

## Introduction and Model Outline

Clouds and deliquescent particles are a complex multiphase and multi-component environment with simultaneously occurring gas and aqueous phase as well as heterogeneous chemical transformations which can potentially alter the physico-chemical composition of tropospheric aerosols.

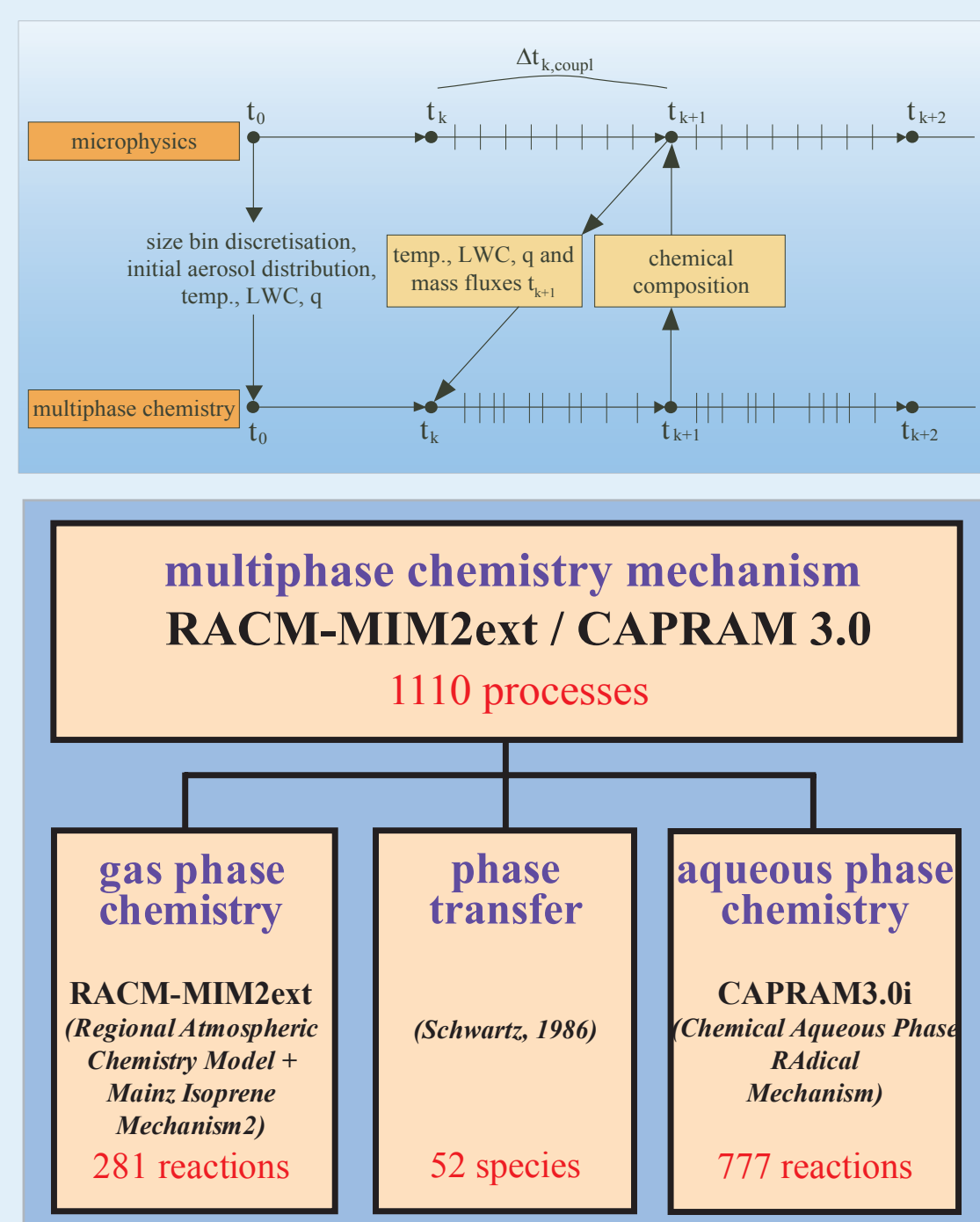


Figure 1: Schematic representation of the microphysics-chemistry model coupling (top) as well as the applied multiphase chemistry mechanism RACM-MIM2ext/CAPRAM 3.0 (down).

## Model Results

### Radical Oxidant Processing

As can be seen from Figure 2 clouds and deliquescent particles can significantly influence the tropospheric radical oxidant gas phase budget. In particular under polluted conditions, the gas phase concentrations are notably reduced due to their direct aqueous phase interaction of the oxidant and/or their precursors. Furthermore, the aqueous radical concentrations of  $\text{NO}_3$  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 from the gas phase.

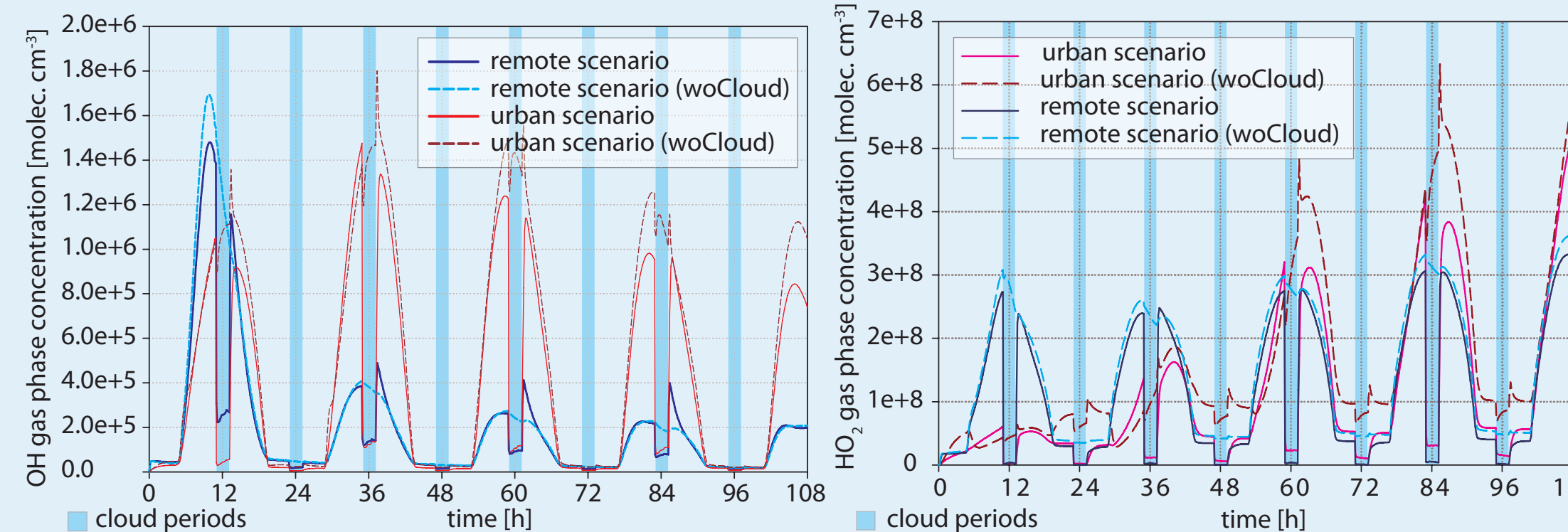


Figure 2: Modelled gas phase concentrations of the OH and  $\text{HO}_2$  radical for the urban and remote scenario with and without (acronym: woCloud) aqueous phase chemistry interaction, respectively.

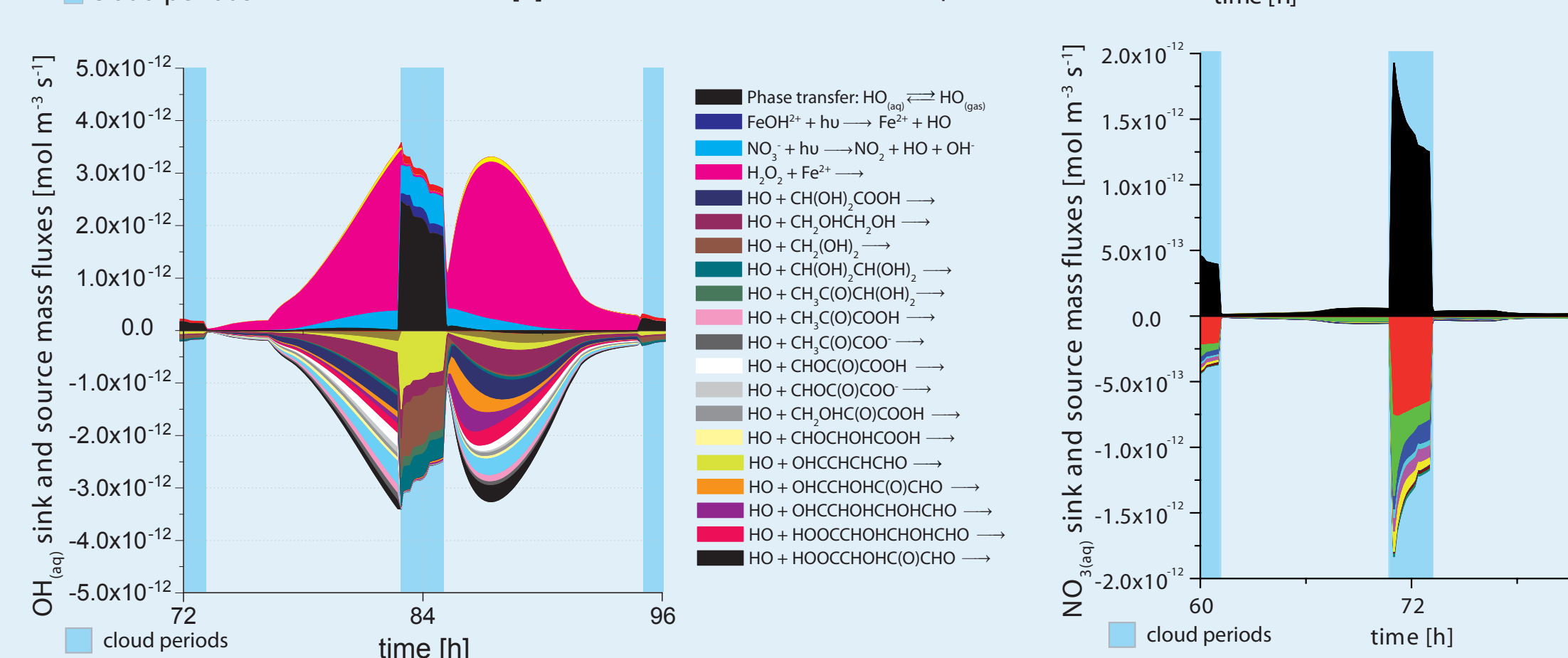
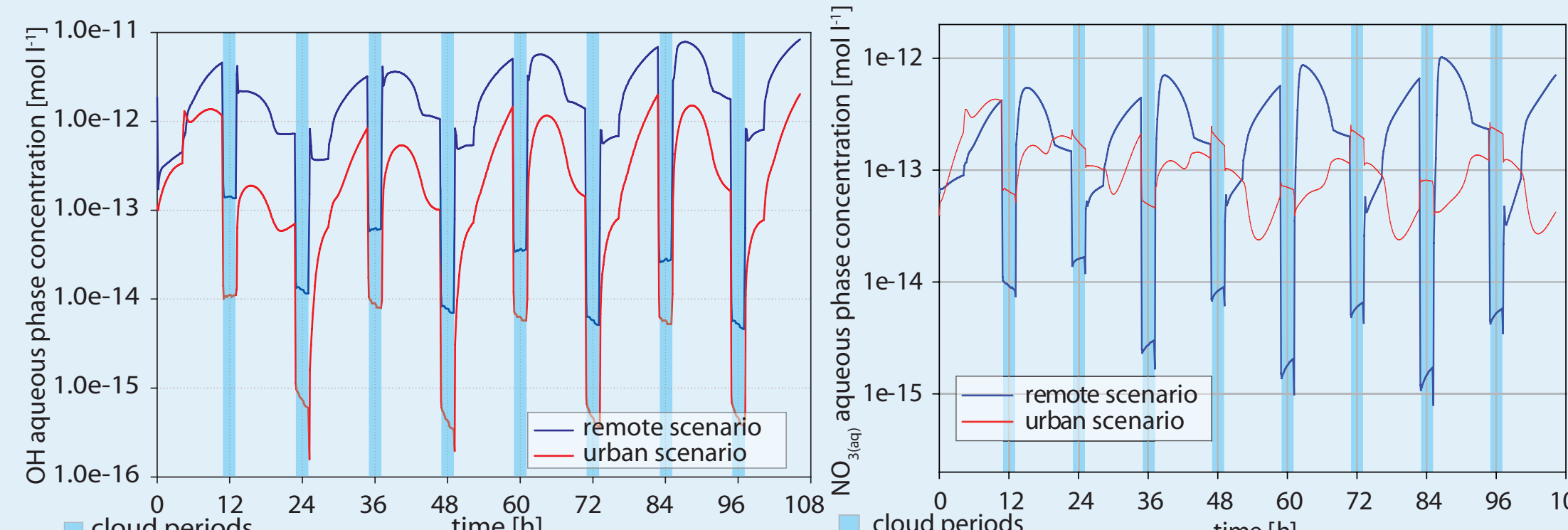


Figure 3: Modelled aqueous phase concentrations of the OH and  $\text{NO}_3$  radical for the urban and remote scenario (top). Chemical flux analysis (down) of the main aqueous phase sink and source processes of the OH and  $\text{NO}_3$  radical in mol m<sup>-3</sup> s<sup>-1</sup> for urban conditions.

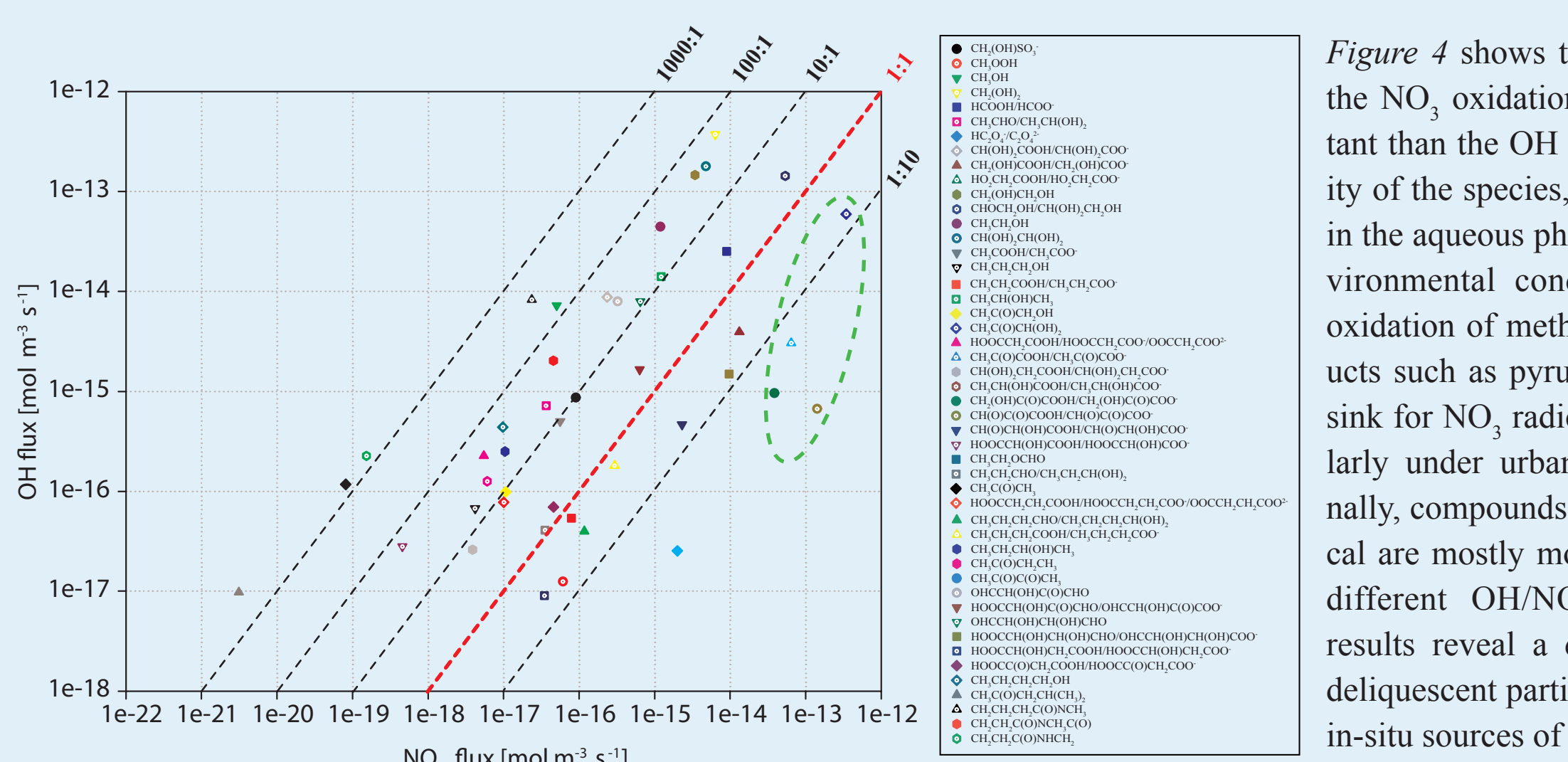


Figure 4: Modelled in-cloud oxidation fluxes [mol m<sup>-3</sup> s<sup>-1</sup>] of the  $\text{NO}_3$  radical vs. the OH radical with different C<sub>1</sub>-C<sub>4</sub> organic compounds under polluted environmental conditions.

### Organic Multiphase Chemical Processing

Figure 5 shows the influence of the aqueous phase oxidation processes on important VOC's such as glyoxal and glycolaldehyde. The concentrations in the gas phase are significantly influenced by both in-cloud processes and the changed gas phase oxidation budget. For emitted gaseous compounds such as ethene, the degradation flux is substantially decreased particularly under daytime cloud conditions mainly due to the reduced gas phase  $\text{HO}_2$  radical budget. A much more complex behaviour was obtained for soluble gas phase oxidation products which interact with the aqueous phase. As Figure 6 and 8 show, aqueous phase oxidation processes can significantly contribute to the multiphase oxidation of soluble VOC's. Under remote conditions the aqueous phase contribute with 7%, 31%, 47% and 93% to the total degradation of methylglyoxal, glyoxal, glycolaldehyde and ethylene glycol, respectively.

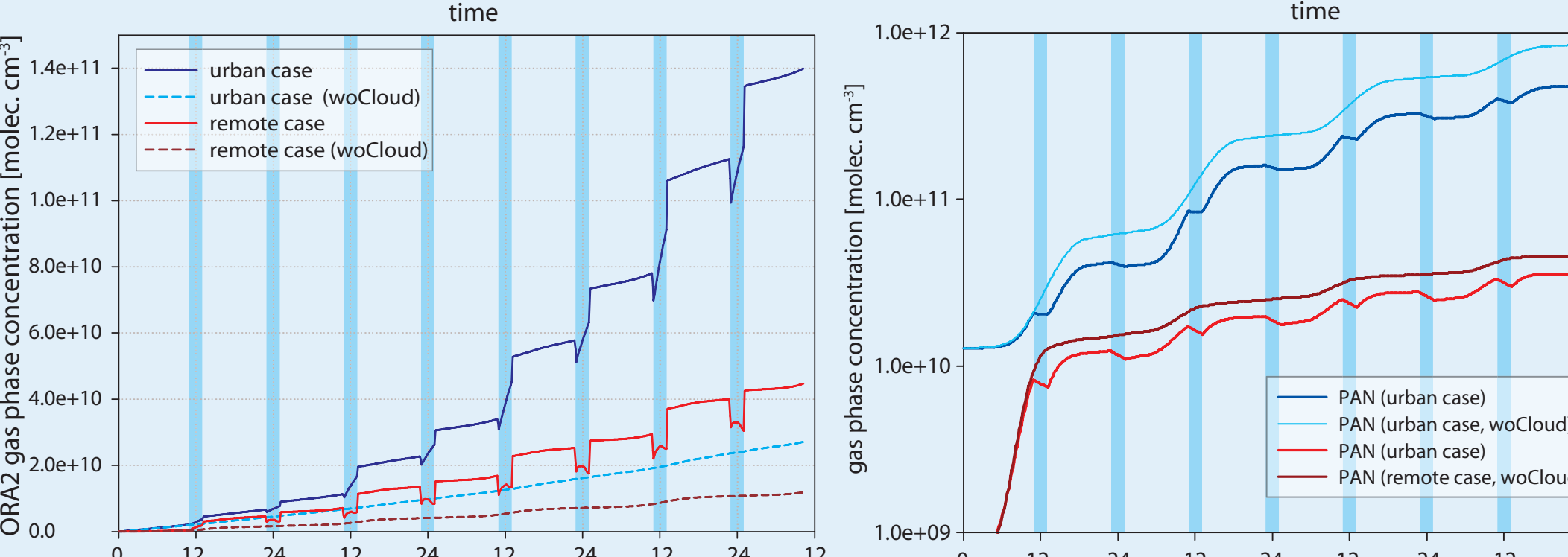


Figure 5: Modelled gas phase concentrations of ethene, xylene, acetic acid, glycolaldehyde, glyoxal and PAN for the urban or/and remote case, respectively.

### Organic Multiphase Chemical Processing (continued)

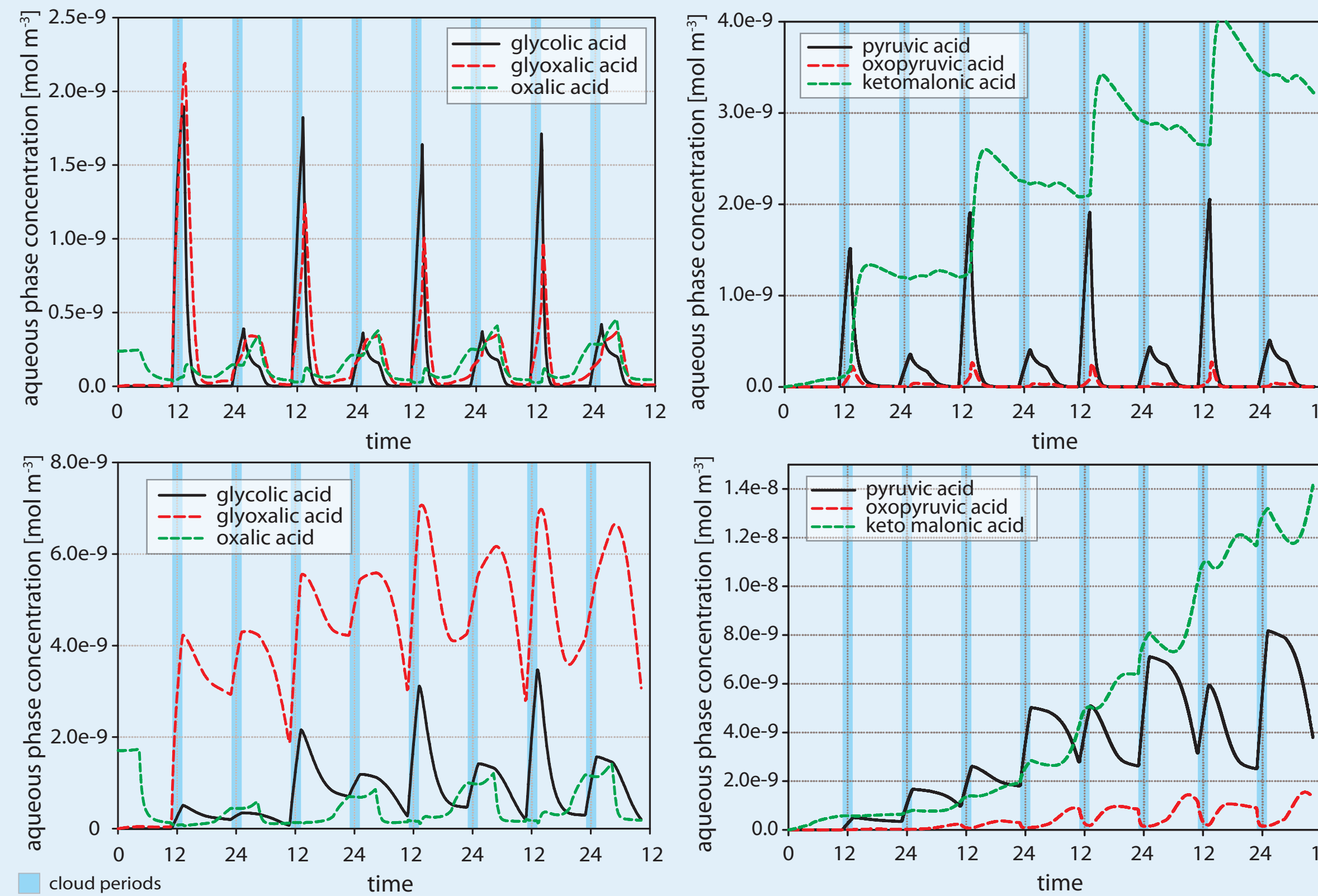
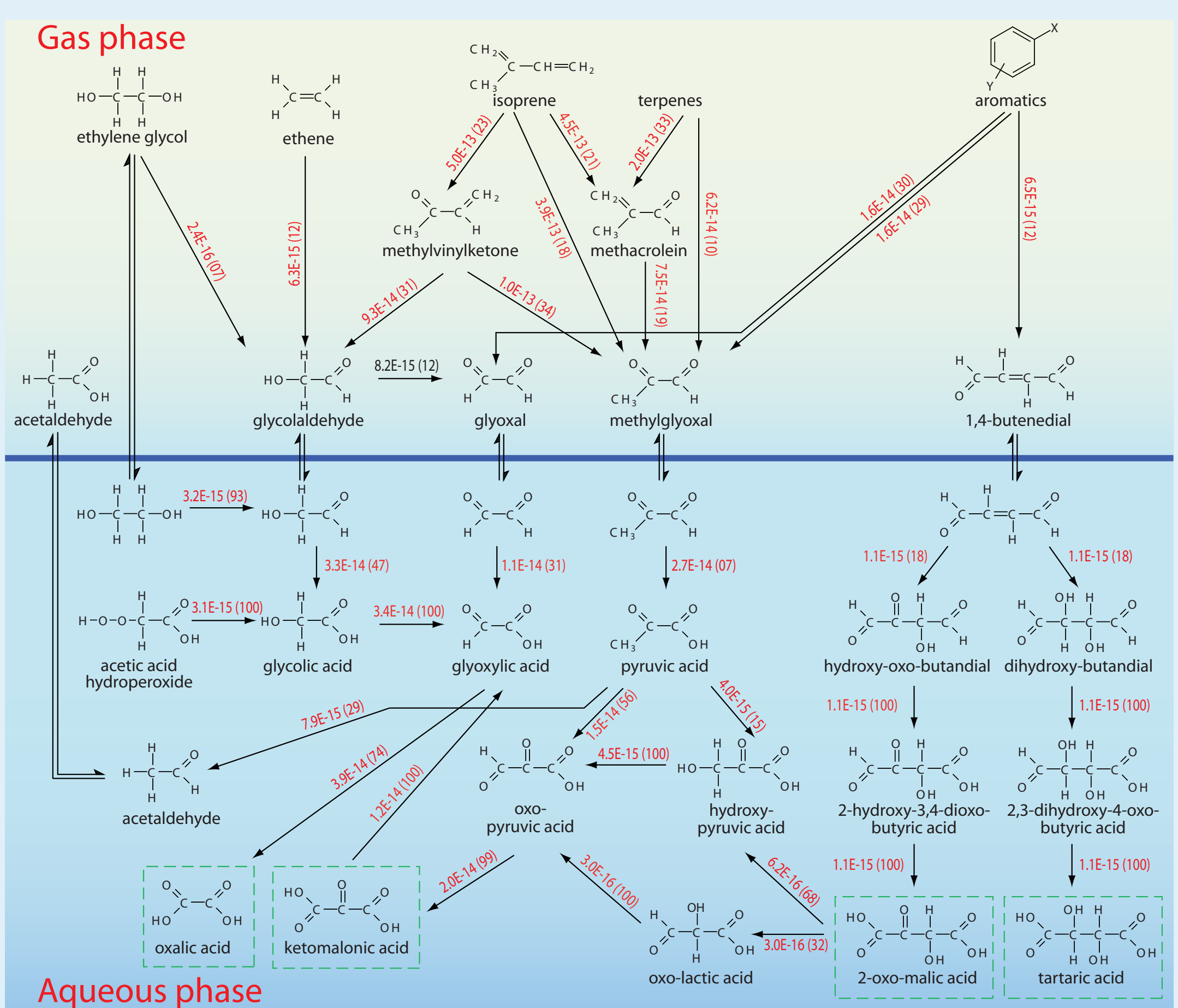


Figure 7: Modelled aqueous phase concentrations in mol m<sup>-3</sup> of the most important C<sub>2</sub> (left) and C<sub>3</sub> (centre) organic oxidation products for the remote (top) and urban (down) atmospheric scenario, respectively. Depiction of the modelled spectral pyruvic acid mass concentration in mol m<sup>-3</sup> as function of time and the corresponding dry initial particle/droplet radius for the two environmental scenarios.

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 7 shows the modelled aqueous phase concentration profiles of the most important C<sub>2</sub> and C<sub>3</sub> organic oxidation products for the remote and urban atmospheric scenario. In the case of the C<sub>2</sub> species particularly glycolaldehyde, glycolic and glyoxylic acid are effectively produced and further oxidised under daytime in-cloud conditions as well as partly in deliquescent particles. Besides the C<sub>2</sub> 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 μg m<sup>-3</sup> per day cloud event to the organic aerosol mass under urban conditions. Furthermore, the model studies (see Figure 3: OH radical sink and source analysis) show that the in-cloud oxidation of methylglyoxal and its oxidation products represents an efficient sink for  $\text{NO}_3$  radical in the aqueous phase particularly under urban but also under remote conditions. Moreover, the aqueous phase oxidations of methylglyoxal and 1,4-butenediol 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 8: Scheme of the most important oxidation pathways of C<sub>2</sub>-C<sub>3</sub> organics contributing to the particulate organic mass for the remote model scenario (mass fluxes in mol m<sup>-3</sup> s<sup>-1</sup> and percentages of the degradation pathways in parentheses).



### Aerosol Mass Processing

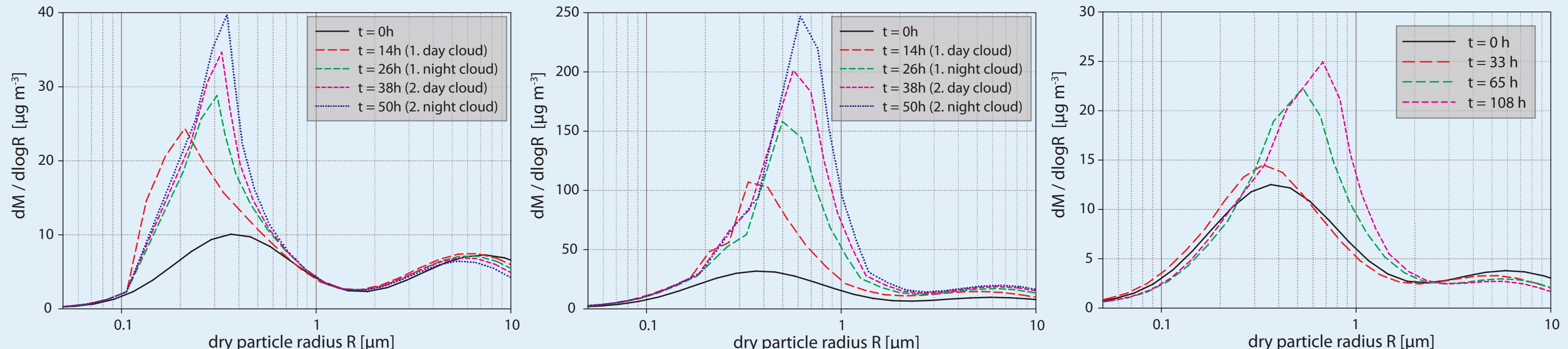


Figure 9: Modelled spectral organic and total dry particle mass distributions at 4 points of modelling time in μg m<sup>-3</sup> for remote (left) and urban (centre: total mass; right: organic mass) tropospheric conditions.

The simulation results plotted in Figure 9 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 μg m<sup>-3</sup> 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.

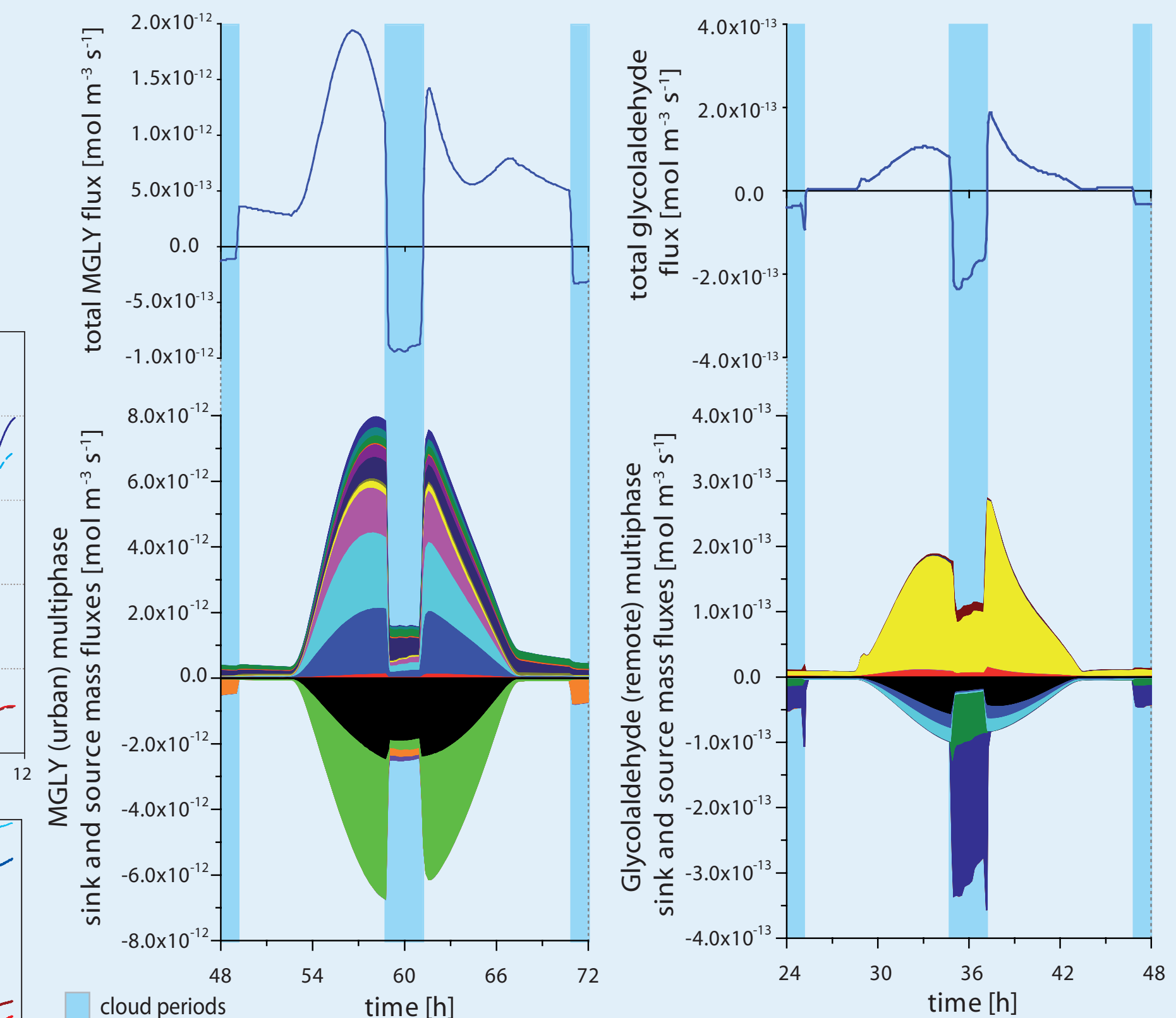


Figure 6: Modelled multiphase formation and degradation fluxes of methylglyoxal (MGly, left, urban case) and glycolaldehyde (right, remote case).

## Summary and Outlook

Simulations with the parcel model SPACCIM have been carried out for different atmospheric conditions considering microphysics and multiphase chemistry to investigate the effect of multiphase processes on 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 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  $\text{H}_2\text{O}_2$ . Moreover, the model studies have revealed 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-butenediol 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  $\text{NO}_3$  radicals in the aqueous phase particularly under urban as well as under remote conditions. Additionally, the model studies have shown in-cloud organic mass productions up to about 1 μg m<sup>-3</sup> preferably under polluted day time cloud conditions mainly due to OH initiated multiphase oxidation processes. Finally, the sum of the results implicates the necessity of the aqueous phase processes to be considered in future higher scale chemistry transport models. Consequently, a reduced CAPRAM mechanism describing the main inorganic and organic aqueous phase chemistry issues has been developed.

## References

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