Answer to Reviewer 2

This manuscript describes measurements made over two summers of sulfur containing aerosols, atmospheric DMS mixing ratio, and seawater DMSP concentrations at the Mario Zucchelli Station in Terra Nova Bay, Antarctica. The authors link the aerosol types to biogenic DMS sea-to-air fluxes. The data from the two summers are compared and contrasted. The authors conclude that polynya close to the station is the most important for producing DMS and subsequent fresh aerosols. They also determine a branching ratio of DMS oxidation for freshly produced aerosols to be ~0.84 (older airmasses have a lower ratio). Biogenic particulate matter makes up an average of 17% (max of 56%) of PM10 measured at the station during the summer season. The article contains interesting and useful data, which are sparse, so it should definitely be published. It is generally well written and the techniques/analyses are robust. There are a few minor to moderate issues that should be addressed before publishing. One general comment is that there a number of minor English errors, so the article should be proofread again before submission.

Firstly, I'd like to thank Prof. Marandino for the positive comments, the constructive suggestions, and the new references. I think the paper will improve a lot in the final version.

Specific comments:

Lines 40-41 – DMSO is overlooked by the authors. The cycling of the three compounds (DMS/P/O) is fast and significant (e.g., Archer et al., 2001).

A sentence (and related references) on the importance of DMSO is added here in the introduction and in the discussion about the pattern of DMSP in sea water and DMS into the atmosphere.

At line 40:

"In surface waters, substantial quantities of dissolved DMSP and DMS can be detected, but another important sulfur cycle compound in sea water is dimethylsulfoxide (DMSO) whose concentrations exceeds the concentration of DMS and DMSP (Asher et al., 2017). DMSO is mainly produced from photochemical and bacterial DMS oxidation, the latter process may serve as an energy source for bacteria (Bodein et al., 2011). The loss processes of dissolved DMS include (i) microbial consumption, (ii) photooxidation, (iii) air-sea gas exchange and 30 (iv) vertical export by mixing (Simo, 2004)."

In the discussion of figure 3:

… the fast biological turnover (leading to the formation of DMSO) helped in producing low DMS concentrations in summer…

Lines 45-47 – Why did the authors pick these reactants and citations? There is a more complete description in the recent publication by Fung et al. (2022) that also includes O3 in the water and Cl in the atmosphere.

Thanks for this suggestion, the reference is used here and above. In particular, here the sentence is changed in:

"Once in the atmosphere, DMS is oxidized both in gas and water phase by O_3 or by the hydroxyl (OH), nitrate (NO_3), Chlorine (Cl), and bromine oxide (BrO) radicals to form either methanesulfonic acid (MSA) or sulfur dioxide (SO_2), which is further oxidized to H_2SO_4 (Gondwe et al., 2003; Read et al., 2008; Fung et al., 2022)."

Paragraph starting on line 74 – This is not true. DMS gas exchange has more of a linear relationship with wind speed, as it is largely transported by interfacial exchange and is not as influenced by bubbles (i.e. whitecaps, Bell et al., 2017; Zavarsky et al., 2018) as other more insoluble gases. This is also true for lines 258-259 and 270-271. The discussed decrease in exchange around 10 m/s winds is not universal (Bell et al., 2013; 2015; Yang et al., 2016; Blomquist et al., 2017; Zavarsky et al., 2018). Also, the argument from lines 272-275 (and line 372) is tenuous, especially without DMS measurements, as DMS in the water is more important for the flux than the wind (Marandino et al., 2007).

I fully agree that DMS in sea water is the main factor affecting DMS concentration into the atmosphere, but precisely because I do not have the DMS measurements, I felt the need to exclude the wind speed (and therefore the sea-atmosphere transfer speed) among the factors determining the highest concentrations of DMS in the atmosphere in one campaign respect to the other. I reinforced the discussion following the referee suggestions, stressing about the need of DMS measurements in sea water to understand these processes.

Line 100 – Should this include other types of aerosol (e.g., primary organics)?

Yes, both secondary inorganic and primary organic are important, but in this paper we focus on inorganic secondary aerosol. This is specified in the text as follow:

"It is necessary to fill the data gap in the knowledge of biogenically-derived aerosols (both secondary inorganic and primary organics) in the Antarctic to improve understanding of the effects of ocean ecosystem on the marine aerosol-cloud-climate system."

Line 115 – Why is the Hulswar et al. (2022) climatology referenced here, but everywhere in the introduction only the earlier Lana (and Kettle) climatology is referenced?

I inserted a wrong reference, the correct one is Hulswar et al., 2021. I use this reference throughout the paper, and I deleted the reference to older climatologies:

Hulswar, S., Simo, R., Galí, M., Bell, T., Lana, A., Inamdar, S., Halloran, P. R., Manville, G., and Mahajan, A. S.: Third Revision of the Global Surface Seawater Dimethyl Sulfide Climatology (DMS-Rev3), Earth Syst. Sci. Data Discuss., 2021, 1-56, 10.5194/essd-2021-236, 2021.

Figure 1 – Formatting is different for reporting the years: 2018/2019 vs 2019-2020; typo – the caption says: figure on top reports enlarged map but should say figure on bottom shows enlarged map.

Yes, will be correct.

Section 2.4 – I think it was a big oversight to not measure DMS in the water. Why was it not done? DMS can be measured reliably after a few hours of storage.

You are right, unfortunately we do not have the instrumentation to perform the measurements of the DMS in sea water. These measurements would have been really useful to understand better these processes. In several part of the paper we stress for the need of these measurements to confirm some speculations we do on the basis of the data we have.

Lines 239-240 – Did the authors see the recent work on new DMS oxidation products and pathways? Perhaps this factors in to the calculation? The work is also referenced in the Fung et al. (2022) paper.

At these lines, the MSA, nssSO_4^{2-} and DMS mean values are presented and we only add the suggested reference. Above in the paper, discussion on the new oxidation products and pathways is added. Thanks for the suggested references that I didn't know.

Line 288 – Are there not more recent studies corroborating this? I think this citation can be used, but it is very old. There is a modelling study by Bock et al. (2021) that may also shed some light on this issue.

Also considering the above comment, the text is here rearranged and simplified by adding more recent references:

"…Therefore, large differences in the DMS sea to air transfer velocity coefficient (k_w) do not seem to occur, and are not expected to be the cause of the different behavior of DMS evolution in the two ACs. Unfortunately, we do not have measurements of DMS in sea water, that could have confirmed this hypothesis, but it is consistent with previous modeling and experimental evidences assessing that the large year-to-year variability of atmospheric DMS concentrations can not be explained by changes of meteorological processes controlling the k_w factor or by changes of atmospheric oxidants, but most likely by changes in oceanic DMS concentrations (Sciare et al., 2000; Kettle and Andreae, 2000; Marandino et al., 2007; Bock et al., 2021)."

Lines 290-291 – I would tend to agree with this statement, but it really needs a chemical transport model and measurements of DMS in the ocean to corroborate.

Lines 292-294 – As the authors mention a bit below, the correlation between biomass and DMS is not reliable (e.g., summer paradox, Simo and Pedros-Alios, 1999). Again, I think not having DMS measurements in the water is a large oversight. In general, these statements are fine (not wrong), but this piece is missing.

The sentences at line 290-294 are changed stressing the need of DMS measurements in sea water.

Paragraph starting on line 298 (and elsewhere e.g., lines 364-367) – The use/analysis of the back trajectories and the reaction times seems too little (line 375 on) – were trajectories over the whole region check and compared with all data (measured/downloaded)? Please also see my comments to lines 403 on.

See answer to the comments below (at line 403)

Figure 2 and surrounding text – it is well known that the relationship between DMSP and DMS (in the water) is not straightforward – not only phytoplankton type but also physiology is important (temperature, light levels, etc.). DMS should be measured when possible and DMSO would have been a helpful measurement. Also, it has been observed that there can be a mismatch between DMS water and atmospheric levels, which has to do with physics and chemistry in the atmosphere. Maybe these discussions can be used to point to what future measurements may help elucidate the connections (that were missing here).

The sentence is rewritten clarifying the role of processes in sea water, in the conclusions we highlight the importance of future measurements of DMS in sea water to understand these processes.

Lines 381-382 – Are there physical explanations here (what is influencing this chemistry) that could be mechanistically helpful?

Here the suggested reference Fung et al., 2022 allow to improve the discussion, the following discussion is added here:

In these conditions, the MSA/nssSO_4^{2-} ratio ranges from 0.68 to 0.94 mol/mol, corresponding to percentages of DMS loss up to 41% and 49% respectively for MSA and nssSO_4^{2-} formation. As reported by Fung et al. (2022) the BrO reaction with DMS in gas phase and O_3 reaction in aqueous phase are the two main processes for DMS loss in southern high latitude ocean accounting for 50-60% and 20-30 % respectively. Both these processes lead to the formation of MSA in aerosol phase (Fung et al., 2022). In particular, the reaction with O_3 in aqueous phase could be particularly efficient at this time when high relative humidity is measured (100%). This high MSA/nssSO_4^{2-} ratio can be measured only in the freshly formed secondary biogenic

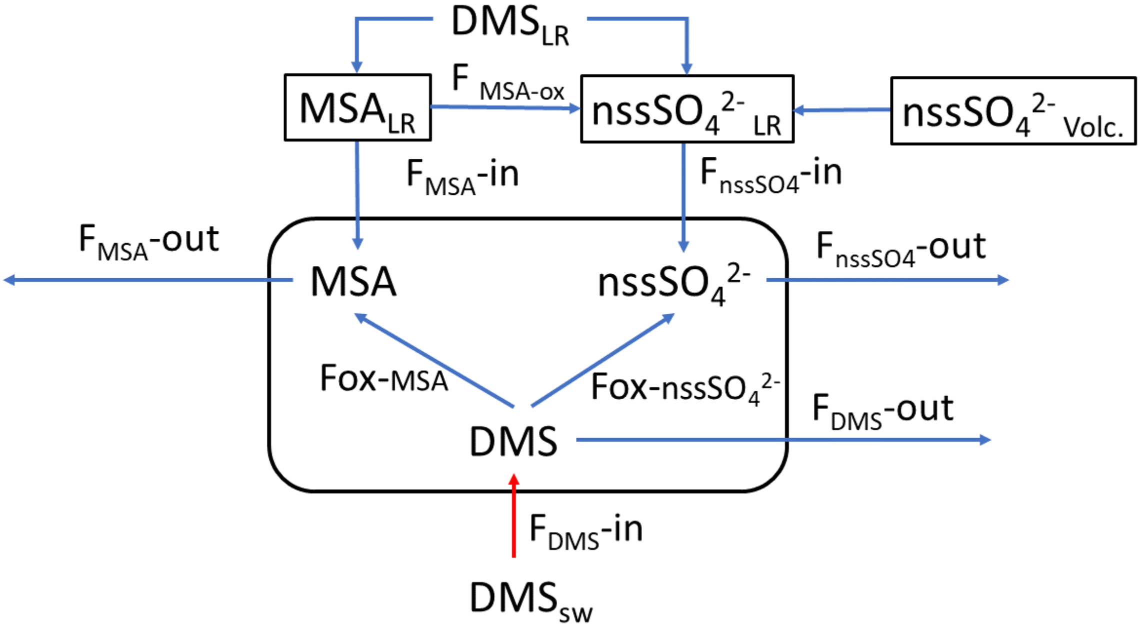
aerosol as MSA in aerosol phase can be transformed in nssSO_4^{2-} by reaction with OH radicals (Fung et al., 2022) leading to a decrease of the MSA/ nssSO_4^{2-} ratio in the aged aerosol.

Figure 6 – What are the trajectory durations?

Trajectories duration is 10 days that will be reported also in the figure caption in the revised version of the paper.

Lines 403-420 – Why are the reaction/transport times only considered important sometimes (no. 1) and not at other times (no. 2)? Even with fresh DMS emissions there will be a reaction time and the DMS laden air masses will be transported away before the relevant products form.

I agree with this, I think the text was not clear, I insert the following figure reporting the box model I've in mind and these further explanations.



Lines 370 and following:

These processes can be summarized by the simple box model reported in figure, where the box represent the atmosphere over the sampling site (and relative concentration of DMS, MSA and nssSO_4^{2-}). F are the flux of DMS, MSA and nssSO_4^{2-} incoming (F…-in), outcoming (F…-out) or formation (F…ox). DMSsw and DMS_{LR} represent the concentration of DMS in sea water and

from sea water far from the sampling site (long range) respectively. MSA_{LR} and $nssSO_4^{2-}{}_{LR}$ represent the concentration of long range transported species and $nssSO_4^{2-}{}_{volc.}$ represent the volcanic $nssSO_4^{2-}$.

From 16 to 17 December2019 we assumed that F_{DMS-in} is constant and quite high; at the beginning of DMS emission (16 December) Fox-MSA and Fox-$nssSO_4^{2-}$ are low therefore the concentration of DMS in the box depend by the equilibrium between F_{DMS-in} and $F_{DMS-out}$. At this wind speed $F_{DMS-out}$ is probably low respect to F_{DMS-in} as the concentration DMS_{sw} (driving the sea-air flux) is high. When Fox-MSA and Fox-$nssSO_4^{2-}$ become relevant (at constant F_{DMS-in} and $F_{DMS-out}$) the concentration of MSA and $nssSO_4^{2-}$ increases and DMS decreases, indeed as described above we experimentally find that

DMS emitted = MSA+nssSO4 +DMS residual

Therefore, in this particular situation of constant wind speed and direction the 17 December we can suppose that flux of MSA and $nssSO_4^{2-}$ in and out are negligible and the concentration of MSA and $nssSO_4^{2-}$ in the box are mainly due to the Fox-MSA and Fox-$nssSO_4^{2-}$ and for this reason reflecting the MSA/$nssSO_4^{2-}$ ratio of freshly formed biogenic aerosol.

In the following day (18 December) the abrupt change of wind direction (Figure 5) transport on the sampling site different air masses, therefore progressively increasing $F_{DMS-out,}$ $F_{MSA-out}$ $F_{nssSO4-out}$ leading to a MSA, $nssSO_4^{2-}$ and DMS concentration decreases in the box of figure.

Lines 204 and followings:

In case 1, due to the presence of sea ice in the proximity of the sampling site F_{DMS-in} is low, therefore is low also the concentration of DMS in the box. MSA and $nssSO_4^{2-}$ come from high MSA_{LR} and $nssSO_4^{2-}{}_{LR}$ therefore from the DMS produced far from the sampling site.

Case 2, in this case due to high variability of wind speed condition and values up to 25-30 m/sec F_{DMS-in} can be high, but in this condition is also high $F_{DMS-out}$ therefore the DMS laden air masses are transported away before a relevant amount of product (MSA and $nssSO_4^{2-}$) are formed. Therefore, even if a small amount of measured MSA and $nssSO_4^{2-}$ in the box can come from Fox-MSA and Fox-$nssSO_4^{2-}$, the main part come from F_{MSA-LR} and $F_{nssSO4-LR}$. As $nssSO_4^{2-}{}_{LR}$ can arise from the further oxidation of MSA in water phase along the transport (FMSA-ox, Fung et al., 2022) and from volcanic sources ($nssSO4_{volc.}$) the measured MSA/$nssSO_4^{2-}$ ratio is lower and more variable respect to those measured in freshly formed biogenic aerosol.

Figure 8 – Are the two slopes related to any other metadata – timing, location, air mass origin?

The split in the two data means low and high biogenic aerosol load and it is related both to the air masses direction and timing. About the 60% of data with nssSO4 concentration lower than 3 μMol/m^3 comes from the ice sheet (direction from 200-350°N as above reported), the remaining 40% are related to a time before the beginning of sea ice melt and therefore before the phytoplanktonic bloom. This is now reported in the text.

Line 465 – What is meant by "…reliable…branch ratio."?

I mean characteristic for freshly formed biogenic aerosol; the sentence is changed in:

"we believe that it is possible to obtain a characteristic MSA/nssSO_4^{2-} branch ratio for the freshly formed biogenic sulfur oxidized aerosol."

References

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Most of these references will be quoted and discussed.