

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:

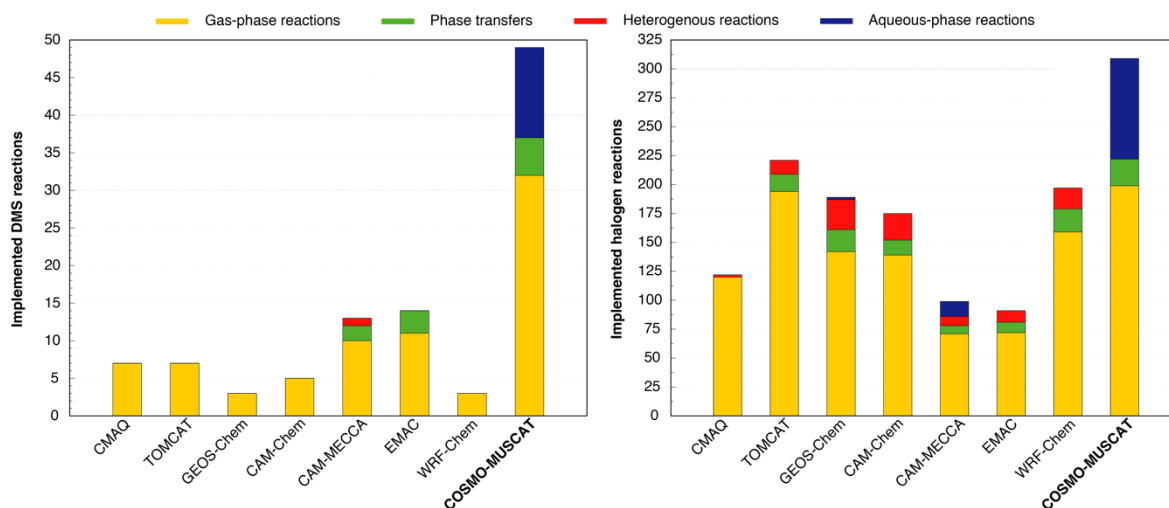


Figure 4 Comparison of applied tropospheric DMS and halogen chemistry mechanisms within the chemical transport models: CMAQ (Muniz-Unamunzaga et al., 2018), TOMCAT (Hossaini et al., 2016), Geos-Chem (Wang et al., 2019), CAM-Chem (Saiz-Lopez et al., 2014), CAM-MECCA (Long et al., 2014), EMAC (Jöckel et 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.'

References

- Hoffmann, E. H., Tilgner, A., Wolke, R., and Herrmann, H.: Enhanced chlorine and bromine atom activation by hydrolysis of halogen nitrates from marine aerosols at polluted coastal areas, *Environ. Sci. Technol.*, 53, 771-778, <https://doi.org/10.1021/acs.est.8b05165>, 2019b.
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- Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordóñez, C.: Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, *Atmos. Chem. Phys.*, 16, 12239-12271, <https://doi.org/10.5194/acp-16-12239-2016>, 2016.
- Xue, L. K., Saunders, S. M., Wang, T., Gao, R., Wang, X. F., Zhang, Q. Z., and Wang, W. X.: Development of a chlorine chemistry module for the Master Chemical Mechanism, *Geosci. Model Dev.*, 8, 3151-3162, <https://doi.org/10.5194/gmd-8-3151-2015>, 2015.