SPACCIM simulations of chemical aerosol-cloud interactions with the multiphase mechanism MCM-CAPRAM3.0

A. Tilgner, R. Schrödner, P. Bräuer, R. Wolke and H. Herrmann

Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, D-04318 Leipzig, Germany

tilgner@tropos.de

Introduction and Motivation

A wide variety of organic compounds is emitted into the troposphere and is then oxidised by complex multiphase degradations leading to secondary organics which partition between the tropospheric gas and aqueous phase, i.e. deliquescent particles and cloud droplets. Secondary organics play a key role in tropospheric chemistry and account for a substantial fraction of tropospheric aerosol mass (Hallquist et al., 2009).
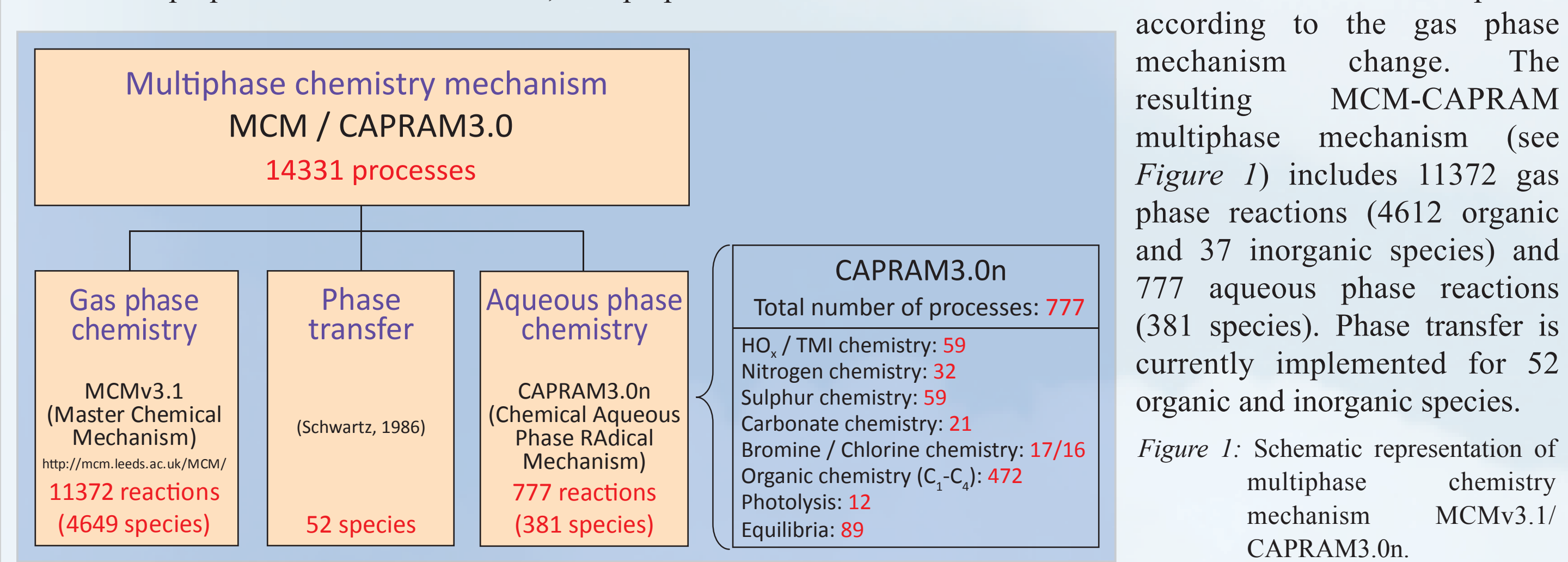
Clouds and deliquescent particles are a complex multiphase and multi-component environment with simultaneously occurring gas and aqueous phase as well as heterogeneous chemical transformations which can potentially alter the physico-chemical composition of tropospheric aerosols on a global scale (Ravishankara, 1997). However, the chemical multiphase processing, i.e. secondary formation and aging mainly of organic aerosols remains poorly considered in current multiphase chemical mechanisms and models. In order to model such complex tropospheric multiphase chemical interactions of cloud and fog droplets as well as deliquescent aerosol particles, chemical mechanisms with a detailed description of chemical processes in both the gas and aqueous phase are required. Currently, near-explicit gas and aqueous phase mechanisms are available. However, a near-explicit chemical multiphase mechanism was still missing. Enhanced mechanisms and models are essential in order to improve the scientific knowledge on the organic aerosol mass evolution, i.e. to better understand atmospheric fate of important atmospheric gas phase constituents, the origin of particulate organic compounds as well as their presence in tropospheric aerosols.

Therefore, further mechanism and model development were firstly aimed to couple the existing near-explicit chemical gas phase mechanism MCMv3.1 (Master Chemical Mechanism, Saunder et al., 2003) and the explicit aqueous phase mechanism CAPRAM 3.0n (Chemical Aqueous Phase Radical Mechanism, Herrmann et al., 2005; Tilgner and Herrmann, 2010) and to integrate them into the model framework SPACCIM (SPectral Aerosol Cloud Chemistry Interaction Model; Wolke et al., 2005). Since the condensed phase organic chemistry processes in CAPRAM are not yet treated in equivalent detail as in the MCM, the present study was secondly aimed to investigate the needs and directions for future aqueous phase mechanism developments.

Mechanism and Model Outline

■ Multiphase chemistry mechanism

In this study, the near-explicit chemical gas phase mechanism MCMv3.1 was linked to the aqueous phase mechanism CAPRAM3.0n. In this process, the MCM code in its SMILES-string nomenclature has been converted into the SPACCIM preprocessor format. Further, the preprocessor and also the SPACCIM model framework were updated according to the gas phase mechanism change. The resulting MCM-CAPRAM multiphase mechanism (see Figure 1) includes 11372 gas phase reactions (4612 organic and 37 inorganic species) and 777 aqueous phase reactions (381 species). Phase transfer is currently implemented for 52 organic and inorganic species.

Figure 1: Schematic representation of multiphase chemistry mechanism MCMv3.1/ CAPRAM3.0n.

■ Model description

The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model which allows a detailed description of the physico-chemical processing of gases, deliquescent particles and cloud droplets. All microphysical parameters required by the multiphase chemistry model are taken over from the microphysical model (see Figure 2). In order to test the mechanism and model developments, first preliminary test simulations with the SPACCIM model have been carried out for remote environmental conditions. Simulations were carried out for a non-permanent meteorological cloud scenario (see Figure 2) which was derived from the global calculations of Pruppacher and Jaenicke (1995). In the model scenario, 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 by neglecting the effects of non-ideality. The model investigations were focused on the multiphase chemistry of tropospheric radical oxidants such as OH and HO₂, organic compounds and closely linked chemical subsystems. The model results have been analysed including time-resolved reaction flux analyses.
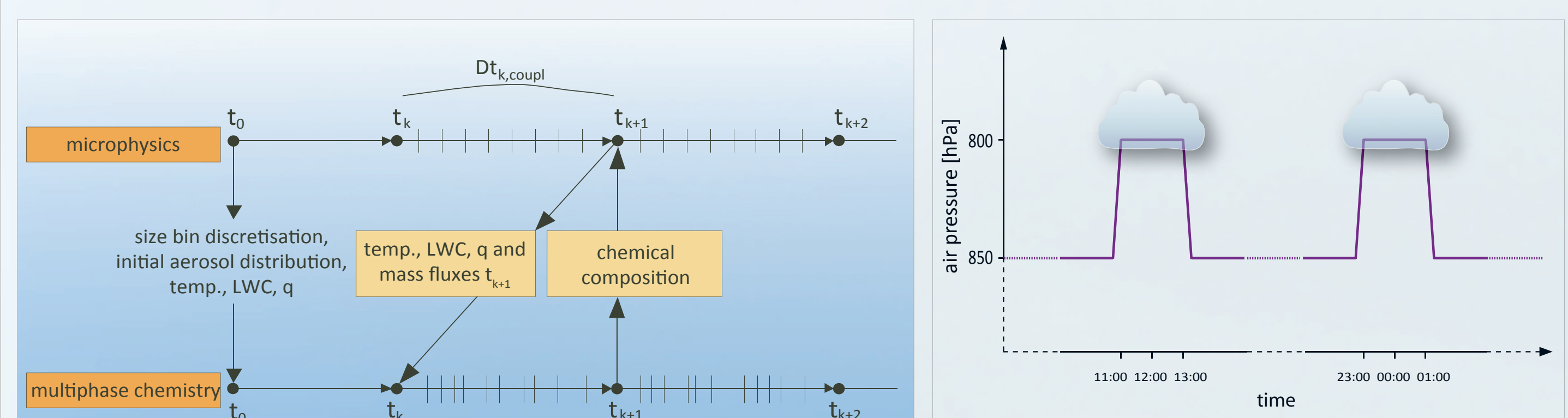

Figure 2: Schematic representation of the microphysics-chemistry model coupling in SPACCIM (left) as well as the applied meteorological scenario for the model simulations (right).

Model results

■ Multiphase oxidant processing

Figure 5: Modelled gas phase concentrations of OH (top), HO₂ (center) and H₂O₂ (down), respectively.

Figure 6: Modelled aqueous phase concentrations of HOₓ radicals (OH and HO₂/O₂⁻).

Figure 7: Chemical source and sink flux analysis of the OH radical in the aqueous phase in mol m⁻³ s⁻¹ for the 2nd simulation day.

■ Multiphase organic processing

Figure 8: Modelled gas phase concentrations of formaldehyde [C=O], formic acid [OC=O], acetic acid [CC(=O)O], glycolaldehyde [OCC=O], glyoxal [O=CC=O] and methylglyoxal [O=CC(=O)C], respectively.

Figure 9: Modelled aqueous mass concentrations in mol m⁻³(air) of glycolic acid, glyoxalic acid, oxalic acid, pyruvic acid, 3-oxo pyruvic acid and ketomalonic acid.

Future MCM-CAPRAM coupling

The MCM and the current CAPRAM3.0n mechanism were investigated regarding links in current versions and future required mechanism enhancements. In the MCM, there is a huge amount of species, which are able to undergo phase transfer (e.g. organic carbonyl compounds, acids, ...) and should be included in future CAPRAM mechanisms.

● An estimation on how many organic MCM species are possible candidates for efficient phase transfers is given in Figure 3

● O/C ratio of organic species was determined to characterise its water solubility.

● Species in the 3rd, 4th and 5th class reflect well soluble species, which might be present in the tropospheric aqueous phase.

➡ Phase transfer and aqueous phase chemistry of approximately 2100 species should be considered in future CAPRAM mechanisms.
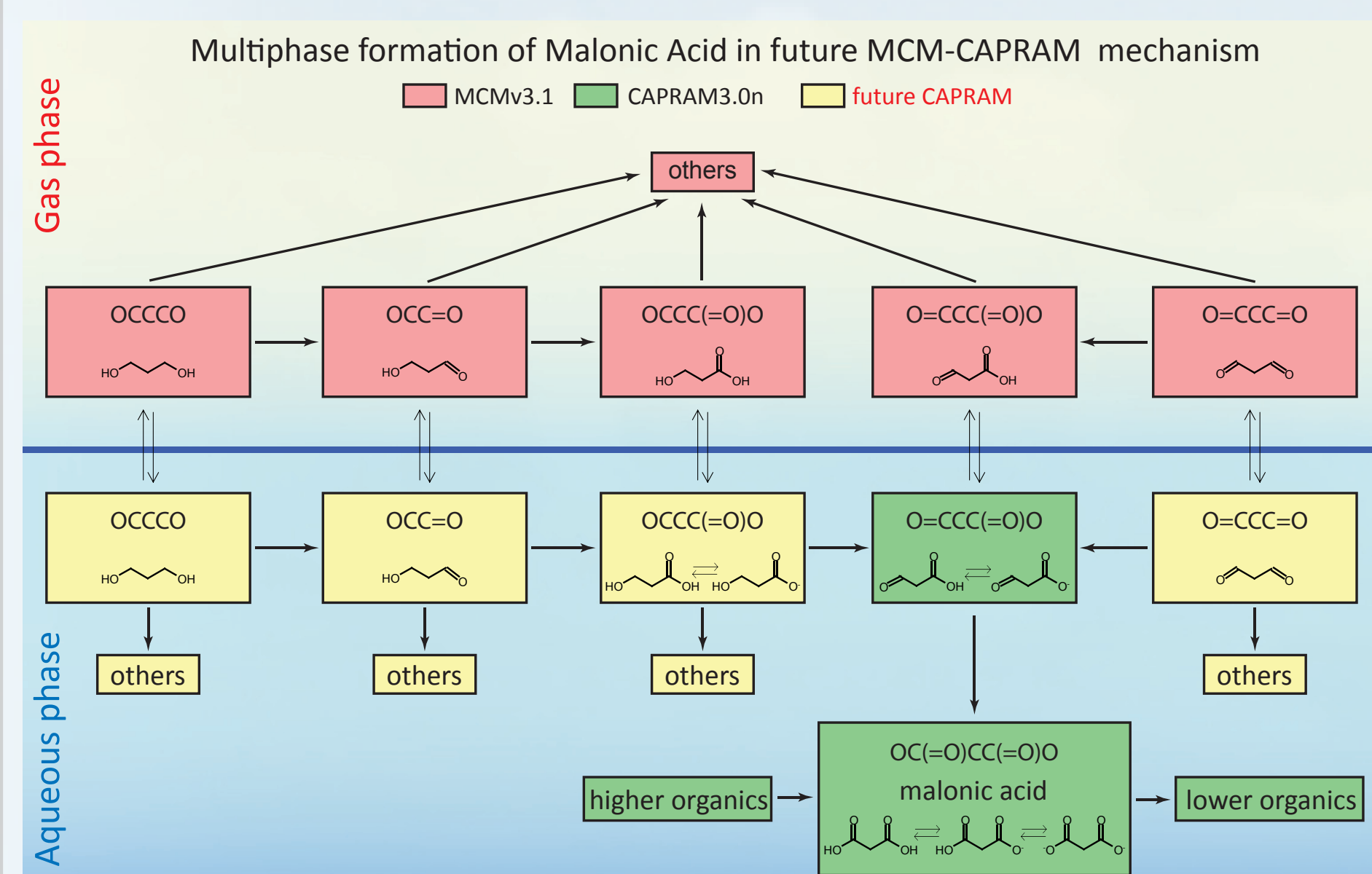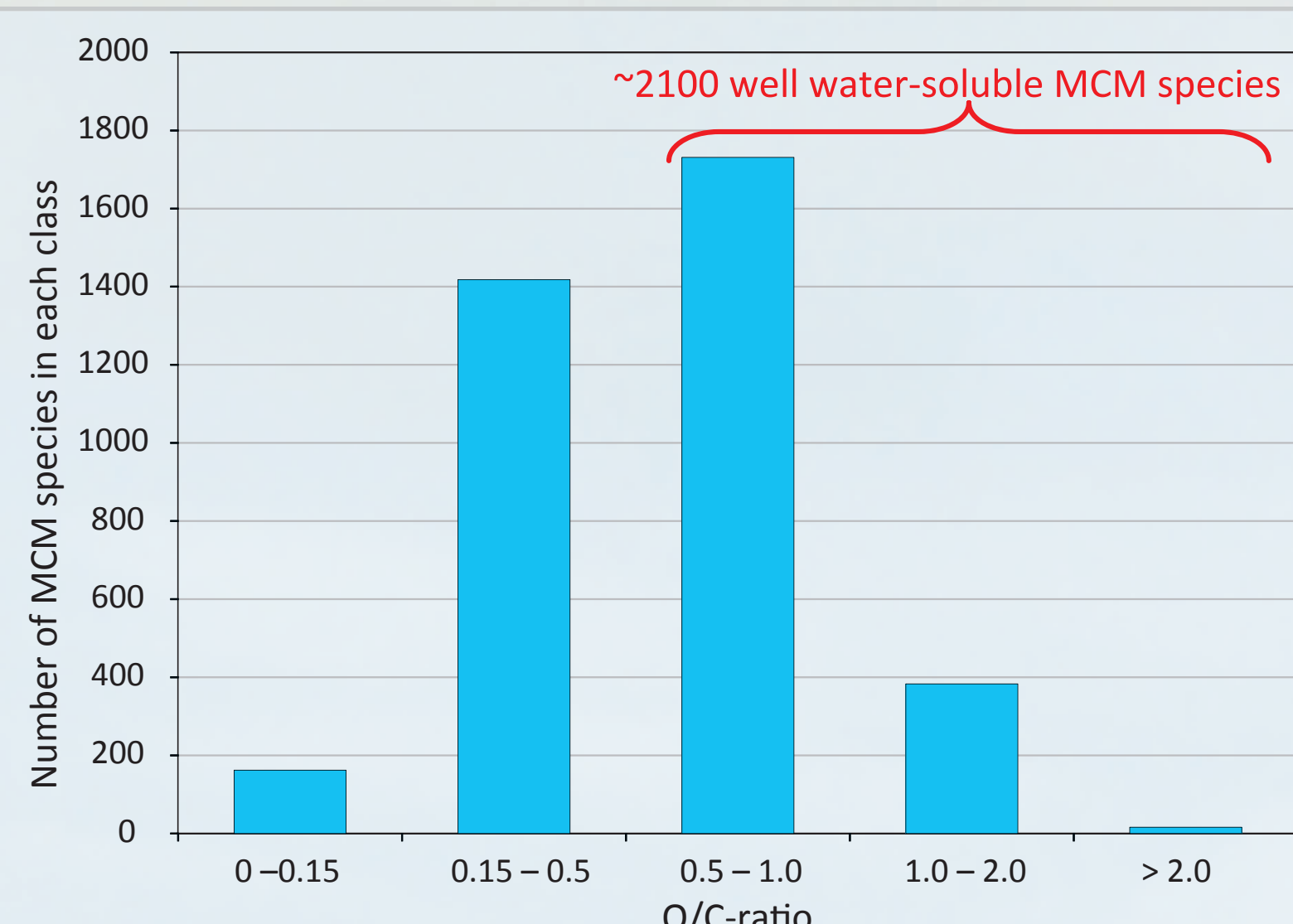

Figure 3: Oxygen/Carbon-ratio of all organic compounds in the MCM excluding organic radicals.

■ Outlook on future CAPRAM mechanism developments

The multiphase formation of many organic compounds, e.g. dicarboxylic acids which are often present in tropospheric aerosols, is still uncertain. Soluble precursors of many particulate organic compounds are available in the MCM. But, not all of these gas phase precursors are implemented in CAPRAM3.0n, yet. In the course of the future CAPRAM mechanism developments, the atmospheric origin of important particulate organics could be investigated for the first time and help to better understand their presence in the atmospheric particles and clouds.

Figure 4 shows an example of a future linkage between the MCM and CAPRAM for malonic acid. As can be seen, there is an existing sub-mechanism in the MCM and the current CAPRAM. The improvements are the phase transfers of all gas phase precursors and their further oxidation in the aqueous phase. As this is just an example for malonic acid, similar work has to be done in the future for many other oxidised organics.

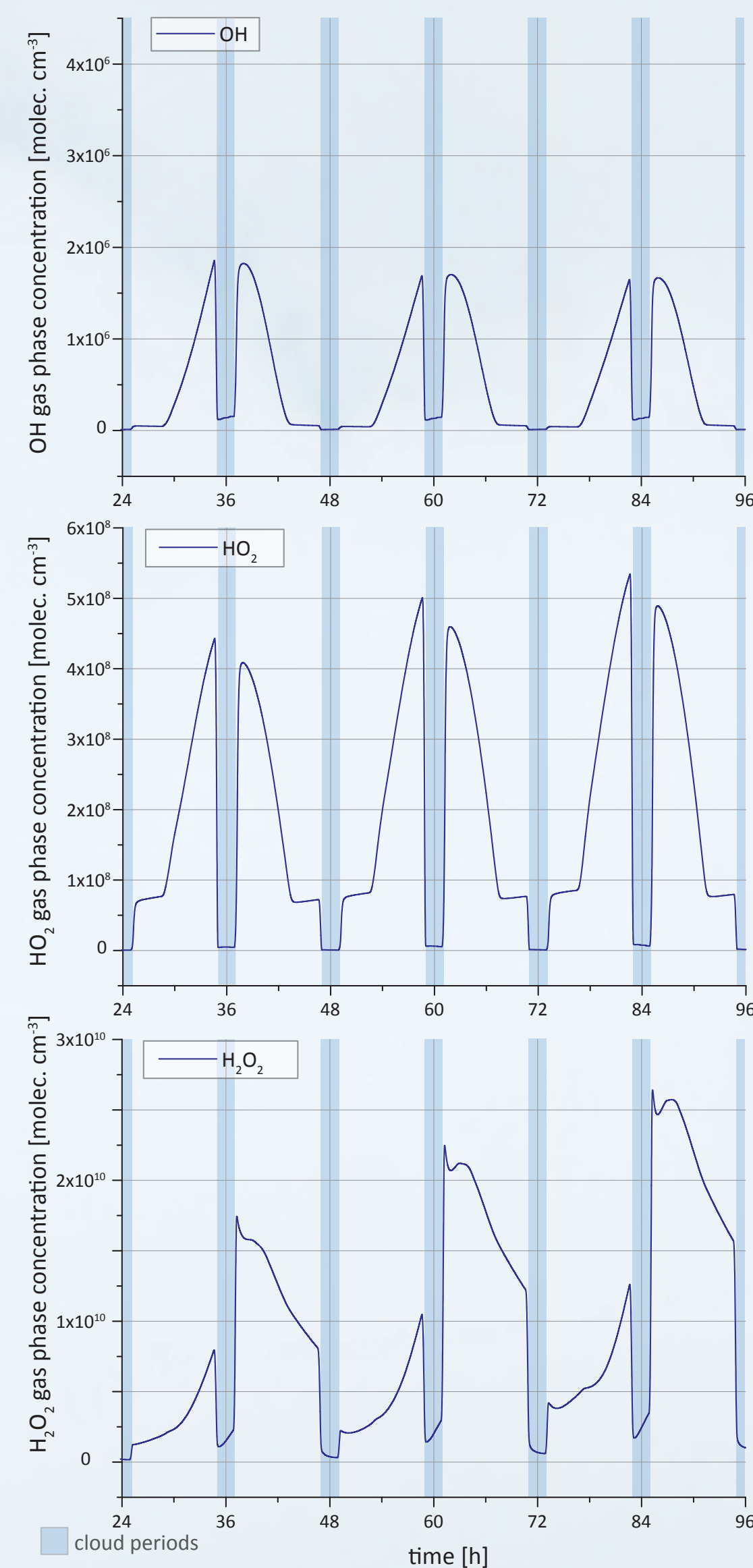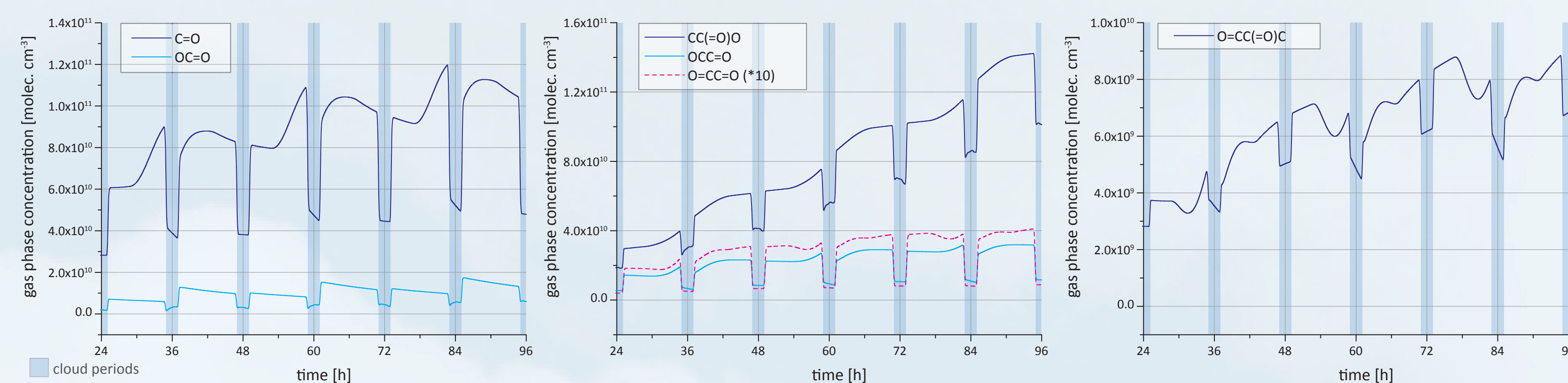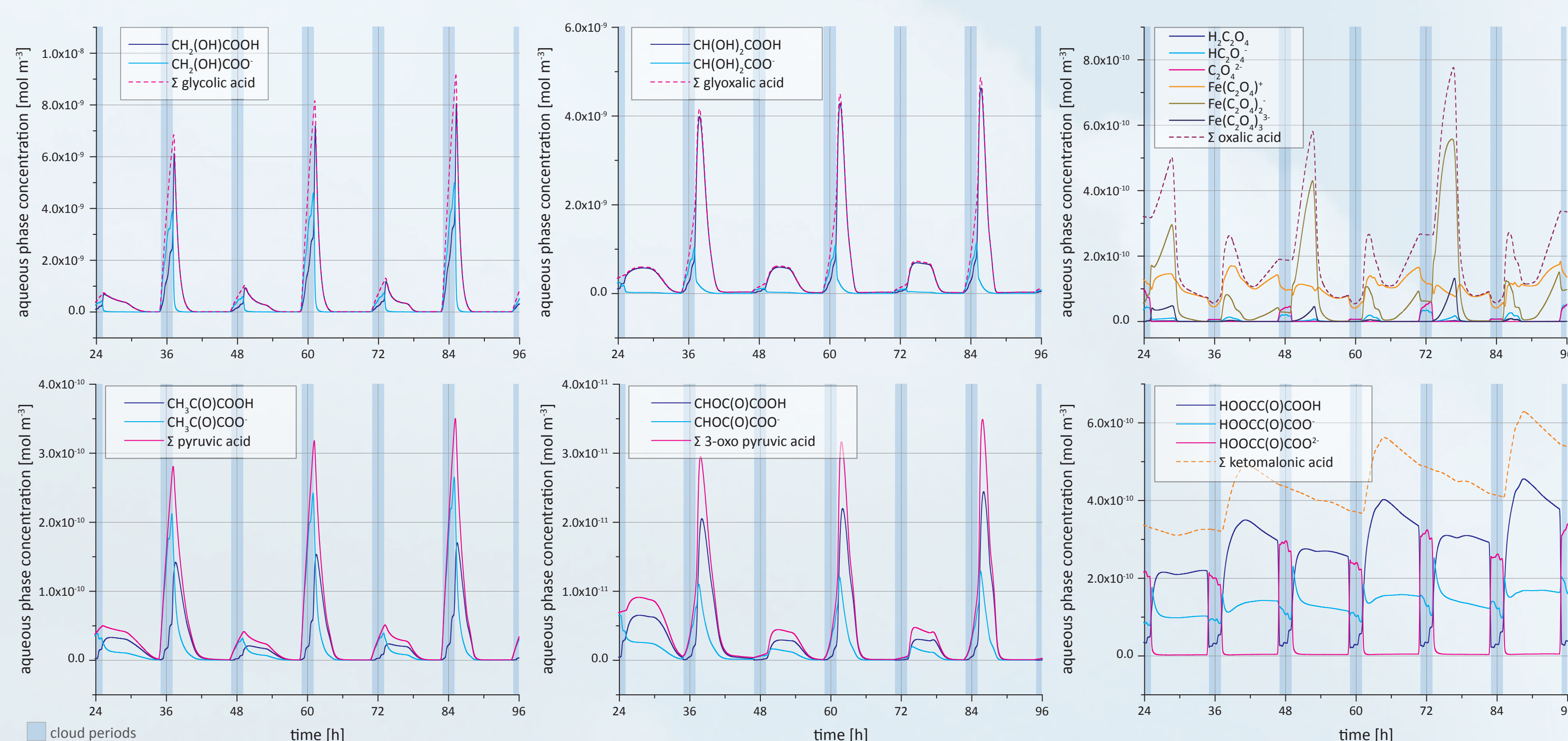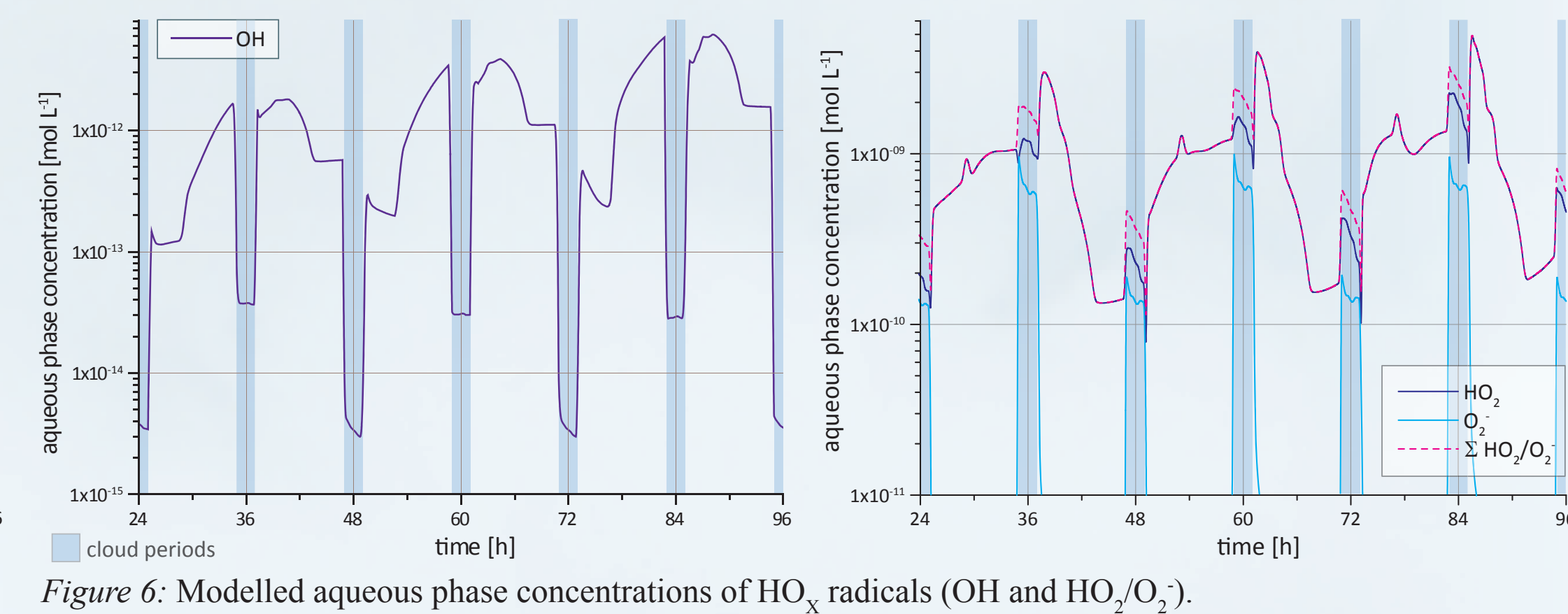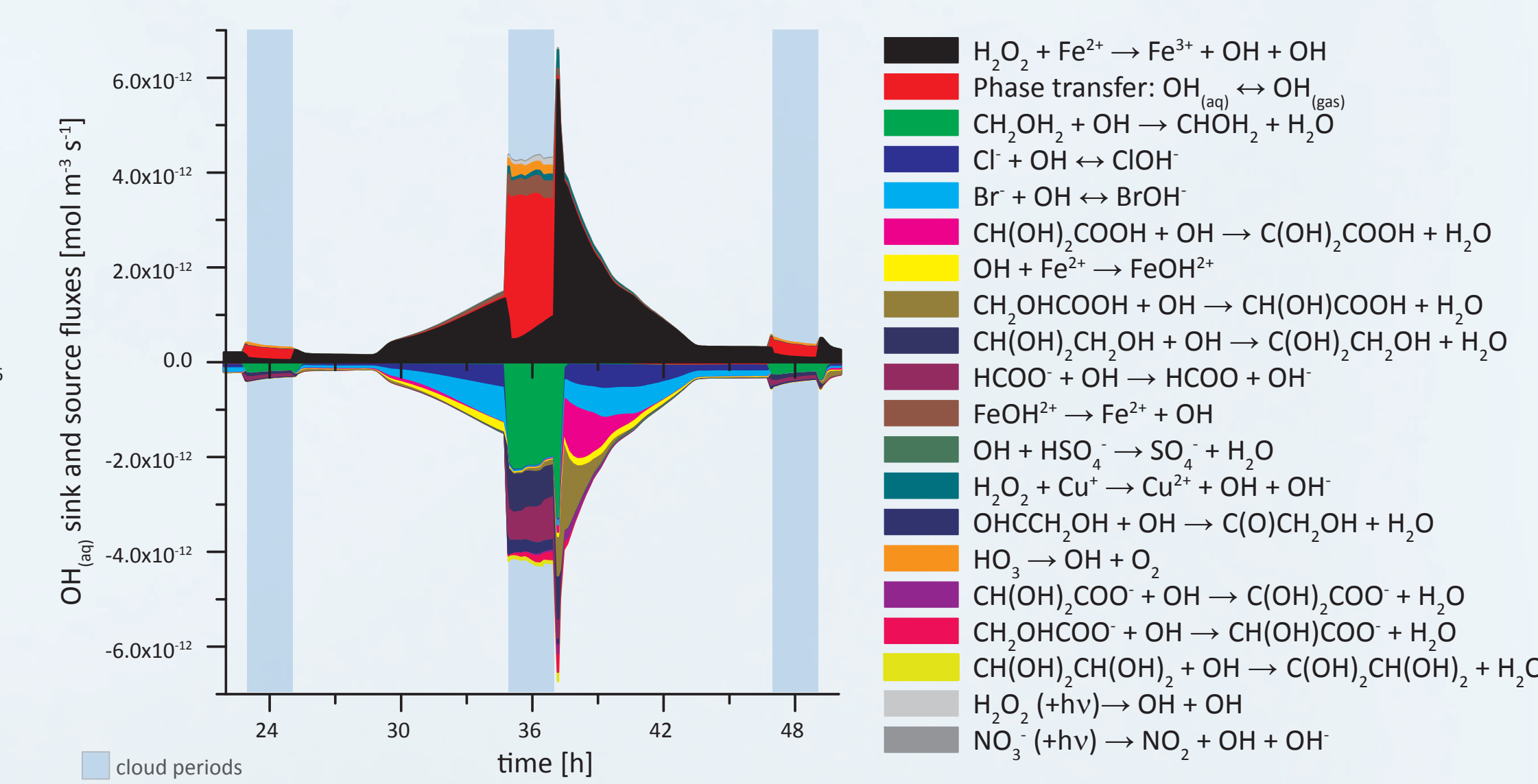Figure 4: Future coupling of the MCM and CAPRAM to study e.g. the tropospheric multiphase formation of malonic acid.

Summary and Outlook

In the present study, the near-explicit chemical gas phase mechanism MCMv3.1 was linked to the aqueous phase mechanism CAPRAM3.0n and integrated into the framework of the parcel model SPACCIM. The multiphase chemistry mechanism MCM-CAPRAM considers 11372 gas phase reactions 777 aqueous phase reactions. First test simulations with the MCM-CAPRAM mechanism have been carried out for remote environmental conditions using a non-permanent cloud scenario. The present model studies were focused on multiphase chemistry of tropospheric oxidants and closely linked organic chemical subsystems. The simulation results agree with findings of former model investigations using the CAPRAM mechanism (see e.g. Tilgner and Herrmann, 2010). The model studies have revealed considerable effects of multiphase aerosol-cloud interactions on the gaseous budget of tropospheric radical and non-radical oxidants such as OH and H₂O₂. Furthermore, the simulations have shown the importance of the aqueous phase for the gaseous concentrations of semivolatile organic compounds and the formation of higher oxidised organic compounds such as substituted mono- and dicarboxylic acids. In particular, the aqueous phase oxidations of formaldehyde, formic acid and glycolaldehyde have been identified as important in-cloud OH radical sinks under remote environmental conditions.

An additional prospect study focusing on future MCM-CAPRAM coupling, has revealed that approximately 60% of the MCM compounds might undergo efficient phase transfer and perhaps aqueous phase chemistry which needs to be considered in future mechanisms. For an equivalent treatment of both gas and aqueous phase chemical processes in the future, the CAPRAM mechanism needs to be further extended with new aqueous phase pathways, triggered by gas phase precursors of the MCM, which were not recognized in the development steps before. The resulting near-explicit multiphase mechanism will allow enhanced model investigations on the tropospheric multiphase chemistry and improve the understanding of the multiphase chemical processing of organic compounds in tropospheric aerosol particles and clouds.

References

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