

Answers to comments on “**Relating dimethyl sulphide and methanethiol fluxes to surface biota in the South-West Pacific using shipboard mesocosms**” article submitted in *ACP*.

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#Editor comments:

After careful reading of the manuscript, I agree with the reviewer that the manuscript requires drastic improvement in order to meet the quality for publication in *ACP*.

- The authors need to properly cite earlier works both with regard to the understanding of the processes of DMS production in the sea water as well as to the DMS observations in the marine environment as already suggested by the reviewer.

The updated version of the Lana climatology is now mentioned in the introduction. This version is very recent (2022) and therefore was not available at the start of writing the present paper, which explains why it was missing. We now include it. However, we contest the reviewer’s assessment that our introduction makes insufficient use of DMS state of the art . We use 32 different references, among which many are from the last 5 years (Novak and Bertram, 2020; McNabb and Tortell, 2021; Lawson et al., 2020; Kilgour et al., 2021; Wang et al., 2020; Galí et al., 2018; Bell et al., 2021).

- They also need to clearly demonstrate and spell out (also in the abstract) the originality and the added value of the work compared to earlier studies.

We provide the first quantitative relationships between emissions of DMS, and also MeSH, with nanophytoplankton abundance, derived across a range of oceanic water types.

We now specify this in the abstract:

“Dimethyl sulphide (DMS) and methanethiol (MeSH) emissions from South Pacific surface seawater were determined in three **shipborne**.”

and in the conclusion:

“We found that fluxes measured in the ASITs could be accurately predicted from seawater concentrations assuming a very low wind speed. The experimental set-up in our study provided a new approach to relating DMS and MeSH fluxes to the biogeochemical properties of surface seawater. Previous empirical relationships linking DMS fluxes and seawater biology have used Chl-a derived from satellite retrievals, which has inherent spatial resolution and biological limitations.”

- In addition, they have to thoroughly discuss the uncertainties introduced by the contamination and losses inside the ASITs.

Regarding contamination, our fluxes are calculated as a difference of concentration between the headspace and flushing air, so any contamination coming from the flushing air would be subtracted (as a “blank”). Moreover, here we focus on DMS and MeSH, which do not suffer from contamination issues (from the system itself).

Furthermore, in a previous report from this study (Rocco et al., 2021) potential contamination from the ASITs and sampling system were investigated for aromatic VOCs which are commonly associated with man-made materials. The aromatic VOCs concentrations in 3 seawater samples collected from the ASITs were close to those measured in samples collected from open ocean water, indicating contamination from ASITs materials was not a significant artefact.

- For instance, they mention that the O₃ levels inside the ASIT are lower than the ambient levels in the control experiment due to losses on the walls and the pipeline. This means that the control experiment is not representative of the ambient atmosphere – so the derived fluxes are not representative either.

A discussion was added section 2.1. on ozone:

“The ASIT-O₃ ozone concentrations (14.5 ± 2.9 ppbv) were closer to the ambient air ozone concentrations (14.6 ± 1.8 ppbv) than the ASIT-control levels (6.7 ± 1.5 ppbv) due to potential wall losses of ozone in the tanks and sampling lines, but also potential increased reactivity in the ASITs headspaces compared to ambient air (as biogenic emission fluxes under low turbulence tend to be more concentrated than in ambient air). **Consequently, the ASITs experiments could only compare sub-ambient O₃ with ambient and so, by combining data from both ASITs, measured fluxes were obtained under the typical ozone range observed over this oceanic region and during this period of the year (Bourgeois et al. 2020).**”

- In addition, if O₃ is lost in the system why not having also artifacts for the other studied species?

We corrected the statement that lower ozone concentrations being lower in the ASITs are attributed to losses: “The ASIT-O₃ ozone concentrations (14.5 ± 2.9 ppbv) were closer to the ambient air ozone concentrations (14.6 ± 1.8 ppbv) than the ASIT-control levels (6.7 ± 1.5 ppbv) due to **potential** wall losses of ozone in the tanks and sampling lines, **but also increased reactivity in the ASITs headspaces compared to ambient air (as biogenic emission fluxes under low turbulence enclosures tend to be more concentrated than in ambient air).**”

We also further discuss the potential losses of other species, such as DMS.

“The estimated headspace concentration of DMS calculated from the Henry’s law equation (Eq. 1) showed an excellent correlation with DMS measured in the headspace (DMS_h) ($R^2 = 0.94$, slope = 1.66, intercept = -0.75), indicating equilibrium conditions were established in the ASITs (Figure 6), and so wall and chemical losses were limited under the flow-through experimental conditions with headspace concentrations reflecting changes in dissolved DMS concentrations in the underlying seawater.”

- However, I cannot find an evaluation of how the errors induced by this artifact propagate to the main findings of the study. I would also like to see a more critical presentation of the results of the ASIT experiments since only 3 pairs of them have been performed. Even though these experiments are logistically heavy to be performed, it is difficult to draw a firm conclusion from a such small number of experimental results and thus the way the results are presented has to be appropriate.

Each experiment lasts several days, and for our study of relationships between chemical concentrations (or fluxes) and seawater biogeochemical variables, we merged both ASIT’s data which doubles the number of points. We do provide a statistical analysis of the robustness of our relationships (p values) provided Table 3.

Regarding the impact of ozone, we clearly acknowledge the small number of data points, and lack of duplicates: “**However, recognising the limited dataset and also the absence of replication in the ASIT experiments further work is required to confirm potential inhibition by ozone.**”

- Furthermore, the authors erroneously mention a lifetime of DMS for its reaction with O₃ at 15 days with reference to Vrekoussis et al., 2004, who do not mention any relevant to that result since that study investigated OH and NO₃ radicals atmospheric levels. To my knowledge there is only a very low upper limit rate for reactivity against O₃. For a thorough review of DMS chemistry – although a bit old now -but very comprehensive the authors are directed to the Barnes et al Chemical Reviews paper Chem. Rev. 106, 940-975, 2006.and recent updates by Veres et al. 2021 <https://doi.org/10.1073/pnas.1919344117>

This is right. We now refer to Burkholder et al. (2015) following Fung et al. (2022). The reactivity of DMS with ozone leads to a chemical lifetime of more than 12 years.

| Gas-phase reactions | k_{298} ($\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$) | $-E_a/R$ (K) | References |
|---|---|-----------------|---|
| $\text{DMS} + \text{OH} \rightarrow 0.6\text{SO}_2 + 0.4\text{DMSO} + \text{CH}_3\text{O}_2$ | See footnote* | – | Burkholder et al. (2015), Pham et al. (1995) |
| $\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$ | 1.13×10^{-12} | 530 | Burkholder et al. (2015) |
| $\text{DMS} + \text{BrO} \rightarrow \text{DMSO} + \text{Br}$ | 3.39×10^{-13} | 950 | Burkholder et al. (2015) |
| $\text{DMS} + \text{O}_3 \rightarrow \text{SO}_2$ | 1.00×10^{-19} | 0 | Burkholder et al. (2015) |
| $\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO} + 0.5\text{HCl} + 0.5\text{ClO}$ | 3.40×10^{-10} | 0 | Burkholder et al. (2015) |
| $\text{DMSO} + \text{OH} \rightarrow 0.95\text{MSIA} + 0.05\text{SO}_2$ | 8.94×10^{-11} | 800 | Burkholder et al. (2015) |
| $\text{MSIA} + \text{OH} \rightarrow 0.9\text{SO}_2 + 0.1\text{MSA}$ | 9.00×10^{-11} | 0 | Burkholder et al. (2015) |
| $\text{MSIA} + \text{O}_3 \rightarrow \text{MSA}$ | 2.00×10^{-18} | 0 | Lucas (2002) |

The Barnes et al. review only mentions the DMS reactivity towards OH, NO₃ and halogenes; it does not contain any information regarding reactivity with ozone. We feel it would be out of scope to include

a review of the DMS reactivity with OH, as in our case most of our DMS fluxes were measured during nighttime. As the Veres et al. study investigates a new pathway which is also initiated by OH, it is also irrelevant here.

- There are also inconsistencies between the numbers provided in the text and the figures as in Figures 4 and 5 pointed out by the reviewer. Although the color scale in Figure 4 does not allow to see the exact value of the concentrations, the high levels of DMS provided in the manuscript, for instance the 1285 ppt of DMS in line 269. In addition, alteration between ppt and ppb for DMS concentration in the text and the figures is rather confusing for the reader.

The value of 1285 ppt has been updated: “**Mixing ratios of DMS ranged from below the detection limit (< 78 pptv) to 753 pptv with a voyage average of 171 ± 118 pptv**”. The unit was changed following the reviewer comment and all concentrations are now given in ppt.

- Furthermore, key references, like Sellegri et al 2023 and Rocco et al. 2021, are provided in the text and are missing from the ref list. The first one, I imagine, should be the Sea2Cloud description published in <https://journals.ametsoc.org/view/journals/bams/104/5/BAMS-D-21-0063.1.xml> and the second should be the paper in Nature Communications E&E <https://www.nature.com/articles/s43247-021-00253-0> where ASIT results are also presented for organics.

Yes, this is now corrected.

The manuscript will also benefit from a careful re-reading and English correction.

- Overall, I consider this manuscript requires a very careful examination of all its statements, the statements need to be supported by observations and statistical analysis (including p-values for all correlations),

Again, p values are provided and therefore we believe our conclusions are supported by a careful statistical analysis.

- and needs to demonstrate its added value compared to earlier studies from different or even the same campaign.

We hope this is now much clearer.

- In addition, the content should reflect on the title. As is now, focused on the ASIT experiments, the title in the supplementary material seems closer to the content of the manuscript than the original title.

The title now reflects the content of the paper.

Bourgeois, I., Peischl, J., Thompson, C. R., Aikin, K. C., Campos, T., Clark, H., Commane, R., Daube, B., Diskin, G. W., Elkins, J. W., Gao, R.-S., Gaudel, A., Hints, E. J., Johnson, B. J., Kivi, R., McKain, K., Moore, F. L., Parrish, D. D., Querel, R., Ray, E., Sánchez, R., Sweeney, C., Tarasick, D. W., Thompson, A. M., Thouret, V., Witte, J. C., Wofsy, S. C., and Ryerson, T. B.: Global-scale distribution of ozone in the remote troposphere from the ATom and HIPPO airborne field missions, *Atmos. Chem. Phys.*, 20, 10611–10635, <https://doi.org/10.5194/acp-20-10611-2020>, 2020.

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical kinetics and photochemical data for use in atmospheric studies: evaluation number 18, Jet Propulsion Laboratory, National Aeronautics and Space Administration, Pasadena, CA, USA, <http://hdl.handle.net/2014/45510> (last access: 30 November 2021), 2015.

Fung, K. M., Heald, C. L., Kroll, J. H., Wang, S., Jo, D. S., Gettelman, A., Lu, Z., Liu, X., Zaveri, R. A., Apel, E. C., Blake, D. R., Jimenez, J.-L., Campuzano-Jost, P., Veres, P. R., Bates, T. S., Shilling, J. E., and Zawadowicz, M.: Exploring dimethyl sulfide (DMS) oxidation and implications for global aerosol radiative forcing, *Atmos. Chem. Phys.*, 22, 1549–1573, <https://doi.org/10.5194/acp-22-1549-2022>, 2022.