Responses to review comments for Drivers of Atmospheric Volatile Methylated Sulfur Variability Across the Southern Ocean and Antarctic Coast

Reviewer 1: Charel Wohl

The authors present a whole suite of measurements centred around MeSH and DMS concentrations via PTR-ToF in air. The authors include oceanic measurements which are relevant to the production of these compounds in seawater and measurements of the oxidative products of MeSH and DMS in air. The methodologies employed are well described and robust. The authors present a very detailed and complete discussion of the data. The claims made in this discussion are well backed up by the available data and are well embedded in the existing knowledge around these compounds. The dataset and discussion are very valuable to the community and I highly recommend this manuscript for publication following a few minor comments around the methodology.

As part of the peer review process and for posterity, it might be worth detailing here how this manuscript differs from "Mynard, C., Franklin, E. B., Alroe, J., Somerville, N., Patti, A., Siems, S. T., et al. (2025). Constraining atmospheric methanethiol estimates over the Southern Ocean. Geophysical Research Letters, 52, e2025GL116470. https://doi.org/10.1029/2025GL116470". The manuscript presented here clearly contains more detailed information on the MISO voyage and it is richer in data from different instruments (air and water).

Response: Thank you for this suggestion. Please see text added to the Introduction from line 65 to the end of the paragraph, explaining more clearly how this publication differs from the previous publication.

"A previous publication reported on atmospheric DMS and MeSH concentrations collected across the Southern Ocean and Antarctic coast during the January--March 2024 austral summer Multidisciplinary Investigations of the Southern Ocean (MISO) voyage (Mynard et al., 2025). In this study, we analyse this dataset in greater detail with the inclusion of atmospheric DMSO concentrations and merge with a much broader array of biogeochemical, oceanographic and meteorological observations collected during the voyage and integrate with modelled air mass backward trajectories. While Mynard et al., 2025 constrained the latitudinal gradients of DMS and MeSH and established spatio-temporal boundaries whereby DMS can be used to predict MeSH in the atmosphere, here we assess in greater detail how physical-biological regimes shape VMS variability, evaluate the potential for remotely sensed Chl-a to predict atmospheric DMS and MeSH, and explore the degree of coupling between primary VMS gases and their oxidation products."

L20: These are CLAW-hypothesis specific references. Suggest changing to a different reference which look at the impact of DMS (and MeSH) specifically, rather than this feedback mechanism.

Response: Thank you for this suggestion. We have updated to include these references: Andreae and Crutzen, 1997; Hodshire et al., 2019; Mahajan et al., 2015.

L28: "… limited anthropogenic and terrestrial influence"

Response: Added this to the text.

Figure 1: The figure is potentially missing some arrows indicating HPMTF losses and how they reduce the yield of SO2 from DMS. Potentially beyond the scope of the manuscript but feels like a detail worth adding to the figure. Also, MSA is potentially playing a role in nucleation, again, not sure if this is important for this manuscript. https://pubs.acs.org/doi/10.1021/acsearthspacechem.3c00017

Response: Thank you for this suggestion. Please see updated Figure 1 with an arrow indicating heterogeneous loss of HPMTF.

L95: The PTR was calibrated every 5 days. Can the authors provide a figure that shows that the analytical system was very stable and not more frequent calibrations were necessary?

Response: The initial aim was to conduct daily calibrations with gas standards, but as mentioned in Mynard et al., 2025, the autocalibration system failed while underway, meaning that there were only nine usable calibrations that were conducted manually (every 5 days of the voyage). At the same time, we were conducting mesocosm experiments, so we needed to optimise ambient/mesocosm sampling periods versus downtime periods from calibration/zero measurements. That being said, our calibrations were stable across the voyage and during post-voyage calibrations at KCG. I have added in calibration factor standard deviations for MISO and KCG datasets in the Table S3 to reflect this.

L100: Why did the authors decide to relate MeSH, DMSO sensitivities to DMS sensitivity using a ratio rather than a regression? After all, there could be an intercept in this relationship.

Response: Thank you for this comment. We chose to relate the MeSH and DMSO sensitivities to DMS sensitivity using a ratio because the post-voyage calibrations indicated that the relative sensitivity between these compounds was stable. The DMSO sensitivity ratio remained constant across the calibration periods, suggesting that a proportional relationship was appropriate for converting DMS sensitivity to DMSO sensitivity.

L163: Did the authors use day and night-time data for this? During the day, the fluorometer measurements could be influenced by photochemical quenching. The authors could consider adding the HPLC measurements to Fig2 c). L188: Please add here that you compared underway and CTD Fluo to check for measurement consistency/contamination.

Response: Yes this is day and nighttime data. Please see updated text in Section 2.6 to clarify the correction factor:

"Underway Chl-a fluorescence measurements were scaled using a correction factor of 3.39, derived from 64 paired in-situ fluorescence and HPLC pigment measurements. These paired observations were obtained from CTD water samples collected between 3.5 and 450 m depth and compared with corresponding fluorescence measurements. Restricting the analysis to samples collected within the underway seawater intake depth (≤10 m) produced a similar correction factor of 3.1 (n = 10). As there was little evidence of near-surface non-photochemical quenching during the voyage, we adopted the correction factor derived from the full dataset (3.39), providing a more robust estimate based on the larger number of paired observations."

Section 3.3: This section is very complete. Have the authors observed any correlations with hourly precipitation Figure S13? We might expect that DMS and MeSH and DMSO are “scavenged” by rain. Have the authors observed any correlations with PAR and the amplitude of a potential diurnal cycle in DMS and MeSH? More PAR – more OH – larger diurnal. Overall there is a lack of discussion of diurnal variability in DMS and MeSH. All MeSH air measurements up to now have found a diurnal change in the mean. Might be worth adding a figure in the supplement and brief discussion e.g. in Sect.3.1.

Response: Thank you for this suggestion. The diurnal variability of VMS (including DMS and MeSH) is discussed in detail in Mynard et al. (2025), particularly in the Supplementary Information. Therefore, we have not further explored diurnal cycles in the present work, as the limited number of periods with optimal conditions to isolate and assess diurnal variability in the voyage dataset are already examined in that publication.

We have added this information on the diurnal variability to Section 3.1 at L222:
“As illustrated by Mynard et al., 2025, the MeSH:DMS diurnal cycle observed during the MISO voyage exhibited stronger diurnal variability at lower latitudes (maximum-to-minimum ratio of ~3.5 at ~38oS) than at higher latitudes (maximum-to-minimum ratio of ~1.5--2 at ~55--60oS). This latitudinal difference was attributed to variations in OH radical abundance and small differences in reaction rates of MeSH and DMS with OH.”

With regards to precipitation scavenging, we have updated the correlation matrix (Figure S11) to include trajectory-integrated precipitation. We do not observe significant correlations between precipitation and DMS, MeSH, or DMSO concentrations, suggesting that wet scavenging was not a dominant control on the observed variability during the voyage.

Mynard, C., Franklin, E. B., Alroe, J., Somerville, N., Patti, A., Siems, S. T., Williams, A., Mallet, M. D., Humphries, R., & Dunne, E. (2025). Constraining Atmospheric Methanethiol Estimates Over the Southern Ocean. Geophysical Research Letters, 52(18), e2025GL116470.
https://doi.org/10.1029/2025GL116470

Supplement

L4: How frequent were the backgrounds?

Response: Zero measurements were conducted during the same time period as the VOC calibrations, approximately every 5 days during the voyage from measurements. Updated to “Ambient data were background corrected by linear interpolation of all nine background measurements to match ambient data cycles and then subtracted to give background-corrected data for each analysed VOC.”

L13: The uncertainty of the Apel-Riemer Cal gas concentration is +- 5 %. Has this been considered?

Response: Yes, this is included in the Dunne et al., 2018 approach to propagating uncertainty for PTR-MS measurements.

Dunne, E., Galbally, I. E., Cheng, M., Selleck, P., Molloy, S. B., & Lawson, S. J. (2018). Comparison of VOC measurements made by PTR-MS, adsorbent tubes-GC-FID-MS and DNPH derivatization-HPLC during the Sydney Particle Study, 2012: A contribution to the assessment of uncertainty in routine atmospheric VOC measurements. Atmospheric Measurement Techniques, 11(1), 141–159. https://doi.org/10.5194/amt-11-141-2018

L21: Why was the sensitivity at KCG 6 times larger than during MISO?

Response: Thank you for identifying this. While this manuscript has been in review, we have re-assessed our calibrations and benchmarking of DMSO. The calibration factors originally provided for the DMS_KCG and DMSO_KCG are falsely high due to problems with our calibration dilution system. We have since rectified this issue and have applied a combined dilution and instrument sensitivity to PerMasCal (m/z 203 and 330) correction factor reducing the reported CF by a factor of ~5. As a result, the final calibration factors from those post-voyage calibrations are CF(DMSO_{KCG}) = 114 cps ppb-1, CF(DMS_{KCG}) = 669 cps ppb-1 (reflected in the SI text). This still maintains the ~1:6 ratio to benchmark for CFMISO(DMSO) = 88 cps ppb-1 and does not affect the final reported DMSO (ppb) in the manuscript.

L26: Did the authors also compare cylinder-derived MeSH sensitivity and MeSH sensitivity from the measured ion counts of protonated species and the collision rate constant for the proton transfer reaction? What was the transmission used for MeSH and how was this derived?

Response: Yes, the comparison between k-rate-derived MeSH concentrations and ppb-calibrated MeSH concentrations was presented in the Supplementary Information of Mynard et al. (2025). During gas standard calibrations, the transmission efficiency of MeSH relative to m/z 21 was determined to be approximately 0.7, which was similar to the relative transmission measured for DMS (~0.75). Using the k-rate approach, based on the measured ion counts of the protonated species and the proton transfer reaction collision rate constant, resulted in MeSH concentrations that were approximately 3.2 times lower than those reported using the ppb calibration approach.

L114: Indicate location of NO3-CIMS? How straight was this inlet?

Response: The NO3-CIMS was located in the Air Chemistry Lab of the RV Investigator alongside the PTR-ToF-MS (see main text Section 2.3) and was only used for ambient measurements not for the mesocosm experiments that are discussed in this Section S5. We have updated the main text about the CIMS inlet here:
"Ambient air was sampled from a separate inlet and included a straight 1.6 m stainless steel 1" line at a flow rate of 60 L min-1 followed by a flow of 10 L min-1 drawn through 1.2 m of PFA 1/2" tubing to NO3-CIMS. Diffusional losses in the sampling line were determined following the procedure described in Cheng 2011, using the diffusion coefficient of SA, which was applied to both SA and MSA."

Figure S1: The authors could include brief (1-2 days) timeseries of m/z 49, 63 and 79 and all peaks they fitted at these nominal masses. This is just to show that the authors have fitted "the right" number of peaks – if there is such a thing. The motivation behind this is very well illustrated in the

supplement of this paper: https://www.pnas.org/doi/10.1073/pnas.2218127120#supplementary-materials

Response: Thank you for this suggestion. The peak fitting procedure used in this study was based on the well-established Ionicon Data Analyser peak fitting method (e.g. Muller et al., 2013). We have carefully inspected the fitted peaks across the dataset and verified that the assigned components were consistent between ambient and calibration measurements (Table S2). We have decided not to add additional time series plots of individual nominal masses as we consider these examples would not provide additional information beyond the quality-control and validation procedures already described in the SI.

Müller, M., Mikoviny, T., Jud, W., D'Anna, B., & Wisthaler, A. (2013). A new software tool for the analysis of high resolution PTR-TOF mass spectra. Chemometrics and Intelligent Laboratory Systems, 127, 158–165. https://doi.org/10.1016/J.CHEMOLAB.2013.06.011

Reviewer 2 – anonymous

This paper presents measurements of gas-phase DMS, MeSH and DMSO during a research cruise near Antarctica and in the Southern Ocean with extensive analysis of air mass backtrajectories and local biogeochemical measurements. The discussion of the case studies is interesting as is the discussion of DMSO. This paper is an important addition to the still fairly sparse body of measurements in this remote and climactically important region. It should be published after consideration of the following comments.

Major comments:

1. I think the paper could benefit from some restructuring and possibly removing some material that doesn't tell a clear story. In particular, I find all the different ways the data is sliced up to be confusing and wonder if they are all necessary. For example, Figure 3 has the data divided in two by ship location and then divided in four by air mass source/productivity. Do the violin plots for ship location explain anything? They are not discussed in Section 3.2. The ratio of MeSH:DMS is discussed in Section 3.4 but in the context of a figure in a previous paper. The violin plots in Figure 3 do not make the same point. Instead, the violin plots look remarkably similar between low and high productivity (except oceanic DMSO). I don't think they demonstrate the point that high productivity regions had higher VMS concentrations. I encourage you to rethink whether violin plots are a good representation of the data. It might be better to plot MeSH vs DMS and DMSO vs DMS and color by the four air mass sources. If that does not show a clear separation between high and low productivity air masses, then maybe remove Section 3.2 and Figure 3 and move on to the next section which makes a more convincing case for correlating concentrations with air mass source.

Response: Thank you for this suggestion. We have proceeded with your suggestion to remove Section 3.2 Influence of Air Mass History and Figure 3 (violin plots), with 3.2 becoming "Predictors

of VMS Variability…". Updated paragraph from line 201 to summarise some of the content about air mass history from the previous 3.2.

"Observations were classified into four air mass history categories based on 12-hour back trajectories and cumulative boundary layer Chl-a exposure (cBLChl-a}): oceanic or Antarctic origin, each with low or high biological productivity (threshold = 1.23 ug m-3; Section 2.7. Antarctic Ice-Edge air masses were predominantly oceanic (83%) and high productivity (78%; Fig. S6 and Fig. S7; marine in-situ underway Chl-a up to 5 ug m-3, >62oS), coinciding with the highest atmospheric concentrations of DMS, with extreme spikes up to 5.7 ppb and median concentrations of 340 ppt. In comparison, MeSH concentrations were up to 200 ppt (median = 23 ppt, Fig. 2) over the same spatial regions. Open Ocean air masses were exclusively oceanic and mostly low productivity (81%; Fig. S6 and Fig. S7; marine in-situ underway measured Chl-a <1 ug L-1, where DMS and MeSH were more tightly coupled (R2 = 0.80, slope = 0.173, p < 0.05) ranging from below detection limits (BDL) to 1.4 ppb (median = 271 ppt) and BDL to 253 ppt (median = 28 ppt), respectively. Across both regions, air masses with high biological productivity consistently exhibited higher concentrations of DMS, MeSH and DMSO than low-productivity air masses (Fig. 2)."

2. Later in the paper, there is a further division into three case studies. The times of the case studies are not indicated on any of the time series plots making it difficult to understand how they relate to the rest of the campaign. In Figure 2 (and Figure S13), I would suggest using vertical lines to mark the start/end of each case study. Also mark the various regions on Fig. S11 which has a different time axis.

Response: Thank you for your suggestions regarding Fig 2, S11 and S13. We have updated to include vertical lines and annotations to indicate the case study time periods, please see updated Fig 2 and SI figs (now Fig S3 and Fig S14).

3. I don't think the mesocosm experiment adds much to this paper and it adds text/figures to the SI. I would remove it from this paper since the authors mention that a more extensive paper on the mesocosm experiments is in progress.

Response: Thank you for the suggestion. We agree that the usage of the mesocosm results is low relative to the complexity of the experimental setup in this manuscript. However, the mesocosm results are critical to interpretation of the ambient results, as the mesocosm maintained an oxidant-free headspace environment. This was a critical line of evidence for interpreting the ambient data in the following ways: 1. the low concentrations of DMSO compared to DMS in the mesocosm headspace is evidence against co-ventillation of DMSO at the air-sea interface. This provides evidence of rapid DMS->DMSO atmospheric oxidation as the key source of ambient DMSO (see Section 3.5). Without the mesocosm headspace evidence, there wouldn't be a clear way to rule DMSO ventilation at the highly biologically active Antarctic Ice-Edge. 2. Evidence of the limited photoinhibition effect with increased atmospheric MeSH concentrations during low light conditions at the Process Station associated with high MeSH and high DMS compared to the low MeSH and high DMS concentrations at the Mertz Polynya Area. We have added the following text to the beginning of the mesocosm section in the SI to clarify this as follows:

"These experiments are the focus of future works and a full analysis is beyond the scope of this publication. However, as described below, the mesocosm headspace maintained negligible

concentrations of atmospheric oxidants, and as such the ratios of VMS species and their oxidation products observed in the experiments serve as vital lines of evidence for investigating the effects of ventilation versus atmospheric oxidation in the ambient dataset."

4. You should state more clearly that the DMS and MeSH measurements in this paper have been published previously, either in the introduction or in the campaign overview section.

Response: We agree with this. Please see text added from line 65 to the end of the paragraph, explaining more clearly how this publication differs from the previous publication.

"A previous publication reported on atmospheric DMS and MeSH concentrations collected across the Southern Ocean and Antarctic coast during the January--March 2024 austral summer Multidisciplinary Investigations of the Southern Ocean (MISO) voyage (Mynard et al., 2025). In this study, we analyse this dataset in greater detail with the inclusion of atmospheric DMSO concentrations and merge with a much broader array of biogeochemical, oceanographic and meteorological observations collected during the voyage and integrate with modelled air mass backward trajectories. While Mynard et al., 2025 constrained the latitudinal gradients of DMS and MeSH and established spatio-temporal boundaries whereby DMS can be used to predict MeSH in the atmosphere, here we assess in greater detail how physical-biological regimes shape VMS variability, evaluate the potential for remotely sensed Chl-a to predict atmospheric DMS and MeSH, and explore the degree of coupling between primary VMS gases and their oxidation products."

Minor comments:

Figure 1. This is a very nice summary of the various processes. I would suggest a few changes that might make it easier to interpret. On the right-hand side, I would flip what is above and below the red dashed line. This would put the higher temperature reactions above the lower temperature reactions and also put the more volatile species above the less volatile species. I think these changes to the layout would enhance interpretation by having the physical layout represent the properties. Can you make the pink and the red boxes more different in color? They are difficult to tell apart. It would be helpful to have a legend for the colors.

Response: Thank you for these suggestions. The reason we have included the lower temperature pathway (OH-addition) at the top of the figure is because this regime is favoured at Ice-Edge, which is what is mostly discussed in Section 3.5. Please see updated Figure 1 with added "(Ice-Edge-favoured)" and "(Open Ocean-favoured)" to the titles and included legend to clarify. We have also included an additional arrow for HPMTF to indicate heterogeneous loss.

Section 2.4. Did you calibrate the TOF-ACSM for MSA and did you see any indication that some of the SO4 measured might have been MSA?

Response: We did not calibrate for MSA for this voyage given that previous laboratory experiments with our capture-vaporiser-ToF-ACSM setup demonstrated extensive fragmentation of MSA within the instrument making it difficult to ascertain the fraction of SO4 related to MSA within an acceptable level of confidence. This is an active area of investigation within this research group – we regularly calibrate a long-term monitoring ToF-ACSM at the Kennaook/Cape Grim station in

Tasmania, Australia with ongoing intercomparison studies involving the calibration and quantification of MSA aerosol in the remote marine atmosphere.

Figure 2. In panel e), the axis is labeled MeSH:VMS but the text says MeSH: DMS. Are the ppb units ppbv? Is there a reason to use different units (molecules/cm3) for DMSO and MSA? In general, the traces are very hard to tell apart. Maybe consider using more contrasting colors in each panel.

Response: Thank you for the feedback. The data is in fact MeSH:VMS with units in ppbV and the caption was updated to reflect this. Thank you for the feedback regarding colours, after passing this figure through multiple colourblind image tests, we have decided to keep the same colour scheme.

The units of molecules/cm3 were used for MSA and sulfuric acid consistent with Miljevic et al., 2025.

Figures 2, 4, S11, S13. Why are the tick marks on the time axis not evenly spaced? Most are 7 days apart but there's a gap of 10 days between Jan 22 and Feb 1. This makes it hard to find specific dates mentioned in the text.

Response: We have updated the x axis ticks. Please see updated Figure 2 in the manuscript and SI figs (Fig S3 and S14).

Figure 3. Why is the sum of the air mass points (1195) 40% higher than the sum of the ship location points (852)? Figure 2 shows the air mass analysis extending longer in time than the ship location but not 40% longer.

Response: Thank you for noticing this, this is due to the 5-95th percentile analysis in Figure 3 – but from your previous we have removed Figure 3 and its interpretation from the text.

Lines 282-3: MeSH is not what you are plotting in Fig. 5a. However, if you mark the Subtropical Front on Fig.2, then you can refer to that.

Response: At this line, we updated the text to: "The highest observed VMS concentrations occurred at the shallowest ocean depths (Fig. 5a), especially MeSH at the Subtropical Front (>200 ppt, <4000 m; Fig. 2e)."

Line 325: Please explain briefly what the nocturnal accumulation method is.

Response: Added the following text to this line: "We estimated sea–air fluxes of DMS and MeSH from their nocturnal accumulation in the marine boundary layer following (Maradino et al., 2007, Lawson et al., 2020, Rocco et al., 2025, see detailed method in Section S4). This approach exploits reduced nighttime photochemical loss, allowing DMS and MeSH to accumulate in the boundary layer and providing an estimate of their net oceanic emissions."

Lines 349 and 356: Please mark the locations of your three case studies on the map in Fig. S4. What is a process station?

Response: Thank you for this suggestion, but including markers for the case studies would obscure the back trajectory data (which is already quite complex). In place of an addition to Fig S6, a reference to Fig S15 (where the case study locations are clearly annotated) has been added to the caption of Fig S6.

Lines 357-367: This description of high DMS/MeSH being associated with shallow water is at odds with the depth profile in Fig S9 which shows the highest DMS at the point where the water became much deeper. Do you have an explanation?

Response: Thank you for this observation. Our intended point illustrated in Fig. S9 was that the enhanced concentrations occur in the vicinity of the continental shelf edge, where the bathymetry changes rapidly, rather than being directly driven by whether the water is becoming shallower or deeper along the transect. We have revised the text to clarify this interpretation and now relate the observed enhancement to the shelf-edge region, consistent with previous studies that have identified elevated biological productivity and DMS production in these environments.

The following was included in 3.4.1:
"During MISO, the RV Investigator transited across the Antarctic continental shelf and shelf-edge within the MPA, where the deep Southern Ocean (>3000 m) transitioned to the shallow (200--1000 m) shelf waters (Fig. S9). The highest atmospheric DMS concentrations coincided with the Antarctic shelf-edge region, which is recognised as a zone of enhanced biological productivity and extremely high DMS fluxes (Webb et al., 2019, Stefels et al., 2018)."

Webb, A. L., van Leeuwe, M. A., den Os, D., Meredith, M. P., J. Venables, H., & Stefels, J. (2019). Extreme spikes in DMS flux double estimates of biogenic sulfur export from the Antarctic coastal zone to the atmosphere. Scientific Reports, 9(1), 2233. https://doi.org/10.1038/s41598-019-38714-4

Stefels, J., van Leeuwe, M. A., Jones, E. M., Meredith, M. P., Venables, H. J., Webb, A. L., & Henley, S. F. (2018). Impact of sea-ice melt on dimethyl sulfide (sulfoniopropionate) inventories in surface waters of Marguerite Bay, West Antarctic Peninsula. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 376(2122), 20170169. https://doi.org/10.1098/rsta.2017.0169

Line 388: There are only a few measurements of dissolved DMSO in the MPA region and they are not higher than the other measurements. Please explain why you consider these high concentrations.

Response: Updated the text to, "High concentrations of dissolved DMSO observed near the Antarctic coast (Fig. S11) have also been observed elsewhere in Antarctic waters." Fig S11 demonstrates increased DMSO seawater concentrations around 2024-01-21 when near the Antarctic coast.

Line 497: I would not call an R2 of 0.04 "signficantly correlated." Plus, you call it decoupled in line 557. Please rephrase.

Response: Thank you for this suggestion. We have updated to "weakly correlated over the Open Ocean…"

Figure 6. Can you use red and blue regions to indicate ice edge and open ocean? Using red and blue bars for the polar front and subtropical front makes it look like you are defining open ocean differently in this graph than in the other ones.

Response: Thanks for the feedback. We have updated Fig. 5 (previously Fig. 6) to distinguish the atmospheric fronts using a solid line for the Subtropical Front and a dashed line for the Polar Front. We have not added shaded regions to indicate ice-edge and open-ocean periods because the x-axis in this figure represents air temperature rather than time (cf Fig 2).

Lines 534-536: Since you have seawater and air DMSO, can you estimate a flux from a two-layer model?

Response: Thank you for this suggestion. We considered this when first writing the manuscript, but due to 1. inconsistent meteorology when sampling seawater DMS/O/P alongside atmospheric DMS/DMSO (e.g., windspeeds that decouple atmospheric DMS from underway seawater) and 2. Too few data points of DMS/O/P coinciding with atmospheric DMS/DMSO. Our research team are currently developing dissolved measurements of VMS to make this possible for future voyages.

Supplementary Information:

Line 13: 11-12% uncertainty seems low for PTR measurements, especially for the compounds that you are not directly calibrating during the campaign. Does this take into consideration the error in fitting two peaks close to each other, as in the examples in Fig. S1, when the target peak is small?

Response: Thank you for this query. The peak fitting procedure used in this study was based on the well-established Ionicon Data Analyser peak fitting method (e.g. Muller et al., 2013). We have carefully inspected the fitted peaks across the dataset and verified that the assigned components were consistent between ambient and calibration measurements (Table S2).

Dunne, E., Galbally, I. E., Cheng, M., Selleck, P., Molloy, S. B., & Lawson, S. J. (2018). Comparison of VOC measurements made by PTR-MS, adsorbent tubes-GC-FID-MS and DNPH derivatization-HPLC during the Sydney Particle Study, 2012: A contribution to the assessment of uncertainty in routine atmospheric VOC measurements. Atmospheric Measurement Techniques, 11(1), 141–159. https://doi.org/10.5194/amt-11-141-2018

Müller, M., Mikoviny, T., Jud, W., D'Anna, B., & Wisthaler, A. (2013). A new software tool for the analysis of high resolution PTR-TOF mass spectra. Chemometrics and Intelligent Laboratory Systems, 127, 158–165. https://doi.org/10.1016/J.CHEMOLAB.2013.06.011

Equation 1: It is confusing that all the subscripts are x. Shouldn't two of them be DMS?

Response: Thank you for noticing this. The equation has been updated to be CF(x_MISO) = CF(DMS_MISO)*CF(x_KCG)/CF(DMS_KCG)

Lines 20-21: Why is the sensitivity of DMS 6 times higher at KCG than during MISO?

Response: Thank you for identifying this. While this manuscript has been in review, we have re-assessed our calibrations and benchmarking of DMSO. The calibration factors originally provided for the DMS_KCG and DMSO_KCG are falsely high due to problems with our calibration dilution system. We have since rectified this issue and have applied a combined dilution and instrument sensitivity to PerMasCal (m/z 203 and 330) correction factor reducing the reported CF by a factor of ~5. As a result, the final calibration factors from those post-voyage calibrations are CF(DMSO_{KCG}) = 114 cps ppb-1, CF(DMS_{KCG}) = 669 cps ppb-1 (reflected in the SI text). This still maintains the ~1:6 ratio to benchmark for CFMISO(DMSO) = 88 cps ppb-1 and does not affect the final reported DMSO (ppb) in the manuscript.

Lines 23-27: Do you have enough compounds in your calibration cylinder to do sensitivity vs kPTR? Can you show the data and where MeSH and DMSO fall relative to the compounds in your cal cylinder? I'm surprised DMSO is off by a factor of 4.5.

Response: Thank you for this query, please see the following text (Section S1) included to clarify our consideration of the k-rate approach for VMS quantification:

"Between each calibration cylinder, acetone was a common reference compound, allowing us to compare instrument sensitivity across standards. Consistent with our previous observations (Mynard et al., 2025, Mynard et al., in prep), we found that concentrations derived using calibration standards and those estimated using the k-rate approach differed by approximately a factor of 1-5. This demonstrates the uncertainty associated with k-rate approach quantification and reinforces the importance of frequent calibrations using appropriate standards for accurate quantification of, in this study, VMS compounds. Similar discrepancies have also been reported for MeSH (see Mynard et al., 2025). Our calibration cylinders did not contain enough compounds spanning a sufficiently wide range of reaction rate constants to robustly establish instrument sensitivity as a function of the k-rate approach."

Section S2: This is a confusing description of OSSCAR since it starts with a lot of detail about the detector. What is in front of the detector? A GC? With a trap? Are you looking at the headspace of a sample? Or bubbling through a sample?

Response: OSSCAR is a purge-and trap system, so it bubbles (sparges) the DMS out of the seawater sample with N2 and has a GC column inline out to the detector.

To clarify the OSSCAR measurement of DMS/O/P we have updated the main text Section 2.6 with the following:

"Seawater DMS, DMSO, and DMSP (DMS/O/P) concentrations were determined via the Organic Sulfur Sequential Chemical Analysis Robot (OSSCAR), a custom-built, semi-autonomous purge-and-trap system (Asher et al., 2015). DMS/O/P concentrations were quantified using a custom chemiluminescence detector coupled to OSSCAR, following a similar approach to Nagahata et al., 2013. Full instrument configuration, operating conditions, and calibration procedures are provided in Supplementary Information Text S2. Briefly, the system first sparges and traps DMS for quantification via chemiluminescence, followed by converting subsequent sub-samples of DMSP

and DMSO to DMS via fast NaOH hydrolysis (Asher et al., 2015) and electrochemical reduction (McCulloch and Tortell, 2023), respectively. The 30-minute electrochemical reduction protocol (McCulloch and Tortell, 2023) was adapted to use a NiSO4 catalyst. Nitrogen carrier gas delivered the analyte from OSSCAR to the reaction chamber, where an ozone–air mixture initiated the chemiluminescence reaction, and the amplified signal was recorded using a dedicated DAQ system."

And in the Supplementary Text:

"Measurement of DMS/O/P concentrations were made using the Organic Sulfur Sequential Chemical Analysis Robot (OSSCAR) (Asher et al., 2015). Briefly, OSSCAR is a custom built, semi-autonomous purge-and-trap system configured to extract DMS from 10 mL seawater samples via nitrogen sparging onto a thermal desorption trap, and the eluted DMS is then separated from other volatiles by a gas chromatography column. Subsequent DMSP and DMSO sub-samples are converted to DMS separately via fast NaOH hydrolysis (Asher et al., 2015) and electrochemical reduction (McCulloch and Tortell, 2023), respectively. The electrochemical reduction procedure was adapted to use a 1 mL addition of 1.8mM NiSO4 (Sigma Aldrich) catalyst to a 10 mL sample, which was determined to produce comparable performance under the 30 min reduction protocol described in McCulloch and Tortell, 2023. DMS/O/P concentrations were quantified by a custom-built chemiluminescence detector coupled to OSSCAR, following similar methodology to Nagahata et al., 2013 (Figure S3)."

Section S4: Since you have both air and seawater measurements for DMS, can you calculate fluxes with a two-layer model? How do they agree with the nighttime accumulation method?

F=k(Cw−HCa)

- F**= DMS flux (µmol m^{-2} s^{-1}, often converted to µmol m^{-2} d^{-1})**
- k**= gas transfer velocity (m s^{-1})**
- C_w**= seawater DMS concentration (µmol m^{-3})**
- C_a**= atmospheric DMS concentration (µmol m^{-3})**
- H**= dimensionless Henry's law constant for DMS (air–water)**

Response: Thank you for this suggestion. We considered this approach when writing the manuscript, but were unable to identify a suitable approach for the following reasons: 1. inconsistent meteorology when sampling seawater DMS/O/P alongside atmospheric DMS/DMSO, meaning that windspeeds were too high and inconsistent for a reasonable degree of coupling between ocean at atmosphere at the times when seawater DMS/O/P were measured, and 2. Too few data points of DMS/O/P coinciding with atmospheric DMS/DMSO. Hence, we proceeded with the nocturnal accumulation method in this instance. Our research team are currently developing dissolved measurements of VMS to make this possible for future voyages.

Lines 104-105: What are the UV transmission characteristics of the PMMA lid and Tedlar film?

Response: Thank you for this query. We have updated the SI text in Section S5 to include the following details:

"These experiments are the focus of future works and a full analysis is beyond the scope of this publication. However, as described below, the mesocosm headspace maintained negligible concentrations of atmospheric oxidants, and as such the ratios of VMS species and their oxidation products observed in the experiments serve as vital lines of evidence for investigating the effects of ventilation versus atmospheric oxidation in the ambient dataset.

Unfiltered seawater was pumped from 5-7 m depth using a trace-metal clean tow fish system. The device was mounted from a boom off the RV Investigator's midship beyond its wake and towed at five knots. Seawater was pumped directly into two 2000 L polypropelene mesocosm tanks. The mesocosm lids were made of polymethyl methacrylate (PMMA); both the tanks and lids were lined with Tedlar film. Light transmission was PMMA-limited across all wavelengths. From post-voyage measurements of the light transmission properties of the PMMA lid, there was ~90 % transmission at all visible light wavelengths 396-1100 nm with a substantial drop off to <1 % transmission into the UV beginning ~395 nm to 200 nm, as has been documented before for this material (e.g., Martinez et al., 2022). These results indicate high transmittance of photosynthetic active radiation (PAR) and low transmittance of ultraviolet radiation into the headspace, supporting the conclusion that the mesocosm headspace approximated an oxidant-free environment. This conclusion is supported by ozone measurements, which were below detection limits at all times in the mesocosm headspaces.

Each tank was simultaneously filled approximately halfway using a two-way flow splitter linked to an all-plastic pump (A100, Wilden) with a trace-metal clean Teflon diaphragm. The mesocosms were filled at select locations during the MISO voyage. One of these sample collection periods corresponded to Process Station 2 (PS2, 64◦ S, 132◦ E). The two tanks were analysed simultaneously, with one tank used to investigate nutrient perturbations to underlying biology and the other acting as an unamended control."

Figure S9: Is there a reason to plot versus latitude instead of as a time-series? It makes it hard to visually compare averages as you do in the text. It would be useful to add the locations of the CTD casts to this figure.

Response: Thank you for this query. We believe this illustrates more clearly the changes in depth and the relationship to observed VMS concentrations as the RV Investigator traversed the Mertz Polynya Area. Readers can compare with the time series figure in Fig. S14.

Figure S10: Please include an axis in units of depth.

Response: Thank you for the suggestion. We have included this in the updated Figure.

Figure S12: It is very difficult to tell the different orange lines apart. Can you use more distinct colors and/or different symbols? Do any of these correspond to the Subtropical Front case? Can you put a label with the region at the top of each column?

Response: Thank you for this suggestion. Please see the updated Figure (now Fig S4) We have updated the Antarctic Ice-Edge data point symbols to more clearly indicate each CTD profile and updated the legend to indicate Ice-Edge and Open Ocean CTD profiles.

Figure S15: Please highlight the region that is the Subtropical Front case in the time-series panels.

Response: Please see updated Figure (now Fig S13).

Typos/corrections:

Line 276: You have not yet defined MPA.

Response: Thank you, the text has been updated to: "Relative to the shallower bathymetry and shallower MLDs in Antarctic shelf regions, such as the Mertz Polynya Area (MPA; 65.33–67o S, 140–150o E; see later in Section 3.4…"

Lines 426-429: This sentence is repetitive and refers to the wrong figure in the SI (CDOM is Fig. S10 not S12).

Response: Please see updated text to reduce repetition and correctly refer to Fig S10: "Potentially indicative of a more heterotrophic phase and downwelling at the shelf was the consistently higher pCO2 (~350 ppm) compared to the MPA (~208 ppm), lower O2 saturation (<100 %) (Fig. S9), and higher CDOM (2--3 ppb throughout the measured water column ~0--200 m; Fig. S10)."

Line 474: I think you mean Subtropical Front, rather than Open Ocean, for the third case study.

Response: Updated to "…and near the Subtropical Front (42-52oS)…"

Line 558: R2 is 0.04 in Fig. 6.

Response: Thank you, updated to R2=0.04

Supplementary Information:

Make sure the figures are in the order mentioned in the text.

Response: Thank you, I have updated the SI to the correct order as mentioned in the main text.

Line 10: Reference missing.

Response: Thank you, updated with "(Bevington et al., 1993)".

Figure S5: Can you use the same orange color for oceanic high productivity in the pie charts as on the map?

Response: Please see updated Figure S7 in SI.

Figure S8: It is very hard to see the blue writing against the blue background.

Response: Updated to white and black text/markers.

Reviewer 3: anonymous

The authors present a valuable contribution to our understanding of marine sulfur cycling by detailing the environmental drivers of DMS and MeSH across the Southern Ocean and Antarctic coastal region. A major strength of this study is its robust integration of atmospheric and biogeochemical data from an austral summer voyage, which combinedly demonstrates that volatile methylated sulfur (VMS) drivers are highly region-specific. By detailing distinct regional mechanisms alongside observations of rapid oxidation processes near the ice edge, the manuscript provides crucial, high-resolution empirical data that will significantly refine how future climate models parameterize climate-cooling sulfate aerosol precursors in these remote marine environments. This timely manuscript is valuable to the community in addressing the knowledge gap for this climatically important region and should be published after the following comments are addressed.

Major Comments:

1. To avoid ambiguity regarding overlapping datasets, please explicitly detail the novelty of this work especially in term of dataset presented by mentioning that in the earlier section like introduction or at the beginning of methodology in contrast with your recently published work Mynard, C., et al. (2025).

Response: Thank you for this suggestion. Please see text added in the introduction:

"A previous publication reported on atmospheric DMS and MeSH concentrations collected across the Southern Ocean and Antarctic coast during the January--March 2024 austral summer Multidisciplinary Investigations of the Southern Ocean (MISO) voyage (Mynard et al., 2025). In this study, we analyse this dataset in greater detail with the inclusion of atmospheric DMSO concentrations and merge with a much broader array of biogeochemical, oceanographic and meteorological observations collected during the voyage and integrate with modelled air mass backward trajectories. While Mynard et al., 2025 constrained the latitudinal gradients of DMS and MeSH and established spatio-temporal boundaries whereby DMS can be used to predict MeSH in the atmosphere, here we assess in greater detail how physical-biological regimes shape VMS variability, evaluate the potential for remotely sensed Chl-a to predict atmospheric DMS and MeSH, and explore the degree of coupling between primary VMS gases and their oxidation products."

2. While Figure 1 provides an excellent and highly useful conceptual framework for VMS oxidation, it is currently missing arrows for heterogeneous loss of HPMTF. I would recommend adding that to provide a more realistic picture of VMS chemistry. Additionally,

the scheme currently links methanesulfonic acid (MSA) solely to particle growth. It would be valuable to indicate that MSA can also play a direct role in nucleation.

Response: Thank you, we have included an arrow for the heterogeneous loss of HPMTF and an arrow to indicate MSA can play a role in nucleation. Please see updated Figure 1.

3. In Figure 4, the authors use a 5-hourly average with a 12-hour back trajectory for the Ice-Edge regression but seemingly use 1-hourly data for the Open Ocean regression with a 24-hour back trajectory. While you justified the choice of time for back trajectory analysis and unless I missed to catch this up, it would be nice to add a justification in the main text for treating the temporal averaging of the data points for two regimes differently (5-hour vs 1-hour).

Response: Thank you for identifying this. We have clarified this in the main text with the following:

"At the Antarctic Ice-Edge, hyper-local and rapidly evolving phytoplakton blooms can develop over timescales of only 1-3 hours, resulting in pronounced short-term variability in atmospheric VMS concentrations (Fig. 2 and Fig. 3). To more appropriately represent the spatial and temporal mismatch between measured atmospheric DMS concentrations and the underlying biogeochemical indicators integrated by the 12-hour air mass back trajectories, atmospheric DMS concentrations were averaged from 1-hour to 5-hour resolution (Fig. 3). This smoothing reduces the influence of transient local-scale variability while retaining the broader signal associated with air-mass exposure to the highly productive Antarctic coastal waters. Consistent with this interpretation, the relationship between DMS and cBLChl-a strengthened following 5-hour averaging (R2 = 0.49) compared with the unsmoothed 1-hour data (R2 = 0.20). In contrast, no temporal smoothing was applied to the Open Ocean analysis because biological productivity was more spatially diffuse and less episodic. Under these conditions, 1-hour atmospheric measurements combined with 24-hour back trajectories provided the most representative relationship between DMS and cBLChl-a (Fig. 3)."

Minor Comments:

Line 282-283: How did you isolate MeSH since you plotted VMS in Figure 5a?

Response: Updated text to say: "The highest observed VMS concentrations occurred at the shallowest ocean depths (Fig. 4a), especially at the Subtropical Front (MeSH>200 ppt and DMS>1 ppb, <4000 m; Fig. 1e and Fig. 4a)."

Fig S1: The figure would benefit from increasing all font sizes and repositioning the legend inside the figure.

Response: Thank you for suggesting this. Note that this is a screenshot taken from the Ionicon Data Analyzer software. I have updated Fig. S1 as best as possible with larger x and y tick labels and enhanced the size of the legend as much as possible without degrading the resolution.

Fig S13: Have the authors investigated any potential correlations between VMS concentrations and the hourly rainfall data presented in Figure S13? The author could consider adding a figure in the supplementary.

Response: Thank you for your suggestion. We have added ERA5 back trajectory-integrated mean total precipitation rate to the Fig. S11 correlation matrix.

Fig S14: Consider increasing the size of the symbols in the legend for clarity.

Response: Recoloured and increased size of the symbols, please see updated figure S16.