

Introduction and Motivation

Organic compounds are a ubiquitous constituent of the troposphere. With either biogenic or anthropogenic sources, they have a major influence on the atmospheric multiphase system and thus have become a main research topic within the last decades.

Modelling can provide a useful tool to explore the tropospheric multiphase chemistry. While in the gas phase several detailed oxidation schemes exist (e.g. MCMv3.1 [1]), in the aqueous phase those chemical mechanisms are very limited. The aim of the current study was to provide a more detailed and near-explicit oxidation scheme for the C3 chemistry in the currently most comprehensive aqueous phase chemistry mechanism CAPRAM 3.0m [2]. The mechanism is based on experimental data if available and estimations such as structure-activity relationships (SARs). The new chemical scheme comprises of 11381 reactions with 4664 species in the gas phase, 1002 reactions with 525 species in the aqueous phase and 92 species undergoing phase transfer as depicted in Fig. 1.

For the mechanism construction a thoughtful literature review of available experimental data and estimation methods was done. First Test simulations have been carried out with the air parcel model SPACCIM [3] for a meteorological scenario with non-permanent clouds under remote conditions.

Mechanism construction

Development of a new chemical scheme for the C3 chemistry in the aqueous phase in addition to the existing multiphase mechanism MCMv3.1/CAPRAM 3.0m [1, 2] with 145 new species and 225 new reactions. Initial species of the new scheme are MCM species taken up from the gas phase. So far, only alcohols, carbonyls, and organic acids are considered including unsaturated compounds.

Experimental data in the aqueous phase are based on an up-to-date database with 474 reactions of OH and 125 reactions of NO₃ with VOCs, respectively.

Prediction methods for stable species have been evaluated (see below) and the SAR of Monod and Doussin [4] was chosen for the mechanism construction whenever possible. Remaining rate constants were predicted with the SAR of Minakata et al. [5].

The fate of radicals was estimated with constant rate constants and branching ratios.

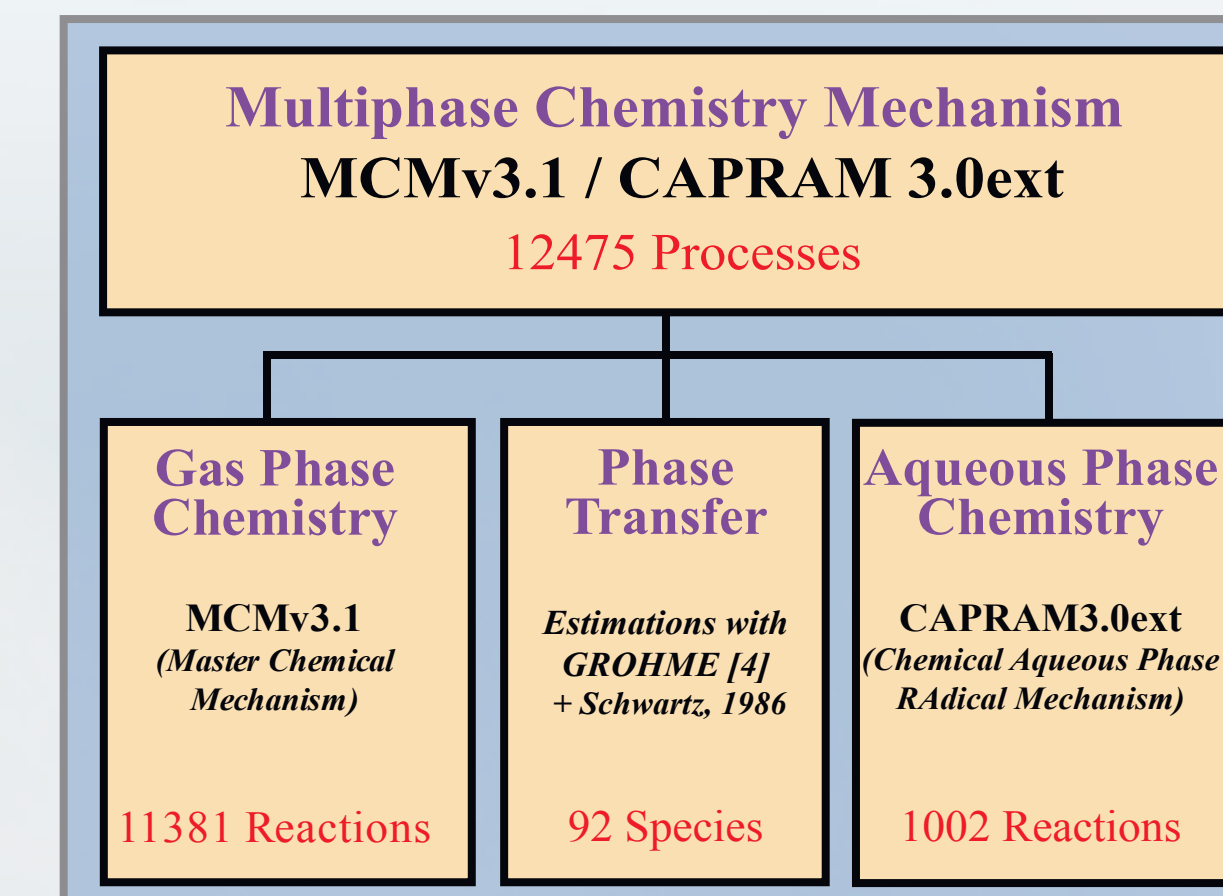


Fig. 1. Schematic representation of the multiphase mechanism.

Evaluation of prediction methods

An evaluation of different prediction methods has been performed including correlations of gas and aqueous phase rate constants, the homologous series of different compound classes, Evans-Polanyi-type correlations, and structure-activity relationships (SARs).

Gas - aqueous phase correlations comprise large uncertainties while homologous series of compound classes work only in some specific cases.

Evans-Polanyi-type correlations [6] consider only H-abstraction reactions of the weakest bonded H-atom, which results in underestimation (Fig. 3a,b). BDEs are needed for the correlations, which have to be estimated with a group additivity method, yet several increments are missing.

SARs seem to be the most accurate prediction tool, however, for more complex molecules with more than one functional group the accuracy decreases (compare Fig. 3). Two different SARs have been tested, the one of Monod and Doussin [4] and the one of Minakata et al. [5], see Fig. 2.

The SAR of Monod and Doussin has a little higher accuracy, however with 22 descriptors for 72 compounds overfitting is likely. Also, the method describes only H-abstraction reactions of OH with aliphatic alkanes, alcohols, acids and bases, and carbonyls coming soon [pers. comm.].

The Method of Minakata et al. has a lower accuracy, yet with 434 species a large database has been used to describe the H-abstraction by OH of almost all atmospherically relevant saturated and unsaturated compounds as well as benzene, furans, pyridines, imidazoles, and triazines.

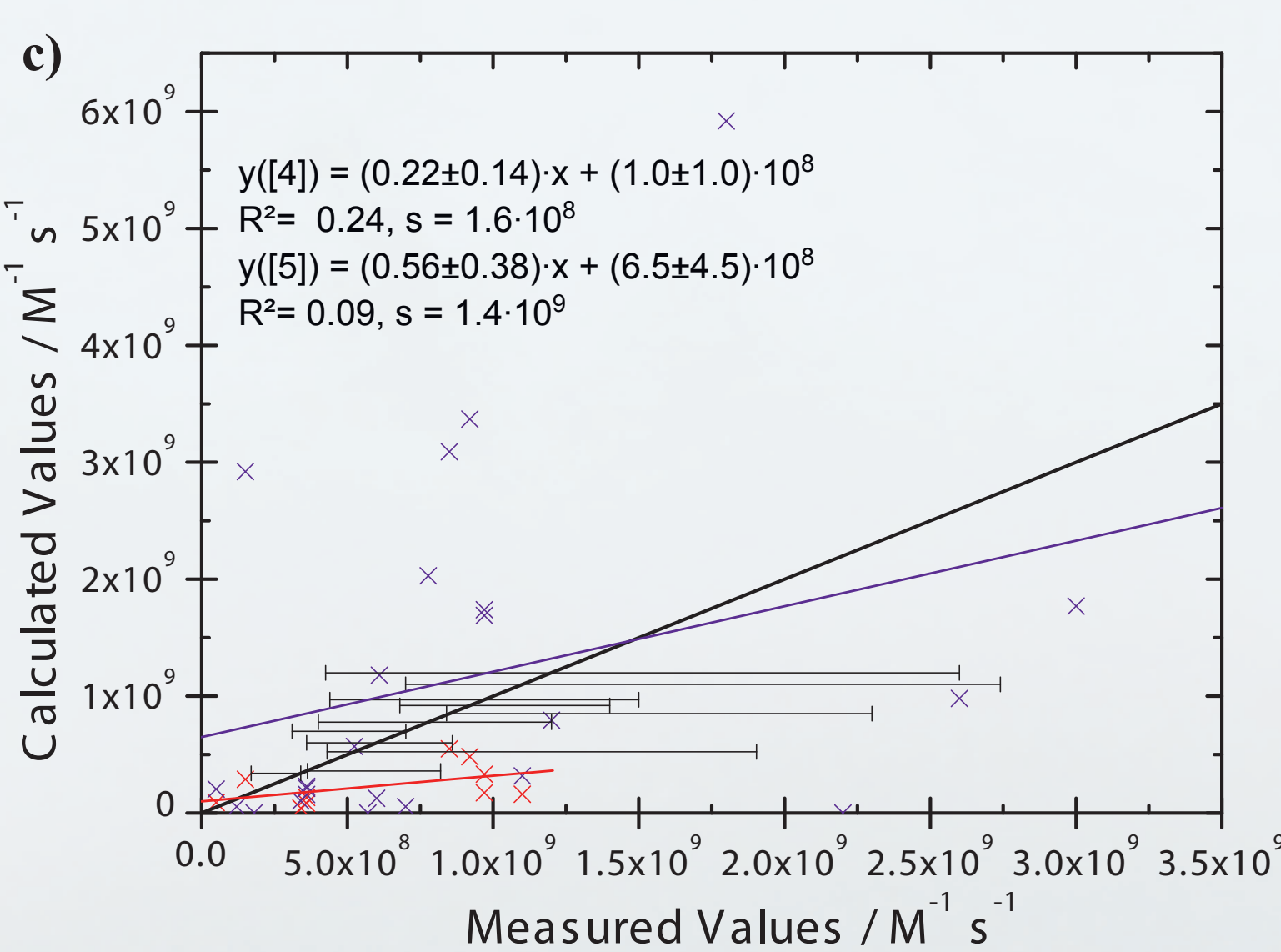
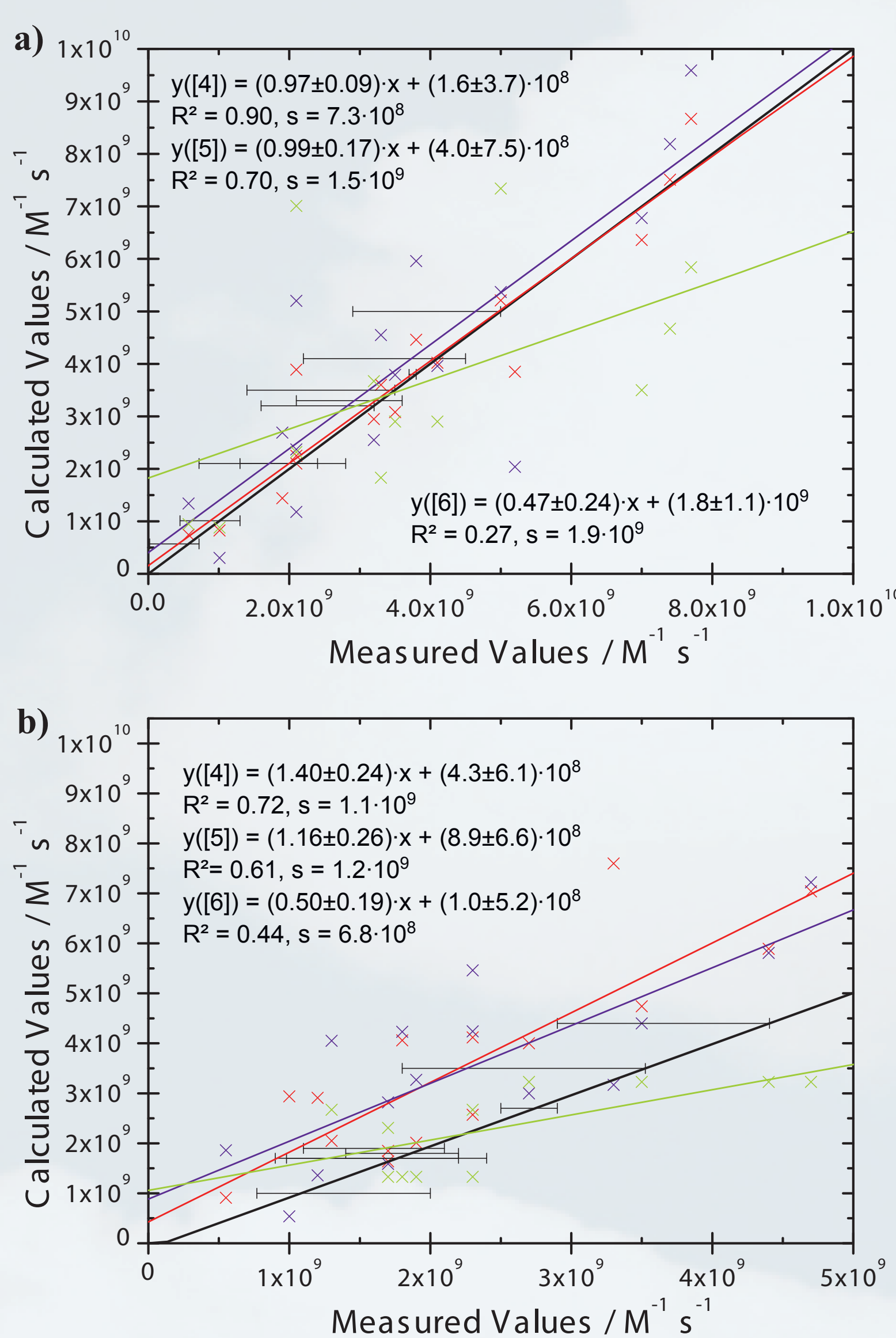


Fig. 3. Comparison of predicted vs. measured Data for the two SARs of Minakata et al. [5] (blue) and Monod et al. [4] (red) and Evans-Polanyi-type correlations [6] (green) for monoalcohols (a), polyols excluding sugars (b), and polyfunctional compounds (c). Error bars indicate range of measurements.

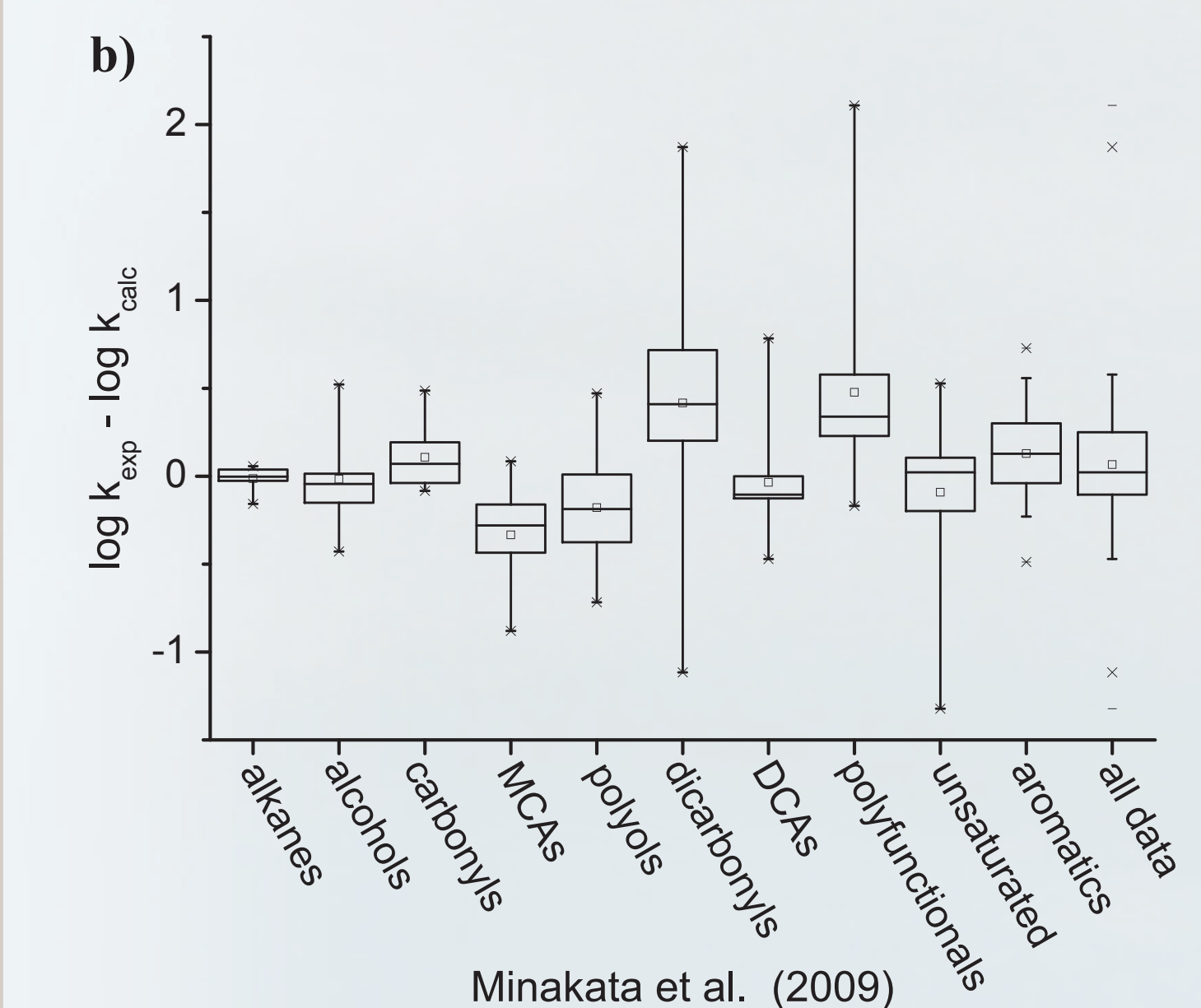
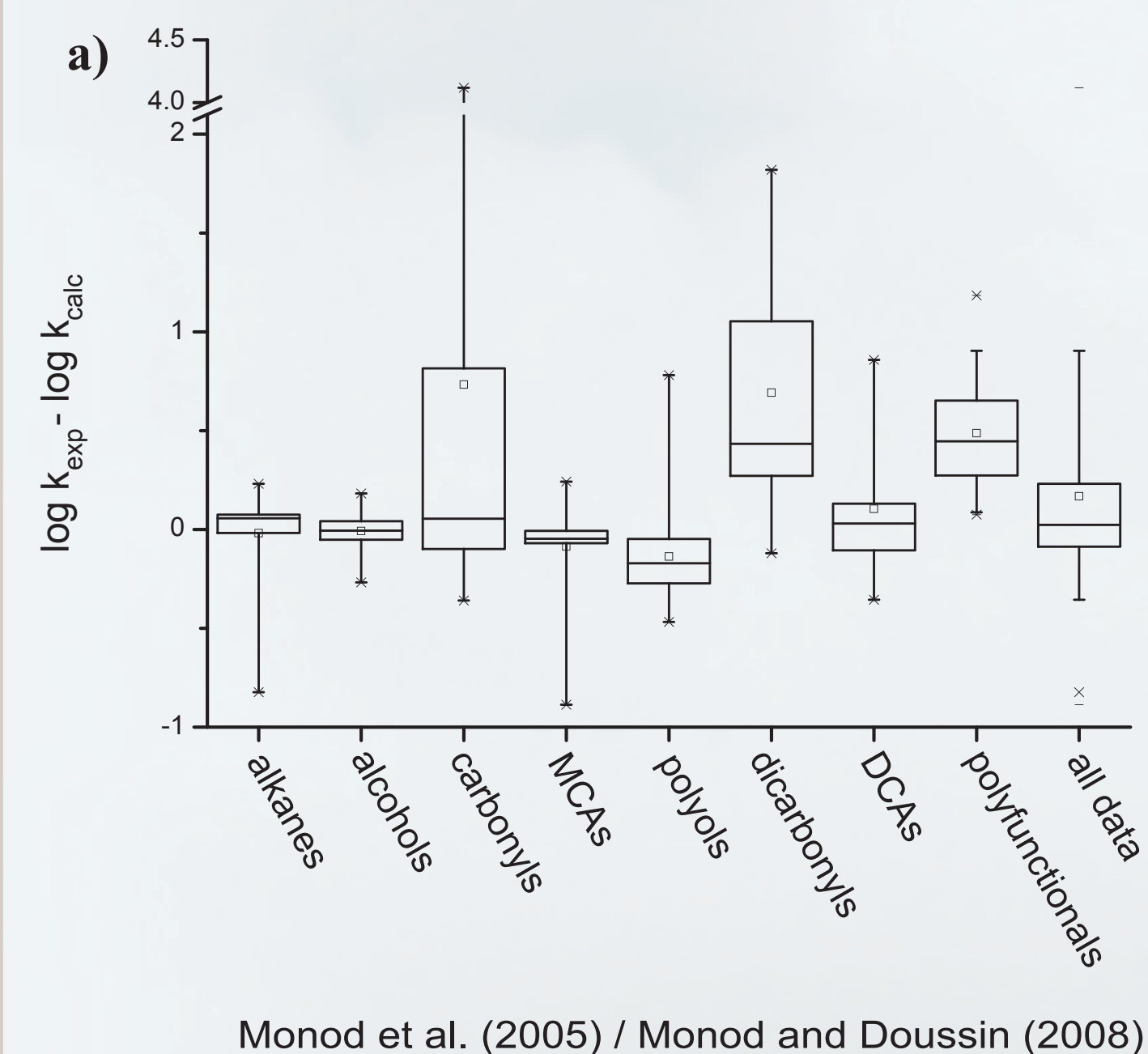


Fig. 2. Comparison of the accuracy of the two different SARs of Minakata et al. [5] and Monod et al. [4, 7]. Boxes represent 25% and 75% percentile, the line in the boxes is the median, squares are the mean value, whiskers are 5% and 95% percentile, crosses are 1% and 99% percentile, minus signs are minimum and maximum. For a) the method of Monod and Doussin [4] was applied except for carbonyl compounds, where the older method of Monod et al. [7] was used. b) shows the method of Minakata et al. [5].

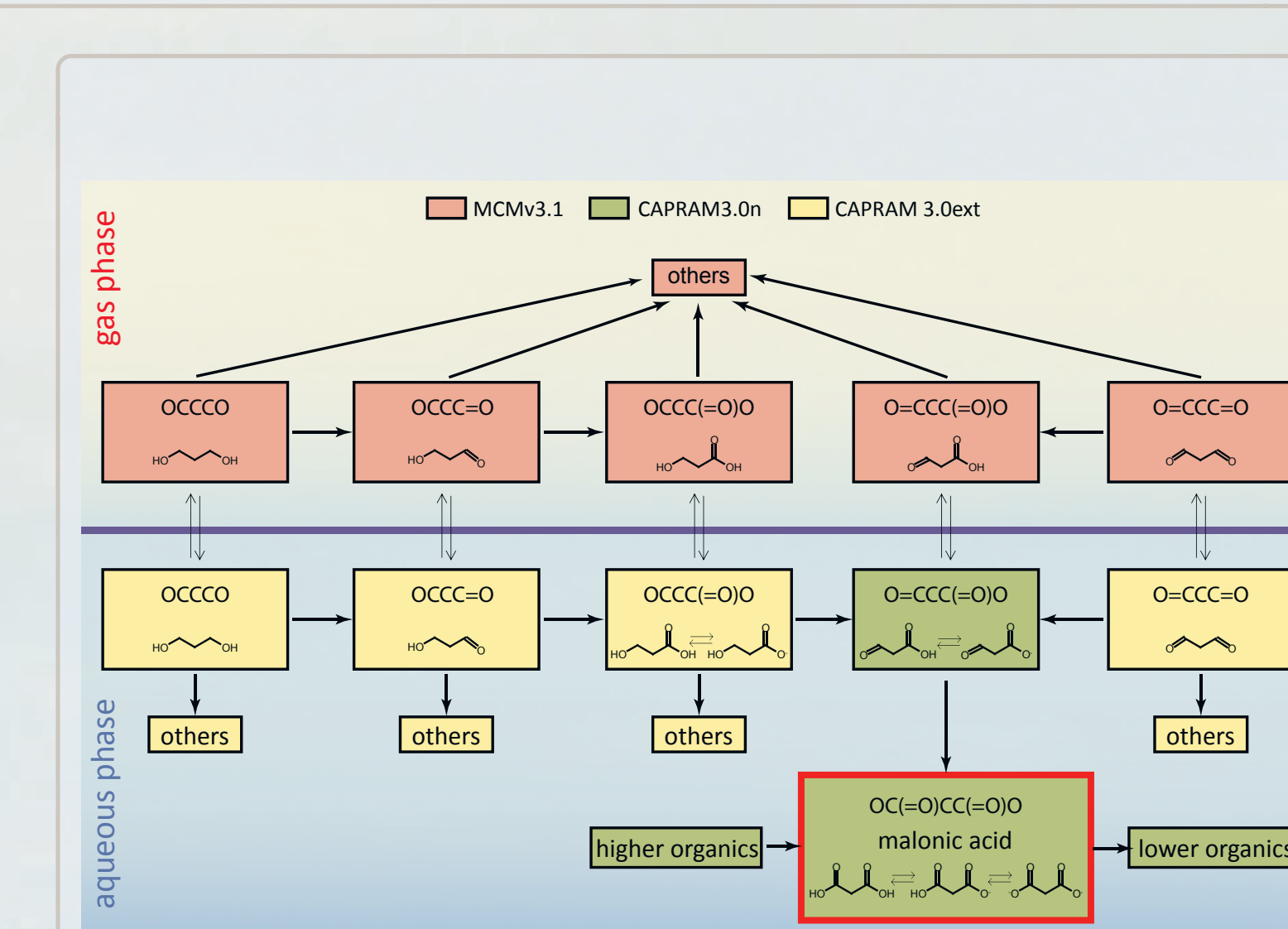


Fig. 8. Schematic of the influence of the new C3 oxidation scheme to the concentration profile of malonic acid.

Model results and discussion

The advancement of the C3 chemistry in CAPRAM influences the concentration profiles of many organics in the gas and aqueous phase (compare Fig.s 5 - 10).

E.g. malonic acid production is enhanced (Fig.s 8, 9). While most precursors are reduced in the gas phase, the direct precursor 3-oxo-propanic acid is enhanced (Fig. 10).

C2 chemistry is also influenced as shown for glyoxylic acid (Fig. 6) and sum of all oxalate forms (Fig. 5).

The addition can lead to totally new regimes as in the case of 3-oxo lactic acid, which is partially owed to the fact of the addition of the hydrated form CH(OH)₂CH(OH)COOH (Fig. 6a).

Aqueous phase OH concentrations are lowered with the introduction of new organic (Fig. 4).

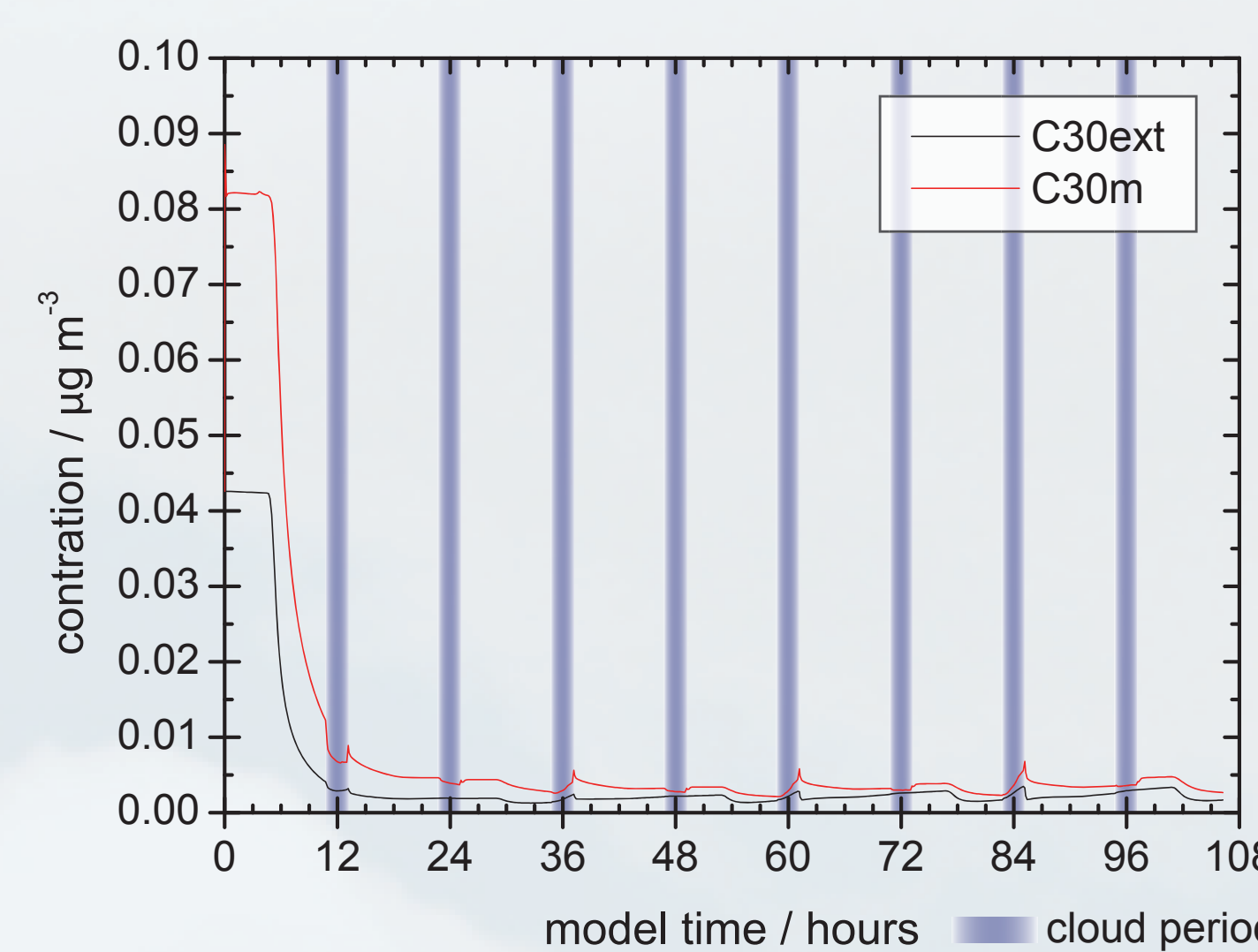


Fig. 5. Modelled aqueous phase concentrations of oxalic acid, oxalate mono- and dianion (including oxalate bound in iron complexes) for the whole modelling period of 108h with and without extension of the C3 chemistry.

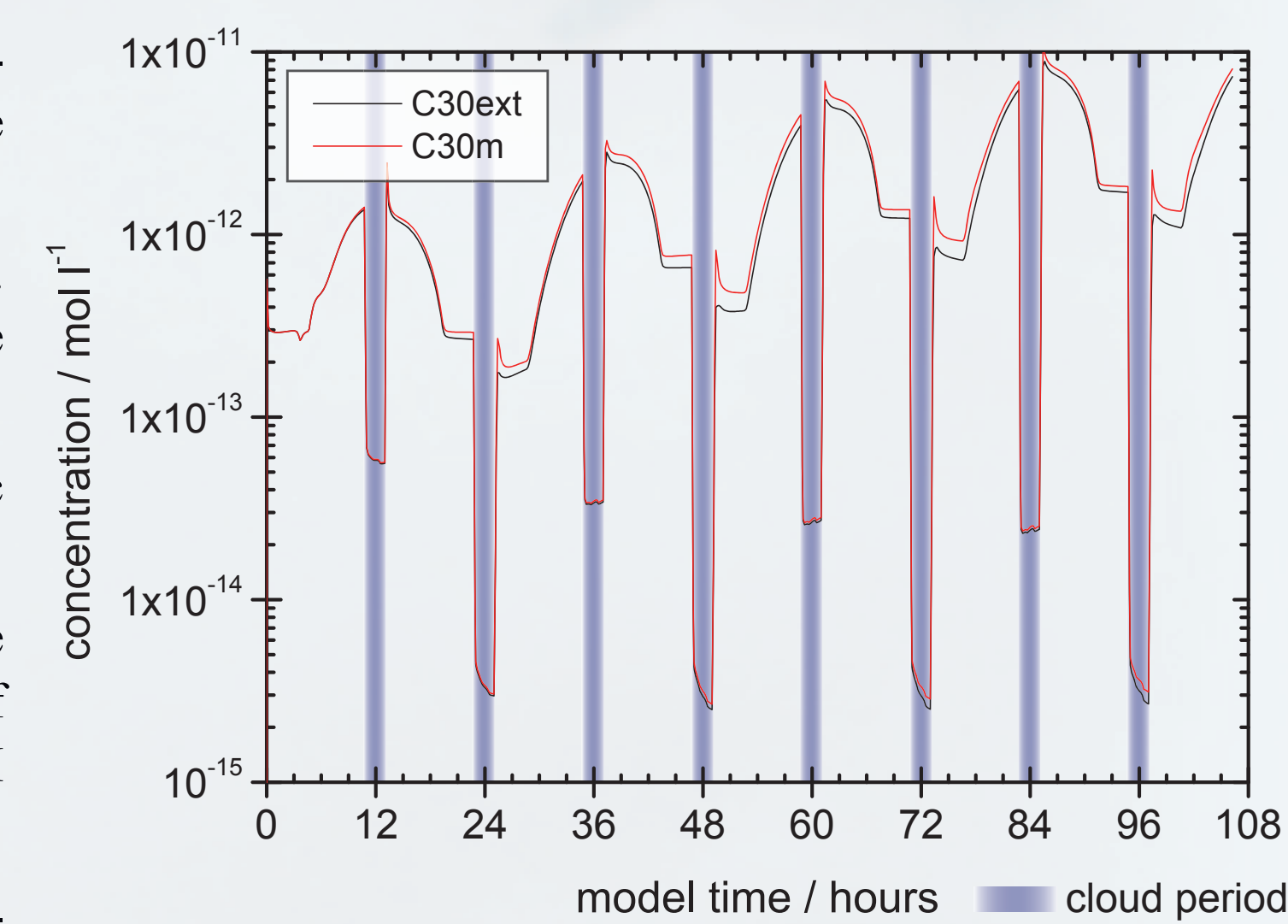


Fig. 4. Modelled OH(aq) concentrations for the whole modelling period of 108h with and without extension of the C3 chemistry.

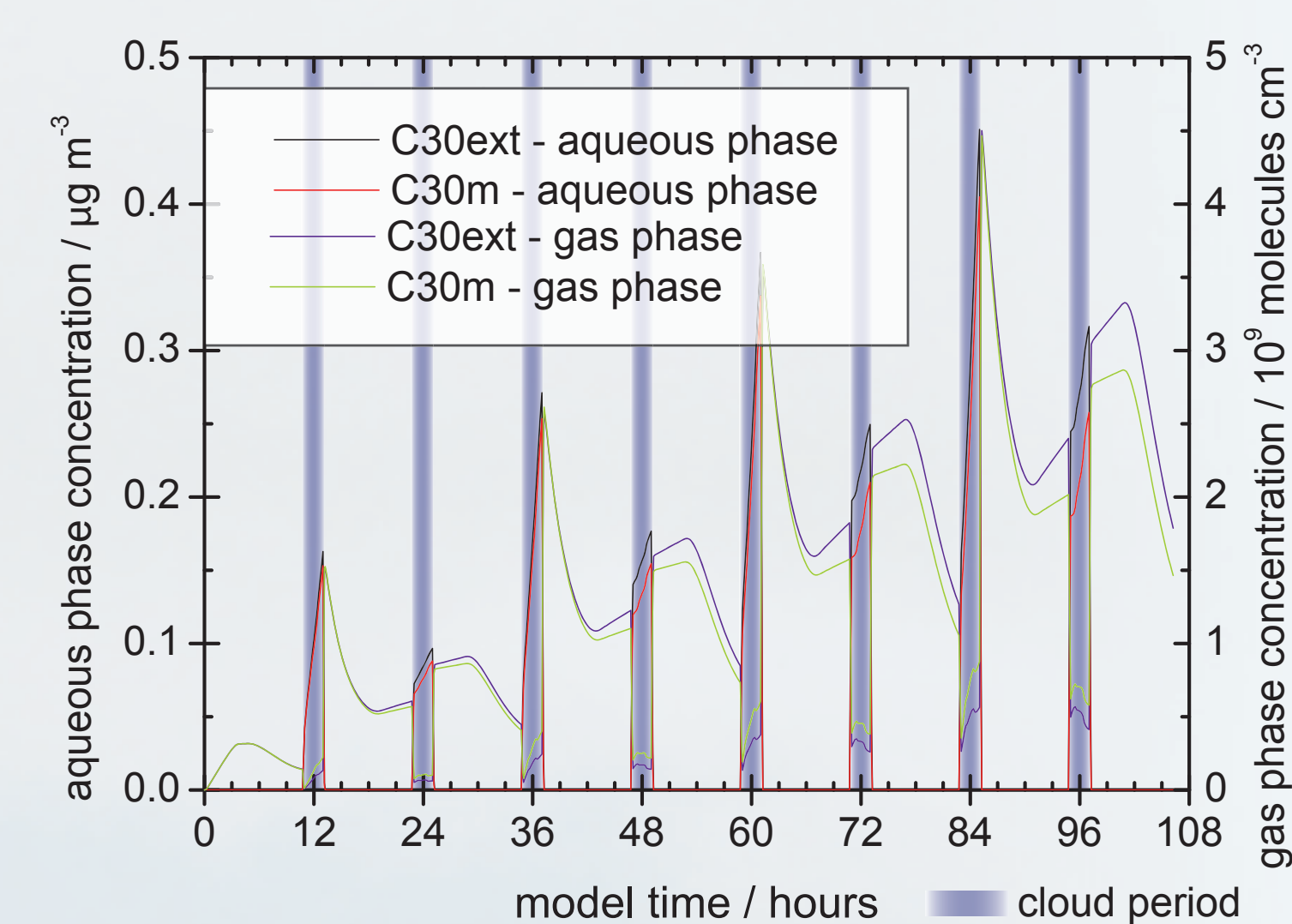


Fig. 6. Modelled gas and aqueous phase concentrations of the sum of glyoxylic acid and glyoxylate for the whole modelling period of 108h with and without extension of the C3 chemistry.

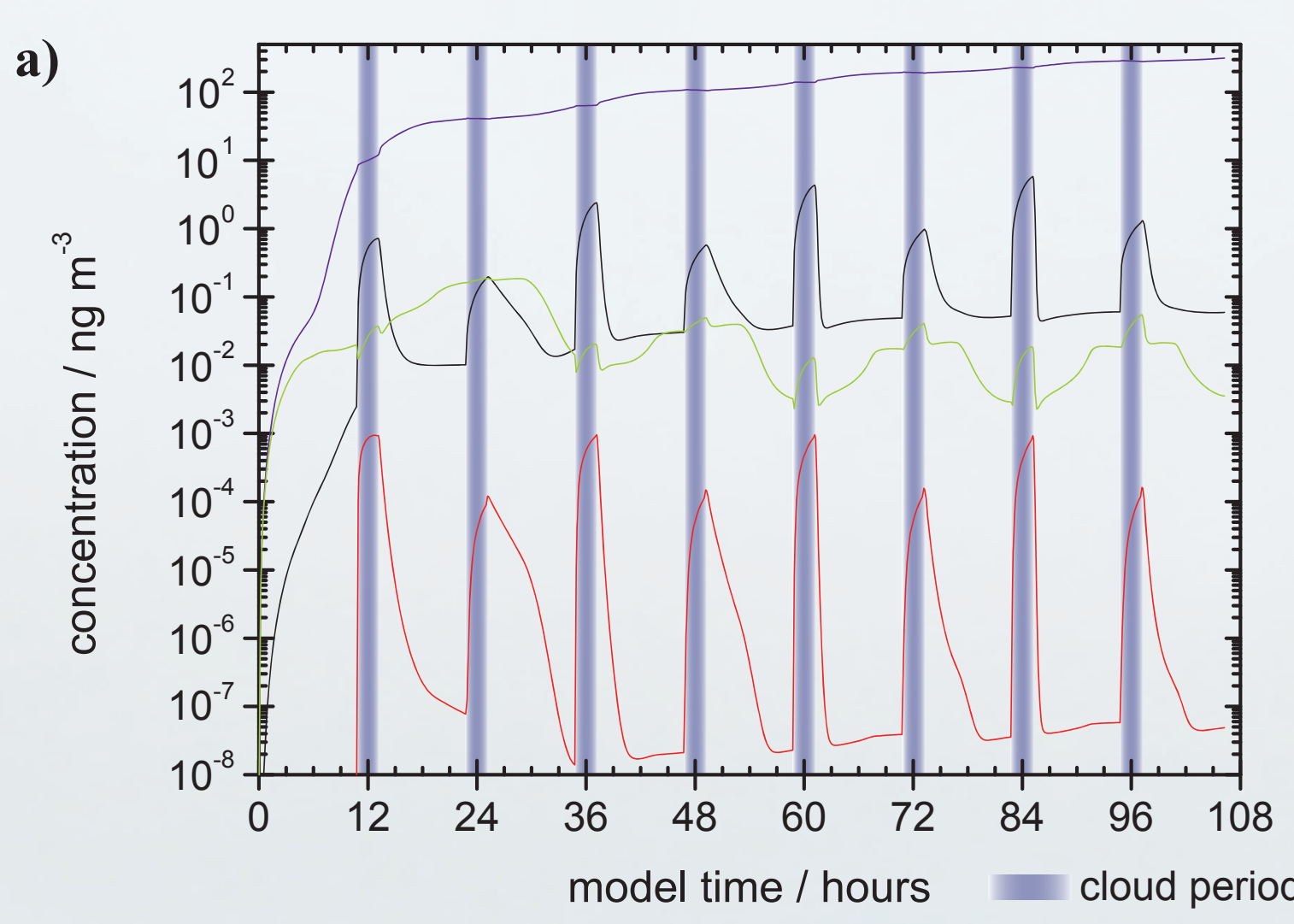


Fig. 7. Modelled aqueous phase concentrations of various C3 compounds for the whole modelling period of 108h with and without extension of the C3 chemistry. Different states in hydration or dissociation are summed up in one model species.

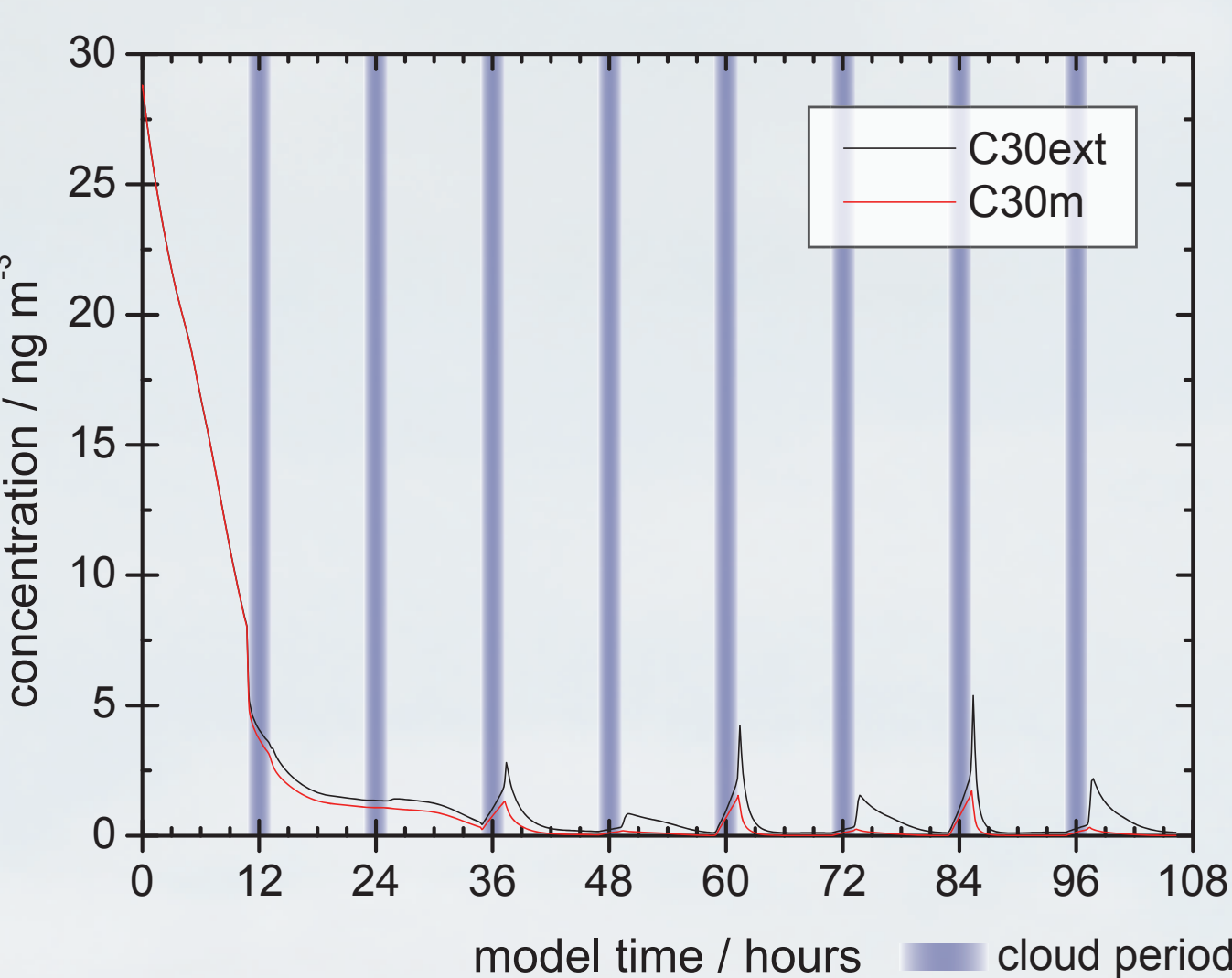
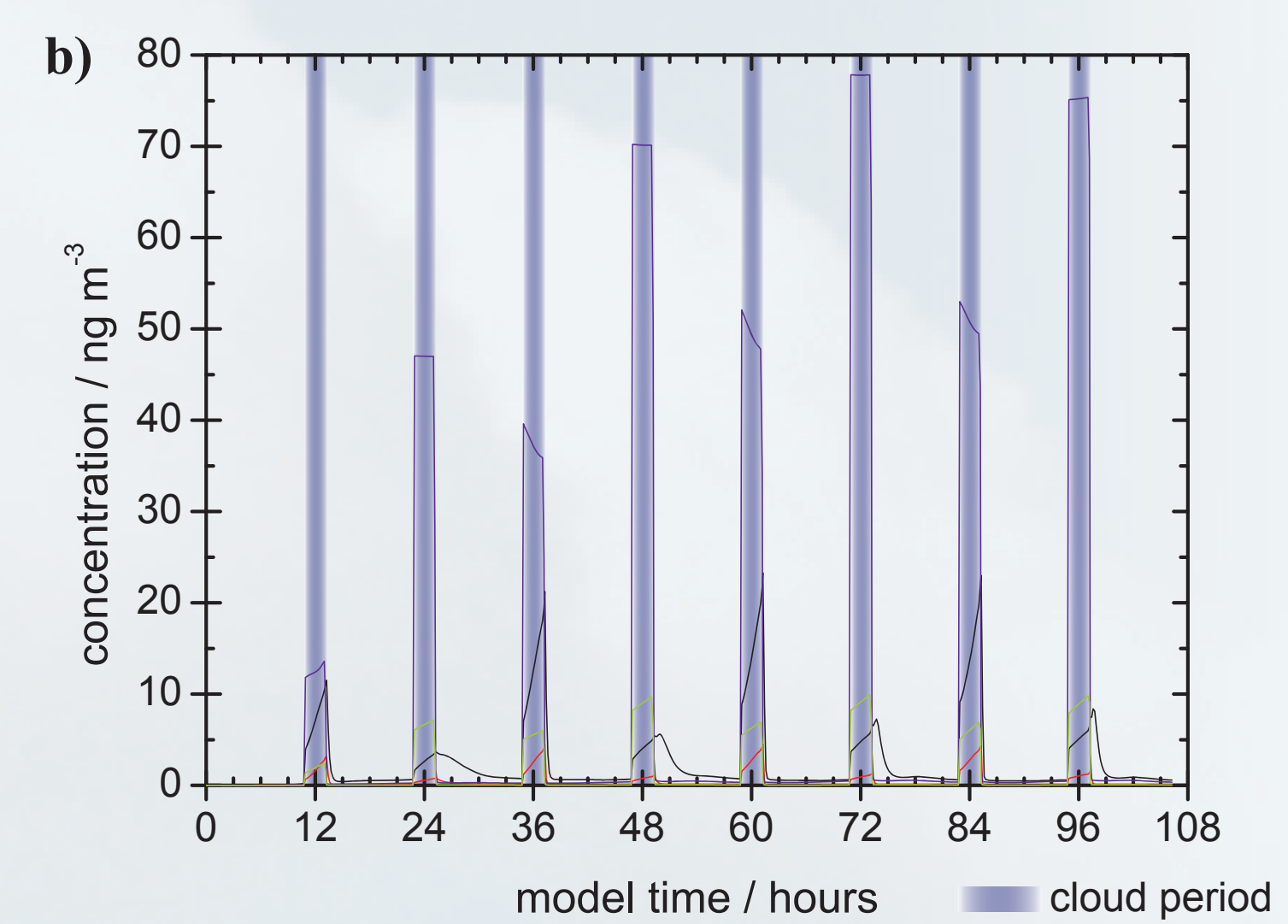


Fig. 9. Modelled aqueous phase concentrations of the sum of malonic acid, malonate mono- and dianion for the whole modelling period of 108h with and without extension of the C3 chemistry.

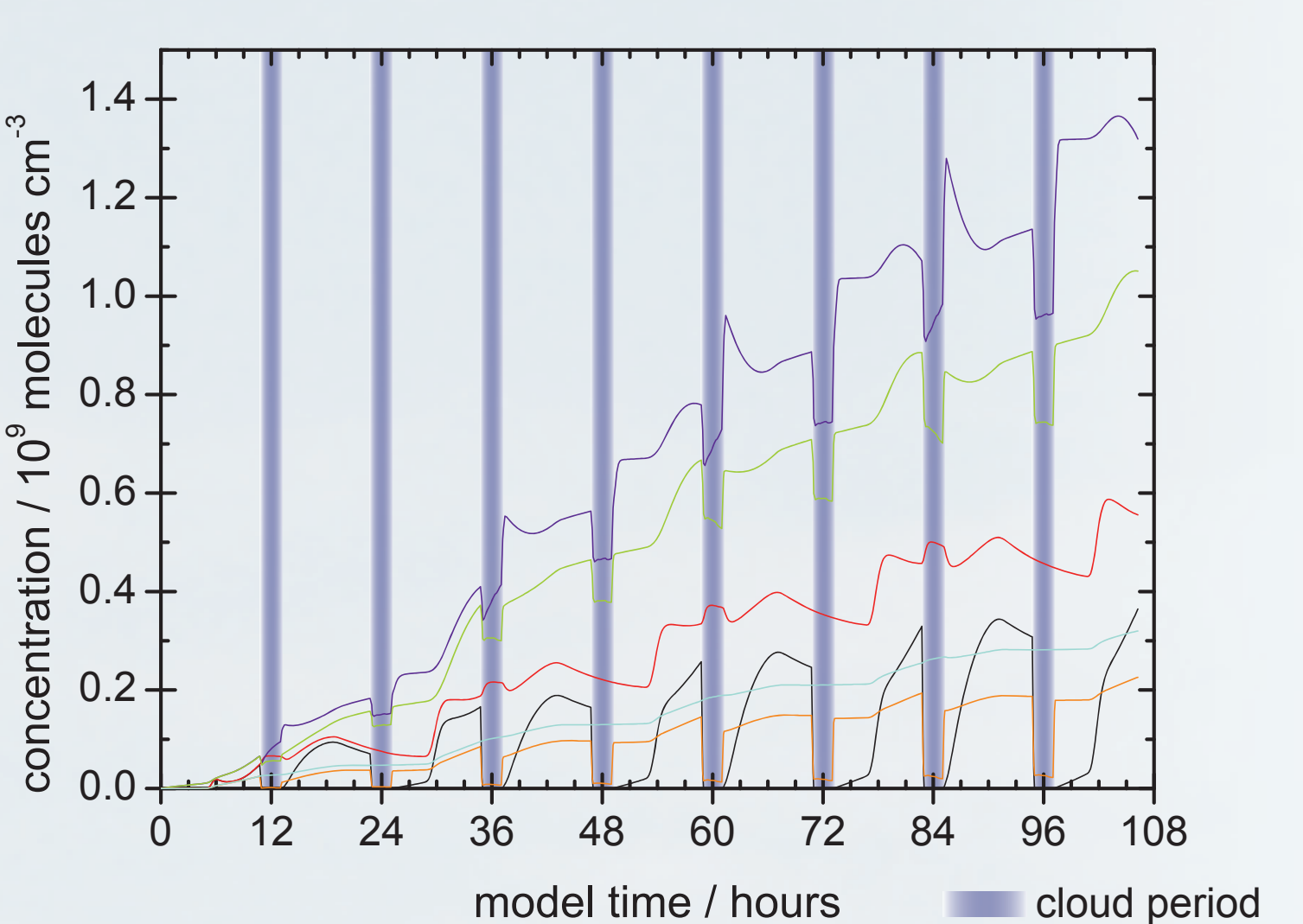


Fig. 10. Modelled gas phase concentrations of various gas phase species for the whole modelling period of 108h with and without extension of the C3 chemistry.

Summary

Organic compounds influence tropospheric multiphase chemical processes. While larger compounds can significantly contribute to those processes they are currently not well described in oxidation schemes of atmospheric models. The current study introduced a new near-explicit chemical aqueous phase oxidation scheme for C3 compounds to the multiphase mechanism MCMv3.1/CAPRAM 3.0m. First results for a remote case show the importance to include higher organics in aqueous phase mechanisms. The update of the CAPRAM 3.0m lead to new insights of the formation of several C3 compounds such as lactic acid, pyruvic acid, or malonic acid. The oxidation of C3 compounds also influenced lower weight compounds, e.g. glyoxylic acid.

The evaluation of prediction methods for aqueous phase rate constants found SARs to be the most precise and an easy-to-use method. With this knowledge it is now possible to create automated mechanisms and explore the tropospheric multiphase chemistry with even more advanced chemistry mechanisms. Further studies will aim to introduce branched OH and NO₃ attacks to organic compounds to the existing CAPRAM mechanism and advance the C4 chemistry.

References

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Acknowledgements

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