**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 stud 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:
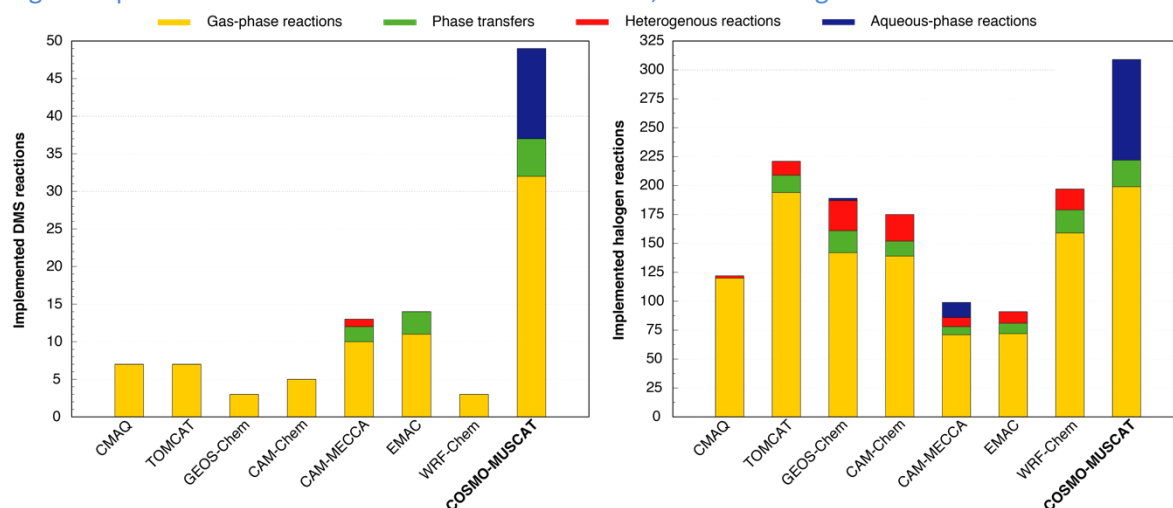


**Figure 4     Comparison of applied tropospheric DMS and halogen chemistry mechanisms within the chemical transport models: CMAQ (Muniz-Unamunzaga et al., 2018), TOMCAT (Hossaini et al., 2016), Geos-Chem (Wang et al., 2019), CAM-Chem (Saiz-Lopez et al., 2014), CAM-MECCA (Long et al., 2014), EMAC (Jöckel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

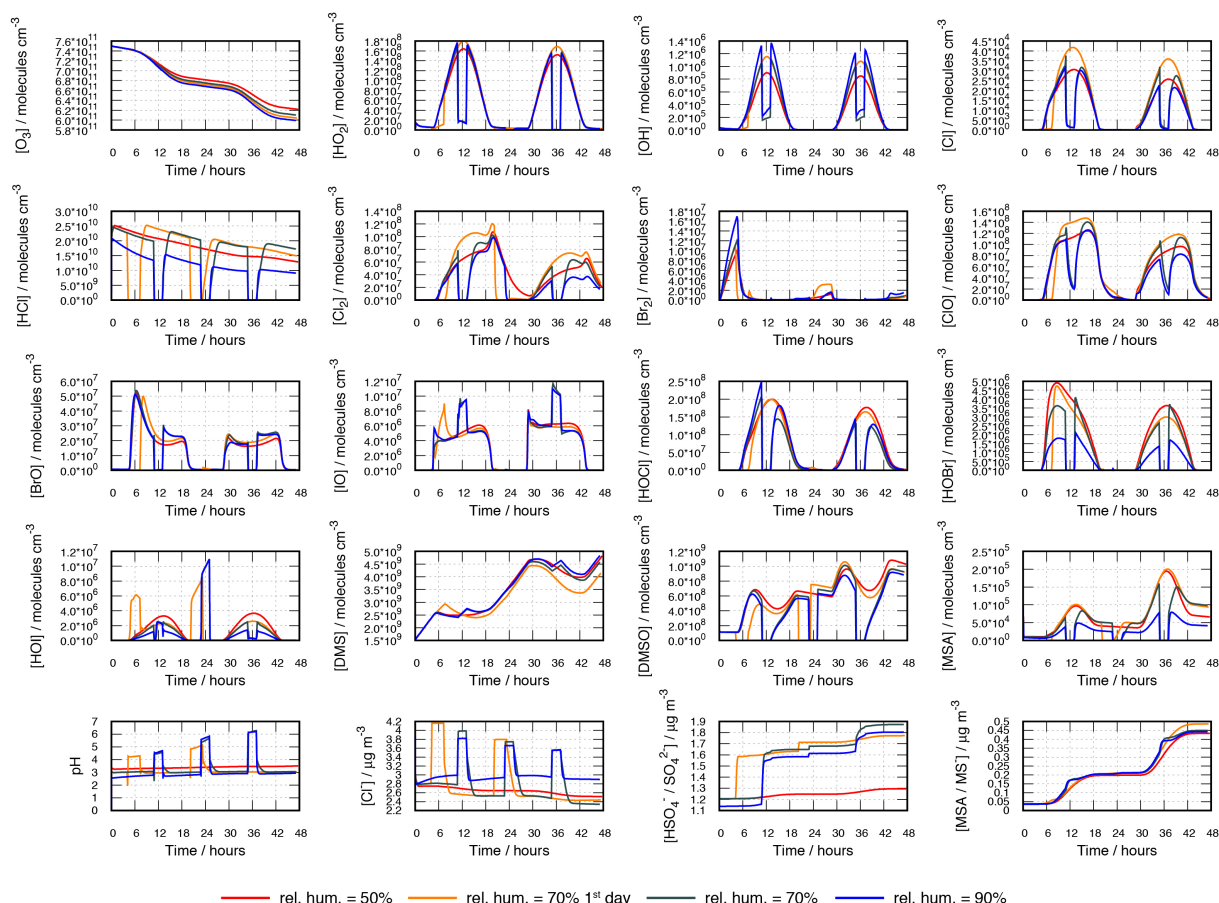An example for the simulation at 45° latitude is given below.

**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.
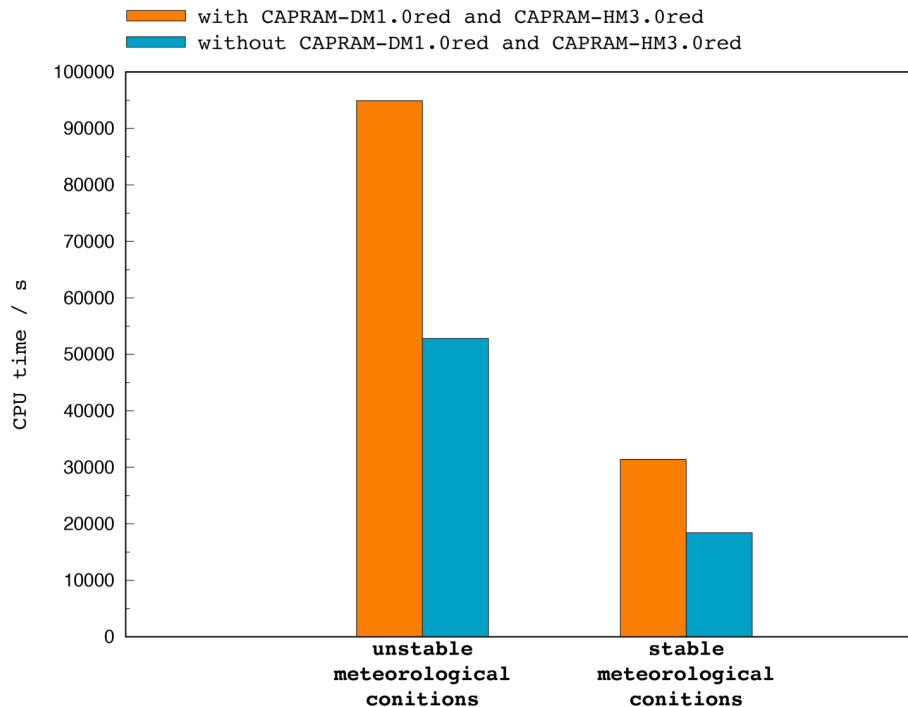


*Figure 1 CPU time when the simulations are performed with and without added CAPRAM-DM1.0red and CAPRAM-HM3.0red.*

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 underlaying 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 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.'

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 $Cl_2$ 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 $Br_2$ formation by HOBr, the higher HOCl does not necessarily lead to a higher modelled $Cl_2$ 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 $Cl_2$ 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 / $10^2$' 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).'
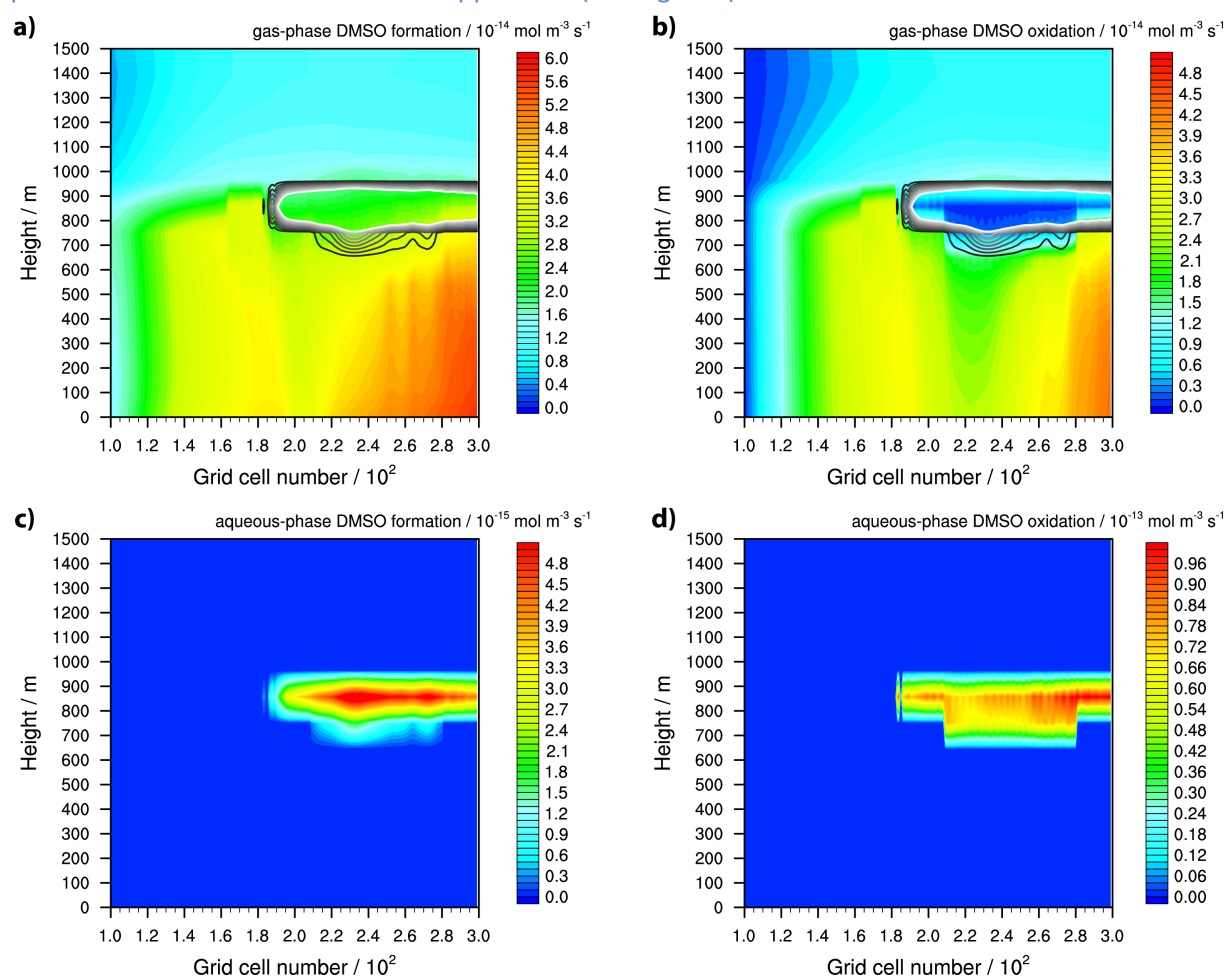


Figure S11 Modelled formation rate of DMSO in (a) the gas phase and (c) the aqueous phase together with the modelled oxidation rate in (b) the gas phase and (d) the aqueous phase in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents 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 "O3 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:

'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:

'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 HOBr+HSO3- 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 places into the supplement. The additional text in manuscript reads as follows:

'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).'
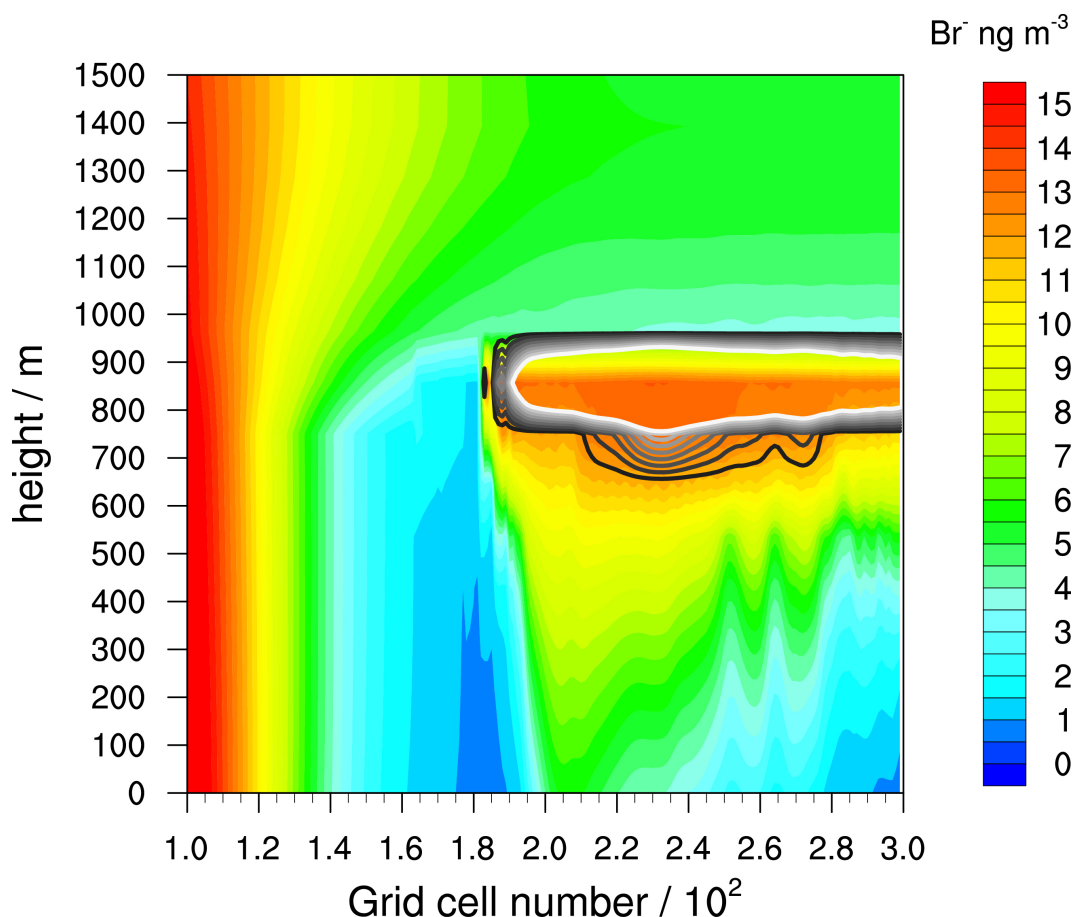
**Figure S12** Simulated aqueous-phase concentration of bromide in the 'stable meteorological condition' simulation with stratiform clouds after 12 hours of modelling time. The x-axis represents the innermost horizontal grid cells divided by 100. The black contour lines represent the simulated clouds. 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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