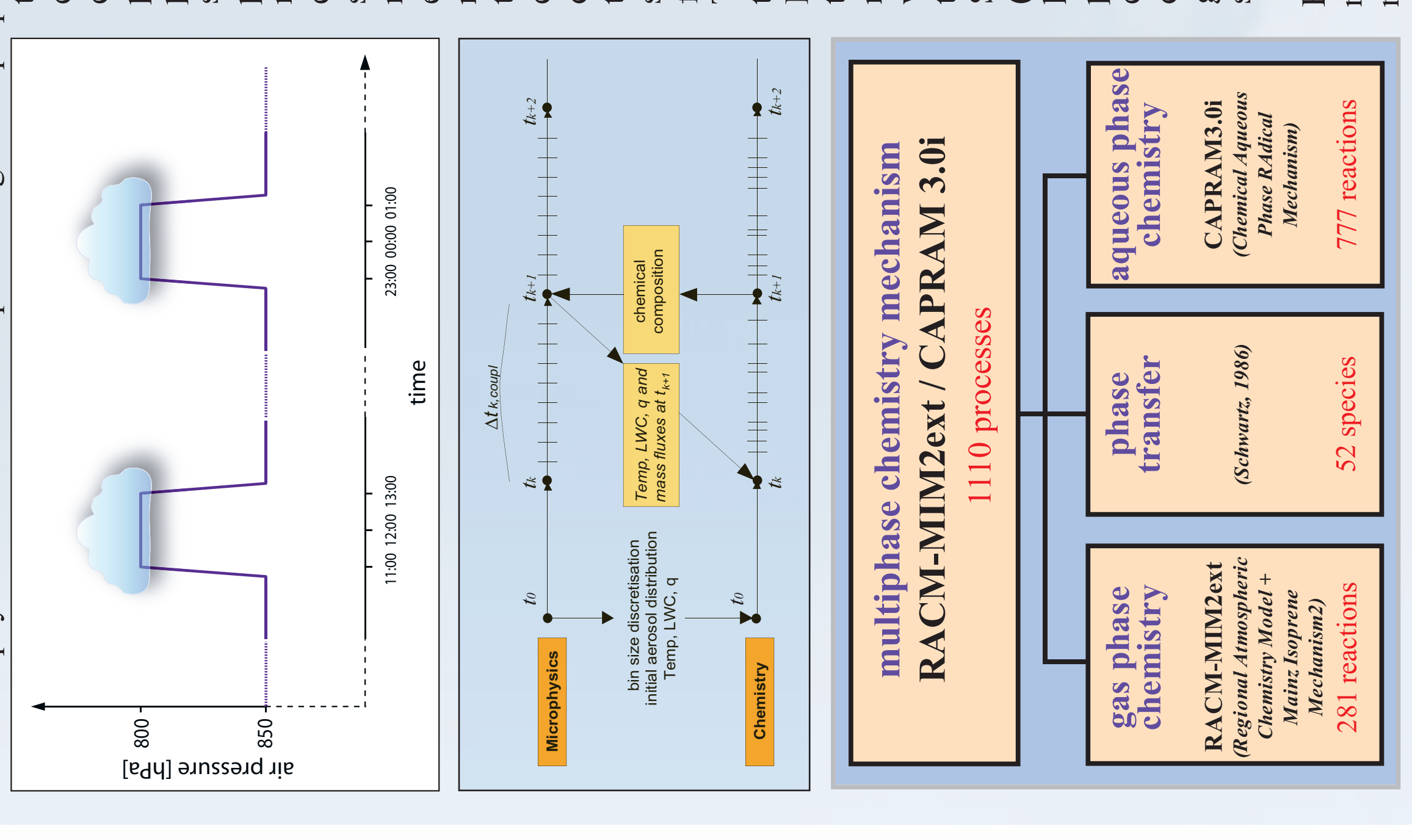


## Introduction and Model Outline

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 aerosols and trace gases resulting from passages through warm tropospheric clouds. The simulations were focused on the multiphase aerosol cloud processing of tropospheric aerosols, in particular organic atmospheric trace constituents and the spectral aerosol particle mass processing as well. 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. All microphysical parameters required by the multiphase chemistry model are taken over from the microphysical model like presented in Figure 1. 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 the aqueous phase mechanism CAPRAM 3.0 (Herrmann et al., 2005) with 777 reactions and an extended version of the gas phase mechanism RACM-MIM2 (Karr et al., 2006) with 281 reactions. CAPRAM 3.0 contains a complex implementation of aqueous phase inorganic as well as organic chemistry including organic species with mainly up to four carbon atoms based on time-dependent size-resolved aerosol particle/cloud droplet 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.

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 8 cloud passages of about 2 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 for three different atmospheric scenarios (marine/remote/urban) beginning at 0:00 on the 19<sup>th</sup> 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 (acronym: woCloud) aqueous phase chemistry to investigate the effect of multiphase aerosol-cloud chemistry interaction on the tropospheric multiphase system.

Figure 1. Scheme of the meteorological model scenario (top), the microphysics-chemistry model coupling (middle) as well as the applied multiphase chemistry mechanism RACM-MIM2ext/CAPRAM 3.0 (down).



## Non-Radical Oxidants

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 compared to a model run with gas phase chemistry only. In the urban case, the  $O_3$  concentration is affected particularly during the daytime cloud passages resulting in a reduction of the gas phase concentration of about 25% at the end of the simulation time. In contrast to the indirect cloud effect on  $O_3$ , the  $H_2O_2$  gas concentration is mainly influenced by the reactivity in the aqueous phase of the cloud droplets as well as deliquescent particles. Consequently, in-cloud processes including e.g. an effective aqueous phase transitional metal ion chemistry can lead to a distinctive increased  $H_2O_2$  gas phase concentration under remote environmental conditions.

## Organic Multiphase Chemistry

Figure 4 shows the influence of the aqueous oxidation processes on important VOC's such as methylglyoxal, glyoxal and glycolaldehyde. The concentrations in the gas phase are significantly influenced by both in-cloud processes and the changed gas phase radical budget. For emitted gas phase compounds like ethene, the degradation flux is substantially decreased particularly under day time cloud conditions mainly due to the reduced gas phase HO<sub>2</sub> radical budget. But for species with relevant NO<sub>2</sub> reaction rates also effects of the night-time clouds can be observed. A much more complex behaviour can be obtained for gas phase oxidation products which are soluble enough to be taken up into and interact with the aqueous phase like methylglyoxal and ethylene glycol. As can be seen from Figure 6, aqueous phase oxidation processes can influence the gas phase concentrations and act as important sinks. Under continental background (remote) conditions the aqueous phase contribute with 7%, 31%, 47% and 93% to the total degradation of methylglyoxal, glyoxal, glycolaldehyde and ethylene glycol, respectively.

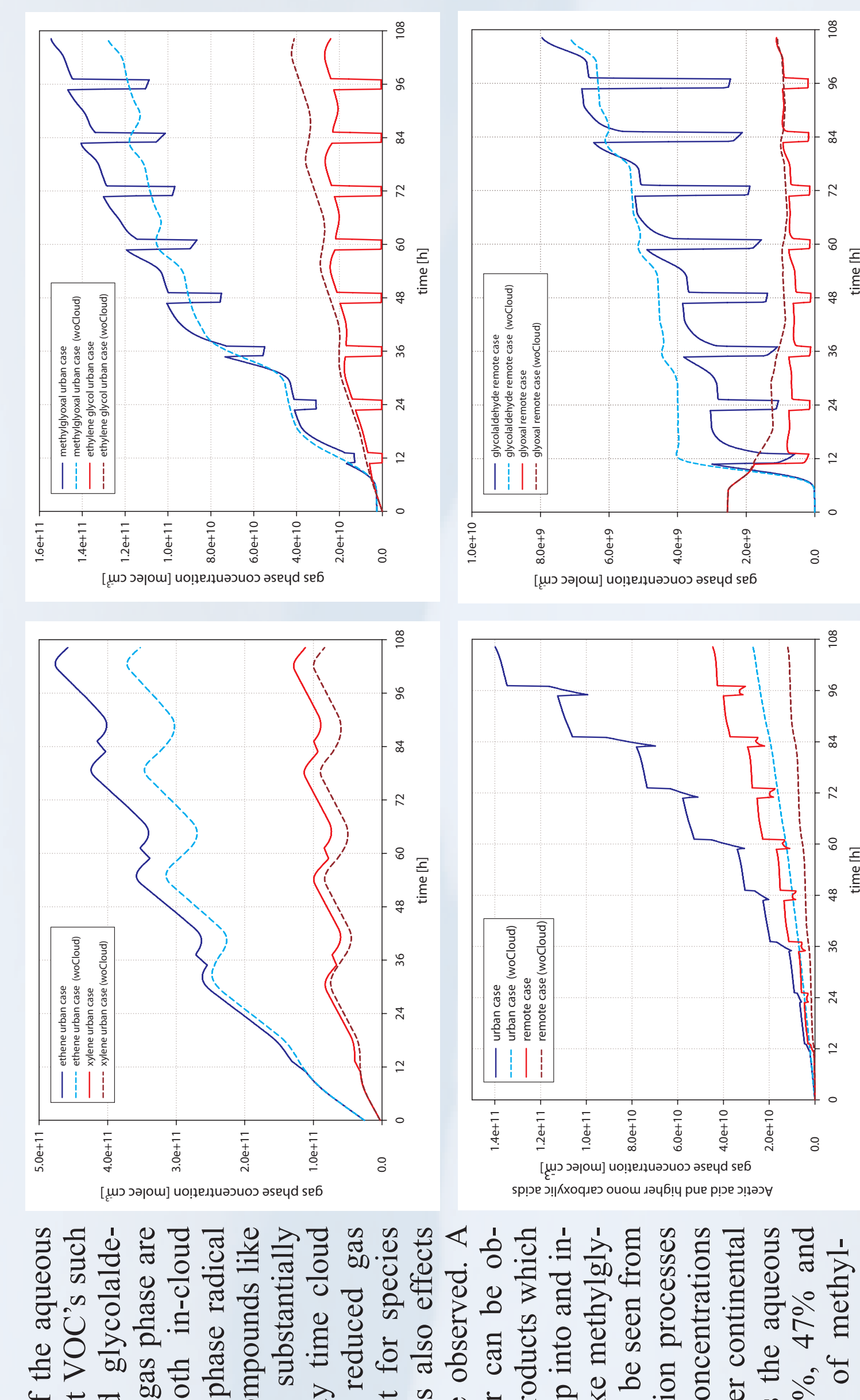


Figure 4. Modelled gas phase concentrations of ethene, methylglyoxal, glyoxal, glycolaldehyde and glyoxal for the urban and remote case, respectively.

## Aerosol Particle Mass Processing

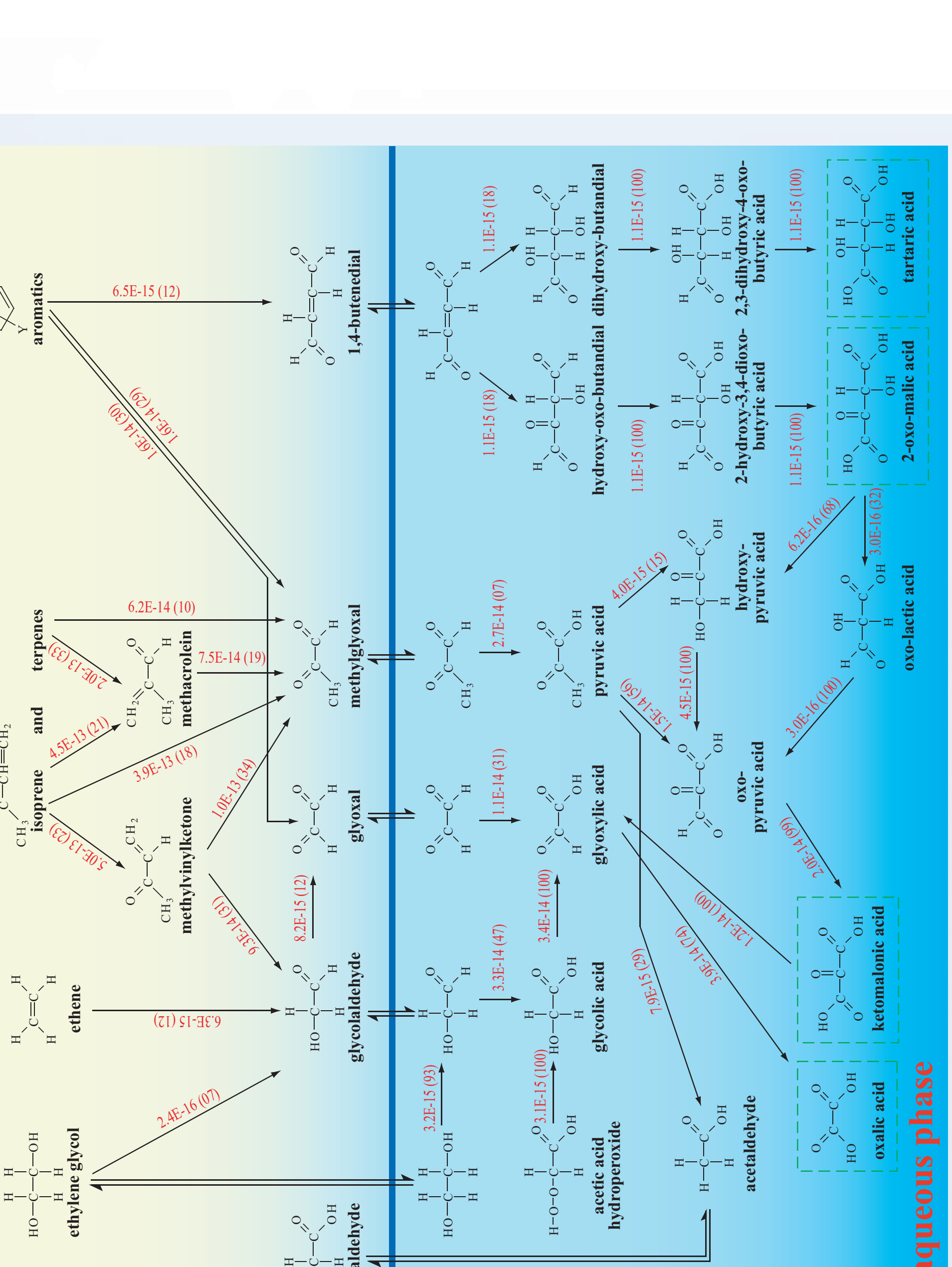


Figure 6. Scheme of the most important oxidation pathways for C-C organics contributing to the particulate organic mass for the remote case (fluxes in mol m<sup>-3</sup> s<sup>-1</sup> percentages in parenthesis).

## Radical Oxidants

As can be seen from Figure 2 and 3 clouds and deliquescent particles can influence the tropospheric radical as well as non-radical oxidant gas phase budget significantly. In particular under polluted conditions, the gas phase concentrations are notably reduced due to the aqueous phase interaction of the gas precursors and their own multiphase behaviour. Furthermore, the aqueous radical concentrations of NO<sub>2</sub> and OH show interesting differences between cloud and two scenarios according to the role of their in-situ sources in the aqueous phase and the direct phase transfer. Contrary to the NO<sub>2</sub> radical, in-situ sources of OH can be significantly contribute to the radical budget in the aqueous phase of both deliquescent particles and cloud droplets beside the direct phase transfer from the gas phase.

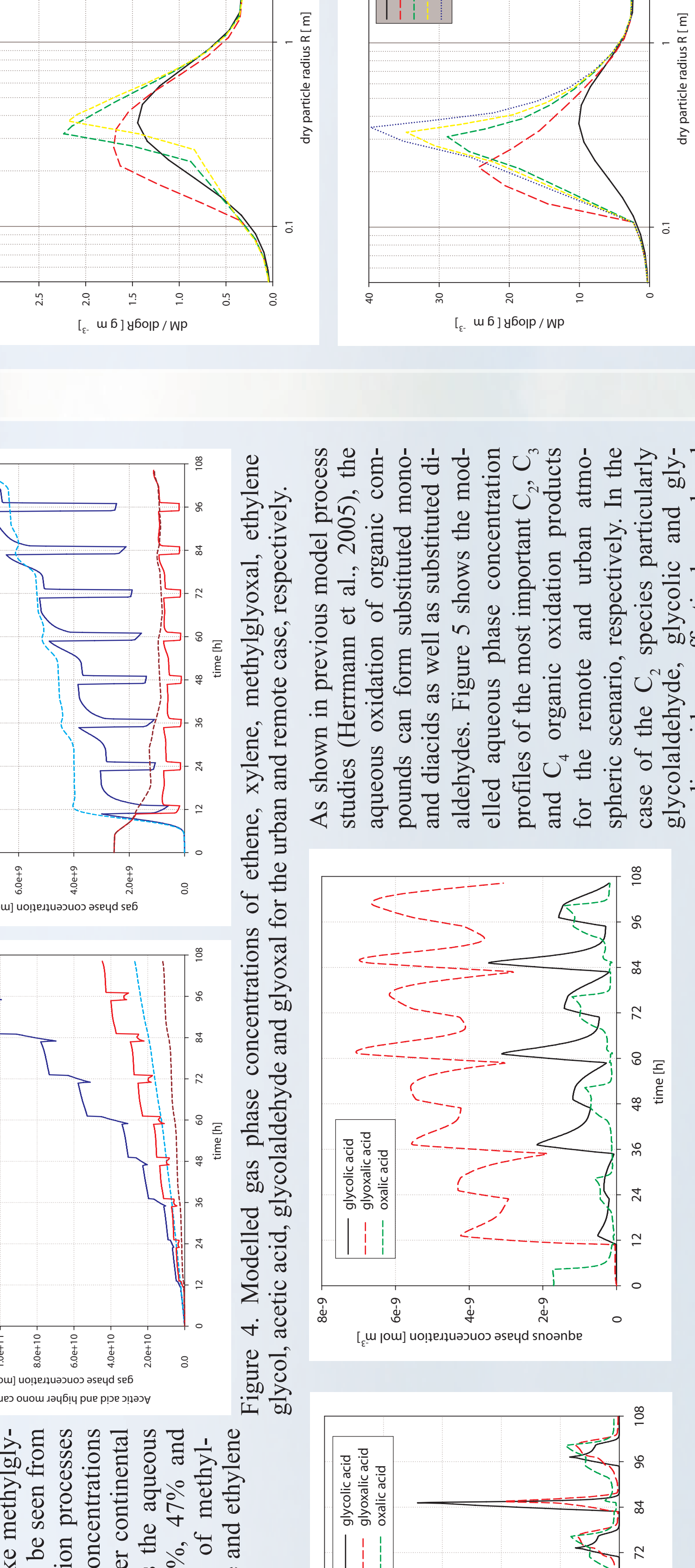


Figure 2. Modelled gas and aqueous phase concentrations of the OH and NO<sub>2</sub> radical for the urban and remote scenario. Chemical analysis (down) of the most important aqueous phase sink and source processes of OH and NO<sub>2</sub> radical in mol m<sup>-3</sup> s<sup>-1</sup> under urban conditions.

## Summary and Outlook

Simulations with the parcel model SPACCIM have been carried out for different atmospheric conditions considering detailed microphysics and multiphase chemistry (RACM-MIM2ext/CAPRAM 3.0) to investigate the effect of multiphase processing of tropospheric aerosol particles and trace gases based on more realistic meteorological non-permanent cloud scheme. The model studies show significant effects of multiphase cloud droplet and deliquescent aerosol particle 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 production of radical oxidants such as OH and non-radical oxidants such as H<sub>2</sub>O<sub>2</sub>. Moreover, the model study shows the importance of the aqueous phase for the formation of higher oxidised organic compounds such as substituted mono- and diatomic OH radical sinks under polluted environmental conditions contributing to the production of less volatile organic compounds and thus the organic aerosol particle mass. Further, in-cloud oxidation of methylglyoxal and its oxidation products seems to be an efficient sink for NO<sub>2</sub> radicals in the aqueous phase particularly under urban as well as under remote conditions. Finally, the sum of the results implicates the importance of the aqueous phase processes to be considered in future higher scale chemistry transport models.

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