

Interactive comment on “A new marine biogenic emission: methane sulfonamide (MSAM), DMS and DMSO₂ 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 artifacts that need to be addressed prior to publication.

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 $3.3\text{-}6.5 \times 10^5 \text{ M / atm}$, 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.

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.

Specific comments:

1) Page 2, line 15: It would be good to include a brief discussion of ammonia / ammonium air-sea gas exchange here.

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?

3) Page 5, line 5: More information should be included on how the background was

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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.

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 $3.3\text{--}6.5 \times 10^5 \text{ M / atm}$, 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.

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

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

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