CAPRAM MODELLING OF THE PHYSICO-CHEMICAL CLOUD PROCESSING OF TROPOSPHERIC AEROSOLS

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ABSTRACT Clouds and deliquescent particles are a complex multiphase and multicomponent environment with simultaneously occurring gas and aqueous phase as well as heterogeneous chemical transformations which potentially alter the physico-chemical composition of tropospheric aerosols. Moreover, chemical cloud interactions contribute significantly to the physico-chemical aerosol processing together with significant effects on the whole multiphase oxidation budget. In order to improve the still limited understanding of the cloud chemistry processing, detailed model studies using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM) have been performed.

The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model. In chemistry model, the multiphase mechanism RACM-MIM2ext/ CAPRAM 3.0i with about 1100 processes was applied incorporating a detailed description of the tropospheric multiphase processes. Simulations were carried out for different environmental conditions using a non-permanent meteorological scenario. Furthermore, simulations were performed with and without aqueous phase chemistry to study the effects of aerosol-cloud interaction. The model results have been analysed including time-resolved source and sinks studies particularly focused on multiphase phase radical as well as non-radical oxidants and multiphase oxidations of C_2–C_4 organic compounds.

The model studies shows significant effects of multiphase cloud droplet and aqueous aerosol interactions on the tropospheric oxidation budget for polluted and remote environmental conditions as well as influenced VOC's oxidation due to the changed oxidation budget within the clouds. Furthermore, the simulations implicate the potential role of deliquescent particles to act as a reactive chemical medium due to the in-situ aqueous phase oxidant productions. Moreover, the model study shows the importance of the aqueous phase for the formation of higher oxidised organic compounds such as substituted mono- and diacids. In particular, the aqueous phase oxidations of methylglyoxal and 1,4-butenedial were newly identified as important OH radical sinks under polluted environmental conditions contributing to the production of less volatile organic compounds and thus the organic aerosol particle mass. Furthermore, the in-cloud oxidation of methylglyoxal and its oxidation products represents an efficient sink for NO_3 radicals in the aqueous phase. Additionally, the model studies have shown in-cloud organic mass productions up to about 1 µg m^{-3} preferably under polluted day time cloud conditions mainly due to OH initiated multiphase oxidation processes. Finally, the sum of the results implicates the importance of the aqueous phase processes to be considered in future higher scale multiphase chemistry transport models. Consequently, also a reduced CAPRAM mechanism describing the main inorganic and organic aqueous phase chemistry issues have been developed.

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1 INTRODUCTION

Clouds and deliquescent particles play a crucial role in the entire tropospheric multiphase system. Tropospheric clouds fill about 15% of the lower half of the troposphere [Pruppacher and Jaenicke, 1995] and are a complex multiphase and multi-component environment with simultaneously occurring gas and aqueous phase as well as heterogeneous chemical proceses. Even if the volume of clouds is relative small, multiphase processes can potentially alter the physico-chemical composition of the tropospheric aerosol on global scale [Ravishankara, 1997]. Moreover, chemical aqueous phase interactions contribute significantly to the physico-chemical aerosol processing together with effects on the whole multiphase oxidation budget.

Chemical aqueous phase components of deliquescent particles and cloud droplets are originated from the soluble fraction of the aerosol particles which can act also as cloud condensation nuclei (CCN) and from the dissolution of soluble trace gases as well as from scavenging processes. The multiphase processing of chemical components in the aqueous phase can influence both the chemical composition of the aerosol and the physical particle properties such as solubility, size and mass distribution. However, the understanding of physico-chemical modifications of the aerosol properties is currently still restricted chiefly because of the high complexity of multiphase interactions. While significant amount of work has been done regarding the in-cloud chemistry of inorganic species such as sulphur [Warneck, 1999], the aqueous phase chemistry of organic aqueous phase constituents and their oxidative effects are investigated to a much smaller extend.

In order to enhance the understanding of the system, a proper knowledge and description of both microphysical and multiphase chemistry processes are therefore crucial to appraise the role of the tropospheric aerosol processing. In this context, tropospheric multiphase models provide a very convenient instrument for investigating individual physico-chemical processes in detail. Consequently, models can help to improve the understanding of the aerosol cloud processing and to assess the relevance of tropospheric chemistry processes in a multiphase context. Recently developed as well as applied multiphase mechanisms [Herrmann et al., 2000, 2003, 2005; Ervens et al. 2003; Tilgner et al., 2005] and multiphase models [Wolke et al., 2005; Knoth, 2005] describe the physico-chemical processes occurring in the tropospheric multiphase environment predominantly in clouds. These more recent mechanisms and model studies have introduced also the importance of the in-cloud processing of soluble organic compounds by aqueous phase chemical processes. In context of an inorganic and organic multiphase environment, the Chemical Aqueous Phase RAdical Mechanism (CAPRAM) was developed for the application in multiphase models. The model studies in the past have been carried out mostly considering permanent cloud conditions which is expedient to investigate in-cloud aerosol modifications. However for more realistic studies of the physico-chemical aerosol cloud interactions as well as processing, model studies are necessary considering non-permanent cloud conditions. For this reason, the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM; Wolke et al. [2005]) has been developed and applied to investigate the effects of the multiphase aerosol-cloud-interaction on tropospheric aerosol particle and trace gas constituents.

2 MULIPHASE CHEMICAL MECHANISM AND MODELLING

2.1 AQUEOUS PHASE CHEMISTRY MECHANISM CAPRAM

The chemical aqueous phase mechanism CAPRAM in its version 3.0 [Herrmann et al., 2005] is the most recent development of the CAPRAM series with a total of 777 reactions. CAPRAM 3.0 incorporates the former version CAPRAM 2.4 [Ervens et al., 2003] and an extended reaction mechanism for atmospherically relevant organic compounds containing more than two and up six carbon atoms. The chemistry of organic compounds containing one to four carbon atoms as well as different functional groups is described in detail with more than 400 reactions. Furthermore, CAPRAM 3.0 includes reactions involving OH, HO_2, NO_3, SO_4^-, Cl_2^-, Br_2^- and CO_3^- radicals with inorganics (transition metal ions (TMI), NO_3^-, Cl^-, Br^-). Both radical and redox reaction pathways are integrated in the N(III) and S(IV) oxidation. In fact, CAPRAM considers an explicit description of the S(IV) oxidation by radicals, iron (Fe^{3+}), peroxides, ozone and peroxy nitric acid as well. CAPRAM 3.0 is currently the most detailed aqueous phase mechanism and an adequate tool for studies of multiphase aerosol processing. Further specific details regarding the CAPRAM mechanism including mechanism tables, references, corrections, revisions and the corresponding CAPRAM 3.0 mechanism data base are available at the CAPRAM homepage[2].

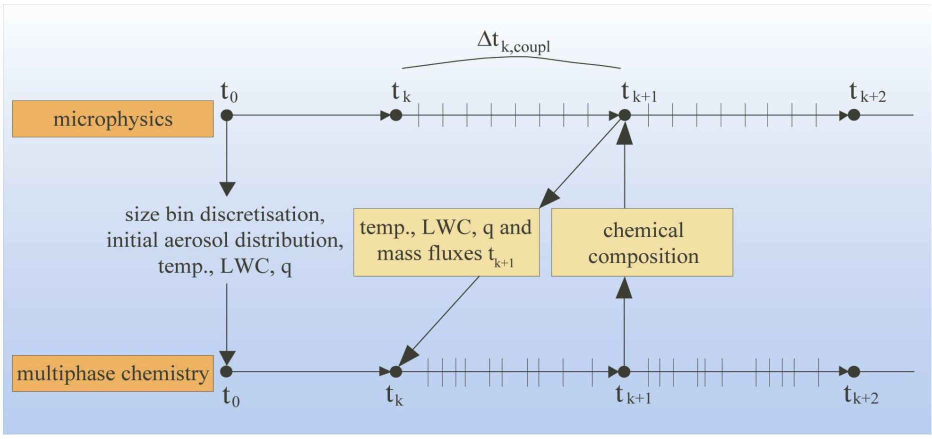

Figure 1. Schematic depiction of the SPACCIM model coupling of microphysics and chemistry.

2.2 ATMOSPHERIC MULTIPHASE MODEL SPACCIM

The air parcel model SPACCIM (Wolke et al. [2005]) was developed for the description of multiphase processes combining a complex multiphase chemistry mechanism and a detailed microphysical model. In SPACCIM the description of both separate processes is performed for a highly size-resolved particle and droplet spectrum. The model allows a detailed description of the processing of gases and deliquescent particles before the cloud formation, under cloud conditions and after cloud evaporation. The adiabatic air parcel model includes a description of microphysical processes of deliquescent particles and cloud droplets. All microphysical parameters required by the multiphase chemistry model are taken over from the microphysical model after a coupling time step (see **Figure 1**). In the performed model studies the coupling time step has been fixed at 10 seconds and the moving bin SPACCIM version has been used.

2.3 ACTUALISATION OF THE SPACCIM MODEL SIMULATIONS

In SPACCIM the complex aqueous phase mechanism CAPRAM 3.0 with 777 reactions was coupled to an updated and revised RACM mechanism (lumped gas phase mechanism with 281 reactions). The uptake processes of 52 soluble compounds are included in the mechanism following the resistance model approach by Schwartz [1986] considering Henry solubility, gas phase diffusion and mass accommodation coefficients.

The original gas phase mechanism RACM (Stockwell et al., 1997) was updated and revised. Particularly, the important iso-

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[2] CAPRAM homepage:
http://projects.tropos.de/capram/

prene oxidation has been updated with about 25 new reactions mainly based on the work Karl et al. [2006] including a detailed description of important oxidation products such as metacrolein and methylvinylketone. The further oxidation of methylvinylketone has been additionally implemented with 4 reactions after Zimmermann and Poppe [1996]. This oxidation chain leads to the formation of glycolaldehyde an important precursor for the formation of oxalic acid in the aqueous phase. To this end, the chemistry of glycolaldehyde is treated now separately using the oxidation scheme of the Master Chemical Mechanism (MCM; Saunders et al. [2003]). Moreover, the gas phase oxidation of ethene and ethylene glycol has been updated and implemented, respectively. Additionally, the inorganic gas phase chemistry has been updated according to available revised reaction rates (see Karl et. al. [2006]). In conclusion, the applied new gas phase mechanism contains 25 new reactions and 10 new species compared to the formerly used RACM mechanism.

The SPACCIM model was initialised with physical and chemical data from the EUROTRAC-2 project CMD (cp. Poppe et al. [2001] and references therein) for 2 different atmospheric scenarios urban (polluted case) and remote (continental background case). For the simulations a finely resolved particle spectrum is considered. The particle number initialisation is based on 3 particle modes which were discretised with 64 size bins within the microphysical model. The corresponding chemically homogeneous initial particle compositions has been derived from the aerosol distributions given by Poppe et al. [2001] and the chemical mass ratios of the different aerosol modes. The chemical initialisation of the gas phase has been used from the previous studies. Moreover, gas emissions and deposition were considered throughout the simulation time.

The simulations have been carried out using a meteorological scenario which is based on the global calculations of Pruppacher and Jaenicke [1995] with an in-cloud residence time about 15% (global average).In the scenario, an air parcel moves along a predefined trajectory including 8 cloud passages (4 day and 4 night clouds) of about 2 hours within 108 hours modelling time and an intermediate aerosol state at a 90% relative humidity level (see **Figure 2**) by neglecting the effects of non-ideal solutions. This means, the deliquescent particles are treated as well dissolved. Simulations have been performed for the two different atmospheric scenarios beginning at 0:00 on the 19th of June (45°N). Simulations have been carried out with and without (used acronym: woCloud) aqueous phase chemistry to investigate the effect of multiphase aerosol-cloud chemistry interaction on the tropospheric multiphase system. Finally, this non-permanent cloud meteorological scenario including more realistic in-cloud and cloud free time periods allows improved investigations of the aerosol cloud interaction compared to the former permanent cloud model studies.

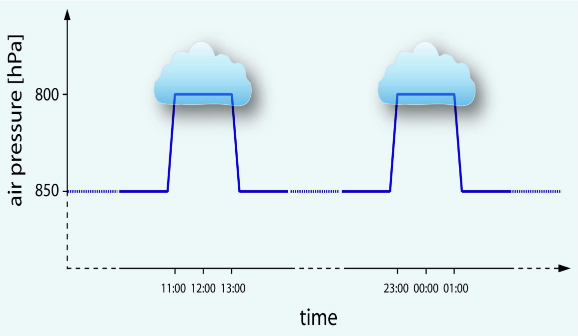

Figure 2. Schematic illustration of the used SPACCIM model scenario.

3 RESULTS AND DISCUSSION

3.1 GAS PHASE OH RADICAL OXIDATION BUDGET

The most important radical oxidant in the tropospheric multiphase system is the OH-radical. In **Figure 3**, the gas phase radical concentrations in molecules per cm^{-3} vs. time are presented for the urban and remote scenario both with and without aqueous phase chemistry interaction. According to the importance of the photochemistry for the OH-radical, the concentration profiles shows a day-time profile which is significantly influenced by the cloud occurrence. This fact can be seen directly in the difference between the case with cloud and without cloud interaction.

Under cloud conditions the radical concentration of OH is decreased by about 90% and 75% in the urban and remote scenario (2. day cloud event), respectively. This reduction is mainly caused by the uptake of very soluble HO_2 and not only by the direct phase transfer into the droplets. The efficient HO_2 uptake leads to an OH precursor separation between the two phases and a remarkable formation flux decrease. As can be seen from **Figure 3**, the reduction in the cloud is more substantial under urban conditions. This is caused by the relevance of the different sources for the OH formation. In contrast to the remote case, the OH formation pathway based on the reaction of HO_2 and NO is more important in the urban case. Therefore, the decrease is more recognisable in the urban case. In conclusion, the in-cloud reduction of the OH gas phase budget is mainly an indirect cloud effect regarding the OH based on a direct effect on HO_2.

The fluctuations which occur for the case without cloud interaction are caused by the relatively fast air pressure change during the air parcel lifting along the trajectory which leads to different fluxes of the pressure depended reactions. Therefore, the OH profile is characterised by chemical balancing effects.

Another interesting observation under remote conditions is the higher OH concentration after the day-time cloud evaporation. This effect is caused by a significant production of H_2O_2 in the remote day-time clouds leading to an increase of H_2O_2 in the gas phase and finally to a changed NO_X/HO_X budget and a short-time OH increase after the cloud evaporation. Furthermore, for the urban case a difference between the two cases can be recognised under wet aerosol conditions. The reduction there is caused also by the interaction of OH itself and it's precursors with the deliquescent particles.

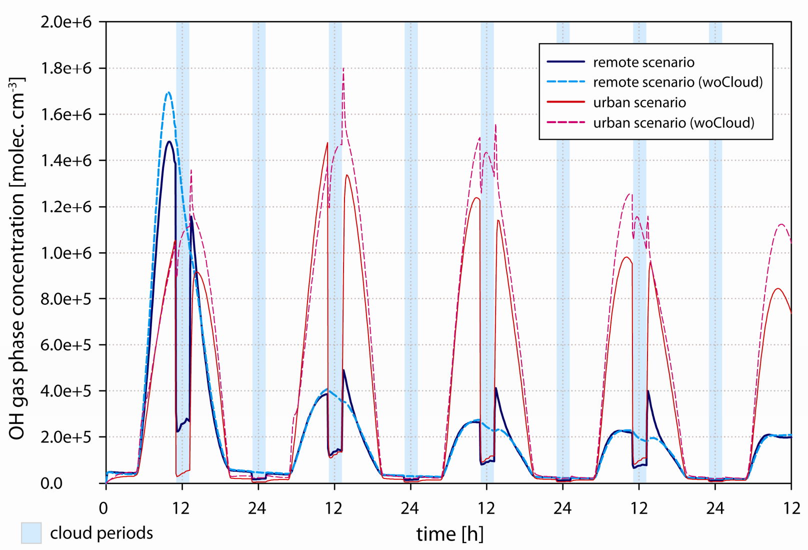

Figure 3. Modelled OH gas phase concentrations in molecules per cm^{-3} vs. modelling time for the urban and remote scenario both with and without (woCloud) aqueous phase chemistry interaction, respectively.

3.2 AQUEOUS PHASE OH RADICAL OXIDATION BUDGET

The OH day profile is also reflected in the aqueous phase. In **Figure 4** the aqueous concentration of OH is plotted for the urban and remote scenario in mol l^{-1}. The aqueous phase concentration itself depends on both the available water this means on the microphysical conditions and on the chemical sinks as well as sources of the species itself. The day-time concentrations of OH reach values of about $6.0 \cdot 10^{-14}$ and $1.0 \cdot 10^{-14}$ mol l^{-1} in the cloud droplets for the remote and urban scenario, respectively. The lower concentrations in the urban case result from the larger possible sink fluxes under polluted conditions. The corresponding night-time cloud concentrations are about 1 order of magnitude lower.

For both scenarios, a reduced OH budget in the aqueous phase can be mostly observed after the cloud evaporation. This reflects the effective oxidation within the cloud. As can be seen form the **Figure 4** the difference between deliquescent particle and cloud droplet concentration is only in the range of about two orders of magnitude and not only in the range of the LWC variation of about 5 order of magnitude. Therefore, other sources of OH in the aqueous phase have to be important for the concentration of the aqueous phase OH. The solution effect is more dominant in the night-time clouds. For this reason in-situ sources of OH act more effectively under day-time conditions. This also results from the flux diagnosis of the most important sinks and sources of the OH radical in the aqueous phase.

In **Figure 5**, the total sinks and sources of OH in the aqueous phase are plotted vs. a selected time interval of the modelling time. The positive reaction fluxes are sources for OH in the aqueous phase; the negative fluxes represent the sinks of OH. The mass fluxes are given in mol m^{-3} s^{-1} for the corresponding OH sink and source reactions. This kind of time resolved sink and source analysis leads to the determination of the most important chemical processes and interactions. Finally this leads to a more comprehensive understanding of the physico-chemical aerosol processing.

As can be seen from the total fluxes, the OH fluxes show also a characteristic day-profile as expected for the gas phase. The colours show significant differences in the sinks and sources between deliquescent aerosol conditions and cloud conditions. This is caused by the phase transfer of soluble compounds into the droplets which can act there as additional sink and sources.

Integrated over all cloud periods, the most important source of OH in the aqueous phase under cloud conditions is the direct transfer from the gas phase with about 73% in the urban case (64% in the remote case). But also the aqueous 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 $FeOH^{2+}$ act with about 3%, 16%, 7%, 7% and 2%, respectively, as important in-cloud sources of the OH radical among the direct uptake from the gas phase.

In contrast to the cloud conditions, the OH formation is dominated by the Fenton reaction of Fe(II) with H_2O_2 in the deliquescent particles. Interestingly, the total source fluxes in the particles are fully comparable with that in the cloud droplets under urban conditions. The model results implicate that the in-situ OH production under wet aerosol particle condition strongly depends on the TMI concentration and especially on the H_2O_2 concentration. Contrary to the almost comparable OH production fluxes in the urban case, the remote case shows mostly somewhat smaller OH formations under particle conditions depending mainly on the availability of H_2O_2.

The above mentioned results are a good agreement with measurements of Arakaki et al. [2006]. They have analysed aqueous extracts of aerosol particles regarding to the photochemical formation of OH in deliquescent particles. They found a direct correlation between the OH formation and the dissolved iron concentration. But more experimental work has to be done to point out the importance of the different formation pathways including the Fenton reaction.

A much more complex picture 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%) which lead to the production of less volatile organic compounds. In a good agreement with the results of simple conceptual model studies of Gelencser and Varga [2005], predominantly organic compounds with effective Henry constants above 10^{-3} M atm^{-1} (mostly bifunctional compounds) acts as important OH sinks under cloud conditions. In contrast to the cloud conditions, the reactions with the various less volatile oxidation products of the mentioned before organics such as pyruvic acid (6%) and glyoxylic acid (12%) act as sinks for OH in the urban scenario in the deliquescent particles. The reaction of these species is less important under cloud conditions because of the competitive reactants which are effectively taken up into the cloud droplets like formaldehyde.

The integrated percentage contributions of the most important OH sources and sinks for the urban case are summarised in **Table 1** and grouped into 4 classes regarding to the different microphysical conditions.

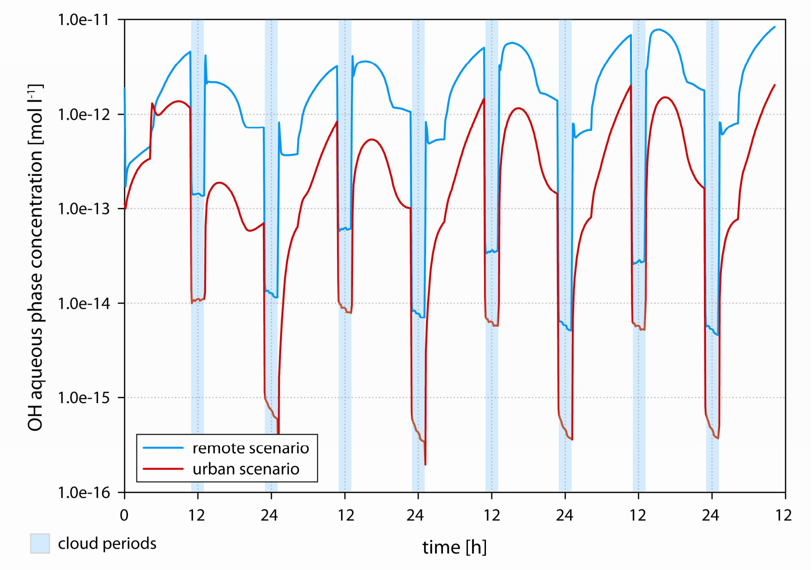

Figure 4. Modelled OH aqueous phase concentrations in mol l^{-1} vs. modelling time for the urban and remote scenario, respectively.

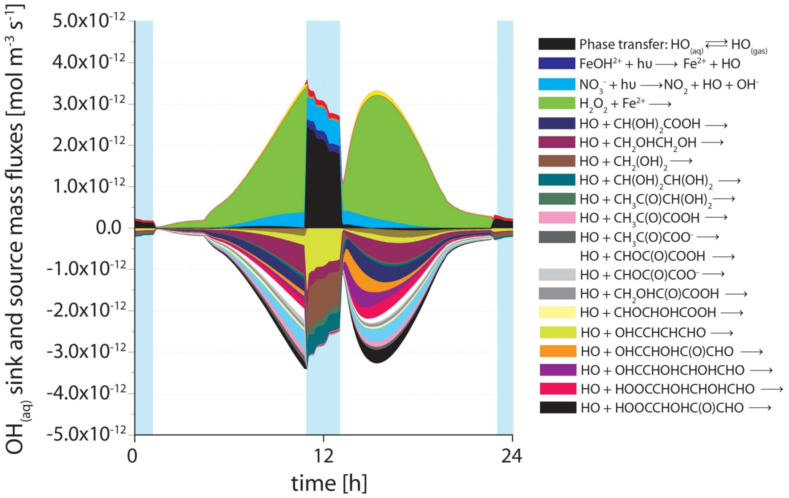

Figure 5. Modelled chemical sinks and sources mass fluxes of OH in aqueous phase mol m^{-3} s^{-1} for the third day of modelling time for the urban.

Table 1. Integrated percentage contributions of the most important $OH_{(aq)}$ radical sources and sink reactions for the urban case classified regarding to the different microphysical conditions during the simulation time (total = total contributions throughout the simulation time, total clouds = contributions throughout all cloud events, day-/nighttime clouds = contributions throughout all day and night cloud events, aqueous particles = contribution throughout the deliquescent particle conditions) (only sinks and sources with contributions larger than ±1 % presented).

reaction	total	Total clouds	Daytime clouds	Nighttime clouds	Aqueous particles
phase transfer: $OH \rightleftharpoons OH_{(aq)}$	18%	73%	73%	76%	1%
$Cl^- + OH \rightleftharpoons ClOH^-$	-2%	0%	0%	2%	-3%
$Br^- + OH \rightleftharpoons BrOH^-$	-1%	0%	0%	0%	-2%
$FeOH^{2+} + h\nu \longrightarrow Fe^{2+} + OH$	2%	7%	7%	0%	0%
$NO_3^- + h\nu \xrightarrow{H_2O} NO_2 + OH + OH^-$	10%	14%	15%	0%	9%
$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH + OH^-$	67%	1%	1%	2%	87%
$H_2O_2 + Cu^+ \longrightarrow Cu^{2+} + OH + OH^-$	2%	0%	0%	0%	2%
$Cu^+ + O_3 \xrightarrow{H^+} Cu^{2+} + OH + O_2$	0%	1%	1%	4%	0%
$HO_3 \longrightarrow OH + O_2$	1%	4%	3%	14%	0%
$SO_4^- + H_2O \longrightarrow SO_4^{2-} + OH + H^+$	0%	0%	0%	2%	0%
$OH + HSO_4^- \longrightarrow$	-3.1%	0.0%	0.0%	0.0%	-4.1%
$OH + Fe^{2+} \longrightarrow$	-8.4%	-0.3%	-0.3%	-0.2%	-10.9%
$OH + CH_2(OH)_2 \longrightarrow$	-7.7%	-28.6%	-28.6%	-29.6%	-1.3%
$OH + HCOO^- \longrightarrow$	-0.4%	-1.6%	-1.6%	-1.5%	0.0%
$OH + CH_2OHCH_2OH \longrightarrow$	-14.1%	-10.8%	-10.7%	-12.3%	-15.1%
$OH + CH_3CH_2OH \longrightarrow$	-0.9%	-3.4%	-3.3%	-3.8%	-0.1%
$OH + CH(OH)_2CH(OH)_2 \longrightarrow$	-4.5%	-13.1%	-13.0%	-13.8%	-1.8%
$OH + CH(OH)_2COOH \longrightarrow$	-9.4%	-0.3%	-0.3%	-0.4%	-12.2%
$OH + CH_3C(O)CH(OH)_2 \longrightarrow$	-1.2%	-4.6%	-4.6%	-5.5%	-0.2%
$OH + CH_3C(O)COOH \longrightarrow$	-2.8%	0.0%	0.0%	0.0%	-3.6%
$OH + CH_3C(O)COO^- \longrightarrow$	-2.1%	-0.2%	-0.2%	-0.3%	-2.7%
$OH + CH_2(OH)C(O)COOH \longrightarrow$	-1.9%	0.0%	0.0%	-0.1%	-2.5%
$OH + CHOC(O)COOH \longrightarrow$	-3.6%	0.0%	0.0%	0.0%	-4.7%
$OH + CHOC(O)COO^- \longrightarrow$	-1.3%	0.0%	0.0%	0.0%	-1.7%
$OH + OHCCHCHCHO \longrightarrow$	-10.5%	-31.1%	-31.3%	-28.1%	-4.2%
$OH + OHCCH(OH)C(O)CHO \longrightarrow$	-5.1%	-0.6%	-0.7%	-0.2%	-6.4%
$OH + OHOCCH(OH)C(O)CHO \longrightarrow$	-5.0%	-0.1%	-0.1%	-0.2%	-6.4%
$OH + OHCCH(OH)CH(OH)CHO \longrightarrow$	-5.1%	-0.6%	-0.7%	-0.2%	-6.4%
$OH + OHOCCH(OH)CH(OH)CHO \longrightarrow$	-4.8%	-0.1%	-0.1%	-0.1%	-6.2%
$OH + CHOCH(OH)COOH \longrightarrow$	-1.7%	0.0%	0.0%	-0.1%	-2.2%

Finally, it has to be noted that all these results imply the potential relevance of deliquescent particles to act as a reactive medium within the tropospheric multiphase system. Moreover, the availability of OH radical sources 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. These so-called “twilight zones” with forming and evaporation cloud fragments as well as hydrated aerosols can extend up to tens of kilometres from the clouds in the free troposphere [see Koren et al., 2007] and can thereby fill large volume of the free troposphere. Therefore, the free troposphere provides conditions in which aqueous phase reactions also in deliquescent particles are conceivable and maybe potentially important.

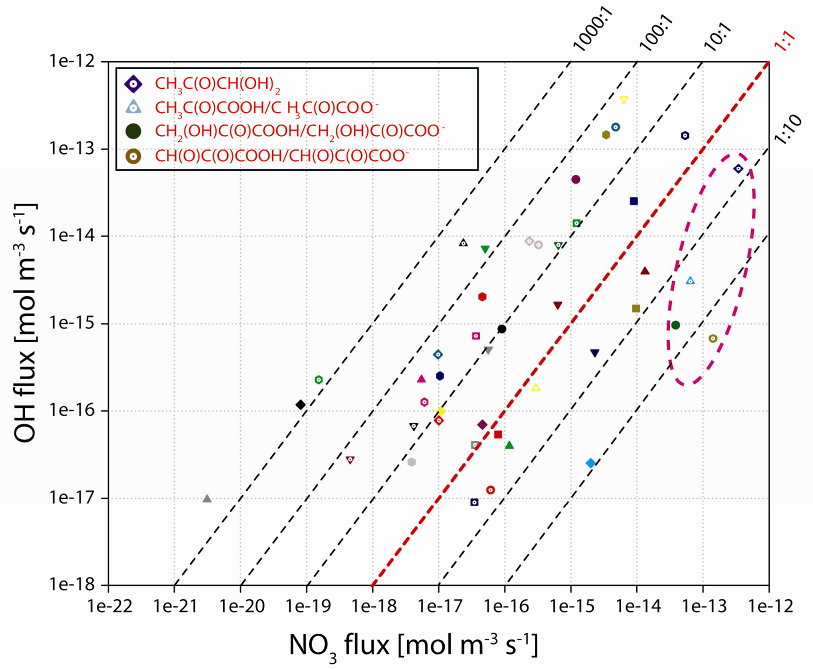

Figure 6. Comparison of the modelled mean in-cloud NO_3 and OH degradation fluxes of organic compounds under urban conditions.

3.3 IMPORTANCE OF THE NO_3 AND OH RADICAL FOR THE IN-CLOUD OXIDATION OF ORGANIC SPECIES

Moreover, the last paragraph has been pointed out the importance of organic compounds for the aqueous phase budget of the main radical oxidant OH. However, among the OH radical, other radical oxidants such as the NO_3 radical can contribute significantly to the oxidation of organic compounds under cloud conditions particularly during the night. Their competitive reactivity for the in-cloud oxidation of organic compounds is shown in **Figure 6**. For the actualisation of this comparison, the aqueous phase OH and NO_3 organic oxidation fluxes have been analysed classified according to the different microphysical conditions during the simulation time. In **Figure 6**, a comparison is shown of the importance of the two main tropospheric radical oxidants for the in-cloud degradation of organic compounds under polluted in-cloud conditions. The red line in **Figure 6** marks the 1:1 ratio. The results point out that for some organic compounds the NO_3 radical oxidation can be potentially more important than the OH pendant. However, for the majority of the species, the OH reaction is the main sink in the aqueous phase also under highly polluted environmental conditions. Moreover, the in-cloud oxidation of methylglyoxal and its oxidation products like pyruvic acid seems to be an efficient sink for NO_3 radicals in the aqueous phase particularly under both urban and remote conditions. Furthermore, the results reveal a dominating OH chemistry under deliquescent particle conditions due to the in-situ sources of OH radical.

3.4 AQUEOUS PHASE IMPACT ON ORGANIC GAS PHASE TRACE GAS BUDGETS

Further investigations following the studies on the tropospheric oxidants were related to the influence of the changed gas phase oxidation budget on the oxidation of organic trace gases. For emitted less soluble gas phase species like xylene, a significant reduction of the degradation rate can be observed if aqueous phase chemistry interactions are considered (see **Figure 7**). In particular, the changed oxidation budget in the day-time clouds leads to the reduction of the gas phase degradation for this kind of compounds. The concentrations of the model run including aqueous phase chemistry are about 20% higher compared to the model run with gas phase consideration only. Moreover, trace gas concentrations of less soluble organics can also be altered by a modified NO_3 radical budget as well as modified O_3 levels.

A much more complex concentration patterns can be obtained for oxidation products which are soluble enough to be taken up into the aqueous phase. For this kind of compounds additionally to the gas phase, the aqueous phase can act as a significant sink as well as source.

For instance in the case of ethylene glycol, the chemical interaction with deliquescent particles as well as droplet leads to decreasing concentrations in comparison to the case without consideration of aqueous phase chemistry. Because of the high Henry-solubility ethylene glycol is transferred efficiently into wet aerosol particles and cloud droplets. It's effectively oxidised there particularly during the high OH day time conditions. As **Figure 7** shows, the aqueous phase oxidation can compensate also the reduced gas phase oxidation budget and leads finally to a lower concentration of ethylene glycol in the gas phase.

Among the species which are well degraded in the aqueous phase, species exist which are efficiently produced and transferred to the gas phase like acetic acid (see **Figure 7**). Without considering multiphase interactions, the productions of the acetic acid are significantly underestimated. Under remote environmental conditions about $^2/_3$ of acetic acid is produced in the cloud droplets and largely degassed to the gas phase with the cloud evaporation.

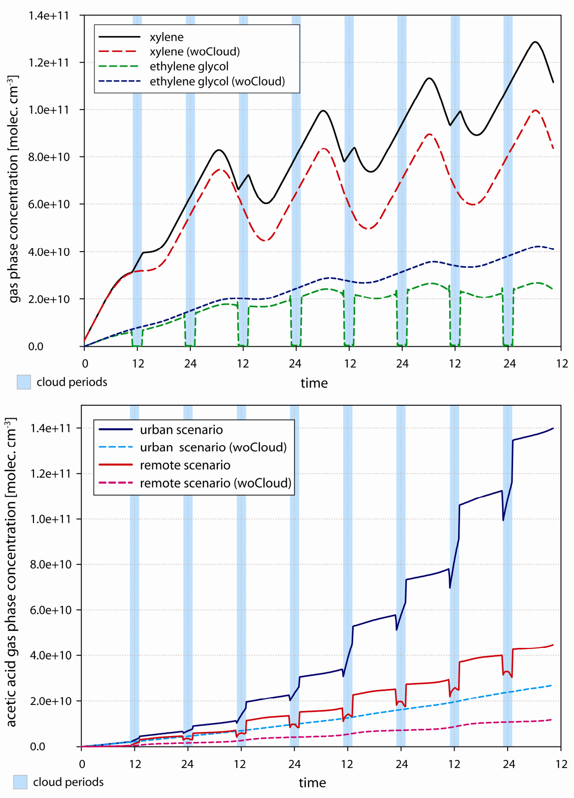

Figure 7. Modelled gas phase concentrations of xylene and ethylene glycol under urban conditions (top) as well as acetic acid under remote and urban conditions (down) both with and without (woCloud) aqueous phase chemistry interaction, respectively.

In conclusion, without reflection of aqueous phase chemical processes organic trace gas concentrations can be significantly under- and overestimated by pure gas phase chemistry models.

3.5 ORGANIC PROCESSING IN THE AQUEOUS PHASE

Based on the studies on oxidation budget, the most important aqueous phase oxidation pathways have been determined by comprehensive flux analyses. In **Figure 8**, the modelled mean sink and source fluxes for the most important multiphase oxidation processes contributing to organic particle mass formation are presented for the remote scenario.

Figure 8 shows the chief aqueous organic oxidations leading to the formation substituted mono- and diacids as well as substituted dialdehydes. The main identified precursors for the organic mass production in the gas phase are 1,4-butenedial, methylglyoxal, glyoxal, glycolaldehyde and ethylene glycol. The aqueous phase contributes with about 36%, 7%, 31%, 47% and 93% to their total multiphase degradation. Under continental background conditions, in particular the oxidation of glycolaldehyde can contribute to the in-cloud C_2 organic particle mass formation. The most important source for glycolaldehyde in the gas phase represents the oxidation of methylvinylketone which is one of the main isoprene oxidation products. As similar shown by Lim et al. [2005], this pathway links the emitted isoprene and oxalic acid which is one of the main identified single organic particle mass components. The oxidation of methylglyoxal has been identified as the most important C_3 oxidation pathway which is moreover able to influence significantly the aqueous phase NO_3 and OH radical budget.

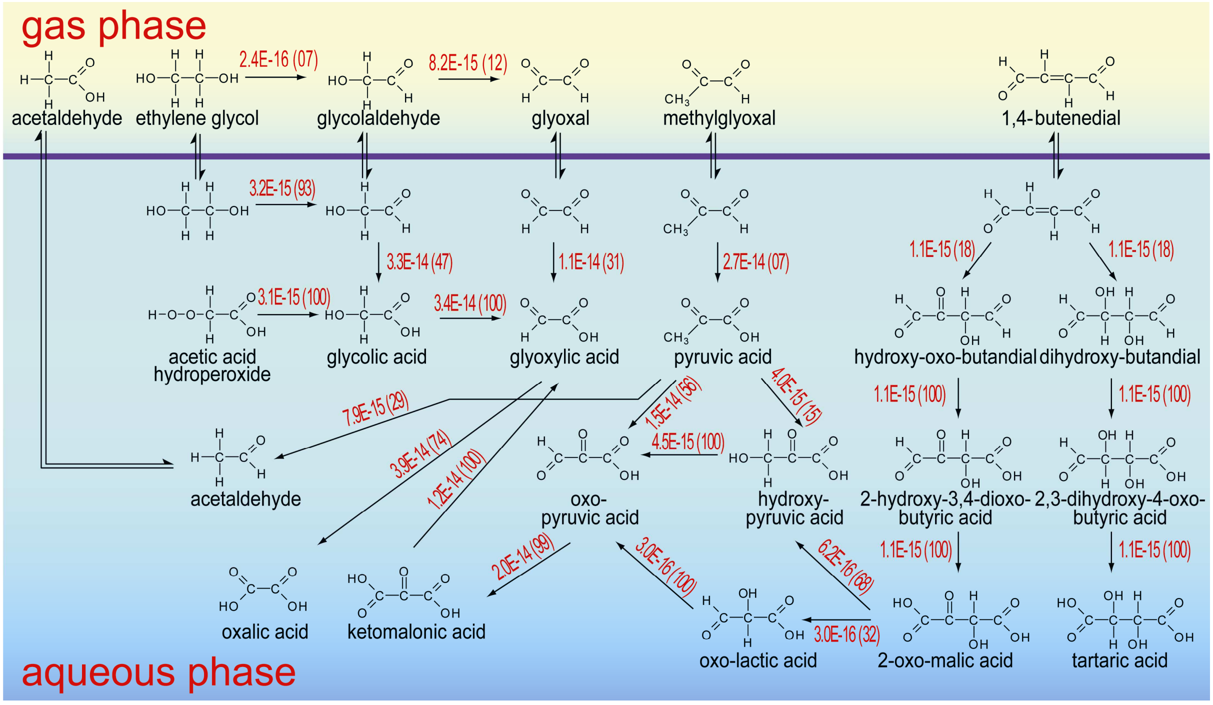

Figure 8. Schematic presentation of the most important aqueous phase C_2-C_4 organic oxidation paths and contributing to the particulate organic matter (remote scenario). The integrated mean oxidation fluxes are given in mol m^{-3} s^{-1} and the corresponding percentages in brackets.

Among the total mass production the spectral processing of the organics has been investigated exemplary shown in **Figure 9** for the pyruvic acid. In **Figure 9,** the spectral pyruvic acid mass concentration in mol m^{-3} is depicted vs. modelling time and the corresponding particle and droplet spectra, respectively.

Figure 9 shows that the aqueous phase pyruvic acid production is mainly restricted to the size interval between the activation radius and about 800 nm. This pattern has been observed quite a lot of the organic compounds and is also reflected in the spectral distribution of the total organic mass, which can be increased after the daytime cloud evaporation by about 1 µg m^{-3} under urban conditions.

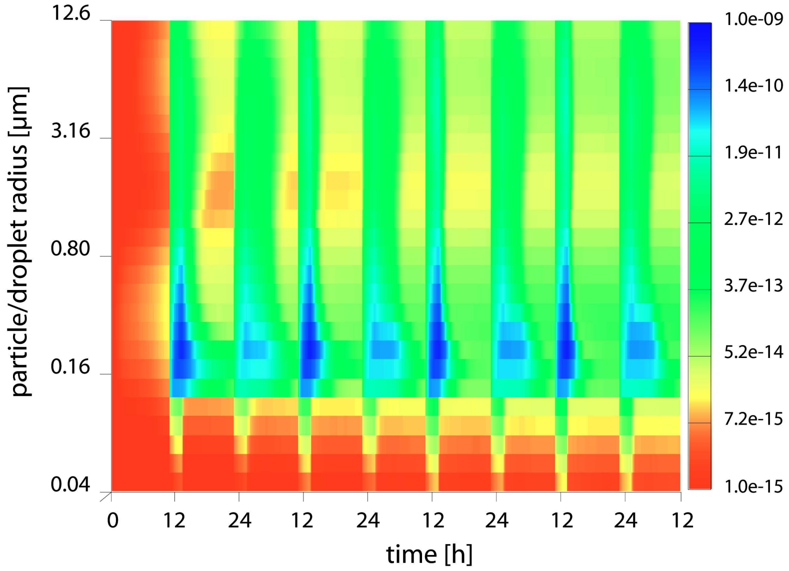

Figure 9. Depiction of the modelled spectral pyruvic acid mass concentration in mol m^{-3} as function of time and the corresponding dry particle/droplet radius.

4 SUMMARY AND OUTLOOK

Simulations with the parcel model SPACCIM have been performed for different atmospheric conditions considering detailed microphysics and multiphase chemistry (RACM-MIM2ext/CAPRAM 3.0i) to investigate the effect of multiphase processing of tropospheric aerosol particles and trace gases using a more realistic meteorological non-permanent cloud model scheme. The model studies show considerable effects of multiphase cloud droplet and deliquescent aerosol particle interactions on the tropospheric oxidation budget for polluted and remote environmental conditions as well as affected VOC's oxidation due to the influenced oxidation budget. Moreover, the simulations implicate the potential role of deliquescent particles to act as a reactive chemical tropospheric medium due to the in-situ aqueous phase production of radical oxidants such as OH and non-radical oxidants such as H_2O_2. Additionally, the model study have revealed the importance of the aqueous phase for the formation of higher oxidised organic compounds such as substituted mono- and dicarboxylic acids such as pyruvic acid and tartaric acid. In particular, the aqueous phase oxidations of methylglyoxal and 1,4-butenedial have been identified as important OH radical sinks under polluted environmental conditions contributing to the production of less volatile organic compounds and thus the organic aerosol particle mass. Further, the in-cloud oxidation of methylglyoxal and its oxidation products have been shown to be an efficient sink for NO_3 radicals in the aqueous phase particularly under urban and remote conditions. Finally, the sum of the results implicates the necessity of the aqueous phase processes to be considered in future higher scale chemistry transport models. Moreover, important cloud effects are mainly not yet considered or less represented in presently available regional scale chemistry transport models (CTM's) because of both the restricted knowledge in the past and the high computational costs of detailed aqueous phase chemistry mechanisms such as CAPRAM 3.0.

To this end, a reduced aqueous phase mechanism with less than 250 reactions has been already developed. This mechanism is able to reproduce the most important aqueous phase chemistry processes for key compounds including reasonable computational costs. Finally, the application of this reduced mechanism will allow further investigations of the multiphase chemical processing on regional scale in the future CTM's.

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