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Comment on egusphere-2022-504

Anonymous Referee #1

Referee comment on "Dimethyl sulfide cycling in the sea surface microlayer in the southwestern Pacific – Part 2: Processes and rates" by Alexia D. Saint-Macary et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-504-RC1, 2022

Review of: '**DMS cycling in the Sea Surface Microlayer in the South West Pacific: 2 Processes and Rates**'

Alexia D. Saint-Macary, Andrew Marriner1, Stacy Deppeler, Karl Safi, Cliff S. Law

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Synopsis

The reported study was undertaken as a component of the Sea2Cloud campaign onboard the R/V Tangaroa in the region of the Chatham Rise east of NZ. The objective was to examine physical and biogeochemical processes affecting the SML to determine if DMS/P enrichment occurs there and, if so, how this might modulate air-sea exchange of DMS. The overall conclusion derived from the time and location of this study was that DMS/P accumulation in the SML was minimal and apparently did not influence air-sea flux/emission of DMS.

General comments

The SML is the interfacial surface zone where exchange of trace gases between the ocean and the atmosphere takes place. This zone, which contains the bacterioneuston, is a zone where accumulation of dissolved organic substances can occur, leading to enhanced biological abundance, activity and metabolic turn-over. It is a zone that may undergo dynamic enrichment of organic carbon, suspended particulates and biofilm material

compared to the underlying water. In lines 53-57 of the introduction it is explained that DMS/P may be enriched in the SML where it can be stabilised through adsorption with dissolved organic compounds. Adsorption of DMS/P to organic compounds may provide an answer to the question posed in lines 11-12 of the abstract as to how enrichment of DMS may occur in the SML while it is also lost to the atmosphere. Organics that are least hydrophilic will partition into the SML where they may chemically interact with DMS to produce weakly-bound complexes, thereby lowering the Henry's law volatility constant of DMS while the adsorption complex exists. Over time, photolysis and microbial catabolism of the organic component of the DMS-organic complex may lead to delayed release of DMS. A natural mechanism such as this is analogous to the analytical technique described at L135 where DMS was adsorbed onto Tenax to be 'held up' for later release by thermal desorption.

Through a delayed release mechanism DMS may be enriched in the SML while also being exchanged to the atmosphere. In my opinion, studies of the SML would require co-measurement of dissolved organics because DMS/P is likely to be a function of the dissolved organics content in the SML. The organic component of the SML can be collectively measured in the form of TOC/DOC; data which is unfortunately absent from the on-board incubation experiments to accompany the DMS/P data. This is an oversight of the experimental design that I suggest is considered to be included in future SML research. Comparison of the SML off-shore at the mouth of an estuary rich in dissolved organics with an open ocean location such as the Chatham Rise is more likely to show significantly contrasting SML properties and air-sea DMS turn-over rates.

While this study reports some unique information about DMSP process rates in the SML (L241), a major limitation of the study is the low number of samples that were collected. It is good to see that this limitation of the SML incubation experiment is made clear to the reader in lines 147-148. Even though a number of SML physico-chemical variables were examined in the current study, the lack of replicate information in the form of duplicates six hours apart (T_0 and T_6) restricts the confidence that can be applied to the findings. Consequently, statements about observed correlations and what they imply need to be made with caution and words such as "confirms" (L 340) & "confirm" (L344) should be avoided. The statement "…the current study confirm that SML DMS enrichment is rare in the SW Pacific" (L344) is based on very limited data made at one location east of NZ in one season that may not be so at other locations at other times of the year in the broad study region. Walker et al., (2016) state that enrichment of DMS in the SML can be variable and is influenced by particular conditions. Given that the overall finding of this particular study contrasts with the report of Walker et al., (2016) from the same study region, caution needs to be exercised in the concluding statements of this report.

In the results and discussion there is detailed analysis of the DMS process rates and turnovers (defined in Table 2) for the three seawater types sampled; however, clear conclusions derived from this analysis are lacking. I would like to see a conclusion (section 5) added that provides concise findings from the complex analysis of data undertaken. Currently section 4.5 brings together some conclusion-like comments on air-sea emission and processes occurring in the SML but I would like to see a conclusion that summarises all the processes examined. On looking for conclusions I focussed on section 4.5. The statement 'Air-sea emission was the dominant process controlling DMS concentration in the SML' (L319) is inevitable regardless of whether DMS is enriched in the SML or not because seawater is supersaturated in DMS relative to the atmosphere which maintains

the net flux of DMS from the ocean. The statement at L321-323 "Consequently, despite net DMS accumulation in the SML (Table 4), the significantly greater air-sea loss should deplete DMS in the SML and so prevent enrichment (Table 5)" does not take into consideration the possibility that DMS may interact with organics in the SML to temporarily lower its volatility leading to enrichment.

This report is identified as a companion to a more substantial part-1 report referred to as Sâ□□M1 that is under revision (L85-86). The many references to S-M1 for methodology (e.g. details about the new sipper collection technique, L101-103) and DMS flux results (L158, 205-207) and references to S-M1 throughout the discussion leave the reader wondering about aspects of the study that are not available. The publication status of S-M1 is unclear. Is it possible to include an Ocean Science manuscript number or information that it has been or will be accepted for publication at L452?

Specific comments

Abstract

L11. "active" makes more sense than "reactive"

L12. Please change "have" to "has"

Introduction

L25. Again, "active" makes more sense than "reactive". Change to "natural sulfate aerosol precursor …"

L26. Please change to "that has been hypothesized to contribute to the regulation of climate ..."

L38. I suggest to say "largely influenced by phytoplankton type and density"

L53-54. This statement requires clarification; I suggest saying "The SML also contributes to possible climate regulation when air-sea exchanged trace gases are oxidised leading to secondary organic aerosol, which may influence atmospheric radiative properties"

L56-57. I suggest it would be better to say "due to stabilization by dissolved organic substances …". Please clarify what the dissolved DMSP is adsorbed to. I presume it is the stabilised dissolved organic substances?

L67. what sort of "material"? particulate organic materials?

L76. Please say "a SML sink for DMS" to clarify the aquatic compartment referred to here.

L79. Comment: The net effect of these enhanced but opposing processes in the SML may cancel each other out, so they might not be particularly significant in the SML.

L86 and L224. Please make it clear that the Walker et al., (2016) report was also a "South West Pacific regional study".

Method

L97-99. It is stated here that were six workboat deployments but information is not included for 6 stations in Table 1. If the workboat went out isn't there a sampling time and data from the vessel sampling system for the parameters given in Table 1 for 5-STW? Even though there was no deck-board incubation carried out for station 5 (L107) the reader would expect to see data in Table 1. I suggest that L107 in the caption for Fig 1 and L114-115 are moved together into L97-99 to explain up front the circumstances for station 5 (STW).

L110. change "5-m" to "5 m". Table 1; Please include the number of measurements (n=?) for each parameter. Add units for salinity (PSU?). Specify time zone (±? h UTC).

L118. Grammar here; "was placed" or "systems were placed"

L127. Please comment on if the DMDS analysed for DMS impurity?

L135. What type of Tenax? TA? TC?

L136. Please change "chromatography" to "chromatograph". Was a chromatography

column used? If so please specify the column type and the applied chromatographic conditions.

L139. It should be explained for those unfamiliar with the analytical approach that DMSP is base catalysed to DMS by the addition of alkali that allows DMSP to be indirectly measured in the form of DMS on a molar conversion basis.

L140. Please say "with analysis of the liberated DMS within 24 h …."

L141. add "DMS" before "calibration". Add "water" after "Milli-Q". Was it an actual Millipore water system? If not, say "deionised water".

L150. There is inconsistency in the description "net DMSP dark bacterial consumption rate," with what is shown in Table 2.

L154. There is inconsistency in the description "net DMS dark bacterial consumption rate," with what is shown in Table 2.

Table 2. Air-sea turnover in minutes is not shown to be so where turnover is (d).

Results

L169. For clarity please state that the "frontal station" are stations 1 & 2.

L180. I suggest to change "showed" to "was indicated"

L185. The shading in Fig 2 is confusing because shading is usually used to represent nighttime periods on plots. This is most confusing for Fig 4 where light and dark treatments are compared. I recommend that the shading is removed and the water mass types are separated by vertical dashed and/or dotted lines in Figs 2, 3 and 4.

L220. Fig 4 caption. Specify “set A (light)” and “set B (dark)” in the caption to improve clarity.

Please comment on the significance of the average values shown in Tables 3 &4.

Discussion

L233. Please define “EF DMS” here in the caption. Was EF previously defined? I presume it means enrichment factor?

L274. Define the “SOAP” experiment and where it was conducted.

L339. State the correlation value/s.

L340. This sentence is not clear, remove “play”. Can you really say the correlation ‘confirms’ that these particular phytoplankton were responsible for the observation given that there are many other marine organisms and factors in play in the SML that were not measured?

L344. Again, can you really say ‘confirms’ here based solely on your Sea2 Cloud campaign findings?

Acknowledgements

L346. Please check the spelling of Theresa B?

References

Some of the references have DOIs inserted but many do not. Please complete the referencing by including all available DOIs.

L457 appears to be out of place and requires revision.

Supplementary Information

The SI requires the same attention to detail as the manuscript.

Please include a title and authors heading for the SI document.

Fig S1 caption. Please provide a legend to explain each abbreviation and also specify what the different treatments are, and I recommend changing the shading to vertical dashed lines to avoid night/day confusion.