

Introduction and Model Outline

The parcel model SPACCIM (Spectral Aerosol Cloud Chemistry Interaction Model; Wolke et al., 2005) has been applied to investigate the effect of physico-chemical cloud processing on tropospheric aerosol particles and trace gases resulting from passages through warm tropospheric clouds. The simulations were focused on the multiphase aerosol cloud processing of tropospheric oxidants as well as in particular organic atmospheric trace constituents. The applied air parcel model SPACCIM (Wolke et al., 2005) combines a complex multiphase chemistry with detailed microphysics. 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. All microphysical parameters required by the multiphase chemistry model are taken over from the microphysical model. The adiabatic air parcel model contains a detailed description of microphysical processes of deliquescent aerosol particles and droplets (Simmel et al., 2005). The applied explicit multiphase mechanism consists of CAPRAM 3.0 (Herrmann et al., 2005) with 777 reactions and the gas phase mechanism RACM (Stockwell et al., 1997) with 261 reactions. CAPRAM 3.0 contains a complex implementation of aqueous phase inorganic as well as organic chemistry including organic species with up to mainly four carbon atoms based on time-dependent size-resolved aerosol/cloud spectra. Phase transfer processes are treated by means of the resistance model of Schwartz considering Henry's equilibrium, gas phase diffusion and mass accommodation coefficients.

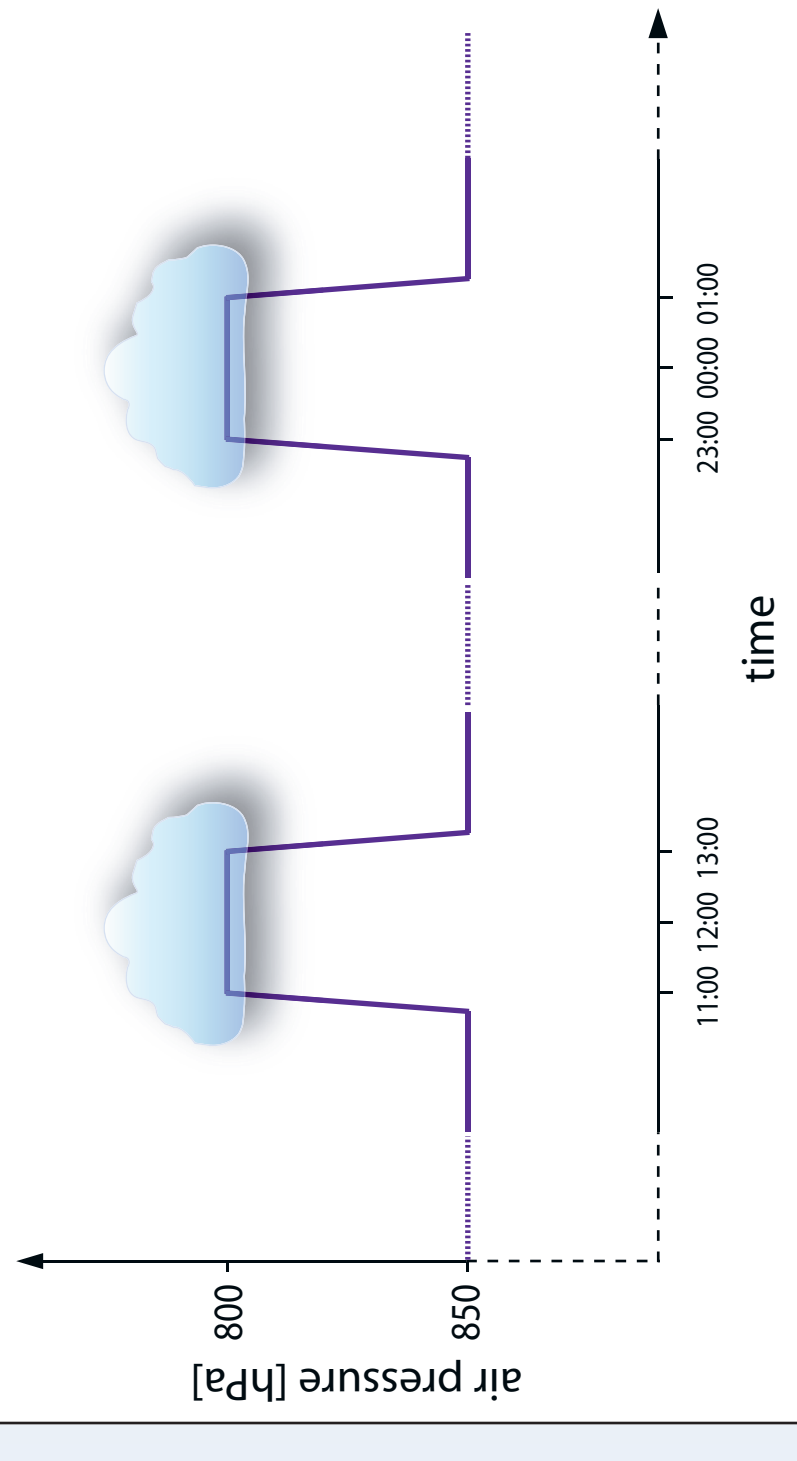


Figure 1: Scheme of the meteorological scenario (model trajectory of the air parcel). The chemical mechanism was initialised with physical and chemical data from the EUROTRAC-2 project CMD (cp. Poppe et al., 2001 and references therein). For the simulations a finely resolved particle spectrum is considered. The simulations have been carried out for a meteorological scenario in which an air parcel moves along a predefined trajectory, including eight cloud passages of about two hours within 108 hours modelling time and an intermediate aerosol state at a 90% relative humidity level (cp. Figure 1) by neglecting the effects of non-ideal solutions. Simulations were performed here only the results of atmospheric scenarios (marine/remote/urban) beginning at 0:00 on the 19th of June (45°N) [presented here only the results of the remote and urban scenario]. The characteristic time periods of in-cloud and intermediate aerosol phases were derived from the global calculations of Pruppacher and Jaenicke (1995). Simulations have been carried out with and without aqueous phase chemistry to investigate the effect of multiphase aerosol-cloud chemistry interaction on the tropospheric multiphase system.

Simulation Results and Discussion

Microphysical Conditions and pH

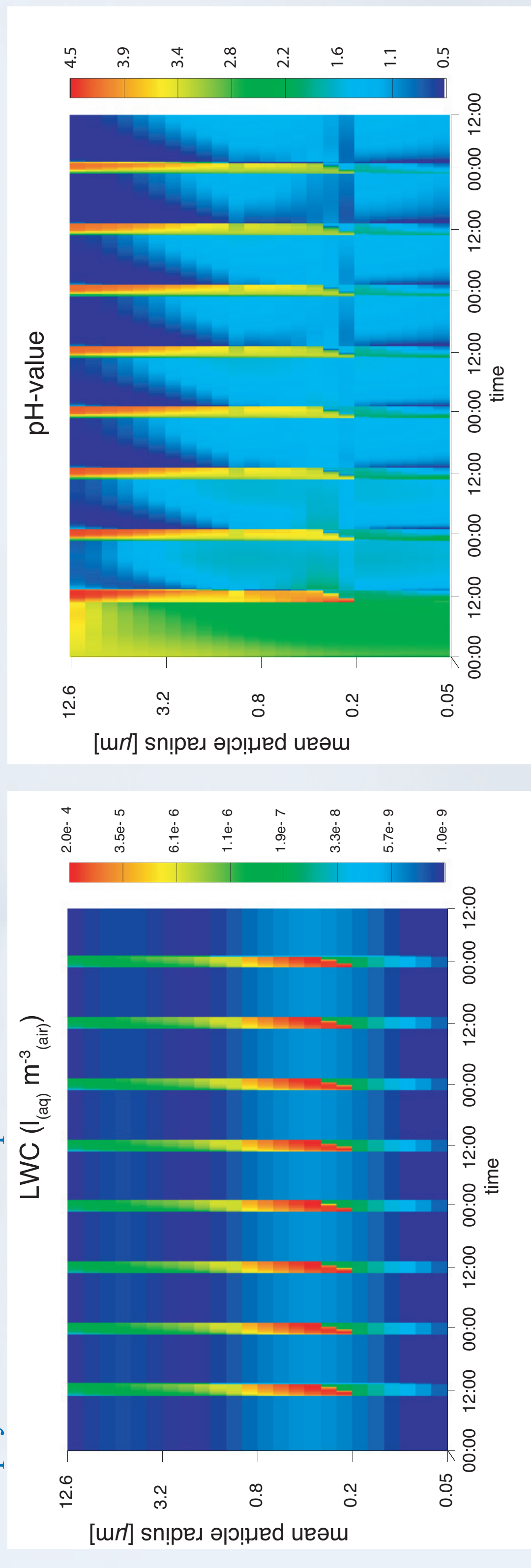


Figure 2: Size-resolved temporal evolution of the liquid water content in $\mu\text{m}^3 \text{ (air)}$ (left) and pH of the urban scenario (right).

Radical Oxidants

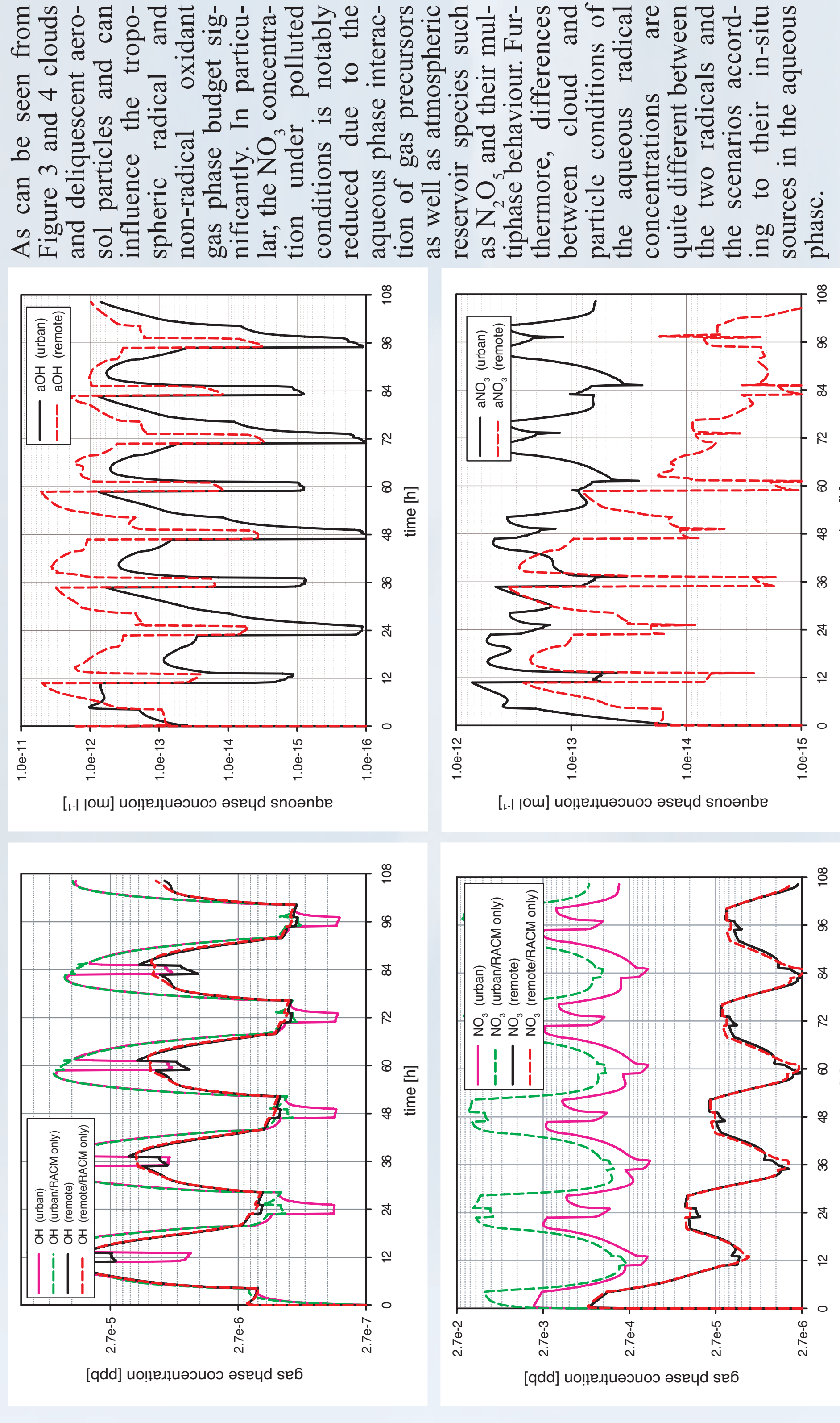


Figure 3: Modelled gas and aqueous phase concentrations of the OH and NO_3 radical for the urban and remote scenario.

Non-Radical Oxidants

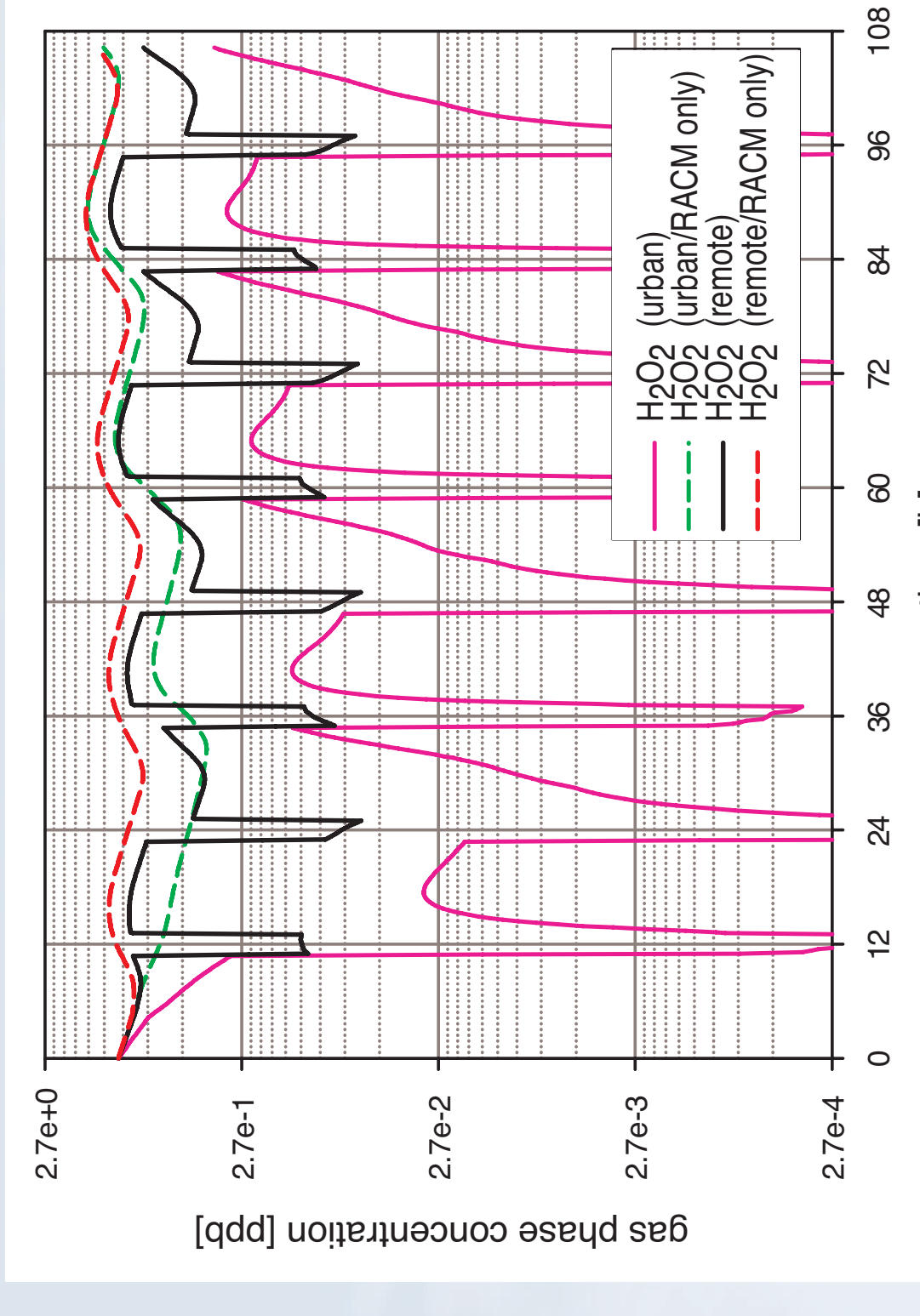


Figure 4: Modelled gas phase mixing ratios of H_2O_2 and O_3 for the urban and remote atmospheric scenario. Due to the higher availability of reactants as well as the separation of chemical precursors between the two phases the non-radical species concentrations are significantly influenced under polluted atmospheric conditions compared to a model run with gas phase chemistry only. Contrary to the urban case, the multiphase effect on H_2O_2 as well as O_3 is of minor importance. In the urban case about 50% of the acetic acid is produced by aqueous oxidations mainly under in-cloud daytime conditions. A more complex behaviour can be observed for glyoxal including different effects of day and night clouds. Due to the significant uptake into cloud droplets the efficient glyoxal gas phase degradation is reduced under day time conditions. For this reason the gas phase concentration is higher after the cloud passage. A different picture can be obtained in the nighttime clouds which show lower concentrations after the cloud passage compared to the model simulation without aqueous phase chemistry. This fact is caused by in-cloud oxidations as well as reduced glyoxal gas phase yields according to the changed gas phase oxidant concentrations. Moreover, also other VOC's show similar concentration profiles as can be seen in figure 5 (down left). The influence on the gas phase concentrations of glyoxal (GLY) as well as the lumped RACM species DCB budget in the cloud as well as by aqueous oxidations of butane-unsaturated dicarbonyls and HCB (reactive hydrocarbons with dial and ethylene glycol, respectively).

Organic Multiphase Chemistry

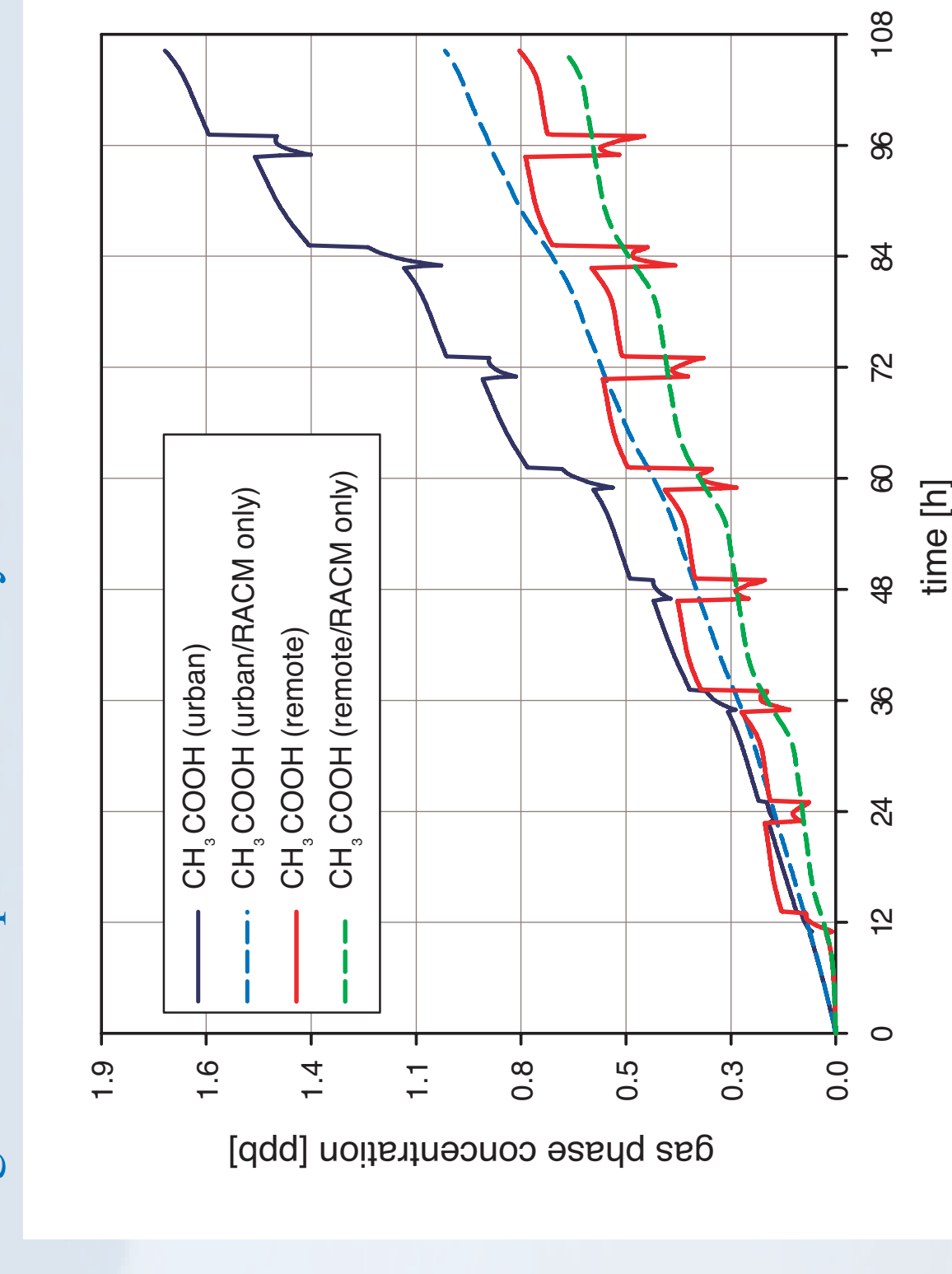


Figure 5 shows the influence of the aqueous oxidation processes on important VOC's such as acetic acid and glyoxal. The concentrations in the gas phase are significantly influenced by in-cloud processing as well as changed gas phase radical budgets. In the urban case about 50% of the acetic acid is produced by aqueous oxidations mainly under in-cloud daytime conditions. A more complex behaviour can be observed for glyoxal including different effects of day and night clouds. Due to the significant uptake into cloud droplets the efficient glyoxal gas phase degradation is reduced under day time conditions. For this reason the gas phase concentration is higher after the cloud passage. A different picture can be obtained in the nighttime clouds which show lower concentrations after the cloud passage compared to the model simulation without aqueous phase chemistry. This fact is caused by in-cloud oxidations as well as reduced glyoxal gas phase yields according to the changed gas phase oxidant concentrations. Moreover, also other VOC's show similar concentration profiles as can be seen in figure 5 (down left). The influence on the gas phase concentrations of glyoxal (GLY) as well as the lumped RACM species DCB budget in the cloud as well as by aqueous oxidations of butane-unsaturated dicarbonyls and HCB (reactive hydrocarbons with dial and ethylene glycol, respectively).

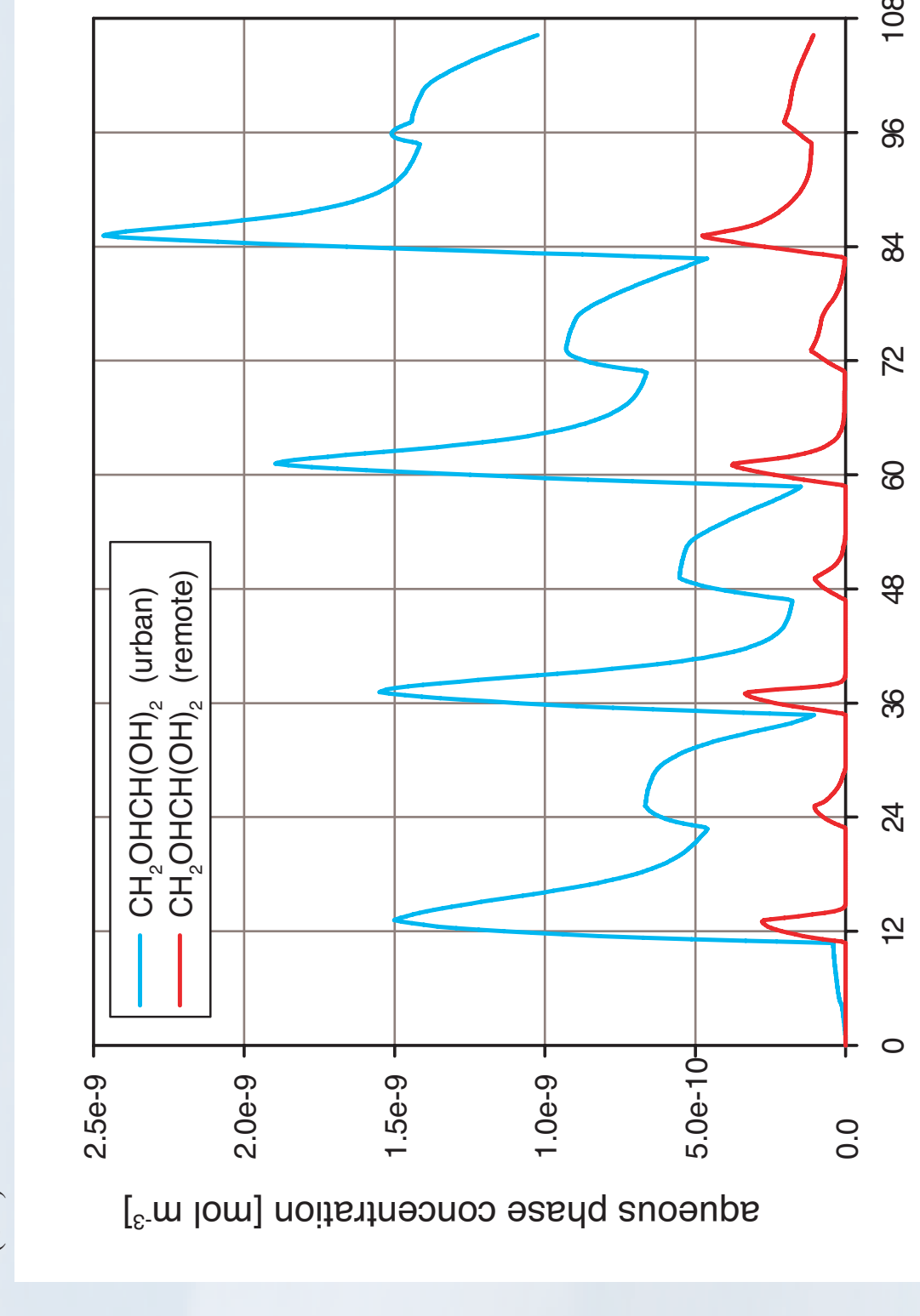


Figure 6: Modelled aqueous phase concentrations of glycolaldehyde, glycolic acid and glyoxylic acid in mol m^{-3} (air).

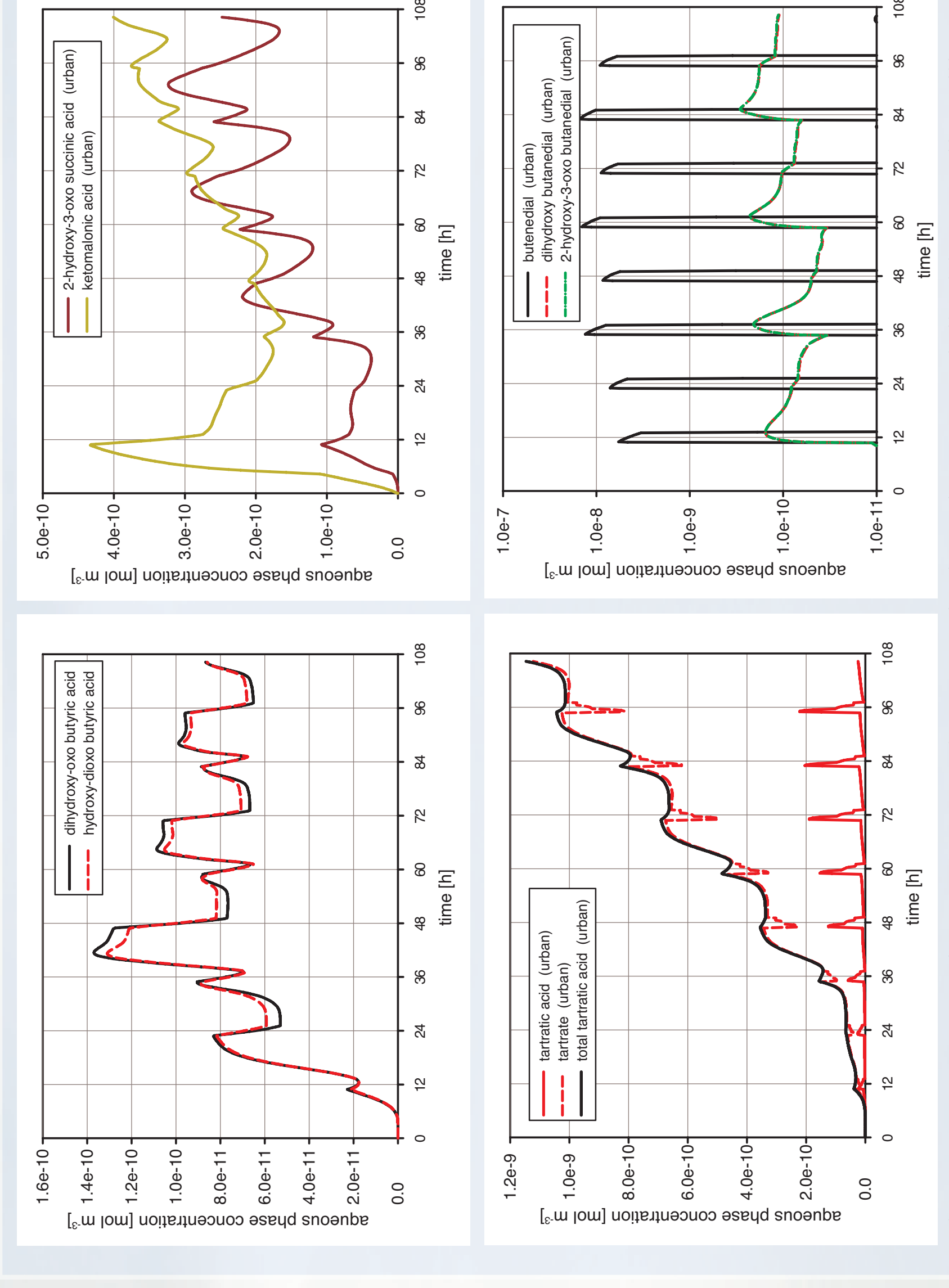
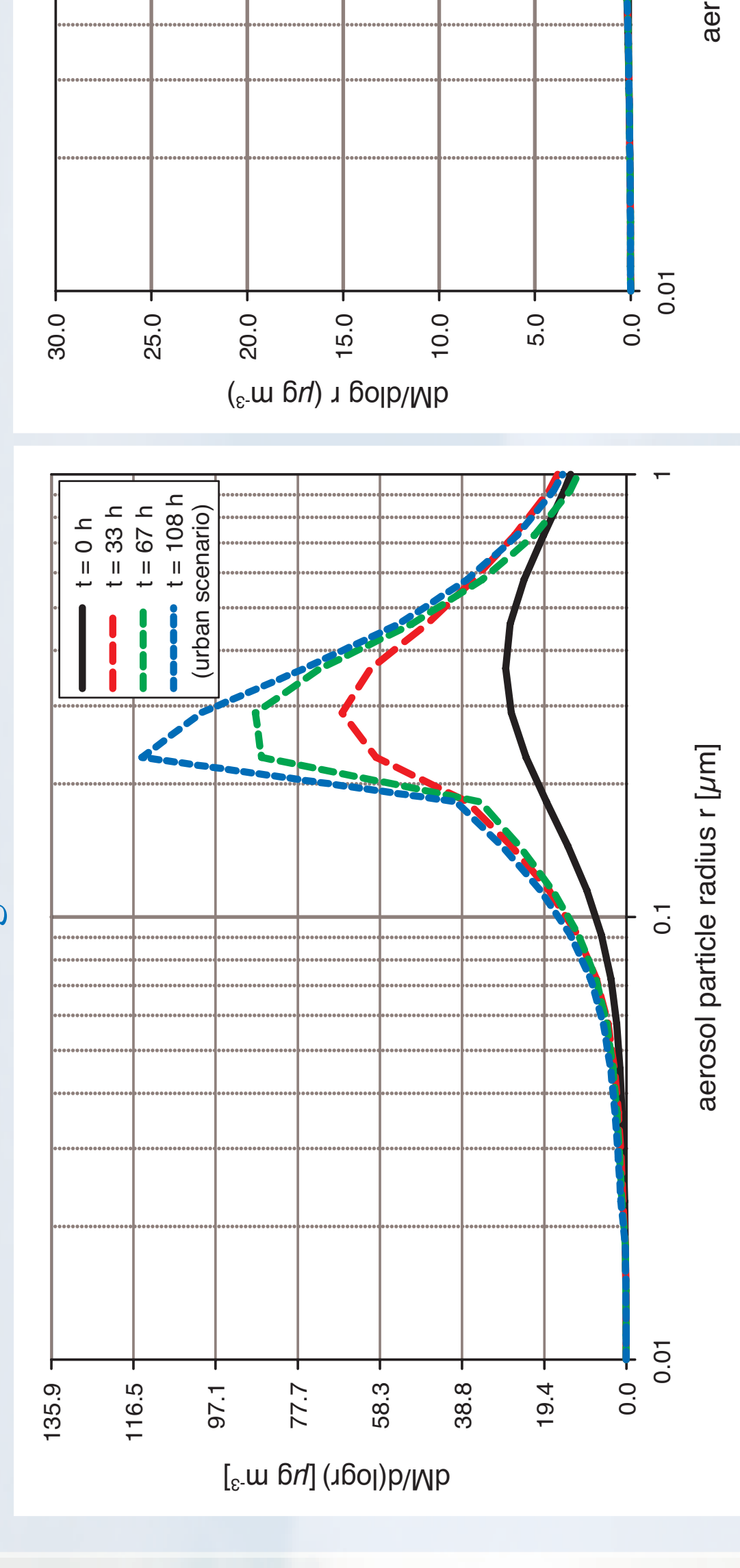


Figure 7: Aqueous phase concentrations of substituted mono and diacids as well as dibutylaldehydes in the urban scenario.

Aerosol Particle Mass Processing



The simulation results plotted in Figure 8 show the modification of the aerosol spectra as well as the total aerosol mass according to the physico-chemical processes. As can be seen from the plots, the aerosol cloud processing is strongly affected by physical losses in the remote case. In contrast, in the polluted case the chemical processing is the dominant process up to a particles size of $1 \mu\text{m}$. In the urban scenario, a mass production of about $30 \mu\text{g m}^{-3}$ during the simulation time can be observed. Furthermore, the comparison of the processed aerosol spectra shows the most significant mass increase in the size interval between the activation diameter and about 500 nm . This result is in a good agreement with previous model findings (Tilgner et al., 2005). As can be seen from Figure 8 (down left), beside the in-cloud processing, the aerosol mass is also affected under the intermediate particle state conditions due to the uptake of volatile trace gases to the deliquescent particles including e.g. a deacidification as can be seen in Figure 2.

Summary

SPACCIM simulations on the multiphase aerosol processing were carried out for different atmospheric environmental conditions considering a detailed microphysics and multiphase chemistry (RACM/CAPRAM 3.0). Significant effects on the tropospheric oxidation capacity due to the multiphase cloud droplet and aqueous aerosol interactions has been modelled for polluted environmental conditions. Furthermore, the model results point out the influence of multiphase processes on gas phase concentrations of important oxidants as well as VOC's. Significant cloud condensation nuclei modifications with sizes mainly up to 500 nm have been modelled considering a mass increase of about $30 \mu\text{g m}^{-3}$ under polluted conditions. Moreover, the results implicate the importance of the aqueous phase for the formation of higher oxidised organic compounds such as substituted mono- and diacids. Organic mass productions of substituted diacids such as tartaric acid in the aqueous phase of about $0.17 \mu\text{g m}^{-3}$ has been modelled in good agreement with the permanent cloud studies of Herrmann et al. (2005).

References

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Acknowledgement

This study was supported by the Scholarship Programme of the German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt, DBU).