particles is mostly just one order of magnitude smaller than the corresponding in-cloud level. Moreover, the diurnal HO_2 gas-phase profile is also reflected in the aqueous phase. The modelled maximum HO_2/O_2^- concentrations of about 1.0 10^{-8} and 2.5 10^{-9} mol L^{-1} in the urban and remote scenario (AqChem case), respectively, are about 5 orders of magnitude

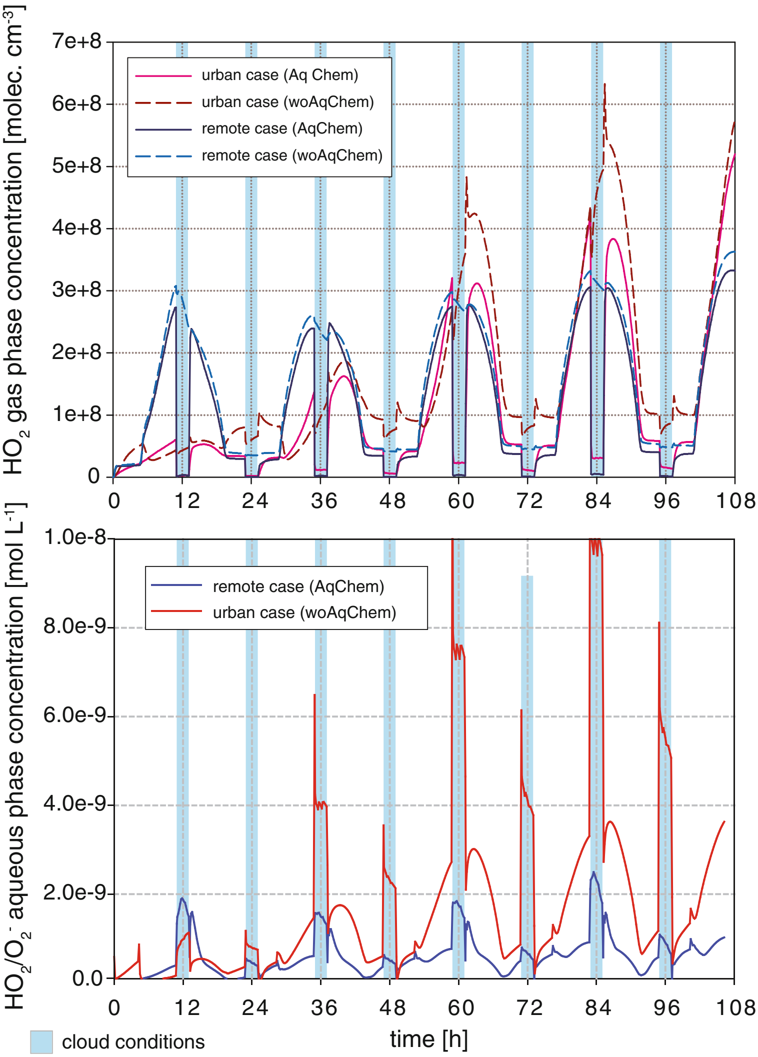

Fig. 7 Modelled gas-phase (*top*) and aqueous-phase (*down*) $HO_2(O_2^-)$ concentrations for the urban and remote case scenario with (AqChem) and without (woAqChem) aqueous-phase chemistry interaction

higher than the respective OH concentrations. In comparison, the concentration difference in the gas phase accounts only for 2–3 orders of magnitude. This results from the very effective reactive uptake of gaseous HO_2 and the efficient in-situ sources. Particularly in the aqueous particles, the uptake is the dominating source besides in-situ sources. Figure S8 in the ESM shows the total sink and source fluxes including the net effect of the HO_2/O_2^- cycling with copper and its backward reaction. The latter processes together with the other TMI reactions lead to a net HO_2/O_2^- destruction in the aqueous phase. Although the reactivity of iron with HO_2/O_2^- is considerably smaller than the copper pendants, the iron reactions contribute with about 10 % to the HO_2/O_2^- loss fluxes.

Another interesting fact seen in Fig. S8 is the importance of the unimolecular decay of the acetyl peroxyl radical (hydrated form) for the in-situ formation of HO_2 in the aqueous phase.

This pathway represents the main in-cloud HO_2 source with an overall relative contribution of about 24 % in the urban case. Besides the acetyl peroxyl radical, other organic peroxyl radicals can substantially add to the total in-situ formation of HO_2/O_2^-. Additionally to the organic peroxyl radicals depicted in Fig. S8, unimolecular decay reactions of other organic compounds contribute to the aqueous formation of HO_2/O_2. About 84 % of the other sources (marked in dark green in Fig. S8) represent unimolecular decay reactions other organics. In total, the organic aqueous-phase chemistry contributes to about 47 % to the total HO_2/O_2^- sources and therefore constitutes a non-negligible source for the multiphase HO_2/O_2^- budget. Furthermore, the currently still incomplete organic aqueous-phase chemistry might still lead to a possible underestimation of the HO_2 formation in clouds and might therefore be also a reason for the considerably higher modelled HO_2 gas-phase reduction in comparison to the field data of Commane et al. (2010). Moreover, it can be seen from Fig. S8 that urban night-time cloud chemistry can lead to a release of HO_2 into the gas phase due to the efficient aqueous formation pathways. This finding is different to the remote case, where the aqueous phase represents just a sink throughout the simulation time. However, this result cannot be compared with field measurements at present.

Another important scientific question concerning HO_2 represents the importance of its heterogeneous and multiphasic removal pathways of HO_2 by clouds and aerosol particles (see e.g. Morita et al. 2004; Thornton et al. 2008; Taketani et al. 2008). Higher scale model studies have revealed the potential relevance of these removal processes to affect significantly the atmospheric HO_x budget. However, there are still quite a lot of uncertainties in the model parameterisations as well as the resulting simulation findings (see Thornton et al. 2008). Moreover, studies of Thornton et al. (2008) and Taketani et al. (2008) have assessed the effects of the aerosol pH, temperature, particle radius, aqueous-phase diffusion and the copper chemistry for the overall HO_2 uptake coefficient (γ_{HO2}).

Thornton et al. (2008) have discussed the main issues, which restrict more precise parameterisations and outputs of higher scale models. One of the mentioned issues is related to the importance of the particulate organics for the HO_2 budget. The former model calculations of Thornton et al. (2008) completely neglect the possibility of an in-situ aqueous-phase HO_2 formation in aqueous particles even though the direct uptake from the gas phase would decrease. The obtained SPACCIM results (AqChem) including aqueous particles at 90 % relative humidity show considerable reduction in both scenarios in comparison to the woAqChem model run (see Fig. 7). The noon concentrations at the end of the simulation time (108 h) show reductions of approximately 10 % in both cases. Moreover, the reaction flux analysis shows that also multiphase oxidations of organics such as glyoxalic acid are potentially important in-situ sources contributing to the aqueous-phase HO_2 source budget besides the direct phase transfer. Even if the current CAPRAM mechanism contains only organics up to mainly C_4, the current results implicate that organic oxidation reactions probably have the potential to lower the direct uptake of HO_2 from the gas phase due to their contributions to the aqueous HO_2/O_2^- concentration budget. Thus, considering the processing of other higher organics in future condensed phase mechanisms, model results might show a lowered gas-phase removal of HO_2 due to the increased aqueous-phase in-situ sources for HO_2/O_2^-.

When, the modelled HO_2 particle uptake fluxes of several size-bins (remote/urban case) are converted into a γ_{HO2}-value (see Jacob 2000), a value almost equal to the mass accommodation coefficient (10^{-2}) applied in the current model results. The calculated values are smaller than values derived from field measurements (see Taketani et al. 2012). This result means that the applied mass accommodation represents the limiting step for the HO_2 uptake process in the present study and that further sensitivity studies on this crucial parameter should be done in the future.

3.3 Multiphase processing involving H_2O_2 and O_3 as non-radical radical oxidant

Beside the radical oxidants, also concentrations of non-radical oxidants such as H_2O_2 and O_3 can be influenced by aqueous-phase chemistry interactions and have been therefore investigated in the present study. The model results for H_2O_2 are presented below because of the various interesting interactions of H_2O_2 with other chemical subsystems such as the HOx and TMI chemistry in both deliquesced particles and cloud droplets. The results for O_3 are given in the ESM.

Figure 8 shows the modelled H_2O_2 gas-phase concentrations vs. modelling time for the remote scenario (AqChem/woAqChem case). The modelled H_2O_2 gas-phase concentrations (AqChem, blue line) are significantly reduced in comparison to the woAqChem model run. The red curve in Fig. 8 (woAqChem case) shows a typical diurnal concentration profile with an increase over the simulation time due to the not considered chemical sinks in the aqueous phase. In contrast, the blue concentration profile is characterised by significant decreases during cloud periods mainly due to the efficient partitioning of H_2O_2 into the cloud droplets. Moreover, a substantial increase of the gaseous H_2O_2 concentration is obvious after daytime cloud evaporation, e.g. during the descent period of the air parcel trajectory and a significant decrease can be obtained after night-time cloud evaporation. Additionally under deliquescent particle conditions, the H_2O_2 is mostly lowered compared to the woAqChem case. Overall, the reduction of the H_2O_2 concentration is caused by both a decreased gas-phase production in the cloud and effective aqueous-phase oxidations in the cloud droplets and deliquescent particles. The aqueous-phase oxidations mainly involve sulphur (IV) oxidation and the transition metal ion chemistry, which are discussed below in more detail. Figure S10 in the ESM depict the modelled chemical sink and source fluxes of H_2O_2 under urban and remote conditions, respectively. Under urban cloud conditions, the sulphur chemistry dominates the aqueous-phase H_2O_2 chemistry leading to reduced H_2O_2 gas-phase concentration levels after the cloud evaporation (see Fig. S10). In the remote case, the TMI-chemistry (particularly reactions of Cu^+/Fe^{2+} with O_2^-) controls the multiphase H_2O_2 budget during the daytime clouds and the sulphur chemistry during the night-time clouds (see Fig. S10 in the

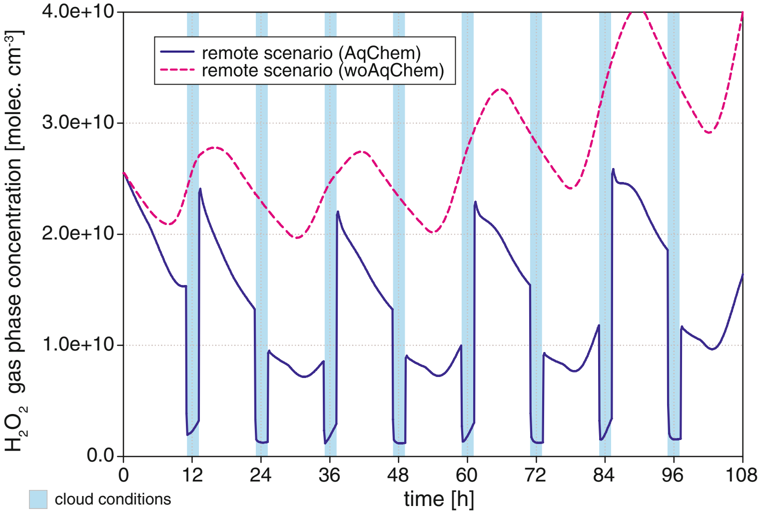

Fig. 8 Modelled H_2O_2 gas-phase concentration vs. modelling time for the remote scenario both with (AqChem) and without (woAqChem) aqueous-phase chemistry interaction

ESM). The reaction flux analysis reveals negative net fluxes during the night clouds and positive values during the day clouds. Consequently, the cloud phase act as source for H_2O_2 in the gas phase and the concentration of H_2O_2 is increased by more than 50 % after the day-cloud evaporation, when the dissolved H_2O_2 is transferred back to the gas phase (see Fig. 8). This result differs from many other former model studies, which usually pointed out clouds just as a sink for H_2O_2. However, the presently modelled direct chemical cloud effect on H_2O_2 confirms both laboratory investigations of Zuo and Holgne (1992), modelled in-cloud H_2O_2 productions by Liu et al. (1997) and conclusions of Anastasio et al. (1994). Zuo and Holgne (1992) expected an effective generation of hydrogen peroxide in daytime clouds and consequently a feedback on the H_2O_2 gas-phase budget. Anastasio et al. (1994) concluded that aqueous photochemistry can be a significant and in some cases the dominant source of H_2O_2 in cloud droplets. However, it should be noted that other studies, e.g. of Marinoni et al. (2011), are not in agreement with the above findings showing that the photolysis is more important than in-situ photochemical production in the investigated cloud water solutions.

The above-mentioned result of Anastasio et al. (1994) is confirmed by the present model findings. The reaction flux plots (see Fig. S10) reveal that the uptake represents an important source for the aqueous H_2O_2 just at the beginning of the cloud episodes. Afterwards, reactions of TMIs (Cu^+/Fe^{2+}) with HO_2 represent the main sources for H_2O_2 under cloud conditions. It is noted that this chemical cloud effect on the gaseous H_2O_2 and thus the $HO_{x,y}$ budget might be of particular importance for processes in the evaporation zones of cloud droplets, e.g. the cloud edges and upper ice formation zones in the cloud. Moreover, the present model results confirm also findings of Arellanes et al. (2006) and Wang et al. (2010), which found that aqueous particles are capable of generating H_2O_2. The reaction flux plots (see Fig. S10) show that particularly under urban particle conditions the TMI chemistry of Cu^+ and Fe^{2+} with aqueous HO_2 acts as source for H_2O_2. This model finding is in good agreement with the studies of Wang et al. (2010), which found a strong correlation of the H_2O_2 with soluble metal such as iron and copper.

3.4 Effects of multiphase chemistry interactions on organic trace gases

As briefly discussed in other multiphase chemistry studies (see e.g. Lelieveld and Crutzen 1991), changed oxidants budgets are expected to perturb the degradation of many organic trace gases. However, up to now, such chemical cloud effects have not been analysed in a systematic manner. Therefore, investigations have been performed on the influence of the changed gas-phase oxidants budget on the degradation of important organic trace gases.

Present model results show that, due to the obtained multiphase chemical effects on oxidants, the concentration patterns of gas-phase trace gases can be considerably affected (see Fig. S12 in the ESM). The observed effects of the organic RACM-MIM2ext gas-phase compounds are summarised in Table 2. Both daytime and/or night-time cloud effects as well as more complex multiphase cloud interaction effects are identified for organic trace gases. According to the observed cloud effects, the organic RACM-MIM2ext gas-phase species were classified into 3 different effect types (see Table 2).

(i) Less water-soluble organics

For the emitted less water-soluble gas-phase species like xylene (XYL) and ethene (ETE), a significant reduction of the degradation rate and higher concentration levels can be observed during the cloud episodes if aqueous-phase chemistry is considered (see Fig. S12 in the ESM). In particular, the reduced oxidant concentrations in the daytime clouds lead to reduced gas-phase degradation for these compounds (type 1 see Table 2). In

Table 2 Summary of the modelled chemical aqueous-phase interaction effects on RACM-MIM2ext gas-phase species for remote and urban environmental conditions

Effect type	Remote case	Urban case
(1) Almost only daytime cloud effect	ALD (11), CAR4 (14), CSL (−7), DIEN (0), ETE (5), ETH (0), HC3 (3), HC5 (2), HC8 (2), KET (0), HKET (−5), ISO (−2), MACR (10), MPAN (2), MVK (24), NALD (3), OLI (2), OLT (0), OP1 (−22), PAA (−52), PAN (−22), TPAN (−10), TOL (−2), UDD (−7), XYL (−2), ISON (23), ONIT (12)	ALD (7), CAR4 (113), ETE (33), HC3 (6), HC5 (10), HC8 (24), HKET (−37), KET (−17), MPAN (−29), MVK (138), NALD (−39), OLI (−52), OLT (50), PAN (−44), TPAN (30), TOL (18), XYL (37)
(2) Day- and night-time cloud effect	API (−5), LIM (−6), OP2 (26),	API (86), CSL (166), DIEN (107), LIM (−57), OP1 (22), OP2 (−33), PAA (−83), ISO (112), UDD (16) ETH (0), ISON (−27), MACR (−15), ONIT (−19)
(3) Complex effect (gas/aqueous phase interaction effects)	CH2OHCH2OH, DCB, GLY, HCHO, MGLY, MO2, ACO3, OHCCH2OH, ORA1, ORA2	CH2OHCH2OH, DCB, GLY, HCHO, MGLY, MO2, ACO3, OHCCH2OH, ORA1, ORA2

Percentage deviations at the end of the simulation time (simulation with vs. simulation without chemical aqueous-phase interaction) are given in brackets (%). However, also more substantial concentration deviations are feasible during the simulation. The percentage deviations have been not given for the third effect type due to the multifaceted temporal concentration pattern deviations

the AqChem run, the concentrations are about 37 % higher for XYL compared to woAqChem run at the end of the simulation. For such trace gases, the most important oxidant in the gas phase is the OH radical. For species with high NO_3 reaction rates such as isoprene (see Fig. S12 in the ESM), the reduced NO_3 budget additionally leads to substantial concentration pattern changes under polluted night-time conditions (type 2 see Table 2). Also, more oxidised compounds such as MACR and HKET reveal influenced concentration levels, which are caused by the reduced degradations of their precursors and their own affected degradation under cloud conditions. Depending on the characteristic chemical sinks and sources of each organic trace gas, both increased and decreased concentrations are modelled (see Table 2).

(ii) Highly water-soluble organics

More complex concentration patterns can be obtained for highly water-soluble compounds, which are soluble enough to be taken up in considerable amounts into the aqueous phase such as ethylene glycol, glyoxal, glycolaldehyde and methylglyoxal (see Fig. S12 in the ESM). For such compounds, the aqueous-phase can act as both a significant sink and source in parallel to the gas phase. Figure 9 shows that during the cloud occurrence their gas-phase concentration is clearly reduced due to the uptake of those species into the cloud droplets. Depending on the solubility and reactivity, the water-soluble compounds are taken up into the droplets to a different degree. For this reason, the concentration behaviour of these compounds can be somewhat different. For ethylene glycol, the chemical interaction with deliquescent particles and droplets leads to decreasing concentrations compared to the woAqChem case. Because of its high Henry solubility, ethylene glycol is transferred efficiently into the aqueous-phase of both wet particles and cloud droplets, and is effectively oxidised there particularly during the high OH daytime conditions (see Tilgner and Herrmann 2010 for further details). The aqueous-phase oxidation can even over-

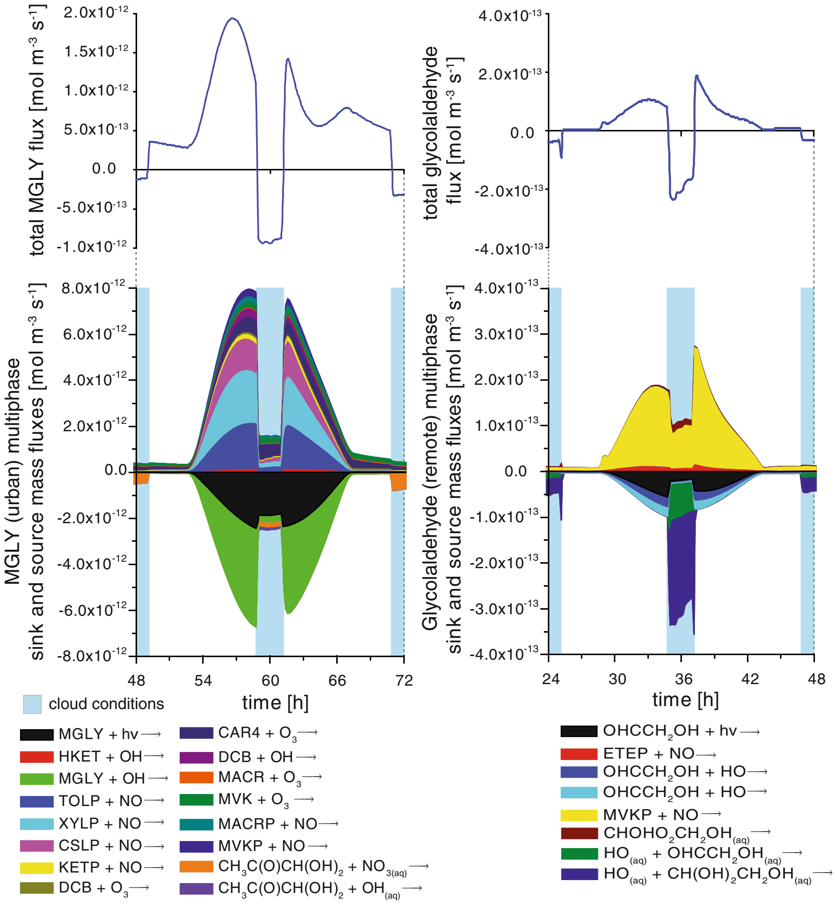

Fig. 9 Modelled multiphase chemical sink and source mass fluxes (mol $m^{-3}_{(air)}$ s^{-1}) of methylglyoxal (MGLY, urban case, left) and glycolaldehyde ($OHCCH_2OH$, remote case, right) for a selected period of the modelling time

compensate the reduced gas-phase oxidation and the coupling of both phases results in a lower concentration of ethylene glycol in the gas phase. A similar behaviour becomes apparent for glycolaldehyde. Figure 9 plots the multiphase sink and source flux analysis for this compound under remote conditions. It can be seen that the in-cloud daytime degradation fluxes are nearly three times larger than the gas-phase formation fluxes and much more important than other gas-phase sinks. Contrary, the behaviour of methylglyoxal (MGLY) is more complex. Besides MGLY itself, its sources in the gas phase are noticeably affected, as can be seen from the sink and source analysis in Fig. 9. Therefore, the concentration profile differences of MGLY result from both the affected precursors and the effects on MGLY in both phases. For MGLY, the aqueous-phase acts both as sink and as a protecting medium. Under cloud conditions, MGLY is transferred into the droplets and is oxidised there effectively, which becomes apparent with the deficit after the cloud evaporation. Additionally to the oxidative effect, the photolysis flux of MGLY in the gas phase is reduced under cloud conditions due to the reduced gas-phase MGLY budget. The less effective gas-phase OH degradation in the cloud is partly compensated by the aqueous-phase oxidations, which contribute to the particulate organic mass production. Smaller aldehydes such as methylglyoxal are present in the aqueous phase in the more reactive hydrated diol form and hence their reactivity can be higher compared to the gas phase. Moreover, it should be noted that further solution phase reactions of importance exist such as photo-reactions and oligomerisation (Kroll and Seinfeld 2008; Hallquist et al. 2009), which should be incorporated into models once the underlying process data are available (see Tilgner and Herrmann 2010 for details).

(iii) Effects on Acetic acid, PAN and denoxification

Besides the species, which are degraded in the aqueous phase, compounds exist which are efficiently produced and subsequently transferred to the gas phase such as acetic acid (see Fig. S12 in the ESM). In the woAqChem cases, the production of acetic acid is significantly underestimated. Under remote conditions, about two thirds of acetic acid are produced in the cloud droplets and largely degassed to the gas phase during cloud evaporation. As Fig. S12 reveals, acetic acid is produced more effectively in the daytime clouds, which is mainly caused by the diurnal concentration profile of the acetic acid precursors and the HO_x radicals. The concentration increase is almost solely related to the aqueous oxidation pathway of the acetylperoxyl radical, which is efficiently transferred into the cloud droplets and into wet particles. Due to the higher acetylperoxyl radical (APR) concentrations under polluted conditions, acetic acid is formed more effectively in urban daytime clouds than in remote clouds. As a result of the reactive APR uptake (Villalta et al. 1996) including the hydrolysis and subsequent acetic acid formation, reduced peroxyl acetyl nitrate (PAN) gas-phase concentrations are modelled for remote and urban conditions (see Fig. S12 in the ESM). The in-cloud APR removal affects its equilibrium with PAN in the interstitial gas phase, so that the PAN budget decreases during the cloud periods. In that way, the NO_y is converted back to NO_x (NO_2) due to the influenced APR/PAN equilibrium. In the field, indirect losses of PAN have been firstly observed by Roberts et al. (1998) during boundary layer fog events. Additionally, uptake studies of Villalta et al. (1996) suggested a significant contribution of the reactive APR uptake to the atmospheric acetic acid and odd hydrogen budget. But in contrast to the gas-phase acid formation pathways (see e.g. Madronich and Calvert 1990), the aqueous-phase pathway does not consume peroxyl radicals (HO_2 and CH_3O_2) and does not lead directly to an ozone formation. In fact, the aqueous oxidation has a positive feedback on the HO_2 multiphase budget as explained in section 3.2.5. Finally, it is noted that similar multiphase effects have also been observed for the propionyl peroxyl radical and its corresponding organic nitrate. Therefore, this effect will need to be considered in future extended mechanisms.

3.5 S(IV) to S(VI) conversion

Various box and higher scale model simulations (see e.g. Warneck 1999; Alexander et al. 2009) have shown that in-cloud oxidation pathways are expected to be preferred because of their higher efficiency leading to the well-known phenomenon of the acid rain formation (Cox and Penkett 1983). Additionally, such studies have modelled aqueous-phase contributions to the total S(IV) oxidation of about 80 %. A major drawback of many model studies is that they usually consider only poor aqueous-phase S(IV) oxidation schemes and often completely neglect interactions with other chemical subsystems. The present model studies have revealed considerable multiphase phase interactions of other chemical subsystems, which are crucial for the sulphur oxidation. Thus, the sulphur processing in the aqueous phase was investigated in the present study with special emphasis on the coupling of the

S(IV) oxidation chemistry with other chemical subsystems and differences between present and former cloud chemistry model results.

Figure S13 in the ESM shows the modelled aqueous-phase sulphur(VI) concentrations as a function of the modelling time for remote and urban atmospheric conditions. From this plot it becomes apparent that the S(VI) formation is predominantly restricted to cloud periods. Turnovers under deliquescent particle conditions are less important due to the restricted uptake of S(IV) into the acidic particles. The concentration profile of the remote scenario clearly differs from the urban concentration patterns. In the remote case, the S(IV) in-cloud oxidation reveals no significant differences between day-and night-time clouds concerning the efficiency of the S(IV) oxidation. On average, about 0.7 $\mu g\ m^{-3}\ h^{-1}$ S(VI) are formed in remote clouds. Contrary, the urban daytime clouds act as source for S(VI) almost three times more effective than their night-time pendants (see Fig. S13). The S(VI) formation averages out to about 5 $\mu g\ m^{-3}\ h^{-1}$ and 1.6 $\mu g\ m^{-3}\ h^{-1}$ in the polluted daytime and night-time clouds, respectively.

Significant differences can also be obtained for the main formation pathways in the two scenarios (see Fig. 10). For remote conditions, H_2O_2 and ozone represent the main oxidants for S(IV) contributing with about 59 % and 36 % to the total S(VI) formation in the aqueous phase. Particularly in the daytime clouds, the ozone pathways are nearly comparable with the H_2O_2 contributions. However, the H_2O_2 oxidation path dominates with about 70 % of the S(IV) oxidation during the night-time cloud episodes. Because of the noon clouds, the OH radical reaction with SO_2 is presumably artificially reduced during its most efficient reaction period.

A different behaviour is found for the polluted model case, where also the NO_y chemistry plays a considerable role for the S(IV) oxidation. The main sources for the S(VI) under polluted conditions are the reactions with H_2O_2 and HNO_4 with contributions to the total formation flux of about 39 % and 42 % , respectively. The simulation results show higher contributions of HNO_4 in the night-time clouds (52 %) because of the much lower H_2O_2 concentrations during urban night-time conditions. Moreover, the model result reveals that organic peroxides are efficient oxidants for S(IV) with about 12 % contribution under night-time cloud conditions.

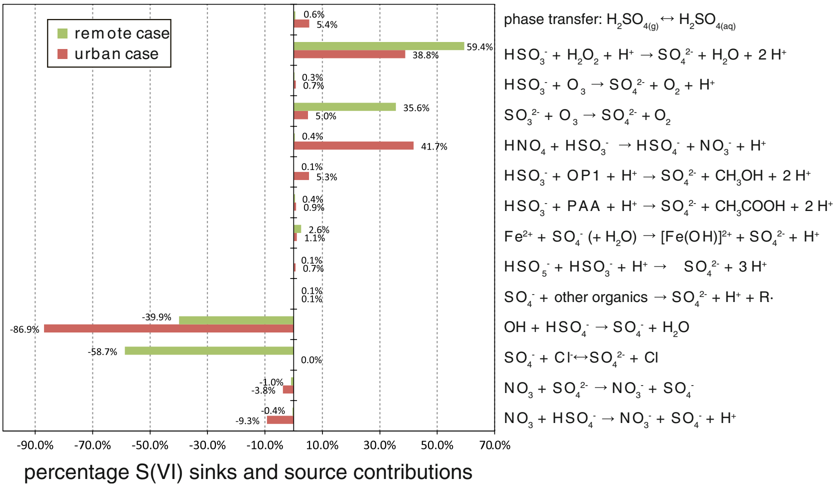

Fig. 10 Relative contributions [%] of chemical sinks and sources to the sulphur(VI) processing in the remote and urban case integrated over the whole simulation time (mean source/sinks fluxes: $6{\cdot}10^{-13}/8{\cdot}10^{-14}$ mol $m^{-3}{}_{(air)}\ s^{-1}$ (remote) and $2{\cdot}10^{-12}/4{\cdot}10^{-14}$ mol $m^{-3}{}_{(air)}\ s^{-1}$ (urban))

Furthermore, the gas-phase contribution of 5 % under urban conditions is somewhat higher compared to the remote conditions. Although, their relevance seems to be underestimated by the model due to the chosen model scenario considering clouds always at noon, the present non-permanent process studies show rather higher contributions of the HNO_4 pathway in the urban case reflecting the more realistic NO_x/NO_y regime in contrast to many permanent cloud chemistry model investigations in the past (e.g. Warneck 1999; Herrmann et al. 2005). The high contributions of the HNO_4 pathway in the urban case confirm model results e.g. of Leriche et al. (2003) and Tilgner et al. (2005), who calculated contributions of about 59 % and up to 30 % for a single cloud events, respectively. However, there are currently no observations in polluted clouds available in order to confirm the model results. However, the HNO_4 findings have to be treated with caution because of the uptake data considered in CAPRAM. The available Henry's Law constants in the literature show a huge variability (see e.g., the compilation of Sander 1999) and the mass accommodation coefficient was estimated in CAPRAM because of missing lab studies. In order to improve the present mechanism and to finally prove the current findings, more laboratory studies are required.

Nevertheless, this result implies that the HNO_4 pathway should be considered in simplified S(IV) oxidations schemes as they are often applied in regional scale chemistry transport models beside the H_2O_2 and O_3 pathways to better predict the S(IV) oxidation in anthropogenically influenced environments. However, it is also noted that H_2O_2 and O_3 pathways will be the main S(IV) oxidants on global scale due to the lower NO_x/NO_y levels.

3.6 Aqueous phase speciation and redox cycling of iron

The most abundant TMI in tropospheric particles is iron, which plays a crucial role in aqueous-phase chemistry of fog and cloud droplets as reviewed by Deguillaume et al. (2005). The redox-cycling of iron is responsible for many chemical interactions such as the HO_x/HO_y processing. However, Deguillaume et al. (2005) showed in their review that still large uncertainties of TMI chemistry including the TMI speciation in the condensed phase exist. Particularly, comparisons between field observations and chemical process model studies exhibit large discrepancies. Even different mechanisms reveal substantial differences (see Deguillaume et al. 2004; Parazols et al. 2006), e.g. in the diurnal in-cloud speciation of iron in its two main tropospheric oxidation states (+II and + III). Accordingly, further investigations of iron speciation and redox-cycling in deliquescent particles and cloud droplets were preformed in the present study. The processing and speciation in deliquescent particles is investigated for the first time by a model. Consequently, no comparisons with literature data were feasible. Moreover, for sake of clarity, just the plots for the urban case are presented here. The corresponding material for the remote case is given in the ESM.

In the present model studies, the iron redox-state is referred to the ratio

$$\delta([Fe(II)]) = \frac{[Fe(II)]}{[Fe(II)] + [Fe(III)]}$$

which represents the quotient of the concentrations of iron in its oxidation state (+II) and the total dissolved iron (+II and + III).

Figure 11 shows the temporal evolution of the percentage contributions of different iron species to the total iron mass under urban conditions. The red line in Fig. 11 illustrates the percentage contribution of Fe(II) species to the total iron aerosol content ($\delta((Fe(II)))$ ratio) throughout the simulation time. The $\delta((Fe(II)))$ ratio shows a characteristic diurnal profile in

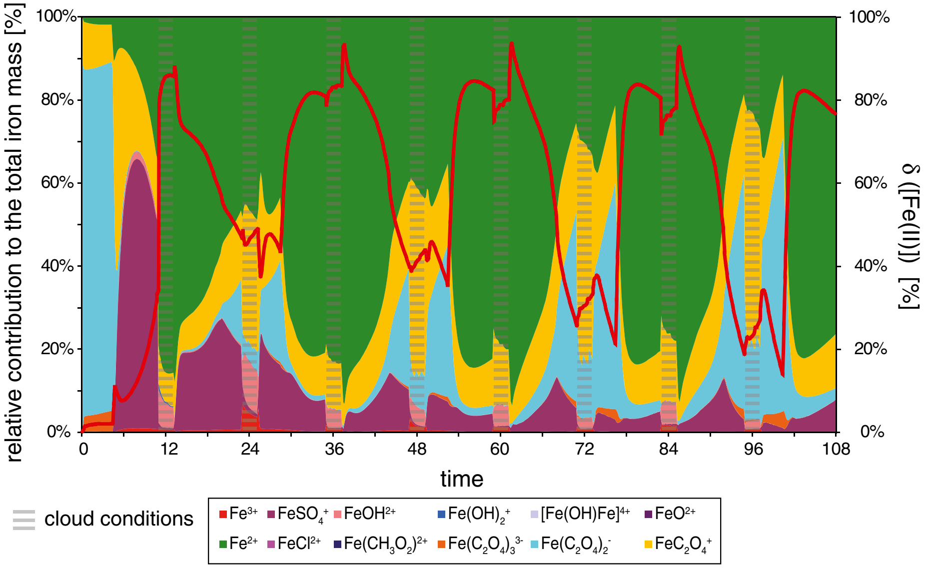

Fig. 11 Temporal evolution of the relative contributions [%] of different iron species to the total iron mass under polluted environmental conditions. The red line shows the percentage contribution of iron(II) species to the total iron aerosol content

both scenarios (see Fig. 11 and Fig. S14 in the ESM). Higher Fe(II) in-cloud concentrations during the day than during the night have been also observed in several field studies (e.g. Behra and Sigg 1990; Erel et al. 1993; Deutsch et al. 2001) including dependencies on e.g. the solar radiation (Behra and Sigg 1990; Kieber et al. 2001; 2003), the oxidant budget (Kieber et al. 2001; Willey et al. 2000) and the presence of organic ligands such as diacids (Erel et al. 1993). The obtained patterns reflect the dynamic time-dependent iron redox-cycling in both cloud droplets and deliquescent particles. The diurnal cycling is more noticeable under urban conditions caused by the more efficient iron processing under high HO_x/HO_y conditions in the particle phase. Consequently, the remote case shows always higher Fe(II) concentrations in clouds than in the aqueous particles. Contrary, differences between cloud and aerosol conditions are relatively small under polluted conditions. At noon (midnight), approximately 80 % (40 %) and 80 % (50 %) of the total soluble iron exists in its oxidation state + II in the urban and remote clouds, respectively. The Fe(II) exists almost completely as Fe^{2+} in clouds and aqueous particles. On the other hand, the Fe(III) fraction consist mainly of Fe(III) oxalate complexes ($[Fe(C_2O_4)]^+$ and $[Fe(C_2O_4)_2]^-$) and the iron-sulphato-complex $[Fe(SO_4)]^+$ in the deliquescent particles under both urban and remote conditions (see Table 3). Moreover, iron-hydroxo-complexes ($[Fe(OH)_2]^+$ and $[FeOH]^{2+}$) on average contribute with 12 % and 46 % to the total Fe(III) budget in urban and remote clouds, respectively. The respective contributions under aqueous particle conditions are negligible due to much lower pH values. However, it is mentioned that the contributions of the iron-oxalato-complexes are presumably underestimated in the present study because of the underpredicted oxalate budget (see Tilgner and Herrmann 2010 for further details). Larger contributions might be possible assuming a higher concentration budget of oxalate caused by additional formation pathways from larger organic compounds not yet considered in the current CAPRAM mechanism. Hence, the contributions of other Fe(III) and Fe(II) compounds are probably overestimated at present.

Table 3 Mean percentage contributions of the main Fe(III) compounds to the total Fe(III) in cloud droplets (CD) and aqueous particles (AP) for the urban and remote case

Species	Urban case		Remote case	
	CD	AP	CD	AP
Fe^{3+}	3.8 %	1.2 %	2.1 %	1.1 %
$FeSO_4^+$	2.4 %	26.2 %	7.2 %	54.7 %
$FeOH^{2+}$	11.9 %	0.4 %	38.2 %	2.8 %
$Fe(OH)_2^+$	0.2 %	0.0 %	8.1 %	0.1 %
$FeCl^{2+}$	0.0 %	0.0 %	0.0 %	0.1 %
$Fe(C_2O_4)^+$	67.9 %	34.1 %	31.2 %	28.3 %
$Fe(C_2O_4)_2^-$	13.6 %	36.8 %	12.9 %	11.6 %
$Fe(C_2O_4)_3^{3-}$	0.1 %	1.3 %	0.2 %	1.4 %

Figure 11 shows that the Fe^{2+} concentration does not decrease close to zero during night compared to other model studies (Ervens et al. 2003; Deguillaume et al. 2004). About 20–50 % of the soluble iron (average: 34 %) is still present as Fe^{2+} depending on model time. This reflects an efficient night-time iron redox cycling in the deliquescent particles and cloud droplets. Previous permanent cloud model studies (Ervens et al. 2003; Deguillaume et al. 2004) have modelled night-time $\delta((Fe(II)))$ ratios of less than 2 % and up to 20 % under urban and remote conditions, respectively. Night-time cloud water measurements of the Fe(II) content (e.g. Behra and Sigg 1990; Erel et al. 1993; Schwanz et al. 1998; Deutsch et al. 2001) have shown rather high values in the range of 20 % and 60 %. Accordingly, the present non-permanent model results seem to be in a better agreement with the observations. In contrast to the above-mentioned observations, recent in-cloud measurements of Parazols et al. (2006) have not shown a diurnal cycle of the Fe(II)/Fe(III) ratio. These authors found no influence of (i) solar radiation intensity, (ii) oxidant concentration levels and (iii) the oxalate concentration on the Fe(II)/Fe(III) ratio, which was nearly constant at 0.75. Their findings were explained with the complexation of the Fe(II) by colloidal organic matter stabilising the reduced iron preventing its further redox cycling. This observed behaviour is currently not reproducible by the present model calculations.

In Fig. 12, the total sinks and sources of Fe(II) in the aqueous phase are plotted vs. a selected time interval of the modelling time (3. day) for polluted conditions. As can be seen from the total fluxes, the redox cycling fluxes show a characteristic daytime profile, which is perturbed by the cloud periods. The total daytime fluxes in the deliquescent particles are about 2 times larger than in daytime clouds. This means that the iron redox cycling is potentially more efficient in the aqueous particles than in clouds under urban conditions. Moreover, Fig. 12 reveals chemical differences in the sink and source reactions between deliquescent aerosol and cloud conditions. This is caused by different pH conditions and the different HO_2/O_2^- budget in the two aqueous environments. The comparison of the total Fe(III) to Fe(II) daytime cloud fluxes (approx. $2.0 \cdot 10^{-12}$ mol m^{-3} s^{-1}) with fluxes of permanent cloud model studies of Deguillaume et al. (2004) (approx. $7.0 \cdot 10^{-12}$ mol m^{-3} s^{-1}) shows the same tendency. However, for the night-time clouds, the modelled fluxes of Deguillaume et al. (2004) are about one order of magnitude lower than in the present model study with approx. $4.0 \cdot 10^{-14}$ mol m^{-3} s^{-1} in this study.

Table S4/S5 show that the most important sources of Fe(III) in the aqueous phase under urban cloud conditions are the reactions of Fe^{2+} with HO_2 and O_2^- with about 37 % and 16 % (1 % and 53 % in the remote case). Interestingly, the Fenton reaction seems to be more important (with about 29 %) under remote conditions than under polluted conditions with about 7 %. Furthermore, reactions of Fe^{2+} with sulphur-containing species (SO_4^-, HSO_5^-) and

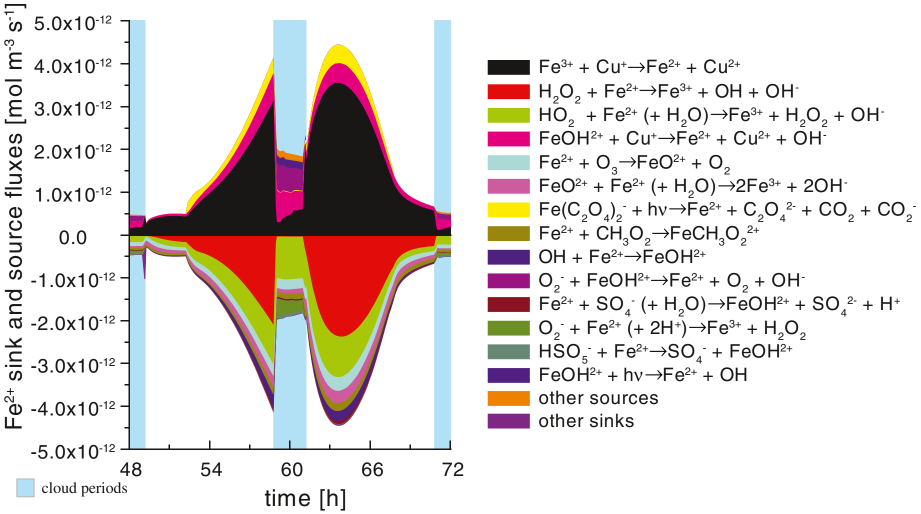

Fig. 12 Depiction of the modelled aqueous-phase chemical sink and source mass fluxes of Fe(II) for a selected period of the modelling time (third day) under urban conditions

reactions of the ferryl ion (FeO^{2+}) with Fe^{2+} and formiate contribute with about 4 %, 9 %, 12 % and 5 % to the in-cloud sources of Fe(III) under polluted conditions. This result is in a good agreement with the permanent cloud model studies of Deguillaume et al. (2004).

In contrast to the cloud conditions, the Fe(III) formation in deliquescent particles is dominated by the Fenton reaction with contributions of about 60 % and 46 % in the remote and urban case, respectively. In the remote case, Fe^{2+} reactions with inorganic radicals such as SO_4^-, OH, Br_2^- and HO_2/O_2^- act with about 11 %, 8 %, 6 % and 4/2 %, respectively, as considerable sources of Fe(III) in the deliquescent particles besides the Fenton reaction. Additional Fe(III) sources are almost exclusively HO_x radical reactions under polluted conditions.

Differences between cloud and particle conditions can also be identified for the sink fluxes (see Table S4 and S5). The Fe(III) in-cloud sinks are dominated by the chemistry of the iron-hydroxo-complexes with contributions of about 95 % and 64 % in the remote and urban case, respectively. In contrast, the reaction of Fe^{3+} with Cu^+ contributes by about 39 % (remote) and 75 % (urban) significantly to the Fe(III) sinks under deliquescent particle conditions. This result differs slightly from the former permanent cloud model studies (see e.g. Deguillaume et al. 2004). These authors calculated much higher photochemical contributions and fewer contributions from the HO_x chemistry, which dominates in remote clouds. This difference reflects the changes in the HO_x budget performing a non-permanent cloud modelling.

Moreover, Table S4 shows that the photolytic reduction of the iron-monohydroxo-complex and iron-dioxalato-complex are an effective Fe(III) sink under cloud conditions and deliquescent particle conditions, respectively. The opposite behaviour of these compounds to photoreactive Fe(III) complexes can be explained with the pH variation (low pH values in the aqueous particles leads to small iron-hydroxo-complex concentrations) and the availability of oxalate, which has higher formation fluxes in the deliquescent particles. The photolytic decay of the iron-di-oxalato-complex in clouds is also noticeable in the iron speciation (see Fig. 12). While the iron-monooxalato-complex do not show a noticeable in-cloud reduction, the iron-dioxalato-complex concentration is substantially decreased. This reduction results from the decreased in-cloud formation flux of oxalate. The different behaviour of the mono and dioxalato-complex is caused by the missing photolysis of the monooxalato-complex $[Fe(C_2O_4)]^+$, which is currently unknown. However, future mechanisms might consider the photo-reduction of the monooxalato-complex $[Fe(C_2O_4)]^+$. Overall, the present study has shown that the water-soluble iron in tropospheric particles is a crucial parameter for a number of chemical subsystems. Therefore, additional sensitivity studies with different available water-soluble iron contents have been performed to study the effects in more detail. The simulation results are presented for the sake of clarity in the ESM.

4 Conclusions

Multiphase chemical processes of tropospheric aerosol constituents, e.g. in clouds and deliquescent particles, as well as their feedback on the gas phase are understood to a much smaller amount than pure gas-phase processes. The present study intended to clarify important chemical aerosol-cloud interaction processes focusing on the multiphase chemistry of oxidants and organic trace gases, the aqueous-phase TMI redox-cycling, and other related inorganic chemical subsystems, using comprehensive time-resolved reaction flux analyses. The present work was performed with parcel model SPACCIM and the up-to-date chemical aqueous-phase mechanism CAPRAM 3.0i. Simulations were carried out for different tropospheric conditions using a more realistic non-permanent cloud model scenario with smaller droplet lifetimes compared to many former permanent cloud chemistry model studies. The performed model studies and subsequent detailed chemical flux analyses showed that:

(1) Multiphase chemical interactions can considerably affect the radical oxidants budget under both cloud and deliquescent particle conditions. Gas phase concentrations of radicals such as OH, NO_3 and HO_2 are significantly reduced under cloud condition, which shows the same tendency than the few available in-cloud radical measurements. The model studies have calculated e.g. OH gas-phase concentration reductions of about 90 % and 75 % under urban and remote cloud conditions, respectively. Moreover, e.g. OH oxidation reaction fluxes in the interstitial gas phase of urban clouds are about 6 times lower compared to cloudless conditions indicating drastically reduced gas-phase oxidation processes.

(2) Mostly functionalised organic compounds such as dicarbonyls are important sinks for OH under cloud conditions. In particular, the in-cloud oxidations of methylglyoxal and 1,4-butenedial have been identified as important OH radical sinks under polluted environmental conditions. In total, the C_3 and C_4 organic chemistry contribute with about 38 %/ 48 % and 8 %/ 9 % significantly to the urban and remote cloud / deliquescent particle OH sinks.

(3) Deliquescent particles might act as an important reactive chemical medium within the troposphere due to an efficient TMI/$HO_{x,y}$ chemical processing including e.g. an effective aqueous-phase in-situ formation of OH radicals. The model results implicate that the in-situ OH production under wet aerosol particle conditions strongly depends on the H_2O_2 and the TMI concentration. Thus, entrainment and detrainment areas of tropospheric clouds (so-called "twilight zones") as well as air masses with high relative humidity conditions might represent quite reactive environments for aqueous chemical processing in addition to tropospheric clouds.

(4) Under urban and remote in-cloud conditions, oxidations of methylglyoxal and its oxidation products can be efficient sinks of the NO_3 with relative contributions of about 84 % and 51 %, respectively. Performed comparisons on the importance of OH and NO_3

reactions of organics revealed that for some organic compounds the NO_3 radical oxidation can be more important than the corresponding OH pendant. This result differs from results of former permanent cloud chemistry modelling. Comparisons have revealed that the relevance of the NO_3 radical for tropospheric oxidations in the aqueous phase appears to be substantially under-determined using permanent cloud chemistry model conditions due to the almost permanent loss of gaseous NO_y in those former studies. Moreover, the studies have found that the importance of the NO_3 radical oxidations increases with the functionalisation of the organic compounds, i.e. the chemical aging of the organic aerosol constituents.

(5) Effective multiphase chemical interactions of HO_2 with both deliquescent particles and clouds can considerably reduce the gaseous HO_x budget. The modelled diurnal HO_2 gas-phase concentration patterns including the HO_2 gas-phase removal by aqueous particles are in a good agreement with recent literature data. However, the presently modelled reductions of about 10 % are less substantial than reductions of other model investigations. The reaction flux analyses have revealed that aqueous-phase oxidations of organics such as glyoxalic acid might play an important role for the aqueous HO_2 budget. The organic chemistry contributes with approximately 50 % significantly to the aqueous-phase budget of HO_2, which consequentially leads to a buffering of the HO_2 gas-phase removal. Hence, current higher scale models with a more simplified chemistry presumably overestimate the gaseous HO_2 removal.

(6) Non-radical oxidants such as H_2O_2 and ozone can be significantly influenced by aqueous processes in clouds and deliquescent particles. The non-permanent cloud model studies demonstrated that remote daytime clouds could potentially act as a considerable source for the multiphase H_2O_2 budget under SO_2 limited background conditions due to an effective TMI chemistry. The present simulations have shown that the gaseous H_2O_2 concentrations can be more than 2 times higher after the cloud evaporation (+ 0.5 ppb per remote daytime cloud). This model result confirmed laboratory investigations, which expected an effective generation of H_2O_2 in daytime clouds and consequentially a feedback on the H_2O_2 gaseous budget. However, the evidence in the field is currently still missing. The model studies on non-radical oxidants implicate that, concentrations of H_2O_2 and ozone are probably over- or underestimated without a description of the multiphase TMI/$HO_{x,y}$ chemistry. The latter can cause, e.g. a less adequate representation e.g. of the sulphur oxidation in simplified atmospheric air pollution models.

(7) Without consideration of aqueous-phase chemical processes, organic trace gas concentrations can be significantly under- or overestimated by pure gas-phase chemistry models, which are usually used in 3-D CTMs. Due to chemical cloud interactions and e.g. the correspondingly reduced gas-phase oxidant concentrations, the tropospheric residence time of less soluble organic trace gases could increase by about 30 %. On the other hand, it was shown that for highly water-soluble compounds the chemical aqueous-phase interactions are partly able to compensate the reduced gas-phase oxidations. Additionally, the present studies demonstrate the potential importance of the reactive acetylperoxyl radical uptake for acetic acid formation and the odd hydrogen budget without consuming aqueous-phase inorganic radicals. This oxidation pathway contributed with about two-thirds more effectively to the multiphase acetic acid formation under remote conditions than gas-phase oxidations.

(8) Interestingly, the reactive uptake of the acetylperoxyl radical including the hydrolysis and subsequent oxidation leads to a perturbation of the gaseous PAN concentration. The effective in-cloud uptake of the acetylperoxyl radical perturbs its equilibrium with peroxyl acetyl nitrate leading to NO_2 recycling from NO_y. This modelled process is an important finding as it confirms, for the first time, field observations. Moreover, the present study

has shown that the chemical cloud interaction of acetylperoxyl radical including its the aqueous oxidation has also a positive feedback on the HO_2 multiphase budget. Overall, the present study has revealed the need to consider similar multiphase effects of other the organic peroxyl radicals and its corresponding organic nitrates in future mechanisms.

(9) Considerable chemical differences exist between the iron redox-cycling in deliquescent particles and cloud droplets. The present study has investigated the redox-cycling of iron in deliquescent particles for the first time and revealed a circa 2 times more efficient daytime iron processing in the deliquescent particle phase. Performed comparisons of the redox states with available cloud water measurements revealed both reasonable agreements and differences. But, the present model studies have better reproduced observed redox states of soluble iron in clouds than former permanent cloud model studies particularly under night-time conditions. Nevertheless, it is noted that a precise modelling of the iron speciation and comparison with field data is still rather complicated and needs further laboratory and field investigations and subsequent aqueous-phase mechanism enhancements.

(10) Differences exist between the present results and those of former permanent cloud model studies. The model studies pointed out that e.g. that the relevance $NO_{x,y}$ chemistry seems to be artificially underestimated by permanent cloud studies with very long droplets lifetimes. This differences lead to changes in the modelled S(VI) formation characteristics. The present non-permanent cloud model studies have revealed that under urban conditions the S(IV) oxidation by HNO_4 contributes with about 41 % more significantly to the S(VI) formation than in former permanent cloud simulations.

Overall, the model studies have implicated close multiphase interactions of different chemical subsystems. Due to these strong interactions, a decoupled treatment of single chemical subsystems such as the S(IV) to S(VI) conversion in other models appears to be less adequate. In conclusion, the present non-permanent cloud model studies provide a deeper insight into the chemical multiphase processing in cloud droplets and deliquescent particles, the latter for the first time. From the SPACCIM model studies including detailed reaction flux investigations, it can be concluded that chemical aerosol cloud interactions can have a major impact on the multiphase photochemistry and hence the tropospheric composition as well as many related issues. To this end, aqueous-phase processes necessarily need to be considered in future higher scale chemistry transport models using condensed mechanisms (see Deguillaume et al. 2009).

Finally, it is noted that, according to the performed simplifications in the current model investigations and the restricted number of simulations for just a few environmental conditions, the present study outlines the requirement for further advanced model, field and laboratory investigations in the future to gain a better understanding of unresolved issues of multiphase aerosol cloud processes for a broader range of tropospheric environments.

References

Acker, K., Wieprecht, W., Moller, D., Mauersberger, G., Naumann, S., Oestreich, A.: Evidence of ozone destruction in clouds. Naturwissenschaften **82**(2), 86–89 (1995)

Adriano, D.C., Johnson, A.H.: Acidic Precipitation. Biological and ecological effects, vol. 2. Springer, New York (1989)

Alexander, B., Park, R.J., Jacob, D.J., Gong, S.L.: Transition metal-catalyzed oxidation of atmospheric sulfur: global implications for the sulfur budget. J Geophys Res-Atmos. **114** (2009)

Anastasio, C., Faust, B.C., Allen, J.M.: Aqueous phase photochemical formation of hydrogen peroxide in authentic cloud waters. J Geophys Res **99**(D4), 8231–8248 (1994)

Arakaki, T., Kuroki, Y., Okada, K., Nakama, Y., Ikota, H., Kinjo, M., Higuchi, T., Uehara, M., Tanahara, A.: Chemical composition and photochemical formation of hydroxyl radicals in aqueous extracts of aerosol particles collected in Okinawa. Japan. Atmos Environ **40**(25), 4764–4774 (2006)

Arellanes, C., Paulson, S.E., Fine, P.M., Sioutas, C.: Exceeding of Henry's Law by hydrogen peroxide associated with urban aerosols. Environ Sci Technol **40**(16), 4859–4866 (2006)

Barth, M.C.: The importance of cloud drop representation on cloud photochemistry. Atmos Res **82**(1–2), 294–309 (2006)

Behra, P., Sigg, L.: Evidence for redox cycling of iron in atmospheric water droplets. Nature **344**(6265), 419–421 (1990)

Bräuer, P., Tilgner, A., Wolke, R., Herrmann, H.: Mechanism development and modelling of tropospheric multiphase halogen chemistry: the CAPRAM Halogen Module 2.0 (HM2). J Atmos Chem **70**(1), 19–52 (2013)

Brunekreef, B., Holgate, S.T.: Air pollution and health. Lancet **360**(9341), 1233–1242 (2002)

Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley, J.A., Hansen, J.E., Hofmann, D.J.: Climate forcing by anthropogenic aerosols. Science **255**(5043), 423–430 (1992)

Clegg, S.L., Seinfeld, J.H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. I. The acids as non-dissociating components. J Phys Chem A **110**, 5692–5717 (2006)

Collett, J.L., Bator, A., Rao, X., Demoz, B.B.: Acidity variations across the cloud drop size spectrum and their influence on rates of atmospheric sulfate production. Geophys Res Lett **21**, 2393–2396 (1994)

Commane, R., Floquet, C.F.A., Ingham, T., Stone, D., Evans, M.J., Heard, D.E.: Observations of OH and HO2 radicals over West Africa. Atmos Chem Phys **10**(18), 8783–8801 (2010)

Cox, R.A., Penkett, S.A.: Formation of atmospheric acidity. In: Beilke, S., Elshout, A.J. (eds.) Acid Deposition, pp. 56–81. Springer, Netherlands (1983)

Deguillaume, L., Tilgner, A., Schrödner, R., Wolke, R., Chaumerliac, N., 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), 1–35 (2009)

Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., Chaumerliac, N.: Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters. Chem Rev **105**(9), 3388–3431 (2005)

Deguillaume, L., Leriche, M., Monod, A., Chaumerliac, N.: The role of transition metal ions on HOx radicals in clouds: a numerical evaluation of its impact on multiphase chemistry. Atmos Chem Phys **4**, 95–110 (2004)

Deutsch, F., Hoffmann, P., Ortner, H.M.: Field experimental investigations on the Fe(II)- and Fe(III)-content in cloudwater samples. J Atmos Chem **40**(1), 87–105 (2001)

Erel, Y., Pehkonen, S.O., Hoffmann, M.R.: Redox chemistry of iron in Fog and stratus clouds. J Geophys Res-Atmos **98**(D10), 18423–18434 (1993)

Ervens, B., Carlton, A.G., Turpin, B.J., Altieri, K.E., Kreidenweis, S.M., Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products. Geophys Res Lett. **35**(2), (2008)

Ervens, B., George, C., Williams, J.E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): an extended and condensed tropospheric aqueous phase mechanism and its application. J Geophys Res Atmos. **108**(D14), (2003)

Finlayson-Pitts, B.J., Pitts, J.N.: Chemistry of the upper and lower atmosphere. (2000)

Frost, G.J., Trainer, M., Mauldin, R.L., Eisele, F.L., Prevot, A.S.H., Flocke, S.J., Madronich, S., Kok, G., Schillawski, R.D., Baumgardner, D., Bradshaw, J.: Photochemical modeling of OH levels during the first aerosol characterization experiment (ACE 1). J Geophys Res-Atmos **104**(D13), 16041–16052 (1999)

Geyer, A., Ackermann, R., Dubois, R., Lohrmann, B., Müller, T., Platt, U.: Long-term observation of nitrate radicals in the continental boundary layer near Berlin. Atmos Environ **35**(21), 3619–3631 (2001). doi:10.1016/S1352-2310(00)00549-5

Gong, W.M., Dastoor, A.P., Bouchet, V.S., Gong, S.L., Makar, P.A., Moran, M.D., Pabla, B., Menard, S., Crevier, L.P., Cousineau, S., Venkatesh, S.: Cloud processing of gases and aerosols in a regional air quality model (AURAMS). Atmos Res **82**(1–2), 248–275 (2006)

Grègoire, P.J., Chaumerliac, N.: Impact of cloud dynamics on tropospheric chemistry: advances in modeling the interactions between microphysical and chemical processes. J Atmos Chem **18**, 247–266 (1994)

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmos Chem Phys **9**(14), 5155–5236 (2009)

Healy, R.M., Wenger, J.C., Metzger, A., Duplissy, J., Kalberer, M., Dommen, J.: Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene. Atmos Chem Phys **8**, 3215–3230 (2008). doi:10.5194/acp-8-3215-2008

Herrmann, H., Hoffmann, D., Schaefer, T., Bräuer, P., Tilgner, A.: Tropospheric aqueous-phase free-radical chemistry: radical sources, spectra, reaction kinetics and prediction tools. Chem Phys Chem **11**, 3796–3822 (2010). doi:10.1002/cphc.201000533

Herrmann, H.: Kinetics of aqueous phase reactions relevant for atmospheric chemistry. Chem Rev **103**(12), 4691–4716 (2003)

Herrmann, H., Ervens, B., Jacobi, H.W., Wolke, R., Nowacki, P., Zellner, R.: CAPRAM2.3: a chemical aqueous phase radical mechanism for tropospheric chemistry. J Atmos Chem **36**(3), 231–284 (2000)

Herrmann, H., Tilgner, A., Barzaghi, P., Majdik, Z., Gligorovski, S., Poulain, L., Monod, A.: Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0. Atmos Environ **39**(23–24), 4351–4363 (2005)

Holgate, S.T.: The epidemic of allergy and asthma. Nature **402**(6760), B2–B4 (1999)

Jacob, D.J.: Chemistry of Oh in remote clouds and its role in the production of formic-acid and peroxymonosulfate. J Geophys Res-Atmos **91**(D9), 9807–9826 (1986)

Jacob, D.J.: Heterogeneous chemistry and tropospheric ozone. Atmos Environ **34**(12–14), 2131–2159 (2000)

Keene, W.C., Pszenny, A.A.P.: Comment on “Reactions at interfaces as a source of sulfate formation in sea-salt particles” (I). Science. **303**(5658), (2004)

Kieber, R.J., Hardison, D.R., Whitehead, R.F., Willey, J.D.: Photochemical production of Fe(II) in rainwater. Environ Sci Technol **37**(20), 4610–4616 (2003)

Kieber, R.J., Williams, K., Willey, J.D., Skrabal, S., Avery, G.B.: Iron speciation in coastal rainwater: concentration and deposition to seawater. Mar Chem **73**(2), 83–95 (2001)

Koren, I., Remer, L.A., Kaufman, Y.J., Rudich, Y., Martins, J.V.: On the twilight zone between clouds and aerosols. Geophys Res Lett. **34**(8), (2007)

Kreidenweis, S.M., Walcek, C.J., Feingold, G., Gong, W.M., Jacobson, M.Z., Kim, C.H., Liu, X.H., Penner, J.E., Nenes, A., Seinfeld, J.H.: Modification of aerosol mass and size distribution due to aqueous-phase SO2 oxidation in clouds: Comparisons of several models. J Geophys Res-Atmos. **108**(D7), (2003)

Kroll, J.H., Seinfeld, J.H.: Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere. Atmos Environ **42**(16), 3593–3624 (2008)

Lelieveld, J., Crutzen, P.J.: Influences of cloud photochemical processes on tropospheric ozone. Nature **343**(6255), 227–233 (1990)

Lelieveld, J., Crutzen, P.J.: The role of clouds in tropospheric photochemistry. J Atmos Chem **12**(3), 229–267 (1991)

Leriche, M., Curier, R.L., Deguillaume, L., Caro, D., Sellegri, K., Chaumerliac, N.: Numerical quantification of sources and phase partitioning of chemical species in cloud: application to wintertime anthropogenic air masses at the Puy de Dome station. J Atmos Chem **57**(3), 281–297 (2007). doi:10.1007/s10874-007-9073-y

Leriche, M., Deguillaume, L., Chaumerliac, N.: Modeling study of strong acids formation and partitioning in a polluted cloud during wintertime. J Geophys Res-Atmos. **108**(D19), (2003).

Leriche, M., Voisin, D., Chaumerliac, N., Monod, A., Aumont, B.: A model for tropospheric multiphase chemistry: application to one cloudy event during the CIME experiment. Atmos Environ **34**(29–30), 5015–5036 (2000)

Li, S.M., Macdonald, A.M., Strapp, J.W., Lee, Y.N., Zhou, X.L.: Chemical and physical characterizations of atmospheric aerosols over southern California. J Geophys Res-Atmos **102**(D17), 21341–21353 (1997)

Liang, J.Y., Jacob, D.J.: Effect of aqueous phase cloud chemistry on tropospheric ozone. J Geophys Res-Atmos **102**(D5), 5993–6001 (1997)

Liu, X.H., Mauersberger, G., Moller, D.: The effects of cloud processes on the tropospheric photochemistry: an improvement of the EURAD model with a coupled gaseous and aqueous chemical mechanism. Atmos Environ **31**(19), 3119–3135 (1997)

Lohmann, U., Feichter, J.: Global indirect aerosol effects: a review. Atmos Chem Phys **5**, 715–737 (2005)

Madronich, S., Calvert, J.G.: Permutation reactions of organic peroxy-radicals in the troposphere. J Geophys Res-Atmos **95**(D5), 5697–5715 (1990)

Madronich, S., Flocke, S.: The role of solar radiation in atmospheric chemistry. In: Boule, P. (ed.) Handbook of Environmental Chemistry, pp. 1–26. Springer, New York (1999)

Mao, J., Fan, S., Jacob, D.J., Travis, K.R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols. Atmos Chem Phys **13**, 509–519 (2013)

Marinoni, A., Parazols, M., Brigante, M., Deguillaume, L., Amato, P., Delort, A.-M., Laj, P., Mailhot, G.: Hydrogen peroxide in natural cloud water: Sources and photoreactivity. Atmos Res **101**, 256–263 (2011)

Mauldin, R.L., Madronich, S., Flocke, S.J., Eisele, F.L., Frost, G.J., Prevot, A.S.H.: New insights on OH: measurements around and in clouds. Geophys Res Lett **24**(23), 3033–3036 (1997)

Monod, A., Carlier, P.: Impact of clouds on the tropospheric ozone budget: direct effect of multiphase photochemistry of soluble organic compounds. Atmos Environ **33**(27), 4431–4446 (1999)

Moore, K.F., Sherman, D.E., Reilly, J.E., Collett, J.L.: Drop size-dependent chemical composition in clouds and fogs. Part I. Observations. Atmos Environ **38**, 1389–1402 (2004)

Morita, A., Kanaya, Y., Francisco, J.S.: Uptake of the HO2 radical by water: molecular dynamics calculations and their implications for atmospheric modeling. J Geophys Res-Atmos. **109**(D9), (2004)

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study. Atmos Chem Phys **11**, 5761–5782 (2011)

Parazols, M., Marinoni, A., Amato, P., Abida, O., Laj, P., Mailhot, G.: Speciation and role of iron in cloud droplets at the puy de Dome station. J Atmos Chem **54**(3), 267–281 (2006)

Pruppacher, H.R., Jaenicke, R.: The processing of water-vapor and aerosols by atmospheric clouds, a global estimate. Atmos Res **38**(1–4), 283–295 (1995)

Pszenny, A.A.P., Moldanov, J., Keene, W.C., Sander, R., Maben, J.R., Martinez, M., Crutzen, P.J., Perner, D., Prinn, R.G.: Halogen cycling and aerosol pH in the Hawaiian marine boundary layer. Atmos Chem Phys **4**, 147–168 (2004)

Ravishankara, A.R.: Heterogeneous and multiphase chemistry in the troposphere. Science **276**(5315), 1058–1065 (1997)

Roberts, J.M., Williams, J., Baumann, K., Buhr, M.P., Goldan, P.D., Holloway, J., Hubler, G., Kuster, W.C., McKeen, S.A., Ryerson, T.B., Trainer, M., Williams, E.J., Fehsenfeld, F.C., Bertman, S.B., Nouaime, G., Seaver, C., Grodzinsky, G., Rodgers, M., Young, V.L.: Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: implications for regional ozone production from biogenic hydrocarbons. J Geophys Res-Atmos **103**(D17), 22473–22490 (1998)

Rosenfeld, D.: TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall. Geophys Res Lett **26**, 3105–3108 (1999)

Rosenfeld, D.: Suppression of rain and snow by urban and industrial air pollution. Science **287**, 1793–1796 (2000)

Sander, R.: Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry (Version 3). http://www.henrys-law.org (1999).

Saxena, P., Hildemann, L.M.: Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. J Atmos Chem **24**(1), 57–109 (1996)

Schwanz, M., Warneck, P., Preiss, M., Hoffmann, P.: Chemical speciation of Iron in fog water. Contrib Atmos Phys **71**(1), 131–143 (1998)

Schwartz, S.: Mass transport considerations pertinent to aqueous phase reactions of gases in liquid water clouds. In: Jaeschke, W. (ed.) Chemistry of Multiphase Atmospheric Systems, NATO ASI Series, pp. 415–471. Springer, Berlin (1986)

Sehili, A.M., Wolke, R., Knoth, O., Simmel, M., Tilgner, A., Herrmann, H.: Comparison of different model approaches for the simulation of multiphase processes. Atmos Environ **39**(23–24), 4403–4417 (2005)

Shen, H., Anastasio, C.: Formation of hydroxyl radical from San Joaquin Valley particles extracted in a cell-free surrogate lung fluid. Atmos Chem Phys **11**, 9671–9682 (2011). doi:10.5194/acp-11-9671-2011

Simmel, M., Wurzler, S.: Condensation and activation in sectional cloud microphysical models. Atmos Res **80**(2–3), 218–236 (2006)

Simmel, M., Diehl, K., Wurzler, S.: Numerical simulation of the microphysics of an orographic cloud: comparison with measurements and sensitivity studies. Atmos Environ **39**, 4365–4373 (2005)

Stelson, A.W., Seinfeld, J.H.: Chemical mass accounting of urban aerosol. Environ Sci Technol **15**(6), 671–679 (1981)

Taketani, F., Kanaya, Y., Akimoto, H.: Kinetics of heterogeneous reactions of HO2 radical at ambient concentration levels with (NH4)(2)SO4 and NaCl aerosol particles. J Phys Chem A **112**(11), 2370–2377 (2008)

Taketani, F., Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Okuzawa, K., Kawamura, K., Wang, Z., Akimoto, H.: Measurement of overall uptake coefficients for HO2 radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China). Atmos Chem Phys **12**, 11907–11916 (2012)

Thornton, J.A., Jaegle, L., McNeill, V.F.: Assessing known pathways for HO2 loss in aqueous atmospheric aerosols: regional and global impacts on tropospheric oxidants. J Geophys Res. **113**(D5), (2008)

Tie, X.X., Madronich, S., Walters, S., Zhang, R.Y., Rasch, P., Collins, W.: Effect of clouds on photolysis and oxidants in the troposphere. J Geophys Res. **108**(D20), (2003)

Tilgner, A., Herrmann, H.: Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM. Atmos Environ **44**, 5415–5422 (2010)

Tilgner, A., Majdik, Z., Sehili, A.M., Simmel, M., Wolke, R., Herrmann, H.: SPACCIM: simulations of the multiphase chemistry occurring in the FEBUKO hill cap cloud experiments. Atmos Environ **39**(23–24), 4389–4401 (2005)

Villalta, P.W., Lovejoy, E.R., Hanson, D.R.: Reaction probability of peroxyacetyl radical on aqueous surfaces. Geophys Res Lett **23**(14), 1765–1768 (1996)

Vrekoussis, M., Mihalopoulos, N., Gerasopoulos, E., Kanakidou, M., Crutzen, P.J., Lelieveld, J.: Two-years of NO3 radical observations in the boundary layer over the Eastern Mediterranean. Atmos Chem Phys **7**(2), 315–327 (2007). doi:10.5194/acp-7-315-2007

von Glasow, R., Crutzen, P.J.: Tropospheric halogen chemistry. In: Heinrich, D.H., Turekian, K.K. (eds.) Treatise on Geochemistry, pp. 1–67. Pergamon, Oxford (2007)

Walcek, C.J., Yuan, H.H., Stockwell, W.R.: The influence of aqueous-phase chemical reactions on ozone formation in polluted and nonpolluted clouds. Atmos Environ **31**(8), 1221–1237 (1997)

Wang, Y., Arellanes, C., Curtis, D.B., Paulson, S.E.: Probing the source of hydrogen peroxide associated with coarse mode aerosol particles in Southern California. Environ Sci Technol **44**(11), 4070–4075 (2010)

Warneck, P.: The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. Phys Chem Chem Phys **1**(24), 5471–5483 (1999)

Williams, J.E., Dentener, F.J., van den Berg, A.R.: The influence of cloud chemistry on HO_x and NO_x in the moderately polluted marine boundary layer: a 1-D modelling study. Atmos Chem Phys **2**, 39–54 (2002)

Willey, J.D., Kieber, R.J., Williams, K.H., Crozier, J.S., Skrabal, S.A., Avery, G.B.: Temporal variability of iron speciation in coastal rainwater. J Atmos Chem **37**(2), 185–205 (2000)

Wolke, R., Sehili, A.M., Simmel, M., Knoth, O., Tilgner, A., Herrmann, H.: SPACCIM: A parcel model with detailed microphysics and complex multiphase chemistry. Atmos Environ **39**(23–24), 4375–4388 (2005)

Yao, X., Ling, T.Y., Fang, M., Chan, C.K.: Size dependence of in situ pH in submicron atmospheric particles in Hong Kong. Atmos Environ **41**(2), 382–393 (2007)

Zaveri, R.A., Easter, R.C., Wexler, A.S.: A new method for multicomponent activity coefficients of electrolytes in aqueous atmospheric aerosols. J Geophys Res **110**, D02201 (2005)

Zuend, A., Marcolli, C., Luo, B.P., Peter, T.: A thermodynamic model of mixed organic–inorganic aerosols to predict activity coefficients. Atmos Chem Phys **8**, 4559–4593 (2008)

Zuo, Y.G., Holgne, J.: Formation of hydrogen-peroxide and depletion of oxalic-acid in atmospheric water by photolysis of iron(III) oxalato complexes. Environ Sci Technol **26**(5), 1014–1022 (1992)