Modelling marine multiphase chemistry in box and chemical transport models with CAPRAM

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Introduction and Motivation

Oceans cover approximately 70% of the earth's surface (1) and influence the emission of sea salt particles and the tropospheric budgets of important trace gases such as dimethyl sulfide (DMS) and halocarbons. Therefore, in the marine boundary layer multiphase halogen and DMS chemistry plays a key role. Furthermore, emitted sea salt particles below a diameter of 130 nm are mainly composed of organic matter representing a strong carbon flux into the atmosphere.

DMS is the most important natural source of sulfate aerosols, thus significantly influencing direct and indirect radiative forcing. DMS oxidation is strongly dependent on the oxidizing agent and the medium (gas or aqueous phase) in which the oxidation takes place. It is closely linked to the chemistry of reactive halogen species (2). In addition, reactive halogen species have a significant influence on oxidation of volatile organic compounds (VOCs) as well as the degradation/production of O_3 and thus the oxidation capacity of the atmosphere (3). This can have strong effects on human health, as in coastal regions live more than 45% of all people worldwide (1).

In contrast to the gas-phase oxidation, the regional and global effect of the DMS oxidation in the aqueous phase is still quite little understood. Therefore, recent studies with the current parameterisation in higher-scale models still have very high uncertainties. Furthermore, multiphase chemistry is also very important for the activation of halogen radicals. The interactions in the aqueous phase are complex so that simple cause-effect principles can often not be derived. However, current implementations in higher scale models implement multiphase chemistry by heteregenous reactions or, if treating multiphase processes, can only be used by offline computing. Hence, effects on aerosol concentration as well as on Earth's radiation budget cannot be represented. It is therefore of central importance to implement the current state of the art multiphase halogen and DMS chemistry in higher-scale models in order to elucidate regional and global effects on air quality and Earth's climate.

Hence, the goal is to develop a marine multiphase chemistry mechanism for application in chemical tranport models and to derive parameterisations for climate models. Therefore, a reduced marine multiphase chemistry mechanism from reduction of near-explicit mechanisms will be developed. Afterwards first 2D and 3D modelling studies will be done.

CAPRAM mechanism development

Development of a near-explicit halogen module

For the development of a reduced marine multiphase chemistry mechanism the Halogen Module 2.0 (4) and the DMS Module 1.0 (5) are used. A realistic description of the atmospheric multiphase chemistry is reached by coupling both modules with the near-explicit gas-phase mechanism MCMv3.2 (6) and the near-explicit aqueous-phase mechanism CAPRAM4.0. However, the Halogen Module 2.0 contains lumped species and thus cannot be simply coupled to near-explicit mechanisms. Therefore, it is extended into a near-explicit mechanism and can now simply coupled to the MCM.
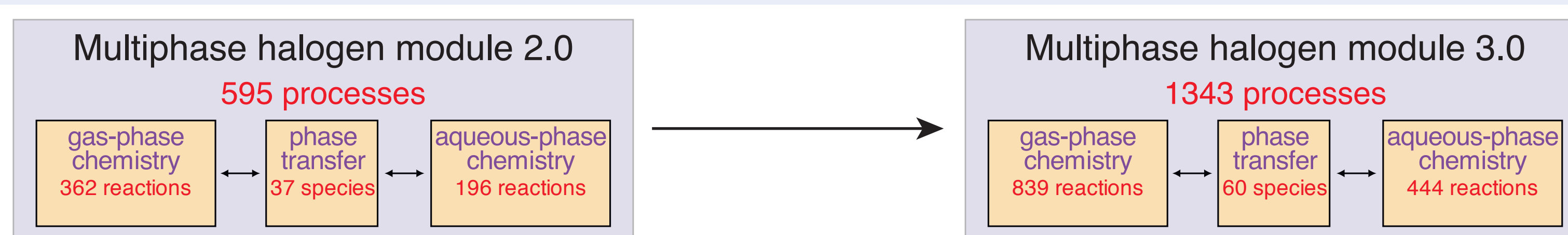

Fig. 1: Overview over the number of processes implemented in the old Halogen Module 2.0 and the new extended Halogen Module 3.0.

Development of a aqueous-phase oxidation module for aromatics

In a prospective study the effect of halogen chemistry on air quality in polluted coastlines will be investigated. Therefore, realistic multiphase chemistry treatment of anthropogenic VOCs is necessary. Aromatic compounds are highly important anthropogenic VOCs. Functionalised aromatic compounds can partition into cloud droplets and be further oxidized by aqueous-phase processes. Hence, they can influence the formation of anthropogenic aqSOA. Currently, no aqueous-phase chemistry mechanism for aromatic compounds is available. Therefore, a detailed aqueous-phase chemistry mechanism is developed, which can easily coupled to the MCMv3.2+CAPRAM4.0 mechanism system.
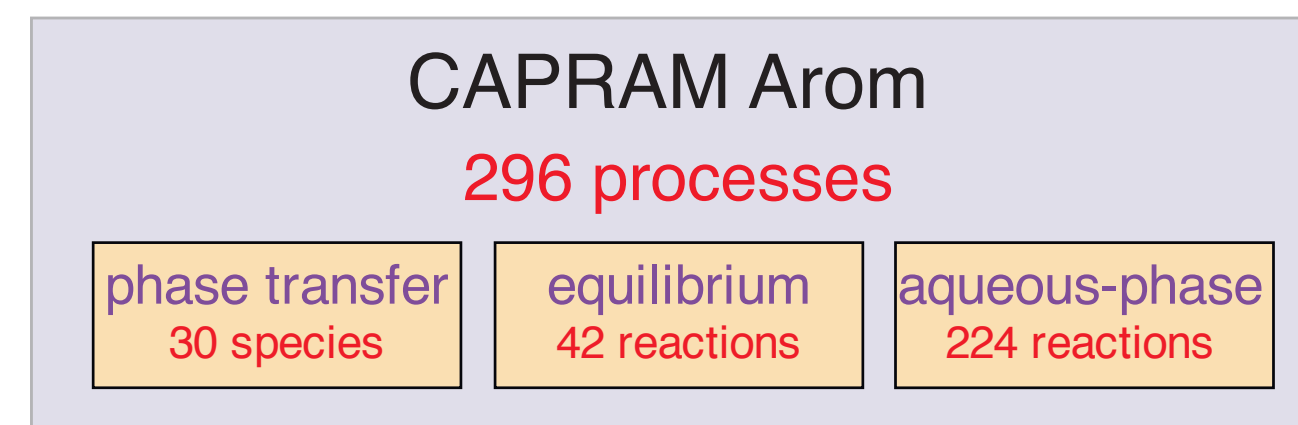

Fig. 2: Overview on process numbers implemented in the CAPRAM Aromatics Module 1.0 .
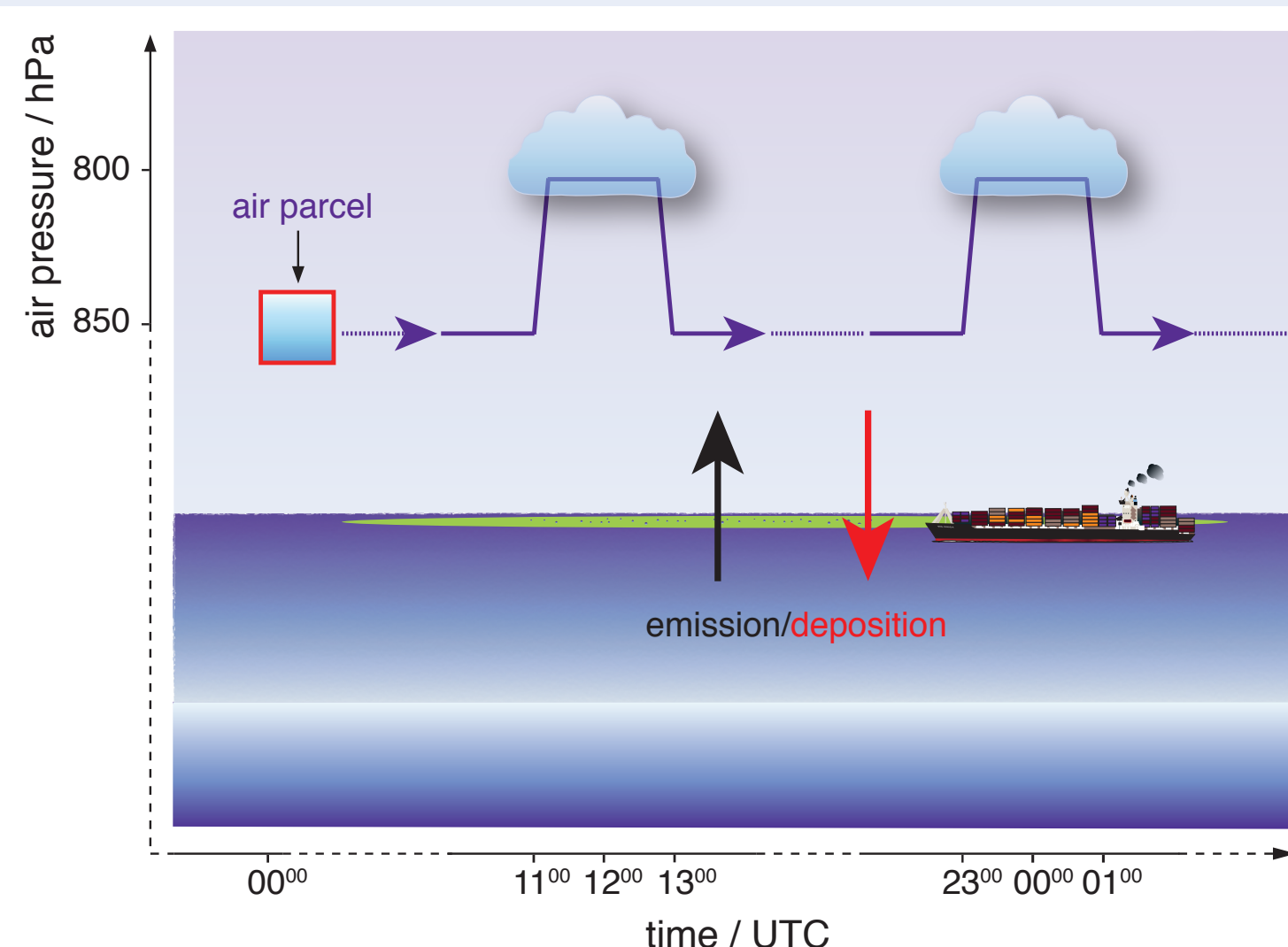
Mechanism reduction

Fig. 3: Applied standard environmental scenario.

Fig. 4: Scheme of the applied multiphase chemistry mechanism for developing the reduced marine multiphase chemistry mechanism.

- Studies with the air parcel model SPACCIM

- Coupling of DMS module 1.0 as well as halogen module 3.0 with the near explicit gas-phase mechanism MCMv3.2 and the aqueous-phase mechanism CAPRAM4.0

- Modelling different environments at different latitudes and seasons of the year

- Determination of the most important reactions by mass flux analysis

Outlook

- Investigating the influence on air quality of halogen chemistry in polluted coastlines

- Performing of 2D and 3D Simulations

- Developing of parameterisations for climate models
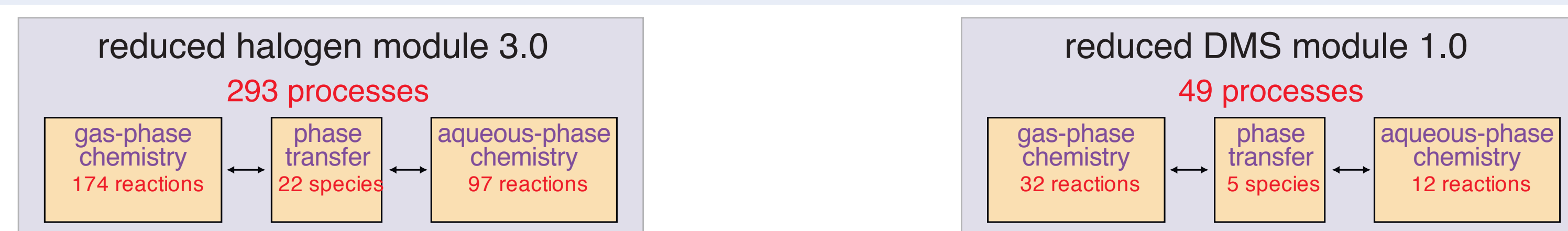
Results

Developed reduced mechanism

Fig. 5: Overview over the number of processes implemented in the reduced Halogen Module 3.0 and the reduced DMS module 1.0.

Evaluation of the reduced mechanism

	mean	standard deviation	median	quartile distance
gas-phase species				
HBr	108%	6%	107%	9%
HCl	101%	1%	100%	1%
Cl	108%	10%	109%	5%
BrO	107%	6%	107%	9%
IO	105%	29%	100%	12%
DMS	98%	2%	98%	2%
SO$_2$	268%	2546%	109%	4%
H$_2$SO$_4$	107%	4%	107%	4%
aqueous-phase species				
Sulfate	101%	0%	101%	1%
MSA	99%	1%	99%	2%

Table 1: Mean and median value between simulations with the full mechanisms and the reduced mechanisms for selected target compounds. The chosen simulations are modelled at 45° latitude for summer conditions.

- Simulation using the reduced DMS and halogen module coupled with MCMv3.2 and CAPRAM4.0.

- Comparison between simulation with the complete mechanisms and with the reduced mechanisms

- CPU time reduced by 11%

- Difference between important target species < 10% (see table 1)

- Same evolution of the concentration profile (see Fig. 6)
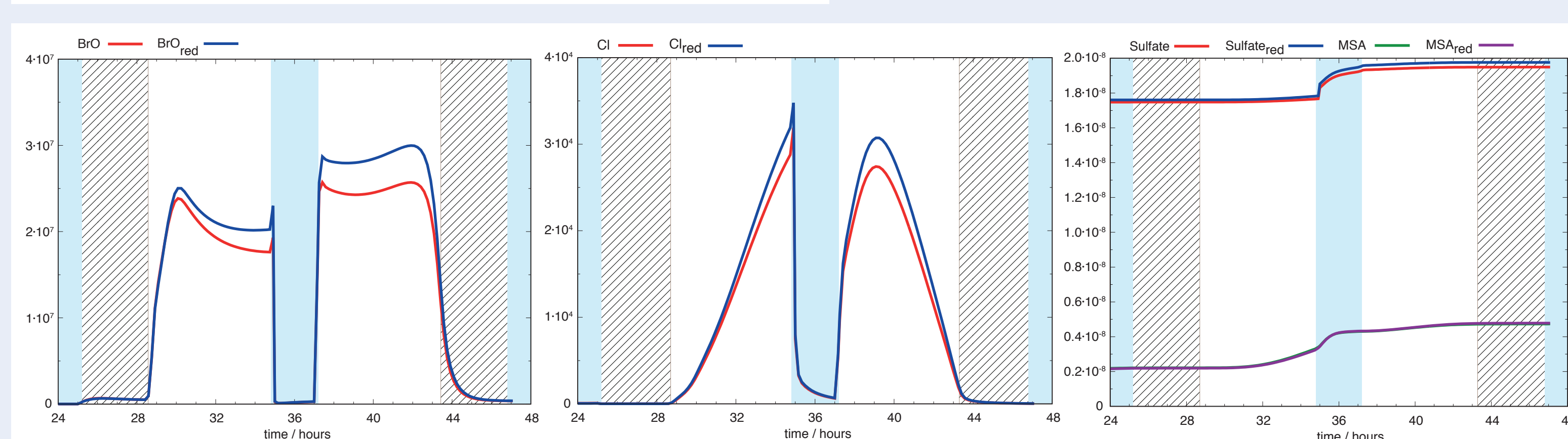

Fig. 6: Comparison between simulations with the full mechanisms and the reduced mechanisms for carefully selected target species. The chosen simulations are modelled at 45° latitude for summer conditions.

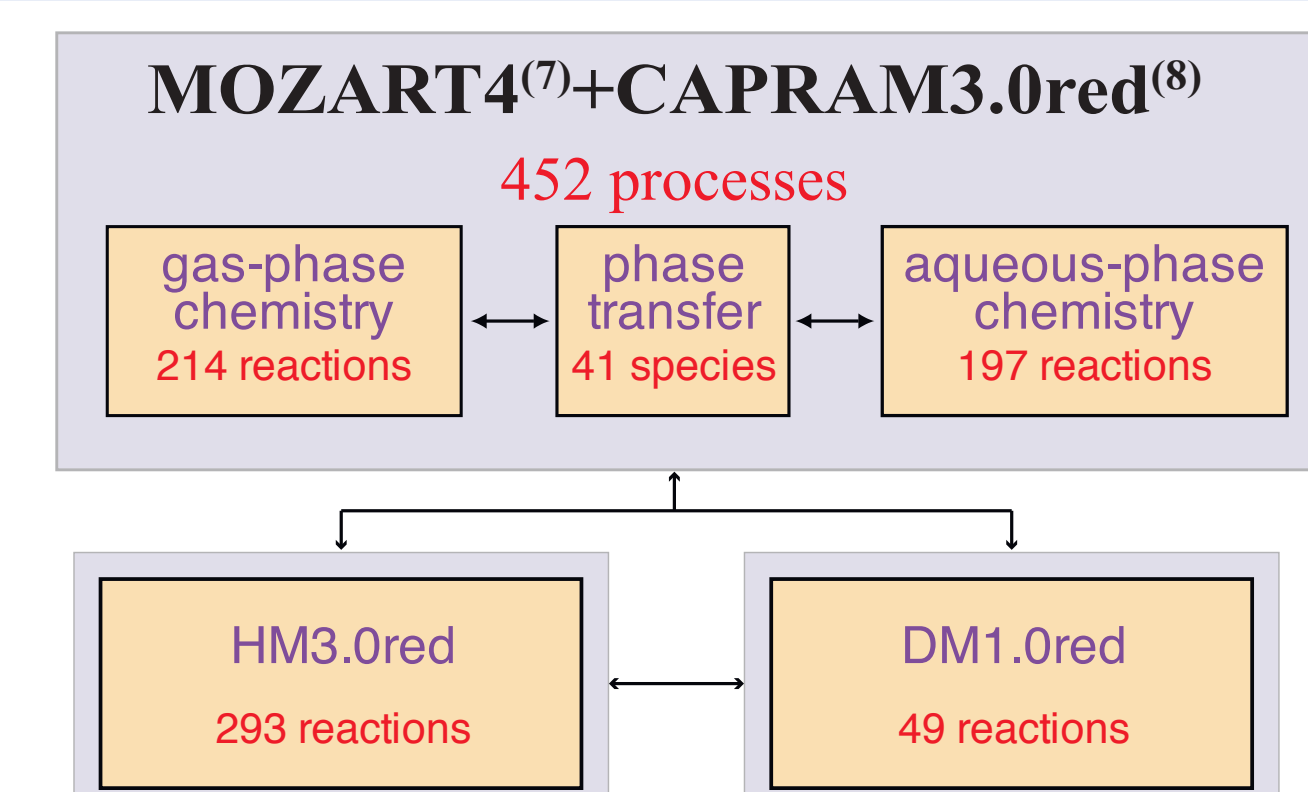### Implementation in COSMO-MUSCAT and first test 2D simulations

Fig. 7: Scheme of the applied multiphase chemistry mechanism for simulation in the chemical transport model COSMO-MUSCAT.
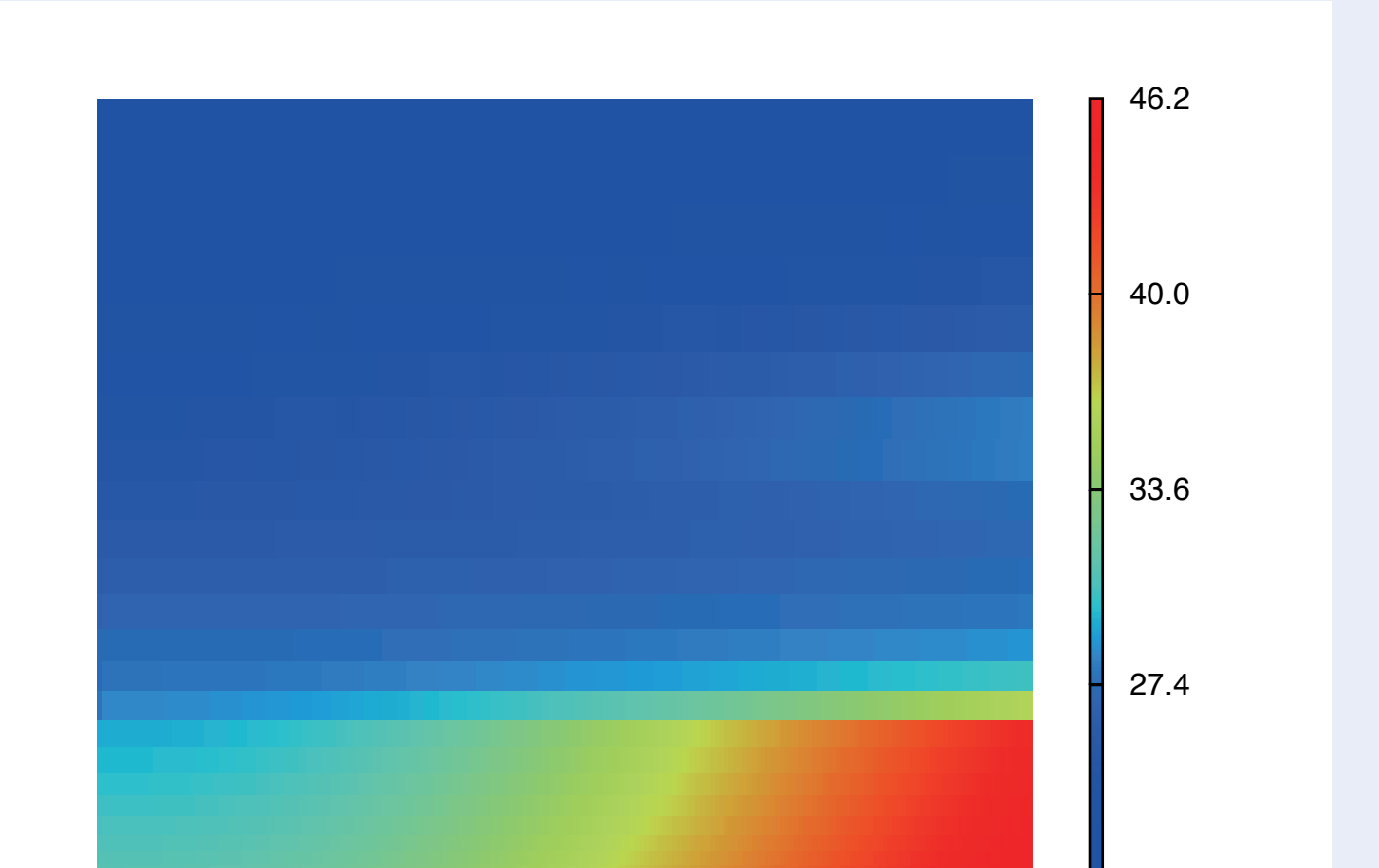

Fig. 8: Modelled temporary mean 2D concentration of methanesulfonic acid in ng m^{-3}.

References

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