

Biogeosciences Discuss., referee comment RC2
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Comment on bg-2022-150

Anonymous Referee #2

Referee comment on "Concentrations of dissolved dimethyl sulfide (DMS), methanethiol and other trace gases in context of microbial communities from the temperate Atlantic to the Arctic Ocean" by Valérie Gros et al., Biogeosciences Discuss.,
<https://doi.org/10.5194/bg-2022-150-RC2>, 2022

General Comments

This manuscript describes a comprehensive set of dissolved reactive gas and microbiological measurements taken on a research cruise from the North Atlantic to the Arctic. The authors extensively discuss the sources and relationships between the measured trace gases and microbiology, and focus their discussion on dimethyl sulfide (DMS) and methanethiol (MeSH). They show that MeSH does not correlate with DMS during the entirety of the cruise. They find that MeSH can contribute on average 20%, and up to 50%, to the total waterside sulfur budget, defined by the sum of DMS and MeSH. Overall, this manuscript is well-structured and presents new findings that are valuable to the biogeosciences and atmospheric chemistry communities and should be published after the following main comments are addressed.

My main comment for this manuscript is that a more nuanced discussion of variations in the measured MeSH/(DMS+MeSH) ratio and the dominant factors controlling it would be extremely helpful. Little information currently exists on how this ratio varies based on environmental parameters, which has impacts for how we think about SO₂ production. This dataset provides measurements of MeSH in a region for the first time with varying temperature and salinity, meaning that we now have data to form more accurate models of SO₂ production based on how this ratio scales with different waterside parameters. Suggestions for discussion on this topic include:

- Addition of a column containing MeSH/(DMS+MeSH) to Table 1. Can any trends from the water classifications (salinity, temperature) explain the observed variations?
- In line 371-372, it's noted that at 78.6 °N, MeSH contributes up to 50% of total sulfur, but only 20-40% in 70-75°N. What is driving this difference?
- Looking at Fig. 2, it looks like in some regions MeSH and DMS covary (>71°N) and in some regions, there is little correlation (<68°N). Some more statistical analysis and

discussion of why there seems to be a correlation in certain water masses/time periods but not others would be useful.

- 5 could be revised to provide more information about any environmental parameters controlling this ratio (colored points by salinity, temperature, chlorophyll?) or additional regressions against these variables instead of just latitude.

Specific Comments – Manuscript

Line 19: It would be helpful to make it clear somewhere in the abstract that all gas measurements are in the dissolved phase in the seawater and not in the air. Potentially could also add “dissolved” to title.

Line 39: Instead of “rapidly oxidized”, can you state the atmospheric lifetime of DMS?

Line 40: It would be useful to add some references to the CLAW hypothesis. Some suggestions:

- Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem.*, 14, 315–337, <https://doi.org/10.1007/BF00115242>, 1992.
- Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, 326, 655–661, <https://doi.org/10.1038/326655a0>, 1987.

Line 41: Suggested references for DMSP demethylation producing MeSH:

- Kiene, R. P.: Production of methanethiol from dimethylsulfoniopropionate in marine surface waters, *Mar. Chem.*, 54
- Kiene, R. P. and Linn, L. J.: The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: tracer studies using ³⁵S-DMSP, *Geochim. Cosmochim. Ac.*, 64, 2797–2810, [https://doi.org/10.1016/S0016-7037\(00\)00399-9](https://doi.org/10.1016/S0016-7037(00)00399-9), 2000b.

Line 42: The atmospheric impacts of MeSH are less well-characterized than DMS, but we do know some about MeSH impacts based on its oxidation and reactivity. See references below:

- Butkovskaya, N. I. and Setser, D. W.: Product Branching Fractions and Kinetic Isotope Effects for the Reactions of OH and OD Radicals with CH₃SH and CH₃SD, *J. Phys. Chem. A*, 103, 6921– 6929, <https://doi.org/10.1021/jp9914828>, 1999.
- Tyndall, G. S. and Ravishankara, A. R.: Atmospheric oxidation of reduced sulfur species, *Int. J. Chem. Kinet.*, 23, 483–527, <https://doi.org/10.1002/kin.550230604>, 1991
- Novak, G. A.; Kilgour, D. B.; Jernigan, C. M.; Vermeuel, M. P.; Bertram, T. H. Oceanic Emissions of Dimethyl Sulfide and Methanethiol and Their Contribution to Sulfur Dioxide Production in the Marine Atmosphere. *Atmospheric Chem. Phys.* **2022**, 22 (9), 6309–6325. <https://doi.org/10.5194/acp-22-6309-2022>.

Line 49: Isoprene has also been shown to have a photochemical source.

- Ciuraru, R.; Fine, L.; Pinxteren, M. van; D’Anna, B.; Herrmann, H.; George, C. Unravelling New Processes at Interfaces: Photochemical Isoprene Production at the Sea Surface. *Sci. Technol.* **2015**, 49 (22), 13199–13205. <https://doi.org/10.1021/acs.est.5b02388>.

Line 52-53: Add a citation for OVOCs affecting the oxidative capacity of the remote atmosphere. Potentially this one could work:

- Singh et al. (2004). Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. *Journal of Geophysical Research Atmospheres*.

Lines 55-59: Acetone, methanol, acetonitrile, and acetaldehyde can also be anthropogenic, affecting whether the net flux is positive or negative. It is worth adding this in addition to whether the flux is positive or negative depending on oligotrophic water.

Lines 58-59: Another reference for acetone and acetaldehyde flux.

- Phillips, D. P., Hopkins, F. E., Bell, T. G., Liss, P. S., Nightingale, P. D., Reeves, C. E., Wohl, C., and Yang, M.: Air–sea exchange of acetone, acetaldehyde, DMS and isoprene at a UK coastal site, *Atmospheric Chem. Phys.*, 21, 10111–10132, <https://doi.org/10.5194/acp-21-10111-2021>, 2021.

Line 115: What do the different blue colors mean in Fig. 1? I suggest adding information

about the water classifications to this figure as well, like Fig. S6.

Line 152: It has been shown previously that other molecules can be measured in PTR-MS at the unit mass 63 where DMS is measured, such as ethylene glycol. Has this been accounted for in background measurements? Otherwise, if these are measured along this transect, they could artificially inflate the DMS measurements. It should be explicitly stated that all VOC measurements were taken at their unit mass $m/z + 1$ mass.

Line 155: Cite Blake et al. (2009) again for the thermodynamics of the proton transfer reaction.

Line 155-156: While PTR-MS can be a soft ionization technique, there is still the possibility for fragmentation of larger molecules to affect your measurements, so quantifying at the $m/z + 1$ mass may be the protonated molecule in addition to fragments of larger molecules. Have there been control experiments to support quantifying the molecules of interest only at the $m/z+1$ mass?

Line 157-158: What is the residence time in your tubing? Does this affect the measurements of any of your molecules, like acetonitrile?

Line 164-164: I don't see information in the SI on how MeSH was calibrated. Was this an assumed equivalent sensitivity as DMS? This calibration should also be included in the SI.

Line 194: I don't see any discussion of uncertainty for the trace gas measurements. Some discussion of this should be included either in the methods or in 3.1.1.

Line 195: What are your detection limits for acetone and acetaldehyde?

Line 205: I'm curious what's causing the high MeSH between 70 and 73-75 °N?

Line 209: I think this figure can be edited to help the story flow better. My suggestions are:

- Since CO presumably has a different source than DMS and MeSH, having it on the same panel is distracting. I'd suggest making this a 4-panel figure with CO on its own.

- Can some information about the water masses (info from Table 4) be included? Perhaps as a shaded background.
- Can information about the timing of these measurements be included? By plotting against latitude, it is hard to understand how many points are represented at each latitude, especially in the horizontal transect region near 70°N.

Line 227: I am unclear what MeSH_DMS is on Fig. 3b x-axis? Is this MeSH/(MeSH+DMS)? If so, should be updated to read more clearly.

Technical Corrections – Manuscript

Line 35: "source and sink" should be "sources and sinks"

Line 99: "some leads present)," should be "some leads present),"

Line 123: "Chl a l concentrations" should be "Chl a concentrations"

Line 156: "at their at their" should be "at their"

Line 254: "but the here found concentrations" should be "but here the concentrations found"

Line 324: "nm" should be "nM"

Technical Corrections – Supplemental

Line 8: There is something cut off in the upper righthand corner of Fig. S1.

Line 61: Fig. S3 is blurry and hard to read.

Line 77-79: I am unclear what it means for the Henry's law constant "whatever the solubility of the compound over 4 to 5 orders of magnitude"

Line 118: Bottom right panel y-axis in Fig. S6 is cut off. What is being plotted on the x-axis – is this both phytoplankton functional group and chlorophyll? Can the x-axis label be adjusted to be more clear?

Line 123: Should read "Supplement S7: "

Lines 131-146: References should be alphabetized and formatting should be consistent.

Line 133: Callahan et al. reference is missing a year.