Response to Reviewers for: “Oceanic emissions of dimethyl sulfide and methanethiol and their contribution to sulfur dioxide production in the marine atmosphere”

We thank both reviewers for the constructive comments on our manuscript. Reviewer comments are reproduced below along with author responses and any significant changes made to the manuscript text.

Reviewer comments are in green

Author responses are in black

Additions to the text are marked in red, and deletions are shown with a red ~~strikethrough~~

Reviewer 1:

This paper report simultaneous flux measurement of DMS (CH_3SCH_3) and MeSH (CH_3SH), which are important sulfur compounds as oceanic sulfur emission and subsequent aerosol formation and climatic effect, from a coastal ocean site. The result shows a linear relationship between DMS and MeSH over the campaign, and this suggests that both have the same source (i.e. oceanic emission). Besides, another important finding is that no other volatile sulfur compounds like DMSO, DMSO2, MSAM, and DMDS were below the detection limit.

The authors then investigated how the MeSH emission is important for the budget of sulfur dioxide (SO_2) in the marine environment. Based on a chemical box model implemented with newly compiled MeSH oxidation mechanisms, 30% of total SO_2 production in the marine boundary layers is from MeSH oxidation. Because this large additional source of marine SO_2 has not been considered in the global modeling studies, the finding for this study has a large impact not only on chemical kinetics but also on climate implications including the elucidation of particle formation/growth and/or CCN activity.

The paper is very well-written and organized. The background of the study, experimental setup, data analysis, and parameters for the modeling are all well described. The discussion of the results is expedient and understandable. I recommend this paper be published after minor/technical corrections. Although I have tried my best to find some problems to provide constructive comments for this study, I could not find any fatal problems that may help this manuscript. For this reason, the followings are my minor comments.

Minor comments

Line18: I guess these values are also interquartile range? If so, please write so.

Yes these are interquartile ranges. This has been clarified.

Line 19: “Campaign mean emission fluxes of DMS (F_{DMS}) and MeSH (F_{MeSH}) were 1.13 ppt m s^{-1} (0.53-1.61 ppt m s^{-1} interquartile range) and 0.21 ppt m s^{-1} (0.10-0.31 ppt m s^{-1} interquartile range) respectively.”

Line 140: You described both DMS and MeSH in this paragraph and different from the section title of 1.3. From this sentence, you can start another section “1.4 Purpose of this study” or something like that.

As suggested we have added a new subsection at line 146 titled "1.4 Study Overview”

Line243: It is hard to understand which parameters are Meteorological inputs from NOAA data. Please specify what you cited.

We use the NOAA buoy data only for ambient temperature and pressure. This has been clarified.

Line 250: “Ambient pressure and temperature data ~~Meteorological inputs~~ were acquired from the NOAA National Data Buoy Center (Stations LJPC1 and LJAC1) as well as from an onsite temperature and relative humidity data logger (OM-62, Omega Engineering).”

Line321: The ranges of the flux of DMS and MeSH are different from Figure 3 as far as I read. As written, 0.53 to 1.61 are the interquartile range, however, the flux is varied over the hour of Day. I do not understand why the author used an interquartile range for the flux data, but the standard deviation is added in Figure 3. To improve the readability, I hope the authors modify the value in the text or the presentation in Figure 3. The same comments are also for MeSH.

The means and interquartile ranges quoted in here are for all data points from the full campaign. In contrast the values shown in Figure 3 are data binned by the hour of the day. We think that the interquartile range is better suited to show the range of observed values for the full campaign because the measured flux values do not follow a normal distribution. The interquartile range then contains some information about the asymmetry of the distribution. For the hourly binned data, the standard deviation is more appropriate as some of the bins contain relatively few data points which would not allow for a robust determination of the interquartile range.

Line372: It is very hard to understand “The poorer model performance at night“ in this context. When I saw Figure 6, the difference between model and observation seems larger in the daytime for DMS.

See response to comment on line 384 below

Line374: Similarly, I do not understand “The model shows generally good performance during daytime” here. What does it mean “good performance” here? The difference between observation and model was larger in the daytime for DMS (Figure 6a).

See response to comment on line 384 below.

Line 384: “reproduce observed DMS and MeSH” are hard to be convinced because of the comments above.

We respond to the three prior comments together here. In general, we agree with the reviewer that it is difficult to interpret the measurement/model agreement as presented. The following are the main points that we aim to express in this section:

1.) We only have direct constraints on DMS and MeSH emissions in the model during daytime.
2.) At nighttime, it is likely that the MBL height changes significantly and that some emission flux of DMS and MeSH is still present, neither of which are easily captured in the model with the available measurements.
3.) DMS has a long lifetime to oxidation relative to MeSH meaning variations in the diel profile of DMS are damped compared to MeSH. MeSH conversely has a short (<3 hrs) lifetime to oxidation during the afternoon. Afternoon mixing ratios of MeSH are therefore the best test of model performance since MeSH mixing ratios in those periods are controlled by the measured daytime emission flux and modelled oxidant loadings which we believe are well captured in the model.

Ultimately, we expect that the model/measurement disagreement is largely driven by parameters (e.g. MBL height, nighttime emission fluxes) which are not well captured in the model. However, that is difficult to state definitively with the available data. Instead we aim to express that while we have no reason to doubt the available oxidation rate equations or our measurements of DMS and MeSH flux and mixing ratios, the model/measurement disagreement points to some factor that is not well represented in the model.

We have made several changes to the text in this section to more clearly express this uncertainty as shown below:

Line 386 – “We assessed the ability of the coupled ocean-atmosphere chemical box model described in **Section 2.4.2** using the Pier Model Case to replicate the observed mean diel profiles of DMS and MeSH mixing ratios from the SIO pier. The model and measurement diel profiles of DMS and MeSH are shown in **Fig. 7**. For MeSH the model agrees with measurements to within 25% during daytime hours (10 – 21) when direct flux constraints were possible but diverges significantly at night where the model underpredicts MeSH. DMS is overpredicted by roughly 25 ppt during daytime (hours 9 to 20) in the model. Modeled DMS also shows less day-night variability in concentration, varying by a factor of 1.25 compared to observations which vary by approximately a factor of 2. The poorer model performance at night is likely related to diel changes in coastal boundary layer dynamics, including boundary layer height and advection, which are not captured in the model. As noted, nighttime emission fluxes of DMS and MeSH are poorly constrained by the EC flux measurements and may also contribute to the larger disagreement at nighttime. We expect the most informative model test case is for MeSH mixing ratios during daytime, where the MeSH emission flux is well constrained by measurements and the oxidative lifetime of MeSH is short (<3 hours), resulting in modeled MeSH mixing ratios being primarily driven by oxidation and not by the uncertain boundary layer dynamics or nighttime emission fluxes. During daytime modeled and measured MeSH mixing ratios agreed to within 25 % while DMS mixing ratios were overpredicted by ~50%. ~~The model shows generally good performance during daytime when winds are consistently from the ocean and direct flux measurements are available as constraints for the model.~~ One additional potential driver of model overprediction of DMS during daytime is the exclusion of BrO chemistry from the base model due to the lack of observational constraints of BrO at the study site. BrO has been suggested to be an important oxidant of DMS which peaks in concentration in the afternoon (Saiz-Lopez et al., 2006, 2008). A model sensitivity run using an afternoon peak BrO concentration ($[BrO]_{max}$) of 1 ppt was performed which brings modeled DMS to within 10 ppt of the observations during daytime but degrades model to observation agreement at night. The $[BrO]_{max}$ of 1 ppt was selected as an intermediate value in the range of measured and modeled BrO in the daytime marine boundary layer, however mean daytime BrO mixing ratios of up to 4 ppt have been observed in some locations (Mahajan et al., 2010; Saiz-Lopez et al., 2004; Wang et al., 2019). Implementing higher BrO mixing ratios in this model would generally serve to decrease modeled DMS and MeSH mixing ratios, especially during daytime. Daytime MeSH mixing ratios are reduced by less than 0.5 ppt in the 1 ppt BrO sensitivity test, as MeSH oxidation is still dominated by OH. Due to the ~~general good model to measurement agreement for DMS and MeSH during daytime for the base case and~~ the lack of observational constraint on BrO during our study, we elect to exclude BrO chemistry from the model base case used in subsequent calculations. Inclusion of BrO chemistry would have minimal impact on model MeSH as described, and would serve to reduce DMS lifetime, increase the yield of DMSO and MSA from DMS oxidation, and reduce the yield of SO_2 from DMS oxidation. While there are clear uncertainties in this modelling effort especially during nighttime, ~~The demonstrated~~ the general model ability to reproduce observed DMS and especially MeSH mixing ratios during daytime when we have robust constraints on the emission flux suggests that the DMS and MeSH oxidation mechanism added to the MCM v3.3.1 in this work is suitably accurate to provide meaningful information on the oxidative fate of DMS and MeSH."

Line 374: Please add an explanation why you use 1 ppt for BrO. I think you need some citations to choose this value for BrO concentration for your model.

We have added some discussion on how we selected 1 ppt as a reasonable estimate of daytime mixing ratios as in intermediate value in the range of previously measured and modeled values. We also add some general discussion of the implications of using a higher BrO mixing ratio.

Line 393: "The $[BrO]_{max}$) of 1 ppt was selected as an intermediate value in the range of measured and modeled BrO in the daytime marine boundary layer, however mean daytime BrO mixing ratios of up to 4 ppt have been observed in some locations (Mahajan et al., 2010; Saiz-Lopez et al., 2004; Wang et al., 2019). Implementing higher BrO mixing ratios in this model would generally serve to decrease modeled DMS and MeSH mixing ratios, especially during daytime."

Line398: For me (perhaps also for readers), "a 43% increase in total SO2 production" has a larger impact compared to 30% of the overall SO2 production. I suggest adding this 43% increase in your abstract in addition to a 30% description.

The abstract text has been changed to highlight the increase in total SO_2 production rate as suggested.

Line 30: "Model results suggest that MeSH emissions lead to afternoon instantaneous SO_2 production of 2.5 ppt hr^{-1}, which results in a 43% increase in total SO_2 production compared to a case where only DMS emissions are considered and accounts for 30% of the instantaneous SO_2 production in the marine boundary layer at the mean measured $F_{DMS}$and F_{MeSH}."

Line424: SI S3? I think you described HPMTF for SI S5.

Corrected, thanks.

Recommendation

It is not easy to follow these complicated chemical networks for sulfur oxidation. If you prepare a Figure to describe the chemical scheme in addition to Table S1, the reader will be able to understand the reaction mechanisms for DMS and MeSH oxidation to SO2 more easily. I suggest drawing something similar to Chen et al. 2018 (Atmos. Chem. Phys., 18, 13617–13637, 2018 https://doi.org/10.5194/acp-18-13617-2018).

Based on comments from both reviewers we have added a diagram of the reaction scheme to the manuscript as Figure 1.

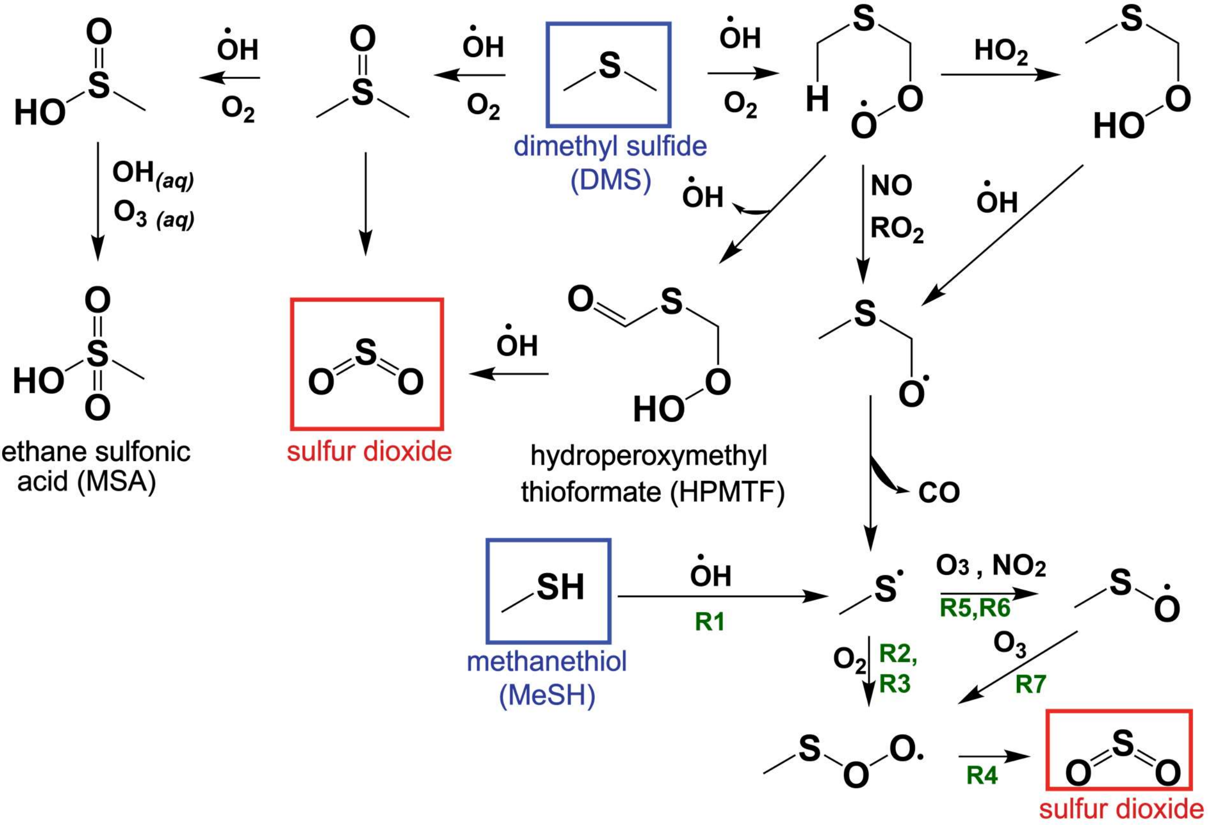

Figure 1. A simplified reaction scheme for the gas phase oxidation of dimethyl sulfide (DMS) and methanethiol (MeSH) that focuses on pathways to SO_2 production. Reactions R1 through R7 described in Section 1.3 are labelled with green text on the schematic. Other

chemical pathways including oxidation by halogens and most condensed phase reactions of DMS and its oxidation products are not shown in this simplified schematic. Refer to Table S1. for a complete list of reactions and rate equations as implemented in this work.

Technical correction

F_{DMS} should be F_{DMS} in the main text, and the *F* (Flux) for the caption in Figures 3,4,5, and 8 should be italic. Likewise, the all variable should be italic throughout the manuscript.

Changed as requested.

Overall, I enjoyed reading your manuscript. Thank you very much.

Thank you for your thoughtful review!

Additional Comment:

Subsequent to submitting this manuscript, a paper was published providing the first measurement of the HPMTF + OH rate constant ($k_{HPMTF+OH}$). $k_{HPMTF+OH}$ was found to be 1.4 (0.27 – 2.4 uncertainty range) × 10^{-11} cm^3 $molec^{-1}$ s^{-1}, which is consistent with the rate constant of 1.1 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} used in this work estimated from the structurally similar molecule methyl thioformate. We add some discussion of this new measurement in SI section S5 where we discuss HPMTF chemistry.

SI Line 104: "The bimolecular rate constant of HPMTF with OH ($k_{OH+HPMTF}$) was approximated to be 1.1 × 10^{-11} × 10^{-11} molecules cm^{-3} s^{-1} which is the rate of OH + methyl thioformate which is structurally similar molecule to HPMTF, which is within the uncertainty range of a recent laboratory determination of 1.4 (0.27 – 2.4 uncertainty range) x 10^{-11} cm^3 $molec^{-1}$ s^{-1} (Jernigan et al., 2022) ~~as $k_{OH+HPMTF}$ has not been experimentally determined~~."

Reviewer 2:

The paper entitled "Oceanic emissions of dimethyl sulfide and methanethiol and their contribution to sulfur dioxide production in the marine atmosphere" is novel, interesting and falls within the scope of ACP. The authors report the first direct eddy covariance flux measurements of MeSH oceanic emissions and perform a comprehensive analysis of the implications of this findings with the help of a chemical model.

In general, the paper is well written and I have only a few minor comments:

We thank the reviewer for their review and suggestions which have improved the quality of our paper!

1. Section 1.1 It would be nice if the authors include the reference to some more recent studies elucidating the methanethiol production pathways by Sun et al. (2016)

Agreed, discussion of the Sun et al. work has been added.

Line 63: "The bacteria *Pelagibacter* HTCC1062 has been shown to simultaneously produce both DMS and MeSH, where the allocation between products may be related to the available supply of DMSP, with DMS production enhanced when the supply of DMSP exceeded the cellular demand for sulfur (Sun et al., 2016)."

2. The work of Sun et al. (2016) should also be discuss the study in the discussion line 353ff.

   Yes, discussion of the Sun et al. (2016) work is warranted here and has been added.

   Line 364: "Sun et al., (2016) have also shown that the bacterium *Pelagibacter* produces both DMS and MeSH from DMSP, where the relative yield of products is related to the amount of excess DMSP compared to the cellular demand for sulfur for biosynthesis."

3. Section 1.3 Can the reaction mechanism be displayed in some form of graphic/schematic? This is a little hard to follow

   A reaction diagram has been added as Figure 1.

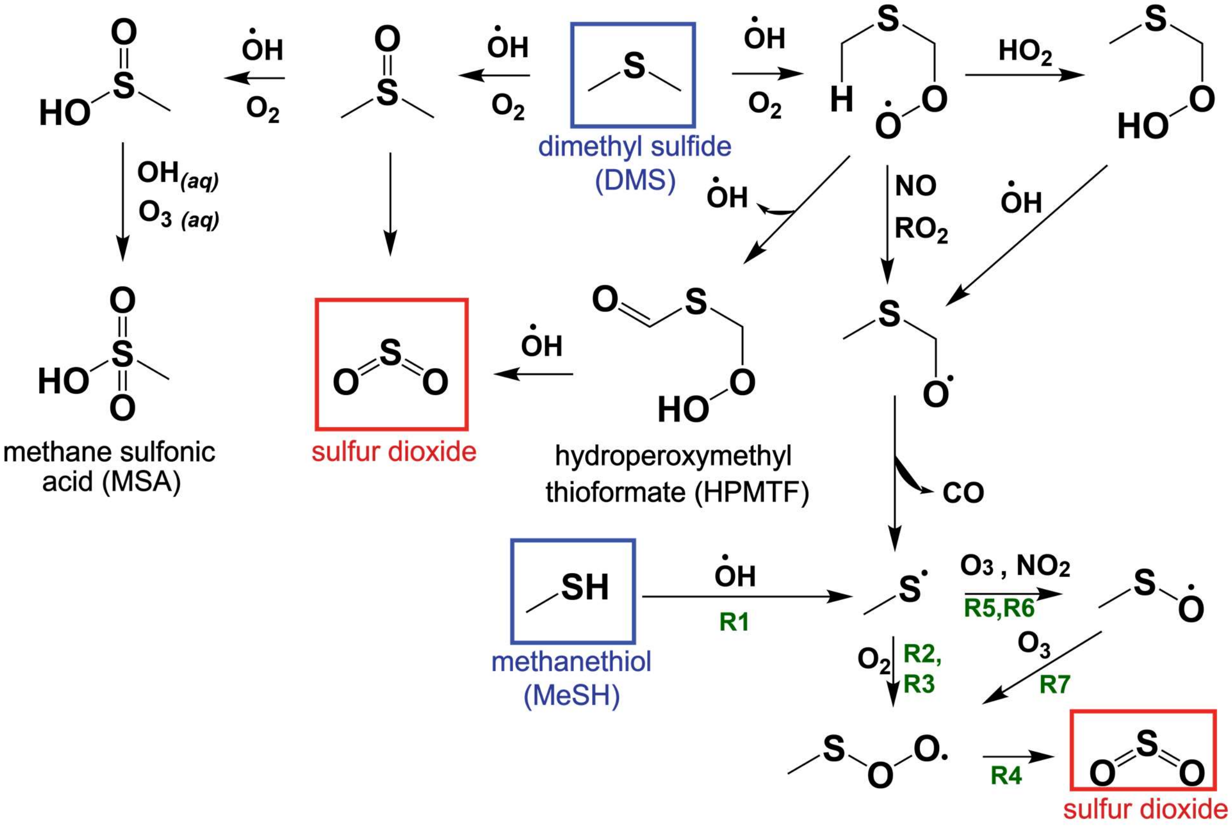

Figure 1. A simplified reaction scheme for the gas phase oxidation of dimethyl sulfide (DMS) and methanethiol (MeSH) that focuses on pathways to SO_2 production. Reactions R1 through R7 described in Section 1.3 are labelled with green text on the schematic. Other chemical pathways including oxidation by halogens and most condensed phase reactions of DMS and its oxidation products are not shown in this simplified schematic. Refer to Table S1. for a complete list of reactions and rate equations as implemented in this work.

4. Methods section: I seem to be unable to find the section where the meteorological measurements and the equipment used for the eddy covariance flux system are described. Can the authors add this description?

   A description of the meteorological measurements for the eddy covariance system were given at line 77 "The ambient inlet sampling point was collocated with a sonic anemometer recording three-dimensional winds at 10 Hz (Gil HS-50). The sonic anemometer and Vocus inlet were mounted on a 6.1 m long boom extended beyond the end of the pier to minimize flow distortions from the pier. The inlet was mounted on the boom at a height of 13 m above the mean lower low tide level."

5. Line 449 the recent ship cruise in the Arabian Sea was not the first study dimethyl sulfone DMSO2 has also been reported in marine air masses in Antarctica. Berresheim et al. 1998 reported it **https://doi.org/10.1029/97JD00695**

   Thank you for bringing this to our attention, we have added some discussion of the Berresheim et al. observations.

   Line 468: "$DMSO_2$ has also been measured at Palmer Station, Antarctica in January to February of 1994 with mean and median mixing ratios of 1.7 and 1.3 ppt respectively (Berresheim, 1998). The higher $DMSO_2$ mixing ratios observed in that study are likely at least in part due to the much lower temperatures (mean 274.5 K), where the DMS + OH addition channel forming DMSO and $DMSO_2$ is more favored."

Additional Comment:

Subsequent to submitting this manuscript, a paper was published providing the first measurement of the HPMTF + OH rate constant ($k_{HPMTF + OH}$). $k_{HPMTF + OH}$ was found to be 1.4 (0.27 – 2.4 uncertainty range) × 10^{-11} cm^3 $molec^{-1}$ s^{-1}, which is consistent with the rate constant of 1.1 × 10^{-11} cm^3 $molec^{-1}$ s^{-1} used in this work estimated from the structurally similar molecule methyl thioformate. We add some discussion of this new measurement in SI section S5 where we discuss HPMTF chemistry.

SI Line 104: "The bimolecular rate constant of HPMTF with OH ($k_{OH+HPMTF}$) was approximated to be 1.1 × 10^{-11} × 10^{-11} molecules cm^{-3} s^{-1} which is the rate of OH + methyl thioformate which is structurally similar molecule to HPMTF, which is within the uncertainty range of a recent laboratory determination of 1.4 (0.27 – 2.4 uncertainty range) x 10^{-11} cm^3 $molec^{-1}$ s^{-1} (Jernigan et al., 2022) ~~as $k_{OH+HPMTF}$ has not been experimentally determined~~."