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Introduction and Motivation

Organic compounds are an ubiquitous constituent of the troposphere influencing air quality and human health and are therefore research topic for the last decades. Clouds influence the multiphase chemistry of organics significantly.

Modelling provides a useful tool to explore the tropospheric multiphase chemistry. However, aqueous phase chemical mechanisms are restricted compared to gas phase mechanisms, e.g. MCM [1]. Therefore, the goal of the current study was to advance the aqueous phase chemical mechanism CAPRAM 3.0n (C3.0n) [2] with the most detailed, near-explicit C3 and C4 chemistry. New oxidation schemes for several case studies have been developed with up to 4798 gas phase species and 11381 gas phase reactions and 2364 aqueous phase species and 3601 aqueous phase reactions out of which 279 compounds can undergo phase transfer (see Figure 1).

Box model simulations with the air parcel model SPACCIM [3] have been performed for a meteorological scenario with non-permanent clouds at 45°N. Runs were performed for remote and urban conditions in summer.

Mechanism Construction

- Creation of a kinetic database with 474 OH and 125 NO₃ reactions with organics
- Evaluation of available prediction methods:
 - structure-activity relationships (SARs)
 - Evans-Polanyi correlations/BDE prediction after Benson [4]
 - Homologous series of various compound classes
 - gas-aqueous phase correlations
- Development of a prediction tool for automated mechanism construction based on GECKO-A [5]
- Methods used for the mechanism self-generation are:
 - SARs of Monod and Doussin [6,7] for aliphatic compounds, except unsaturated compounds, where Minakata et al. [8] was used.
 - GROMHE [9] for phase transfers
 - Dissociations according to Perrin et al. [10] as provided by GECKO-A
 - Radical decay estimated with constant values based on experimental data

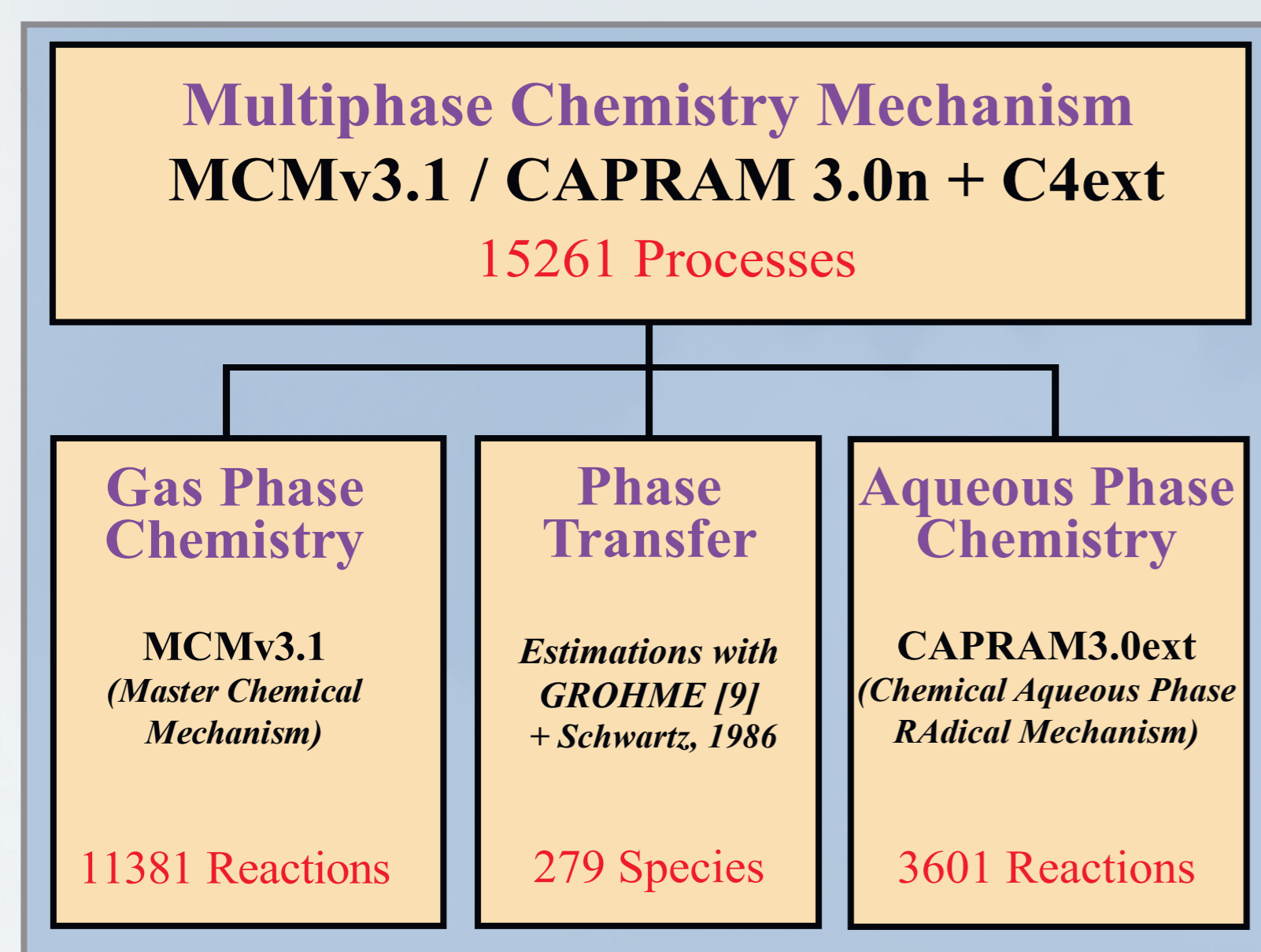


Fig. 1 Schematic representation of the multiphase mechanism.

➤ Expansion of the C3 and C4 chemistry in the aqueous phase in CAPRAM 3.0n (C3.0n) and coupling to the gas phase mechanism MCMv3.1 (see Figure 1 for details of the new mechanism)

1. step: Introduction of branching ratios to C3.0n (up to C4 compounds)
2. step: Addition of new C3 and C4 organic compounds taken up from the MCM gas phase mechanism, which were not yet present in C3.0n

➤ Only results from the first step (scenario C4branch) are shown on this poster together with a test scenario (C3ext), where the original MCM/CAPRAM version has been extended by the aqueous phase oxidation of 1,2- and 1,3-propanediol, 3-hydroxy propanoic acid, allyl alcohol, allyl aldehyde, and acroleic acid.

- C4branch: 1533 additional aqueous species and 2221 additional aqueous phase reactions
- C3ext: 210 additional aqueous species and 299 additional aqueous phase reactions
- LEAK: 6406 aqueous species and 9451 aqueous phase reactions

Summary and Outlook

An aqueous phase mechanism with about 3600 reactions has been developed by means of automated self-generation and coupled to the gas phase mechanism MCMv3.1. First results are shown for an extended C3 chemistry with about 1000 aqueous phase reactions and an extended C4 chemistry with about 3000 aqueous phase reactions. Box model simulations with a non-permanent cloud scenario have been performed focusing on the tropospheric aqueous phase. The studies included detailed time-resolved flux analyses to investigate malonic acid production. With the extended C4 scheme, discrepancies between model results and experimental data from the field could be resolved during cloud periods. However, during non-cloud periods, malonic acid exists almost exclusively in the gas phase in contrast to field measurements.

In current experiments at the LEAK chamber, data were not suitable to validate the mechanism as the particulate concentrations of all organics were close to the detection limit and thus not detected in the current experiment. However, gas phase concentration profiles show a good agreement with model results, such as the decrease of about 200ppb of hexane in the gas phase. Future experiments should be aimed at even more water soluble reaction products to assure aqueous phase concentrations above the detection limits of the instruments used.

Moreover, further mechanism development already includes the introduction of RO₂ cross reactions and the oxidation of organics by NO₃. Detailed studies with the non-permanent cloud scenario under different meteorological conditions are planned. Besides the multiphase investigations of the concentration profiles, highly time-resolved reaction flux investigations will be performed to improve the understanding of cloud chemistry.

Model Results and Discussion

Modelling of tropospheric cloud processing

- Comprehensive investigations of the organic multiphase chemistry including detailed time-resolved reaction flux analyses for the different scenarios (see Figure 2) have been performed.
- Investigations include different subsystems, e.g. malonic acid production (see Figure 2), using the original CAPRAM 3.0n version (ORIG) and the extended schemes C3ext and C4branch.
- The extended scenario C4branch greatly improves the understanding of malonic acid production during cloud periods. The modelled concentrations of 80 ng m⁻³ fall in the range of field measurements, e.g. by Bao et al. [11], who measured between 32.7 and 122 ng m⁻³.
- Implementation of the phase transfer of malonic acid leads to an overestimation of gas phase concentrations and an underestimation of aqueous malonic acid concentrations during non-cloud periods (see Figure 3). Almost all of the up to 80 ng m⁻³ malonic acid are released to the gas phase despite the high Henry's Law constant of 3.7·10⁶ M atm⁻¹ during non-cloud periods. Measurements of Bao et al. [11] give maximum gas phase concentrations of only 26.8 ng m⁻³.
- The extended C3 scheme only slightly improves the underestimation of malonic acid production of only a few ng m⁻³ in the original CAPRAM 3.0n version.
- 3-oxo propanoic acid being already part of CAPRAM 3.0n (ORIG) shows increased in-cloud production in the extended schemes (C3ext/C4branch) with increased concentration levels in the aqueous phase during cloud periods and, due to phase transfer, in the gas phase during non-cloud periods (see Figure 4, solid lines).
- Due to the newly implemented uptake of 3-hydroxy propanoic acid as a potential precursor of malonic acid, gas phase concentrations decrease and cause an in-cloud production (see Figure 4, dashed lines). Differences between the two extended schemes are small.
- Aqueous OH concentrations decrease in the C4branch scenario compared to ORIG due to the increased number of reactions with organic compounds (see Figure 5).
- Colour code in the following pictures (3 - 5) concerning the advancement of the mechanism is the following: remORIG (red), remC3ext (green), remC4branch (blue).

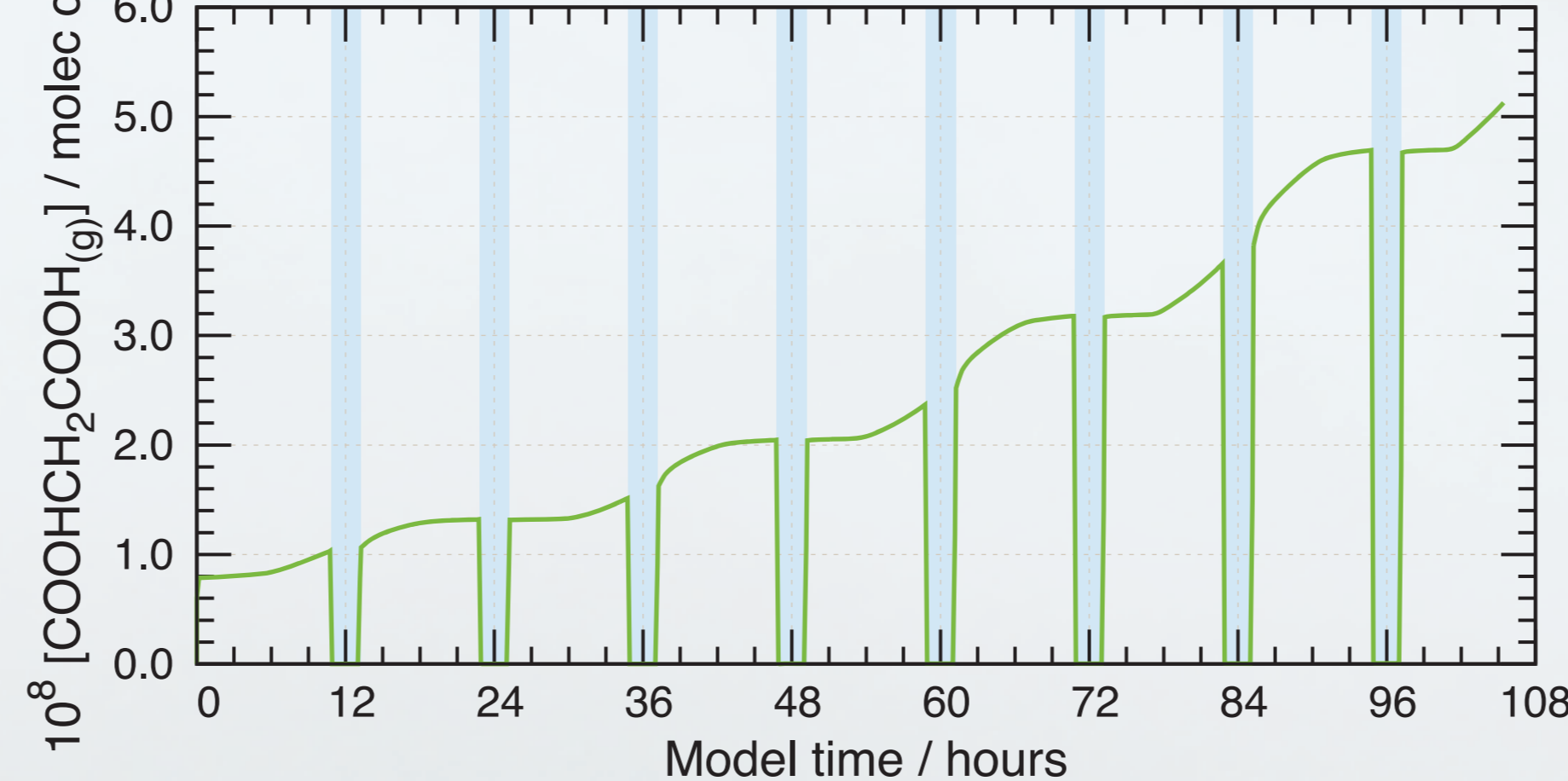
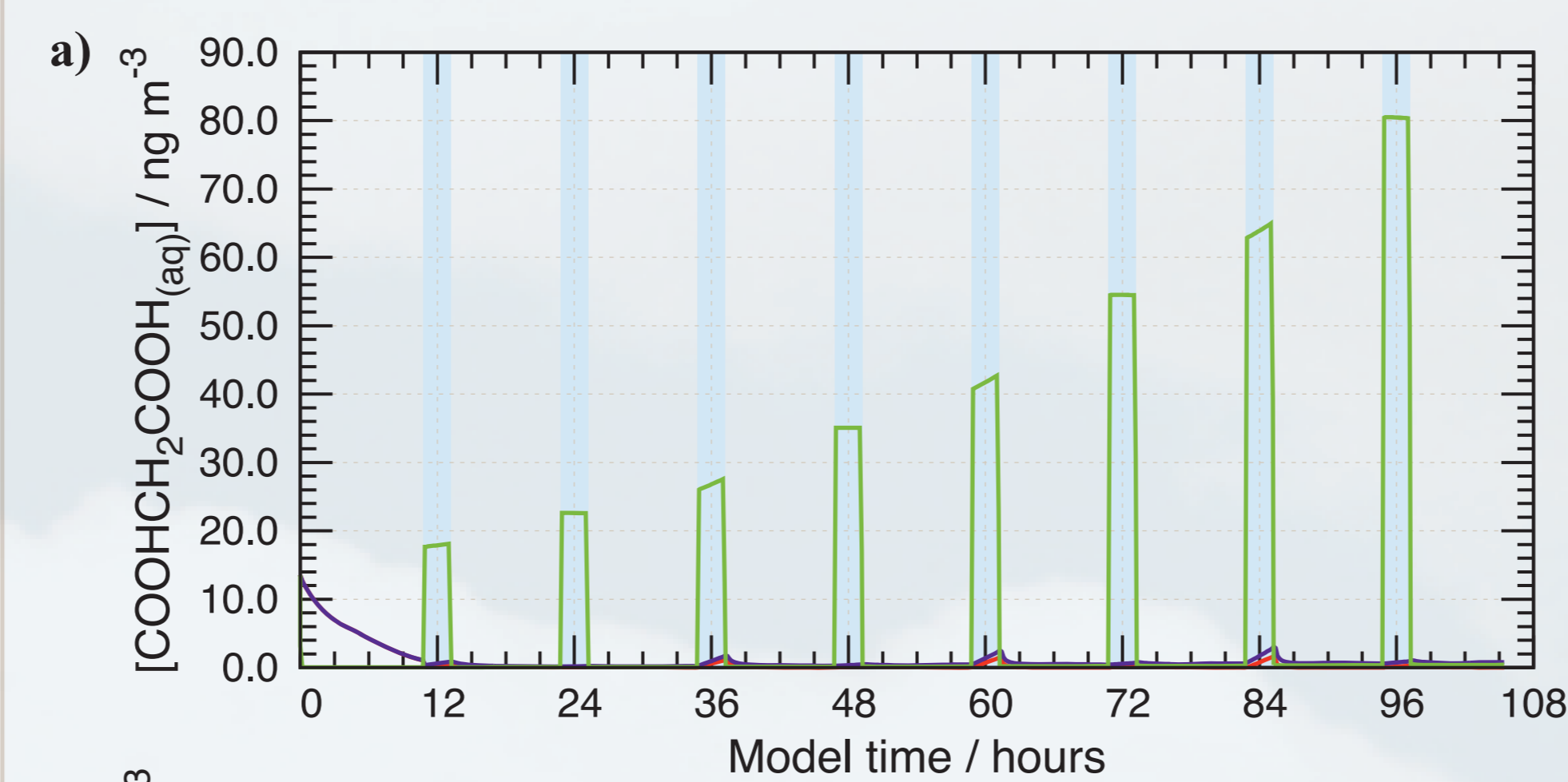


Fig. 3 Concentration-time profile of malonic acid in the aqueous phase (a) and the gas phase (b) for the different scenarios (colour-coded as described in the text) over the whole modelling period of 108h.

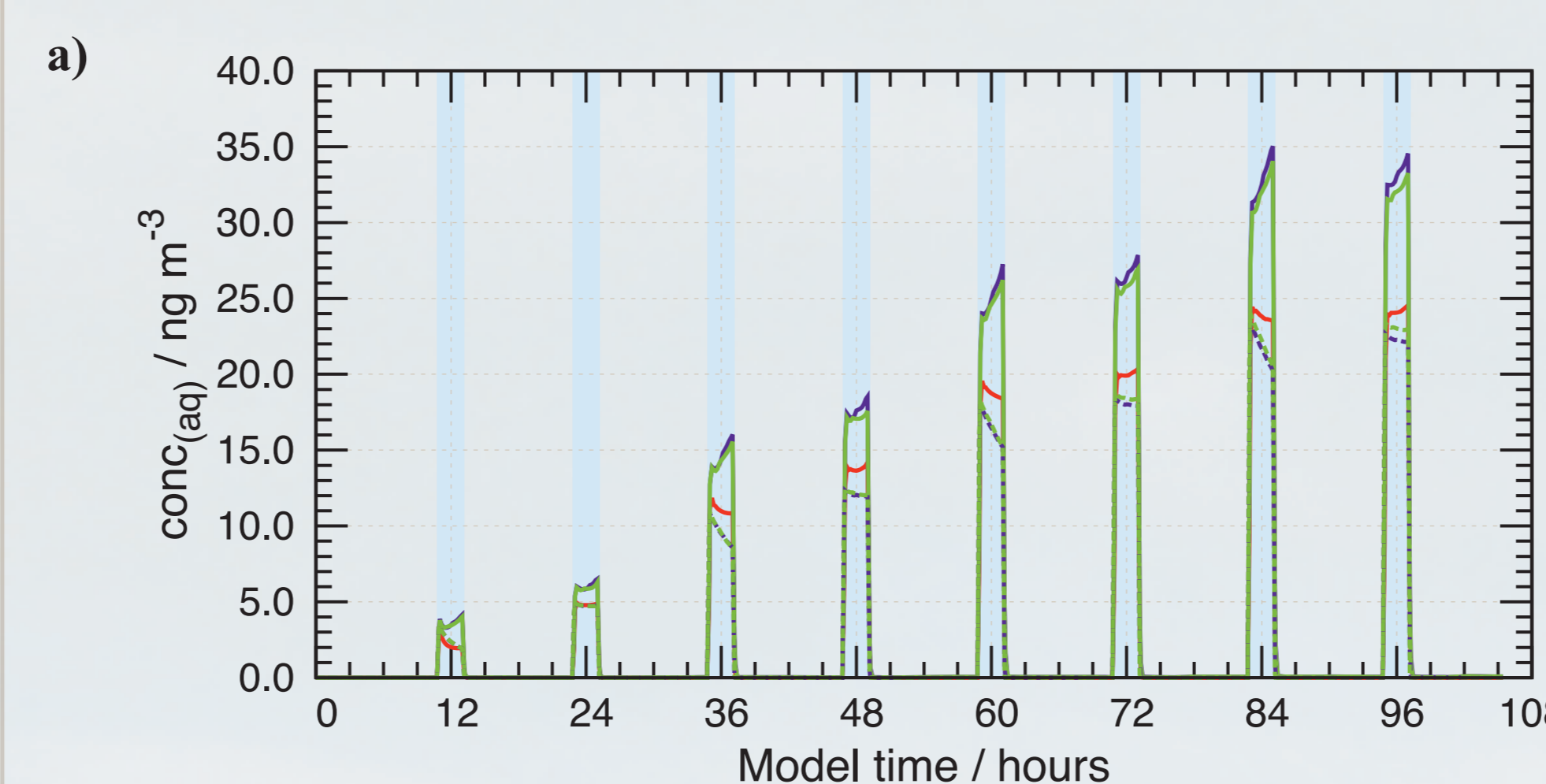


Fig. 4 Concentration-time profile of 3-oxo propanoic acid (solid lines) and 3-hydroxy propanoic acid (dashed lines) in the aqueous phase (a) and the gas phase (b), respectively, for the different scenarios (colour-coded as described in the text) over the whole modelling period of 108h.

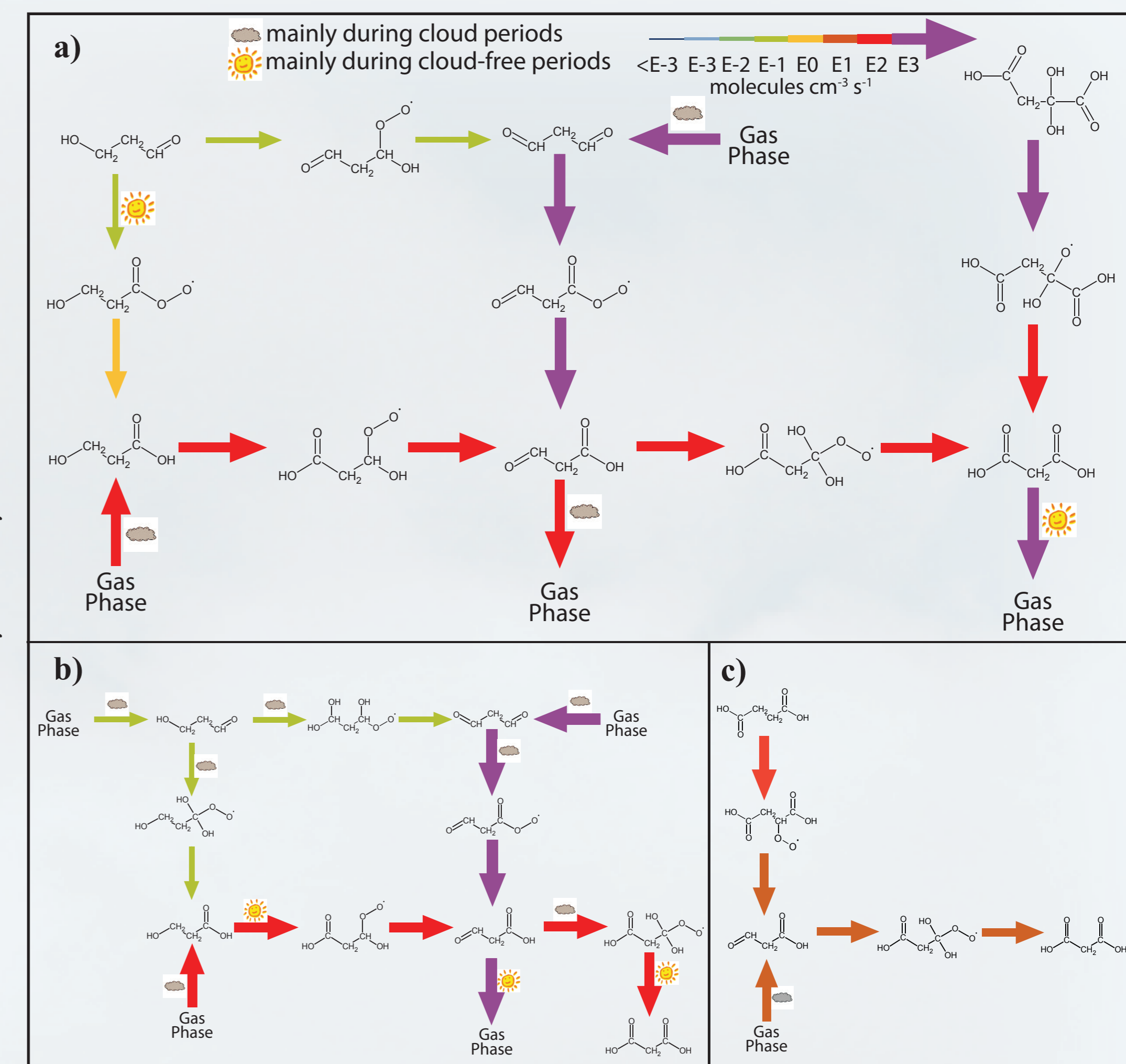


Fig. 2 Reaction flux scheme for malonic acid production for the scenarios C4branch (a), C3ext (b), and ORIG (c). Colour code and size of the arrows correspond to the order of magnitude of the reaction flux. A cloud symbol next to an arrow indicates that the reaction flux is important mainly during cloud periods, while a sun indicates that the reaction flux is mainly important during non-cloud periods.

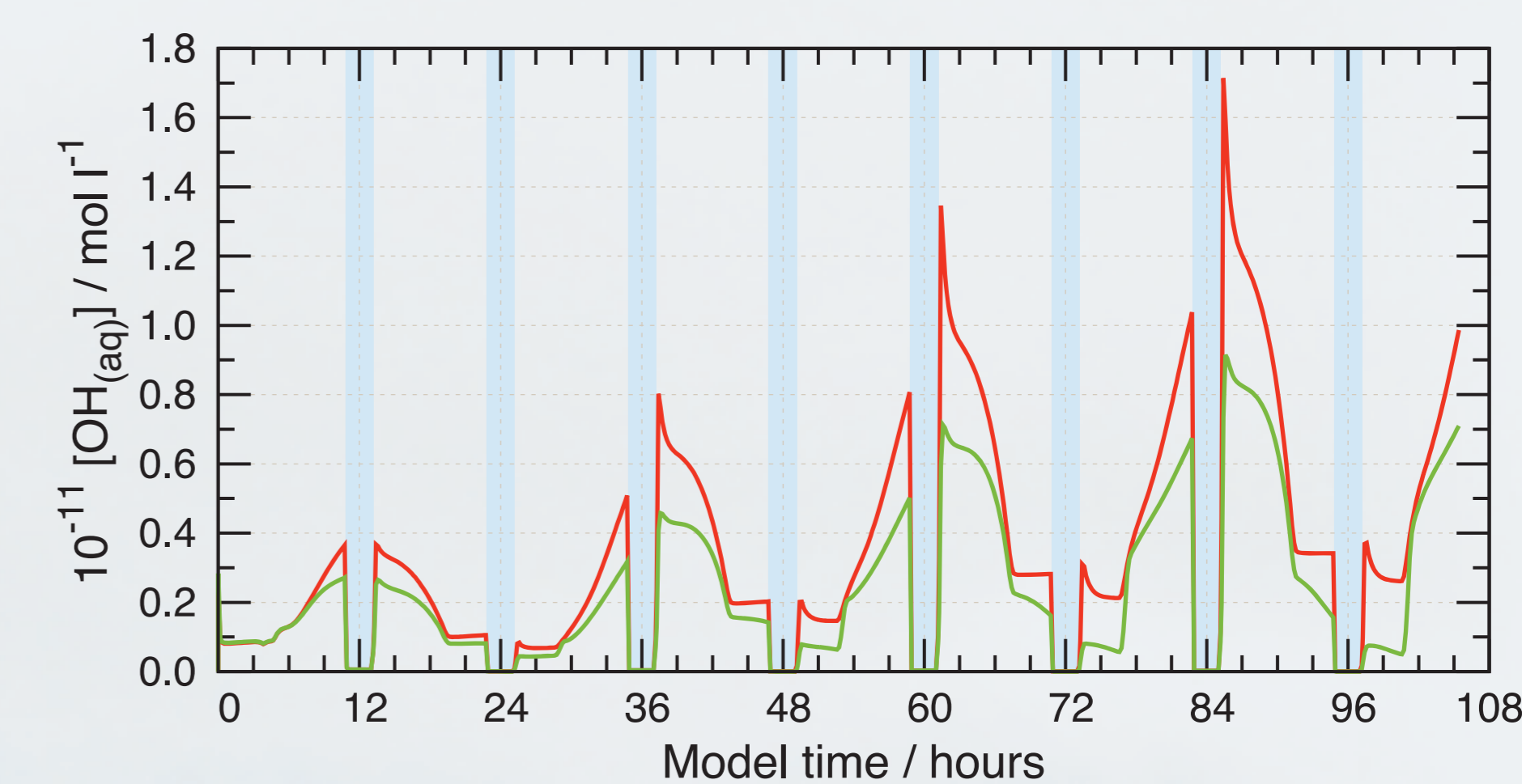


Fig. 5 Concentration-time profile of aqueous OH radicals for the different scenarios (colour-coded as described in the text) over the whole modelling period of 108h.

Chamber Runs

- Chamber experiments at the LEAK chamber [12] have been performed at 70%rH, room temperature (~20°C) to validate the created mechanism.
- 0.5ppm hexane were initiated in the gas phase and oxidised by OH.
- OH production was via reaction of TME (30ppb) with ozone (30ppb).
- Gas phase decrease of 200ppb hexane could be reproduced by the model in the run LEAK (compare Figure 6).
- Increase in aqueous phase concentrations of organics (see Figure 7) were not found in the chamber experiments, as all concentrations were close to the detection limits of the instruments used.

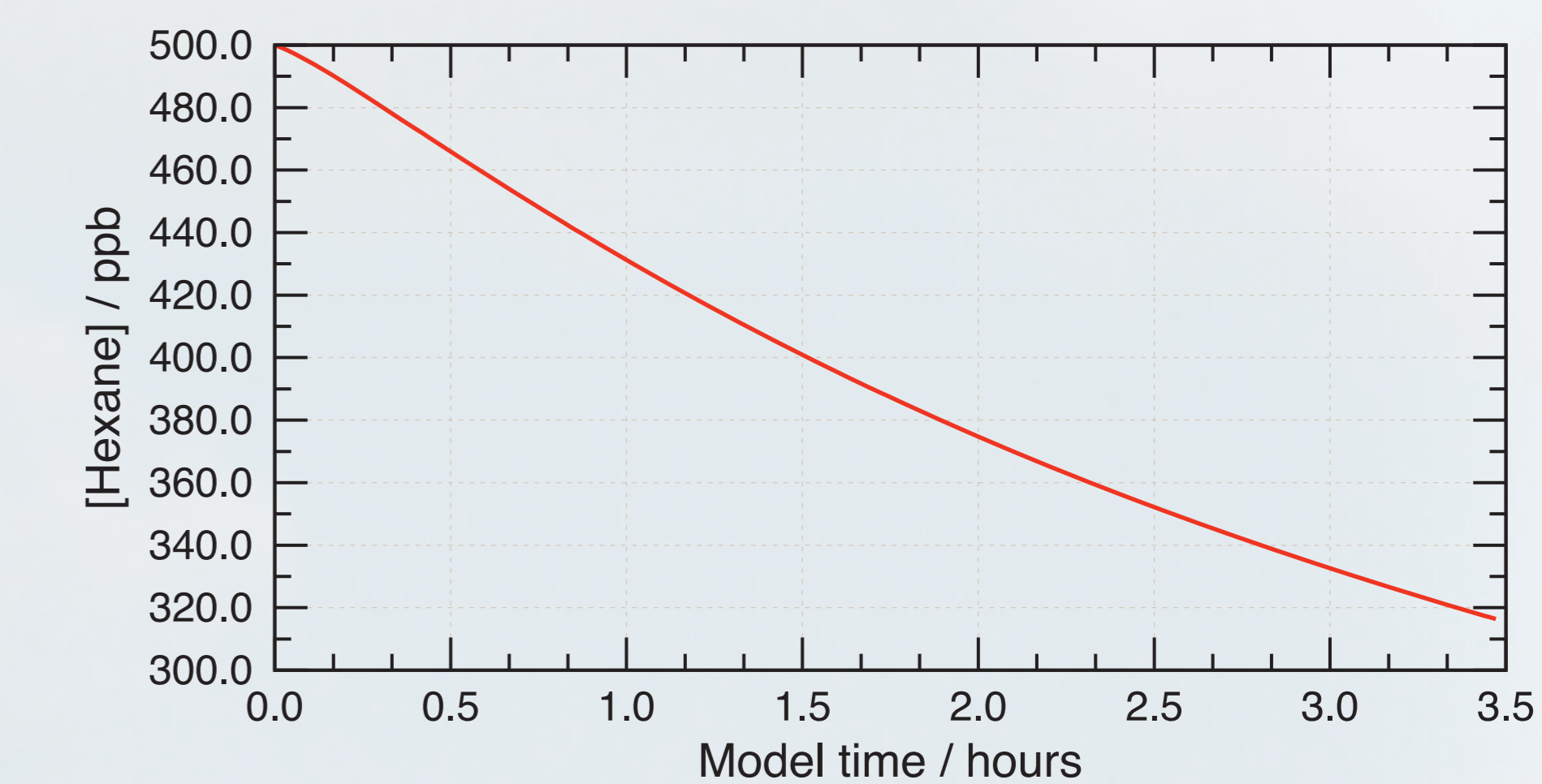


Fig. 6 Modelled concentration-time profile of gaseous hexane for comparison with LEAK chamber experiments.

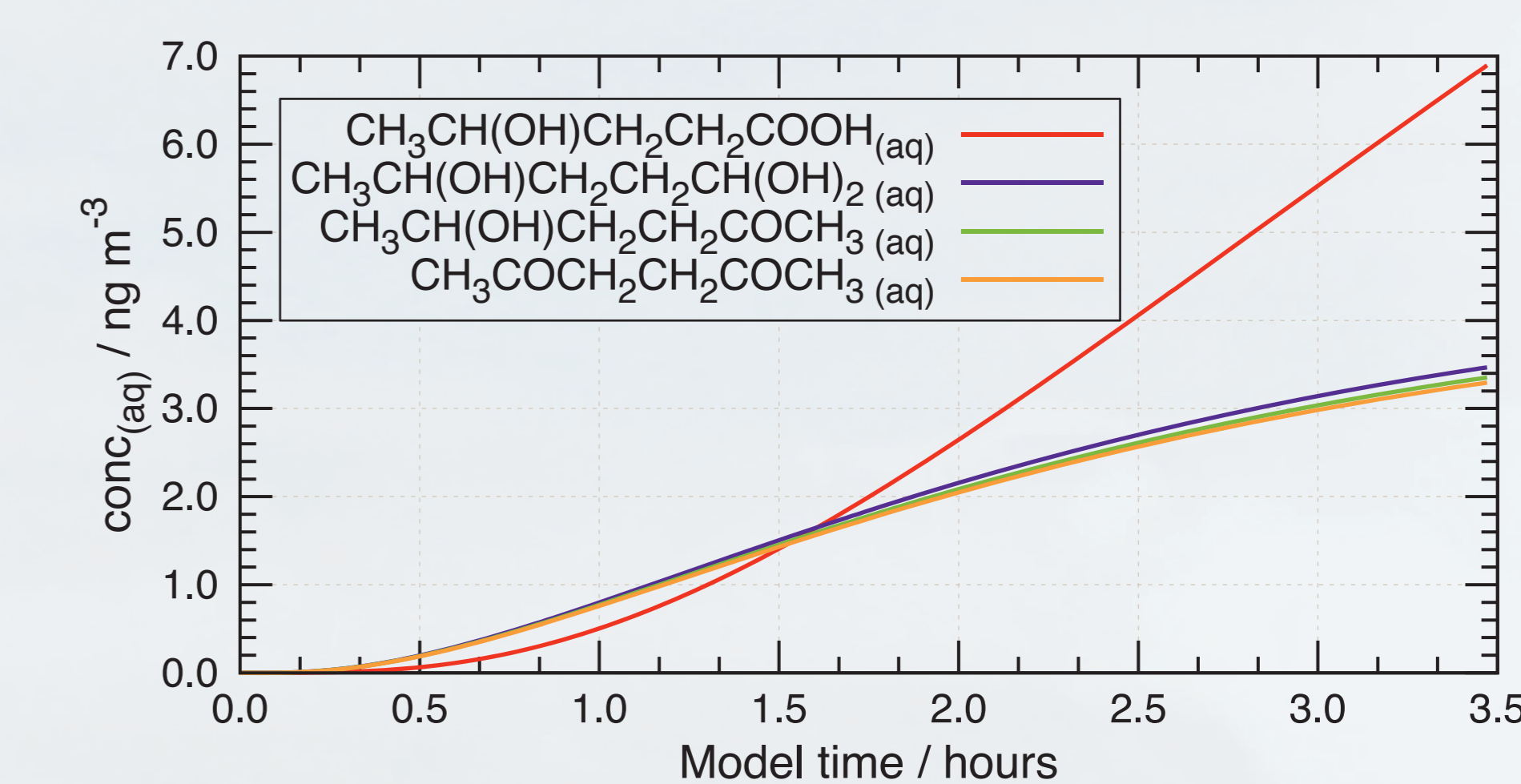


Fig. 7 Modelled concentration-time profiles of potential particulate oxidation products of hexane for comparison with LEAK chamber experiments.

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Acknowledgements

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