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Modeling the multiphase processing of an urban and a rural air mass with COSMO–MUSCAT

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A B S T R A C T

A reduced version of the complex aqueous phase mechanism CAP-RAM3.0i (C3.0RED) was used in the regional chemistry transport model COSMO–MUSCAT in a 2-D application. Besides sulfate and nitrate production, the mechanism treats a complex HOx-chemistry, transition metal ion chemistry and organic species up to C4. The effects of the cloud chemistry on the chemical composition of air and particles were investigated. Sensitivity studies were conducted for an urban and a rural air mass. For this purpose simulations with C3.0RED were compared to ones with a simple inorganic aqueous phase mechanism (INORG) and without aqueous phase chemistry. A reduction of the gas phase concentrations of major oxidants was observed especially in the urban environment. Compared to INORG, C3.0RED is always more acidic leading to shifts in several chemical subsystems, (e.g. production of sulfate). Using C3.0RED instead of INORG, differences in sulfate mass of 3% to −15% occurred. The modeled O/C-ratio tends to be higher than observations as C3.0RED does not consider the whole population of organics and no insoluble organic mass. Nevertheless, the modeled concentration of glyoxalic acid is in the range of atmospheric measurements in both environments, whereas oxalic acid and pyruvic acid are underestimated in the urban case.

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1. Introduction

Clouds play a crucial role in the atmospheric multiphase system. They have the ability to influence highly coupled and often non-linear processes such as transmission of radiation through the atmosphere or chemical reactions in the gas and aqueous phase thus altering the chemical composition of the air and the particle population (Ravishankara, 1997). This cloud chemical processing of aerosols includes activation of cloud condensation nuclei (CCN), scavenging, partially solving of particle constituents, dissolution of trace gases, aqueous phase chemical reactions, deposition via precipitation and evaporation (Fig. 1). Chemical cloud processes can therefore affect the distribution (in time, space and size) and chemical composition of atmospheric particles leading to aged particles with different microphysical and radiative properties (Donahue et al., 2009; Cubison et al., 2008). It is reported that 80–90% of particulate sulfate is produced by aqueous phase chemistry inside of cloud droplets (Lelieveld and Heintzenberg, 1992). Besides inorganic species, also a huge variety of organic species is involved into aqueous phase chemistry leading to the formation of aqueous secondary organic aerosol (aqSOA; Ervens et al., 2011; Hallquist and et al., 2009; Kanakidou and et al., 2005). Sorooshian et al. (2006) showed a strong correlation between sulfate and oxalate in cloud residuals. It was also reported that a large fraction of ambient organic aerosol is oxygenated (Jimenez et al., 2009), which is expected to occur via aqueous phase pathways. Additionally, SOA has higher O/C and OM/OC ratios than what could be expected by dry gas-to-particle conversion represented by smog chamber experiments (Aiken et al., 2008).

Urban and rural air masses differ substantially in their chemical composition and particle loading. In rural sites anthropogenic pollutants such as NO_x, SO_2, O_3 and many organic species have considerably lower concentrations (Seinfeld and Pandis, 1998). In contrast, there are some species from biogenic sources (e.g. isoprene, alpha-pinene, limonene, sesquiterpene) with elevated concentrations. Usually, the pH of cloud droplets is lower in urban areas (Herrmann, 2003, and references therein). As many chemical subsystems show a strong pH-dependency (e.g., sulfate formation), it can be expected that such systems behave different in rural or urban sites, respectively.

Up to now, cloud processing of gases and aerosol particles is responsible for the highest uncertainties in air quality models (Gong et al., 2011). Unfortunately, a detailed description of aqueous phase
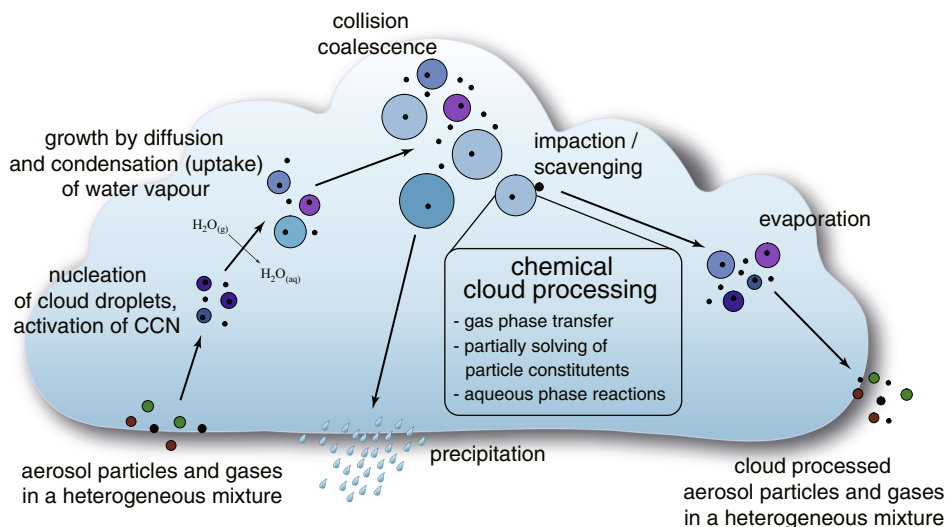

Fig. 1. Schematic depiction of cloud processing and the relevant physical and chemical sub-processes (modified from Tilgner, 2009).

chemistry and cloud microphysics causes high computational costs. Therefore, most chemistry transport models (CTMs) use a highly parameterized description or simple aqueous phase chemical mechanisms focusing on sulfate production. But, there are also CTMs available, which treat inorganic and organic species (up to C2) in the aqueous phase (see review of Gong et al. (2011)). Recently, the formation of oxalate was investigated using a 3-D-model with an explicit aqueous phase mechanism (Myriokefalitakis et al., 2011; Lim et al., 2005). In the work of Leriche et al. (2013), an aqueous chemistry mechanism including organic species up to C2 was used in a regional model in 2-D and 3-D studies.

In the present study, the comprehensive aqueous phase mechanism CAPRAM 3.0i (Chemical Aqueous Phase Radical Mechanism, (Tilgner and Herrmann, 2010) in a reduced version, which was announced as applicable for multi-dimensional models (C3.0RED, Deguillaume et al., 2009), was used in the coupled regional CTM COSMO-MUSCAT (Wolke et al., 2012, 2004) and compared to the simpler inorganic mechanism INORG (Sehili et al., 2005). A short description of the model and both mechanisms is given in section 2. Sensitivity studies on the behavior of both mechanisms on several chemical targets (major oxidants, sulfate mass, organic mass, pH) were conducted in an urban and a rural air mass.

2. The chemistry transport model COSMO–MUSCAT

COSMO–MUSCAT is an online-coupled model system consisting of the CTM MUSCAT and the forecast model of the German Weather Service (DWD) COSMO (Baldauf et al., 2011; Schättler et al., 2012). The meteorological fields are provided by COSMO and are used by MUSCAT for transport and chemical processes. The chemical mechanisms are imported from ASCII-files, whereby changes to the mechanism can be performed in a simple way without recompiling. Therefore, it is easy applicable to use chemical mechanisms of different complexity. In previous applications, the model system was used for process studies and regional simulation of pollutants or Saharan dust (Heinold et al., 2007; Hinneburg et al., 2009; Renner and Wolke, 2010). Besides an already included description of the gas phase chemistry the treatment of aqueous phase chemical processes has been implemented recently (Deguillaume et al., 2009). Up to now, two aqueous phase mechanisms are available for COSMO–MUSCAT. All chemical conversions are described explicitly and solved in a prognostic way.

The reduced CAPRAM 3.0i mechanism (C3.0RED) provides a less computationally intensive mechanism, which considers inorganic and organic aqueous phase processes occurring in tropospheric warm clouds. A comparison using a box model showed C3.0RED to be ~40% less time consuming (Deguillaume et al., 2009). The C3.0RED mechanism with 198 aqueous phase processes is almost a factor of 4 smaller than the full CAPRAM 3.0i mechanism. The mechanism contains 130 aqueous phase species and 157 aqueous phase reactions, and treats the phase transfer of 41 species. In addition to a detailed description of the inorganic chemistry (HO_x, transition metal ions (TMI), sulfate, nitrate), C3.0RED takes into account also the aqueous phase chemistry of important organic compounds with up to 4 carbon atoms. To simulate both gas and aqueous chemical processes, the gas phase chemistry mechanism RACM-MIM2ext (see Tilgner and Herrmann, 2010) is coupled to C3.0RED.

In contrast to the complex C3.0RED, a very simple inorganic mechanism INORG can be used. INORG focuses on the description of sulfate via the oxidation of S(IV) with O_3 and H_2O_2. Additionally, the uptake and dissociation of HNO_3, H_2SO_4, HCl, NH_3 and CO_2 are considered. So, it is comparable to aqueous phase mechanisms used in state-of-the-art air quality models (Gong et al., 2011) and several chemical weather forecast models (Kukkonen et al., 2012).

In both mechanisms, the pH is described explicitly and is therefore variable. All dissociation equilibriums, which depend on the pH, have to be balanced by the solver within every time step leading to increased computational costs compared to the more common treatment of a fixed or prescribed pH.

3. Scenarios and model setup

As the treatment of aqueous phase chemistry in 3-D-studies increases the computation time by a huge amount, an artificial 2-D-domain describing the streaming over a mountain was used in this

study (see Fig. 2). Besides that, this 2-D-case is easier to understand and hence is more suitable for process studies. The domain spans 400 cells with a grid resolution of ~1 km in the horizontal of which an inner domain of 136 cells is used for MUSCAT. In the vertical, 50 layers are used in the meteorological driver with a thickness between 25 and 2000 m. Of those, the lowest 26 layers (i.e. up to 3 km with a maximum thickness 250 m) are treated for MUSCAT. The mountain is 500 m high and 20 km wide. The air is streaming from left to right. After a short spin-up two clouds are evolving, one directly at the mountain top, the other in a wave above the lee side. To ensure a stable cloud over the whole simulation time of 48 h, radiative processes are turned off for the meteorology (i.e. no heating or cooling). Incoming radiation and shading effects are taken into account for photolysis. In this work, the bulk liquid water provided by COSMO is used for the aqueous phase chemistry. The droplet number of this monodisperse distribution is held constant at 150 cm^{-3} leading to maximum cloud droplet radii of 6.2 μm. Aqueous chemical processes are switched on above a liquid water content (LWC) threshold of 0.01 g m^{-3} (i.e. ~2 μm radius). When aqueous phase chemistry was turned on in a grid cell, the chemical system is imbalanced instantaneously due to fast dissociations of e.g. sulfate, nitrate or acetic acid. This problem could be solved by introducing a minimal LWC (0.01 g m^{-3}), which is present in the whole model domain. At this level, these fast dissociations and appropriate uptake processes are treated even in cloud-free grid cells. In that case, the chemical system is less stiff and more balanced.

For the sensitivity study, simulations with C3.0RED were compared to simulations with INORG and without aqueous phase chemistry in an urban and a rural environment. Therefore, the behavior of chemical targets such as major oxidants (OH, HO$_2$, H$_2$O$_2$, NO$_3$, O$_3$), sulfate mass, pH, organic mass and the O/C-ratio was examined. Compared to the rural case, the urban case is characterized by higher initial concentrations of anthropogenic gas phase pollutants (e.g. NO$_x$, SO$_2$), lower initial concentrations of biogenic precursors (e.g. isoprene, limonene), a higher particle load and different initial particle composition (for more details see (Deguillaume et al., 2009)). The initial concentrations were provided by a 24 h box model run and are distributed over the height of the MUSCAT domain with a constant mixing ratio. This initial composition of the first column is used to define constant in-flow conditions for the left edge of the computational domain. The pH was initialized with charge balancing leading to values of ~2.5 in the beginning. The simulations started at midnight and were carried out for 48 h.

4. Results and discussion

4.1. Oxidants

The oxidative capacity of the atmosphere is controlled by its main oxidants. These species are known to start reaction chains in the gas and aqueous phase and, in case of HO$_x$, for its ability to recycle each other. Fig. 3 shows the concentration of H$_2$O$_2$ in the gas phase during the second day (after
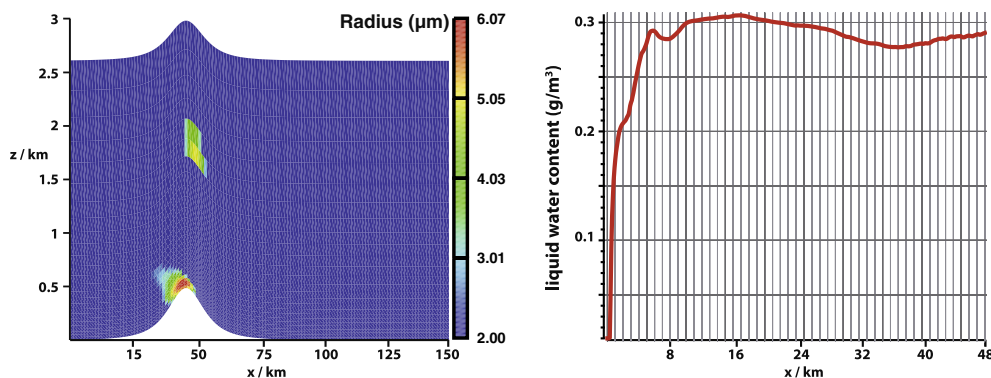

Fig. 2. Left: Cloud droplet radius (μm) after 36 h. Right: Time series of liquid water content (g m^{-3}) in the middle of the lower cloud.
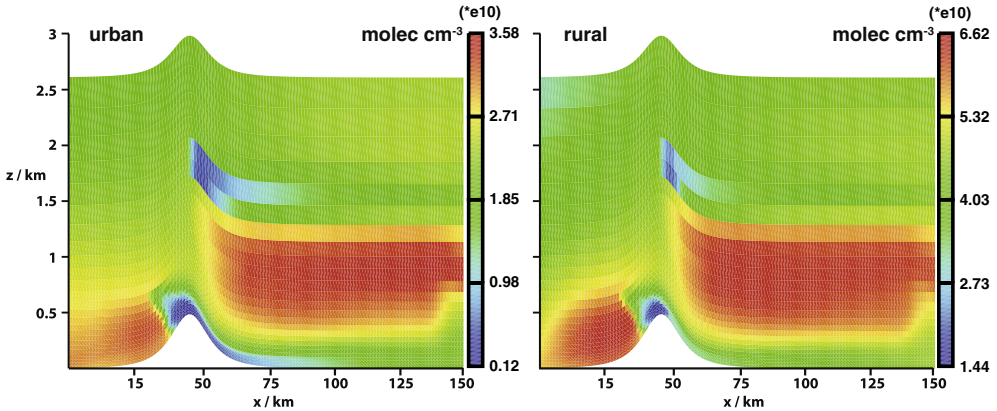
Fig. 3. Modeled gas phase concentration of H_2O_2 (molec cm^{-3}) in urban (left) and rural (right) environment using C3.0RED.

36 h). H_2O_2 is the major oxidant that converts S(IV) to S(VI). Furthermore, it is very soluble in water. Because of that, the gas phase concentration drops by 75–95% in the area of the cloud in both environments. In Fig. 4, horizontal profiles of the concentration of OH, HO_2, H_2O_2 and NO_3 are presented for C3.0RED, INORG and without aqueous phase chemistry in the height of the middle of the lower cloud. The relative loss using C3.0RED or INORG compared to the simulation without aqueous phase chemistry at the cloud passage and ∼30 km downwind of the cloud is given in Table 1. Like H_2O_2, using C3.0RED gas phase OH, HO_2 and NO_3 are reduced by the clouds especially in the urban case due to more reaction partners present also in the aqueous phase. For gas phase NO_3, the highest sink is the uptake and dissociation of N_2O_5. Contrary to H_2O_2, the loss of OH and HO_2 is compensated after the cloud very fast because of the high gas phase production fluxes. Note that except of H_2O_2 and O_3, none of the other oxidants is treated in INORG. Therefore using INORG, no significant reduction
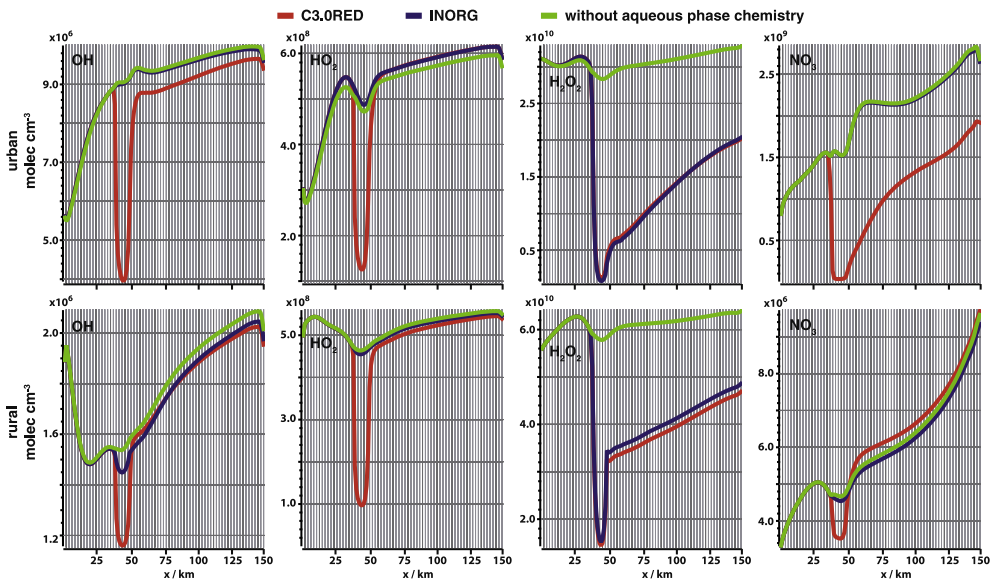

Fig. 4. Horizontal profile of gas phase concentration (molec cm^{-3}) after 36 h (for NO_3 after 48 h) through the lower cloud for the urban case (upper panel) and the rural case (lower panel).

Table 1

Relative deviation (%) of C3.0RED and INORG from simulation without aqueous phase chemistry during cloud passage and ~30 km downwind of the cloud in the same height after 36 h (NO_3 after 48 h).

		urban in-cloud	urban after cloud	rural in-cloud	rural after cloud
C3.0	OH	−56.0	−5.7	−24.6	−2.7
	HO_2	−73.4	3.2	−78.9	−3.6
	H_2O_2	−95.1	−69.5	−74.2	−41.9
	NO_3	−97.7	−58.6	−23.7	5.3
INORG	OH	−0.5	−0.5	−5.8	−2.9
	HO_2	3.0	3.1	−1.9	−1.2
	H_2O_2	−96.6	−70.7	−72.0	−39.0
	NO_3	−0.35	−0.6	−2.6	−2.3

is observed for OH, HO_2 and NO_3. As the major sink of H_2O_2 is the production of sulfate, which is described similarly in both mechanisms, no substantial differences between C3.0RED and INORG occur for the H_2O_2 gas phase concentration.

With a loss of less than 3% in both mechanisms, the effect of the aqueous phase chemistry on the ozone concentration is of minor importance (not shown). The small deviations seen for all oxidants between the runs with and without aqueous chemistry upwind of the cloud are due to the use of the minimal LWC in cloud-free areas, where uptake and dissociation of e.g. HNO_3 and HNO_4 are treated. Because of shading effects by the cloud, also the run without aqueous phase chemistry shows a slight reduction of gas phase oxidants.

4.2. pH

Many chemical subsystems, such as the production of sulfate or organic acids, are dependent on the pH due to pH-sensitive dissociation equilibriums of their precursors and themselves. Fig. 5 shows the pH in C3.0RED and the difference between the pH modeled with C3.0RED and INORG for both environments after 36 h (day). Modeled in-cloud pH is ~6 in the rural and 3.5–4.5 in the urban case. Generally, it can be seen that the pH decreases up to 4.5 (rural) and 2.5 (urban), respectively, when the cloud evaporates and the droplets become smaller. This is because of the high concentration inside of the deliquescent aerosols after the cloud passage. Furthermore, INORG is always less acidic than C3.0RED. The highest deviations with up to −0.2 for the rural case and −1 for the urban case occur inside of the clouds and during the day (see Fig. 6). For the rural case, the differences after the clouds are smaller compared to the surrounding air due to strong acidification by the sulfate production, which is comparable between C3.0RED and INORG. The slight difference between both mechanism upwind of the cloud is caused by uptake and dissociation of some organic acids, which are not treated in INORG, at the minimum LWC.

Possible causes for the additional acidifying in C3.0RED are various chemical subsystems such as production of organic acids, additional nitrate production pathways (via N_2O_5, HNO_4) or TMI-chemistry, which are not treated in INORG. To clarify this question, simulations were done where these chemical subsystems were turned off in C3.0RED. In Fig. 6 time series of the pH inside lower cloud for this sensitivity study are presented. It can clearly be seen that for the urban air mass, the pH shows a diurnal cycle, whereas such cannot be observed for the rural case. Most of the pH-difference in the rural environment can be explained by organic acidification and TMI-chemistry. Here, additional nitrate pathways are of minor importance for the pH. In the urban case, the problem seems more complex. When neglecting the organic chemistry, the difference between INORG and C3.0RED becomes a little smaller during the night. If also the additional nitrate production pathways are neglected somewhat more of the deviation can be explained. The TMI-chemistry has only slight effects on the pH in the urban case.

4.3. Sulfate

The modeled sulfate mass and the relative difference between C3.0RED and INORG can be seen in Fig. 7. Due to in-cloud oxidation of S(IV), the sulfate mass is increased by a factor of 2–3 and ~1.3 for
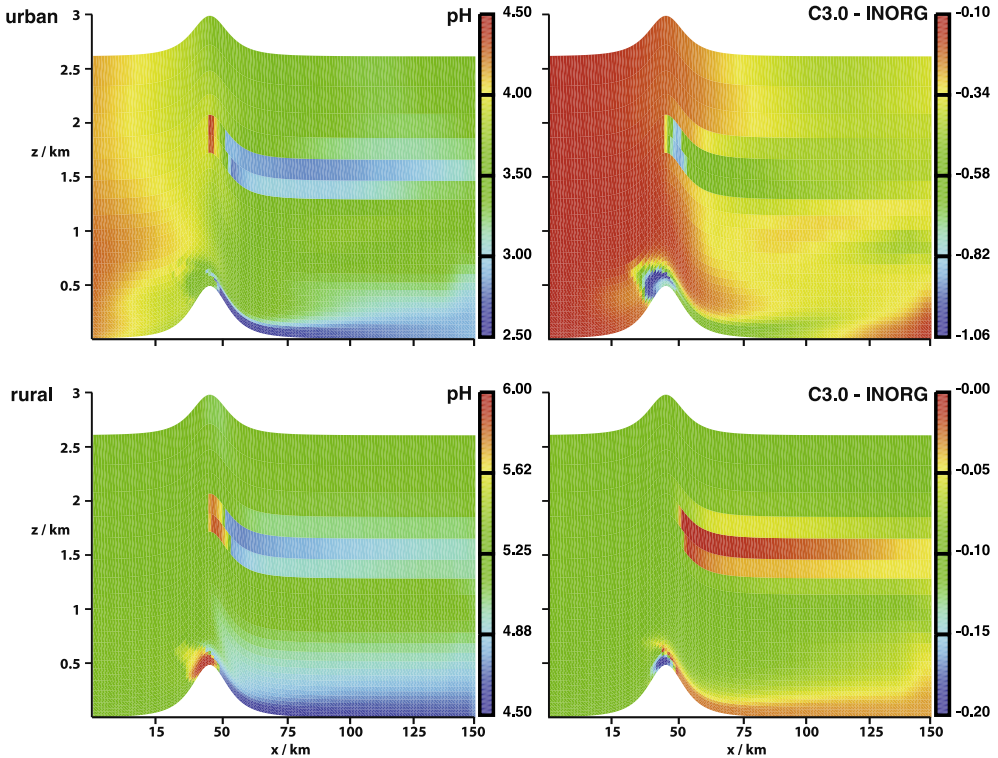
Fig. 5. Modeled pH (left) and difference between C3.0 and INORG (right) for the urban (upper panel) and rural case (lower panel).
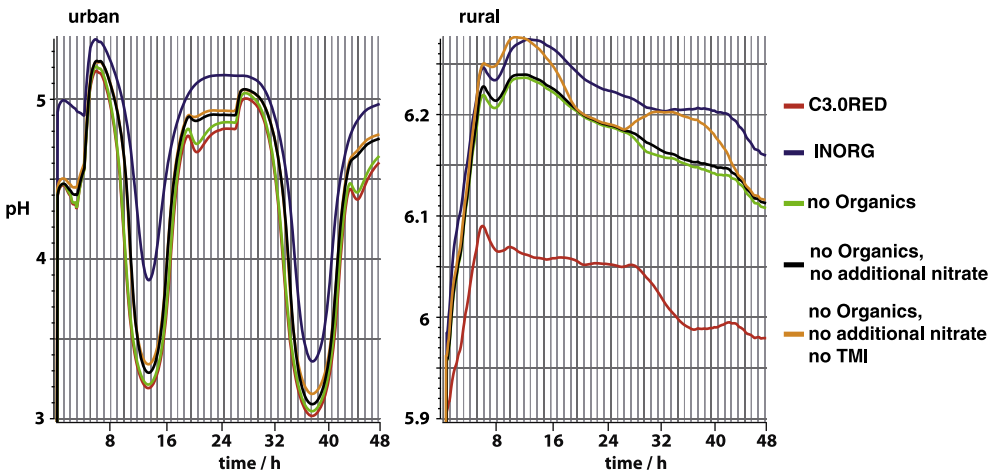

Fig. 6. Time series of modeled pH in the lower cloud for the urban (left) and rural case (right).

the rural and the urban case, respectively. In the aerosol after the cloud passage, the modeled sulfate mass reaches 6–9 μg m^{-3} for rural air and 20–23 μg m^{-3} for urban air. In the rural environment INORG produces generally slightly more sulfate. The relative difference between C3.0RED and INORG

downwind of the hill is up to −5%. The daytime clouds of the urban case produce slightly more sulfate in C3.0RED with a deviation of 3–5% after the cloud passage. During the night, a difference of up to −15% is found, but only for the lower cloud. Overall, these differences are of minor importance in most cases (rural; urban daytime). However, as the different sulfate production pathways are sensitive on the pH, no general conclusion can be given. That means, whether there is a difference in the produced sulfate mass between both mechanisms or not is depending on the difference of the pH and where on the pH-scale this difference occurs. The relative importance of the fluxes of the most important reactions leading to S(VI) are shown in Fig. 8 for the rural air mass and the urban air mass. A diurnal cycle can be seen in the urban environment. The most important reaction in the urban case is the oxidation via H_2O_2. For the less acidic urban nighttime cloud, also the pathway via O_3 becomes important
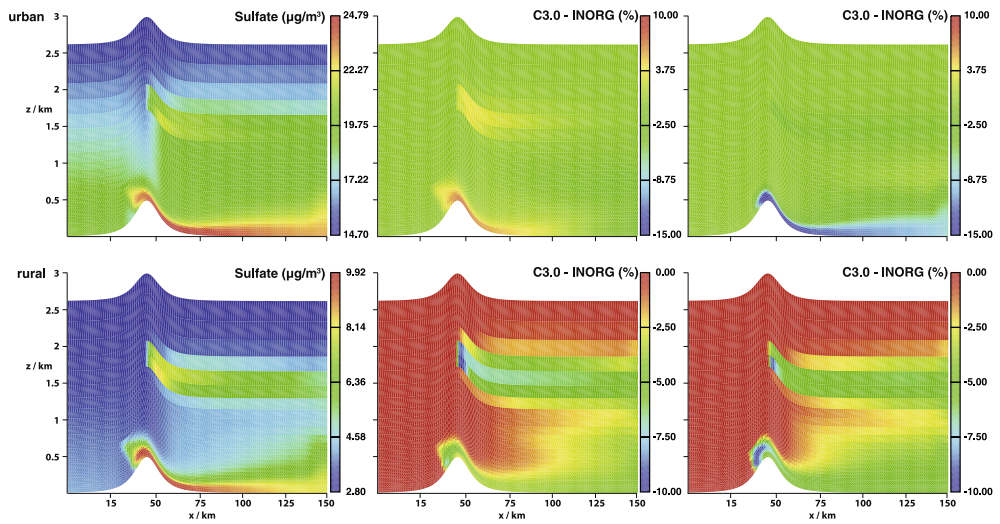

Fig. 7. Modeled sulfate mass (left, $\mu g\ m^{-3}$) after 36 h and relative differences between C3.0RED and INORG during the day (middle) and the night (right) for the urban (upper panel) and rural case (lower panel).
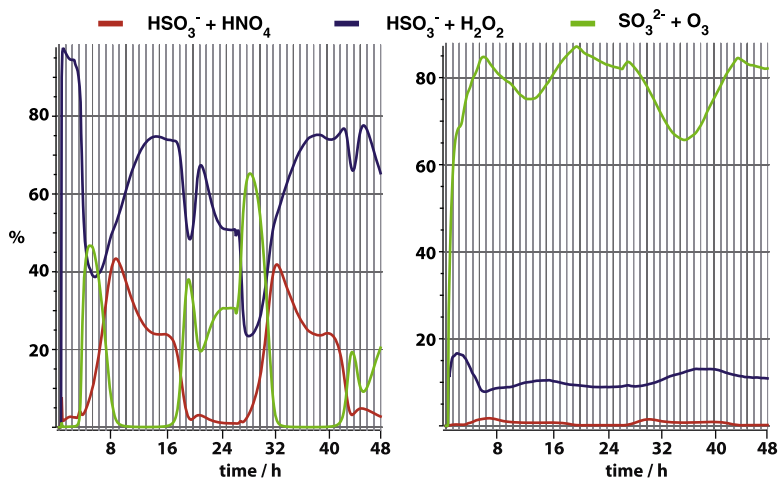

Fig. 8. Relative contribution of the modeled reaction fluxes leading to sulfate in the lower cloud for the urban (left) and rural case (right).

because it reacts with SO_3^{2-}, whereas H_2O_2 reacts with HSO_3^-. The rural case has the least acidic clouds, whereby the ozone reaction becomes most important. Both, the oxidation via H_2O_2 and O_3 are described in C3.0RED as well as in INORG. The reaction of HSO_3^- with HNO_4, which can play a little role in more acidic clouds (e.g. as urban daytime in this study), is only included in C3.0RED.

4.4. Organic aerosol mass

As C3.0RED treats a variety of organic species with up to 4 C-atoms, the cloud processing of these organics was investigated. Fig. 9 shows the modeled organic mass in the aqueous phase after 36 hours. Due to many soluble but volatile compounds it reaches in-cloud maximum values of up to 3.1 $\mu g\,m^{-3}$. After the cloud evaporation many of these substances degas and only less volatile organics stay in the particulate phase. Although the in-cloud organic mass is higher for the rural scenario, the organic mass on the cloud residuals is with $\sim 1\ \mu g\,m^{-3}$ roughly 0.2 $\mu g\,m^{-3}$ higher in the urban air mass. Compared to the particulate organic mass upwind of the clouds, this is an increase by a factor of 3–5. In the atmosphere many organic species with more than 4 C-atoms are present, which are expected to contribute significantly to the organic aerosol mass. Besides that, processes such as oligomerization leading to very low volatile high molecular weight compounds are not treated in C3.0RED. Additionally, C3.0RED does not consider insoluble organic mass as it focuses on the formation of organic acids.

For comparison with available measurements (Sun and Ariya, 2006), the modeled mass of the dicarboxylic acids oxalic acid, glyoxalic acid and pyruvic acid in the cloud residuals was analyzed. Table 2 shows the modeled mass in both environments during the day and the night and the range of reported measurements in brackets. The mass of glyoxalic acid is in the range of the measurements. Oxalic acid tends to be underestimated especially for the urban case, but is at the lower edge of reported atmospheric values. This underestimation is associated with an overestimation of the
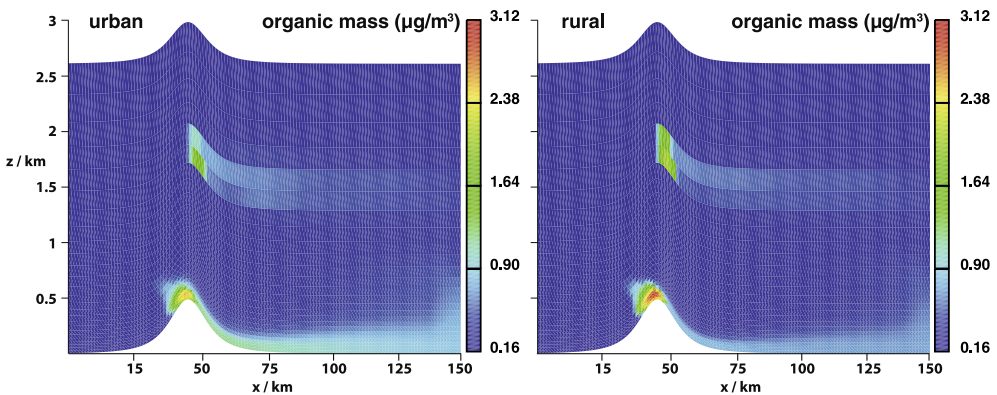

Fig. 9. Modeled organic mass in aqueous phase ($\mu g\,m^{-3}$) for the urban (left) and rural case (right) after 36 h.

Table 2
Modeled concentration of dicarboxylic acids (ng/m^3) after 36 h (daytime) and 48 h (nighttime) for the urban and rural case. Values in brackets show the range of available measurements for urban and rural cases as presented by Sun and Ariya, 2006.

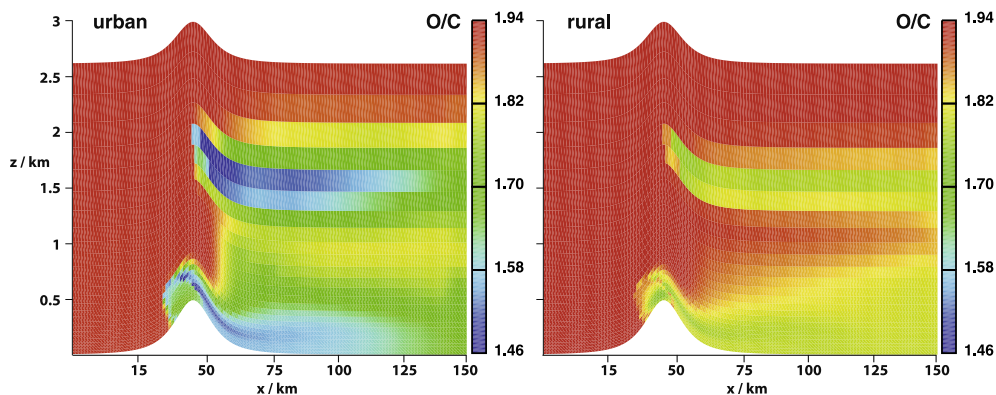|	urban, daytime	urban, nighttime	rural, daytime	rural, nighttime
Oxalic acid	37	186	7	32
	(58 – 1423)		(3.9 – 193)	
Glyoxalic acid	93	93	32	20
	(22 – 174)		(0.9 – 38)	
Pyruvic acid	7	3	8	2
	(27 – 103)		(0.9 – 19.9)	

Fig. 10. Modeled O/C ratio of the organic aerosol for the urban (left) and rural case (right) after 48 h.

photolysis of iron-oxalate complexes in CAPRAM (see Tilgner and Herrmann, 2010). Pyruvic acid is represented well in the rural air mass, but is underestimated in the urban environment. Additionally oxalic acid and pyruvic acid show a strong diurnal cycle due to formation and reduction via OH and NO_3 with different importance.

In recent studies, the O/C-ratio of organic aerosol was measured (e.g. Aiken et al., 2008). For highly oxygenated aerosol an O/C-ratio of ∼1 was reported. Fig. 10 shows the modeled O/C-ratio for both air masses after 48 hours. Upwind of the cloud the ratio is ∼2 because of uptake of some soluble gas phase species (e.g. formic and acetic acid) and oxalate, which is initialized at the beginning of the simulation. Due to cloud chemistry the O/C-ratio drops to 1.6–1.8 with higher values for the rural case. This indicates that in the rural air, the organic aerosol becomes more oxygenated, which agrees with findings from measurements. However, the modeled ratios are much too high compared to atmospheric observations. The reason for that can again be expected to be the lack of an adequate description of high molecular weight substances with usually lower O/C-ratios and neglecting of an insoluble organic mass.

5. Conclusion

The coupled regional chemistry transport model COSMO–MUSCAT was used for investigation of the cloud processing in a rural and an urban air mass. Therefore, the flow over a mountain, where orographic clouds evolve, was investigated in a 2-D domain. The cloud phase chemistry was represented by the complex aqueous phase mechanism CAPRAM3.0i in a reduced version (C3.0RED), which includes a detailed HO_x-, TMI- and organic (up to C4) chemistry as well as the production of sulfate and nitrate. In contrast, a simpler inorganic mechanism (INORG) that focuses on the suitable description of the sulfate production was used. Simulations with both mechanisms were compared to each other and to simulations without aqueous phase chemistry. This model system was applied for sensitivity studies on the behavior of major oxidants (OH, HO_2, H_2O_2, NO_3 and O_3), pH, sulfate mass and organic aerosol mass. Due to cloud phase chemistry of C3.0RED, a strong reduction of the oxidant concentrations, except for ozone, occurs in the area of the cloud. This depletion is stronger in the urban air mass as there are more reaction partners present also in the aqueous phase. After the cloud passage, OH and HO_2 are re-produced very fast, whereas the difference to the pure gas phase run remains substantial for H_2O_2 and NO_3 especially in the urban case. The cloud phase chemistry showed no important effects on the gas phase ozone concentration. In INORG, only H_2O_2 and O_3 are treated in the aqueous phase. The behavior of both substances is comparable to that in C3.0RED.

The modeled cloud water pH reached values of ∼6 in the rural case and ∼3.5–4.5 in the urban case. The comparison of the pH showed that INORG is always less acidic than C3.0RED (with higher

differences for the urban case compared to the rural) leading to potential shifts in other chemical sub-systems such as the sulfate production. For the rural air mass, most of this additional acidification in C3.0RED is caused by organic acid production and TMI-chemistry. In the urban environment, also additional nitrate sources (HNO_4 and N_2O_5) have an effect on the pH.

As the pH influences the oxidation of S(IV) to form S(VI), differences between C3.0RED and INORG were observed for the sulfate mass. The deviations reached from 3% to -15% when using C3.0RED instead of INORG, whereas the highest differences occurred during the night in the urban case. The investigation of reaction fluxes of the aqueous sulfate production in C3.0RED showed that during day and night and in both environments different S(IV) oxidation pathways are relevant. Besides the most important oxidants H_2O_2 and O_3, also HNO_4 can play a role. The importance of the sulfate production pathways is depending on the pH as H_2O_2 and HNO_4 react with HSO_3^- and O_3 reacts with SO_3^{2-}. The latter reaction becomes more important in less acidic regimes, whereas the pathways via H_2O_2 and HNO_4 are more relevant the more acidic the cloud droplet is.

The modeled organic mass in cloud residuals reached values of ~ 1 μg m^{-3} and ~ 0.8 μg m^{-3} for the urban and rural case, respectively. Due to the lack of higher molecular weight compounds and other processes such as oligomerization, this organic mass is smaller than observed by field studies. Hence, also the modeled O/C-ratio (1.6–1.8) is higher than what could be expected from atmospheric observations.

The mass of glyoxalic acid, oxalic acid and pyruvic acid have been compared with reported values of atmospheric measurements. In the rural case, the modeled concentrations are in the range of available measurements. For the urban air mass, glyoxalic acid is comparable to atmospheric conditions, whereas oxalic acid and pyruvic acid are underestimated.

Further development of the chemical mechanism in combination with an enhanced microphysical approach is required for a more appropriate description of the atmospheric multiphase system in 3-D models. This system should be applied in 2-D and 3-D sensitivity studies and realistic scenarios.

Acknowledgement

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