Interactive comment on ‘DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry’ by Chen et al.

The present paper represents a first 3D simulation of the dimethyl sulphide (DMS) oxidation by multiphase chemistry processes in the troposphere into SO_2 and methane sulfonic acid (MSA). For this purpose, the authors apply the global chemical transport model GEOS-Chem and have strictly revised the implemented DMS oxidation scheme following recent insights in tropospheric multiphase DMS oxidation. Therefore, the authors include 12 new reactions describing the oxidation in the gas (7) and aqueous phase (5). For the first time, the aqueous-phase oxidation of DMS oxidation products are treated in a global simulation. Therefore, two new important oxidation intermediates are implemented, dimethyl sulfoxide (DMSO) and methane sulphinic acid (MSIA). While DMSO was already implemented in other global modelling studies, the oxidation of MSIA is dealt in a global chemical transport model for the first time to the reviewer knowledge.
The results show that multiphase chemistry processes decrease the yield of SO_2 and increases the yield of MSA. Multiphase chemistry processes are important for a better representation of measured DMS concentrations and MSA/nss-SO_4^{2-} ratios.

The paper is well-written and organized. The implementation of multiphase chemistry, the mechanism and the technical implementation is well described. The discussion of the results is expedient and understandable.
However, the mechanism has to be strictly revised to be consistent with the current box and 1D modelling studies as well as laboratory results.

General comments

1) The oxidation of DMS by OH happens by two pathways: H-abstraction from the methyl group and OH-addition onto the sulphur atom. The H-abstraction pathway leads predominantly to SO_2. The OH-addition pathway leads predominantly to DMSO (Barnes et al. 2006). The DMSO is then further oxidised into MSIA and subsequently into MSA or SO_2 (see von Glasow and Crutzen, 2004; Zhu et al., 2006; Barnes et al. 2006; Hoffmann et al., 2016). A direct conversion of DMS into SO_2 is unlikely and only convenient if the OH-addition pathway is parameterised. As the present study aims at the investigation on how the formation of DMSO and subsequent multiphase chemistry affects the SO_2 yield, I do not understand why the authors produce DMSO

only in a yield of 0.4 and the residual yield is SO_2. The addition pathway has to be revised according to the literature to consider the DMSO formation more adequately including higher yields.

DMS + OH → DMSO + HO_2 (Schultz et al., 2018)

2) MSIA and MSA are acids. The dissociation of these acids will increase the effective uptake coefficient. In the present study, no dissociation is implemented. Especially, MSA is a strong acid (pKa = -1.92) and should reside predominantly in its dissociated form in aerosol particles and cloud droplets. Hence, as dissociated MSA will not undergo phase transfer, a much higher amount partitions in the aqueous phase as it is calculated by the modelling approach. However, if the pH of aerosols and cloud droplets would be fixed in the model, the effective Henry's Law coefficient can easily be calculated. Then, the implementation of the effective Henry's Law coefficient can be an appropriate way to restrict the numerical costs. Still, in the present model study the pH value is predicted. Thus, the effective Henry's Law coefficient cannot be used. Therefore, the dissociation has to be treated in the model to enable a realistic partitioning and chemistry of MSIA and MSA.
3) The implemented kinetic reaction rate constant for MSA with the OH radical is nearly five times higher than the two other ones given in Barnes et al. (2006). Given the comments on the high rate constant in Barnes et al. (2006), I think the lower ones has to be preferred. This will significantly affect also the oxidation of MSA.
4) The oxidation of DMSO in the gas phase yields only 0.95 MSA. The residual 0.05 should be dimethyl sulfoxide ($DMSO_2$), which will be predominantly being further, but slowly, oxidised into SO_2. Thus, to close the mass balance, a 0.05 yield of SO_2 should be implemented.
5) The oxidation of DMS can also affect new particle formation. As the authors have stated the formation of MSA by aqueous-phase chemistry will not result in new particle formation. I am missing a discussion how the newly implemented multiphase DMS chemistry scheme affects new particle formation. Have the authors investigated how new particle formation is changed between R_{all} and R_{std}? Please address this issue in the discussion of the model results.

Minor comments

1) The term 'multiphase' means connection of oxidation in gas and aqueous phase. Therefore, the usage of multiphase mechanism or multiphase oxidation addressing

oxidation in the aqueous phase is wrong. It has to be stated aqueous-phase mechanism or aqueous-phase oxidation.

2) The conversion yield of DMS into SO_2 and MSA with the new approach is 78% and 13%, respectively. The addition of these numbers does not reach 100%. What are the residual 9%? Are this DMSO and MSIA? These also needs to be stated.
3) Can the authors please provide how much dry and wet deposition contribute to the lifetime of DMSO, MSIA and MSA?
4) Page 2, Line 25: 'DMS + BrO' and 'DMS + $OH_{(g)}$' spaces are missing
5) Page 3, Line21-22.: Recently, cooking was mentioned as an anthropogenic source for MSA by Dall'Osto et al. (2015)
6) Page 5, Line 8-11: The authors have mentioned that no Cl is produced from the heterogenous reaction 'HOBr + Cl^- + H^+' in the model system. This reaction will lead to BrCl formation. Box model studies show that the photolysis of BrCl is an important source for both Cl and Br radicals in the atmosphere (Bräuer et al., 2013), because it recycles HOBr effectively back to Br. As the authors did not include this production pathway for Cl radicals, I wonder if it is implemented for Br radicals? Please clarify this.
7) Page 4, Line 13-14: Can you please provide the resolution of the vertical levels?
8) Page 5, Line 15: 'DMS + $O_{3(aq)}$', 'DMSO + $OH_{(aq)}$', 'MSIA + $OH_{(aq)}$', 'MSIA + $O_{3(aq)}$', 'MSA + $OH_{(aq)}$' spaces are missing
9) Page 5, Line 29-30: Model simulations show that the concentration of OH in the aqueous phase of marine cloud droplets and aerosols can differ up to two orders of magnitude (see Herrmann et al., 2010 or Bräuer et al., 2013). This cannot be derived from the approach of Jacob (2005). Have the authors tried to implement these differences in OH concentration between the bulk of aerosol particles and cloud droplets into the modelling framework?
10) Page 6, Line 7: Usually, these rate constants are measured at 298K not 273K.
11) Page 7, Line 16-17: Measured concentrations of Cl radicals are often in the range of 10^4 molecules cm^{-3} (Saiz-Lopez and von Glasow, 2012). Have the authors performed a sensitivity study with higher concentrations (e.g. $5x10^3$ molecules cm^{-3})? How is the contribution then affected?
12) Page 9 Line 1: Once MSIA is formed, it is quickly, nearly instantaneous, further oxidised in the atmosphere. If 66% of the precursor DMOS stay below 2 km altitude, which processes trigger the 17% smaller contribution of MSIA?

13) Page 9, Line 8-10: The addition of all percent leads to 99%, please revise to give 100%.
14) Page 9 Line 17: 'Hoffmann' not 'Hoffman'
15) Page 10, Line 13-14: Which OH concentrations are used in these studies? Are these comparable to the present study?
16) Page 11, Line 9-10: Are there no data of DMS available for 2007? What is with the Cape Verde Observatory at which DMS is permanent measured since 2006 (Carpenter et al., 2010)? Why are these data not used?
17) Page 26, Fig. 4: Over Central Asia, the oxidation of DMS by BrO shows the highest source for DMSO. Why is this reaction so strong in this region? Please provide proper reasons. Furthermore, the authors should consider to discuss the modelled concentration patterns of key oxidants.

Overall, I think this paper is appropriate for publication in Atmospheric Chemistry and Physics after successful revision and consideration of the major issues.

Comments on the formatting of the references

1) Page 15, Line 19: Formatting error of the DOI number.
2) Page 15, Line 27: Please provide the DOI number.
3) Page 16, Line 3: Formatting error of the DOI number.
4) Page 16, Line 6: Formatting error of the DOI number.
5) Page 16, Line 8: Please provide the DOI number.
6) Page 16, Line 11: Please provide the DOI number.
7) Page 16, Line 26: Please provide the DOI number.
8) Page 17, Line 11: Formatting error of the DOI number.
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28) Page 22, Line 14: Formatting error of the DOI number.
29) Page 22, Line 19: Please provide the DOI number.
30) Page 22, Line 24: Please provide the DOI number.

References

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