

Introduction and Model Outline

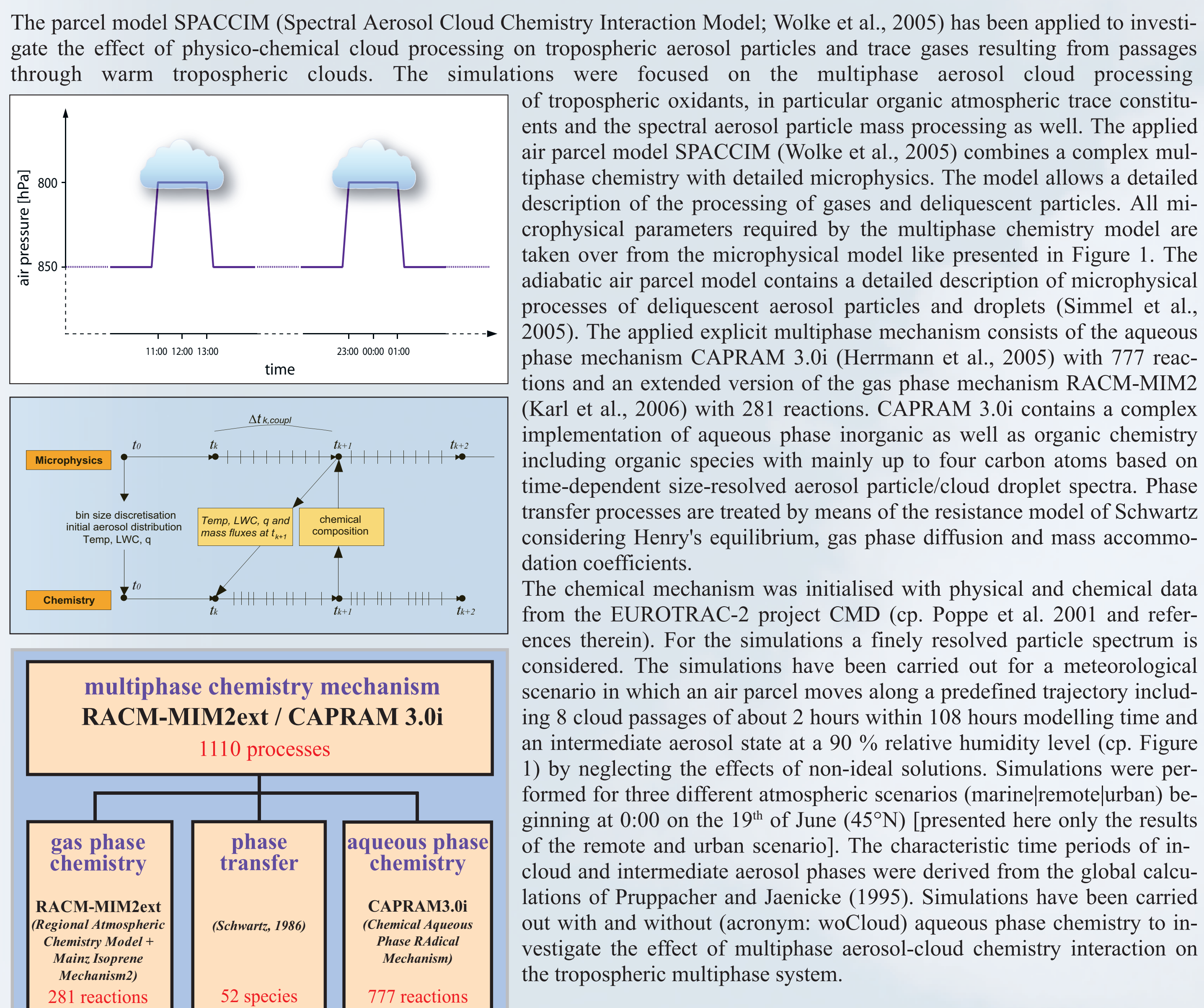


Figure 1. Scheme of the meteorological model scenario (top), the microphysics-chemistry model coupling (center) as well as the applied multiphase chemistry mechanism RACM-MIM2ext/CAPRAM3.0i (bottom).

Results and Discussion

Radical Oxidants

As can be seen from Figure 2 clouds and deliquescent particles can influence the tropospheric 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_3 and OH show interesting differences between cloud and particle conditions as well as the two scenarios according to the role of their in-situ sources in the aqueous phase and the direct phase transfer. Contrary to the NO_3 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.

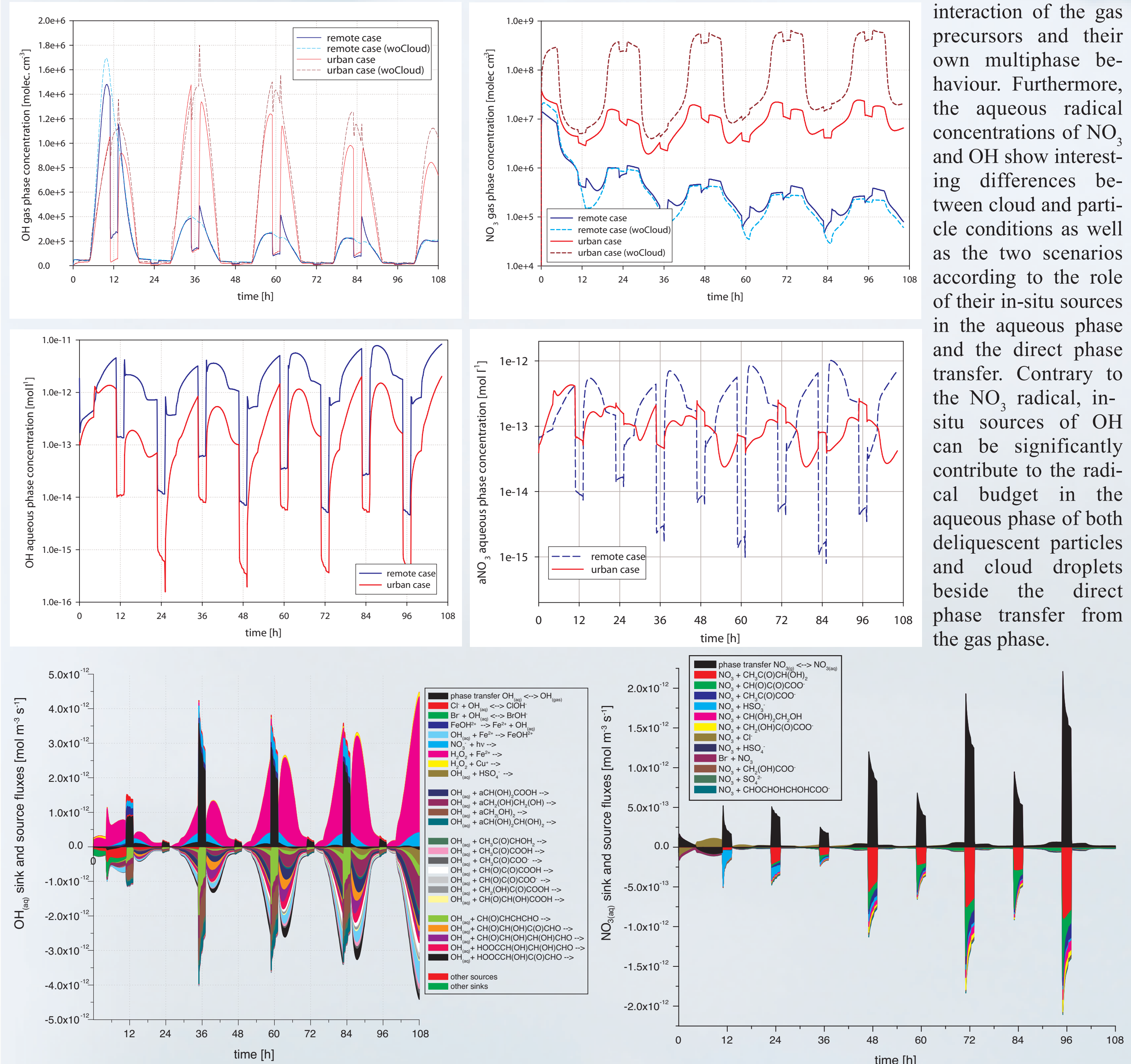


Figure 2. Modelled gas and aqueous phase concentrations of the OH and NO_3 radical for the urban and remote scenario. Chemical analysis (bottom) of the most important aqueous phase sink and source processes of the OH and NO_3 radical in $\text{mol m}^{-3} \text{s}^{-1}$ under urban conditions.

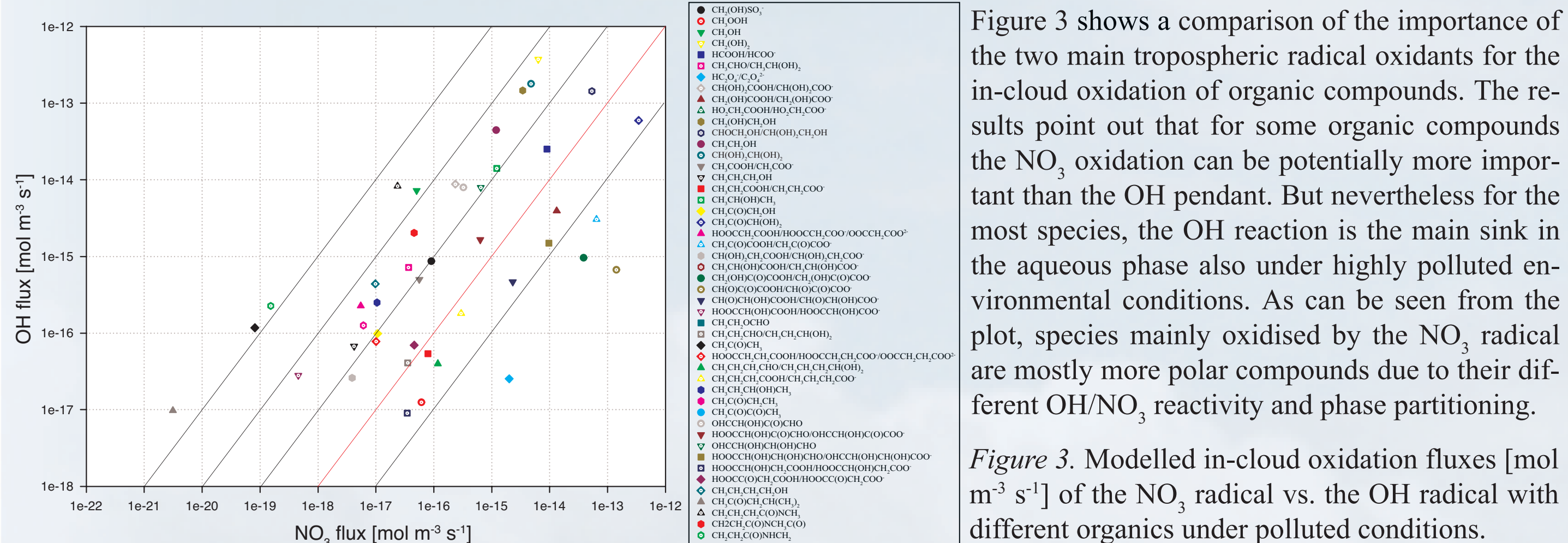


Figure 3 shows a comparison of the importance of the two main tropospheric radical oxidants for the in-cloud oxidation of organic compounds. The results point out that for some organic compounds the NO_3 oxidation can be potentially more important than the OH pendant. But nevertheless for the most species, the OH reaction is the main sink in the aqueous phase also under highly polluted environmental conditions. As can be seen from the plot, species mainly oxidised by the NO_3 radical are mostly more polar compounds due to their different OH/ NO_3 reactivity and phase partitioning.

Figure 3. Modelled in-cloud oxidation fluxes [$\text{mol m}^{-3} \text{s}^{-1}$] of the NO_3 radical vs. the OH radical with different organics under polluted 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 HO₂ radical budget. But for species with relevant NO_3 reaction rates also effects of the night-time clouds can be observed. A much more complex behaviour has been 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, xylene, methylglyoxal, ethylene glycol, acetic acid, glycolaldehyde and glyoxal for the urban and remote case, respectively.

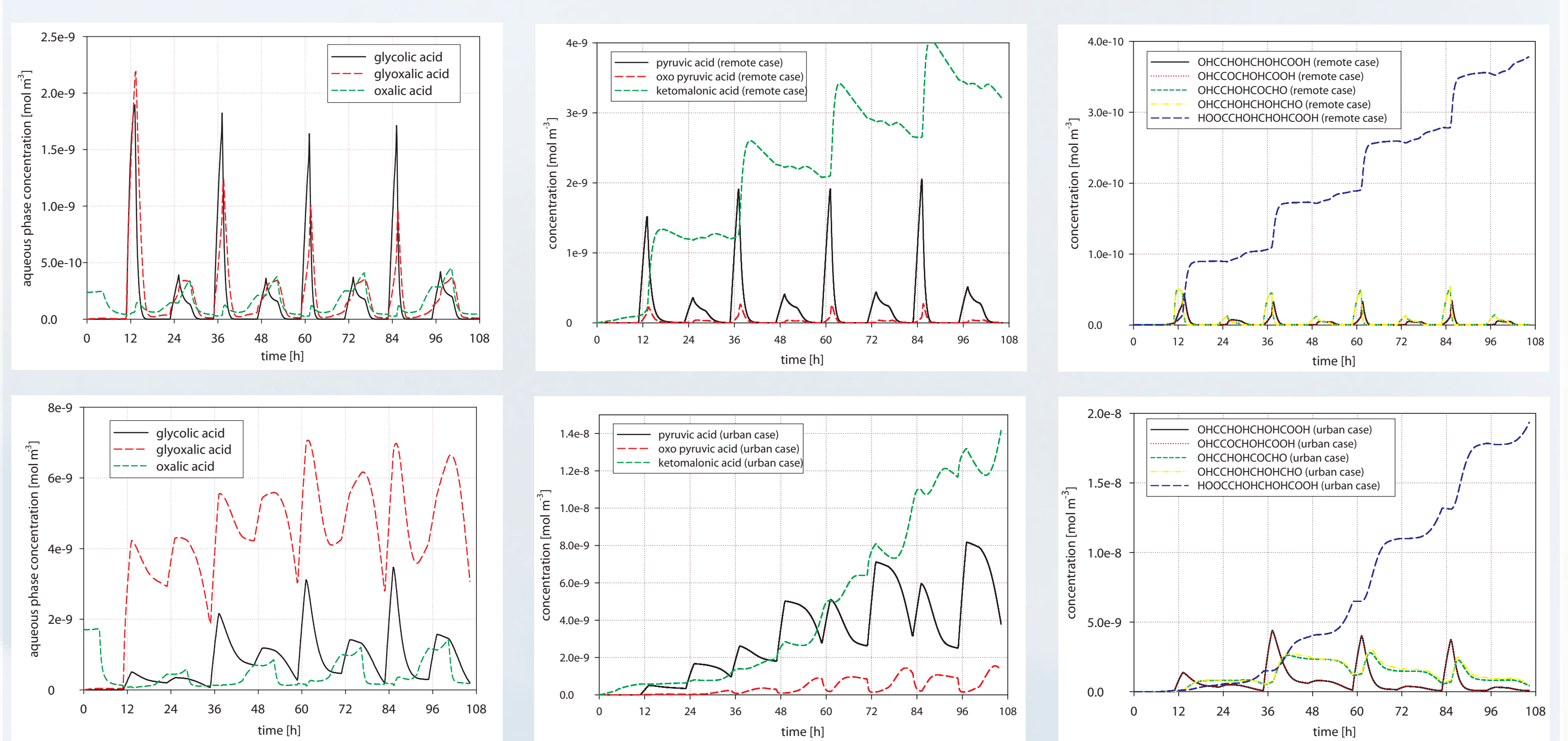
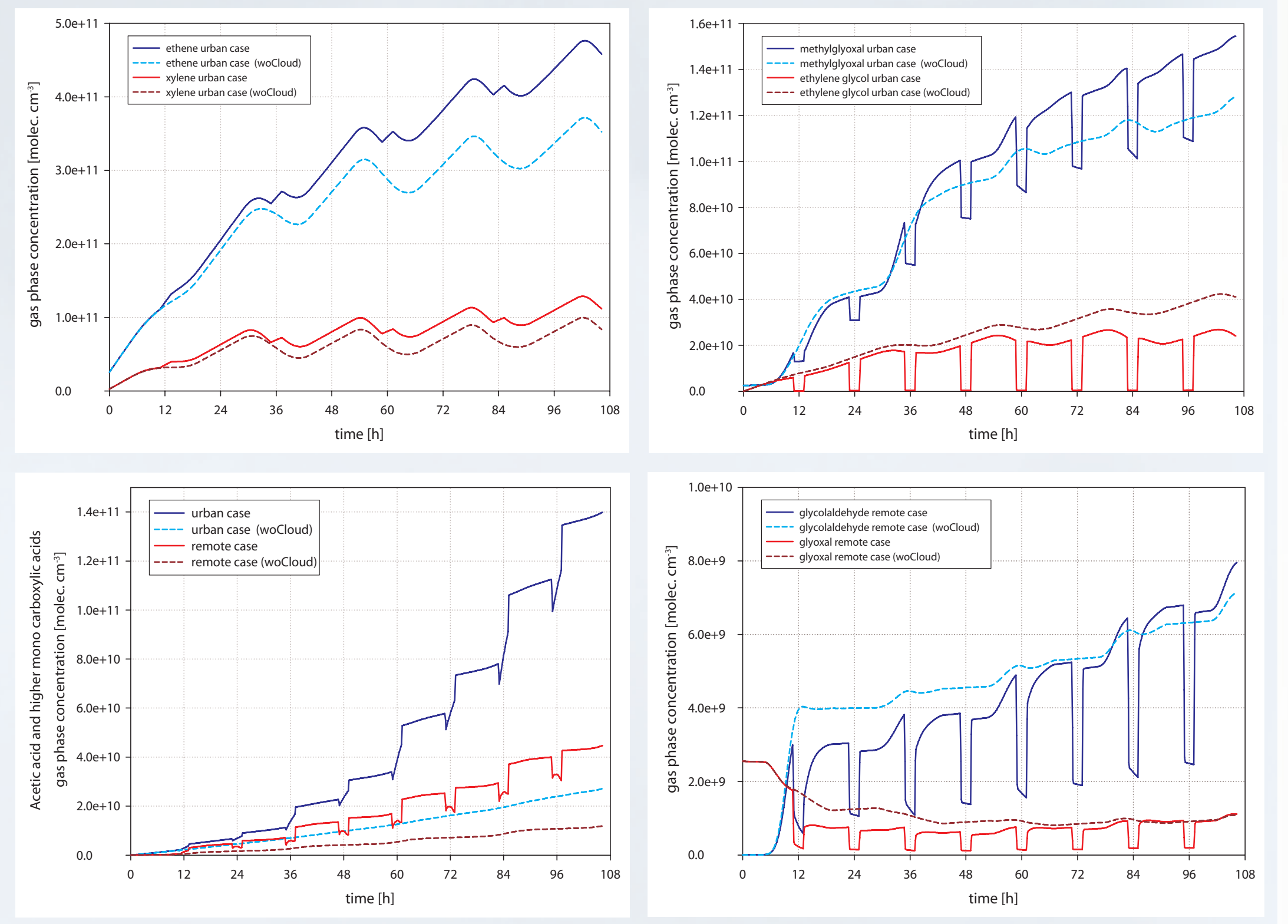
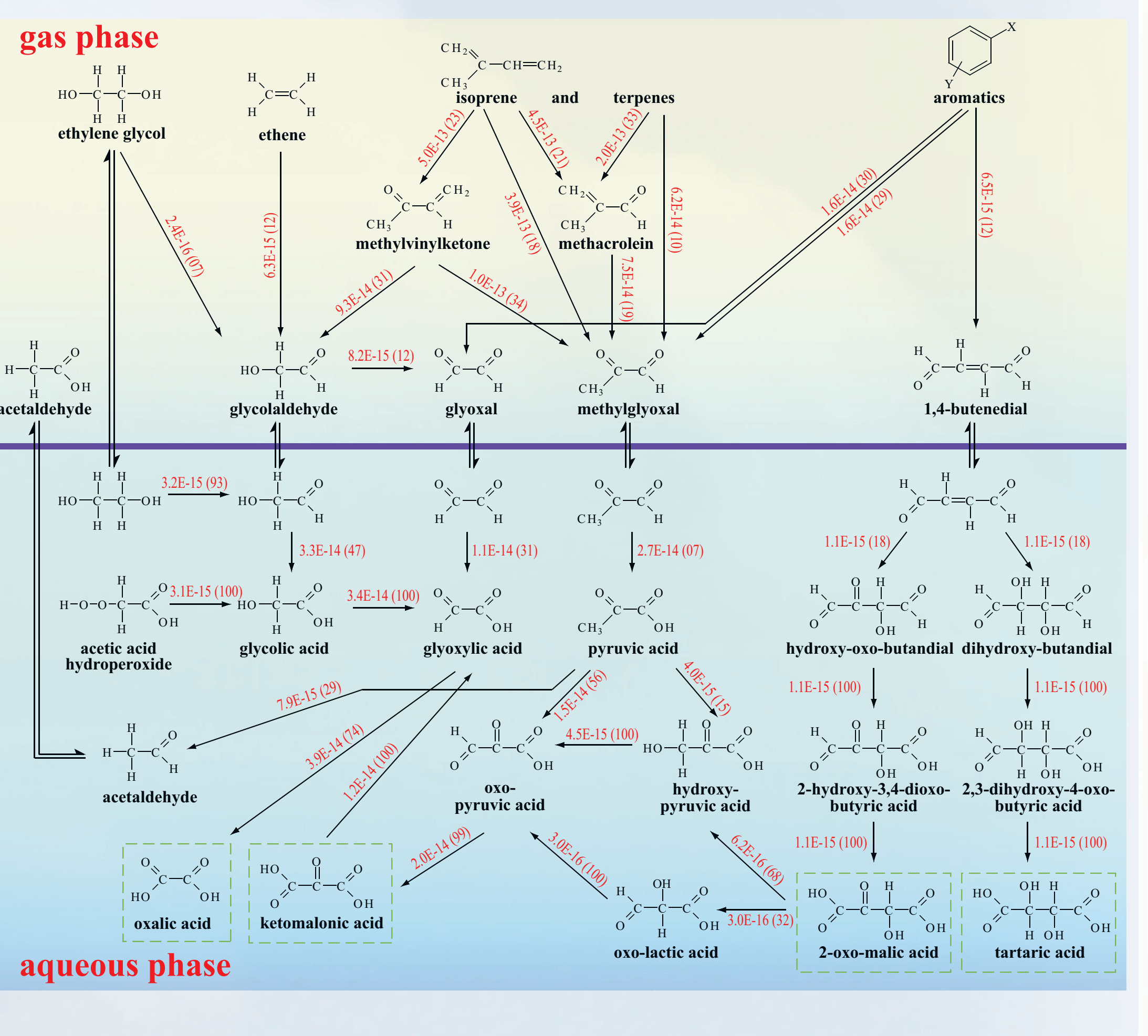


Figure 5. Modelled aqueous phase concentrations in mol m^{-3} (air) of the most important C_2 , C_3 and C_4 organic oxidation products for the remote (top) and urban (bottom) atmospheric scenario, respectively.

As shown in previous model process studies (Herrmann et al., 2005), the aqueous oxidation of organic compounds can form substituted mono- and diacids as well as substituted dialdehydes. Figure 5 shows the modelled aqueous phase concentration profiles of the most important C_2 , C_3 and C_4 organic oxidation products for the remote and urban atmospheric scenario. In the case of the C_3 species particularly glycolaldehyde, glycolic and glyoxalic acid are effectively produced and further oxidised under daytime in-cloud conditions as well as partly in deliquescent particles. Besides the C_3 chemistry also the oxidation of higher organics can contribute to the organic mass. For example the formation of pyruvic acid contributes with up to $0.15 \mu\text{g m}^{-3}$ per day cloud event to the organic aerosol mass under urban conditions. Furthermore, the model studies (cp. Figure 2: radical sink and source analysis) show that the in-cloud oxidation of methylglyoxal and its oxidation products represents an efficient sink for NO_3 radical in the aqueous phase particularly under urban but also under remote conditions. Moreover, 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 potentially to the organic aerosol particle mass.

Figure 6. Scheme of the most important oxidation pathways of C_2 - C_4 organics contributing to the particulate organic mass for the remote case (fluxes in $\text{mol m}^{-3} \text{s}^{-1}$ and percentages in parenthesis).



Aerosol mass processing

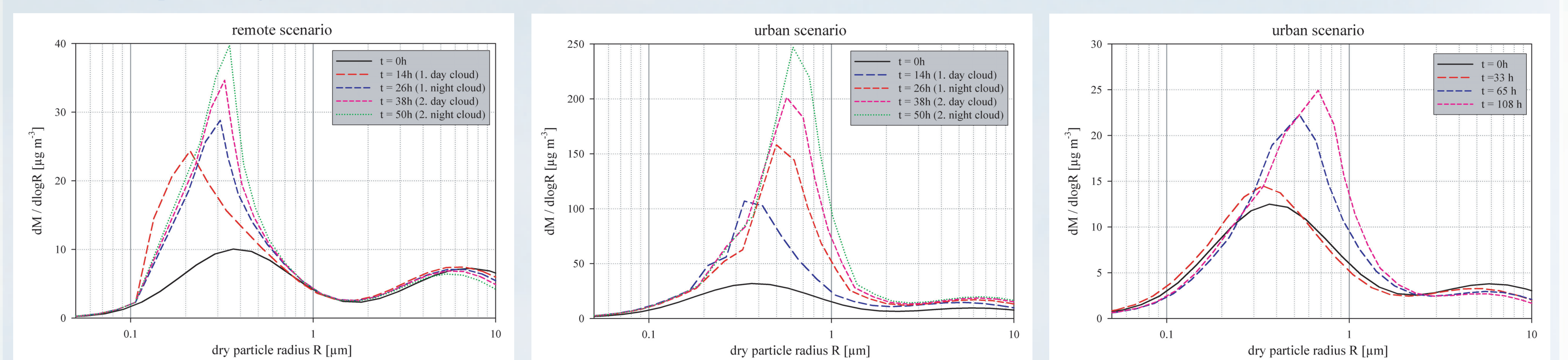


Figure 7. Modelled spectral organic and total dry particle mass distributions at 4 points of modelling time in $\mu\text{g m}^{-3}$ (air) for remote (left) and urban (center): total mass; right: organic mass) tropospheric conditions.

The simulation results plotted in Figure 7 show the modification of the total organic and total dry aerosol particle mass spectra according to the physico-chemical aerosol cloud processing. The model results show in-cloud organic mass productions up to $1 \mu\text{g m}^{-3}$ preferably under polluted day time cloud conditions and mainly due to OH initiated multiphase oxidation processes. However, the size-resolved organic mass productions are restricted to the size interval between 100 – 800 nm. But the noticeable spectral particle size processing is mainly caused by inorganic chemical processes. As can be seen from the plot, the cloud processing of the dry particle mass spectra leads narrower spectra under remote and to a significant CCN size increase including a maximum shift of the mass spectra to about 600 nm under urban cloud conditions, respectively.

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 3.0i) to investigate the effect of multiphase processing of tropospheric aerosol particles and trace gases based on more realistic meteorological non-permanent cloud model 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_2O_2 . 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 like pyruvic 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 seems to be an efficient sink for NO_3 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.

References

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Acknowledgement

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