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Manuscript for Geoscientific Model Development Discussions (MS No.: gmd-2019-322)
'CAPRAM reduction towards an operational multiphase halogen and DMS chemistry treatment in the chemistry transport model COSMO-MUSCAT(5.04e)' by Erik H. Hoffmann, Roland Schrödner, Andreas Tilgner, Ralf Wolke, and Hartmut Herrmann

Dear Dr. Andrea Stenke,

please find attached our answers to the reviewer comments for the manuscript mentioned above together with its revised version. We like to thank the reviewers for all of their valuable comments.

Yours sincerely,



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Response to Anonymous Reviewer #1

Hoffmann et al. developed simplified multiphase halogen and DMS chemistry schemes that consumed less CPU time and could be implemented into the chemical transport models. Along with the development of observation techniques, halogen chemistry is getting more attention in the atmospheric chemistry community during recent years. DMS chemistry is critical for the climate through formation of sulfate aerosols and clouds. Both halogen and DMS chemistry involves many chemical species and reactions and thus are difficult to model, especially the multiphase chemistry parts that are generally not included in CTMs. The chemistry schemes developed in this study will benefit the atmospheric chemistry community. It is within the scope of GMD. However, I think the manuscript can be improved through more discussion about the results (some unclear scientific reasoning), doing sensitivity tests, and adding references to the reaction coefficients used in this study. I recommend it to be accepted after some revisions.

We thank the anonymous reviewer 1 for the recommendation and constructive comments to improve the manuscript. The comments of the reviewer are carefully addressed point by point in the sections below. The answers to the reviewer comments are marked as blue text.

Because of the comment of reviewer 2 the whole manuscript has been checked for grammar by an English language professional at the C2 level. For further information, please see the manuscript version with highlighted changes.

Besides, due to a personal comment from the community regarding that ECHAM-HAMMOZ and EMAC are chemistry climate models, we have deleted ECHAM-HAMMOZ from Figure 4 and added to the Figure caption that EMAC can be run as a CTM. Please, see the changes below:

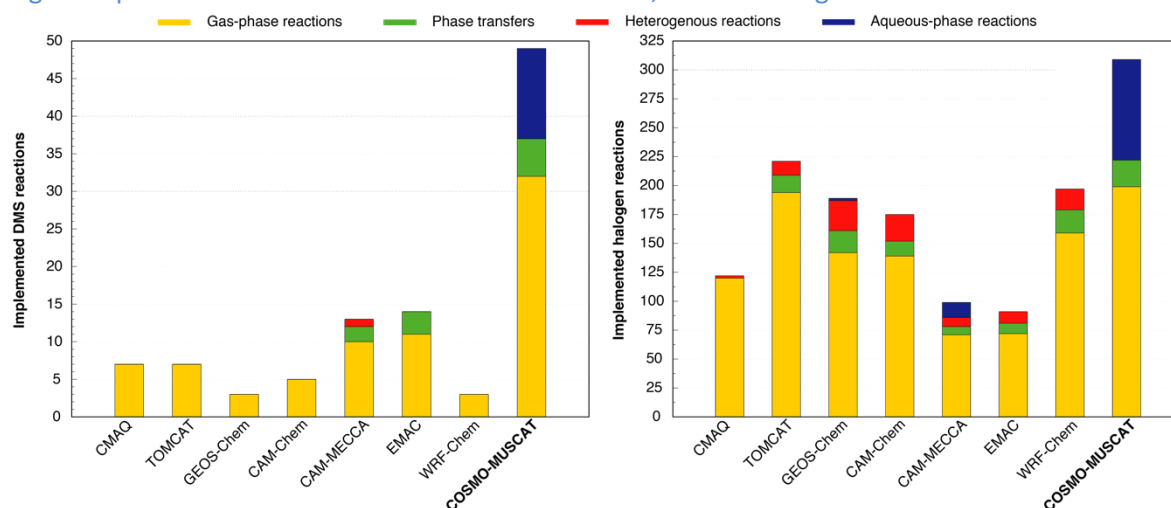


Figure 4 Comparison of applied tropospheric DMS and halogen chemistry mechanisms within the chemical transport models: CMAQ (Muniz-Unamunzaga et al., 2018), TOMCAT (Hossaini et al., 2016), Geos-Chem (Wang et al., 2019), CAM-Chem (Saiz-Lopez et al., 2014), CAM-MECCA (Long et al., 2014), EMAC (Jöckel et al., 2016), and WRF-Chem (Badia et al., 2019). EMAC is a chemistry climate model that can be run as a CTM.

General comments

1. In the Model Setup section, Lines 105-110, it states that the simulations were performed at 48 hours, different latitudes, different seasons, and different relative humidity levels. But I was not able to find where the results for all these simulations are in the manuscript. Please clarify this.

As outlined in the main manuscript, we analysed the modelled sink and source fluxes in detail to receive the reduced mechanisms. For the analysis, we calculated the mean contribution of specific pathways directly from the model output, but did not analyse all concentration time-profiles. In the opinion of the authors, the implementation of such results will not help to better understand the manuscript, but might lead to more confusion. Furthermore, in the term of the coastal simulations, the most important model outcomes are already published (see Hoffmann et al., 2019a; Hoffmann et al., 2019b). Thus, it is not necessary that these results are again included in the present manuscript. However, in terms of completeness, we have included modelled concentration time profiles of target compounds from the pristine ocean simulations into the supplement and linked to the previous published papers covering the results for the coastal simulations, which reads as follows:

Lines 123-124

'The modelled concentration time profiles of specific important trace gases and aerosol compounds within the pristine boundary layer are given in Fig. S1 to S10 in the supplement.'

Lines 132-134

'Details on the model configurations of the first simulation are explicitly given in Hoffmann et al. (2019b) and those of the second simulation in Hoffmann et al. (2019a). The main model results of both simulations do not differ from the present work.'

An example for the simulation at 45° latitude is given below.

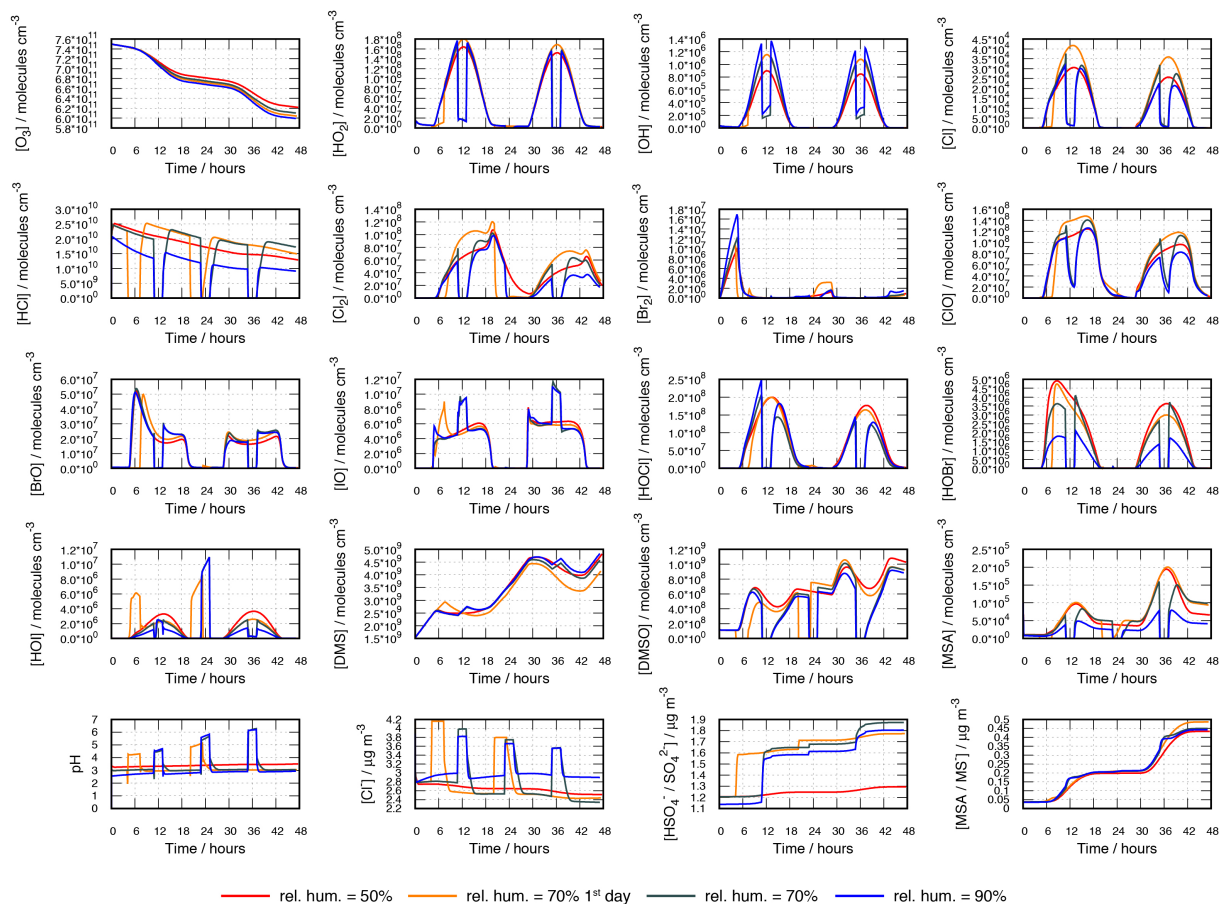


Figure S5 Modelled concentration time-profile of key compounds within the pristine marine boundary layer for the summer simulations at 45° latitude. Red: simulation at rel. humidity of 50% (red). Orange: simulation at relative humidity of 70% and cloud occurrence at early morning and evening of the first model day. Dark green: simulation at relative humidity of 70% and cloud occurrence at noon and midnight. Blue: simulation at relative humidity of 90% and cloud occurrence at noon and midnight.

Besides, we have found a wrong statement regarding the simulation description for the simulations with rel. humidity of 70% and cloud occurrence at early morning. In these simulations cloud occurred at the first model day at early morning and evening. The sentence has been rewritten and reads now as follows:

Lines 119-121

‘The in-cloud residential time of the air parcel is two hours in the simulations with cloud occurrences at noon and midnight and three hours in those with cloud occurrences in the early morning and evening of the first model day.’

2. The CPU time evaluation was shown for the box model with the new chemistry schemes. It will be worth showing the CPU time evaluation for the 2-D modeling before and after using the new schemes.

Before this study, COSMO-MUSCAT did not treat multiphase chemistry of reactive halogen species and DMS. To investigate the additional CPU costs with regard to the DMS and halogen chemistry, we have

performed a simulation without CAPRAM-DM1.0red and CAPRAM-HM3.0red. The CPU time increases by 171% (from 18,420 s to 31,432 s) and 180% (from 52,815 s to 94,896 s) when the simulations are performed with CAPRAM-DM1.0red and CAPRAM-HM3.0red in the ‘stable meteorological conditions’ and ‘unstable meteorological conditions’ simulations, respectively.

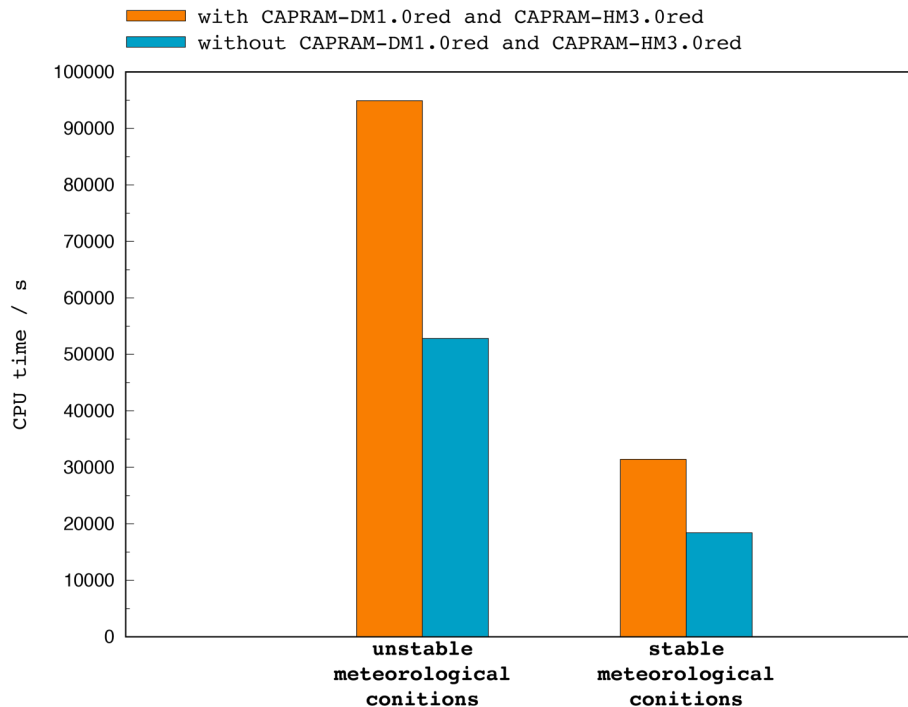


Figure 1 CPU time when the simulations are performed with and without added CAPRAM-DM1.0red and CAPRAM-HM3.0red.

3. References should be added or clarified to all the coefficients shown in the tables in the Supplement.

References have been added (see Tables S2 to S10).

4. There should be discussions about wet scavenging of reactive halogens by clouds when explaining the cloud impacts on halogen and sulfur chemistry.

Thanks for this suggestion which will improve the manuscript. The current COSMO-MUSCAT(5.04e) treats wet scavenging of gases by a first-order scavenging rate without underlying aqueous-phase chemistry. However, a more detailed scheme is implemented for fog droplets, only. The modelled clouds do not precipitate and, thus, this effect would not be of interest in this study. The implementation is a necessary approach that is planned in the future. We have added a discussion on the potential impacts into the section conclusion and outlook which reads as follows:

Lines 718-721

‘The important effect of wet scavenging by clouds was not investigated as the current COSMO-MUSCAT(5.04e) did not implement it in detail, but represented it using a first-order scavenging rate.

Future studies aim to implement a more precise scheme. Since the clouds modelled in this study are not known to precipitate, the propagated error should be small.'

5. It will be useful to have a section discussing the main uncertainties of the new chemistry schemes (e.g. reaction coefficients).

We agree with the reviewer that the uncertainties have to be discussed. However, we have to mention that the new reduced chemistry mechanism is focused on the CAPRAM-DM1.0 and CAPRAM-HM3.0. In the original publication, a discussion of the uncertainties of the main reaction rate constants and products is already given. Furthermore, uncertainties and their discussion are given in the original literature in which the kinetics were determined, too. Therefore, in the first place, we did not include such a section. However, due to the application of the PSSA for the DMS oxidation some uncertainties could exist, because of the changes in the oxygen concentration with height. These were checked and found to be rather small.

A short section that discusses the uncertainties is now added to the revised manuscript and reads as follows:

Lines 421-439

2.5 Uncertainties of the new chemistry scheme

'The downsizing of the CAPRAM-HM3.0 and CAPRAM-DM1.0 solely considering the most important reactions, has led to two new reduced mechanisms, which consist of reactions that sensitively impact the model outcome. Hence, the uncertainty of these reactions can be crucial for the model results. A discussion of the uncertainties of the mechanism development has already been performed in the previous papers describing the mechanism development of the CAPRAM-HM2.0 (Bräuer et al., 2013), CAPRAM-HM3.0 (Hoffmann et al., 2019a; Hoffmann et al., 2019b) and CAPRAM-DM1.0 (Hoffmann et al., 2016) as well as in the cited laboratory work. That's why only a short discussion is given here.

For the oxidation of DMS in the gas-phase, most of the rate constants are based on recommended values of the IUPAC database (<http://iupac.pole-ether.fr/>) or JPL panel (Burkholder et al., 2015). Nevertheless, the application of the PSSA has modified the oxidation pathways, in particular the OH-addition reaction for DMS. The incorporation of the oxygen concentration might increase the uncertainty influencing the DMSO formation rate. As oxygen is in excess under tropospheric conditions and the oxygen concentration is treated in the new derived reaction rate constant specifically, minor changes are expectable. By contrast, no recommended values are available for the aqueous-phase reaction rate constants and can hence be stated as more uncertain (Hoffmann et al., 2016). Further laboratory work is required to minimize their uncertainties.

Regarding the CAPRAM-HM3.0red, certain gas-phase reaction rate constants of the halogen chemistry are based on recommended values (Atkinson et al., 2006, 2007; Atkinson et al., 2008; Burkholder et al., 2015). However, for the oxidation of VOCs/OVOCs by the Cl or Br atom often only one reaction rate constant has been measured by laboratory studies. This is also true for many aqueous-phase chemistry reactions. The highest uncertainties are related to iodine chemistry. Here, often reaction rate constants, which might be of high atmospheric significance are based on estimations, only.'

Other comments

1. Page 3, Line 32: What is the HOX-driven sulfite oxidation? Was it included in the model?

The term HOX refers to hypohalous acids. The model includes HOCl, HOBr, and HOI. These hypohalous acids are very reactive compounds and are known to oxidise effectively sulfite into sulfate in the aqueous phase (Chen et al., 2017; Pechtl and von Glasow, 2007; von Glasow et al., 2002). This chemistry is included. For a better clarification, we have added a description what X means, which reads as follows:

Lines 32-33

'The photolysis of hypohalous acids (HOX, X = Br, Cl, or I) is reduced as well, resulting in higher HOX-driven sulfite to sulfate oxidation in aerosol particles below stratiform clouds.'

2. Line 120: Please give references.

We have added some references to our previous model studies and additionally cite three literature reviews on the topic. These are:

Hoffmann et al. (2019a)

Hoffmann et al. (2019b)

Faxon and Allen (2013)

Saiz-Lopez and von Glasow (2012)

von Glasow et al. (2013)

Lines 125-129

'The lower diversity of the simulations compared to the pristine ocean scenario is chosen because previous model studies had revealed that high NO_x concentrations suppress gas-phase halogen radical cross reactions and lead to a domination of halogen nitrate and nitryl chloride photolysis in halogen atom activation (Hoffmann et al., 2019a; Hoffmann et al., 2019b; Faxon and Allen, 2013; Saiz-Lopez and von Glasow, 2012; von Glasow et al., 2013).'

3. Fig.1: Please clarify shading in the figure. Nighttime?

Yes, the shading in the figure is representing the nighttime. We have added a description into the Figure caption, which reads as:

Lines 358-359

'Grey shaded periods denote the night periods.'

4. Lines 362-363: Please clarify this sentence.

This sentence was included to outline that the difference for the HOCl concentrations are not a driving factor for Cl₂ activation, because different to bromide, the chloride concentrations in sea spray aerosol are still in excess. We have rephrased the sentence in terms of clarity, i.e. It reads now as follows:

Lines 392-394

'As opposed to Br₂ formation by HOBr, the higher HOCl does not necessarily lead to a higher modelled Cl₂ formation, which is related to the significant higher chloride content in sea spray aerosols compared to bromine. It so concludes that the enhanced HOCl seems not to be a driving factor for Cl₂ formation under pristine ocean conditions.'

5. Line 489: 200 horizontal columns – does it mean 222 km?

Yes, it means 222 km. We have added the value in brackets and did this also for the vertical levels. The text reads now as follows:

Lines 537-538

'Whereas COSMO is run on the full domain, only the inner 200 horizontal grid cells (overall 222 km) and lowermost 15 vertical levels (overall 1500 m) are used for the multiphase chemistry simulations with MUSCAT.'

6. Fig. 5: Please clarify the x-axis "Distance in grid". What does it mean and what unit.

This term refers to the model grid resolution, which means the distance from 1 to 2 is 111 km. We added the following sentence to the corresponding figure captions and changed the x-axis in the figures to 'Grid cell number / 10²' for clarification. Furthermore, because of the grammar checking we have rephrased the sentence describing the clouds modelled in the 2D simulations. The caption text for all 2D simulation reads as follows:

Line 559

'The x-axis represents the innermost horizontal grid cells divided by 100.'

Lines 561-562

'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.'

7. Line 515, BrO gas-phase concentration section: Please explain the differences of BrO in two scenarios shown in Fig. 6.

A discussion of the differences has been added, which reads as follows:

Lines 569-576

'Apart from that, the vertical distribution significantly differs between both simulations resulting into distinct spatial pattern. At the left-hand side of the model domain, the BrO concentration is similar, which is related to the activation of reactive bromine species from the initialised marine aerosols. However, when clouds are formed the profiles change. This is related to the high differences in the vertical wind field (see Fig. 7a and b). Because of the stronger updrafts in the 'unstable meteorological condition' simulation, the reactive halogen compounds are advected towards higher altitudes compared to the slow vertical winds in the 'stable meteorological condition' simulation. A second remarkable difference is the much lower BrO concentration at the right-hand side of the model domain

in the 'stable meteorological condition' simulation. This effect is more explicitly discussed in Sect. 3.3.3.'

8. Sect. 3.3.2 Vertical DMSO distribution: It will be useful to show plots of DMSO production and loss rates when discussing the DMSO profiles.

A figure with the modelled DMSO production and loss rates separated into gas and aqueous-phase reactions has been added to the supplement (see Fig. S 11). The link in the manuscript reads as follow:

Lines 626-627

'Furthermore, the overall modelled DMSO production and loss rates separated into gas and aqueous-phase reactions were added to the supplement (see Fig. S11).'

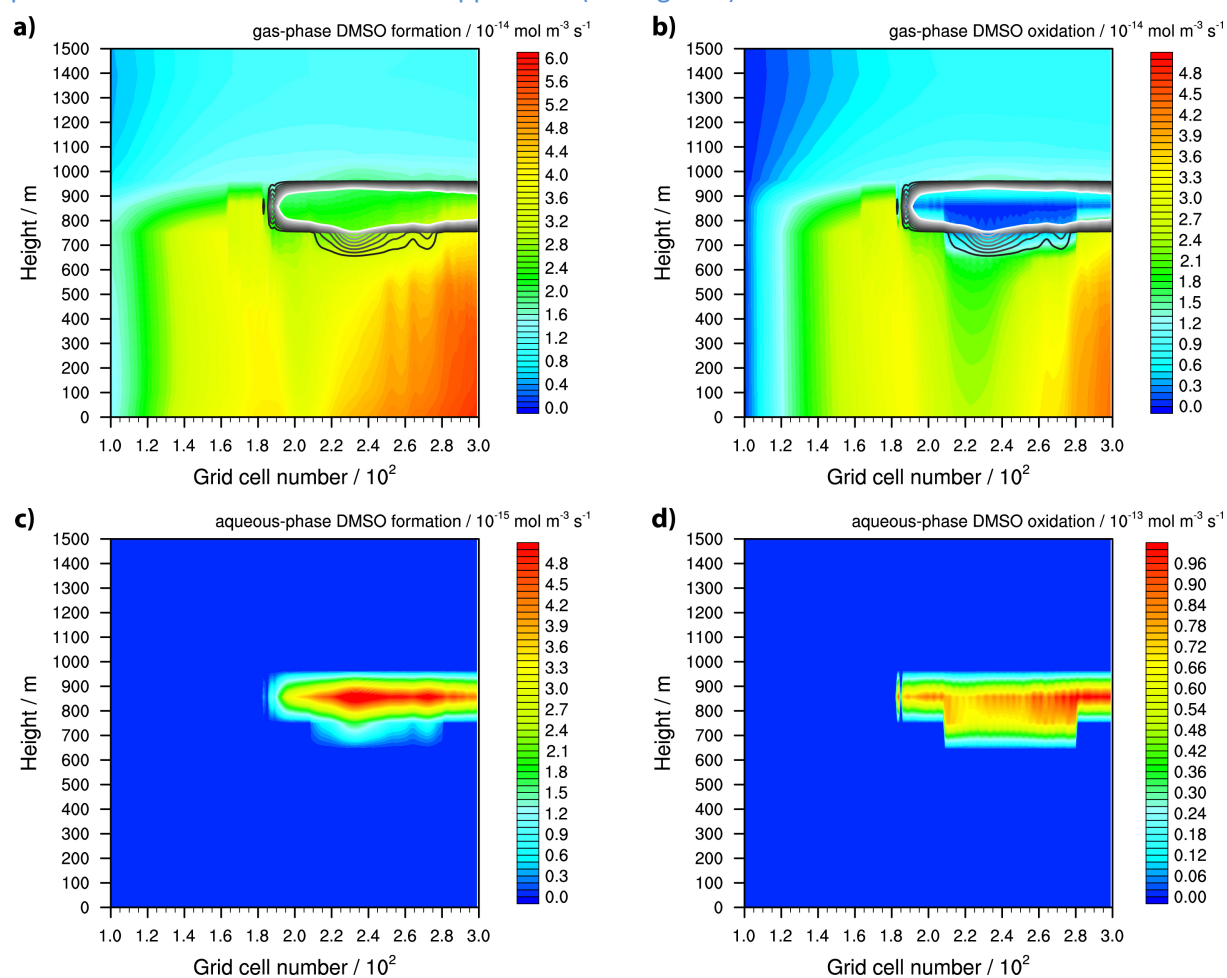


Figure S11 Modelled formation rate of DMSO in (a) the gas phase and (c) the aqueous phase together with the modelled oxidation rate in (b) the gas phase and (d) the aqueous phase in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100.

9. Line 595: Why particularly BrCl? What about Br₂?

Because of the much higher concentration of Cl⁻ in the modelled aerosol particles, the HOBr is modelled to preferably react with Cl⁻ to form BrCl. The modelled BrCl concentrations under the cloud

are one order of magnitude higher than the Br_2 concentrations. However, because of the higher photolysis rate constant, Br_2 is enhanced under the cloud and thus this also important. We have added Br_2 to the text and deleted the word “particularly”. The text reads now as follows:

Lines 651-654

‘This cycle is disturbed by the reaction of BrO with HO_2 , yielding HOBr , which can be photolyzed back into the Br atom again or converted by multiphase chemistry into BrCl or Br_2 . Overall, the photolysis of HOBr , Br_2 and BrCl determine the DMS to DMSO conversion. Clouds suppress the photolysis of Br_2 , BrCl and HOBr due to the reflection of incoming solar radiation.’

10. Lines 598-599: Please clarify more why DMSO concentration profile is shifted to the right compared to the BrO one.

A more detailed explanation is given in the revised manuscript now, which reads as follows:

Lines 656-659

‘Due to a longer lifetime against further oxidation and corresponding horizontal advection, the DMSO concentration profile is shifted towards the right compared to BrO . The lowest oxidation flux between DMS and BrO is modelled between grid cell 2.0 and 2.15. The effect on DMSO concentration is modelled between grid cell 2.1 to 2.4.’

11. Line 612: Please explain “ O_3 is the preferred oxidant in the aerosol phase whereas OH is in the cloud droplets”?

These statements were derived from the results of our previous modelling study Hoffmann et al. (2016) and focused on MSIA oxidation. We have added the reference and rephrased the corresponding text, which reads now as follows:

Lines 671-674

‘ DMSO is rapidly oxidised into MSIA and thus a similar MSIA profile is modelled. As MSIA is highly reactive in the gas and aqueous phases as well as highly soluble, it is rapidly oxidised into methane sulfonate (MS^-) in both the aerosol and the cloud phases. There, O_3 is the preferred oxidant in the aerosol phase, whereas in cloud droplets it is the OH radical (Hoffmann et al., 2016).’

12. Line 617: Please explain “In the grid cells before cloud occurrence, the DMSO concentration is high and consequently the MS^- formation is as well”.

This sentence is related to the rapid oxidation of DMSO in gas and aqueous phase. The formed MSIA is rapidly taken up by sea salt aerosols and is fast oxidised to MS^- and sulfate. We have changed the sentence to make it clearer. The sentence reads now as follows:

Lines 677-679

'In the grid cells left of the cloud, the DMSO concentration is high and consequently the aerosol particle chemistry of DMSO and of the subsequent oxidation product MSIA leads to a sharp increase of MS-formation at the grid cells below the left cloud edge (see Fig. 10a).'

13. Line 625: Please clarify "As for MSA, the formation of sulfate is enhanced in the grid cells directly or indirectly affected by clouds".

The sentence refers to the similar concentration profiles of MSA and sulfate at the left cloud edge. The sentence has been rewritten for more clarity and reads now as follows:

Lines 689-690

'Also, the concentration of sulfate (see Fig. 10b) is enhanced in the grid cells at the left cloud edge, but because of different reasons.'

14. Line 649: How much does the $\text{HOBr} + \text{HSO}_3^-$ in clouds affect the bromine budget through converting HOBr into Br^- ?

The concentration of Br^- is increased inside the cloud droplets by up to one order of magnitude. An additional text discussing this issue has been added and a corresponding figure has been placed into the supplement. The additional text in manuscript reads as follows:

Lines 691-693

'The reaction of HOBr results into the formation of bromide. In addition to the uptake of HBr, this increases the bromide concentration in cloud droplets by up to one order of magnitude compared to the ground level concentration before the left cloud edge (see Fig. S12).'

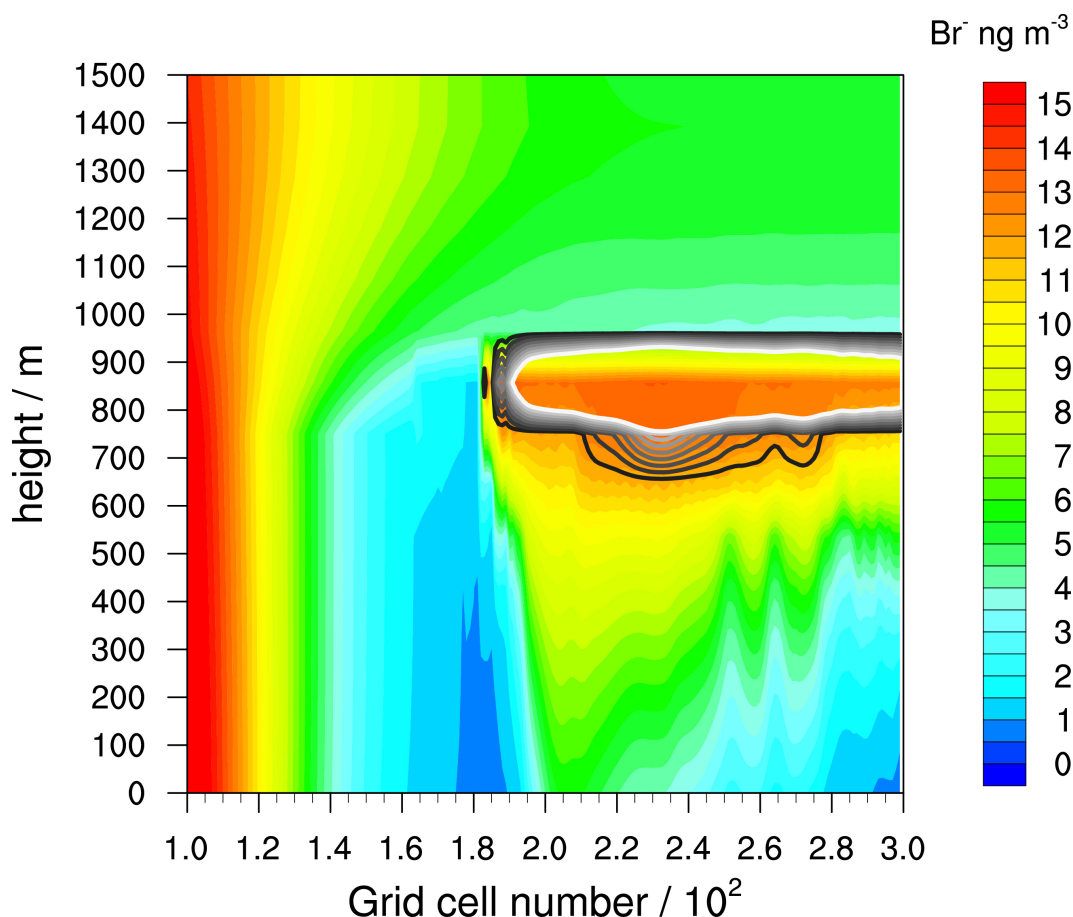


Figure S12 Simulated aqueous-phase concentration of bromide in the ‘stable meteorological condition’ simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The black contour lines represent the simulated clouds. The 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} . The initial background concentration is at about 16 ng m^{-3} .

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Response to Anonymous Reviewer #2

The authors have developed a reduced version of two chemical mechanisms that consider multiphase reactions of dimethylsulfide and reactive halogen species by identifying the primary pathways through which key atmospheric products are formed. The goal of this work is to be able to account for the combined effects of these important multiphase mechanisms in large-scale models for which more comprehensive mechanisms are computationally infeasible. The reduced mechanism is evaluated against a detailed scheme including the two “pre-reduction” versions of the mechanisms under several atmospherically relevant sets of conditions. The authors use the reduced mechanism to draw conclusions on the various factors contributing to DMS oxidation in cloudy environments and reveal strong direct and indirect effects of clouds on this process.

The work is novel in that it provides a new means to account for the combined effects of multiphase dimethylsulfide oxidation and reactive halogen chemistry in large-scale models. The methodology by which the reduction is performed is well reasoned and follows established approaches for such reductions. The evaluation of the reduced mechanism is convincing and the conclusions drawn from the results of incorporating these chemical processes in a chemical transport model are well argued. It is recommended that this article be published in GMD after consideration of a few comments.

The only major comment is that the grammar in certain sections of the manuscript makes interpretation of the arguments difficult at times. I would recommend that the manuscript be edited for grammar by a native English speaker, or someone similarly fluent in English. Some examples (but not all cases) of such passages are included the following comments.

We thank the reviewer for the very positive comments, recommendations and suggestions to improve the manuscript. The comments of the reviewer are carefully addressed point by point in the sections below. The answers to the reviewer comments are marked as blue text. According to the reviewer’s comment, the manuscript has been thoroughly checked for grammar by ourselves again. Furthermore, the manuscript has been checked by an English language professional at the C2 level. The corresponding changes are provided in the manuscript version with tracked changes. The further discussion of the comments can be seen below.

Because of the manuscript checking we have rephrased the figure caption describing the clouds modelled in the 2D simulations. The caption text for all 2D simulation reads as follows:

Lines 561-562

‘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} .’

Besides, due to a personal comment from the community regarding that ECHAM-HAMMOZ and EMAC are chemistry climate models, we have deleted ECHAM-HAMMOZ from Figure 4 and added to the Figure caption that EMAC can be run as a CTM. Please, see the changes below:

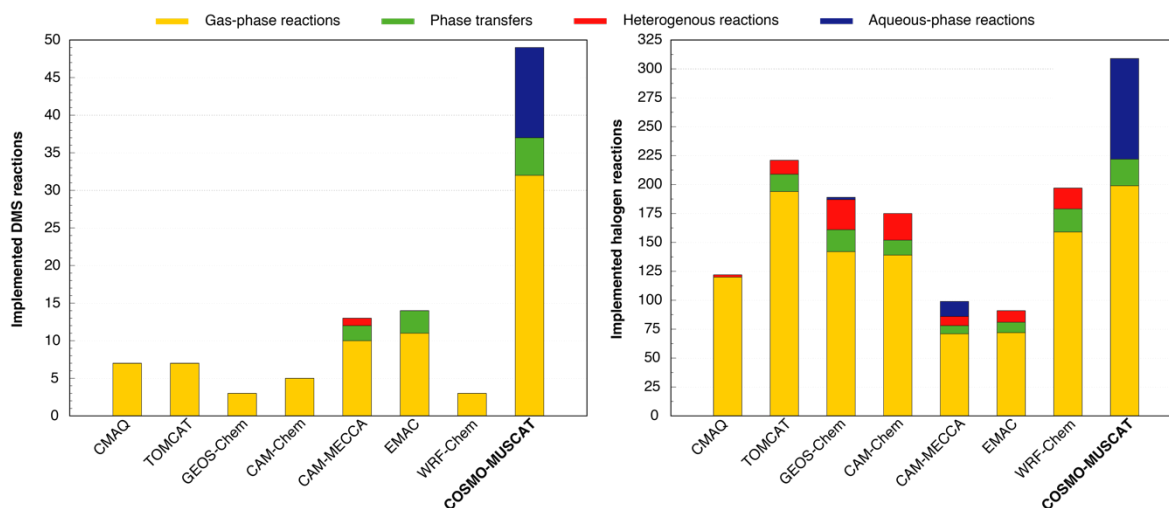


Figure 4 Comparison of applied tropospheric DMS and halogen chemistry mechanisms within the chemical transport models: CMAQ (Muniz-Unamunzaga et al., 2018), TOMCAT (Hossaini et al., 2016), Geos-Chem (Wang et al., 2019), CAM-Chem (Saiz-Lopez et al., 2014), CAM-MECCA (Long et al., 2014), EMAC (Jöckel et al., 2016), and WRF-Chem (Badia et al., 2019). EMAC is a chemistry climate model that can be run as a CTM.

Lines 80–81: “not only the solvation of the high CPU consumption is necessary”

“Solvation” refers to solvent–solute interactions. Also, it is not entirely clear what is meant here. Is not the point of reduced mechanisms to reduce CPU consumption? Does this refer to efforts to develop more efficient numerical solvers for chemical systems?

The sentence intends to say that besides reduction of CPU consumption due to effective numerical solutions in CTMs an appropriate mechanistic description is important, too. We have changed “solvation” to “solution”. The text passage now reads:

Line 83

‘not only a solution for the high CPU consumption is necessary’

Line 83–84: “An adequate mechanism does not currently exist and can only be derived by reducing detailed multiphase chemistry mechanisms.”

I’m not sure that I agree that this is the “only” means to generate such a mechanism. For example, have there not been some machine learning-based techniques applied to simulating atmospheric chemical species transformations based purely on observations? It seems these types of approaches could lead to similarly predictive models, but may shed less light on the underlying chemistry.

We agree with the reviewer that a machine learning approach could lead to a simple predictive model. However, for such an approach to get there a high amount of measurement data is required and a prediction might only be suitable for the current applied location. Thus, the underlaid chemistry is still required, as otherwise a huge number of parameterisations must be included slowing down CPU performance. Furthermore, a simple machine learning approach from observations will not help to understand the pathways responsible for the formation, as it will rely on statistical correlation, nor will

be able to take deposition into account. For example, rain will reduce the sulfate and nitrate concentration, but not necessarily the DMS and NO_x concentration.

Hence, only the reduction of comprehensive mechanisms by sophisticated model studies is able to generate such a detailed but reduced mechanism. To make the statement clearer, we have rephrased the sentence in the revised manuscript. It now reads:

Lines 84-86

‘Currently, an adequate mechanism does not exist and can be derived by reducing detailed multiphase chemistry mechanisms, because important chemical pathways could otherwise be missed resulting in a misinterpretation of field data.’

Line 91 “the various effects of clouds essentially on halogens and DMS.”

It is not clear what the word ‘essentially’ means here.

We have deleted the word “essentially” as it is not really necessary at this point.

Lines 103–104: “The goal of reducing the CAPRAM-DM1.0 and CAPRAM-HM3.0 is that both modules can be applied in different marine atmospheric environments in CTMs.”

This is somewhat unclear. It seems that the results of this work are a single combined reduced mechanism. However, this sentence makes it seem like the goal is to develop two separate reduced mechanisms, and that a CTM can choose which to apply (possibly together or separately?) to particular grid cells. If this is the case, maybe this could also be included in the introduction when the goals of the work are first stated.

Yes, the overall result of this work is a single combined reduced mechanism as it was currently not available for COSMO-MUSCAT. However, as can be seen from the tables in the supplement, the reduction is designed that also only one reduced mechanism or specific reactions could be implemented into CTMs. Because of this, interested modellers could use still their own core mechanism, but can add the marine mechanism module or insights developed in this study, too. This goal was added into the introduction. The new added sentences read as follows:

Lines 90-95

‘During the reduction procedure, two mechanisms are derived, which are afterwards combined into a single one. The combined reduced mechanism is implemented into the CTM MUSCAT (MULTiScale Chemistry Aerosol Transport; Wolke et al., 2004; Wolke et al., 2012), which now treats detailed marine multiphase chemistry. Finally, the combined reduced mechanism is applied in idealised 2D simulations with a focus on multiphase DMS oxidation in the MBL and the various effects of clouds on halogens and DMS.’

Lines 132–140

I find it somewhat unclear how the ‘importance’ of a chemical species is determined here and would prefer a slightly more specific description of why certain species are included in the evaluation. Do you expect that the choice of which species to include in the evaluation, and at what acceptable level of accuracy, would have a large effect on which chemical pathways end up in the reduced mechanism?

Our 5% goal has been determined for the known 'classical' air pollutants, ozone, SO₂, NO_x and PM mass. For the DMS chemistry, we have chosen the most important stable DMS oxidation products DMSO and MSA that are often incorporated in higher scale models. For the reactive halogen chemistry, compounds were chosen that are relevant to understand the gas-phase chemistry of reactive halogens as outlined in review articles. Given the limitations of available measurement techniques, especially for the high reactive halogen compounds, in our opinion 10% deviation is acceptable for these species. Indeed, reducing the goal for example down to 2% will increase the number of reactions that have to be considered, but will not necessarily improve the predictions for air pollutants or greenhouse gases such as ozone. Furthermore, an appropriate reduction is not possible anymore. We have included a more specific description, why these compounds are chosen in the revised manuscript which is given in the following.

Lines 142-158

'The goal of the mechanism reduction firstly is that the modelled concentration of chemical species that are classically treated as important in CTMs, e.g. ozone, SO₂, NO_x, sulfate or nitrate, only deviate from the modelled concentration obtained from the complete scheme by less than 5 % on average over the full modelling time. Secondly, concentrations of oxidants and important chemical compounds of marine multiphase chemistry should only differ by less than 10 % on average. Important chemical compounds of DMS multiphase oxidation are DMS, dimethyl sulfoxide (DMSO), and methane sulfonic acid (MSA), which represent the key stable compounds from DMS oxidation. Dimethyl sulfone (DMSO₂) is not considered, because, according to current scientific knowledge, the oxidation of DMSO₂ is negligible under atmospheric conditions of the pristine ocean. Additionally, the deviation of the concentration of methane sulfinic acid (MSIA) is not a reduction criterion. MSIA is very reactive, so that even slight changes will immediately result in differences of the MSA and sulfate concentrations. In the case of halogen multiphase chemistry, important species for the mechanism reduction are the Cl, Br, and I atoms as well as the ClO, BrO, and IO radical and stable halogen compounds, which can act as important reservoir or activation species for halogen radicals, i.e. hypohalous acids, nitryl chloride, and dihalogen molecules. These halogen reservoir/activation species are of high importance as strong changes in their budget will obviously affect the overall oxidation processes in the MBL. For other halogen radicals, it has been shown by previous studies (e.g. see Saiz-Lopez et al. 2012 and Simpson et al., 2015) that these are rapidly converted into the above-mentioned compounds and thus strong concentration changes will show up in the concentration of X atoms or XO radicals. Lastly, the pattern of the concentration time profile for all species has to match between the reduced and the full mechanism ($R^2 \geq 0.75$).'

Line 268: "As already modelled in other studies, the analyses revealed that the Cl atom is an important oxidant for VOCs and OVOCs"

References for these other studies should be included.

References have been added. These are:

Hoffmann et al. (2019a)

Sherwen et al. (2016)

Xue et al. (2015)

Pechtl and von Glasow (2007)

Lines 290-292

'As already modelled in other studies, the analyses revealed that the Cl atom is an important oxidant for VOCs and OVOCs, e.g. alkanes, non-oxidised aromatic compounds, alcohols, and aldehydes (e.g. Hoffmann et al., 2019a; Sherwen et al., 2016; Xue et al., 2015; Pechtl and von Glasow, 2007).'

Lines 274–277: "Therefore, a first screening on treated VOCs and OVOCs in the mechanisms MOZART4.0 (Schultz et al., 2018), 275 RACM2 (Goliff et al., 2013), MECCA (Jöckel et al., 2016), GEOS-Chem (Wang et al., 2019), and SAPRC11 (Yan et al., 2019) has been performed for the main VOCs and OVOCs. As a result, only the Cl atom oxidation of the lumped VOCs and OVOCs that are treated within all of these mechanisms is considered further."

This could be clarified. Do you first determine which organic species are included in the various lumped species in each model? Do the lumped species in the various models comprise the same sets of actual organic species? How do you determine the rate at which Cl reacts with a lumped species? If one mechanism excludes a specific organic species, are its reactions with Cl automatically excluded from the reduced mechanism?

I am not clear on why this is necessary.

First, the mechanisms were screened for lumped species. Then, the lumped species were analysed on included organic species. Obviously, the models did not comprise the same sets, but mostly the same VOC/OVOC compound classes, e.g. all mechanisms contain a lumped alkane, aldehyde, ketone and aromatics compound. Therefore, the lumped species implemented in our mechanism are also present in the other mechanisms. As we considered the implementation to the new MOZART mechanism, our mechanism contains a lot of VOC/OVOC oxidations. This set can be applied to the other mechanisms, but has to be adjusted if certain species are missing. The chosen reaction rate constant is based on the first lumped product. As example, for aldehydes the lumped species is C₂H₅CHO and the first implemented aldehyde is CH₃CH₂CHO. Here, the reaction rate constant *k* of CH₃CH₂CHO with Cl is chosen. As the reaction rate constants are getting higher with longer chain length, this approach is suitable, as it gives the lower limit of the reaction rate constant. Thus, no overestimation will occur. The statement has been added to better understand the model results from the simulation comparisons. The text now reads as given below.

Lines 292-307

'In order to restrict computational costs, chemical mechanisms in state-of-the-art CTM applications do not contain a high number of organic compounds as the near-explicit MCM. In order to still represent the chemistry of important VOCs and OVOCs in CTMs, species of the same compound classes or of equal reactivity are typically merged into 'lumped' species in condensed mechanisms applied in CTMs (Baklanov et al., 2014). Based on these limitations, the reduced CAPRAM-HM3.0 has to be linkable with the chemical mechanisms used in CTMs. A first screening on treated VOCs and OVOCs in the gas-phase chemical mechanisms MOZART4.0 (Schultz et al., 2018), RACM2 (Goliff et al., 2013), MECCA (Jöckel et al., 2016), GEOS-Chem (Wang et al., 2019), and SAPRC11 (Yan et al., 2019) has been performed for the main VOCs and OVOCs for this purpose. It has been shown that most of the mechanisms contain the same set of primary VOC/OVOC compound classes, for example, aldehydes and alcohols are often treated up to a carbon number of two. As outlined in Sect. 3, the gas-phase mechanism MOZART4 is chosen for further modelling with COSMO-MUSCAT. As a result, only the Cl atom oxidation of the lumped VOCs and OVOCs that are treated within MOZART4 are considered

further. These sets can be applied to the other mechanisms, but have to be adjusted if species are missing. The chosen reaction rate constant is based on the first lumped product. As the k 's are higher with longer carbon chain, this approach is suitable, as it gives a lower limit of the reaction rate constant. Thus, no overestimation will occur. However, when the simulations with the reduced version of the CAPRAM-HM3.0 are compared to the simulations with the non-condensed CAPRAM-HM3.0 this approach results in lower HCl but higher ClO formation.'

Line 317–319: "The evaluation simulations are carried out for 45 latitude with a relative humidity of 70 % under pristine ocean (Hoffmann et al., 2016) and polluted coastal conditions (Hoffmann et al., 2019a)."

In the previous section, several latitudes and relative humidities are modeled. Why are these not used in the evaluation of the reduced model? Can you provide an argument that these scenarios are sufficient to evaluate the reduced mechanism?

Within the analysis of the different simulations it turned out, that reactions that were not important under a specific condition, for example 15° latitude summer, are more important under another specific condition, for example 75° latitude winter, and vice versa. When such case occurred, the corresponding reaction is considered in the reduced mechanism to make it applicable to all regimes. Therefore, it is enough to perform only this meteorological setup. We have outlined this specific mechanism development process in more detail, which reads as follows:

Lines 176-177

'To provide a reduced mechanism applicable for a wide range of conditions, a chemical reaction is included in the reduced scheme in any case if the reaction is important under a single simulation condition.'

Lines 288-289

'Again, as for the CAPRAM-DM1.0 reduction, a chemical reaction is included in the reduced scheme in any case if the reaction is important under a single simulation condition.'

Lines 352-355

'The evaluation by these three simulation cases is appropriate, because both reduced mechanisms contain reactions that were both important and not important under the different performed simulations. Thus, other possible evaluation simulations would also treat reactions that are not necessary under specific conditions. Regardless of the simulation setup a similar performance is expected as a consequence.'

Line 378–379: "Consequently, the high CPU time required overlay the CPU time consumption from the reduction."

This should be clarified.

We have rephrased the sentence for clarity. It now reads:

Lines 408-409

'Therefore, the still high CPU time is caused by requirements of the standard multiphase chemistry mechanism. These high requirements cover the reduction of CPU time achieved by the reduction efforts.'

Line 560 Figure 8

These is an unusually square feature in Fig. 8b for aqueous-phase DMSO directly under the cloud. Is this a result of the way cloud grid-cells and aerosol grid-cells are treated in the model (Fig. 3)?

It is related to the treatment and the interpolation of the grid cells by the used graphic program (ncl). If the resolution of the grid cells would be increased, this feature might not be seen. However, this would increase our CPU time and result into a spatial resolution below 1 km that is normally not covered by regional CTMs.

Line 617–618: "Due to the advection of the stable MS⁻ to the right-hand side of the model domain, the spatial DMSO profile is not modelled."

Is this not shown in Figure 8?

Yes, the DMSO profile is shown in Figure 8. Thus, we have linked on that figure. The corresponding sentence reads now as follows:

Lines 680-681

'Due to the advection of the stable MS⁻ to the right-hand side of the model domain, the spatial profiles of DMSO (Fig. 8) and MS⁻ differ.'

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CAPRAM reduction towards an operational multiphase halogen and DMS chemistry treatment in the chemistry transport model COSMO-MUSCAT(5.04e)

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10 **Abstract.** A condensed multiphase halogen and dimethyl sulfide (DMS) chemistry mechanism for application in **chemistry** transport models is developed by reducing the CAPRAM DMS module 1.0 (CAPRAM-DM1.0) and the CAPRAM halogen module 3.0 (CAPRAM-HM3.0). The reduction is achieved by determining the main oxidation pathways from analysing the mass fluxes of complex multiphase chemistry simulations with the air parcel model SPACCIM. These simulations are designed to cover both pristine and polluted marine boundary layer conditions. Overall, the reduced **CAPRAM-DM1.0** contains 32 gas-phase reactions, 5 phase transfers, and 12 aqueous-phase reactions, of which two processes are described as equilibrium reactions. The reduced CAPRAM-HM3.0 contains 199 gas-phase reactions, 23 phase transfers, and 87 aqueous-phase reactions. For the aqueous-phase chemistry, 39 processes are described as chemical equilibrium reactions. A comparison of simulations using the complete **CAPRAM-DM1.0** and CAPRAM-HM3.0 mechanisms against the reduced ones indicates that the **relative** deviations are below 5 % for important inorganic and organic air pollutants and key reactive species under pristine ocean and polluted conditions. The reduced mechanism has been implemented into the chemical transport model COSMO-MUSCAT and tested by performing 2D-simulations under prescribed meteorological conditions that investigate the effect of stable (stratiform cloud) and more unstable **meteorological** conditions (convective clouds) on marine multiphase chemistry. The simulated maximum concentrations of HCl are in the range of 10^9 molecules cm^{-3} and those of BrO are at around 1×10^7 molecules cm^{-3} reproducing the range of ambient measurements. Afterwards, the oxidation **pathways** of DMS in a cloudy marine atmosphere **have** been investigated in detail. The simulations demonstrate that clouds have both a direct and an indirect photochemical effect on the multiphase processing of DMS and its oxidation products. The direct photochemical effect is related to in-cloud chemistry that leads to high DMSO oxidation rates and a subsequently enhanced formation of methane sulfonic acid compared to aerosol chemistry. The indirect photochemical effect is characterised by cloud shading, which occurs particularly in the case of stratiform clouds. The lower photolysis rate affects the activation of Br atoms and consequently lowers the formation of BrO radicals. The corresponding DMS oxidation flux is lowered by up to 30 % under thick optical clouds. Moreover, high updraft velocities lead to a strong vertical mixing of DMS into the free troposphere predominately

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under cloudy conditions. The photolysis of hypohalous acids (HOX, X = Br, Cl, or I) is reduced as well, resulting in higher HOX-driven sulfite to sulfate oxidation in aerosol particles below stratiform clouds. Altogether, the present model simulations have demonstrated the ability of the reduced mechanism to be applied in studying marine aerosol cloud processing effects in regional models such as COSMO-MUSCAT. The reduced mechanism can be used also by other regional models for more adequate interpretations of complex marine field measurement data.

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1 Introduction

In the marine and coastal atmosphere the chemical composition of the gas-phase, particles, and clouds as well as the size-distribution of particles are significantly influenced by emissions of sea spray aerosols (SSA) and volatile organic compounds from the sea surface (Simpson et al., 2015; Farmer et al., 2015; Quinn et al., 2015). Sea salt is an important compound of SSA (Quinn et al., 2015) and represents a primary source for reactive chlorine and bromine compounds in the troposphere (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). For reactive iodine compounds however, emissions of gaseous iodine compounds from the ocean surface dominate (Carpenter et al., 2012; Carpenter et al., 2013; Carpenter and Nightingale, 2015; Saiz-Lopez et al., 2012). Additionally, the ocean is the main source for dimethyl sulfide (DMS), which is the biggest natural source for atmospheric sulfur (Andreae, 1990; Lana et al., 2011). The oxidation of DMS is the key to understanding the natural radiative forcing as it affects both aerosol and cloud condensation nuclei (CCN) concentrations (Charlson et al., 1987). The chemical systems of halogens and DMS interact with each other strongly and are highly influenced by multiphase chemistry (Barnes et al., 2006; Hoffmann et al., 2016; von Glasow and Crutzen, 2004). As oceans cover around 70 % of the Earth's surface (Joshi et al., 2017; Law et al., 2013) and are in strong interaction with densely populated coastal areas (Kummu et al., 2016; von Glasow et al., 2013), this ocean-related atmospheric chemical subsystem is important for both Earth's climate and air quality.

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The chemistry of reactive halogen compounds as well as of DMS is very sensitive to anthropogenic pollution. The advection of NO_x and ozone has strong effects on the activation of reactive halogen compounds (Hoffmann et al., 2019b; Shechner and Tas, 2017; Mahajan et al., 2009b; Mahajan et al., 2009a; McFiggans et al., 2002) and on DMS oxidation (Breider et al., 2010; Barnes et al., 2006; Chen et al., 2018). Moreover, reactive halogen compounds can significantly influence the depletion of NO_x, ozone, SO₂, volatile organic compounds (VOCs), and oxidised volatile organic compounds (OVOCs) (von Glasow et al., 2002b, a; Sherwen et al., 2017; Schmidt et al., 2016; Sherwen et al., 2016). As the NO₃ radical concentration in anthropogenically influenced atmospheric environments is enhanced (Brown and Stutz, 2012), the NO₃ radical-related DMS oxidation is reinforced (Breider et al., 2010; Chen et al., 2018), which influences the formation of sulfate aerosol particles and correspondingly leads to an increase of aerosol acidity (Muniz-Unamunzaga et al., 2018). The changed aerosol acidity further affects the formation of secondary organic aerosol (SOA) (Surratt et al., 2010; Surratt et al., 2007; Gaston et al., 2014) as well as the activation of reactive halogen compounds (Keene et al., 1998). Apart from that, 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 the

Gelöscht: Furthermore, in anthropogenically influenced atmospheric environments, the NO₃ radical concentration is enhanced (Brown and Stutz, 2012). Thus,

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formation of sulfate aerosol particles even in the Northern Hemisphere (Perraud et al., 2015). Therefore, it is important that chemical transport models (CTMs) treat the crucial multiphase chemistry pathways of both reactive halogen compounds and DMS.

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85 Currently, only a couple of multiphase chemistry mechanisms of halogens and DMS have been developed and applied within CTMs, e.g. EMAC, CAM-MECCA, and GEOS-Chem (Chen et al., 2017; Chen et al., 2018; Jöckel et al., 2016; Long et al., 2014). Nevertheless, the applied model core of these CTMs does not treat aqueous-phase chemistry of halogens and DMS by default. In CTMs that deal with the chemistry in the marine boundary layer (MBL) and the free troposphere, the activation of reactive halogen compounds and its dependence on aerosol acidity is often described by heterogeneous reactions. The parameters of these reactions have been determined in laboratory studies for aerosol solutions that are more ideal than they naturally occur, e.g. pure sulfate or sodium chloride/bromide aerosol. Hence, the accuracy of the description of these processes is restricted and it cannot easily be assumed that they are representative under heterogeneous atmospheric conditions (Ammann et al., 2013). The treatment of multiphase chemistry in models allows for more detailed investigations concerning complex sea spray aerosol matrices. However, the level of detail for the implementation of aqueous-phase chemistry into CTMs is limited because of numerical restrictions, since the implementation of aqueous-phase chemistry usually consumes huge amounts of CPU time. Consequently, mostly only specific small sub-systems are investigated, including a low number of halogen or DMS multiphase chemistry reactions (Chen et al., 2018; Chen et al., 2017). Both discussed aspects, consumption of CPU time and investigating only small sub-systems, highlight that an overall picture of multiphase marine chemistry cannot be drawn by chemical transport modelling yet and might lead to an over- or underestimation of important chemical pathways.

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100 To achieve the goal of adequately treating the multiphase chemistry of DMS and reactive halogen compounds within CTMs, not only a solution for the high CPU consumption is necessary, but also the development of a condensed multiphase chemistry mechanism dealing with the complexity of these chemical systems. Currently, an adequate mechanism does not exist and can be derived by reducing detailed multiphase chemistry mechanisms, because important chemical pathways could otherwise be missed resulting in a misinterpretation of field data.

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105 In the present study, a reduced multiphase chemistry mechanism describing halogen and DMS chemistry is developed through a manual reduction using box model studies with the CAPRAM halogen module 3.0 (CAPRAM-HM3.0, Hoffmann et al., 2019a) and the CAPRAM DMS module 1.0 (CAPRAM-DM1.0, Hoffmann et al., 2016). Both modules currently contain the most detailed mechanisms dealing with the multiphase chemistry of these chemical systems. During the reduction procedure, two mechanisms are derived, which are afterwards combined into a single one. The combined reduced mechanism is implemented into the CTM MUSCAT (MultiScale Chemistry Aerosol Transport; Wolke et al., 2004; Wolke et al., 2012), which now treats detailed marine multiphase chemistry. Finally, the combined reduced mechanism is applied in idealised 2D-simulations with a focus on multiphase DMS oxidation in the MBL and the various effects of clouds on halogens and DMS.

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125 2 Reduction of the CAPRAM-DM1.0 and the CAPRAM-HM3.0

2.1 Model setup

The reduction of the marine multiphase chemistry modules CAPRAM-DM1.0 and CAPRAM-HM3.0 is achieved through modelling studies with the air parcel model SPACCIM (Spectral Aerosol Cloud Chemistry Interaction Model, Sehili et al., 2005; Wolke et al., 2005). SPACCIM is a model framework designed to solve complex multiphase chemistry systems and has already been used for the development of reduced aqueous-phase chemistry mechanisms (Deguillaume et al., 2010). The description of the simultaneously occurring chemical and physical processes in tropospheric cloud droplets and aqueous aerosol particles in SPACCIM is realised by combining a complex size-resolved cloud microphysical model and a detailed multiphase chemistry model. The standard atmospheric multiphase chemistry is represented by the near-explicit gas-phase mechanism MCMv3.2 (Jenkin et al., 2003; Saunders et al., 2003) and the near-explicit aqueous-phase mechanism CAPRAM4.0 (Bräuer et al., 2019).

The goal of reducing the CAPRAM-DM1.0 and CAPRAM-HM3.0 is that both modules can be applied in different marine atmospheric environments in CTMs. To this end, simulations are carried out under two environmental conditions: (i) pristine ocean and (ii) polluted coastal area. The simulations run for 48 hours and are equivalent to former simulations of atmospheric marine environments studied with CAPRAM (Bräuer et al., 2013; Hoffmann et al., 2016; Hoffmann et al., 2019b).

140 In the simulations with pristine ocean conditions, an air parcel is moved along a predefined trajectory at a 900 hPa pressure level. The simulations are carried out at different latitudes (15°, 30°, 45°, 60° and 75°) and in different seasons of the year (summer and winter). The air temperature in the simulations is adjusted accordingly. Furthermore, the simulations are performed at different relative humidity levels (50 %, 70 %, and 90 %). In the simulations with relative humidity levels of 70 % and 90 %, cloud passages of the air parcel are considered. The cloud occurrence is modelled by uplifting the air parcel to an 800 hPa pressure level either at noon and midnight or in the early morning, and evening of the first model day. Due to adiabatic cooling, the relative humidity increases, reaching the critical supersaturation so that a cloud is formed. After the cloud passage, the air parcel descends again to 900 hPa. The updraft and downdraft of the air parcel requires half an hour of modelling time in each case. The in-cloud residential time of the air parcel is two hours in the simulations with cloud occurrences at noon and midnight and three hours in those with cloud occurrences in the early morning, and evening of the first model day. The simulations with 50 % relative humidity have no cloud passages of the air parcel included. For a detailed description of the emission and initialisation of chemical species within the pristine ocean scenario, the reader is referred to Bräuer et al. (2013) and Hoffmann et al. (2016). The modelled concentration time profiles of specific important trace gases and aerosol compounds within the pristine boundary layer are given in Fig. S1 to S10 in the supplement.

150 The scenario at the polluted coastal area is divided into two sub-simulations at 45° latitude and 70 % relative humidity. The lower diversity of the simulations compared to the pristine ocean scenario is chosen because previous model studies had revealed that high NO_x concentrations suppress gas-phase halogen radical cross reactions and lead to a domination of halogen nitrate and nitryl chloride photolysis in halogen atom activation. (Hoffmann et al., 2019a; Hoffmann et al., 2019b; Faxon and

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Allen, 2013; Saiz-Lopez and von Glasow, 2012; von Glasow et al., 2013). The effect of photolysis and temperature change does not affect these four important halogen activation precursors (ClNO₂, ClNO₃, BrNO₃, and INO₃). In the first simulation, the air parcel represents the composition of a pristine marine environment, which is advected over a polluted coastal urban area. The second simulation describes an air-sea breeze circulation system. Details on the model configurations of the first simulation are explicitly given in Hoffmann et al. (2019b) and those of the second simulation in Hoffmann et al. (2019a). The main model results of both simulations do not differ from the present work.

The reduction of both modules is performed by analysing the modelled ten-minute time-resolved source and sink fluxes of key chemical compounds of marine multiphase chemistry. These cover all DMS oxidation intermediates and, for halogen chemistry, all X_y species (X, X₂O₂, XNO₂, XNO₃, XO, XO₂, OXO, XY, HOX, and HX, with X/Y = Cl, Br, or I). At first, the CAPRAM-DM1.0 is reduced and afterwards the CAPRAM-HM3.0. In the following Sect 2.2 and Sect 2.3, the development of the reduced CAPRAM-DM1.0 and CAPRAM-HM3.0 is described.

The final reduced marine multiphase chemistry mechanism is evaluated through control simulations, which are carried out by using not only the full but also the reduced marine multiphase chemistry mechanism.

The goal of the mechanism reduction firstly is that the modelled concentration of chemical species that are classically treated as important in CTMs, e.g. ozone, SO₂, NO_x, sulfate or nitrate, only deviate from the modelled concentration obtained from the complete scheme by less than 5 % on average over the full modelling time. Secondly, concentrations of oxidants and important chemical compounds of marine multiphase chemistry should only differ by less than 10 % on average. Important chemical compounds of DMS multiphase oxidation are DMS, dimethyl sulfoxide (DMSO), and methane sulfonic acid (MSA), which represent the key stable compounds from DMS oxidation. Dimethyl sulfone (DMSO₂) is not considered, because, according to current scientific knowledge, the oxidation of DMSO₂ is negligible under atmospheric conditions of the pristine ocean. Additionally, the deviation of the concentration of methane sulfinic acid (MSIA) is not a reduction criterion. MSIA is very reactive, so that even slight changes will immediately result in differences of the MSA and sulfate concentrations. In the case of halogen multiphase chemistry, important species for the mechanism reduction are the Cl, Br, and I atoms as well as the ClO, BrO, and IO radical and stable halogen compounds, which can act as important reservoir or activation species for halogen radicals, i.e. hypohalous acids, nitril chloride, and dihalogen molecules. These halogen reservoir/activation species are of high importance as strong changes in their budget will obviously affect the overall oxidation processes in the MBL. For other halogen radicals, it has been shown by previous studies (e.g. see Saiz-Lopez et al. 2012 and Simpson et al., 2015) that these are rapidly converted into the above-mentioned compounds and thus strong concentration changes will show up in the concentration of X atoms or XO radicals. Lastly, the pattern of the concentration time profile for all species has to match between the reduced and the full mechanism ($R^2 \geq 0.75$).

Gelöscht:) species.

Gelöscht: The goal of the reduction is that the concentration of chemical species important for chemical transport modelling, e.g. ozone, sulfate or nitrate, only deviate by less than 5 % on average over the full modelling time. A subordinate goal is that oxidants and important chemical compounds of marine multiphase chemistry only diverge by less than 10 % on average. The important chemical compounds of DMS multiphase oxidation are DMS, dimethyl sulfoxide (DMSO), and methane sulfonic acid (MSA). In the case of halogen multiphase chemistry, they are the Cl, Br, and I atoms as well as ClO, BrO, and IO and stable halogen compounds, which act as important reservoir or activation species for halogen radicals, i.e. hypohalous acids, nitril chloride, and dihalogen molecules. Lastly, the evolution of the concentration time profile for all species has to match ($R^2 \geq 0.75$).

2.2 Development of the reduced multiphase DMS chemistry module

The oxidation of DMS in the tropospheric multiphase system leads to gaseous SO₂, sulfuric acid, DMSO₂, MSA, dissolved sulfate, or methane sulfonate through a sequence of steps (Hoffmann et al., 2016; Barnes et al., 2006). To cover the important intermediate oxidation steps, the reduction consists of six individual ones:

- i) Consideration of main multiphase DMS oxidation pathways only;
- ii) Lumping of simple reactions;
- iii) Application of the pseudo-steady-state approximation;
- iv) Neglect of production/oxidation of DMSO₂ in the aqueous phase;
- v) Lumping of the aqueous-phase oxidation of MSIA;
- vi) Reduction of oxidation/production pathways of specific chemical compounds unimportant in the gas or aqueous phase.

In the following, these mechanism reduction steps are outlined in more detail.

2.2.1 Main pathways of multiphase DMS oxidation

In the first reduction step, the main pathways of the multiphase oxidation of DMS and its oxidation products are investigated by analysing the time-resolved source and sink fluxes of all simulations. Main pathways are defined here as chemical production or loss processes that contribute more than 5 % to the overall average mass flux of the investigated compound. This analytical approach has proven its applicability in manual mechanism reduction (Deguillaume et al., 2010; Ervens et al., 2003).

To provide a reduced mechanism applicable for a wide range of conditions, a chemical reaction is included in the reduced scheme in any case if the reaction is important under a single simulation condition. The present analyses provide the important DMS multiphase reaction pathways within the troposphere, similar to a former CAPRAM study dealing with multiphase DMS chemistry (Hoffmann et al., 2016). This approach determines the subsequent reduction steps.

2.2.2 Lumping of simple reactions

According to the current knowledge, in the gas phase, the oxidation of DMS or its oxidation products through H-abstraction lead to a corresponding peroxy radical, which can be further oxidised into an alkoxy radical. Recently, it was suggested that the methylthiomethylperoxy radical (CH₃SCH₂O₂) undergoes a rapid unimolecular H-shift (Wu et al., 2015; Berndt et al., 2019). The final stable product will be an oxidised organic sulfur compound that is characterised by an aldehyde and an organic hydrogen peroxide functionality. This compound can be oxidised in both gas and aqueous phase. Currently, the chemistry of this compound is not further investigated and therefore not treated in the CAPRAM-DM1.0. However, when more laboratory data are available, further mechanisms have to consider this chemistry to improve the modelling of DMS chemistry and its effects.

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Gelöscht:)

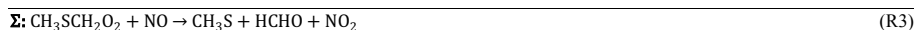
Gelöscht: methane sulfinic acid (

Gelöscht:);

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Gelöscht: then

245 Then, the DMS oxidation derived alkoxy radical can undergo thermal decomposition, a reaction with oxygen, or isomerization (Lightfoot et al., 1992). Nevertheless, the current gas-phase chemistry of the CAPRAM-DM1.0 is based on the MCMv3.2, which only treats thermal decomposition for the CH₃SCH₂O, i.e. C-C bond scission leading to the release of formaldehyde (HCHO). Since the analyses of the mass fluxes reveal that decomposition appears immediately after formation, further decomposition products are directly incorporated in every reaction in which an alkoxy radical is formed and the corresponding decomposition reaction is deleted (see Eq. R1-3).



Further simple integrated reactions correspond to reactions of DMS oxidation products in the aqueous-phase, i.e. reactions with water. The reduction of the CAPRAM3.0 has already revealed that peroxy radical formations in the aqueous phase are not reaction-rate determining steps (Deguillaume et al., 2010). The same is true if reactions of oxidation intermediates occur with water only. Therefore, such aqueous-phase reactions are deleted and the products are directly implemented on the right-hand side of the affected reaction equations.

2.2.3 Application of the pseudo-steady-state-approximation

260 The oxidation of DMS by the OH radical and the Cl atom occurs not only through H-abstraction but also through the addition of these radicals onto the sulfur atom. The formed DMS adduct is unstable and decompose back into DMS and the corresponding radical if it is not stabilised through a reaction with oxygen, which adds to the sulfur atom (Barnes et al., 2006). It is possible that the DMS adduct reacts with NO_x or decomposes into methane sulfenic acid (CH₃SOH) and a methyl (CH₃) radical (Barnes et al., 2006; Yin et al., 1990). The first reduction step has already revealed that even at polluted coastlines, with NO_x concentrations above 10 ppb, NO_x related decompositions are not of atmospheric importance, though. Overall, the analysis shows that oxygen is too reactive against DMS adducts.

The pseudo-steady-state-approximation (PSSA) is a fundamental way to deal with such reactive intermediates to derive the overall rate of a chemical reaction (Seinfeld and Pandis, 2006). The same method is applicable on the oxidation of DMSO, whose oxidation by the Cl atom also leads to a DMSO adduct.

$$\frac{d[\text{DMS}]}{dt} = -k_1[\text{DMS}][\text{X}] + k_2[\text{DMS-X}]; (\text{X} = \text{OH or Cl}) \quad (1)$$

$$270 \frac{d[\text{DMS-X}]}{dt} = k_1[\text{DMS}][\text{X}] - k_2[\text{DMS-X}] - k_3[\text{DMS-X}][\text{O}_2] \quad (2)$$

$$\hookrightarrow \frac{d[\text{DMS}]}{dt} = -\frac{k_1 k_3 [\text{O}_2]}{k_2 + k_3 [\text{O}_2]} [\text{DMS}][\text{X}] \quad (3)$$

As outlined, apart from the DMSO formation, a considerable amount of CH₃SOH is also formed through DMS adduct decomposition. Hence, a PSSA is also effective for this reaction sequence. The implemented rate constant of the DMS adduct decomposition within the CAPRAM-DM1.0 is given temperature independent. The same is true for the oxygen addition

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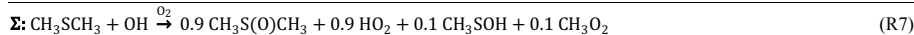
Gelöscht: decomposes

Gelöscht: (Barnes et al., 2006). It is recommended that the DMS adduct can also react with NO_x or decompose

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reaction. Therefore, under tropospheric conditions both reactions can be aggregated into first order reaction rate constants and merged. This merging gives a ratio between decomposition and oxygen addition that is implemented into the overall reaction (see Eq. R4-7).



The PSSA is also applicable on the oxidation of DMSO by the Cl atom and for the methylthiyl radical (CH_3S) reaction with oxygen, leading to the methylthio peroxy radical (CH_3SOO), which has multiple reaction pathways. On the one hand, it can react with NO_x , decompose back into CH_3S , or SO_2 and CH_3 , or rearrange itself into the sulfonyl radical (CH_3SO_2) on the other hand. The first reduction step reveals that the reaction with NO_x is negligible, since only a decomposition into SO_2 as well as the formation of the sulfonyl radical occur. For that reason, the PSSA is also applied to these two reaction pathways as well.

$$\frac{d[\text{CH}_3\text{S}]}{dt} = -k_1[\text{CH}_3\text{S}][\text{O}_2] + k_2[\text{CH}_3\text{SOO}] \quad (4)$$

$$300 \quad \frac{d[\text{CH}_3\text{SOO}]}{dt} = k_1[\text{CH}_3\text{S}][\text{O}_2] - k_2[\text{CH}_3\text{SOO}] - k_3[\text{CH}_3\text{SOO}] \quad (5)$$

$$\hookrightarrow \frac{d[\text{CH}_3\text{S}]}{dt} = -\frac{k_1 k_3}{k_2 + k_3} [\text{CH}_3\text{S}][\text{O}_2] \quad (6)$$

2.2.4 Neglect of production/oxidation of DMSO₂

Though the analysis of the sink and source fluxes has revealed that aqueous-phase chemistry contributes a little more than 5 % to DMSO₂ formation and oxidation, yet the modelled overall DMSO₂ formation and oxidation flux is negligible compared to that of MSIA. Furthermore, DMSO₂ has low reactivity towards OH oxidation in the gas ($k_{\text{OH}} < 3.0 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$; Falbe-Hansen et al., 2000) and aqueous phase ($k_{\text{OH}} = 1.77 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$; Zhu et al., 2003). Because of the low measured background gas-phase concentrations of DMSO₂ in the single-digit ppt range (Davis et al., 1998; Berresheim et al., 1998), the gas-phase oxidation of DMSO₂ by the OH radical is likely to be suppressed through methane oxidation ($k = 3.5 \times 10^{-15}$ to $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in the temperature range of 270 to 298 K), plus dry and wet deposition can be assumed as the major atmospheric removal processes for DMSO₂. In order to shrink the mechanism, DMSO₂ production in the aqueous phase as well as the oxidation of DMSO₂ in both the gas- and aqueous phase are neglected as a consequence.

2.2.5 Lumping of the aqueous-phase oxidation of MSIA

In the fifth reduction step, the oxidation of MSIA in the aqueous phase has been simplified. Having a pK_a value of 2.28 (Wudl et al., 1967) MSIA occurs in both its non-dissociated and its dissociated form under atmospheric aerosol as well as cloud conditions. At this point, the only important oxidant for the non-dissociated form is ozone. The deprotonated MSIA reacts with

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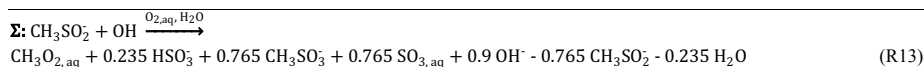
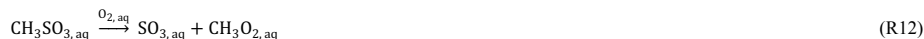
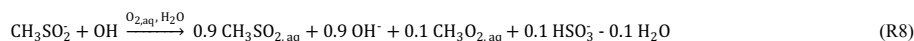
Gelöscht: The

both the OH and the Cl_2^- radical via an electron transfer reaction into aqueous CH_3SO_2 . The formed CH_3SO_2 further reacts with O_2 into the methylsulfonylperoxyl radical ($\text{CH}_3\text{SO}_2\text{O}_2$) or decomposes into the CH_3 radical and dissolved SO_2 that is immediately dissociated into $\text{HSO}_3^-/\text{SO}_3^{2-}$. Because of its high atmospheric abundance, in our study the O_2 concentration is modelled to be almost constant within the tropospheric aqueous phase. Furthermore, both reaction rate constants are implemented as temperature-independent, which is why a ratio between these reactions can be calculated. The reaction of the $\text{CH}_3\text{SO}_2\text{O}_2$ with MSIA yields MSA and the methylsulfonylalkoxyl radical (CH_3SO_3). The latter decomposes into the CH_3 radical and sulfate. Both reactions occur immediately. As a whole, all reactions of the deprotonated MSIA oxidation can be summarized into one reaction for each oxidant, covering the overall MSIA loss (see below Eq. R8-13 for MSIA oxidation by the OH radical).

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2.2.6 Reduction of oxidation/production pathways of specific chemical compounds less important in gas or aqueous phase

In the last reduction step, the mechanism is again analysed for residual multiphase chemistry pathways to be combined. These are, for example, reactions of radicals that now treat only one fast reaction sequence and thus are merged into the previous reaction.

2.3 Development of the reduced multiphase halogen chemistry module

The goal of reducing the CAPRAM-HM3.0 is to enable the description of key halogen chemistry affecting ozone, NO_x , SO_2 , VOCs, and OVOCs by a reduced mechanism that almost conserves the concentration time profile of the reactive halogen compounds listed earlier. The following three reduction steps are applied to achieve this:

- i) Consideration of chemical production or loss processes that contribute more than 5 % to the overall mass flux of halogen compounds only;
- ii) Lumping of simple reaction sequences;
- iii) Neglect of oxidation/production of specific chemical species modelled to be unimportant in tropospheric gas or aqueous-phase chemistry.

In the following, these mechanism reduction steps are outlined in more detail.

2.3.1 Main pathways of multiphase halogen chemistry

An analysis of the main pathways is performed in a similar manner as for the multiphase DMS chemistry. However, the development of a DMS-like stepwise oxidation scheme is impossible, due to important side pathways and interconnections with other chemical subsystems, e.g. NO_x or HO_x chemistry and various halogen cross interactions (Saiz-Lopez and von Glasow, 2012). Furthermore, halogen multiphase chemistry is characterised by large differences in aqueous-phase oxidation within aerosol particles and cloud droplets (Bräuer et al., 2013; Hoffmann et al., 2019b; von Glasow et al., 2002a). Therefore, an appropriate reduced representation of multiphase halogen chemistry requires the focus of the reduction on different halogen species. Hence, the determination of the main pathways is done for a huge number of halogen compounds covering key halogen atoms, halogen radicals, halogen nitrates, halogenated organics such as halogenated aldehydes, as well as halogen oxo-carboxylic acids. Again, as for the CAPRAM-DM1.0 reduction, a chemical reaction is included in the reduced scheme in any case if the reaction is important under a single simulation condition.

As already modelled in other studies, the analyses revealed that the Cl atom is an important oxidant for VOCs and OVOCs, e.g. alkanes, non-oxidised aromatic compounds, alcohols, and aldehydes. (e.g. Hoffmann et al., 2019a; Sherwen et al., 2016; Xue et al., 2015; Pechtl and von Glasow, 2007). In order to restrict computational costs, chemical mechanisms in state-of-the-art CTM applications do not contain a high number of organic compounds as the near-explicit MCM. In order to still represent the chemistry of important VOCs and OVOCs in CTMs, species of the same compound classes or of equal reactivity are typically merged into ‘lumped’ species in condensed mechanisms applied in CTMs (Baklanov et al., 2014). Based on these limitations, the reduced CAPRAM-HM3.0 has to be linkable with the chemical mechanisms used in CTMs. A first screening on treated VOCs and OVOCs in the gas-phase chemical mechanisms MOZART4.0 (Schultz et al., 2018), RACM2 (Goliff et al., 2013), MECCA (Jöckel et al., 2016), GEOS-Chem (Wang et al., 2019), and SAPRC11 (Yan et al., 2019) has been performed for the main VOCs and OVOCs for this purpose. It has been shown that most of the mechanisms contain the same set of primary VOC/OVOC compound classes, for example, aldehydes and alcohols are often treated up to a carbon number of two. As outlined in Sect. 3, the gas-phase mechanism MOZART4 is chosen for further modelling with COSMO-MUSCAT. As a result, only the Cl atom oxidation of the lumped VOCs and OVOCs that are treated within MOZART4 are considered further. These sets can be applied to the other mechanisms, but have to be adjusted if species are missing. The chosen reaction rate constant is based on the first lumped product. As the k’s are higher with longer carbon chain, this approach is suitable, as it gives a lower limit of the reaction rate constant. Thus, no overestimation will occur. However, when the simulations with the reduced version of the CAPRAM-HM3.0 are compared to the simulations with the non-condensed CAPRAM-HM3.0 this approach results in lower HCl but higher ClO formation.

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Gelöscht: However, because of limited computational costs, state-of-the-art chemical mechanisms of CTMs do not contain a high variability of organic compounds as the near-explicit MCM. In order to still represent the chemistry of important VOCs and OVOCs in CTMs, species of the same compound classes or of equal reactivity are typically merged into ‘lumped’ species in condensed mechanisms applied in CTMs

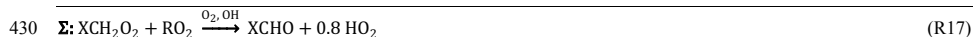
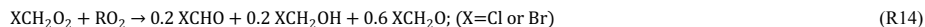
Gelöscht: (Baklanov et al., 2014)

Gelöscht: Because of these limitations, the reduced CAPRAM-HM3.0 has to be linkable with the chemical mechanisms used in CTMs. Therefore, a first screening on treated VOCs and OVOCs in the mechanisms MOZART4.0 (Schultz et al., 2018), RACM2 (Goliff et al., 2013), MECCA (Jöckel et al., 2016), GEOS-Chem (Wang et al., 2019), and SAPRC11 (Yan et al., 2019) has been performed for the main VOCs and OVOCs. As a result, only the Cl atom oxidation of the lumped VOCs and OVOCs that are treated within all of these mechanisms is considered further. However, this approach results in lower HCl but higher ClO formation when the reduced version of the CAPRAM-HM3.0 is compared to the non-condensed MCMv3.2/CAPRAM4.0/ CAPRAM-DM1.0/CAPRAM-HM3.0.

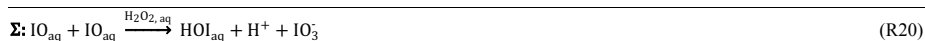
2.3.2 Lumping of simple reaction sequences

In the gas-phase, halogen atoms react rapidly with O₂- and CO-yielding unstable molecules that, as the model simulations show, immediately decompose again. Still, within the CAPRAM-HM3.0, specific oxidation pathways lead to unstable molecules (e.g. the oxidation of halogenated oxidised organics). Consequently, in every reaction in which such an unstable molecule occurs as a product it is replaced by the halogen atom and O₂ or CO.

The further processing of halogenated organic peroxy radicals in the gas phase result in halogenated organic alkoxy radicals. As for DMS, the halogenated organic alkoxy radical decomposition, which is modelled not to be the overall rate-determining step is integrated into these reactions. Overall, the recombination of the halogenated organic peroxy radicals with other organic peroxy radicals (RO₂) leads exclusively to halogenated carbonyls (see Eq. R14-17).



If the analysis of the main pathways leads to only one further reaction of a compound being left, this reaction has been screened for two criteria: (i) Does the follow-up reaction occur rapidly and (ii) is the overall concentration of the product so low that it would not be a significant interfering factor for the modelling. If both issues are true, the overall reaction is merged together. For example, the recombination of IO in the aqueous phase leads to iodite (HIO₂) which is an intermediate in the conversion between iodide and iodate (IO₃). It is quickly oxidized into iodate by H₂O₂, which is ubiquitous in the marine atmospheric multiphase (Jacob and Klockow, 1992; Benedict et al., 2012; Kim et al., 2007; Yuan and Shiller, 2000), and also has a very low modelled concentration. Overall, the IO recombination together with the oxidation of HIO₂ by H₂O₂ results in iodate (see Eq. R18-20).



2.3.3 Neglect of oxidation/production of specific chemical species modelled to be less important in tropospheric gas or aqueous-phase chemistry

For the reduction of the halogen chemistry part, less important chemical halogen species are defined as such with low (< 0.1 ppt for non-radical species) modelled concentrations or high chemical stability ($k_{\text{OH}} < 6.4 \cdot 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ that is the k_{298} of methane; Atkinson et al., 2006) in order that their non-consideration does not affect the concentrations of the target species under conditions in the lower troposphere. While typical species with a rather high chemical stability are chlorinated and brominated organics (e.g. CH₂Cl), except bromoform (CHBr₃), for which oxidation in the lower troposphere is negligible.

Gelöscht: Typical

Gelöscht: . Typical

typical species with low modelled concentrations are oxidised halogenated organics derived from the OH oxidation of methylated halogens (e.g. ICHO or ICIO from CH₃I oxidation). As the reduced mechanism is developed to deal with tropospheric multiphase chemistry, the oxidation of such species is not treated within the reduced CAPRAM-HM3.0.

Gelöscht:), precursors of which are mainly removed through photolysis.

2.4 Evaluation of the reduction steps

455 By comparing simulations with the reduced and with the original CAPRAM-DM1.0 and CAPRAM-HM3.0 added to the multiphase chemistry mechanism MCMv3.2/CAPRAM4.0, the performed reduction steps are evaluated. Being referred to as
460 'Pristine', 'Breeze' and 'Outflow' scenario the evaluation simulations are carried out for 45° latitude with a relative humidity of 70% under pristine ocean (Hoffmann et al., 2016) and polluted coastal conditions (Hoffmann et al., 2019a). While the
abbreviations 'Pristine' and 'Breeze' stand for the scenarios of the pristine ocean as well as of an air-sea breeze circulation system, 'Outflow' represents the scenario of the advection of polluted air masses over a marine environment. The simulations run for 96 hours in total including cloud passages between 11 am and 1 pm and between 11 pm and 1 am in both scenarios 'Pristine' and 'Outflow' as well as between 1 pm and 2 pm in the third scenario 'Breeze'. The longer simulation time compared to that of previous simulations was chosen in order to investigate the effect of a longer modelling time on concentration divergence. The evaluation by these three simulation cases is appropriate, because both reduced mechanisms contain reactions
465 that were both important and not important under the different performed simulations. Thus, other possible evaluation simulations would also treat reactions that are not necessary under specific conditions. Regardless of the simulation setup a similar performance is expected as a consequence.

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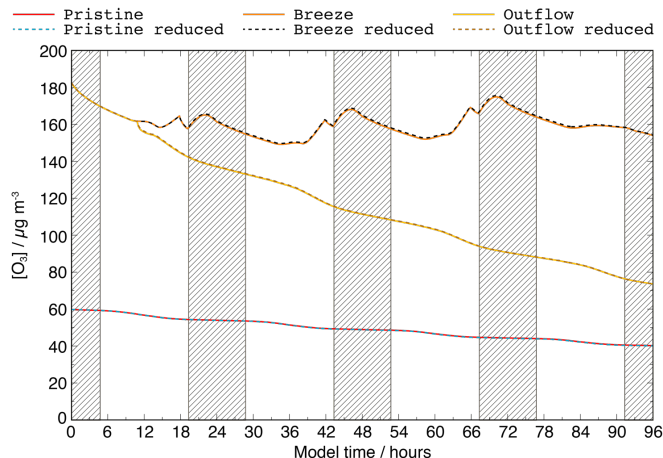


Figure 1 Modelled concentrations of ozone within the scenarios 'Pristine', 'Breeze', and 'Outflow' compared between the simulations with the full (solid lines) and reduced (dotted lines) CAPRAM-DM1.0 and CAPRAM-HM3 mechanism. Grey shaded periods denote the night periods.

The investigation of the modelled evolution of the concentration time profile of ozone is shown in Figure 1, revealing an excellent agreement for all the scenarios ($R^2 = 1$). Moreover, the average ozone concentrations diverge by less than 5% throughout the entire modelling time, demonstrating that the reduced mechanism is able to reproduce the modelled ozone concentrations of the complex mechanism.

The same analysis is performed for other air pollutants and key aerosol compounds important for air quality modelling, which are NO , NO_2 , SO_2 , HNO_3 , HCl , and DMS in the gas-phase, and also the dry mass as well as the organic mass of the aerosols together with nitrate, sulfate, chloride, and methane sulfonate. Furthermore, the analysis is performed for reactive halogen compounds and the OH , NO_3 , and HO_2 radicals. Table 1 shows the average percentage deviation for these chemical species. The main target species, except MSA in the 'Breeze' scenario, do not exceed the 5% threshold, what is also true for the OH , HO_2 , and NO_3 radical in both the gas and aqueous phases. Even for reactive halogen compounds, the deviation rarely exceeds the 5% mark.

However, especially in the 'Outflow' scenario, reactive bromine compounds exceed the 10% threshold, being caused by missing brominated organics in the reduced CAPRAM-HM3.0 that trap the bromine from further reaction. For example, 3 ppt of bromine are trapped on average in brominated alcohols formed through Br atom-related oxidation of alkenes and further RO_2 recombination. Regarding the low concentration and the fact that alcohols are further oxidized into carbonyls, only the formation of brominated carbonyls is considered in the reduced CAPRAM-HM3.0 to minimize the mechanism. Consequently, the bromine radical is recycled faster by the following reaction sequence:

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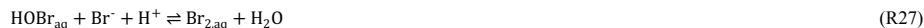
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Overall, this increases the modelled concentrations of reactive bromine compounds, particularly in the afternoon after cloud occurrence and under high alkene as well as low ozone. However, the evolution of the concentration time profile fits very well ($R^2 = 0.98, 0.95, 0.97,$ and 0.75 for Br, BrO, HOBr, and Br₂, respectively). Apart from bromine, larger differences also occur for HOCl in the ‘Breeze’ and ‘Outflow’ scenarios. This is related to the restricted VOC and OVOC oxidations within the

525 reduced CAPRAM-HM3.0 in order to match the condensed gas-phase chemistry mechanisms implemented in the CTMs.

Therefore, the HCl concentration is more than 2 % smaller and more Cl atoms react with ozone into ClO that quickly reacts with HO₂ to yield HOCl. As opposed to Br₂ formation by HOBr, the higher HOCl does not necessarily lead to a higher modelled Cl₂ formation, which is related to the significant higher chloride content in sea spray aerosols compared to bromine. It so concludes that the enhanced HOCl seems not to be a driving factor for Cl₂ formation under pristine ocean conditions.

530 Finally, the methane sulfonate anion (MS⁻) is around one quarter lower in the ‘Breeze’ scenario, which is caused by the Cl₂ radical oxidation. This reduction revealed that the Cl₂ radical is an important oxidant for oxalic acid and MS⁻. Consequently, other OVOC oxidations are discarded for treatment in the reduced CAPRAM-HM3.0. The modelled Cl₂ radical concentrations are around one order of magnitude higher in the ‘Breeze’ scenario compared to the ‘Pristine’ and ‘Outflow’ scenarios, resulting in much higher MS⁻ oxidation rates. Yet, the development of the MS⁻ concentration time profile agrees very well ($R^2 = 1$). In

535 addition, the MSA concentration deviates by only 6% at the end of the model simulations.

Since, the evaluation reveals that the reduced mechanism system is able to reproduce similar results as the full mechanism system, it is basically appropriate for implementation into CTMs. The reduced mechanisms of the CAPRAM-DM1.0 and CAPRAM-HM3.0 will be called CAPRAM-DM1.0red and CAPRAM-HM3.0red in the following text.

Also, the modelling studies reveal that computational (CPU) time is decreased, especially within the scenario ‘Pristine’ (see

540 Figure 2). Compared to the base runs, the CPU time is reduced by 16 %, 5 %, and 6 % in the scenarios ‘Pristine’, ‘Breeze’, and ‘Outflow’, respectively. Overall, the CPU time reduction is low, but is accounted to the usage of the MCMv3.2 and CAPRAM4.0 that still treats more than 21000 reactions. Furthermore, the calculation of microphysical processes consumes a huge amount of CPU time, too. Therefore, the still high CPU time is caused by requirements of the standard multiphase chemistry mechanism. These high requirements cover the reduction of CPU time achieved by the reduction efforts. Very low

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initialised NO_x concentrations in the pristine scenario induced the stronger decrease of computation time unlike the other scenarios. When it comes to the scenarios 'Breeze' and 'Outflow', the high initialised NO_x concentrations effectively suppress halogen radical cross-interactions in the gas phase. These cross-interactions are very fast and establish reaction cycles that induces high fluxes. Therefore, under high NO_x conditions, much lower CPU time is required to solve these reactions. However, in the scenario 'Pristine', the rapid occurring gas-phase cross-interactions of halogen radicals still exist hindering stronger amplified CPU time reductions.

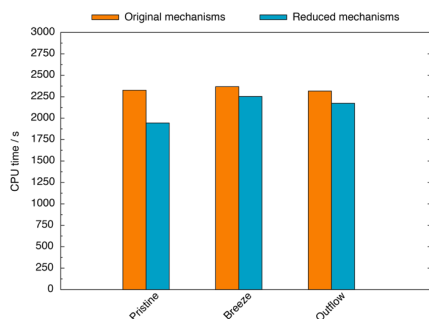


Figure 2 Required CPU time within the scenarios 'Pristine', 'Breeze', and 'Outflow' considering the original multiphase chemistry mechanism system MCMv3.2/CAPRAM4.0/CAPRAM-DM1.0/CAPRAM-HM3.0 and the multiphase chemistry mechanism system with the CAPRAM-DM1.0red and CAPRAM-HM3.0red. The CPU costs include gas and aqueous-phase chemistry, microphysics, model initialization, and output.

2.5 Uncertainties of the new chemistry scheme

The downsizing of the CAPRAM-HM3.0 and CAPRAM-DM1.0 solely considering the most important reactions, has led to two new reduced mechanisms, which consist of reactions that sensitively impact the model outcome. Hence, the uncertainty of these reactions can be crucial for the model results. A discussion of the uncertainties of the mechanism development has already been performed in the previous papers describing the mechanism development of the CAPRAM-HM2.0 (Bräuer et al., 2013), CAPRAM-HM3.0 (Hoffmann et al., 2019a; Hoffmann et al., 2019b) and CAPRAM-DM1.0 (Hoffmann et al., 2016) as well as in the cited laboratory work. That's why only a short discussion is given here.

For the oxidation of DMS in the gas-phase, most of the rate constants are based on recommended values of the IUPAC database (<http://iupac.pole-ether.fr/>) or JPL panel (Burkholder et al., 2015). Nevertheless, the application of the PSSA has modified the oxidation pathways, in particular the OH-addition reaction for DMS. The incorporation of the oxygen concentration might increase the uncertainty influencing the DMSO formation rate. As oxygen is in excess under tropospheric conditions and the oxygen concentration is treated in the new derived reaction rate constant specifically, minor changes are expectable. By contrast, no recommended values are available for the aqueous-phase reaction rate constants and can hence be stated as more uncertain (Hoffmann et al., 2016). Further laboratory work is required to minimize their uncertainties.

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605 Regarding the CAPRAM-HM3.0red, certain gas-phase reaction rate constants of the halogen chemistry are based on recommended values (Atkinson et al., 2006, 2007; Atkinson et al., 2008; Burkholder et al., 2015). However, for the oxidation of VOCs/OVOCs by the Cl or Br atom often only one reaction rate constant has been measured by laboratory studies. This is also true for many aqueous-phase chemistry reactions. The highest uncertainties are related to iodine chemistry. Here, often reaction rate constants, which might be of high atmospheric significance are based on estimations, only.

3 First applications in chemistry transport modelling with COSMO-MUSCAT

610 The CTM applied in this study is MUSCAT (Wolke et al., 2004; Wolke et al., 2012). It is either coupled to the weather model COSMO (Consortium for Small Scale Modelling; Steppeler et al., 2003; Baldauf et al., 2011) or ICON (ICOsahedral Non-hydrostatic; Zängl et al., 2015), which provide all required meteorological fields (e.g. wind, temperature, relative humidity, liquid water content, and precipitation) to MUSCAT that are necessary to calculate the advection, diffusion, and physico-chemical interaction of particles and trace gases. While the emission files of gases and aerosols within MUSCAT are generated by pre-processors, the chemical mechanism is imported from ASCII files, which allows for changes without code recompilation. In terms of dust (Heinold et al., 2007) and sea spray aerosols (Barthel et al., 2019), emissions can also be calculated online.

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- Gelöscht: (Barthel et al., 2019)

3.1 Implementation of the CAPRAM-DM1.0red and the CAPRAM-HM3.0red into COSMO-MUSCAT

620 Within the present study, the model framework COSMO-MUSCAT is used, which has recently been extended to be able to treat multiphase chemistry in clouds (Schrödner et al., 2014; Schrödner et al., 2018). The chemistry of DMS and detailed halogen chemistry are still missing. In order to consider them, the mechanisms CAPRAM-DM1.0red and CAPRAM-HM3.0red are implemented into the atmospheric multiphase chemistry core of COSMO-MUSCAT, in which gas-phase chemistry is described by the MOZART4 mechanism (Schultz et al., 2018) and aqueous-phase chemistry by the CAPRAM3.0red mechanism (Deguillaume et al., 2010). MOZART4 treats comprehensive halogen and DMS gas-phase chemistry that is replaced, as well as specific lumped VOCs and OVOCs. As outlined, these lumped species notably cover the VOCs and OVOCs, where the oxidation by the Cl atom is significant. To link the CAPRAM-HM3.0red to the MOZART4, the overall rate constants of the Cl atom are derived for the following lumped VOCs: (i) BIGALK, (ii) ALKOH, (iii) C₂H₅CHO, (iv) BIGALD1, (v) XYL, and (vi) BZALD. The lumped species C₂H₅CHO represents all aldehydes with more than three carbon atoms and is newly implemented into MOZART4, which makes it consistent with CAPRAM3.0red. Accordingly, the oxidation pathways are adjusted and the C₂H₅CHO oxidation by the OH radical and the Br atom has also been implemented.

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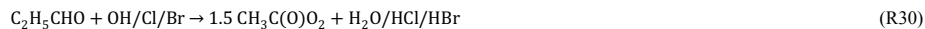
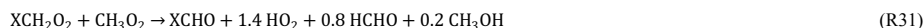


Table 2 provides the implemented reaction rate constants of lumped VOCs. A full mechanistic description of the adjusted CAPRAM-DM1.0red and CAPRAM-HM3.0red is given in the supplement (Table S2-S10).

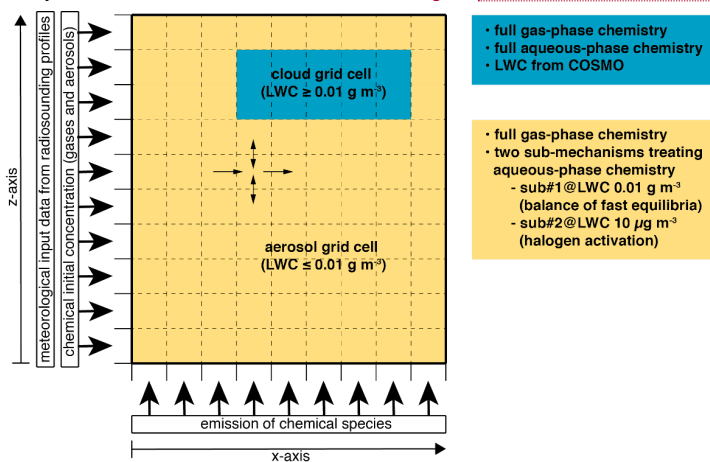
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The recombination of halogenated peroxy radicals as described above is adjusted to fit into MOZART4. In the MCM, this recombination is implemented for the sum of all RO₂, whereas in MOZART4 it is often only for CH₃O₂ and CH₃C(O)O₂. The ratio of the MCM is applied in the RO₂ recombination reaction, but RO₂ is considered as CH₃O₂. The reaction rate constant is adopted from the corresponding [CAPRAM-HM2.0 reaction \(Bräuer et al., 2013\)](#).



Currently, the calculation of aqueous-phase chemical processes in MUSCAT is limited to cloudy conditions, i.e. a liquid water content (LWC) of above 0.01 g m⁻³. Furthermore, the chemical equilibria are treated dynamically as forward and backward reactions, which represents a critical challenge for the numerical solver. Deviations from the equilibrium state of rapid phase transfers and dissociations may lead to large chemical fluxes and hence small timesteps, i.e. high computational costs. The robustness of the numerical integration is particularly affected at phase boundaries between cloud and non-cloud grid cells.

Pre-balancing the aqueous-phase equilibria of CO₂, NH₃, HNO₃, HCl, SO₂, H₂SO₄, and organic acids in cloud-free grid cells at a predefined threshold LWC under cloud conditions (0.01 g m⁻³, abbreviated with 'sub#1') results in a robust numerical integration. This approach is similar to the pH calculation parameterisation described by Alexander et al. (2012) but is designed to describe cloud chemistry and its effect on cloud droplet acidity in detail. In order to describe the activation of reactive halogen compounds by the chemistry in deliquesced aerosols, an additional sub-mechanism is introduced, assuming an LWC of 10 µg m⁻³ in cloud-free grid cells (abbreviated with 'sub#2'). A schematic on how both sub-mechanisms enable the multiphase chemistry treatment in COSMO-MUSCAT can be seen in [Figure 3](#).



665 **Figure 3** Schematic representation of the multiphase chemistry treatment in COSMO-MUSCAT in an idealised 2D-simulation.

The main halogen chemistry reactions treated in the 'sub#2' sub-mechanism are:

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The activation of halogens is in accordance with the heterogeneous reactions used in other CTMs (Badia et al., 2019; Hossaini et al., 2016; Jöckel et al., 2016; Long et al., 2014; Muniz-Unamunzaga et al., 2018; Saiz-Lopez et al., 2014; Wang et al., 2019).

690 However, the 'sub#2' sub-mechanism is able to treat pH-dependent processes, including (i) the activation of reactive halogen compounds and (ii) sulfite formation induced by HOX and H₂O₂ in the MBL online. Tables S8-S10 in the supplement provide here a complete overview of the treated aqueous-phase reactions and phase transfers in both the 'sub#1' and the 'sub#2' sub-mechanism in the CAPRAM-DM1.0red and CAPRAM-HM3.0red. Overall, COSMO-MUSCAT now represents the CTM with the most detailed description of marine multiphase chemistry (see Figure 4).

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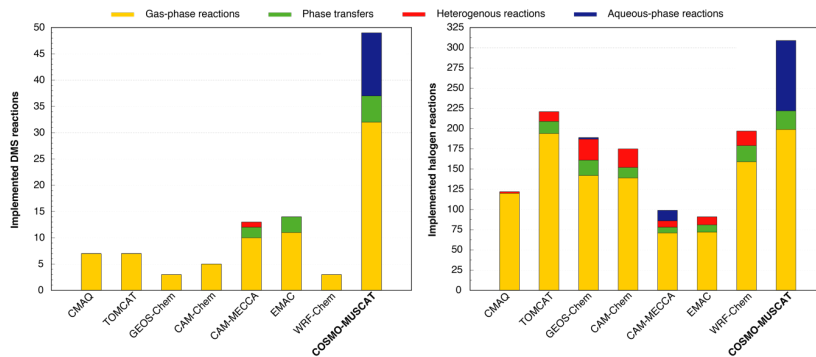


Figure 4 Comparison of applied tropospheric DMS and halogen chemistry mechanisms within the chemical transport models: CMAQ (Muniz-Unamunzaga et al., 2018), TOMCAT (Hossaini et al., 2016), Geos-Chem (Wang et al., 2019), CAM-Chem (Saiz-Lopez et al., 2014), CAM-MECCA (Long et al., 2014), EMAC (Jöckel et al., 2016), and WRF-Chem (Badia et al., 2019). EMAC is a chemistry climate model that can be run as a CTM.

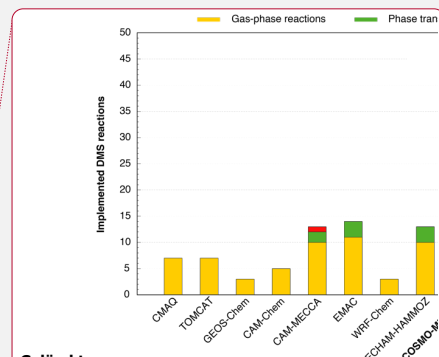
3.2 Evaluation of the 2D-implementation

The **evaluation** of the implementation is carried out by two 2D-simulations (x-z-cross section) dealing with a ‘pristine ocean’ scenario under two meteorological conditions, **namely** a convective and stable atmospheric layer, **which** will result in modelled convective and stratiform clouds, respectively. **Both scenarios are further** applied to investigate DMS oxidation in more detail. The **evaluation** of the implementation is performed by investigating the activation of halogen compounds in the MBL and comparing it with available ambient measurements and other model data. 2D-simulations are preferred over 3D ones because they are based on the same meteorological dynamics but have one lower degree of freedom. As a result, the system under investigation is less computationally expensive. Additionally, 2D-simulations enable a comprehensive understanding of multiphase chemistry in the atmospheric column, including vertical mixing processes.

3.2.1 2D model setup

The chemical model setup, i.e. the initialisation, deposition, and emission of trace gases and VOCs as well as the aerosol composition to describe the atmospheric composition of the pristine ocean, is the same as the one used **during the mechanism** reduction. Because of the lumped species within MOZART4, specific VOC emissions are merged, **Table S1** in the supplement **provides the emission rates**. Initialised concentrations of gas-phase and aerosol compounds represent ground values and are distributed vertically as constant mass mixing ratios within the model domain of MUSCAT. These values are used as constant boundary conditions on the left-hand side of the model domain (see **Figure 3**).

Two different meteorological cases are simulated: One with a high diversity of clouds and a strong vertical wind velocity (further called ‘unstable meteorological condition’) and another with a stable cloud cover at the top of the marine boundary



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3.2 Verification

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layer and a weak vertical wind velocity (further called ‘stable meteorological condition’). These two different meteorological ‘pristine ocean’ simulations are chosen to evaluate the numerical robustness of the model. The meteorological scenarios are initialised using radiosonde profiles (‘unstable meteorological condition’ station: Camborne Observations, station identifier: 3808 on 12Z 21.06.2016 and ‘stable meteorological condition’ station: GVAC Sal Observations, station identifier: 8594 on 12Z 12.06.2017), which can be read and processed by COSMO by default and are considered constant meteorological boundary conditions on the left-hand side of the model domain (see [Figure 3](#)).

The model domain spans 400 horizontal grid cells with a resolution of 1.11 km per grid cell and 100 vertical levels with a resolution of 100 m. Whereas COSMO is run on the full domain, only the inner 200 horizontal [grid cells \(overall 222 km\)](#) and lowermost 15 vertical levels ([overall 1500 m](#)) are used for the multiphase chemistry simulations with MUSCAT. [MUSCAT uses a smaller domain as](#) the interaction is sufficient to describe the multiphase chemistry in the marine boundary layer (MBL). Furthermore, the height of the MBL is often lower than 1000 m (Norris, 1998; Carrillo et al., 2016), which enables an investigation of the interactions between the MBL and the free troposphere and significantly saves computation time compared to the full domain. [So, this chosen model setup](#) can capture almost all essential chemical processes as well as the distribution of important species in the marine troposphere. Overall, the modelling domain for multiphase chemistry encompasses 3000 grid cells.

3.2.2 Comparison with measurements

HCl gas-phase concentration

Firstly, the modelled concentration range of gaseous HCl [is](#) compared to actual measurements. [Figure 5 shows](#) that very high HCl concentrations are modelled, especially in the ‘stable meteorological condition’ simulation above the MBL. These are [results](#) of the constant vertical distributed mass mixing ratios of the initial values. Since the evaluation focuses on the activation of HCl within the MBL, these values can be neglected. The modelled values below 1000 m outside of clouds are in the order of 10^9 molecules cm^{-3} after 12 hours of modelling time and thus in the range of both other modelled (Hossaini et al., 2016; Wang et al., 2019) and measured values within the marine pristine boundary layer (e.g., Keene and Savoie, 1999; Sander et al., 2013; Pszenny et al., 2004). The higher LWC of clouds results in strongly reduced HCl gas-phase concentrations due to the phase partitioning shift from the gas to the aqueous phase. Further chemical cloud processing increases aerosol acidity, yielding higher HCl gas-phase concentrations behind the cloud in wind direction (see [Figure 5](#)).

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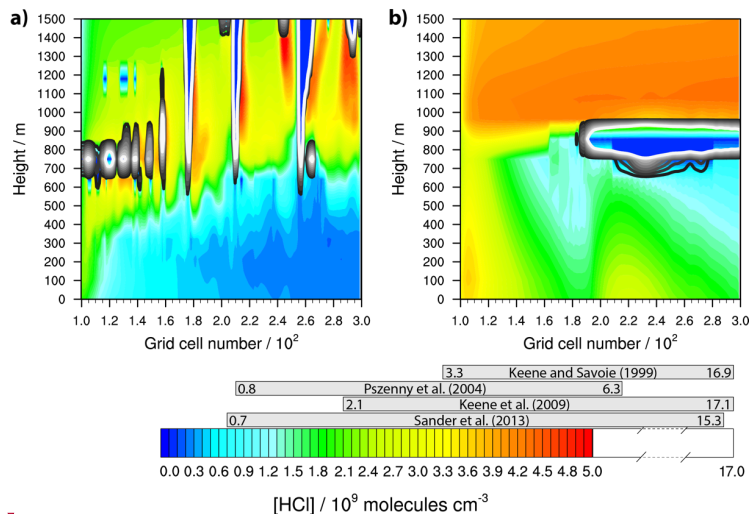
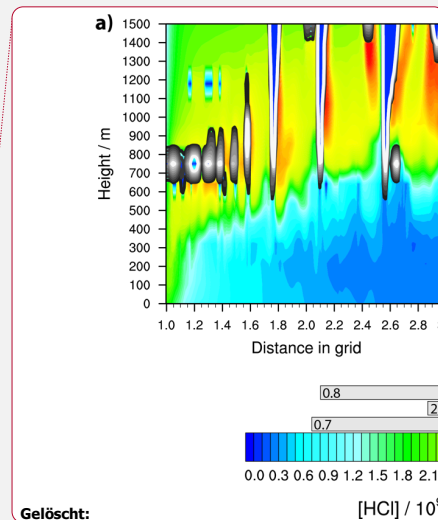


Figure 5 Simulated concentrations of HCl in the gas phase by COSMO-MUSCAT (a) in the ‘unstable meteorological condition’ simulation with convective clouds and (b) in the ‘stable meteorological condition’ simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The grey bars represent measured values in most likely pristine marine environments (see Table S11 for further details). 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.

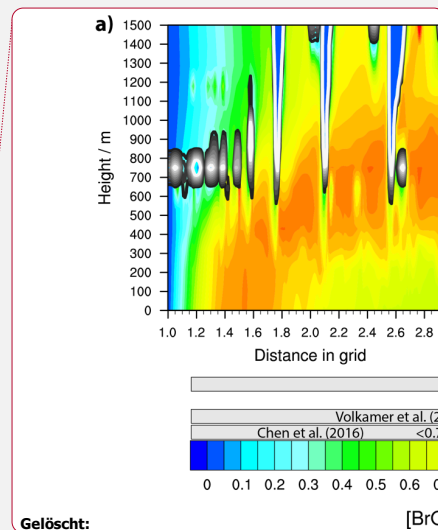
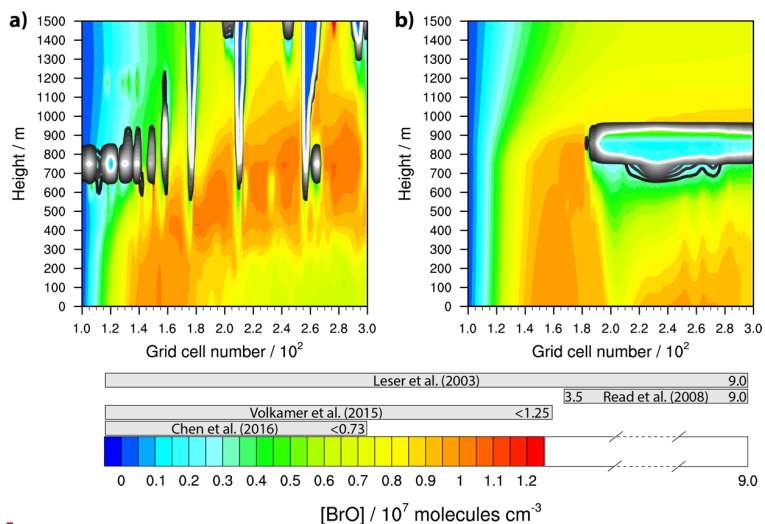
BrO gas-phase concentration

Contrary to HCl, the measured concentrations of HBr over the pristine ocean are missing. However, a high number of measured gas-phase BrO concentrations in the MBL are available (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Therefore, as a second step, the modelled gas-phase BrO concentration range is compared to measurements. Figure 6 shows that the modelled values outside of the cloud grid cells ranging between 10⁶ to 10⁷ molecules cm⁻³ after 12 hours of modelling time. Thus, they are in the range of other modelled (Zhu et al., 2019) as well as measured values within the pristine MBL (e.g., Leser et al., 2003; Read et al., 2008; Chen et al., 2016). Apart from that, the vertical distribution significantly differs between both simulations resulting into distinct spatial pattern. At the left-hand side of the model domain, the BrO concentration is similar, which is related to the activation of reactive bromine species from the initialised marine aerosols. However, when clouds are formed the profiles change. This is related to the high differences in the vertical wind field (see Fig. 7a and b). Because of the stronger updrafts in the ‘unstable meteorological condition’ simulation, the reactive halogen compounds are advected towards higher altitudes compared to the slow vertical winds in the ‘stable meteorological condition’ simulation. A second remarkable



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- Gelösch: in the ‘unstable meteorological condition’ and ‘stable meteorological condition’ simulations, respectively).
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difference is the much lower BrO concentration at the right-hand side of the model domain in the 'stable meteorological condition' simulation. This effect is more explicitly discussed in Sect. 3.3.3.



810 Figure 6 Simulated concentrations of bromine monoxide in the gas phase by COSMO-MUSCAT (a) in the 'unstable meteorological
 815 condition' simulation with convective clouds and (b) in the 'stable meteorological condition' simulation with stratiform clouds after
 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The grey bars represent
 measured values in most likely pristine marine environments (see Table S11 for further details). 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} .

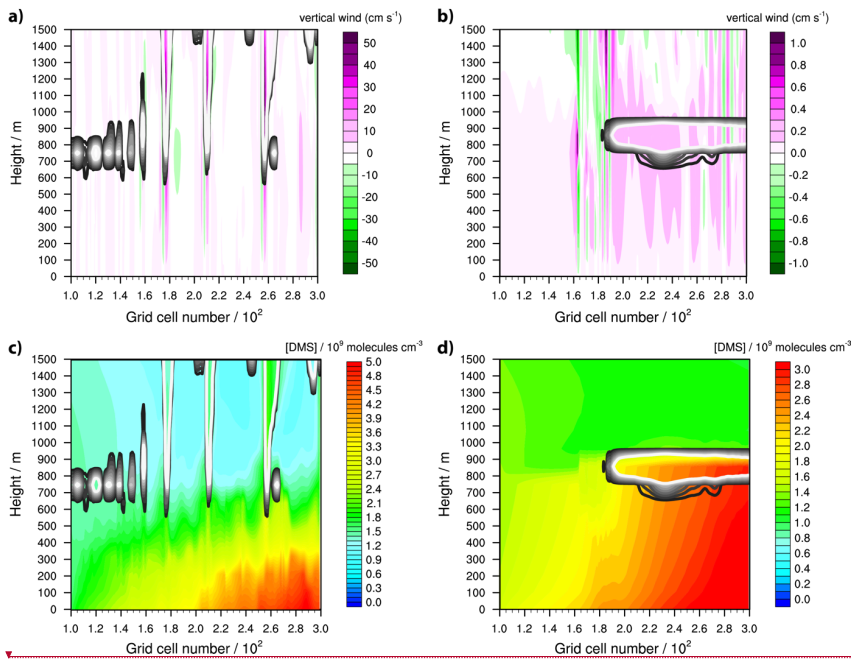
Apart from that, many field studies had the problem that the BrO concentration in the MBL was always below the detection
 limit (Sander et al., 2003). In a recent measurement study, the measured BrO in the MBL was also always below the detection
 limit of 0.5 pptv, i.e. around $1.2 \cdot 10^7 \text{ molecules cm}^{-3}$ (Volkamer et al., 2015). Hence, the BrO concentrations are modelled
 adequately. Since the activation of reactive bromine is highly related to that of chlorine, the mechanism is able to represent the
 activation of reactive halogen compounds within the MBL. A comparison of reactive iodine compounds with measurements
 is not performed, because the concentration range is highly sensitive to the chosen emission values of molecular iodine and
 iodinated organics from the sea surface and is thus uncertain.

Overall, the new marine multiphase chemistry model can represent marine aerosol chemistry and linked halogen activation
 under consideration of meteorological dynamics and shows a good agreement to other field as well as model data. Thus, it is
 825 applicable for further detailed 3D studies.

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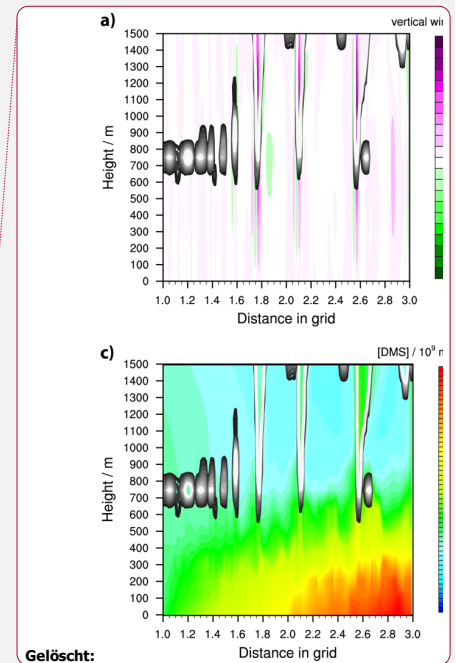
3.3 Results of pristine ocean scenarios

3.3.1 Vertical wind and DMS distribution



840 **Figure 7** Modelled vertical winds (cm s^{-1}) (a) in the 'unstable meteorological condition' simulation with convective clouds and (b) in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. 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} . Further, the modelled concentrations of DMS in the gas phase ($10^9 \text{ molecules cm}^{-3}$) are shown (c) in the 'unstable meteorological condition' simulation with convective clouds and (d) in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time.

850 Both scenarios are further applied to investigate the multiphase oxidation pathways of DMS in a cloudy marine atmosphere in detail. Figure 7 shows the modelled distribution of clouds and the strength of the vertical wind field as well as the modelled DMS concentration distribution for both simulations after 12 hours of modelling time. In the 'unstable meteorological condition' simulation, the clouds extend up to a height of more than 2000 m, whereas in the 'stable meteorological condition' simulation, the top of the cloud is capped below an inversion layer at around 1000 m. Also, the vertical winds are much stronger in the 'unstable meteorological condition' simulation. Because of the strong vertical winds, gas-phase DMS concentrations of



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around $2 \cdot 10^9$ molecules cm^{-3} are transported into the lower free troposphere. The strong inversion and low magnitude of the vertical wind speed in the 'stable meteorological condition' simulation hinders effective DMS transportation into the free troposphere, resulting in a DMS concentration of around $1 \cdot 10^9$ molecules cm^{-3} above the MBL. This is consistent with the initialised background DMS concentration. Below the inversion, DMS concentrations are more homogeneously distributed, which is different to the 'unstable meteorological condition' simulation, with a stronger variability related to the vertical wind field, i.e. the peaking of DMS concentrations into higher vertical levels because of strong updrafts (cp. Figure 7).

3.3.2 Vertical DMSO distribution

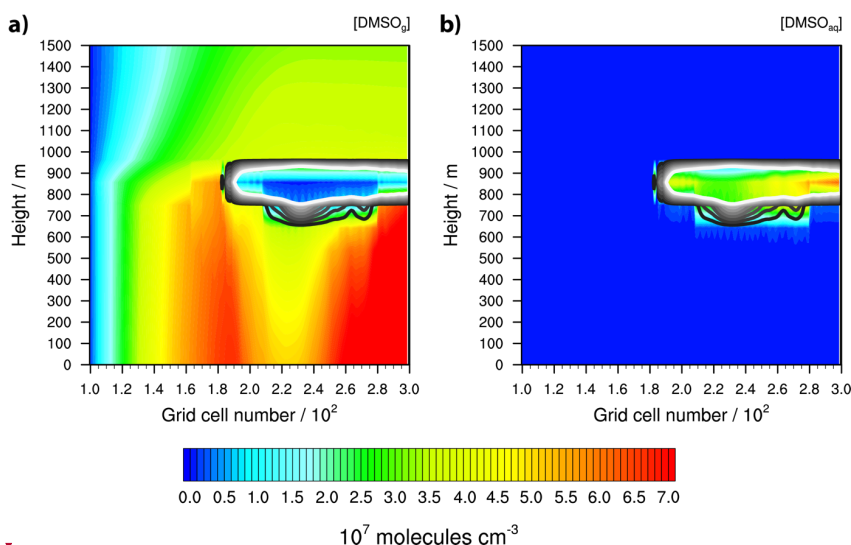


Figure 8 Simulated concentrations of DMSO (a) in the gas phase and (b) in the aqueous phase under the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The black contour lines 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} .

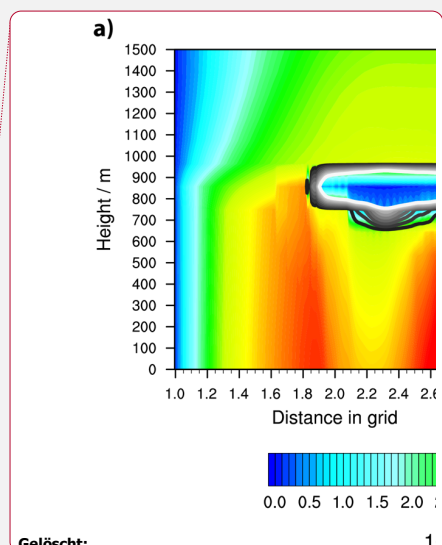
If such homogeneously distributed DMS concentrations are modelled as in the 'stable meteorological condition' simulation in a clear sky atmosphere, a similar concentration distribution for the first stable DMS oxidation products will be modelled. Hence, the concentration distribution of DMSO is a good indicator to investigate the effect of clouds on DMS oxidation. In Figure 8, the distribution of DMSO in the gas and aqueous phases in the 'stable meteorological condition' simulation after 12 hours of modelling time is shown. Furthermore, the overall modelled DMSO production and loss rates separated into gas and aqueous-phase reactions were added to the supplement (see Fig. S11).

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890 The stratiform clouds have a very high influence on the DMSO concentration in both the gas and the aqueous phase. The spatial gas-phase DMSO concentration distribution differs from the DMS concentration. Below the optically thickest clouds, the gas-phase DMSO concentration is significantly reduced, whereas above the cloud it slightly increases. In the cloud grid cells, the gas-phase DMSO concentration is reduced significantly because of the uptake into the aqueous phase. The reduced gas-phase concentrations below the cloud cannot be explained by vertical or horizontal transportation because, as can be seen in [Figure 7](#), an updraft would result in observable concentration peaks in the higher vertical levels. Therefore, the gas-phase DMSO formation in the MBL is somehow influenced by the cloud above what makes it necessary to investigate the cloud-
895 induced effect on such crucial DMS oxidants in the pristine MBL.

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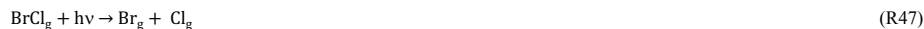
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3.3.3 Effects of stratiform clouds on DMS oxidation

900 Within the pristine MBL, the BrO radical is a primary DMS oxidant that forms DMSO (Barnes et al., 2006; Breider et al., 2010; Hoffmann et al., 2016; von Glasow and Crutzen, 2004; Chen et al., 2018). This radical is formed through reaction of O₃ by the Br atom that is activated by multiphase chemistry. The following [reactions](#) are important pathways of activation in a clear sky [MBL \(von Glasow and Crutzen, 2004; von Glasow et al., 2002b\)](#):

Gelöscht: (von Glasow and Crutzen, 2004; von Glasow et al., 2002b)



910 In the pristine marine boundary layer, two competing pathways determine the main fate of the BrO radical through (i) a reaction with DMS and (ii) a reaction with HO₂. The oxidation of DMS leads to DMSO and the Br atom, so that a cycle is established that continuously depletes O₃ and forms DMSO as long as DMS is emitted or ozone is available. This cycle is disturbed by the reaction of BrO with HO₂, yielding HOBr, which can be photolyzed back into the Br atom again or converted by multiphase chemistry into BrCl or Br₂. Overall, the photolysis of HOBr, Br₂ and BrCl determine the DMS to DMSO conversion. Clouds suppress the photolysis of Br₂, BrCl and HOBr due to the reflection of incoming solar radiation. The thicker the cloud, the
915 lower the radiation flux below. Consequently, Br atom activation below the cloud is hindered, affecting the BrO concentration and thus the reaction rate of BrO with DMS that yields DMSO (see [Figure 9](#)). Due to a longer lifetime against further oxidation and corresponding horizontal advection, the DMSO concentration profile is shifted towards the right compared to BrO. The lowest oxidation flux between DMS and BrO is modelled between grid cell 2.0 and 2.15. The effect on DMSO concentration is modelled between grid cell 2.1 to 2.4.

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Gelöscht: to

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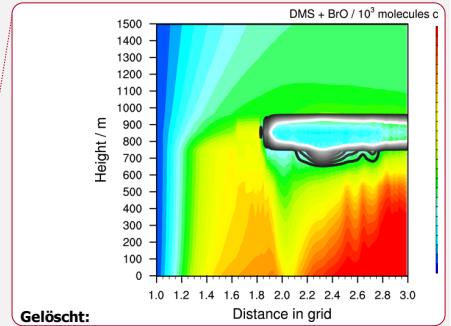
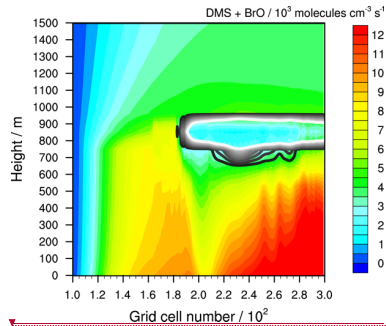


Figure 9 Simulated oxidation rate of DMS by BrO in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The black contour lines represent the simulated clouds. The black line 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} .

Gelöscht: The denser the crowding, the higher the simulated

Gelöscht: the clouds

Gelöscht: compounds

Gelöscht: Furthermore

The photolysis of BrCl and Br₂ is highly sensitive to cloud shading and thus has a high impact on the formation of reactive bromine and the linked DMS oxidation. Moreover, model studies suggest that BrCl photolysis is an important contributor to Cl atom activation in the MBL (Wang et al., 2019; von Glasow et al., 2002b). Hence, the outlined model results reveal that the shading effect of clouds is also very important for the atmospheric Cl atom concentration budget, affecting the atmospheric oxidation capacity within the MBL.

Gelöscht: However, because of its high reactivity

Gelöscht: its high solubility, MSIA

Gelöscht: OH is

Gelöscht: . In

Gelöscht: next time step, the

Gelöscht: as can be seen from

Gelöscht: Figure 7

Gelöscht: Figure 8

Gelöscht: before

Gelöscht: occurrence

Gelöscht: is as well.

Gelöscht: DMSO profile is not modelled

Gelöscht: (see Figure 10).

3.3.4 The formation of MSA and aqueous sulfate

DMSO is rapidly oxidised into MSIA and thus a similar MSIA profile is modelled. As MSIA is highly reactive in the gas and aqueous phases as well as highly soluble, it is rapidly oxidised into methane sulfonate (MS⁻) in both the aerosol and the cloud phases. There, O₃ is the preferred oxidant in the aerosol phase, whereas in cloud droplets, it is the OH radical (Hoffmann et al., 2016). The MS⁻ formed in-cloud can be transported towards the ground by downdrafts. However, comparing the DMSO concentrations in Figure 7 with the DMSO concentrations in Figure 8, the up- and downdrafts in the 'stable meteorological condition' simulations have little effect on the concentration distribution in height. The strongest effect relates to the advection from the left-hand to the right-hand side of the model domain and continuous emission from the surface. In the grid cells left of the cloud, the DMSO concentration is high and consequently the aerosol particle chemistry of DMSO and of the subsequent oxidation product MSIA leads to a sharp increase of MS⁻ formation at the grid cells below the left cloud edge (see Figure 10a). Due to the advection of the stable MS⁻ to the right-hand side of the model domain, the spatial profiles of DMSO (Figure 8) and MS⁻ differ. The high modelled chemical fluxes in cloud droplets indicate the highest MS⁻ concentrations to be within and below the cloud grid cells.

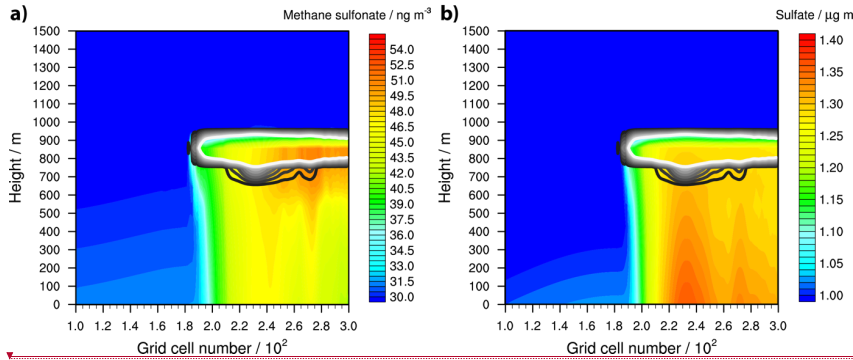
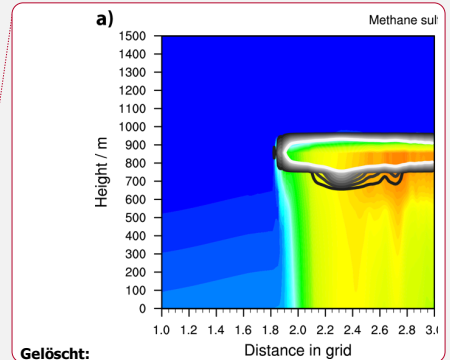


Figure 10 Simulated aqueous-phase concentrations of (a) methane sulfonate and (b) sulfate in the ‘stable meteorological condition’ simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The black contour lines represent 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} . The initial background concentration of methane sulfonate is at about 30 ng m^{-3} and that of sulfate at 1 µg m^{-3} .

Also, the concentration of sulfate (see Figure 10b) is enhanced in the grid cells at the left cloud edge, but because of different reasons. At the left cloud edge, the lower photolysis rates increase the SO_2 oxidation into sulfate by HOX and H_2O_2 . Hence, a stronger HOX-related (especially HOI) reactive SO_2 uptake on the aerosols is modelled. The reaction of HOBr results into the formation of bromide. In addition to the uptake of HBr, this increases the bromide concentration in cloud droplets by up to one order of magnitude compared to the ground level concentration before the left cloud edge (see Fig. S12). The uptake is highest under the optically thickest modelled clouds, resulting in the highest modelled sulfate concentrations. Therefore, the modelled spatial concentration is contrary to that of DMSO.

4 Conclusion and Outlook

Reduced multiphase chemistry mechanisms of DMS and reactive halogen compounds are developed through the reduction of the near-explicit multiphase chemistry mechanisms CAPRAM-DM1.0 and CAPRAM-HM3.0. Simulations that compare the reduced with the original mechanisms revealed that the reduced mechanisms are able to reproduce the concentrations and time evolutions of main air pollutants as well as key reactive halogen compounds. Additionally, CPU time in the box model simulations is reduced by 16 %, 5 %, and 6 %, depending on the model scenario. Afterwards, the reduced mechanisms are implemented into the chemistry transport model COSMO-MUSCAT. This process is evaluated by idealised 2D-simulations of an atmospheric pristine ocean environment. It was proven that the reduced marine multiphase chemistry mechanism can represent marine aerosol chemistry and linked halogen activation as it matches measured field concentrations, e.g. HCl and BrO.



Gelöscht:

Gelöscht:

Gelöscht: As for MSA

Gelöscht: formation

Gelöscht: directly or indirectly affected by clouds.

Gelöscht: beginning

Gelöscht: being there

Gelöscht: A reduced

Gelöscht: mechanism

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Gelöscht: The implementation

Gelöscht: The verification has

1010 Following that implementation, 2D-simulations of a pristine ocean scenario are carried out, investigating the effect of stable (stratiform cloud) and more unstable meteorological conditions (convective clouds) on multiphase DMS oxidation. The simulations reveal that clouds have both strong direct and indirect photochemical effects on the oxidation and vertical distribution of DMS in the marine atmosphere. Firstly, locally high updraft velocities in the unstable scenario result in fast transport of DMS from the marine boundary layer into the free troposphere. Hence, transport and further oxidation of DMS can be an important source of SO₂ within the free troposphere, particularly in the Southern Ocean region that is less affected by anthropogenic pollution. Secondly, clouds enhance the formation of MSA via the DMS addition channel. The formed DMSO is effectively consumed by cloud droplets where it is rapidly oxidised into MSA. Thirdly, the shading of clouds has a high impact on the photolysis of dihalogens that are the main contributor to Cl and Br atom activation. Thus, a much lower oxidation of DMS into DMSO occurs below stratiform clouds. In contrast, the lower HOX photolysis induces stronger sulfate formation. The results indicate that clouds strongly affect the oxidation of DMS directly because of enhanced aqueous-phase oxidation into MSA and indirectly by suppressing the DMSO formation due to lower halogen atom activation. In total, a strong possible effect on the atmospheric oxidation capacity within the MBL of the pristine ocean is assumed. The important effect of wet scavenging by clouds was not investigated as the current COSMO-MUSCAT(5.04e) did not implemented it in detail, but represented it using a first-order scavenging rate. Future studies aim to implement a more precise scheme. Since the clouds modelled in this study are not known to precipitate, the propagated error should be small.

1020 Overall, the 2D-simulations demonstrate the capability of COSMO-MUSCAT to now cover the multiphase chemistry in marine influenced atmospheric environments. This allows for deeper investigations of multiphase chemistry in a wide range of temporal and spatial resolutions together with transport and microphysical processes in the future. In a next step, the mechanism will be applied in simulations with COSMO-MUSCAT for modelling measurement campaigns at the Cape Verde Atmospheric Observatory (Carpenter et al., 2010), supporting the interpretation of the measurement data and enabling further model/mechanism evaluation. Finally, the reduced mechanism is designed in such a way that new findings in DMS or halogen chemistry can easily be implemented, e.g. improved understanding of the multiphase chemistry of the unimolecular H-shift of CH₃SCH₂O₂.

1030

Gelöscht: Afterwards

Gelöscht: weather

Gelöscht: a

Gelöscht: transportation

Gelöscht: the transportation

Gelöscht: Hence

Gelöscht: formations

Gelöscht: marine boundary layer is assumed

Gelöscht: transportation

Gelöscht: to model

Gelöscht: validations. Furthermore

Code and Data availability

The code for the COSMO model is available according to the Software License Agreement by Deutscher Wetterdienst (German Weather Service, <http://cosmo-model.org>). The source code of MUSCAT and SPACCIM, external parameters, and applied mechanisms are archived on a local Git server and can be obtained by request through Ralf Wolke (wolke@tropos.de). Access to the model code used in the paper has been granted to the editor.

1035

Author contribution

EHH, AT, and RW did the model development on SPACCIM. EHH, AT, and HH designed the SPACCIM modelling work. EHH performed the SPACCIM simulations. EHH, AT, and HH analysed the SPACCIM model results. EHH, RS, and RW did
1050 the model development on COSMO-MUSCAT. EHH, RS, and RW designed the COSMO-MUSCAT modelling work. EHH
performed the COSMO-MUSCAT simulations. EHH analysed the COSMO-MUSCAT model results. EHH, RS, AT, and HH
wrote the paper.

Competing interests

The authors declare that they have no conflict of interest.
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Table 1 Average percentage deviations [%] of some inorganic and organic target compounds between the simulations with the full and reduced CAPRAM-DM1.0 and CAPRAM-HM3 mechanisms (deviations calculated throughout the full SPACCIM simulation). Exceedances of the threshold are marked in *italic*.

Species	'Pristine'		'Breeze'		'Outflow'	
	Average	R ²	Average	R ²	Average	R ²
Gas phase						
<i>5% threshold</i>						
O ₃	-0.2%	1.00	0.3%	1.00	0.1%	1.00
NO	-3.9%	1.00	0.4%	1.00	-0.8%	1.00
NO ₂	-2.1%	1.00	0.7%	1.00	-0.1%	1.00
SO ₂	1.5%	1.00	1.3%	1.00	0.6%	1.00
HNO ₃	1.2%	1.00	-0.5%	1.00	-1.0%	1.00
DMS	-4.2%	1.00	-1.6%	1.00	-3.2%	1.00
HCl	0.6%	1.00	-2.1%	1.00	-0.6%	1.00
<i>10% threshold</i>						
DMSO	6.1%	1.00	-1.5%	1.00	<i>10.6%</i>	0.99
OH	0.0%	1.00	0.0%	1.00	0.1%	1.00
HO ₂	-0.5%	1.00	0.1%	1.00	-0.1%	1.00
NO ₃	-0.5%	1.00	0.6%	1.00	0.0%	1.00
H ₂ O ₂	0.0%	1.00	-3.3%	1.00	-2.4%	1.00
Cl	6.4%	1.00	5.1%	1.00	0.8%	1.00
Br	9.8%	1.00	4.2%	1.00	<i>29.0%</i>	0.98
I	-0.6%	1.00	-6.1%	0.99	-1.2%	0.99
ClO	7.4%	1.00	7.9%	1.00	2.0%	1.00
BrO	9.7%	0.99	4.2%	1.00	<i>24.5%</i>	0.95
IO	-1.8%	1.00	-3.1%	0.99	-0.9%	1.00
HOCl	5.0%	1.00	<i>37.5%</i>	0.96	<i>17.8%</i>	1.00
HOBr	8.9%	1.00	<i>10.2%</i>	1.00	<i>27.7%</i>	0.97
HOI	-2.4%	1.00	3.5%	0.98	-3.4%	0.98
Cl ₂	0.4%	1.00	5.6%	0.97	-2.4%	0.97
Br ₂	<i>36.0%</i>	0.96	-1.1%	0.93	<i>24.0%</i>	0.75
ClNO ₂	-0.9%	1.00	0.0%	1.00	0.3%	1.00
Aqueous phase						
<i>5% threshold</i>						
OrgMass	1.1%	1.00	-0.2%	1.00	0.0%	1.00
DryMass	0.2%	1.00	-0.3%	1.00	0.1%	1.00
H ⁺	0.2%	1.00	-1.2%	1.00	-0.2%	1.00
Sulfate	1.1%	1.00	-0.6%	1.00	-0.1%	1.00
Nitrate	0.0%	1.00	0.8%	1.00	1.7%	1.00
Cl ⁻	-0.4%	1.00	0.0%	1.00	0.7%	1.00
Methane sulfonate	2.5%	1.00	<i>18.7%</i>	1.00	2.1%	1.00
<i>10% threshold</i>						
OH _{aq}	-1.9%	1.00	2.0%	0.99	2.1%	0.99
HO _{2, aq}	0.2%	1.00	0.7%	1.00	0.1%	1.00
O _{2, aq}	-0.1%	1.00	2.8%	1.00	3.0%	1.00

Gelöscht: red

Formatiert: Schriftart: 10 Pt., Kursiv, Schriftfarbe: Automatisch

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1370 Table 2 Description of the lumped MOZART4 species and the corresponding kinetic reaction rate constants.

Species	Comment	k	Comment on k
BIGALK	Alkanes with $C \geq 4$	2.05×10^{-10}	same as for butane
ALKOH	Alcohols with $C \geq 3$	$2.7 \times 10^{-11} e^{525/T}$	same as for propanol
C_2H_5CHO	Aldehydes with $C \geq 3$	$4.9 \times 10^{-12} e^{405/T}$	OH; same as for propionaldehyde
		1.3×10^{-10}	Cl; same as for propionaldehyde
		$5.75 \times 10^{-11} e^{-610/T}$	Br; same as for propionaldehyde
BIGALD1	Unsaturated dialdehyde	1.35×10^{-10}	same as for 2-butenedial
XYL	Lumped xylenes	1.4×10^{-10}	mean value of o-, p- and m-xylene
BZALD	Lumped aromatic aldehydes	1.0×10^{-10}	same as for benzaldehyde


 Formatierte Tabelle