Towards an operational CAPRAM multiphase halogen and DMS chemistry treatment in the chemistry transport model COSMO-MUSCAT

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Chemical Aqueous Phase Radical Mechanism CAPRAM TROPOS

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Introduction and Motivation

Oceans are the general emitter of dimethyl sulfide (DMS), the major natural sulfur source, and halides and cover approximately 70 % of Earth's surface. Therefore, marine multiphase chemistry is dominated by DMS and chemistry of reactive halogen species (RHS). DMS is the most important natural source of sulfate aerosols and its oxidation is strongly dependent on the oxidizing agent and the medium (gas or aqueous phase) where the oxidation occurs. It is closely linked to the chemistry of RHS(1). In addition, RHS strongly affect the oxidation of volatile organic compounds (VOCs), the NO_x and HO_x ratio as well as the degradation/production of O_3 and thus the oxidation capacity of the atmosphere(2). This can have strong effects on human health, as in coastal regions live more than 39% of all people worldwide(3). Moreover, the ongoing reduction of fossil fuel combustion emissions in some parts of the world will promote the oxidation of DMS as an important contributor to sulfate aerosol formation even in the Northern Hemisphere(4). Therefore, it is important that chemical transport models (CTMs) treat the crucial multiphase chemistry pathways of both DMS and RHS.

Current representations of marine multiphase chemistry in chemical transport models are done by heteregenous reactions or by using offline computing or using small multiphase mechanisms. Hence, modelled effects on aerosol concentration and composition, VOC oxidation, O_3 degradation/production as well as on Earth's radiation budget are limited. Therefore, it is crucial to consider the current state-of-the-art multiphase halogen and DMS chemistry in CTMs in order to elucidate regional and global effects on air quality and Earth's climate. Here, a condensed multiphase halogen and dimethyl sulfide (DMS) chemistry mechanism for application in CTMs is developed by reducing the CAPRAM DMS module 1.0 (CAPRAM-DM1.0)(5) and the CAPRAM halogen module 3.0 (CAPRAM-HM3.0)(6). The reduced mechanism has been implemented into the CTM COSMO-MUSCAT and tested by performing 2D-simulations under prescribed meteorological conditions that investigate the effect of stable (stratiform cloud) and more unstable weather conditions (convective clouds) on marine multiphase chemistry.

Development of the reduced mechanisms

Development of reduced marine multiphase chemistry mechanism

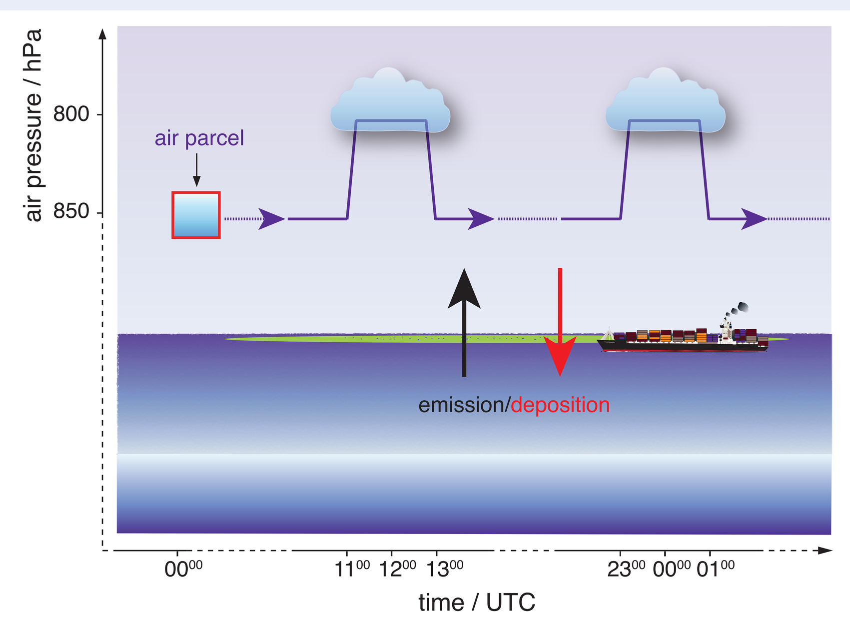

Fig. 1: Applied standard environmental scenario.

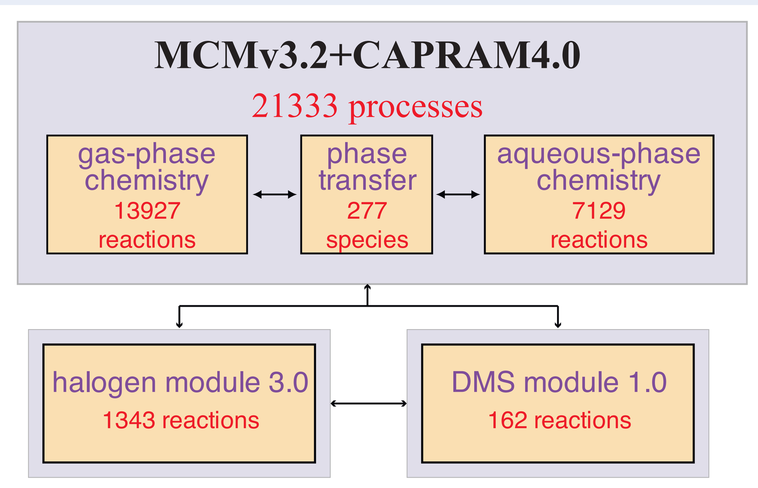

Fig. 2: Scheme of the applied multiphase chemistry mechanism for developing the reduced marine multiphase chemistry mechanism.

- Studies with the air parcel model SPACCIM(7)
- Modelling different environments at different meteorological conditions, latitudes and seasons of the year
- Determination of the most important reactions pathways for DMS oxidation and RHS chemistry by mass flux analysis (pathways that contribute at least 5% to the average mass flux over full simulation)

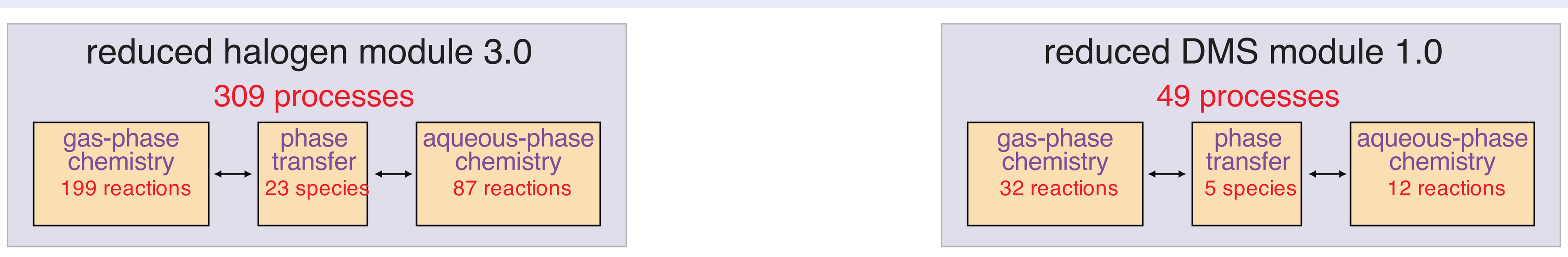

Fig. 3: Overview over the number of processes implemented in the reduced Halogen Module 3.0 and the reduced DMS module 1.0.

Evaluation of the reduced mechanism

- Comparison between simulation with the complete mechanisms and with the reduced mechanisms for different scenarios
  - (i) 'Pristine' - pristine ocean conditions
  - (ii) 'Breeze' - sea breeze conditions at polluted coastal area
  - (iii) 'Outflow' - advection of polluted air over the pristine ocean
- CPU time reduced by 16%, 5% and 6%
- Difference between set of target compounds (e.g. O_3, SO_2, NO_x, OH, sulfat, H^+) below 5% and same evolution of the concentration profile

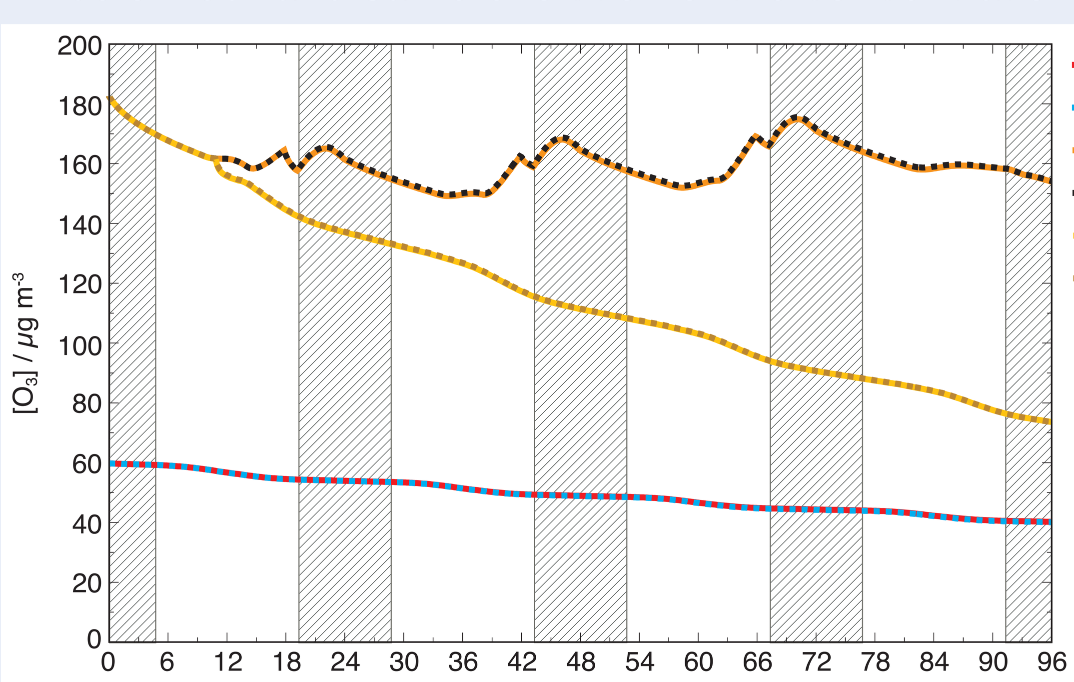

Fig. 4: Modelled concentrations of ozone within the scenarios 'Pristine', 'Breeze', and 'Outflow' compared between the simulations with the full (solid lines) and reduced (dotted lines) CAPRAM-DM1.0 and CAPRAM-HM3 mechanism. Grey shaded periods denote the night periods.

2D-simulations with COSMO-MUSCAT

Implementation into COSMO-MUSCAT(8) and 2D simulations

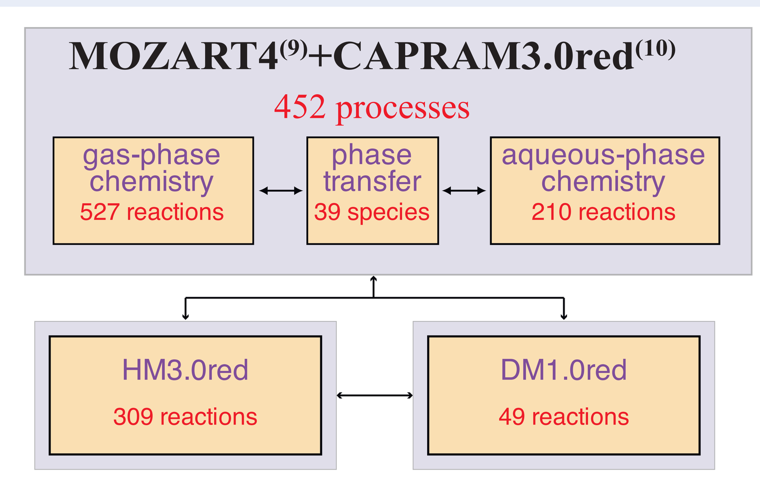

Fig. 5: Scheme of the applied multiphase chemistry mechanism for simulation in the chemical transport model COSMO-MUSCAT.

- 2D-simulations for more unstable and more stable weather conditions performed
- Simulated HCl and BrO concentrations in the range of measurements
- Investigations of DMS oxidation under these conditions
- Direct and indirect (shading of radiation) effect by clouds on DMSO formation
- Effective suppression of Br atom activation and thus low rate of DMS + BrO reaction

The multiphase chemistry of DMS

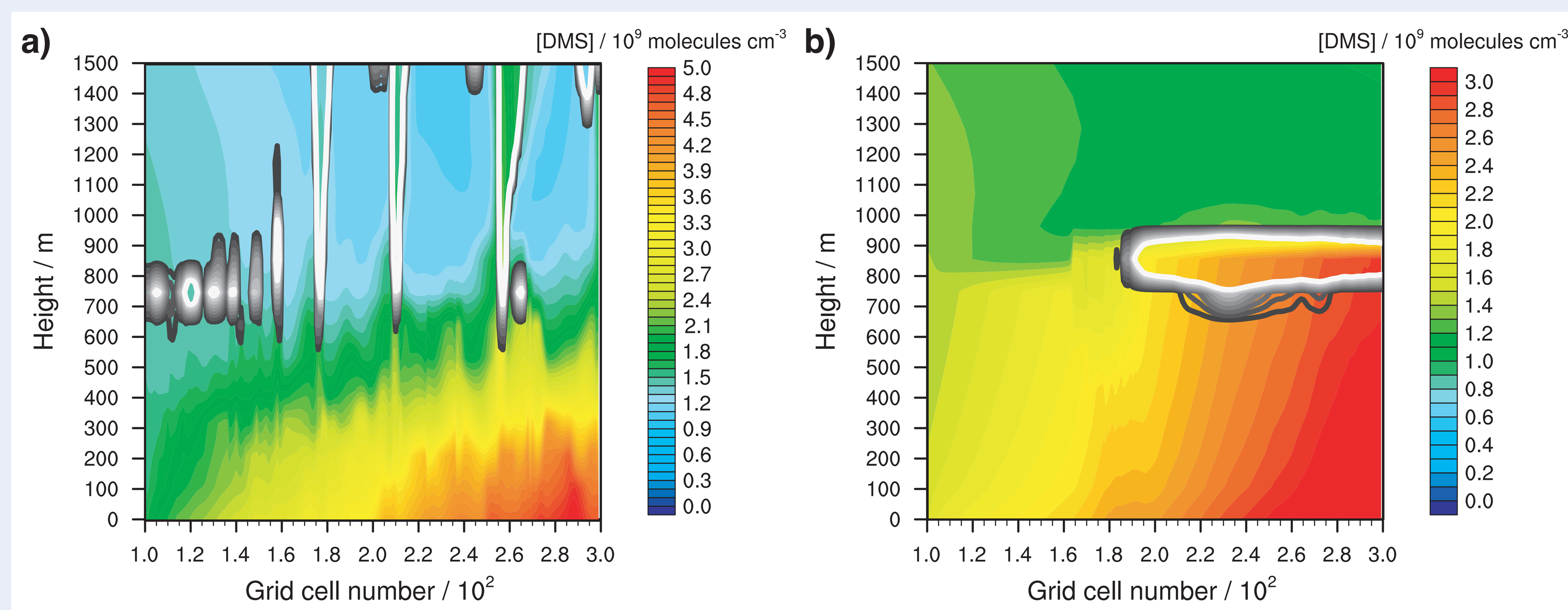

Fig. 6: Simulated DMS concentrations by COSMO-MUSCAT under (a) more unstable and (b) more stable weather conditions after 12 hours modelling time. The black contour lines represent the simulated clouds. The black line corresponds to a liquid water content of 0.01 g m-3 and the white line to 0.1 g m-3. The area framed by the white line includes LWC above 0.1 g m-3.

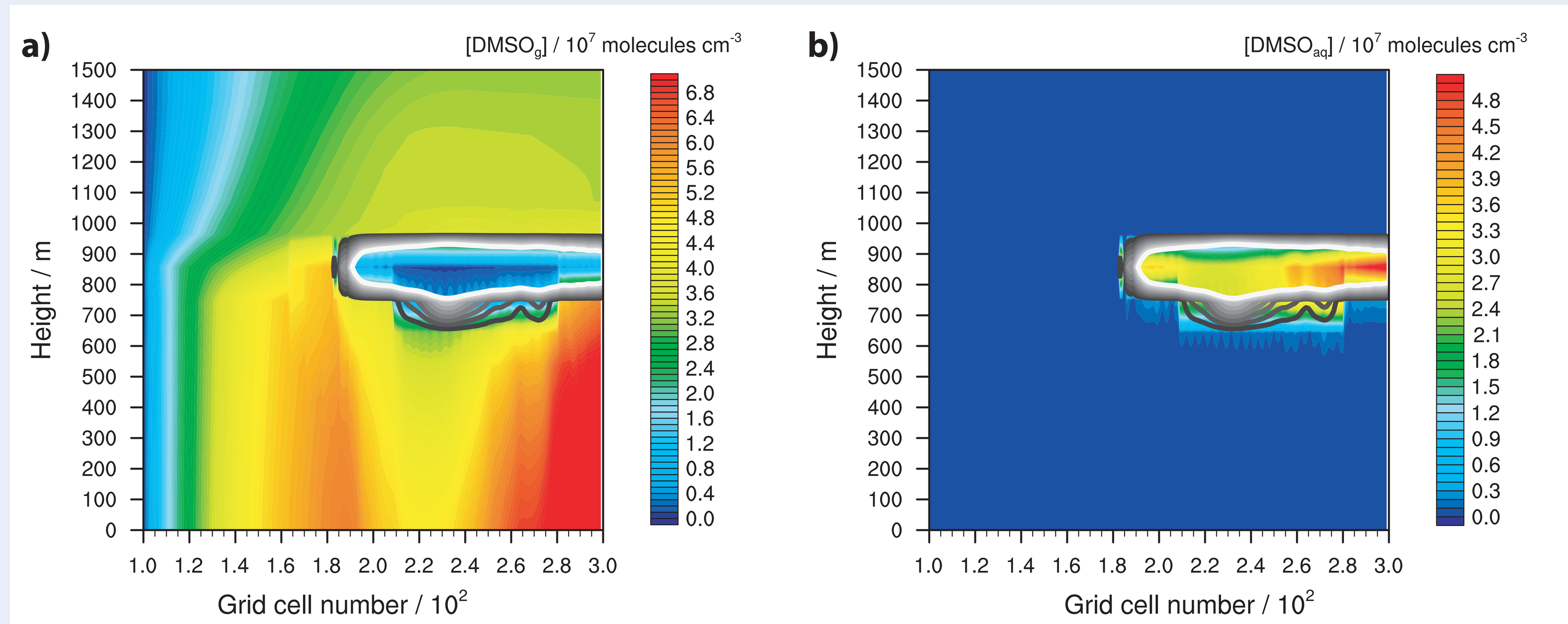

Fig. 7: Simulated DMSO concentrations by COSMO-MUSCAT under (a) more unstable and (b) more stable weather conditions after 12 hours modelling time.

Summary and Outlook

- Development of a reduced multiphase DMS and halogen chemistry mechanism by reduction of near-explicit mechanisms
- Mechanism applicable for wide range of environmental conditions
- Successful implementation in and testing with the CTM COSMO-MUSCAT
- Study recently published in Geoscientific Model Development(11)
- Further planned activities:
  - (i) Investigating influence of halogen chemistry on air quality in polluted coastlines
  - (ii) Performing of 2D and 3D Simulations of MARPARCLOUD(12) campaign

References

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