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.

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 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 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.

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.

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_2O) (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.

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

Received and published: 6 March 2020

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

A new marine biogenic emission: methane sulfonamide (MSAM), DMS and $DMSO_2$ measured in air over the Arabian Sea

Achim Edtbauer[1], Christof Stönner[1], Eva Y. Pfannerstill[1], Matias Berasategui[1], David Walter[1,2], John N. Crowley[1], Jos Lelieveld[1,3], and Jonathan Williams[1,3]

[1]Atmospheric Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
[2]Department Biogeochemical Processes, Max Planck Institute for Biogeochemistry, Jena, Germany
[3]Energy, Environment and Water Research Center, The Cyprus Institute, Nicosia, Cyprus

Correspondence: Achim Edtbauer (a.edtbauer@mpic.de)

Abstract. We present the first ambient measurements of a new marine emission methane sulfonamide (MSAM: CH_5NO_2S), along with dimethyl sulfide (DMS) and dimethyl sulfone ($DMSO_2$) over the Arabian Sea. Two shipborne transects (W → E, E → W) were made during the AQABA (Air Quality and Climate Change in the Arabian Basin) measurement campaign. ~~DMS mixing ratios~~ Molar mixing ratios in picomole of species per mole of air (throughout this manuscript abbreviated as ppt) of DMS were in the range ~~0.3–0.5~~300–500 ~~ppb~~ ppt during the first traverse of the Arabian Sea (first leg) and ~~0.1 to 0.3~~100–300 ~~ppb~~ ppt in the second leg. In the first leg $DMSO_2$ was always below ~~0.04~~40 ~~ppb~~ ppt and MSAM was close to the limit of detection. During the second leg $DMSO_2$ was between ~~0.04–0.12~~40–120 ~~ppb~~ ppt and MSAM was mostly in the range ~~0.02–0.05~~20–50 ~~ppb~~ ppt with maximum values of ~~0.06~~60 ~~ppb~~ppt. An analysis of HYSPLIT back trajectories combined with calculations of the exposure of these trajectories to underlying *chlorophyll*~~*a* content in the~~ in the surface water revealed that most MSAM originates from the Somalia upwelling region, known for its high biological activity. MSAM emissions can be as high as one third of DMS emissions over the upwelling region. This new marine emission is of particular interest as it contains both sulfur and nitrogen, making it potentially relevant to marine nutrient cycling and marine atmospheric particle formation.

1 Introduction

~~Sulfur and nitrogen are essential for all lifeforms and the~~

The ocean plays an important role in the ~~global cycling of both elements. The ocean represents a large reservoir for sulfur, some of which can enter the atmosphere in organically bound forms such as dimethyl sulfide~~ atmospheric chemistry of many trace gases and profoundly influences the global sulfur and nitrogen cycles (Brimblecombe, 2014; Sievert et al., 2007; Bentley and Chastee . Dimethyl sulphide (DMS) ~~. DMS~~ emitted from the ~~oceans~~ ocean accounts for roughly half of the natural global atmospheric sulfate burden. ~~A recent estimate of~~ The global DMS flux to the atmosphere ~~is~~ was recently estimated to be 28.1 (17.6~~–34.4) Tg S per year which amounts to around~~ –34.4) Tg S per year, equivalent to 50 % of the anthropogenic sulfur inputs (Webb et al., 2019). ~~In contrast, nitrogen is usually~~ Nitrogen is often a limiting nutrient for phytoplankton growth ~~(Voss et al., 2013), with nitrate deposition from the air and oceanic upwelling being important factors in the oceans primary productivity~~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_2O) (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 in the oceans 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)and in which highly specialized marine organisms can proliferate. 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).Upwelling generally leads to eutrophic zones in the surface ocean and therefore to regions of high phytoplankton activity, resulting in high 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; B . These species can impact ozone formation and loss in the marine boundary layer (e.g. Williams et al. (2010))

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.

In the oceans, DMS is known to stem from biochemical reactions within phytoplankton result in the production of that produce its precursor dimethylsulphoniopropionate (DMSP) , the primary biological precursor for DMS in the ocean (Kiene et al., 2000) . A (Kiene et al., 2000). Although only a small fraction of the DMS produced in within the ocean is released into the atmosphere (Vila-Costa et al., 2006), where it is oxidized predominantly by the hydroxyl radical (OH), ultimately yielding sulfates which may act as cloud condensation nucleii (see Fig. 1). Even though only a small fraction of DMS is released to the atmosphere, it is it is still the most abundant form in which the ocean releases gaseous sulfur (Kloster et al., 2006; Quinn and Bates, 2011; Lana et al., 2011; .This makes DMS an important component of the global sulfur cycle (Bentley and Chasteen, 2004; Barnes et al., 2006; Zavarsky et al., 201 . The oxidation mechanisms 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 are 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 from OH oxidation of DMSdirectlydirectly 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).

Marine emissions containing reactive nitrogen are generally found at much lower mixing ratio. This is likely as nitrogen is a limiting nutrient to pelagic ecosystems.Alkyl nitrates ($RONO_2$)have been observed in equatorial upwelling areas at low ppt levels (Chuck et al., 2002) and methylated amines were also present at similarly low concentrations (Ge et al., 2011). To date, no compound containing both sulfur and nitrogen has been identified as a marine emission.In this study 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 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 a new sulfur containing species, methane sulfonamide (MSAM). The provenance of these species is investigated with respect to chlorophyll exposure of the airmasses sampledthe new marine emission MSAM in the region of the Arabian Sea.

2 Materials and Methods

2.1 AQABA campaign

From June 25th to September 3rd 2017, the Air Quality and Climate Change in the Arabian Basin (AQABA) cruise took place on the research vessel *Kommandor Iona*. The first leg of the cruise started from La-Seyne-sur-mer near Toulon (France), and headed through the Suez Canal, around the Arabian Peninsula and ended in Kuwait. The second leg took the same route back (see Fig. 2). Onboard the ship were a weather station and four laboratory containers equipped with instrumentation for on- and offline measurement of a large suite of (trace) trace gases, particles and radicals (Bourtsoukidis et al., 2019) (Bourtsoukidis et al., 2019, 2020; Wang et al., 2020).

2.2 Sampling

A 5.510 m high (above deck sea level) high volume-flow inlet (HUFI) (diameter 15 cm) was used to draw ambient air down to the containers at a flow rate of 10 m^3/min. The HUFI was situated between the four containers on the foredeck so that when the ship headed into the wind no interference from the vessel's smokestack or indoor ventilation were measured. From the center of the HUFI, air was drawn continuously at a rate of ca. 5 standard liter per minute (slpm) (first leg) or 3 slpm (second leg) into an air-conditioned laboratory container via an insulated FEP (fluorinated ethylene propylene) tube (1/2" = 1.27 cm o.d., length ca. 10 m). The tube was heated to 50–60 °C to avoid condensation inside the air-conditioned container. To prevent sampling of sea spray and particles, a weekly routinely changed PTFE (polytetrafluorethylene) filter was installed in the inlet line before it entered the container. This inlet system was employed for the measurements of VOCs and total OH reactivity (Pfannerstill et al., 2019) simultaneously. The inlet residence time for the VOC measurements was determined by a spiking test with acetone, and was 12 s during the first leg and 26 s during the second leg.

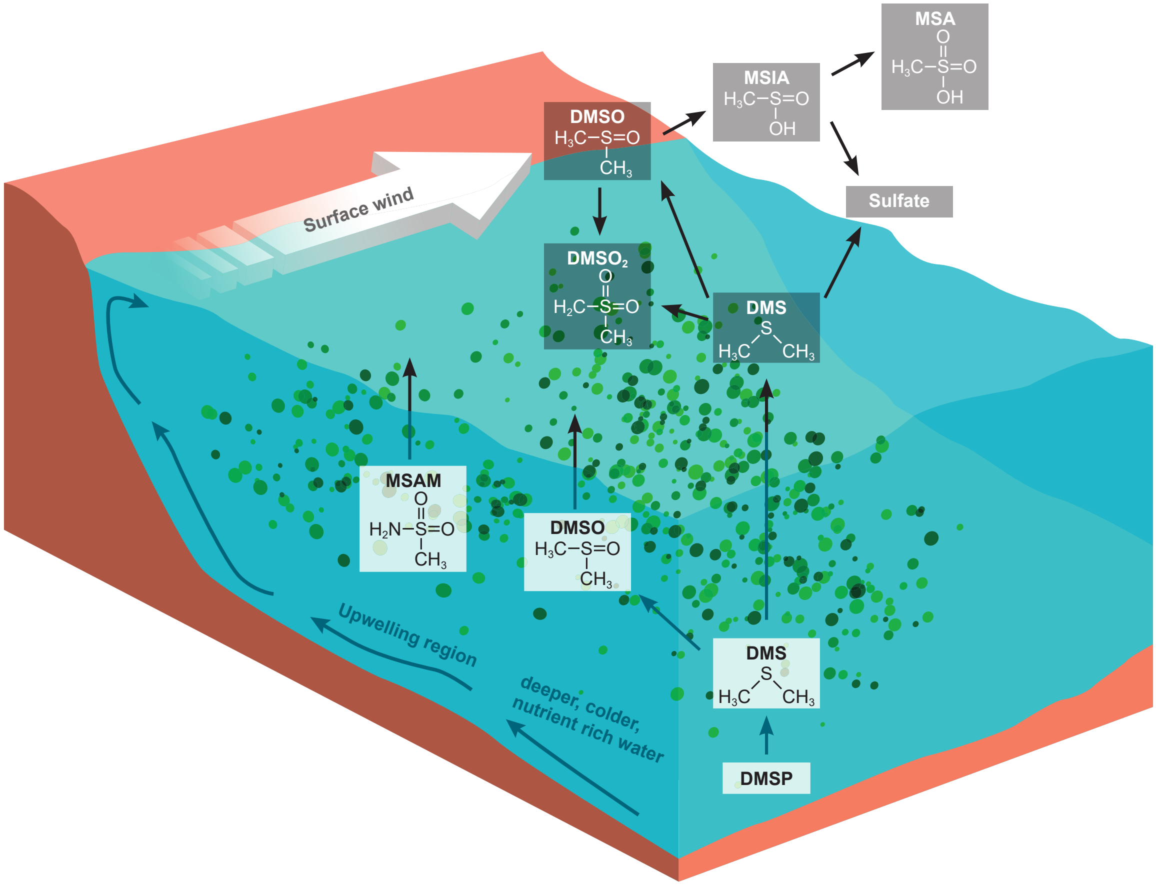

Figure 1. DMS oxidation scheme focusing on the trace gases discussed (Barnes et al., 2006). DMSP production within phytoplankton yields DMS in the surface water where it can be oxidize directly to DMSO. A small fraction of DMS is emitted to the atmosphere. Where it is predominantly oxidized by the OH radical yielding methane sulfonic acid (MSA) and sulfates. Additionally we sketched a possible formation pathways for $DMSO_2$. We suggest that MSAM could be formed in the water as a result of microbial activity and parts of it are then emitted to the atmosphere. The bottom part of the figure illustrates the principle of the Somalia upwelling. Wind blowing along the coast displaces surface water and leads to upwelling of cold nutrient rich water which can support a phytoplankton bloom (Kämpf and Chapman, 2016).

2.3 Volatile Organic Compounds (VOCs) measurements

Online volatile organic compounds (VOCs) measurements were performed using a ~~Proton~~ proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS 8000, Manufacturer: Ionicon Analytik GmbH, Innsbruck, Austria). Detailed descriptions of the instrument can be found in Jordan et al. (2009); Graus et al. (2010); Veres et al. (2013). ~~Proton transfer is a soft ionization technique resulting in little fragmentation which simplifies molecular identification.~~ Drift pressure was maintained at 2.2 mbar and the drift voltage at 600 V (E/N 137 Td). For mass scale calibrations, 1,3,5-trichlorobenzene was continuously fed

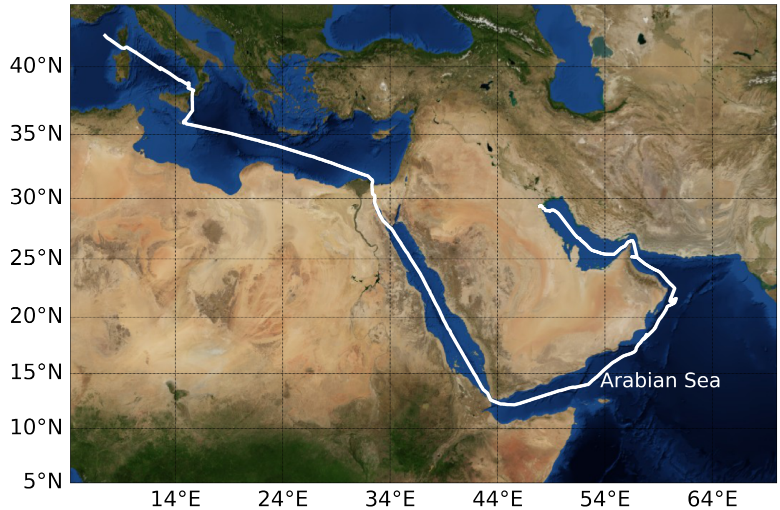

Figure 2. Ship track of AQABA cruise. Beginning of July 2017 the campaign started in the south of France near Toulon, the ship arrived in Kuwait at the end of July, started its return back to France beginning of August and was back at its starting point beginning of September 2017. On the way towards Kuwait it entered the Arabian Sea on the 19^{th} of July and left it on the 24^{th} of July. On the way back it entered the Arabian Sea on the 11^{th} of August and left it on the 15^{th} of August. Credit: NASA Earth Observatory.

into the sample stream. The PTR-TOF-MS was calibrated at the beginning, during and at the end of the campaign (in total five humidity dependent calibrations were conducted as described by Derstroff et al. (2017)). Calibrations were performed by using a standard gas mixture (Apel-Riemer Environmental inc., Broomfield, USA) of several VOCs with ~~known,~~ gravimetrically determined mixing ratios. The VOCs included in the calibration gas were: methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, methyl vinyl ketone, methacrolein, methyl ethyl ketone, benzene, toluene, o-xylene, 1,3,5-trimethylbenzene and α-pinene. Clean synthetic air was measured every three hours for ten minutes to determine the instrument background. Synthetic air was supplied to the instrument only and not the whole inlet. The time resolution of the measurement was 1 minute and the mass range extended to 450 amu. Mass resolution (full width half maximum) at mass 96 amu was ca. 3500 during the first leg and > 4500 during the second leg~~at mass 96 amu~~.

The total uncertainty of the DMS measurement was < 30% (main sources of uncertainty: standard gas mixture 5 %, flow meter 1 %, calibration ≈ 10 %), and the precision < 5 %. $DMSO_2$ and MSAM were not present in the calibration gas. Calculation of the mixing ratio was therefore conducted based on ~~theory and more specifically on~~ the rate coefficients for proton transfer (Su and Chesnavich, 1982; Chesnavich et al., 1980), the knowledge of transmission factors, amount of H_3O^+ ions and parameters of the drift region (Lindinger et al., 1998). Applying this method results in a greater uncertainty than for compounds included in the calibration gas mixture of approximately 50%. Due to the fact that we do not know the inlet transmission for these two substances, we conservatively estimate an uncertainty of up to a factor of 2 for MSAM %. The limit of detection (LOD: 3×standard deviation of background) was 20 ppt for DMS, 25 ppt for $DMSO_2$ and 5 ppt for MSAM.

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 0.4 m in length and a flow rate of 100 sccm. 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 10 m, 1/2" Teflon tubing, flow of 3 slpm) 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.

2.5 HYSPLIT back trajectories

Air mass back trajectories were calculated to investigate the origin of air masses encountered. The Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4, 2014), a hybrid between a Lagrangian and an Eulerian model for tracing small imaginary air parcels forward or back in time (Draxler and Hess, 1998), was used to derive 3D back trajectories from a ~~start~~ starting height of 200 m above sea level, going 216 hours back in time on an hourly grid beginning at the ship position.

3 Results

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 a . 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, $DMSO_2$ and MSAM characterize this part of the cruise as mostly influenced by clean marine air.

3.1 Dimethyl sulfide (DMS)

Measurements of DMS (m/z 63.0263) during AQABA showed elevated mixing ratios when the vessel traversed the Arabian Sea during both legs (brown shaded region in Fig. 3 a). During the first leg over the Arabian Sea (Fig. 3 b), DMS mixing ratios were generally in the range of ~~0.3–0.5~~300–500 ~~ppbv~~ppt, with occasional peaks of ~~0.8~~800 ~~ppbv~~ppt. During the second leg (Fig. 3 c), the DMS mixing ratios over the Arabian Sea were significantly lower in the range of ~~0.1–0.3~~100–300 ~~ppbv~~ppt, again with elevated peaks of short duration (around 2 h).

3.2 Dimethyl sulfone ($DMSO_2$)

~~Dimethyl sulfone (~~$DMSO_2$ ~~) is an oxidation product of DMS by the OH radical (Arsene et al., 2001; Barnes et al., 2006). It~~ was measured by the PTR-ToF-MS at m/z 95.0161. ~~A thorough investigation of other plausible mass formulas, which would yield a m/z value inside the error margins due to the mass resolution, gave no plausible alternative~~ Within the range of uncertainty for that mass we did not find another plausible molecular structure. Additionally, the head space of the pure compound (TCI Deutschland GmbH, purity > 99 %) was sampled yielding a peak at the same position as found in ambient air. ~~Therefore we assigned this mass to $DMSO_2$.~~ Measurements of $DMSO_2$ in the Arabian Sea region showed elevated levels between ~~0.04–0.12~~40–120 ~~ppb~~ ppt during the second leg (Fig. 3 c)) but more modest levels (< ~~0.04~~40 ~~ppb~~ppt) in leg 1 (Fig. 3 b)). To our knowledge, there have been no measurements of $DMSO_2$ performed in this region previously.

3.3 New atmospheric trace gas: Methane sulfonamide (MSAM)

At m/z 96.0144, a signal was observed which displayed a strong correlation with $DMSO_2$ (Pearson correlation coefficient: r around 0.8) over the Arabian sea during the second leg (see Fig. 4). This mass corresponded to methane sulfonamide (MSAM), which has a similar structure to $DMSO_2$, ~~the difference being that one methyl group is replaced by~~ with an amine group substituted for a methyl group (see Fig. 1 for the chemical structures of the molecules). This molecule has not previously been measured in ambient air. To confirm the assignment of mass m/z 96.0144 to MSAM, the head-space of the pure substance MSAM (Alfa Aesar, purity > 98 %) was sampled by the PTR-ToF-MS. The analysis of the pure compound MSAM by PTR-ToF-MS matched the mass found in ambient air. No other plausible molecular structures could be found for this mass within the ~~error margins due to the massresolution~~uncertainty for that mass. Based on the correlation of mass m/z 96.0144 to $DMSO_2$ in ambient data, the mass spectral match to the pure compound, and the absence of alternative structures at that exact mass we identify the measured signal as MSAM. In order to test whether MSAM can be observed outgassing from seawater, we flushed the headspace of solutions of 4.2 mol L^{-1}, 0.05 mol L^{-1} and 0.0005 mol L^{-1} MSAM in artificial seawater with 100, 50 and 25 ml min^{-1} of synthetic air (Air Liquide, Krefeld, Germany) each. The resulting mixing ratios measured ranged from ~~0.65~~650 ~~ppb~~ ppt (lowest concentration and lowest flow rate) to ~~130~~130000 ~~ppb~~ ppt (highest concentration and highest flow rate). Up to a certain flow value the increase in dilution due to an increase in flow is overcompensated through an enhanced emission of the substance from the seawater. Therefore we measured the highest MSAM mixing ratios at the highest flow rate. During the Arabian Sea section of the second leg, values of up to ~~0.06~~60 ~~ppb~~ ppt were measured, but mostly it was found in the range of ~~0.02–0.05~~20–50 ~~ppb~~ppt. In the first leg, MSAM was occasionally detected in the Arabian Sea, but concentrations were generally close to the ~~limit of detection (LOD) which was 5 ppt (3×standard deviation of background)~~LOD.

4 Discussion

Here we discuss DMS, $DMSO_2$ and MSAM measurements in air from a rarely sampled region, the Arabian Sea. First we discuss the difference in DMS abundance between the two legs. Secondly we evaluate the source regions of these trace gases based on knowledge of their atmospheric lifetimes and chlorophyll exposure. Then finally we address the implications of these measurements to marine boundary layer chemistry.

4.1 DMS

~~Sea~~ We observed higher values of DMS in July (leg 1) than in August (leg 2) over the Arabian Sea (see 3.1). This finding is consistent with DMS fluxes predictions by Lana et al. (2011) for this region. Sea surface DMS concentrations can be used to estimate DMS fluxes to the atmosphere and a global climatology of DMS ~~flux values~~ surface water concentrations has been derived by Lana et al. (2011) from over 47000 seawater measurements worldwide. ~~Lana et al.~~ Lana et al. (2011) predict strong fluxes of DMS in the Arabian Sea region, particularly in June, July and August, coincident with the AQABA campaign. Seawater concentration data for DMS from the Lana climatology relevant for AQABA has been plotted in Fig. 5 for July and

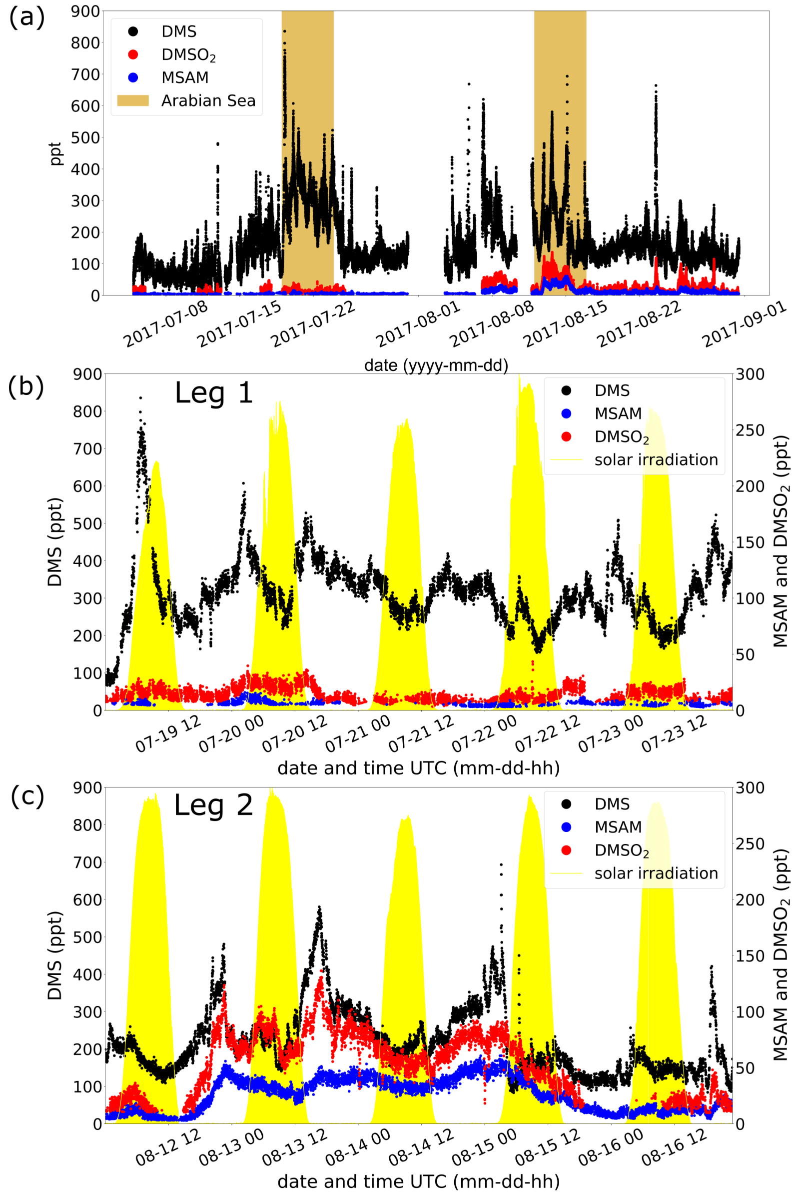

Figure 3. In panel (a) the mixing ratios of for DMS, $DMSO_2$ and MSAM during the whole AQABA cruise are displayed. The Arabian Sea parts of leg 1 and 2 are marked with brown. A zoom-in on measurements over the Arabian Sea is given for leg 1 in panel (b) and for leg 2 in panel (c). The ~~y-axis for MSAM and $DMSO_2$ (panels (b,c)) is on the right (DMS on the left) and the~~ yellow filled curves in panels (b,c) show the solar irradiation in arbitrary units.

August. In the regions south of the Arabian Peninsula, higher concentrations of DMS in seawater are expected in July than in August. ~~The observed higher measured values of DMS seen on the AQABA first leg are consistent with this .~~ Therefore the

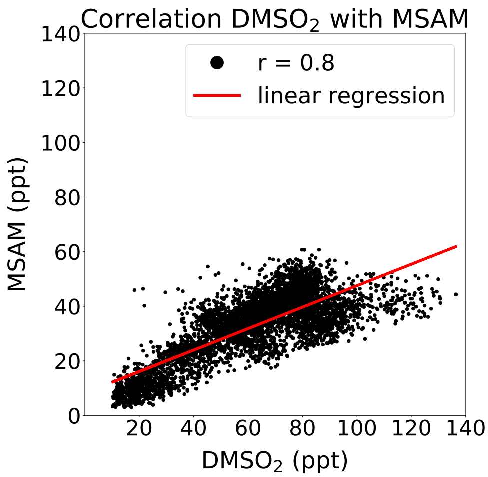

Figure 4. Correlation of MSAM with $DMSO_2$ during the second leg in the Arabian Sea. Displayed in red the is the linear regression ($[MSAM] = 0.393 * [DMSO_2] + 8.245$ ppt). The Pearson correlation coefficient is 0.8.

measured higher mixing ratios of DMS in July than August are supporting the results of the climatology for this region.

The highest DMS mixing ratios occurred during the first leg over the Gulf of Aden with around ~~0.8~~800 ~~ppb~~ppt. The peak values are likely related to the ship crossing directly through patches of phytoplankton as evidenced by the observation of strong bioluminescence around the ship during the night. The DMS mixing ratio values of up to ~~0.3~~300 ~~ppb~~ ppt during the second leg can be compared to measurements made previously in that region~~: During a cruise on the Dutch research vessel Pelagia in April 2000,~~. DMS values up to ~~0.25~~250 ~~ppb~~ ppt associated with upwelling in the Gulf of Aden were reported during a ship cruise in April 2000 (Warneke and de Gouw, 2001). More recent measurements during a ship cruise in July and August 2018 in the western tropical Indian Ocean reported values of up to ~~0.3~~300 ~~ppb~~ ppt DMS (Zavarsky et al., 2018). The DMS measurements presented here are therefore consistent with the very limited previous measurements in this region.

4.2 Atmospheric lifetimes of DMS, $DMSO_2$ and MSAM

The lifetime of DMS in the atmosphere with respect to the primary oxidant OH is around 1.3 days (~~reaction rate~~ bimolecular rate constant = 7.8×10^{-12} cm^3 $molec^{-1}$ s^{-1} ~~,~~ (Albu et al., 2006)). For all lifetimes with respect to OH we use the global average concentration [OH] = 1.1×10^6 molec/cm^3 ~~(Albu et al., 2006))~~(Prinn et al., 2005). In some regions of the marine boundary layer, BrO may also contribute to the oxidation of DMS leading to shorter DMS lifetimes (Breider et al., 2010; Khan et al., 2016; Barnes et al., 2006).~~The high and variable levels of DMS encountered during the Arabian Sea crossing suggest that DMS mixing ratios are influenced by local variation of the sources (i.e. phytoplankton patches). The~~

The reaction rate of OH and $DMSO_2$ is $< 3 \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}, which leads to a tropospheric lifetime of more than 35 days ([OH] = 1.1×10^6 molec/cm^3) (Falbe-Hansen et al., 2000), over twenty times longer than DMS. A recent study

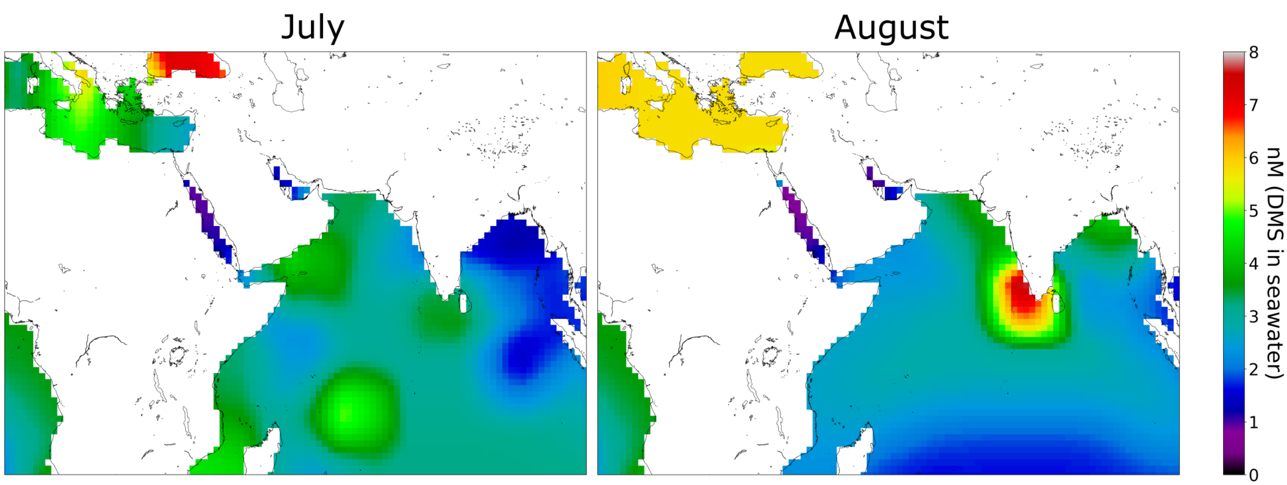

Figure 5. Climatology for DMS sea surface water concentrations in July and August (Lana et al., 2011). Over 47 000 DMS seawater measurements were used together with interpolation/extrapolation techniques in order to obtain a monthly DMS surface water concentration of the whole earth. In the regions south of the Arabian Peninsula the climatology estimates higher values in July than in August.

(?) Berasategui et al. (2020) measured a rate constant of $1.4 \pm (0.2) \times 10^{-13}$ cm^3 molec^{-1} s^{-1} for the reaction of OH with MSAM, which results in a tropospheric lifetime of 75 days ([OH] = 1.1×10^6 molec/cm^3). As MSAM has a long lifetime with respect to reaction with OH, we must also consider its physical removal by deposition to the ocean surface. We therefore carried out experiments to determine the Henry's law constant for MSAM (details see Sect. S2) and found it to be in the range 3.3×10^4 M atm^{-1}–6.5×10^5 M atm^{-1}. $DMSO_2$ has a similarly large Henry's law constant $> 5 \times 10^4$ M atm^{-1} (de Bruyn et al., 1994). The A two-layer model can predict the exchange flux between the gas and aqueous phase can be described phenomenologically to derive an estimate of the effective lifetimes (Schwartz, 1992; Yang et al., 2014). Because of the (Liss and Slater, 1974; Schwartz, 1992; Yang et al., 2014). For substances with a high Henry's law constantfor both , like MSAM and $DMSO_2$, to a good approximation their lifetime is dependent on knowledge of the wind speed and the marine boundary layer height is sufficient to get a prediction of the deposition lifetime (details see Sect. S1). The lifetimes for a This gives a lifetime of 30.5 ± 23.5 hours (marine boundary layer heightof : 750 ± 250 meters and wind speeds in the range from 4 m s^{-1} to 14 m s^{-1}, as encountered during the second leg in the Arabian Sea, is 40 ± 14 hours and 11 ± 4 hours respectively). The lifetimes for MSAM and $DMSO_2$ are therefore controlled by the deposition rate to the ocean surface and not by OH oxidation. This means that DMS, $DMSO_2$ and MSAM have similar lifetimes. During August the 12th and 13th, airmasses from the Somalia upwelling most of the time traveled for 10 h up to a day before reaching the ship. On the 14th and 15th of August, airmasses from the Somalia upwelling were around 4 h old (determined from the HYSPLIT back trajectories). A common oceanic source and the similar lifetimes of $DMSO_2$ and MSAM help explain the observed good correlation of MSAM with $DMSO_2$ (see Fig. 4).

4.3 Chlorophyll exposure of HYSPLIT back trajectories

MSAM and $DMSO_2$ were close to the LOD during the first leg, despite the fact that DMS mixing ratios were even higher than during the second leg. This observation excludes a simple relationship between the emissions of DMS and $DMSO_2$/MSAM. $DMSO_2$ is known to be an oxidation product of DMS and is therefore linked to marine biogenic activity (Barnes et al., 2006). We hypothesize that the newly detected trace gas MSAM is also linked to marine biogenic activity. This is based on the observation that MSAM displays the highest values when influenced mainly by remote marine air without recent contact with land, it correlates well with $DMSO_2$ (see Fig. 4 (c)) and is similar in chemical structure to DMS and $DMSO_2$. A good indicator for marine biogenic activity is phytoplankton. Phytoplankton in the water can be detected from space via the *chlorophyll a* pigment used for photosynthesis. Satellite images of regional chlorophyll can be exploited to investigate emission areas of marine biogenic VOCs. In the following sections we will investigate, with the help of HYSPLIT back trajectories and *chlorophyll a* water content, where the source of MSAM and $DMSO_2$ is located.

4.3.1 *Chlorophyll a* water content

We used data from the satellite MODIS-aqua (Jackson et al., 2019). In Fig. 6 ~~a-d~~a,b and d,e) the *chlorophyll a* concentration averaged over 8 days is plotted for the time periods relevant for our measurements. During the first leg (Fig. 6 a, b) the ship entered the Arabian Sea region on the 19^{th} of July and left it around the 23^{rd} of July 2017. Figure 6 a) displays the average chlorophyll distribution from the 12^{th} until the 19^{th} of July, since air masses reaching the ship from July 19^{th} onwards will have traveled over *chlorophyll a* regions before the time of observation. For the second leg (Fig. 6 ~~c,d~~d,e) (12^{th} of August till the 16^{th} of August 2017) we used the average *chlorophyll a* content from the 5^{th} of August till the 12^{th} of August and from the 13^{th} till the 20^{th} of August. The highest chlorophyll concentrations in the region are found off the Horn of Africa/Somalia coast, a strong upwelling region.

4.3.2 Back-trajectory-chlorophyll analysis

~~Air-masses arriving at the ship which have traveled over marine areas with high biological activity (meaning high phytoplankton content) will likely contain higher levels of marine emissions~~A trajectory analysis was carried out to investigate whether air masses traveling over regions of high chlorophyll are associated with higher atmospheric levels of $DMSO_2$, and MSAM. To investigate the provenance of air-masses sampled at the ship in relation to the chlorophyll distributions shown above, HYSPLIT back-trajectories were calculated (9 days back) for every full hour of the cruise. ~~A weighting factor was applied to emphasize regions closer to the ship. In~~ For each point of the trajectory the underlying *chlorophyll a* content was weighted with respect to the arrival time at the ship to account for oxidation and dispersion effects (see Fig. 6 c and f). These values were then added up for each trajectory individually in order to determine quantitatively to what extent the air sampled had passed over areas of high ~~phytoplankton content (indexed with *chlorophyll a*) we summed up the *chlorophyll a* content detected by satellite~~ chlorophyll content (indicator for phytoplankton in the water~~for each trajectory~~). Only time points when the trajectory was within the marine boundary layer, as calculated from the HYSPLIT model, were considered. ~~The weighting factor (w) was~~

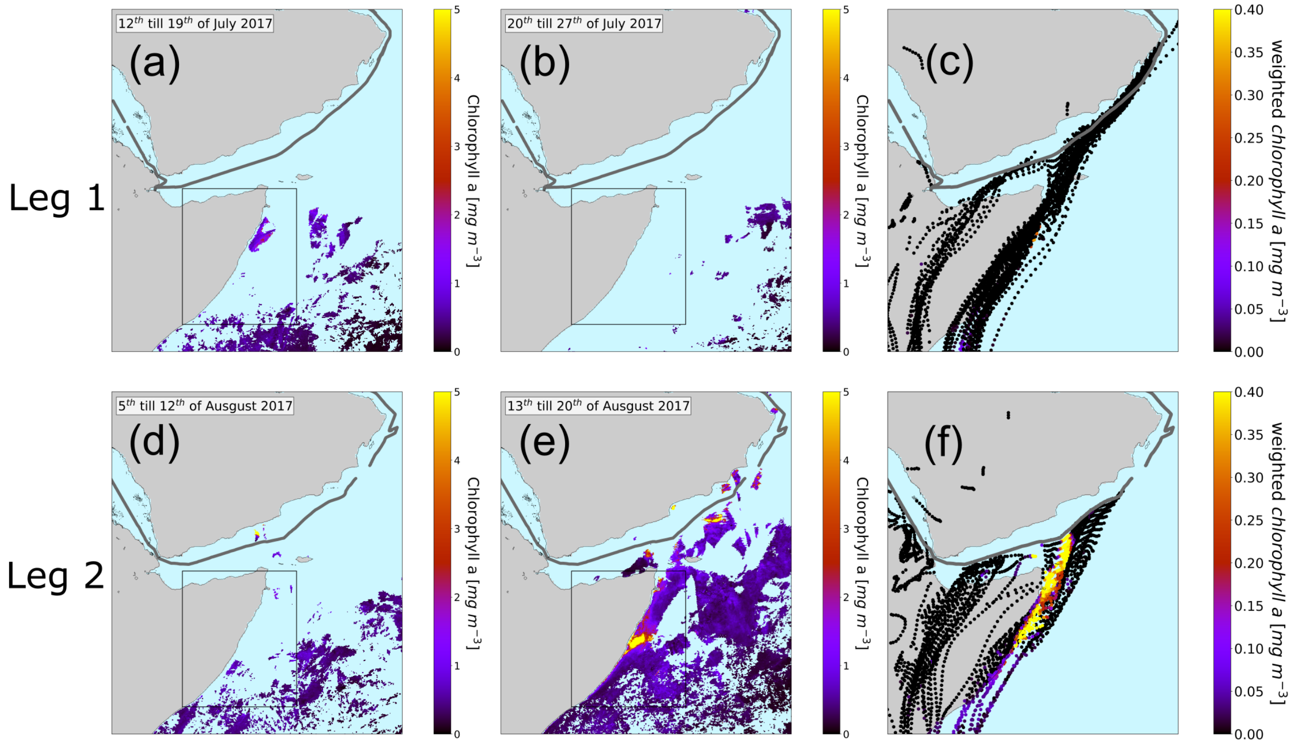

Figure 6. Eight day averaged *chlorophyll a* concentration in the Arabian Sea. The relevant time periods for the first leg (a,b) and for the second leg (~~c,~~d,e) are pictured here. Plot (a) represents the average *chlorophyll a* concentration from the 12^{th} until the 19^{th} of July, plot (b) from the 20^{th} until the 27^{th} of July, plot (~~c~~d) from the 5^{th} till the 12^{th} of August and plot (~~d~~e) from the 13^{th} till the 20^{th} of August. The black rectangle represents the region of the Somalia coast upwelling. The ship track is plotted in ~~black~~gray. The light blue means no *chlorophyll a* content. Plots (c) and (f) display the HYSPLIT back trajectories. The color code of the trajectories represents the weighted amount of *chlorophyll a* concentration in the water underneath the trajectory.

~~applied to this calculation by multiplying the *chlorophyll a* water content by: $w = \frac{1}{1+p*t}$, where p is the weighting parameter and t is the number of hours before arrival at the ship's location. This was to account for the fact that marine emissions from phytoplankton closer to the ship will have a bigger impact on the measured mixing ratios as they will undergo less oxidation and dispersion. Several weighting factors were applied in order to determine the impact of the various parameters on the results. The weighting parameters p ranged from $p = 0.02$ to $p = 1$ and for exponential weighting factors in the form $w_{exp} = p^t$, p was varied from $p = 0.8$ to $p = 0.99$ (details~~ Changing of the weighting did not materially affect the results. For details on the weighting procedure see Sect. S3~~). Varying these parameters did not affect the conclusions drawn.~~.

The results of these calculations are displayed in Fig. 7. The graphs show the total chlorophyll exposure and the exposure of chlorophyll specifically from the region of the Somalia upwelling (see Fig. 6 the region in the black rectangle). In the first leg (Fig. 7 (a)), when both $DMSO_2$ and MSAM mixing ratios were low, air reaching the ship did not cross *chlorophyll a* rich

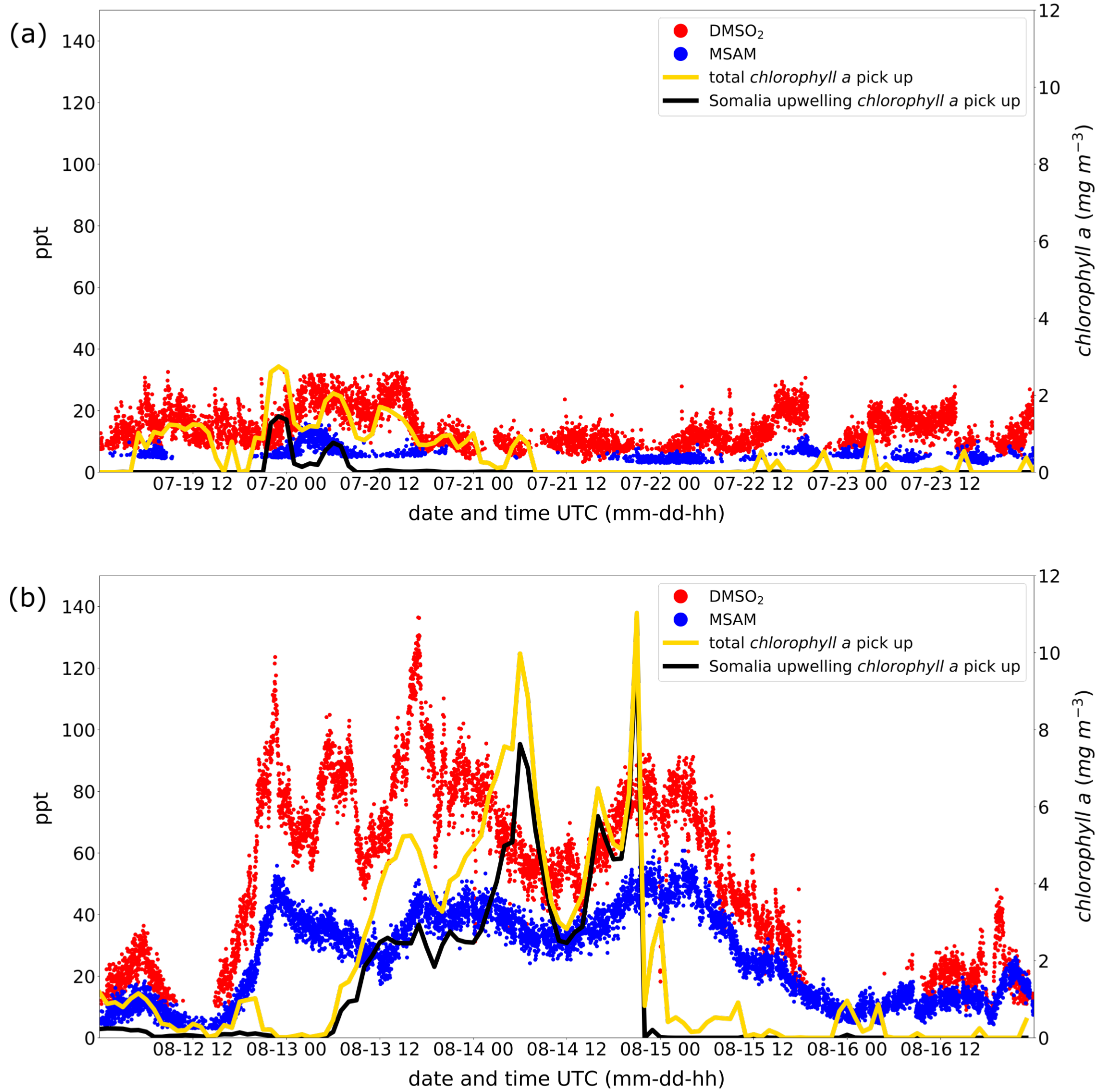

Figure 7. Weighted amount of *chlorophyll a* trajectories crossed over before arrival at the ship for leg 1 (a) and leg 2 (b). The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure for both graphs (a,b) is displayed on the right side. ~~Measured ambient mixing~~ Mixing ratios in ~~ppb~~ ppt for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side.

waters in the previous 1 to 2 days. This is the case for the total exposure as well as for the exposure to chlorophyll in the Somalia upwelling region.

However, during the second leg (Fig. 7 (b)), when $DMSO_2$ and MSAM levels were high, the air measured had traveled over extensive *chlorophyll a* rich waters. In general, the exposure in the Somalia upwelling region always constituted the majority of the total exposure, except for one peak in the beginning (August 13^{th} from 12:00 till 19:00) where chlorophyll patches closer to the ship constituted roughly half of the total chlorophyll exposure. From these calculations we can conclude that the occurrence of $DMSO_2$ and MSAM is related to marine emissions in the Somalia upwelling region. MSAM and $DMSO_2$ mixing ratios started to increase around midday of August 12^{th} but the chlorophyll exposure only started to increase around 6:00 on August 13^{th} (Fig. 7 (b)). ~~The reason for this being that trajectories arriving~~ A possible explanation for the delay in chlorophyll exposure could be that the bloom already started on August 12^{th} ~~had seen low *chlorophyll a* water content, as displayed~~ and not just on August 13^{th} as indicated in Fig. 6 ~~(c),where no phytoplankton bloom was present in the Somalia upwelling region resulting in low chlorophyll exposure. This bloom developed afterward as seen in Fig. 6 (d) but might have started already on August 12^{th} and~~ d,e. Possibly the earlier start of the bloom escaped detection by MODIS-aqua ~~.~~ as it sees every point on earth every 1–2 days. Around the equator some regions escape detection on any given day. An inspection of daily data from MODIS-aqua revealed that parts of the Somalia upwelling were in a blind spot of the satellite on August 12^{th}. The chlorophyll exposure sharply fell to zero at the beginning of the 15^{th} of August, roughly 8 h before $DMSO_2$ and MSAM values start to decline as well (Fig. 7 (b)). In this case the calculated HYSPLIT back-trajectories no longer pass over the Somalia upwelling but cross Somalia before arriving at the ship. Our measurements thus indicate that we were impacted by the Somalian upwelling region for longer than calculated from the trajectories. This is not unexpected as meteorological data for this region are sparse, and the trajectories therefore correspondingly uncertain.

4.4 $DMSO_2$, DMSO, MSIA and MSA

~~We observed $DMSO_2$ mixing ratios during the second leg between 0.04 and 0.12 ppb, which is high compared to previous measurements of 0.2–11 ppt (Berresheim et al., 1998; D. Davis et al., 1998) made in Antarctica. As mentioned in the introduction, $DMSO_2$ is known to be formed from oxidation of DMS with OH, BrO or NO_3 (see Fig. 1). However laboratory studies indicate that OH oxidation of DMS, via the intermediate DMSO, forms mainly methane sulfinic acid (MSIA) and not $DMSO_2$ (Barnes et al., 2006; Kukui et al., 2003; Hoffmann et al., 2016). BrO oxidation of DMSO generating $DMSO_2$ will be negligible for concentrations of 2 ppt for BrO, which have been proposed to be ubiquitous in the marine troposphere (Read et al., 2008; Platt and Hönn , due to the slow reaction compared to the reaction with OH. NO_3 oxidation of DMSO was found to only yield $DMSO_2$ (Falbe-Hansen et al., 2000), but during the night, due to the lack of OH and BrO producing DMSO, $DMSO_2$ generation will be hindered.With the data presented here it is not possible to decide which of the above mentioned mechanisms is responsible for the observed $DMSO_2$. We~~ In the following we will discuss briefly why we did not detect DMSO, MSIA ~~or~~ and methane sulfonic acid (MSA). These are important oxidation products from DMS.

DMSO is known to be an important intermediate in the oxidation of DMS with OH (Hoffmann et al., 2016). The reaction rate of DMSO with OH is 15 times faster than that of DMS with OH, making it a potentially important sink in the remote marine atmosphere (Barnes et al., 2006). A model study of the sulfur cycle in the global marine atmosphere suggested values of around 10 ppt for DMSO in the region of the Arabian Sea (Chen et al., 2018). This is below the limit of detection (LOD) of around 15 ppt for DMSO in our instrument and probably the reason why we do not observe it in this dataset. Measurements of DMSO made on Amsterdam Island ranged from 0.36 to 11.6 ppt (Sciare et al., 2000).

MSIA has a very high reaction rate of 9×10^{-11} cm^3 molec^{-1} s^{-1} with OH radicals (Burkholder et al., 2015; Kukui et al., 2003; Hoffmann et al., 2016). In the model study mentioned above, this leads to concentrations over the Arabian Sea of around 2 ppt which again is below the LOD for MSIA with our instrument (around 20 ppt) (Chen et al., 2018).
MSA, on the other hand, is predicted to be around 20–40 ppt over the Arabian Sea (gas phase and aqueous phase combined), which is above its LOD, but almost all of it will be in the aqueous phase (Chen et al., 2018; Hoffmann et al., 2016). In the gas phase, the maximum MSA values reported to date are below 1 ppt, which is far too low to be measured with our setup (LOD around 15 ppt) (Eisele and Tanner, 1993; Chen et al., 2016; Berresheim, 2002).

We observed $DMSO_2$ mixing ratios during the second leg between 40 and 120 ppt, which is high compared to previous measurements of 0.2–11 ppt (Berresheim et al., 1998; D. Davis et al., 1998) made in Antarctica. In the following we will shortly describe and discuss formation pathways for $DMSO_2$. This will be done for formation via OH, BrO and NO_3.

4.4.1 OH

$DMSO_2$ formation from OH oxidation, via the intermediate DMSO, has been observed in laboratory studies (Falbe-Hansen et al., 2000) . However it has to be noted that newer studies indicate that mainly methane sulfinic acid (MSIA) and not $DMSO_2$ is formed (Barnes et al., 2006; Kukui et al., 2003; Hoffmann et al., 2016). Another pathway is formation from the OH-DMS adduct followed by sequential reactions with NO and O_2 (Arsene et al., 2001; Barnes et al., 2006). Due to the low NO_x of the remote marine atmosphere this pathway seems unlikely as well. There are speculations about a possible formation from the initial formed OH-DMS adduct by O_2 addition and a subsequent complex process which is not yet fully understood (Berndt and Richters, 2012; Arsene et .

4.4.2 BrO

BrO can form $DMSO_2$ from DMSO. But these reaction seems rather unlikely because of the slow reaction rate compared to the fast reaction rate of OH and DMSO. This reaction therefore would only play a role for much higher concentrations of BrO and not for concentrations of 2 ppt for BrO, which have been proposed to be ubiquitous in the marine troposphere (Read et al., 2008; Platt and Hönninger, 2003).

4.4.3 NO_3

Most studies show no formation of $DMSO_2$ from NO_3 oxidation (Barnes et al., 2006). NO_3 oxidation of the intermediate DMSO is known to only yield $DMSO_2$ (Falbe-Hansen et al., 2000). However, NO_3 oxidation is not thought to produce DMSO (Barnes et al., 2006). Maybe the increase in $DMSO_2$ after sunset (see Fig. 3 c) is an indication that NO_3 is oxidizing the remaining DMSO from OH oxidation of DMS produced during daytime.

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 $DMSO_2$ values. A diel analysis of DMS, MSAM and $DMSO_2$ was made. But due to the fact that we only have two consecutive days with elevated $DMSO_2$ 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).

4.5 MSAM

We are not aware of a possible formation pathway for MSAM in the gas phase~~, therefore~~ . Therefore we consider it rather unlikely that it is formed via DMS gas phase oxidation. A microbial formation from DMS or DMS products in the water of the highly biological active upwelling region ~~and~~ with subsequent emission into the atmosphere seems plausible (see Fig. 1).
To our knowledge ~~, no measurements~~ 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).
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.
To our knowledge, no measurements of MSAM have been reported in the atmosphere so far and thus no information about the potential role it could play there is available. SO_2 ~~, which oxidizes to~~ is an oxidation product of MSAM (Berasategui et al., 2020) and a precursor for sulfuric acid (H_2SO_4)~~, is an oxidation product of MSAM (Berasategui et al. , 2019).~~ . H_2SO_4 is known to be a key contributor to new particle formation (Li et al., 2018; Kulmala et al., 2014; Almeida et al., 2013; Sipilä et al., 2010; Weber et al., 2001, 1996; Chen et al., 2016). However, due to the slow reaction of MSAM with OH, the contribution of MSAM to SO_2 is negligible ~~(Berasategui et al. , 2019).~~ (Berasategui et al., 2020). Acid-base reactions (e.g. H_2SO_4 with ammonia/amines) are very important in new particle formation (Chen and Finlayson-Pitts, 2017; Almeida et al., 2013). MSAM is an acid and therefore could participate in acid-base reactions, but since MSAM is only a weak acid ($pK_a = 10.8$ (Junttila and Hormi, 2009)) its role as an acid in these reactions is probably limited.
Studies indicate, that the dominant driving force in new particle formation and growth are the hydrogen bonds formed between common atmospheric nucleation precursors (Xie et al., 2017; Cheng et al., 2017; Li et al., 2018). The newly found trace gas MSAM is very intriguing because it contains a sulfonamide group, which is a sulfonyl group connected to an amine group. The sulfonyl and the amine group both support hydrogen bonding, giving MSAM a high hydrogen-bonding capacity, potentially enabling nucleation.
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]). We only included ratios observed in the afternoons of 14^{th} and 15^{th} of August,

when the ship was in closest proximity to the Somalia upwelling. The afternoon was chosen to ~~ensure that~~ make sure that both MSAM and DMS have roughly the same atmospheric lifetime when estimating the relative emission. Deposition to the ocean surface will happen all the time for MSAM however OH, the ~~primary oxidant of DMS, was present~~ main loss process for DMS, is only present during the day. We derived ratios ranging from 0.1 to 0.27, meaning that emissions of MSAM over the Somalia upwelling can be almost a third of the DMS emissions. Therefore, MSAM could play an important role in particle formation and/or growth over and downwind of upwelling regions. To verify these possibilities, further experiments regarding particle growth and formation with MSAM need to be performed.

5 Conclusions

During the AQABA campaign we made the first measurements of MSAM in ambient air. Back-trajectories-chlorophyll analyses suggest that it is a marine biogenic emission from the highly productive upwelling region off Somalia. During the first leg of the AQABA campaign the ship encountered mostly biogenic emissions from sources located along the ship route when crossing the Arabian Sea. The enhanced DMS values observed there could be attributed to seasonally enhanced DMS fluxes~~and small local phytoplankton blooms visible from space along the Arabian Sea transect~~. No oxidation products or other organosulfur compounds were detected in substantial amounts from the local emissions. In contrast, during the second leg not only DMS but also $DMSO_2$ and MSAM were measured. $DMSO_2$, like MSAM, was shown to originate from the Somalia upwelling region. $DMSO_2$ mixing ratios of up to ~~0.12~~120 ~~ppb~~ ppt were measured during the second leg, which is quite substantial considering that previous studies indicate it to be a minor or negligible product in DMS gas phase oxidation. ~~MSAM is a~~ The main loss mechanism for MSAM and $DMSO_2$ is deposition to the ocean surface with lifetimes of a few hours to a few days. MSAM is a molecule which, to our knowledge, was never reported in the atmosphere. We detected it in concentrations up to ~~0.066~~60 ~~ppb~~ ppt during the second leg in the Arabian Sea. Emissions of MSAM over the Somalia upwelling can reach close to a third of the DMS emissions.

A marine emission containing a nitrogen atom is somewhat surprising since under most circumstances primary productivity in the ocean is nitrogen limited. The emission of a nitrogen containing compound may be related to the abundance of reactive nitrogen provided by the upwelling. ~~Emissions of reactive nitrogen containing species have been previously measured from upwelling (alkyl nitrates in equatorial upwelling (Chuck et al., 2002)).~~ Due to its sulfonyl and amine group, MSAM has a high hydrogen-bonding capacity enabling hydrogen bonding to other atmospheric nucleation precursors. These hydrogen bonds are known to be a critical factor in particle growth and formation (Li et al., 2018; Xie et al., 2017; Cheng et al., 2017). Therefore MSAM could prove to be of importance for particle formation and/or growth over upwelling regions. The mechanisms in which gas phase precursors lead to new particle formation is an active research area in atmospheric chemistry because it is subject to large uncertainties (Li et al., 2018; Chen et al., 2016, 2018; Carslaw et al., 2013).

Data availability. Data available via: https://dx.doi.org/10.17617/3.3o

Author contributions. AE and CS were responsible for VOC measurements and data. AE analysed the data and drafted the article. EP contributed laboratory experiments concerning Henry's law constant. MB and JC contributed to data interpretation. DW calculated the back trajectories. JL designed and realized the campaign. JW supervised the study. All authors contributed to manuscript writing and revision, read and approved the submitted version.

Competing interests. The authors declare that they have no conflict of interest.

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Supplement

1 Deposition lifetime

The exchange flux F of various gases between an air and water interface can be phenomenologically be described through [4, 5]predicted with the help of a two-layer model [3, 4, 5]:

$$F = K_G(G - \frac{A}{H}). \tag{1}$$

Where K_G 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. If we assume that the aqueous phase concentration is zero (e.g. outside of the Somalia upwelling when travelling traveling towards the ship) then equation 1 simplifies to:

$$F = K_G G. \tag{2}$$

The mass-transfer coefficient K_G can be expressed as:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{\frac{1}{4}\nu\alpha} + \frac{1}{Hk_L\beta}. \tag{3}$$

In this equation k_G is the gas phase and k_L the liquid phase mass-transfer coefficient, ν the mean molecular speed of the molecule, α the mass-accommodation coefficient and β an enhancement coefficient of the aqueous phase mass transfer flux due to removal of the molecule by chemical reactions. No enhancement means $\beta = 1$. The middle term which describes the interfacial resistance can be generally neglected in the natural environment because α is always sufficiently large [4]. If the molecule under investigation has a solubility of $H \gg H_{crit} = \frac{k_G}{k_L}$ then gas phase mass transport is dominant and the flux is independent of H. We determined a Henry's law constant in the range of 3.3×10^4 M atm^{-1} - 6.5×10^5 M atm^{-1} for methane sulfonamide (MSAM) (see Sect. S2) and for $DMSO_2$ literature indicates a value greater than 5×10^4 M atm^{-1} [1]. This means that both are sufficiently soluble substances for which the assumption holds true that gas phase mass transport is controlling and the overall mass-transfer coefficient is given in the form:

$$\frac{1}{K_G} = \frac{1}{k_G}. \tag{4}$$

The gas phase mass-transfer coefficient for oceanic applications can be estimated with the help of the wind speed v [2]:

$$k_G = 0.0013v \tag{5}$$

for an observation height of 10 m which is the approximate height of observation during the AQABA campaign. The wind speed during the Arabian sea part in the second leg varied around 4 m s^{-1} and 14 m s^{-1} which yields: $K_G = 0.52$ cm s^{-1} (v=4 m s^{-1}) and $K_G = 1.82$ cm s^{-1} (v=14 m s^{-1}).
This in turn gives a lifetime (1/e) of 40 ± 14 hours for a wind speed of v=4 m s^{-1} and about 11 ± 4 hours for v=14 m s^{-1}. The average marine boundary layer height used for the lifetime calculation was 750 ± 250 m.

2 Henry's law constant measurement

~~Artificial seawater was prepared by adding~~ In order to resemble sea water more closely we added 35 g NaCl and 0.5 g $NaHCO_3$ 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. The MSAM mixing ratio of the headspace of 0.05 mol L^{-1} and 0.0005 mol L^{-1} MSAM in sea water, flushed with 100 ml min^{-1} of synthetic air (Air Liquide, Krefeld, Germany) each, was measured with a PTR-MS instrument. A range for the Henry's law constant was derived from these measurements as the ratio of the concentration of MSAM in solution (in M) vs. the measured partial pressure in the gas phase (in atm): 3.3×10^4 M atm^{-1} – 6.5×10^5 M atm^{-1}. Measurements were performed at 25° C and 995 mbar.

3 Weighting factors

Chlorophyll a water content encountered during transport of the airmasses towards the ship was weighted according to time before arrival at the ship. We employed a linear and an exponential weighting factor.

3.1 Linear weighting factors

The linear weighting factor is in the form $w = \frac{1}{1+p*t}$, where p is the weighting parameter and t is the number of hours before arrival at the ship's location. The *chlorophyll a* water content is multiplied by the weighting factor w to get the weighted *chlorophyll a* water content. We varied the p in the range from $p = 0.02$ to $p = 1$. The resulting plots are displayed in Fig. 1 ~~and Fig. 2~~till Fig. 4. A weighting parameter of $p = 0.02$ results in a high contribution and a $p = 1$ in a low contribution of *chlorophyll a* water content further away of the ship. 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~~(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. MSAM and $DMSO_2$ are low or not detected during leg 1, therefore chlorophyll exposure in regions further away than the Somalia upwelling does not appear to play a role. The calculations in leg 2 are generally quite similar and therefore independent of the weighting parameter p.

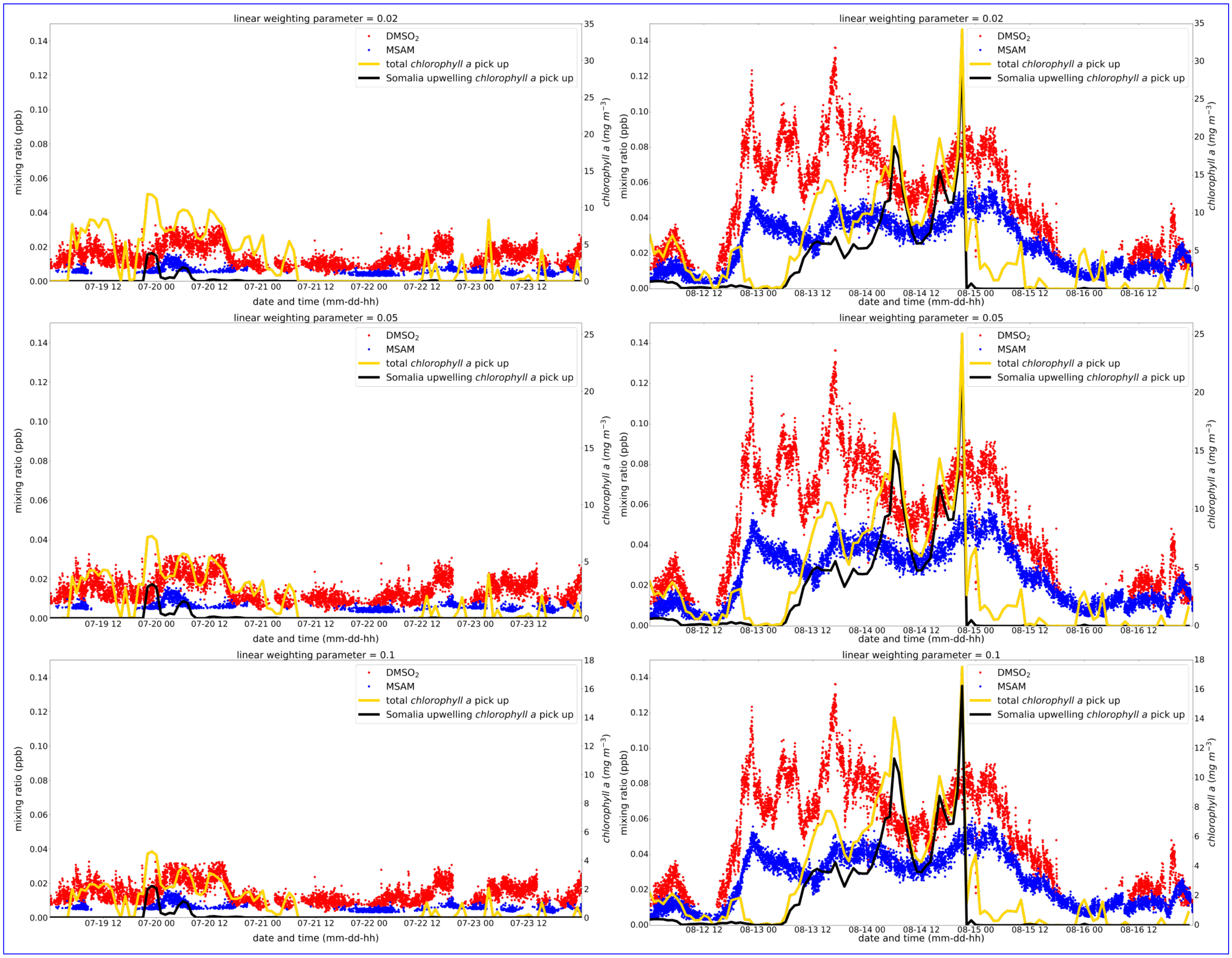

Figure 1: Linear weighting parameters from ~~$p = 0.02 - 0.4$~~$p = 0.02 - 0.1$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

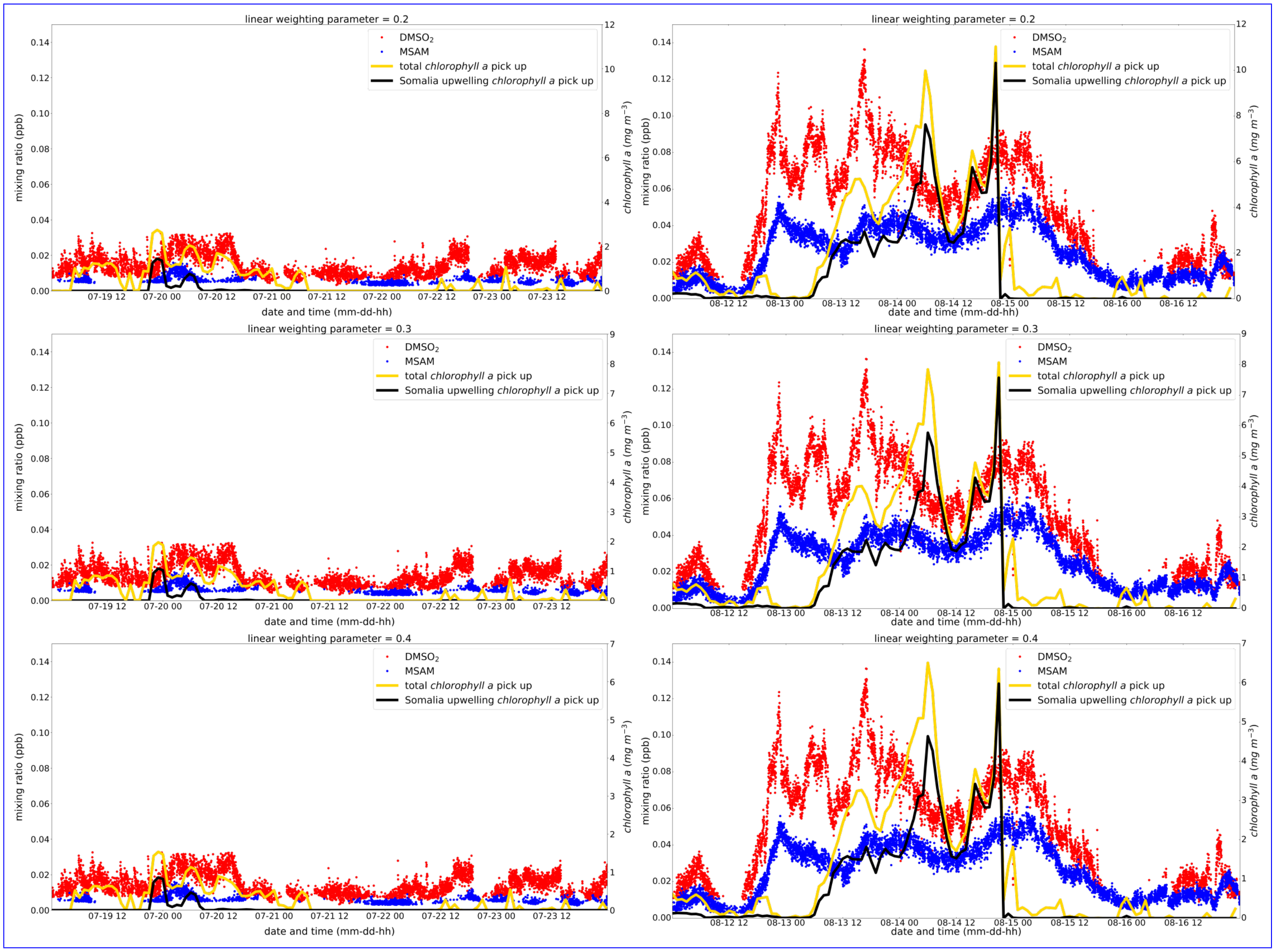

Figure 2: Linear weighting parameters from ~~$p = 0.5 - 1$~~$p = 0.2 - 0.4$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

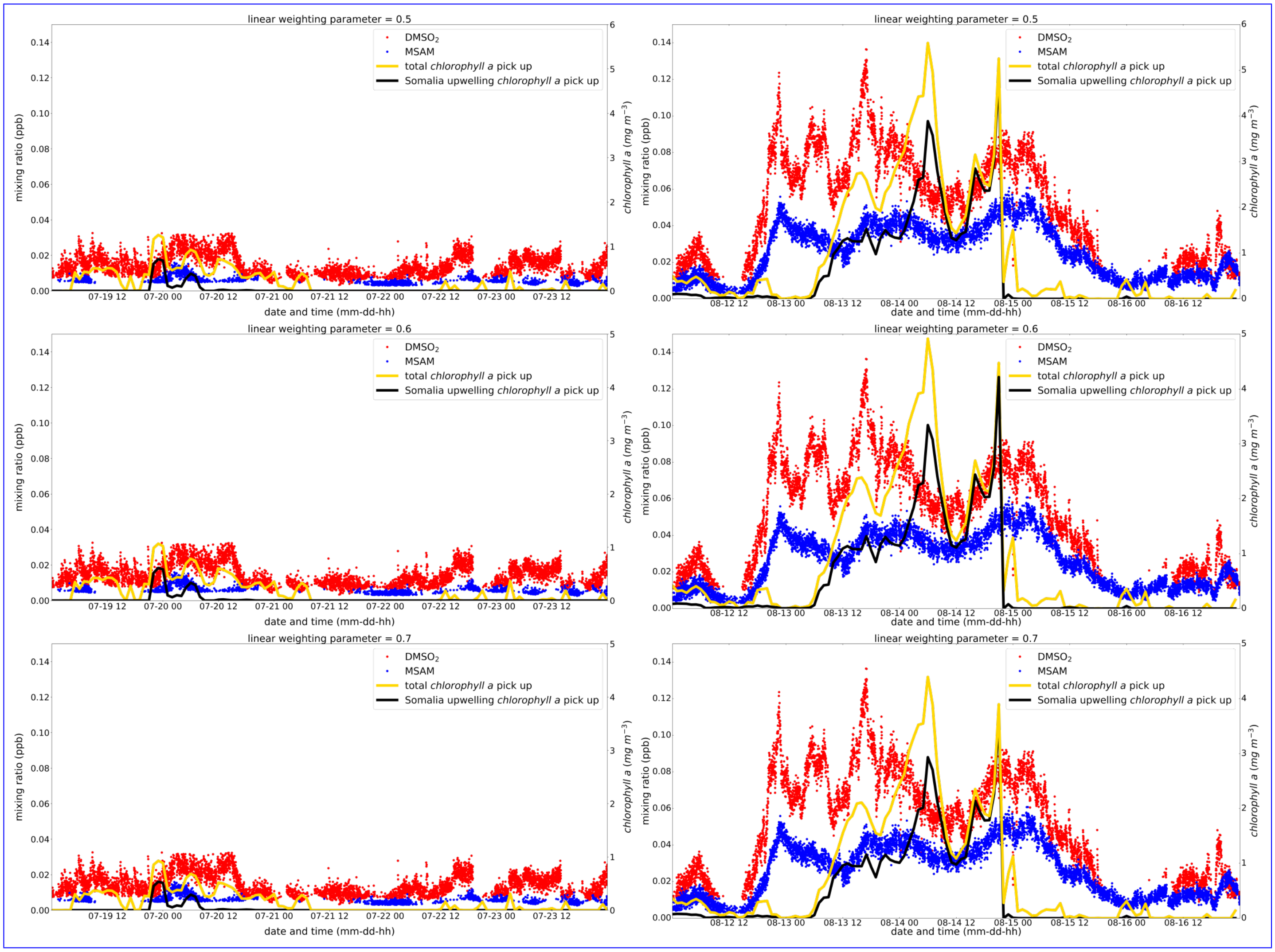

Figure 3: Linear weighting parameters from $p = 0.5 - 0.7$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

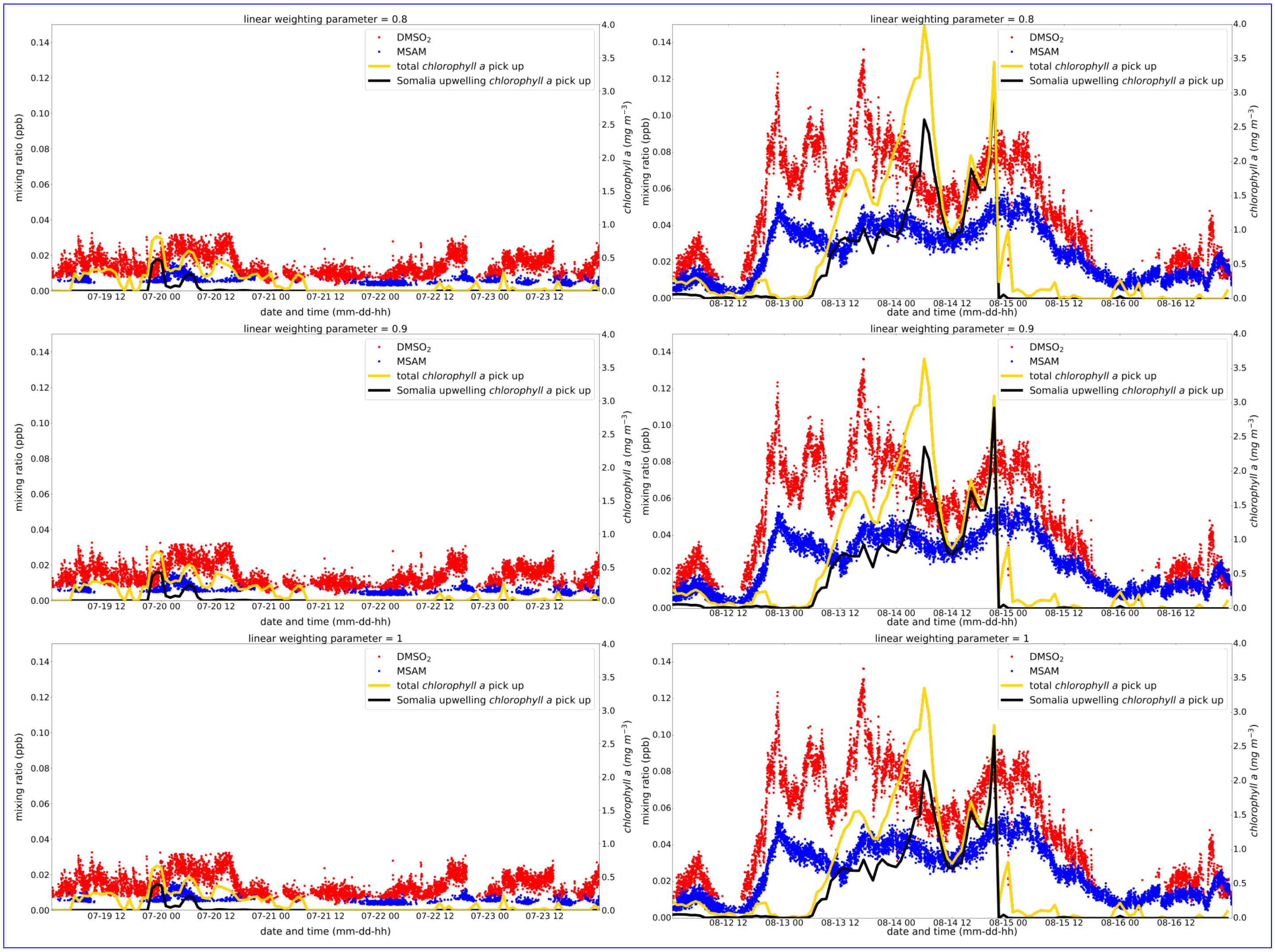

Figure 4: Linear weighting parameters from $p = 0.8 - 1$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

3.2 Exponential weighting factors

The exponential weighting factor has the form $w_{exp} = p^t$, p, where p is the weighting parameter and t is the number of hours before arrival at the ship's location. The weighting factor is then multiplied with the respective *chlorophyll a* water content to yield the weighted *chlorophyll a*. The weighting parameter was varied from $p = 0.8$ to $p = 0.99$ (see Fig. 5 ~~and Fig. 6~~till Fig. 8). A weighting parameter of 1 means that all *chlorophyll a* water content is weighted equally. If p is close to 1 we see in the first leg a small increase in total *chlorophyll a* exposure coming from *chlorophyll a* pick up further away as the Somalia upwelling (as for the linear case). For the other cases we see in leg 2 that the Somalia upwelling region always constitutes the mayor part of the total *chlorophyll a* exposure, even in the case of $p = 0.8$, which discriminates strongly against chlorophyll exposure further away from the ship.

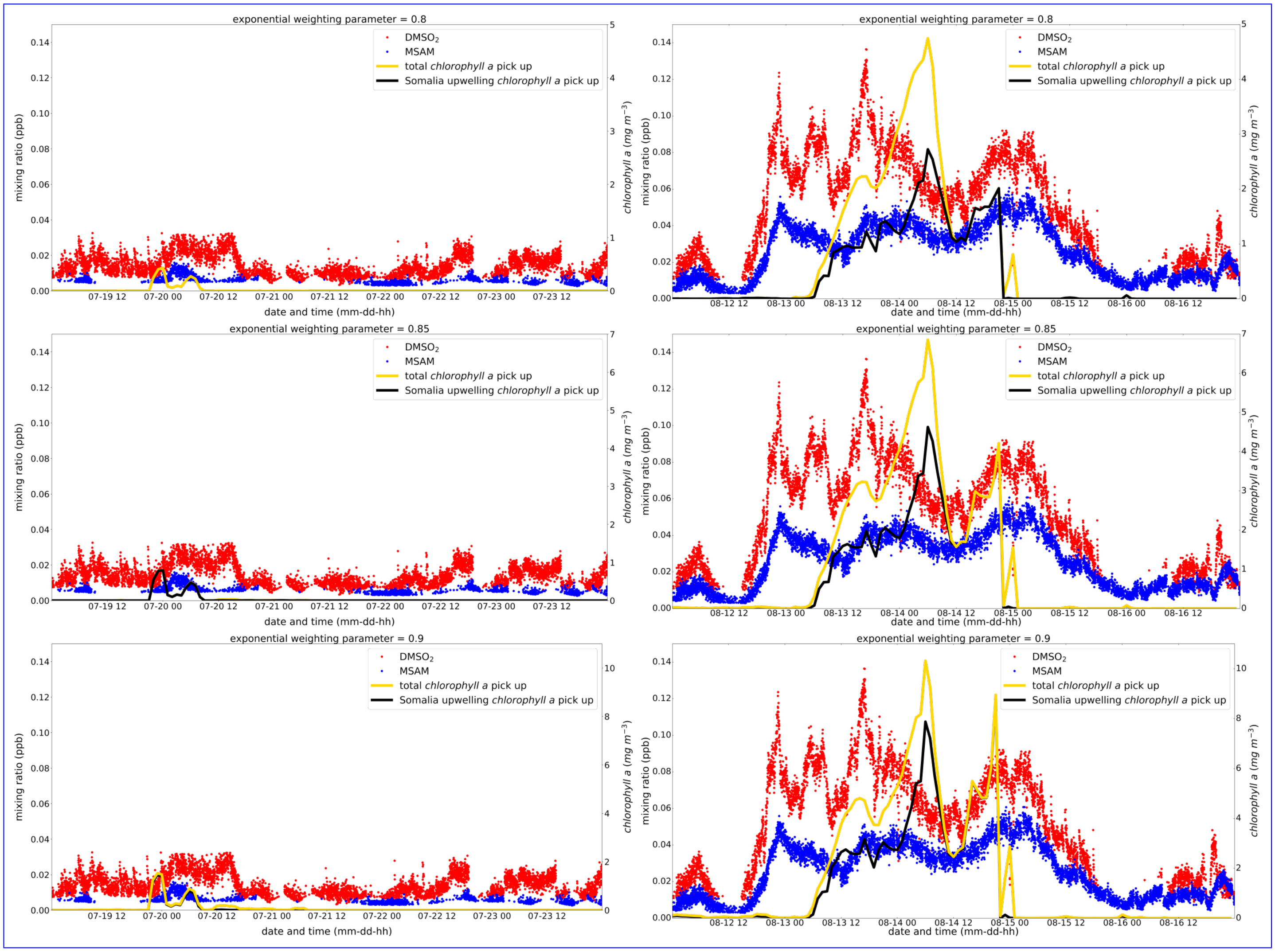

Figure 5: Exponential weighting parameters from ~~$p = 0.8 - 0.93$~~ $p = 0.8 - 0.9$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

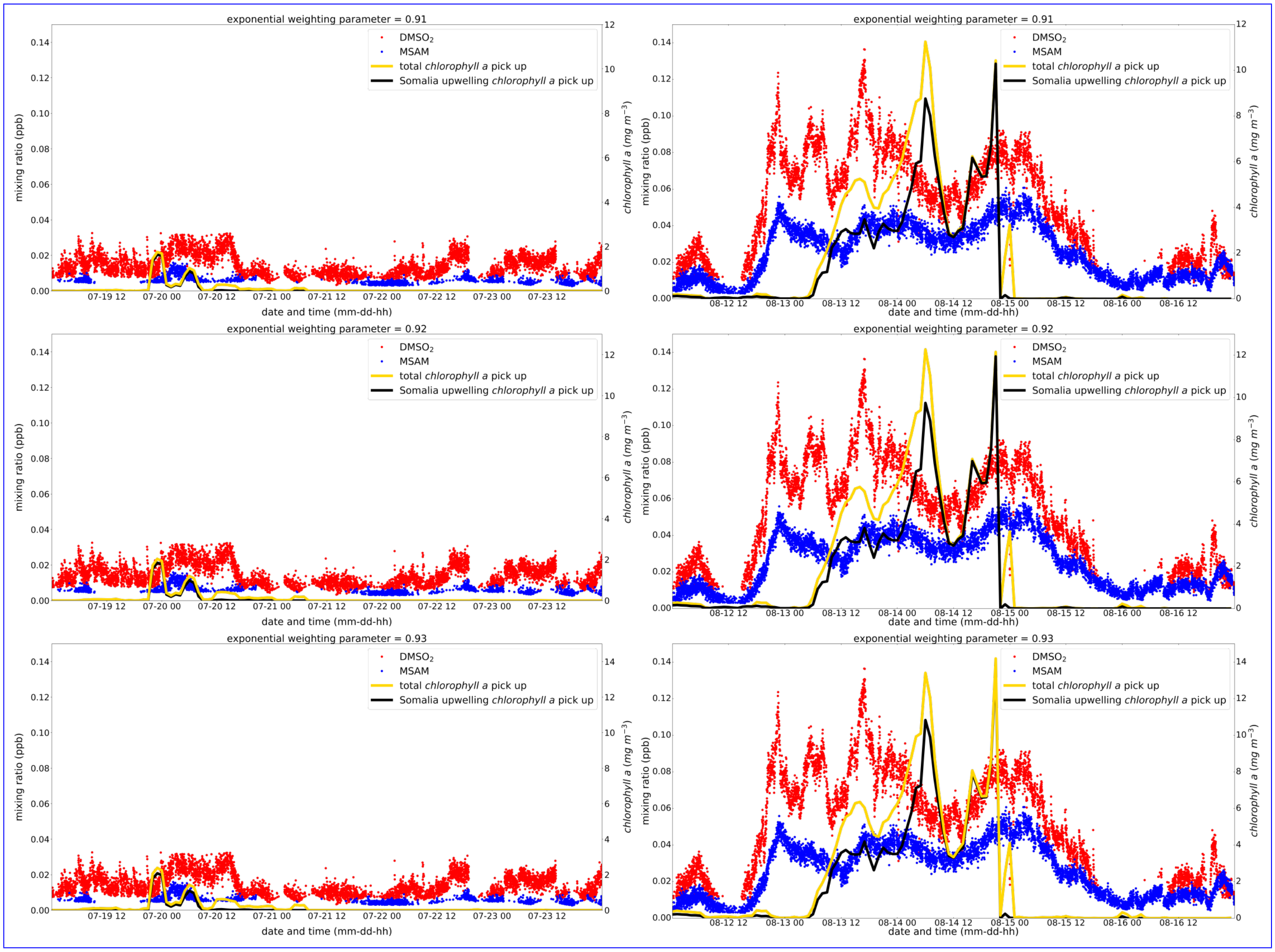

Figure 6: Exponential weighting parameters from ~~$p = 0.94 - 0.99$~~$p = 0.91 - 0.93$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

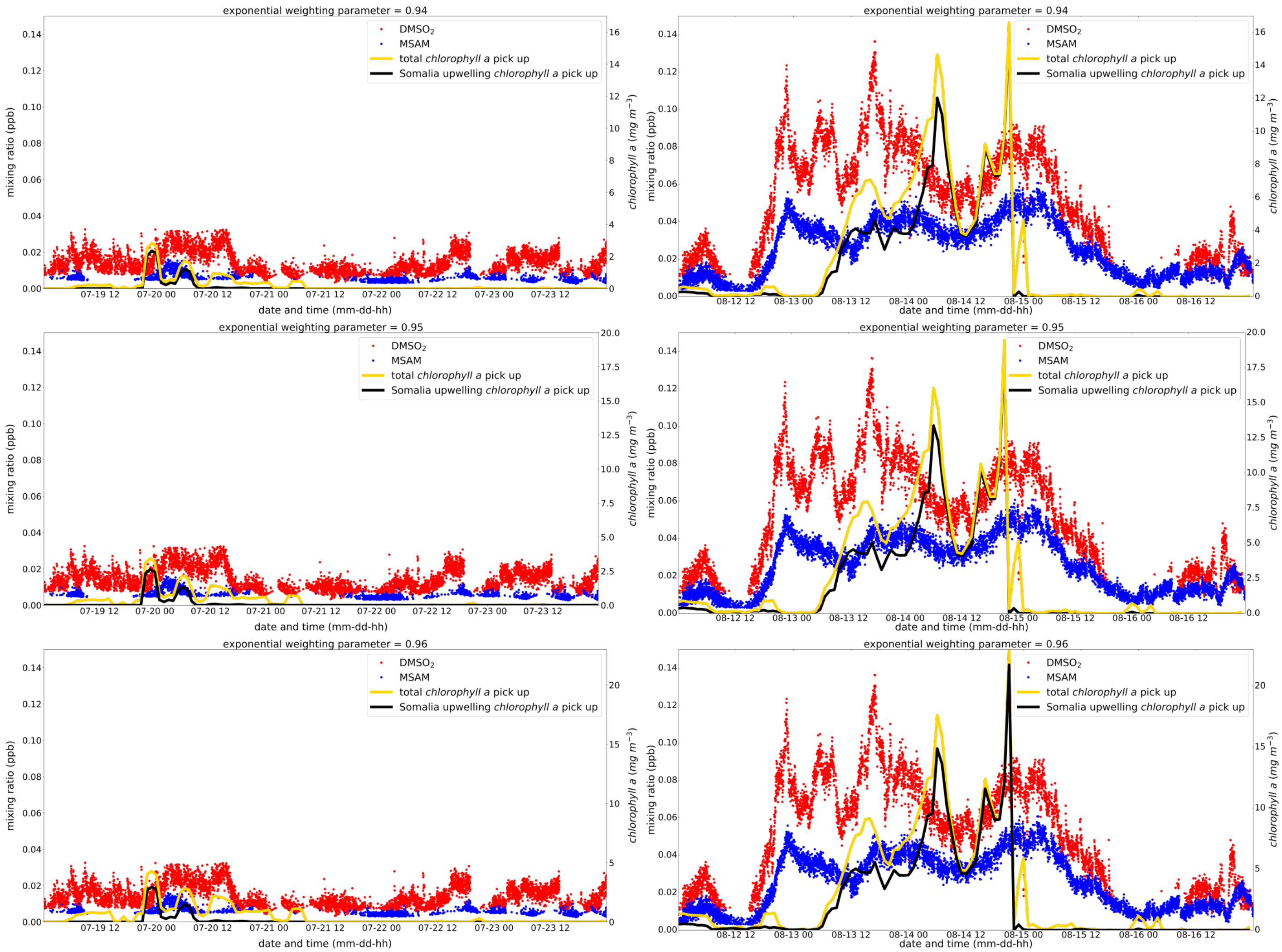

Figure 7: Exponential weighting parameters from $p = 0.94 - 0.96$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

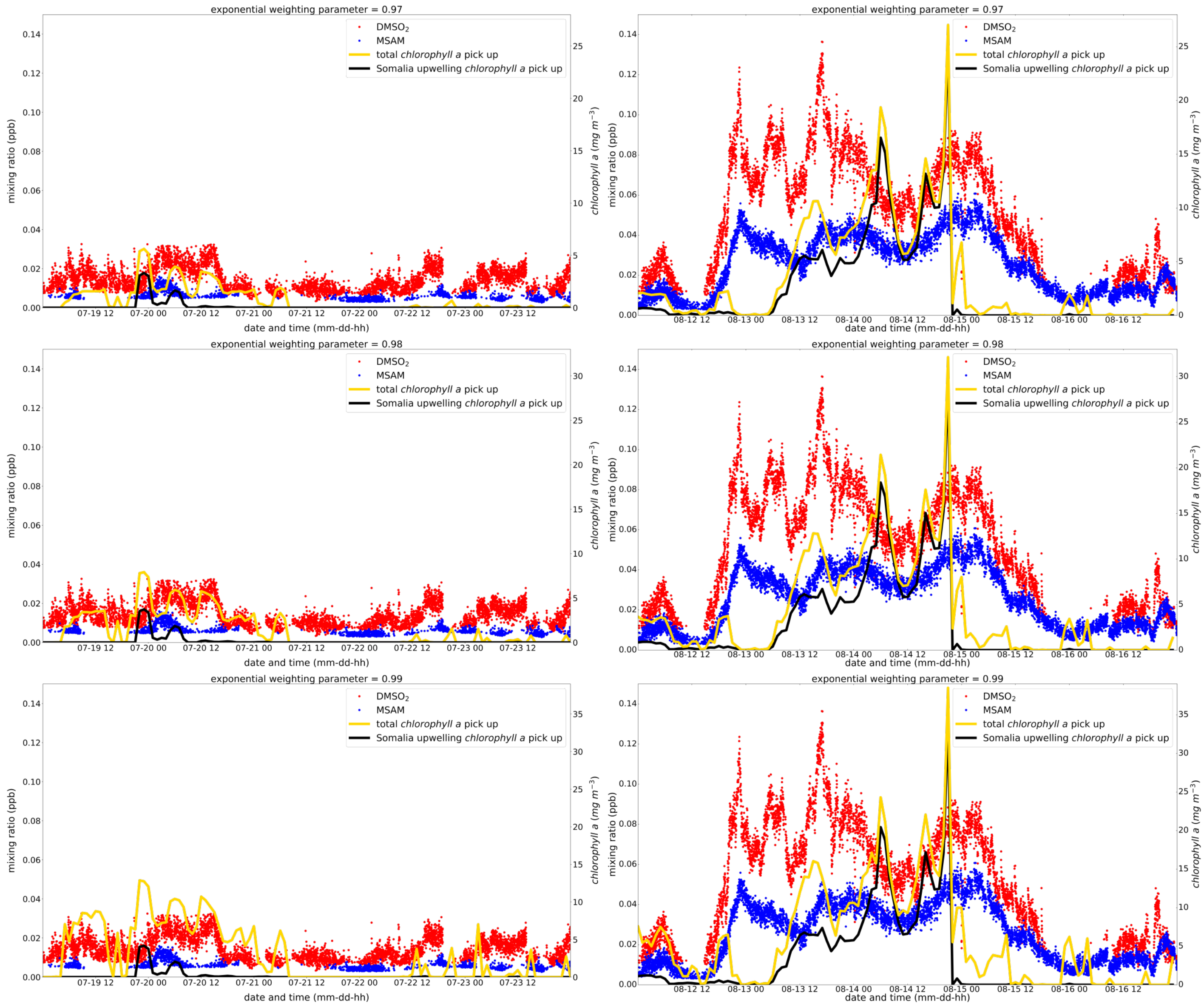

Figure 8: Exponential weighting parameters from $p = 0.97 - 0.99$. The total *chlorophyll a* exposure (yellow line) and the *chlorophyll a* exposure originating from the Somalia upwelling region (black line) is plotted. The corresponding y-axis for the *chlorophyll a* exposure is displayed on the right side. Measured ambient mixing ratios in ppb for $DMSO_2$ and MSAM are plotted in red and blue with the corresponding y-axis on the left side. In the left column leg 1 and in the right column leg 2 is displayed.

4 Diel variability plots

Diel variability of DMS, $DMSO_2$ and MSAM was calculated using only days when the wind was coming from the Somalia upwelling region. For whole days this only occurred on the 13th and 14th of August. On the 12th of August MSAM and $DMSO_2$ only started to increase and on the 15th they started to decline. The relatively short duration of the dataset available for diel variability calculations (2 days), taken on a moving platform means that variations can be interpreted as diel variations (driven by emission or atmospheric removal) or as source variations. Conclusions drawn from these plots should be treated with caution.

DMS seems to be higher at night than during the day (see Fig. 9 (a)). That is expected under stable conditions as DMS gets oxidized during daytime with OH.

$DMSO_2$ shows a tendency to be lower during daytime than at night (see Fig. 9 (b)). After sunset there is an increase in $DMSO_2$ which could hint at formation via NO_3 from the remaining DMSO concentrations.

MSAM we suggest is produced in the waters of the Somalia upwelling not in the atmosphere and subsequently transported to the ship. The time it took airmasses from the Somalia upwelling to reach the ship was 10 h to a day on the 13th and around 4 h on the 14th of August. So if we roughly assume an average travel time of 10 h for the diel cycle we have to shift the solar irradiation by 10 hours to the left (see orange filled curve in 9 (c)) in order to get the solar irradiation at the time of release from the Somalia upwelling. This hints at a production of MSAM in relation with photosynthetic activity since the higher values of MSAM occur together with higher solar irradiation in the Somalia upwelling region.

But as already stated above other effects like changes in transport time from the Somalia upwelling due to changes in wind speed and ship movement could have played a more important role.

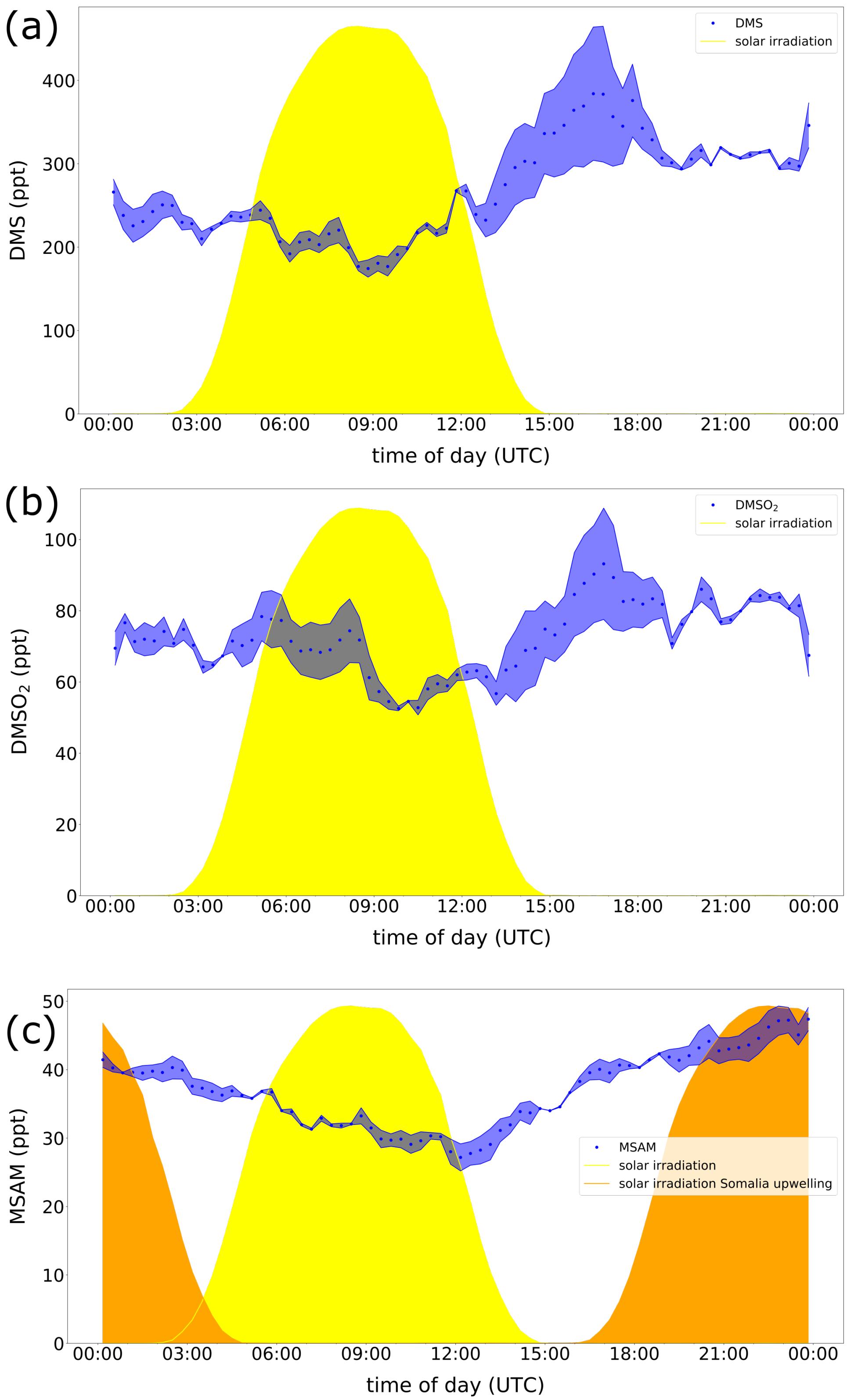

Figure 9: Diel variability of DMS (a), $DMSO_2$ (b) and MSAM (c). The blue dots are the mean and the light blue shading represents the 25th to 75th percentile. The yellow filled curve represents the solar irradiation. The diel variability was calculated using only days when the wind was coming the whole time from the Somalia upwelling region. Therefore we could only used the 13th and 14th of August for this calculations. The orange filled curve in (c) is the solar irradiation at the Somalia upwelling at the time of release of MSAM (assuming an average travel time of 10 h).

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