Interactive comment on “A new marine biogenic emission: methane sulfonamide (MSAM), DMS and $DMSO_2$ measured in air over the Arabian Sea” by Achim Edtbauer et al.

Anonymous Referee #1

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Edtbauer et al. present new measurements of a previously unreported sulfur/nitrogen molecule (methane sulfonamide) measured in the gas-phase during a research cruise in the Arabian Sea. MSAM is observed to be strongly correlated with DMSO2 suggesting a common marine biogenic source. Given the lack of gas-phase pathways for MSAM formation from DMS oxidation, the authors suggest that MSAM is directly emitted to the atmosphere. I think the paper presents new insight and uncovers a potentially interesting new set of reactions that could impact particle formation in marine environments. However, given the Henry’s law constant for MSAM, I have several concerns regarding inlet transmission and inlet articfacts that need to be addressed prior to publication.

We thank the reviewer for the encouraging remarks and insightful comments.

General comments:

1) Is the ocean a net source or sink for MSAM? The authors argue in section 4.2 that the lifetime of MSAM is set by deposition back to the ocean surface (due to the slow OH reaction rate). Based on a Henry’s law constant of 3.3-6.5 x 105 M / atm, the authors find that MSAM has a lifetime with respect to deposition of 10-40 hours. It is completely reasonable that a molecule that is this soluble will dry deposit to the ocean surface promptly (likely with little to no water side resistance). However, this argument seems inconsistent with the premise that MSAM is directly emitted from the ocean surface? The surface water concentrations that would need to be maintained to support an emission flux for MSAM must be enormous. This begs the question how this could be sustained.

We now include the following text in the discussion section 4.5 to make this point more clearly:

From the dataset presented in this paper, the ocean is expected to be a sink for MSAM. This is shown through our calculations of the lifetime (few hours to a few days) which are dominated by deposition. The ocean can only become a source of MSAM to the atmosphere if the concentration of MSAM in surface seawater is so large that emission locally dominates over deposition. Our measurements indicate that this was the case in the region of the Somalia upwelling. Although, no seawater measurements were made in that region to confirm this, the trajectory data presented here indicate that biologically active areas are able to produce sufficiently large MSAM concentrations.

2) Inlet transmission: I would expect that molecules like MSAM have very poor inlet transmission. The authors note that they sampled through a Teflon membrane to remove sea-spray. There was no mention in the paper of inlet characterization experiments to defend that MSAM was not produced on the Teflon membrane or on the walls of the inlets. The correlation with DMSO2 is very interesting, but also begs the question

whether a surface reaction of DMSO2 (or analogous species) with adsorbed NH3 or NH4+ can drive the production of MSAM. This would still be an interesting result, but is a different picture than what is discussed in the manuscript.

This is a valid point which was also raised by reviewer 1. We have addressed this by adding a new section 2.4 (Discussion inlet effects) into the manuscript which discusses inlet effects. The second paragraph of this new section addresses the likelihood of MSAM formation in the inlet:

The partitioning of MSAM to the inside wall of the Teflon tubing raises the question whether the observed MSAM could be generated there on surfaces. No inlet test was done during the campaign to address this issue since this discovery was a surprise. Therefore, we cannot rule out completely that such an effect occurs. However we do consider it highly unlikely that MSAM was formed via a surface reaction of DMSO2 (or an analogous species) with NH3 or NH4+. DMSO2 as well as NH3 and NH4+ are both very unreactive molecules and the interaction would be taking place on a non-catalytic Teflon surface. Additionally, we see no way of how NH4+ and NH3 could lose their hydrogen atoms in order to form the requisite NH2 group. A chemical synthesis pathway for sulfonamides from sulfonic acids has been published (de Luca and Giacomelli, 2008). The first step towards the production of MSAM would be removal of the whole OH group of methane sulfonic acid (MSA), creating a CH3SO2+ ion. In an aqueous solution, the preferred reaction is, however, the removal of H+, i.e. forming CH3SO3-. In this chemical synthesis, aggressive reagents such as trichlorotriazine and high energy (e.g. from a microwave) are used to create an intermediate CH3SO2Cl which reacts as a CH3SO2+ ion. In the second step, this CH3SO2+ ion reacts with an amine (for MSAM formation this would need to be replaced by NH3) in a strong basic solution (NaOH(aq)), abstracting an H from NH3 to form MSAM. The fact that sulfonic acids and not sulfones are used as precursors in synthesis of sulfonamides points out that formation from sulfones is either not possible or more difficult than with sulfonic acids. Formation of MSAM therefore needs aggressive reagents, input of energy and strong basic conditions which were not present in our inlet.

De Luca et. al. 2008: https://pubs.acs.org/doi/10.1021/jo800424g

Specific comments:

1) Page 2, line 15: It would be good to include a brief discussion of ammonia / ammonium air-sea gas exchange here.
The potential of NH3 to affect MSAM in the inlet is now discussed (see above and reply to comment 1 by reviewer 1). Further discussion of ammonia/ammonium is beyond the scope of this paper.

2) Section 2: Were any other trace gases measured on this cruise that can be used for air-mass characterization. If not, are there other VOCs from the PTR that can be used?

Other VOCs were measured during the cruise. We draw the reviewer's attention to the regional characterization of NMHCs by GC-FID (Bourtsoukidis et. al. ACP 2019) and the discovery of new hydrocarbon sources (Bourtsoukidis et al. Nat. Comms. 2020). The overall OH reactivity has been documented by Pfannerstill et al. ACP 2019. Furthermore selected VOCs from the PTR-TOF with particular emphasis on carbonyl compounds have been recently published by Wang et al. ACPD 2020). As shown in all the aforementioned works, the Arabian Sea part under investigation in this paper is characterized by low values of these VOCs measured. Especially VOCs related to anthroprogenic activities were very low. The three molecules presented in this study are the exception. They are higher in the Arabian Sea region than in the other regions. So the absence or very low concentrations of the other molecules plus the high values (compared to other regions) of

DMS, DMSO2 and MSAM characterize this part of the cruise as mostly influenced by clean marine air. See Bourtsoukidis et. al. 2019, Pfannerstill et. al. 2019 and Wang et. al. 2020.

Bourtsoukidis et. al. 2019: https://doi.org/10.5194/acp-19-7209-2019
Bourtsoukidis et. al. 2020: https://doi.org/10.1038/s41467-020-14375-0
Pfannerstill et. al. 2019: https://doi.org/10.5194/acp-19-11501-2019
Wang et. al. 2020: https://doi.org/10.5194/acp-2020-135

We now include the following short paragraph at the beginning of section 3:

This study focuses on the two crossings of the Arabian Sea during the AQABA campaign. The Arabian Sea was generally characterized by low values of VOCs, especially VOCs related to anthropogenic activities (Bourtsoukidis et al., 2019, 2020; Pfannerstill et al., 2019; Wang et al., 2020). The three molecules presented in this study are the exception. They were higher in the Arabian Sea region than in the other regions. So the absence or very low concentrations of the other molecules plus the high values (compared to other regions) of DMS, DMSO2 and MSAM characterize this part of the cruise as mostly influenced by clean marine air.

3) Page 5, line 5: More information should be included on how the background was conducted. Was the synthetic air added to the entire inlet manifold (including the filter) or just to the instrument? If the background air was added to the full inlet manifold, there may be useful information in the decay curves following synthetic air additions.

We included the following sentence into section 2.3:

Synthetic air was supplied to the instrument only and not the whole inlet.

4) Page 5, line 10: If inlet transmission was not measured, how can a conservative estimate of a factor of 2 be stated? If the molecules are lost at the diffusion limit to the walls of the inlet or formed on the inlet walls, this uncertainty could be much larger than this. Inlet transmission should be measured for DMSO2 and MSAM to constrain this number. At a solubility of 3.3-6.5 x 105 M / atm, I would expect that every collision with a wet wall or wet filter would lead to mass accommodation and likely a very high net reactive uptake coefficient.

We included the following discussion about inlet transmission into the new section 2.4 (Discussion inlet effects):

Semi-volatile and especially low-volatile compounds can partition from the gas phase to the walls in Teflon tubing and therefore delay the instrument response to these compounds (Pagonis et al., 2017). The delay in instrument response caused by the inlet can be measured by applying a step concentration change and determination of the time it takes for the compound signal response to reach 90% of the final signal response. We therefore performed tests with step concentration changes of MSAM in the laboratory. After a step concentration change the delay time was about 2 minutes for a 1/8" Teflon inlet of 0.4m in length and a flow rate of 100sccm. It is known that the delay depends proportionally on tubing length and diameter and inversely on the flow rate and saturation concentration (Pagonis et al., 2017). On this basis we can estimate the delay time of our AQABA inlet setup (length 10m, 1/2" Teflon tubing, flow of 3slpm) to ≈ 7 minutes. This implies that larger concentration changes on timescales of minutes will be underestimated for DMSO2 and MSAM. In this paper we show that DMSO2 and MSAM originated from the Somalia upwelling and not from local sources around the ship. Therefore, we do not expect abrupt concentration changes on the timescale of minutes. Even if the delay of DMSO2 and MSAM through the inlet was considerably *longer than estimated it would be still sufficient to measure accurately the concentration since these species were detected over considerably longer time periods. We will only underestimate if large changes of concentration happen on timescales close to the inlet delay time. To take account of such circumstances, that we cannot rule out completely, we state that the reported molar mixing ratios are considered to be a lower limit.*

Pagonis et. al. 2017: https://doi.org/10.5194/amt-10-4687-2017

5) Figure 5: The colorbar legend is not legible. Please consider increasing the font size.

Done, we have increased the colorbar legend size in Figure 5.

6) Page 9, line 21: Have the authors looked at the ammonia signals from the PTR-MS. If so, are they correlated with MSAM?

We examined the ammonia signal from the PTR-MS but it displayed no correlation with MSAM. In our opinion we do not think that the protonated signal of NH3 is representative of the ammonia concentration. When using the H3O+ mode, NH3 is produced in very large amounts in the source itself, giving a very high background which complicates quantification (Norman et. al. 2007). Therefore, often the signal observed can be more influenced by small changes in the source discharge then by variations in ambient ammonia levels.

Norman et. al. 2007: https://doi.org/10.1016/j.ijms.2007.06.010