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.

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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 ad-dress. 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 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 DMSO2 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 DMSO2 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 a 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.

We thank Prof Salzmann for the encouraging comments and are pleased that he shares our enthusiasm for this discovery. We greatly appreciate his critical comments on this manuscript and we have revised the paper accordingly.

Regarding the possibility of inlet production, although we consider it unlikely, we agree that this point should be discussed along with inlet effects in general. We have now added the following section into the manuscript to cover these points:

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 $DMSO_2$ and MSAM. In this paper we show that $DMSO_2$ 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 $DMSO_2$ 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.

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 $DMSO_2$ (or an analogous species) with NH_3 or NH_4^+. $DMSO_2$ as well as NH_3 and NH_4^+

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 NH_4^+ and NH_3 could lose their hydrogen atoms in order to form the requisite NH_2 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 $CH_3SO_2^+$ ion. In an aqueous solution, the preferred reaction is, however, the removal of H^+, i.e. forming $CH_3SO_3^-$. In this chemical synthesis, aggressive reagents such as trichlorotriazine and high energy (e.g. from a microwave) are used to create an intermediate CH_3SO_2Cl which reacts as a $CH_3SO_2^+$ ion. In the second step, this $CH_3SO_2^+$ ion reacts with an amine (for MSAM formation this would need to be replaced by NH_3) in a strong basic solution (NaOH(aq)), abstracting an H from NH_3 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.

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 up-welling 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.

On reflection we agree. We have shortened that discussion and moved the detailed examination of the weighting factor dependence to the Supplemental. As requested we added HYSPLIT trajectories plots for the first and second leg in Figure 6. These more clearly show the origin of the air containing MSAM measured at the ship.

Another issue of concern is the last paragraph of the discussion about MSAM (p14, line12) 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.

We agree that this is confusing. The key point is that the lifetimes of MSAM and DMSO2 are controlled by deposition rather than OH oxidation. This was not well phrased in section 4.2. Therefore we added the following sentences to the manuscript in section 4.2, 4.5 and 5:

4.2 Atmospheric lifetimes of DMS, DMSO2 and MSAM

The lifetimes for MSAM and DMSO2 are therefore controlled by the deposition rate to the ocean surface and not by OH oxidation. This means that DMS, DMSO2 and MSAM have similar lifetimes.

4.5 MSAM

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.

5 Conclusions

The main loss mechanism for MSAM and DMSO2 is deposition to the ocean surface with lifetimes of a few hours to a few days.

As food for thought...perhaps consider analyzing the diurnal variability of DMS,DMSO2, 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 NO3 plays a role in DMSO2 formation, whether the variations in MSAM are consistent with the very long estimated photochemical lifetime, or whether diurnal variability in MSAM emissions are required.

We had also considered putting this in the original manuscript but decided against it since the interpretation would have been ambiguous. The relatively short duration of the dataset containing MSAM and DMSO2, taken on a moving platform means that variations can be interpreted as diel variations (driven by emission or atmospheric removal) or as source variations. However, now for completeness we include 24 hour cycles of DMS, DMSO2 and MSAM in the supplement section. The time period of interest is from the 12th till the 15th of August (second Leg Arabian Sea). In that time period on the 12th we start to get influenced by the upwelling emission and on the 15th we see it declining. This leaves us with only two complete days (13th and 14th of August) for our diel variability analysis.

We included the following at the end of section 4.4 to address the issues of DMSO2 formation from NO3 and the diel variability analysis:

4.4.3 NO3

Most studies show no formation of DMSO2 from NO3 oxidation (Barnes et al., 2006). NO3 oxidation of the intermediate DMSO is known to only yield DMSO2 (Falbe-Hansen et al., 2000). However, NO3 oxidation is not thought to produce DMSO (Barnes et al., 2006). Maybe the increase in DMSO2 after sunset (see Fig. 3 c) is an indication that NO3 is oxidizing the remaining DMSO formed during the day.

With the data presented here it is not possible to decide if one or some of the above mentioned mechanisms are responsible for the observed DMSO2 values. A diel analysis of DMS, MSAM and DMSO2 was made. But due to the fact that we only have two consecutive days with elevated DMSO2 on a moving platform the results must be viewed with caution since variation may come from source or removal process variation. Nevertheless, for completeness the plots and description of these diel variability plots are in the supplement (see Sect. S4).

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 de-position 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.

The new ocean emission MSAM contains both nitrogen and sulfur atoms. To our knowledge this is unique, making this molecule potentially relevant to nitrogen and sulfur cycles in the ocean. In the introduction, we therefore gave examples of organo- nitrogen containing (alkyl nitrates) and sulfur containing (DMS) emissions from the ocean. We agree with Prof. Salzmann that a full discussion of the potential implications for nitrogen deposition is beyond the scope of this paper. We have therefore revised the introduction. It is now more concise and focused on the results of the paper.

The revised introduction is as follows:

1 Introduction

The ocean plays an important role in the atmospheric chemistry of many trace gases and profoundly influences the global sulfur and nitrogen cycles (Brimblecombe, 2014; Sievert et al., 2007; Bentley and Chasteen, 2004; Fowler et al., 2013, 2015). Dimethyl sulphide (DMS) emitted from the ocean accounts for roughly half of the natural global atmospheric sulfate burden. The global DMS flux to the atmosphere was recently estimated to be 28.1 (17.6–34.4)Tg S per year, equivalent to 50% of the anthropogenic sulfur inputs (Webb et al., 2019). In contrast, nitrogen is often a limiting nutrient for phytoplankton growth in the ocean (Voss et al., 2013). Nonetheless, ocean emissions of organic nitrogen do occur in the form of amines (R-NH$_2$) (Ge et al., 2011; Gibb et al., 1999) and in inorganic forms such as nitrous oxide (N$_2$O) (Arévalo-Martínez et al., 2019) and ammonia (Gibb et al., 1999; Johnson et al., 2008; Paulot et al., 2015), particularly in upwelling regions (Carpenter et al., 2012).

Upwelling regions of the ocean are those where nutrient rich waters from depths of 100 to 300 meters are brought to the surface (Voss et al., 2013; Kämpf and Chapman, 2016). Upwelling leads to nutrient richer zones in the surface ocean and therefore to regions of high phytoplankton activity, resulting in strong carbon dioxide uptake and the release of various volatile organic compounds including sulfur, halogen and alkene containing trace gases (Arnold et al., 2010; Colomb et al., 2008; Bonsang et al., 2010; Lai et al., 2011; Yassaa et al., 2008). In the Arabian Sea, the location of this study, the Somalian coastal upwelling is a major feature. It is considered the fifth largest upwelling system in the world (deCastro et al., 2016; Ajith Joseph et al., 2019).

Here we present trace gas measurements taken on a shipborne circumnavigation of the Arabian Peninsula. Relatively few measurements have been made in this region due to political tensions and piracy. Transects of the Arabian Sea (the most southerly section of the route) showed high levels of sulfur containing gases. These include DMS, Dimethyl sulfone ($DMSO_2$*) and methane sulfonamide (MSAM), a new marine emission that unusually contains both sulphur and nitrogen atoms. DMS is known to stem from biochemical reactions within phytoplankton that produce its precursor dimethylsulphoniopropionate (DMSP) (Kiene et al., 2000). Although only a small fraction of the DMS produced within the ocean is released into the atmosphere (Vila-Costa et al., 2006), it is still the most abundant form of oceanic sulphur emission (Kloster et al., 2006; Quinn and Bates, 2011; Lana et al., 2011; Liss et al., 2014). The oxidation mechanism of DMS in the atmosphere is complex and still not fully understood (Mardyukov and Schreiner, 2018; Barnes et al., 2006; Ayers and Gillett, 2000; Chen et al., 2018).* $DMSO_2$*, the second sulphur containing species measured in this study, is a product of DMS oxidation by the OH radical (Arsene et al., 2001; Barnes et al., 2006). It can be formed directly from DMS, via the intermediate dimethyl sulfoxide (DMSO) and from oxidation of DMSO with BrO and* NO_3 *(Barnes et al., 2006). Even though oxidation of DMS in the atmosphere is still not fully understood, reaction with the hydroxyl radical (OH) is considered the dominant loss pathway (Khan et al., 2016). Significantly DMS oxidation ultimately yields sulfates which may act as cloud condensation nucleii (see Fig. 1). In the case of MSAM, there are no previously reported measurements of this species. The MSAM data are assessed here through comparison with the better known DMS and* $DMSO_2$ *species and with respect to airmass back trajectories and chlorophyll exposure, in particular in relation to the upwelling region. In summary, we examine the provenance, distribution and fate of DMS,* $DMSO_2$ *and the new marine emission MSAM in the region of the Arabian Sea.*

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

We added the following lines into section 4.5:

To our knowledge there have been no reports of MSAM occurring or being produced in biological systems. MSAM belongs to the class of sulfonamides which is known for its antibacterial properties and it has therefore been used in antibacterial drugs Sköld (2010). The only mentioning of MSAM in this context was as a metabolite of a drug detected in human urine (Anacardio et al., 2009).

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.

We thank the reviewer for these helpful annotations. We incorporated them into the manuscript!

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.

Done. We now define the term molar mixing ratio in the abstract and use ppt instead of ppb throughout the manuscript. The following sentences in the abstract was included:

Molar mixing ratios in picomole of species per mole of air (throughout this manuscript abbreviated as ppt) of DMS were in the range 300 - 500 ppt during the first traverse of the Arabian Sea (first leg) and 100 to 300 ppt in the second leg.

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?

We altered the sentence describing the exchange flux equation in the supplement stating the dimensions of the individual variables. The altered sentence is now as follows:

Where KG is the overall mass-transfer coefficient (has dimensions of velocity), G is the gas phase concentration, A the aqueous phase concentration and H the Henry's law constant in the dimensionless form.

Note fyi: NaCl+NaHCO3 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.

We rephrased the corresponding sentence as follows:

In order to resemble sea water more closely we added 35 g NaCl and 0.5 g NaHCO3 to a combined volume of 1 L in MilliQ water. The obtained water is in the following referred to as sea water. Strictly speaking it does not classify as artificial sea water because some ingredients like magnesium and calcium salts are missing.

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

We rewrote this sentence in the supplement to:

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 (yellow lines in graphs) but no increase is seen when only the Somalia upwelling region is considered (black lines in graphs). This means that chlorophyll a pick up further away than the Somalia upwelling is responsible for this.

“Fonts on the plots in supplement are way too small.

Done: We increased the plot size to make them legible.