

## ***Interactive comment on “A new marine biogenic emission: methane sulfonamide (MSAM), DMS and DMSO<sub>2</sub> measured in air over the Arabian Sea” by Achim Edtbauer et al.***

**Eric Saltzman (Referee)**

esaltzma@uci.edu

Received and published: 21 January 2020

This paper reports on the first detection of an organic sulfur compound in the atmosphere over the ocean. If this compound is actually present in marine air, it would be a very exciting finding and certainly raise new questions about reduced sulfur cycling in the surface oceans. Identification of the compound by PTR-TOF seems convincing to me. I do have some further analytical questions that the authors can hopefully address. It is exciting to see a new observation like this, and I congratulate the authors on looking deeply at their data for more than the usual suspect molecules. This paper potentially opens a new chapter in understanding of the ocean/atmosphere sulfur

C1

cycle.

Below are some specific issues that I think should be addressed prior to publication. A number of others are noted in the annotated manuscript attached.

My main question about the finding relates to inlets. Both DMSO<sub>2</sub> and MSAM are low volatility compounds. Even in a heated inlet, these compounds likely experience considerable wall interactions and I suspect that the inlet response time for these molecules is considerably longer than the time resolution of 1 minute quoted for other gases. The inlet walls are likely coated with a complex mixture of ambient compounds, including ammonia, and DMSO<sub>2</sub> and MSAM experience exposure to a range of reactive oxidants like ozone, peroxides, reactive halogens, etc. that can give rise to free radicals on surfaces. Is there any observational evidence that MSAM is NOT generated on the inlet walls? An example of such evidence might be that ambient levels don't change after replacing or cleaning the inlet tubing or sampling with only a very short inlet tube. If there is no empirical evidence, it should be noted in the paper, with a statement that such artifacts cannot be ruled out at this time. I don't have any specific reaction precursor or reaction pathway in mind, but I think the reader should know if it remains a possibility.

The paper has a lengthy discussion about trajectory analysis and chlorophyll a with the goal of identifying the source region for MSAM. The discussion is overly complicated by the introduction of weighting factors (both linear and exponential) to correct for dispersion and atmospheric losses. These weighting factors do little to alter the results but will certainly confuse many readers. The relationship to chlorophyll a and the upwelling region would be pretty convincing, even without the weighting. Unfortunately, the trajectories are never shown, so the reader can't decide for themselves. I strongly suggest superimposing some illustrative trajectories over the MODIS data on Figure 6. I would recommend simplifying the discussion in the paper, and simply noting that weighting doesn't materially change the results. As far as I am concerned the weighting discussion could be entirely pushed into the Supplement.

C2

Another issue of concern is the last paragraph of the discussion about MSAM (p14, line 12) where the paper states: Because of the comparable lifetimes of MSAM and DMS, we can estimate the relative emission of MSAM to DMS from the ratio of the mixing ratios of ([MSAM]/[DMS]). This directly contradicts the earlier statement that the lifetime of MSAM is 75 days and the lifetime of DMS as 1.3 days. I see no way to reconcile these statements and conclude that perhaps there was an error in production of the final text. Either I missed the point completely, or this paragraph needs rethinking.

As food for thought...perhaps consider analyzing the diurnal variability of DMS, DMSO<sub>2</sub>, and MSAM further as they might provide useful insight into the processes controlling their cycling. The data is there in the time series plots but it is not analyzed in the manuscript. I suggest extracting some of the data (maybe periods with consistent trajectories) and computing average diurnal cycles. At the very least, this could shed some light on whether NO<sub>3</sub> plays a role in DMSO<sub>2</sub> formation, whether the variations in MSAM are consistent with the very long estimated photochemical lifetime, or whether diurnal variability in MSAM emissions are required.

Putting aside the exciting science, I think the manuscript needs editing prior to publication. In particular, the introduction is not well framed. It almost looks like the introduction was written before the paper, then not revised to match the paper. For example, the issue of alkyl nitrates is raised and never mentioned again in the manuscript. Alkyl nitrates have little to do with the subject at hand, since the paper does not stress the role of MSAM as a nitrogen source to the oceans. If the author thinks that MSAM deposition of N to the oceans is important, then there should be a paragraph in the intro dedicated to that subject, and another in the conclusions to explore the implications. Personally, I think the scope of the paper is good as is, and the intro should be revised accordingly.

I also think there should be at least some statement about what is known about the biosynthesis or utilization of this MSAM. If the answer is "nothing is known", that's fine. Many readers will want to know that. If this molecule is known to occur in biological

C3

systems, then some citations to that would be very helpful.

Grammatical editing is needed to improve readability. There are many instances where sentences are far more complex than required to convey the intended meaning, detracting from the clarity of the paper. I have attached an annotated copy of the manuscript noting some of these. There is also a tendency for imprecise language referring to oceanographic or biological phenomena. For example, the relationship between chlorophyll a and biological activity is not described in terms that a biological oceanographer would deem accurate. Another was this: "Upwelling generally leads to eutrophic zones in the surface ocean and therefore to regions of high phytoplankton activity. . ." Eutrophication is not needed for phytoplankton growth, just nutrients and sunlight.

Some additional issues: Mixing ratios are not a great unit because of past confusion in the literature (molar vs volume basis). I would recommend switching to mole fraction, which is unambiguous. Define the term (i.e. molar mixing ratio) early on, then use ppb throughout without confusion. Personally, I was surprised that they used ppb instead of ppt, which is much more common in the DMS literature. All the mixing ratios discussed are considerably less than 1 ppb anyway.

Supplement:

The discussion of gas deposition was well done, except that no units are specified for several of the terms. I presume kg is in m/s?

Note fyi: NaCl+NaHCO<sub>3</sub> is not usually considered artificial seawater, and is generally not a good chemical analog. Typically Mg, Ca salts are included because these have very different ion pairing characteristics than Na.

Some of the grammar in the supplement is not good. For example, I have no idea what this is intended to mean: "Calculations of leg 1 with low weighting parameters  $p = 0.02-0.1$  lead to a small increase in total chlorophyll a exposure of the trajectories

C4

but not in the exposure in the Somalia upwelling compared to other higher weighting parameters “

Fonts on the plots in supplement are way too small.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-1021/acp-2019-1021-RC1-supplement.pdf>

---

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1021>, 2020.