Modelling marine multiphase chemistry using box and chemical transport models

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Sponsored by the Scholarship Programme of the DBU Deutsche Bundesstiftung Umwelt www.dbu.de

Introduction and Motivation

Marine multiphase chemistry is dominated by dimethyl sulfide (DMS) and halogen chemistry. DMS is the most important natural source of sulfate aerosols. DMS oxidation is strongly dependent on the oxidizing agent and the medium (gas or aqueous phase) in which the oxidation occurs. It is closely linked to the chemistry of reactive halogen compounds(1). In addition, reactive halogen species 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).Therefore, there is a great interest to understand interactions of marine and continental air masses in coastal areas.

Current representation of marine multiphase chemistry in chemical transport models is 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 implement the current state of the art multiphase halogen and DMS chemistry in chemical transport models in order to elucidate regional and global effects on air quality and Earth's climate.

This goal is achieved by combining mechanim development with advanced mechanism reduction. Finally, a marine multiphase chemistry mechanism for application in chemical tranport models is developed and applied in 2D modelling studies.

CAPRAM mechanism development

Development of a near-explicit halogen module

- Coupling of Halogen Module 2.0(4) and the DMS Module 1.0(5) with near-explicit gas-phase mechanism MCMv3.2(6) and near-explicit aqueous-phase mechanism CAPRAM4.0
- Halogen Module 2.0 contains lumped species and cannot be simply coupled to MCMv3.2
- Not valid for treating polluted coastlines because of VOC oxidation limitations
- Extended into a near-explicit mechanism for simple coupling to the MCMv3.2

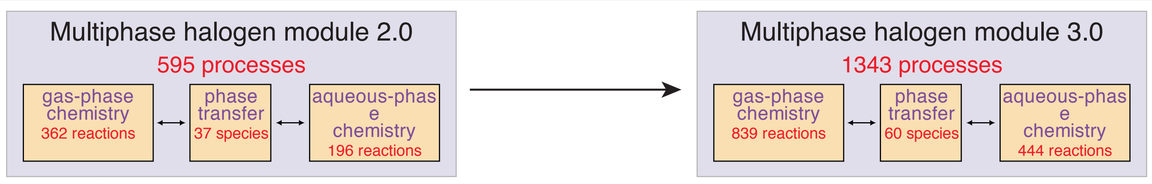

Fig. 1: Overview on the number of processes implemented in the old Halogen Module 2.0 and the new extended Halogen Module 3.0.

Development of an aqueous-phase oxidation module for aromatics

- Monocylclic aromatic compounds are important anthropogenic VOCs.
- Functionalised aromatic compounds partition into cloud droplets and be further oxidized by aqueous-phase processes.
- Influence the formation of anthropogenic aqSOA
- Development of a detailed aqueous-phase chemistry mechanism for functionalised aromatic compounds

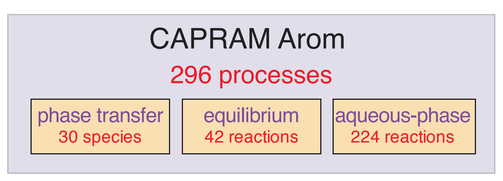

Fig. 2: Overview on process numbers implemented in the CAPRAM Aromatics Module 1.0 .

Development of reduced marine multiphase chemistry mechanism

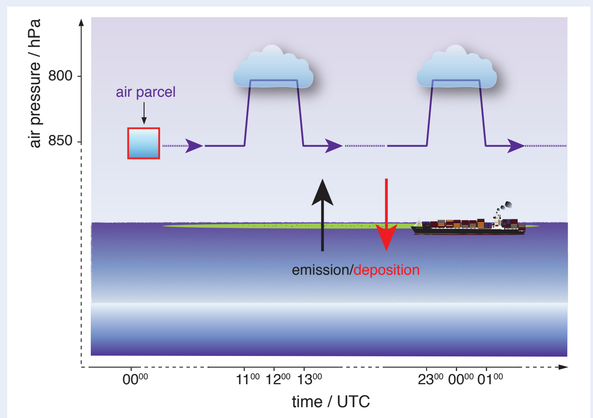

Fig. 3: Applied standard environmental scenario.

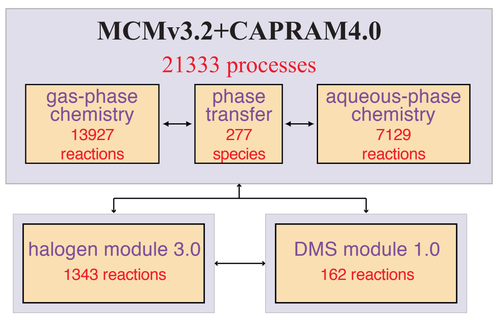

Fig. 4: Scheme of the applied multiphase chemistry mechanism for developing the reduced marine multiphase chemistry mechanism.

- Studies with the air parcel model SPACCIM (7)
- Modelling different environments at different latitudes and seasons of the year
- Determination of the most important reactions by mass flux analyses

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

Outlook

- Investigating the influence of halogen chemistry on air quality in polluted coastlines
- Performing of 2D and 3D chemical transport modelling simulations of e.g. MarParCloud campaign
- Development of parameterisations for climate models

Model results

Evaluation of the reduced mechanism

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.

	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_2SO_4	107%	4%	107%	4%
aqueous-phase species				
Sulfate	101%	0%	101%	1%
MSA	99%	1%	99%	2%

- 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
- 11% CPU time reduction
- Difference between important target species < 10% (see table 1)
- Same evolution of the concentration profile (see Fig. 6)

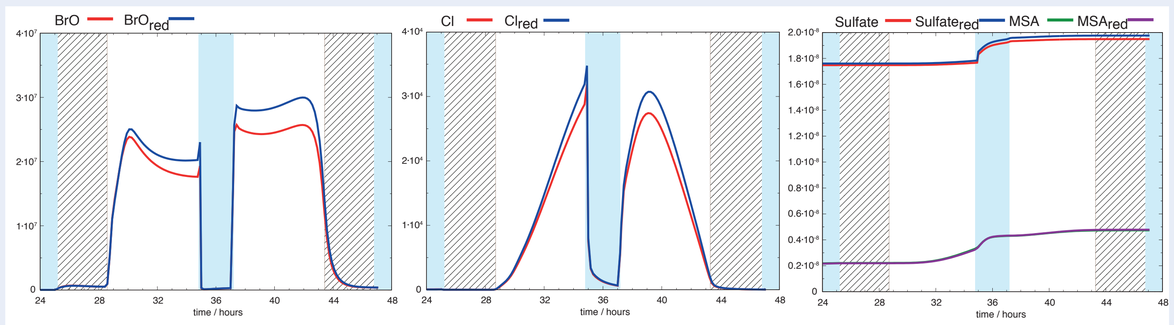

Fig. 6: Comparison between simulations with the full mechanisms and the reduced mechanisms for carefully selected target species. The chosen simulations are modelled at 45° latitude for summer conditions.

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

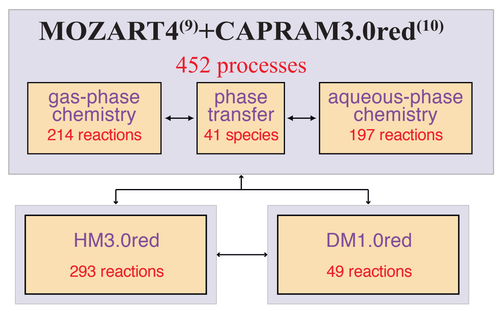

Fig. 7: Scheme of the applied multiphase chemistry mechanism for simulation in the chemical transport model COSMO-MUSCAT.

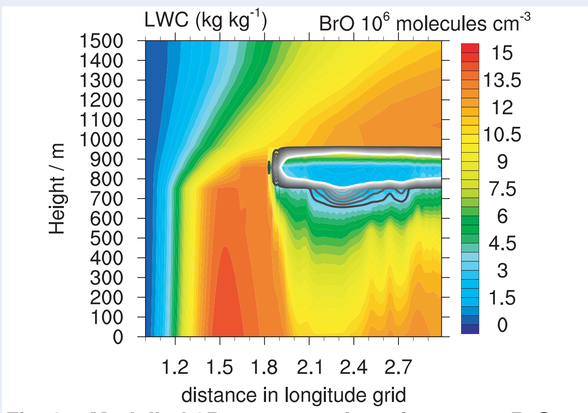

Fig. 8: Modelled 2D concentration of gaseous BrO at noon.

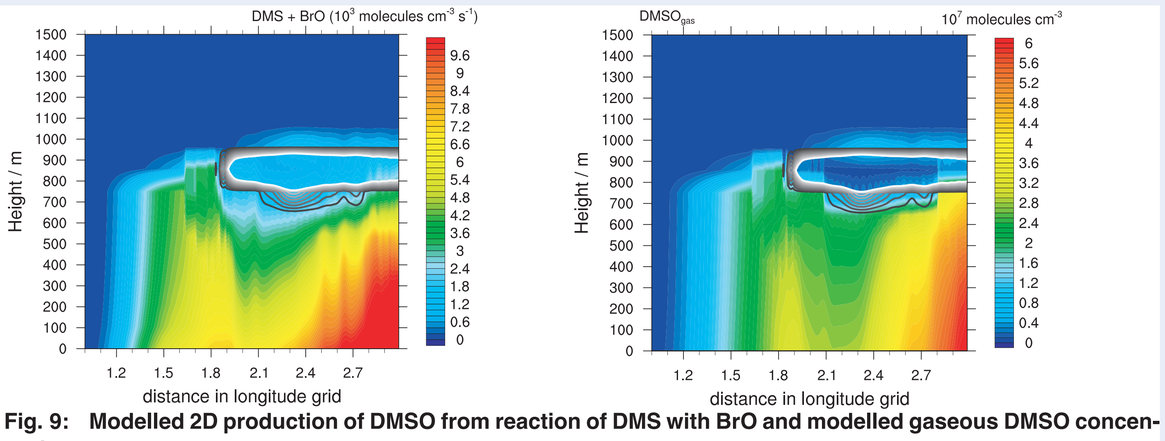

Fig. 9: Modelled 2D production of DMSO from reaction of DMS with BrO and modelled gaseous DMSO concentration at noon.

References

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