

Advanced modelling of the multiphase DMS chemistry with the CAPRAM DMS module 1.0

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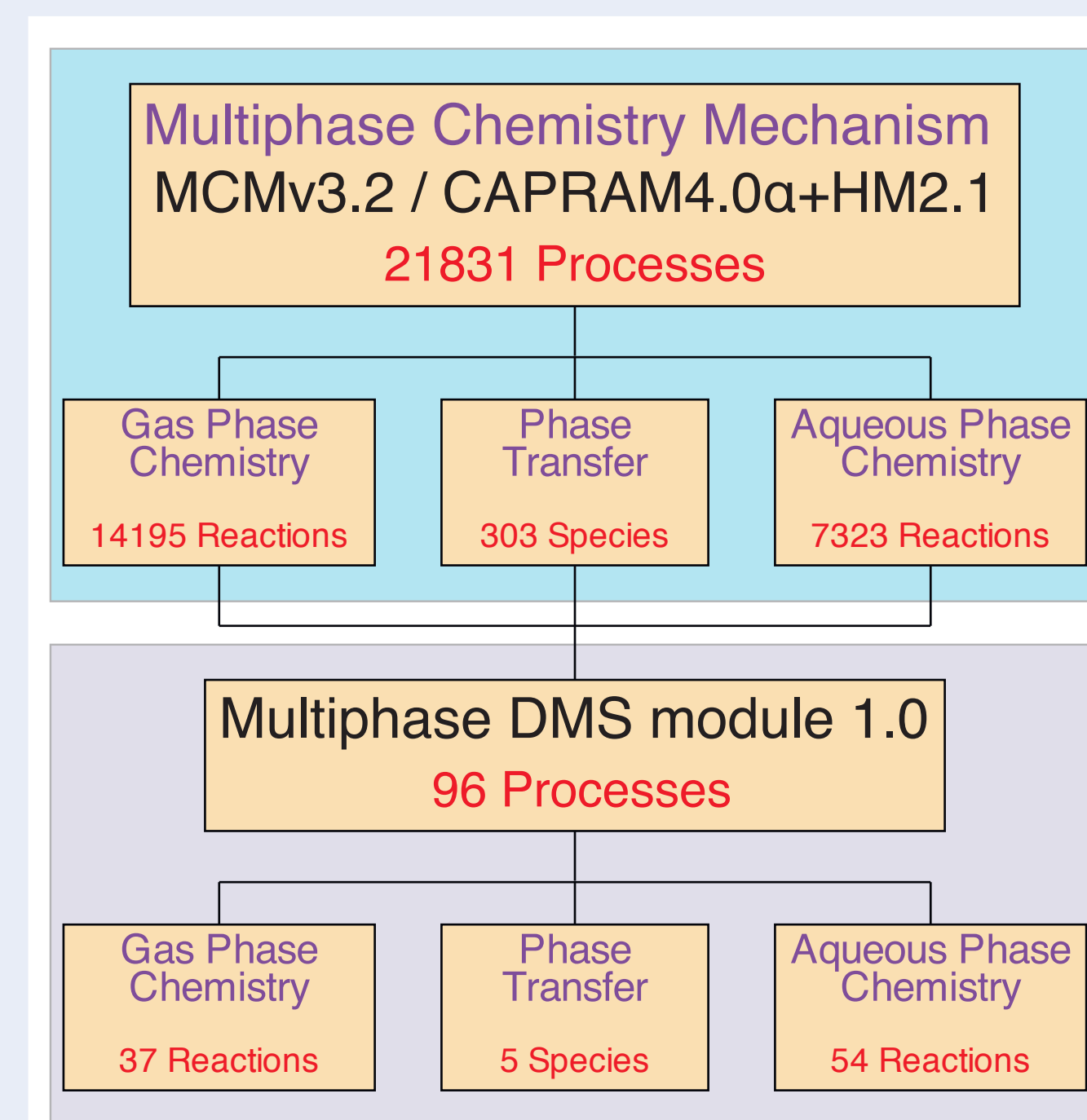


Introduction and Motivation

Dimethyl sulphide (DMS) is the most important precursor for non-sea salt sulphate aerosols over the open ocean (1). Because of their high hygroscopicity, sulphate aerosols can act very well as cloud condensation nuclei (CCN). Furthermore, sulphate aerosols have a strong negative radiative forcing. As oceans cover about 70% of Earth's surface and have low albedo, DMS oxidation therefore plays a major role in influencing the natural radiative forcing of sulfate aerosols as well as changes to cloud properties (2).

Despite different investigations on DMS multiphase chemistry, the tropospheric DMS oxidation processes including its oxidation products are not completely understood (1). First mechanism only treated gas phase chemistry of DMS and were not able to reproduce measured oxidation products, for e.g methyl sulfonic acid (MSA) (3). Later developed mechanism, which treated multiphase DMS chemistry considered only simplified schemes of aqueous phase chemistry, although detailed kinetic data are available in literature. Hence, to improve the understanding of DMS oxidation, simulations with advanced DMS multiphase chemistry mechanisms are necessary.

Thus, the current study was aimed at (i) the development of a detailed multiphase DMS chemistry mechanism, (ii) coupling of the new CAPRAM DMS module 1.0 (DM1.0) on the existing MCM-CAPRAM-HM2.0 mechanism and (iii) its application for simulations with the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, (4)).



Multiphase modelling

- Coupling of DM1.0 with the multiphase chemistry mechanism MCMv3.2/CAPRAM4.0a+HM2.1 leads to overall 21927 processes (schematic description presented in Fig. 2)
- Simulations carried out for an open ocean scenario with non-permanent diurnal and nocturnal clouds
- Several sensitivity studies performed (see Table 1)

Table 1: Overview on the different sensitivity runs

Model run	Specification
full	MCMv3.2, CAPRAM4.0a, HM2.1 and DM1.0
wolodine	'full' without iodine chemistry
woHM2	'full' without HM2.1
O3	'full' with high initial conc.s of NO ₂ , O ₃ and HNO ₃
woCloud	'full' without cloud passages
woAqua	'full' without aqueous phase chemistry of DM1.0

Fig. 2: Schematic description of the multiphase chemistry mechanism MCMv3.2/CAPRAM4.0a+HM2.1 with the DMS module 1.0.

Mechanism Development and Modelling

Mechanism development

- Update of the halogen module 2.0 (HM2.0) to HM2.1 based on the latest updates on IUPAC (5)
- Development of an extensive multiphase DMS chemistry mechanism, gas phase mechanism based on MCMv3.2 and a new aqueous phase mechanism
- Kinetic data are based on the latest IUPAC or JPL recommendations (6) and the most recent literature data
- DM1.0 includes 103 gas phase reactions (66 reactions already implemented in MCMv3.2), 5 phase transfers and 54 aqueous phase reactions (full aqueous phase mechanism is presented schematically in Fig. 1)

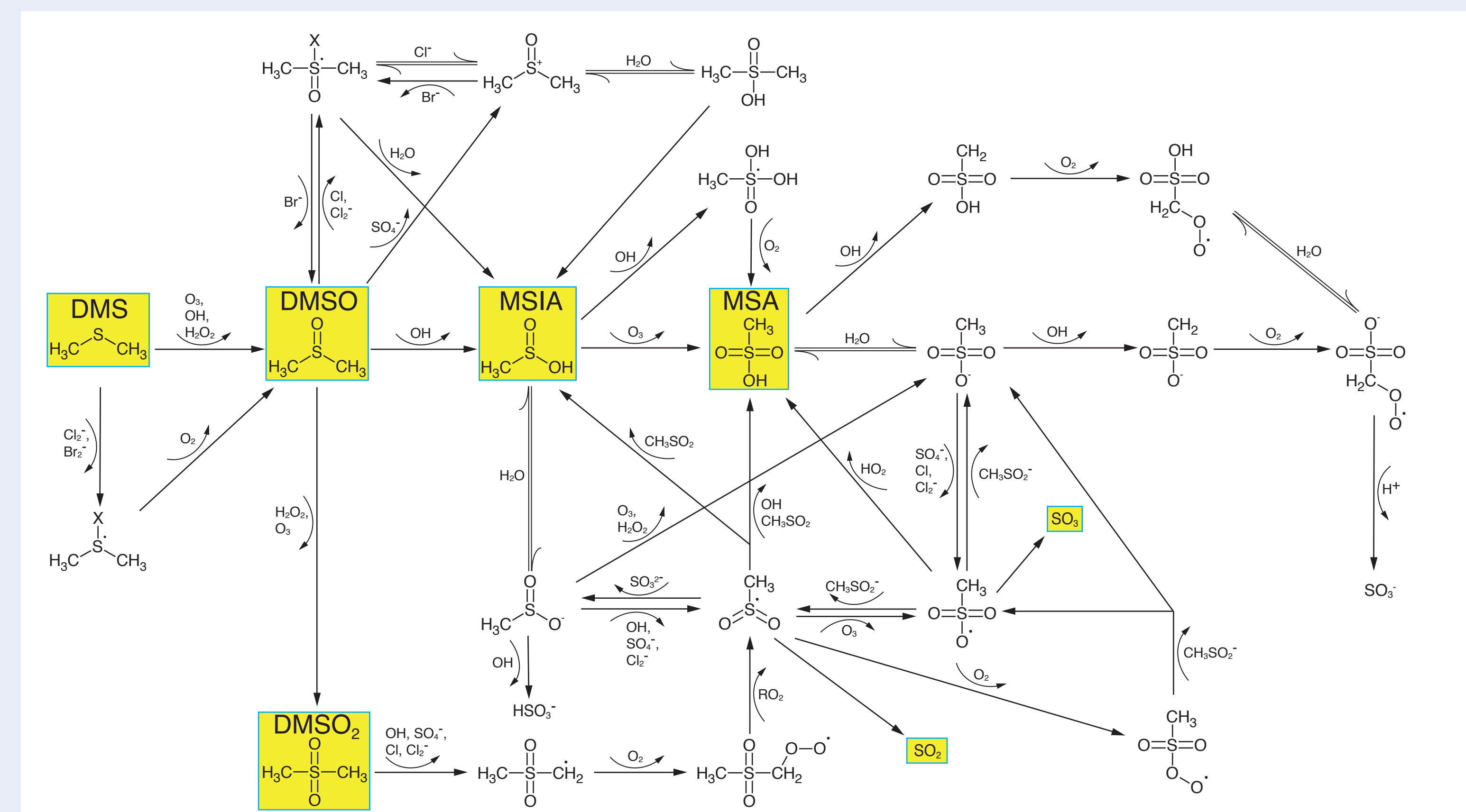


Fig. 1: Scheme of the aqueous phase mechanism in DM1.0. Stable species are underlined yellow and species, which undergo phase transfer are framed blue. The X in the chemical structure describes a chlorine or bromine atom.

Model Results and Discussion

Multiphase oxidation of DMS

- In-cloud periods show reduced gas phase oxidations of DMS and main sink is the aq. phase reaction with dissolved O₃
- High gas phase NO_x and O₃ conc.s lower DMS conc. significantly (run 'O3')
- In high NO_x regimes, reaction with Cl₂ act as new important nocturnal sink
- Strong influence of reactive halogen species on DMS oxidation due to chosen scenario

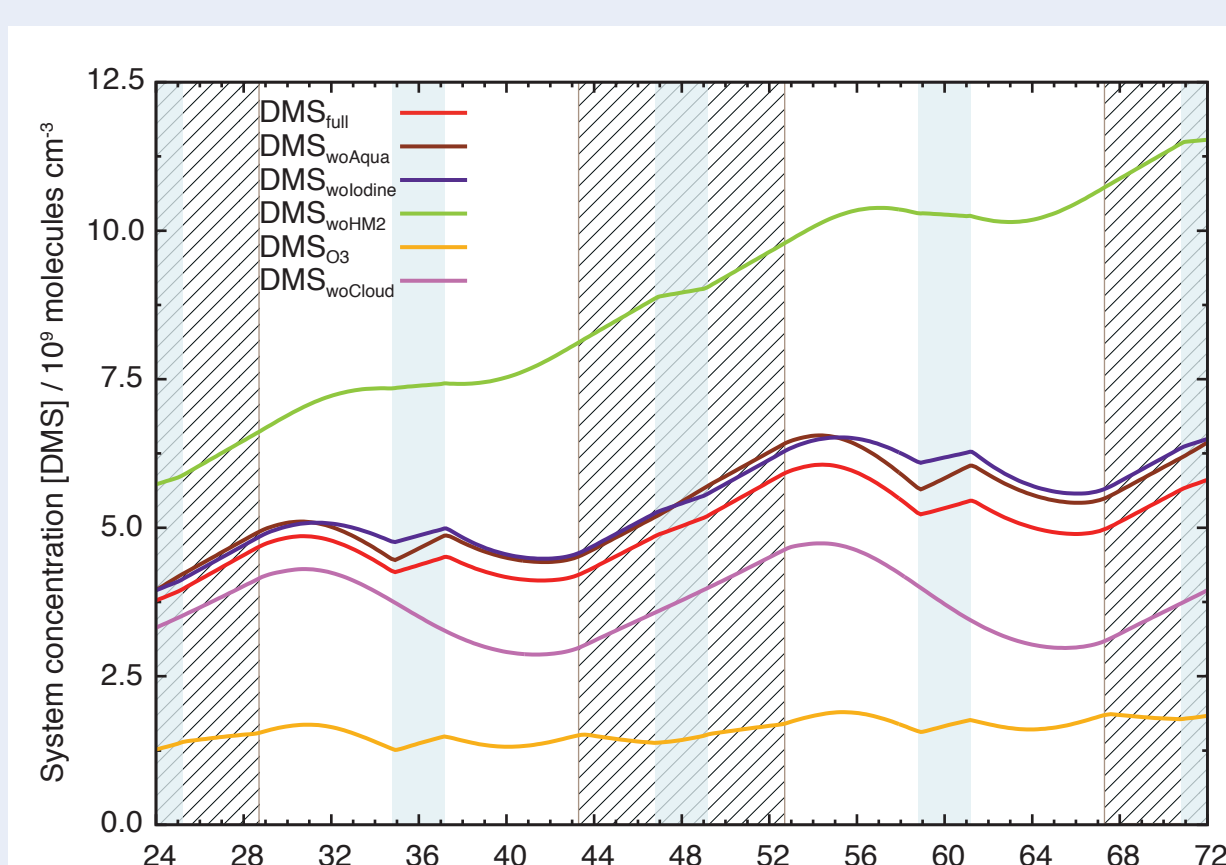


Fig. 3: Modelled system concentration (conc. in gas and aq. phase) of DMS for all sensitivity studies on the second and third model day.

Multiphase chemistry of DMSO

- Modelled conc.s magnitude at sunset are consistent with measurements of 1.8 · 10⁸ molec cm⁻³ (7)
- Unlike diurnal clouds, nocturnal clouds lead to conc. increase

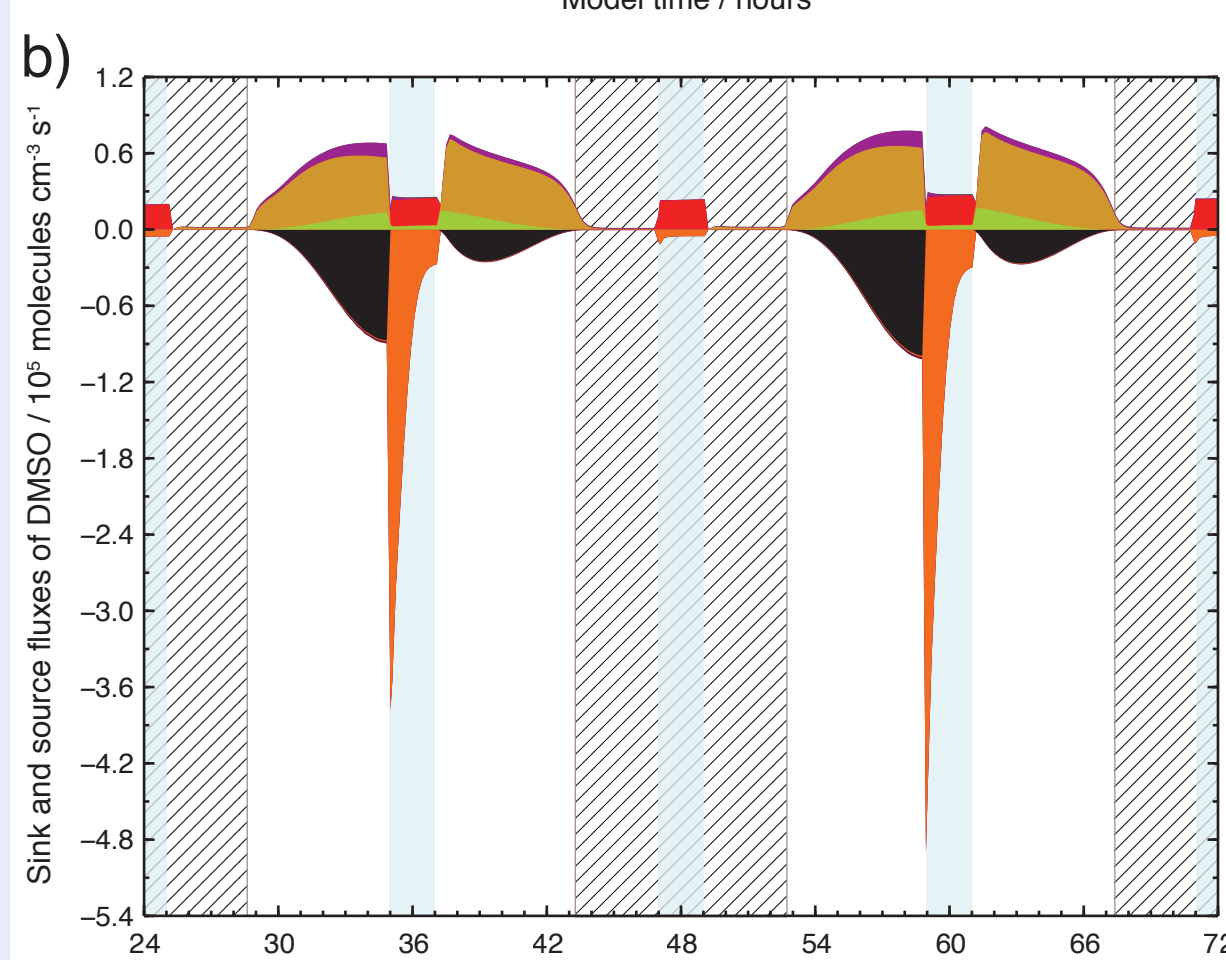
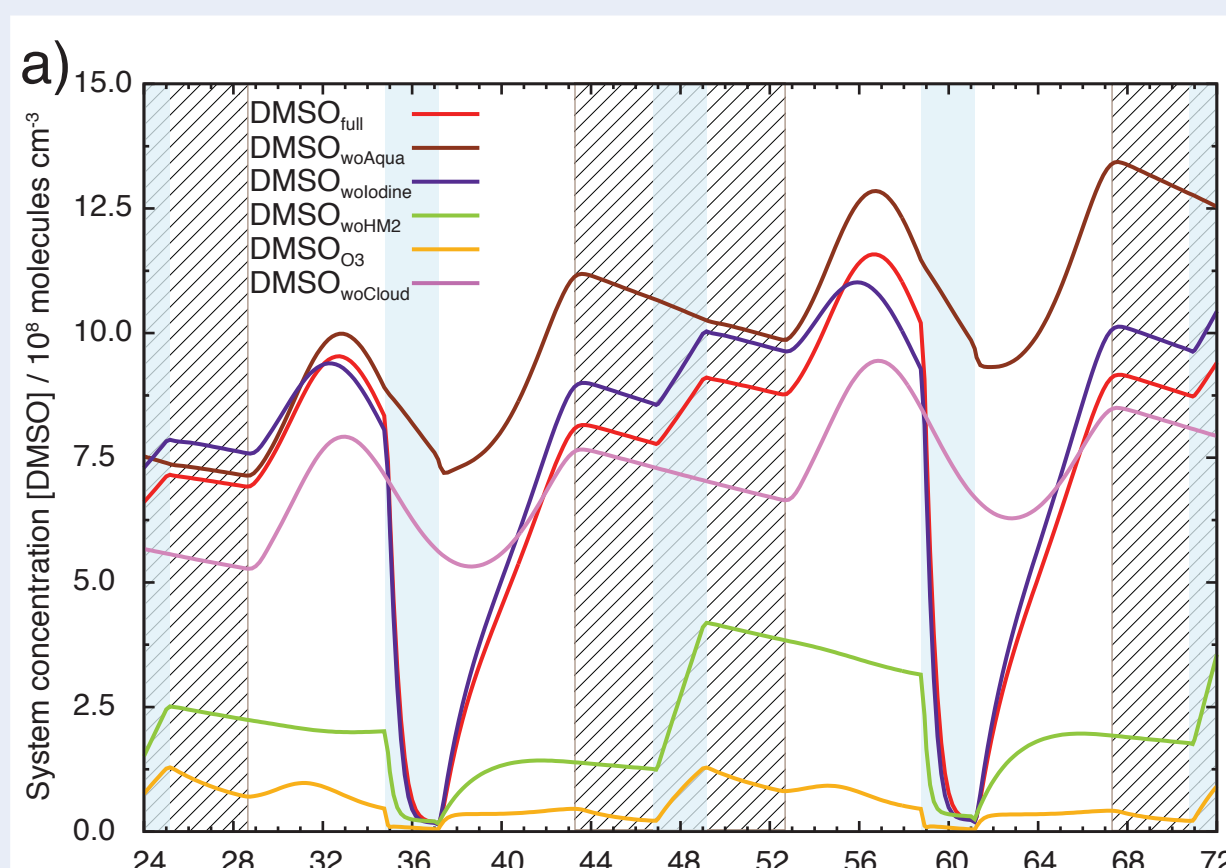


Fig. 4: Modelled time-resolved sink fluxes of the model run 'full' (a) and 'O3' (b) contributing to the destruction (negative) of DMS on the second and third model day in gas and aq. phase.

Multiphase chemistry of MSIA and MSA

- Distinct diurnal profiles identified
- Most MSIA produced during daytime by OH
- Main sinks of MSIA are the aq.-phase reactions with Cl₂, dissolved OH and O₃
- No significant conc. decrease of MSA
- MSA is predominantly formed by aq.-phase chemistry
- Strong influence of cloud periods, BrO and high NO_x/O₃ conc.s on MSA conc.

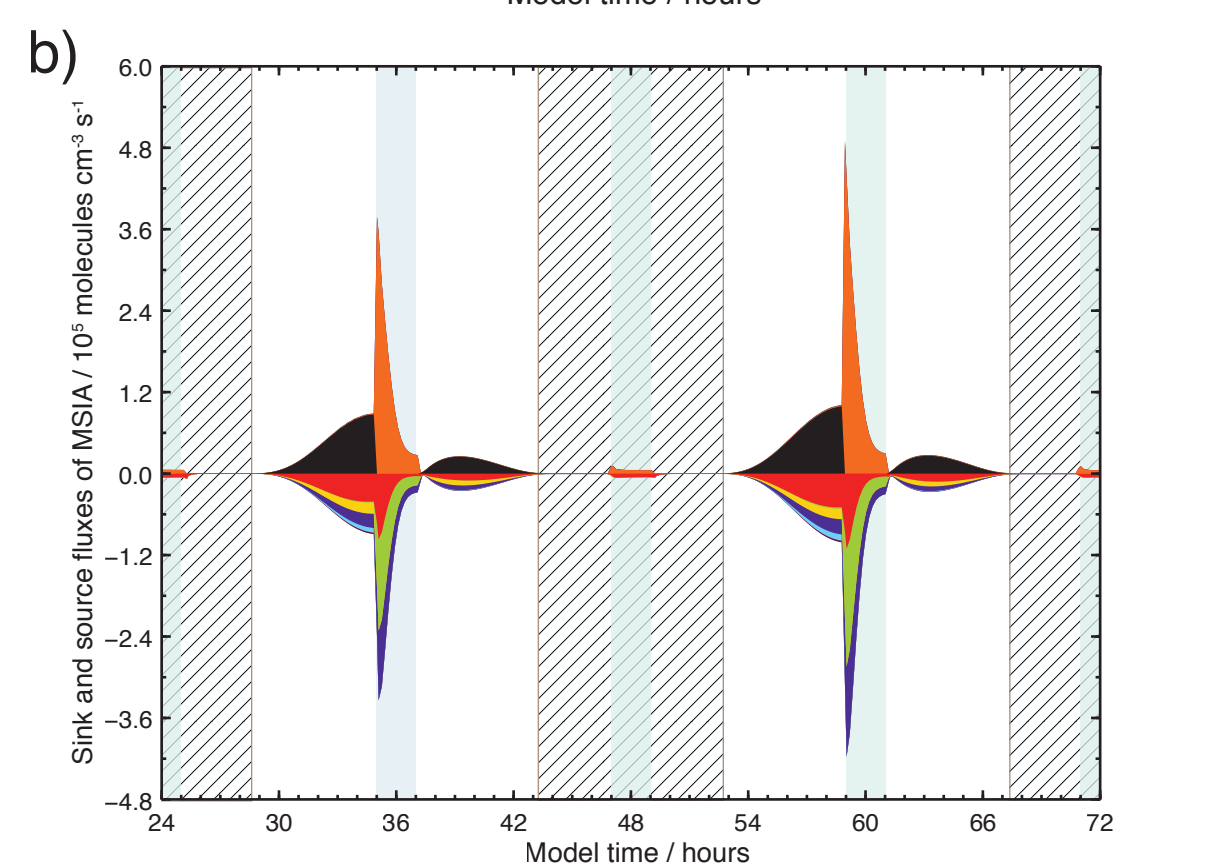
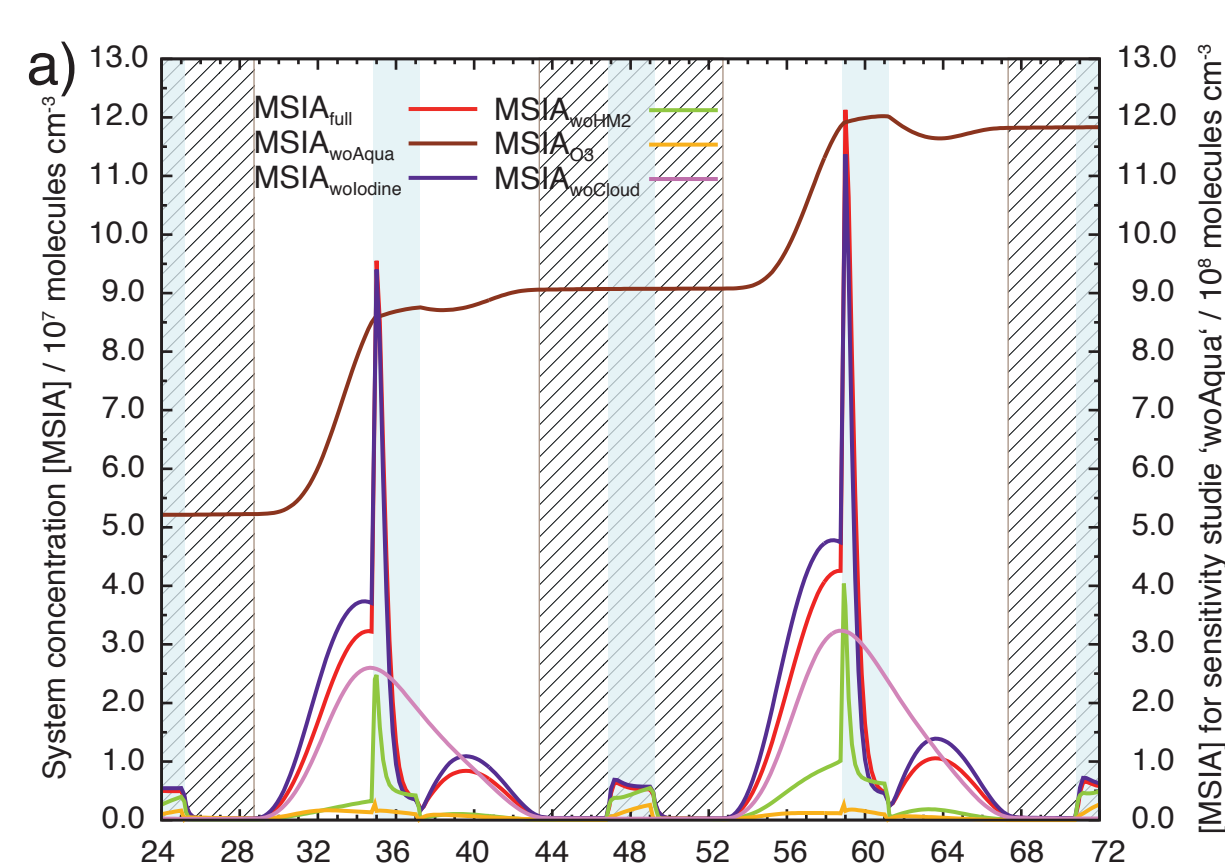


Fig. 6: Modelled system concentration (conc. in gas and aq. phase) of MSIA for all sensitivity studies (a) and modelled time-resolved source and sink fluxes of the model run 'full' (b) in gas and aq. phase on the second and third model day.

Fig. 5: Modelled system concentration (conc. in gas and aq. phase) of DMSO for all sensitivity studies (a) and modelled time-resolved source and sink fluxes of the model run 'full' (b) in gas and aq. phase on the second and third model day.

Main reaction fluxes

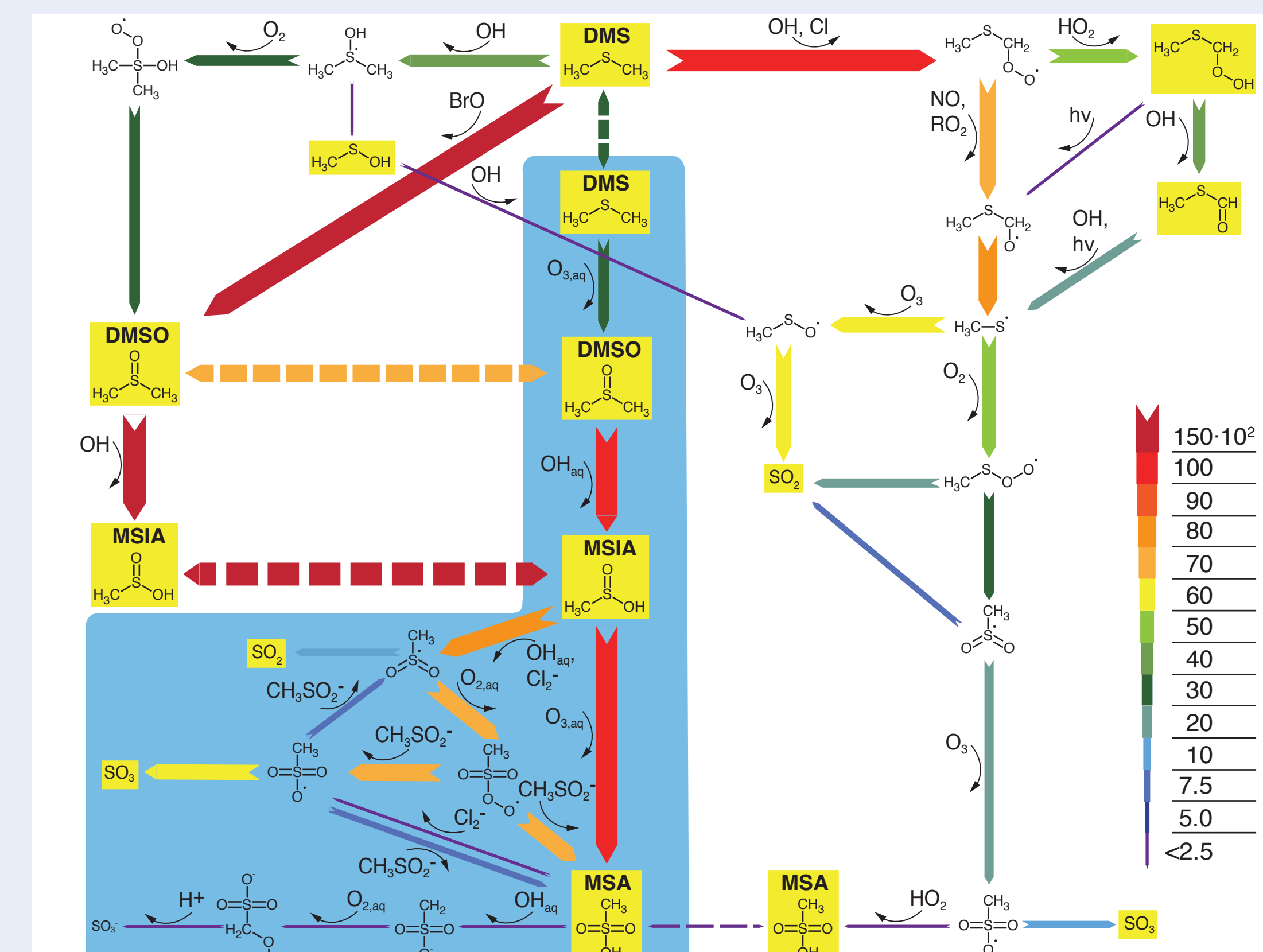


Fig. 8: Depiction of mean source and sink fluxes (in molecules cm⁻³ s⁻¹) of the 'full' scenario run throughout the whole model (fraction of oxidation fluxes > 5%). Arrows indicate the magnitude of the mass flux, where the thickness and colour of the arrows is related to the mass fluxes strength. Dashed arrows represent phase transfer processes. The blue area highlights aqueous-phase reactions. Stable compounds are shaded yellow and dashed lines represent phase transfer processes.

SO₂ and MSA conversion yields

- The higher the MSA yield the lower the SO₂ yield
- Increased SO₂ yield in non-cloud conditions
- Main source of gaseous H₂SO₄ is not SO₂ oxidation but thermal decay of CH₃SO₃ (in total 4.3 %)

Table 2: Summary of effective conversion yields of DMS to SO₂, DMS to MSA and MSA to S(VI) for all sensitivity runs.

Sensitivity run	DMS → SO ₂	DMS → MSA	MSA → S(VI)
'full'	23.6 %	41.0 %	2.2 %
'O3'	56.5 %	14.9 %	34.4 %
'wolodine'	20.5 %	46.9 %	2.5 %
'woHM2'	30.7 %	29.2 %	3.9 %
'woCloud'	32.7 %	30.3 %	0.8 %
'woAqua'	60.3 %	0.9 %	0.1 %

Summary and Outlook

An advanced multiphase DMS chemistry module with totally 162 reactions has been developed and first simulations with the SPACCIM model have been performed for open ocean conditions. The studies revealed the importance of aqueous phase chemistry for the DMS oxidation in the marine boundary layer (MBL) including the formation of marine particulate matter. Compared to former model studies, we first considered aqueous phase reactions of MSIA and dissociated MSIA with O₃, which is shown to be a main sink for MSIA in the aqueous phase triggering the MSA production. Furthermore, the simulations revealed that the conversion of DMS to SO₂, sulphate and MSA is strongly influenced by reactive halogen species, the presence of clouds, and high background concentrations of NO_x and O₃. Beyond, it is shown that over the open ocean, the thermal decay of CH₃SO₃ seems to be the main source for gas phase H₂SO₄.

Our study reveals the importance of the halogen-DMS interaction and DMS aqueous phase chemistry on (i) the conversion of DMS into SO₂ and MSA, (ii) the aging of marine aerosols, (iii) the production of nss-SO₄²⁻ aerosols, and (iv) the radiative properties of marine clouds and aerosols. Currently applied oxidation mechanisms in chemical transport (CTMs) and global climate models (GCMs) only treat DMS gas-phase chemistry. Thus, the implementation of multiphase DMS chemistry in CTMs and GCMs is strongly needed to avoid high prediction uncertainties of natural radiative forcing. Therefore, further studies will aim at the development of reduced DMS multiphase chemistry mechanisms/parameterisation for application in regional CTMs and GCMs.

References

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