

## ***Interactive comment on “Environmental control on the variability of DMS and DMSP in the Mauritanian upwelling region” by C. Zindler et al.***

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We thank the referee for the intensive examination and work on our ms. The comments and advices were really helpful and gave us a frame to improve our paper. We changed parts of our ms to get a better connection between content and title. We clarified some misleading statements and improved our data presentation.

R1: This paper aims to address relevant questions using an interesting dataset. However, the authors make some strong statements based on indirect evidence and, at some points, their argumentation suffers from incomplete data analysis. A greater data mining effort, followed by an improved data synthesis and graphical representation, is needed in order to 1) achieve the goal that the title promises, and 2) place their work adequately in the context of preexisting studies. First of all, there is a conceptual con-

C4290

fusion between descriptive and process studies. Since no fluxes are reported, but only stocks, the authors should not make abuse of words suggesting fluxes or rates, like production, when they refer only to DMS(P) stocks. For instance, hotspots of DMS production and DMS concentration may co-occur (and will probably do in most occasions), but they might not, if DMS consumption processes were able to offset high production rates (as suggested by the authors themselves in the case of DMS photooxidation). A: We thank the referee #1 for the useful comment and it is right that we only measured concentrations not production rates. We clarified this in the ms.

R1: The relationship between environmental (“biotic” and “abiotic”) variables and sulfur compounds is treated in an uneven way. The authors focus on phytoplankton community composition and their trophic status as key environmental controls, which is very interesting. But if they are to understand the relative influence of other factors such as mixing depth and irradiance climate, they should treat these variables in the same way (e.g. binning, smoothing, etc.). A: We thank the referee for this comment. We tried to bin the phytoplankton, MLD and solar radiation data as we have done with the nutrients. The results were not useful. Unfortunately, these parameters were not directly linked to the nutrients, thus, it was not helpful to bin the data dependent on the N/P ratio to examine the influence of these parameters on the sulfur compounds. We also could not find other binning criteria than the N/P ratio to group the data in a reasonable way.

R1: Data concerning the vertical structure of the water column and the underwater irradiance climate are not even reported. All these variables have an obvious influence on the dynamics of microbial communities and, thus, on the surface distribution of dimethylated sulfur compounds. A: During the ATA03 cruise no underwater irradiance was measured, unfortunately. Moreover, the vertical structure of the water column was not investigated (e.g. to understand the microbial dynamics). Thus, we could not present further details about the water column to interpret the DMS and DMSP distribution as we have already stated in the ms.

C4291

R1: The discussion is incompletely referenced and, at times, misleading, and some argumentations are inconsistent. For example, the authors contradict themselves as to whether the vertical mixing and the irradiance regime have an effect at all on DMS(P) distributions. They quote the “intensive solar radiation” of the tropics as an important factor in the abstract, but then, they dismiss SRD as an important driver of DMS(P) variability in their study area. These two facts may not be fully incompatible, but the authors should be able to put in a clear way why this can happen. A: It seems counterintuitive: our failure to predict the surface DMS concentrations by using algorithms based on MLD, chl a and SRD and our assumption that intensive solar radiation in the tropics effect DMS(P) concentrations. However, we explained in the discussion on P8601, L20-28, that the algorithms were working best when the biological effect on DMS concentration is low, which is not the case in the Mauritanian upwelling region. Moreover, it was shown in several studies (references in the ms) that oxidative stress is an important factor for DMS(P) production and conversion. Additionally, the combination of SR and NO<sub>3</sub><sup>-</sup> could photochemically degrade DMS (P 8603 L 21-28). In both cases we discuss the influence of SR on the sulfur cycle and we believe that only in combination with other factors like nutrients and Br<sub>2</sub><sup>-</sup> solar radiation may be contribute to the DMS(P) distribution pattern in the coastal water of Mauritania. We clarified this statement in our ms.

R1: The statistical analysis used seems appropriate, though limited, in part because the authors do not use all its capabilities. Additional statistical tools (e.g. multivariate methods) might throw more light on this dataset. Stepwise regression is useful to explore how much variance is left after fitting, in a stepwise manner, for decreasingly good predictors. Surprisingly, the authors do never report correlations including more than one factor, nor do they report regression coefficients or p values (in some cases). They should also explain whether questions like the homogeneity of the variance and the normality of the variables have been addressed and, if not, consider using nonparametric tests. I suggest summarizing the most relevant statistical results in a table. A: We applied linear and multilinear regression (stepwise fit) to find parameters explaining

C4292

the DMS and DMSP distribution. Unfortunately, multilinear regression identified only one parameter which influenced the sulfur distribution. The upwelling region was too heterogeneous to find algorithms by using multilinear regression to explain the distribution with different parameters. Thus, we could not present correlations with several factors. We added the missing relevant p values in the ms. However, we think that the presentation of statistical factors like p values or regression coefficients in a table will not improve the results and conclusions of our paper. Other statistical tools could not apply because the dataset included only one or two data points per station and the stations were distributed in a large region. Overall we had only 55 data points for each sulfur compound, thus, a more extensive statistical analysis would be difficult to conduct. Additionally, the data were patchy because of the mixed pattern of upwelled and oligotrophic waters. Many statistical tools that assume homogeneous distribution could not apply.

R1: In my view, the most striking feature of this study is the sharp spatial gradients encountered in DMS:DMSPt ratios and, especially, the extremely low DMS:DMSPt at some stations located in the nitrogen replete area. This is clearly suggested by Fig. 7 and 8, but the authors fail at providing a conclusive explanation for their observations. This stresses the need for actual process studies in areas with strong environmental gradients, which are naturally favorable for identifying the major drivers of sulfur cycling. A: We discussed these findings on P 8602-8604. Unfortunately ATA-03 cruise was not designed as a process studies. We agree with the reviewer, that this is interesting work for the future.

Specific comments R1: P 8592 (Abstract): I suggest rewriting the whole abstract, according to the general comments and to the specific comments listed below. A: We have changed parts of the abstract to clarify between real findings and hypotheses which we deduced from our findings. We think that the abstract summaries the most important conclusions in our work and with the changes we believe that the abstract is feasible.

C4293

R1: L7-10: "Dinoflagellates were responsible for DMS production": Tone down the affirmation or rephrase, since it is based only on indirect evidence (correlations between DMS and diagnostic pigment concentrations). A: Statement was changed.

R1: L11-12: Please tone down: "presumably" instead of "most likely". A: done

R1: L14-16: Suggested rewording: "... which results in strong gradients in DMS and DMSP concentrations and DMSP to DMS conversion yields". Actually, the word yield suggests rate, so perhaps "DMS:DMSP ratios" is even more appropriate. A: Unfortunately, we cannot find this sentence in our article.

P 8593 (Introduction) R1: L10: Eliminate "the most". Depending on the system and time of the year considered, coccolithophorids might not be the most important DMSP producers. Perhaps the authors meant haptophytes (including non-calcifiers), instead of coccolithophorids. A: done

R1: L17-24: I suggest rewriting the whole paragraph. First, no DMS(P) production and consumption rates are reported in this study, so it cannot be properly called a "process study". Moreover, most of the studies cited are not process studies either. A: We thank the referee for this advice. We changed the misleading statements which suggested process studies when no production or consumption rates were investigated.

R1: Second, coastal upwelling areas are not among the least visited by oceanographic cruises, even less the North African upwelling. This can be checked in the PMEL database or in the Lana et al. (2011) updated climatology. In the 3.3 section the authors themselves say that DMS measurements in their area have been conducted since 1972. A: Although many cruises in upwelling regions were performed only a few papers have been published discussing sulfur cycles in upwelling regions. Referee #1 is right that several groups listed in the PMEL measured DMS in Mauritanian coastal region. However, only Franklin et al (2009) discussed their data in conjunction with upwelling. Additionally, other groups, with the exception of Putaud et al. (1993), collected only few data points in the Mauritanian region. These were too little to investigate the sulfur

C4294

cycle. Putaud et al. discussed their data in conjunction to atmospheric distribution. The results presented here are the very first data from the coastal upwelling off Mauritania during the upwelling season. It is worth noting that the actual upwelling occurs only in a narrow band along the Mauritanian coast. Except from our campaign and the one by Franklin et al. all other cruises did performed measurements only in waters adjacent to the actual coastal upwelling.

P 8594 (Methods) R1: L11: In terms of DMS(P), there can be large differences between 5 and 30 m, depending on the vertical mixing regime. Did the authors make vertical profiles of DMS(P) concentrations, or did they, at least, establish a clear criterion to choose the sampling depth? (e.g., samples within the upper mixed layer?). The emphasis of the article is on the 5 m depth samples, so I suggest eliminating samples deeper than 5 m or from below the mixed layer. A: We measured one time at 30 and one time at 20 m depth. We always measured at 5 m depth and for every second station also at 10 m depth. At three stations we measured at 15 m depth. 5 sampling points are below the MLD. The other 50 data points are within the MLD. We used all samples and, separately, all 5 m samples for analyzing sulfur compounds with pigments and with nutrients data. In 15m depth very low DMS concentrations were measured. We decided to present all sulfur data for the nutrients analysis because we found nutrient depletion already in 10m depth, thus, the vertical distribution was important. For the analysis of phytoplankton influences, there was no difference between using all data or only in 5 m depth, so we presented only the 5m (in the MLD) depth samples.

R1: P 8595, L8-9: Was the error of DMS measurements accounted for in the DMSPd error? Since the two measurements were done on the same sample, the long purging time (15 minutes, which prevents incomplete purging of DMS) would allow some of the released DMSPd to be converted to DMS. In my experience, filtered seawater always undergoes significant DMS accumulation upon filtration. A: Test runs in the lab before the cruise showed that DMS was completely sparged out of the sample after 15 minutes using a sample volume of 25 ml. Thus, we can exclude that DMS was left

C4295

in the samples. Additionally, we discussed in the Material and Methods sections that DMSPd can be slightly overestimated due to filtration procedure. We could not test directly how much DMSP got converted to DMS during the sparging time. We stored also some of the samples until we could measure them. Also in these samples DMSP could convert into DMS. Leck and Bagander (1988) showed that DMSP is converted into DMS over time. They recommended storing the samples for less than 4 hours to avoid a significant change. By comparing stored and directly measured samples we could not find a significant difference, thus we excluded a significant error in our DMS and DMSPd samples.

R1: P 8597 (Results and discussion): There is some relevant information missing, namely the ranges of chlorophyll concentration in the different regions, as related to upwelling activity. A: We added the information in the ms: range was 0 – 7.4  $\mu\text{mol L}^{-1}$ . The distribution of chl a according to upwelling activity is given the Fig. 2 and 4.

R1: L1-5: Please add some punctuation marks. A: done

R1: L17-18: Does the sentence add relevant information? The “most recently upwelled water” south of 17 N does not seem to display very distinct patterns compared to neighbor transects. A: The 16°N transect showed high silicate and nitrate concentrations with low chl a concentrations compare to the other transects. These still refer to fresh upwelled waters. The referee is right, the phytoplankton pattern is not very distinct different. Thus, we changed our statement in the ms.

R1: L23: Did diatoms actually get replaced by haptophytes, if haptophytes were never >11%? Diatoms seemed to be replaced by a diverse community, with relatively higher haptophyte and dinoflagellate biomass, but even higher abundance of unknown phytoplankton groups. This is important because dinoflagellates and haptophytes are suggested to carry most of the DMSPp in the study area. A: The referee is right, in the Mauritanian upwelling haptophytes and dinoflagellates did not replace diatoms. This happens in boreal region of the North Atlantic. We changed this.

C4296

R1: P 8599 and 8600, section 3.3: I find this whole section poor, considering that sulfur measurements constitute the core of the paper. DMS(P) concentrations say little if they are not compared to, at least, phytoplankton biomass (i.e chlorophyll). DMS:Chla and DMSPp or DMSPt:Chla ratios could be highly informative, and they could unveil interesting modes of seasonal or spatial variability. A: Section 3.3 is only a descriptive section about the DMS and DMSP distribution. We described in the following sections of the ms the influence of the different pigments and chl a on the sulfur compounds. We added the DMS:chl a and DMSP:chl a values in section 3.4.1. The distribution pattern of DMS(P) and chl a is also shown in Fig. 4.

R1: P8600: DLA is only a potential activity (i.e., maximum in-vitro activity), and it does not tell us much about actual DMSP to DMS conversion rates in seawater, even though the association between DLA and dinoflagellates seems solid. Moreover, it is not clear whether a positive or a negative correlation should be expected between DLA and DMSP stocks or DMS:DMSP ratios. Still, there is no clear indication that dinoflagellates or haptophytes were the major DMSP carriers, according to the weak correlations found. A simple calculation shows that, if dinoflagellates and haptophytes were assumed to carry all the DMSPp, the DMSPp:(haptophyte-Chla) ratio would be as high as ca. 6  $\mu\text{mol g}^{-1}$  (that is, 6000  $\text{nmol g}^{-1}$  or  $\text{mmol g}^{-1}$ ) at the spot where DMSPp was 990 nM (where dinoflagellates were virtually absent according to HPLC). This value is one of magnitude higher than the DMSPp:Chla of very strong DMSP producers (see Stefels et al. 2007). Converting haptophyte pigment biomass to carbon biomass (assuming a C:Chl of 50), we find that DMSP carbon could account for far more than 100% of cell carbon, which is unrealistic. Doing it another way, applying a C:S molar ratio of 20 (which is low!), we find that haptophyte DMSP should be around 30 nM, which is almost 2 orders of magnitude lower than 990 nM. In summary: either grazers or unknown phytoplankton groups were carrying a lot of DMSP at some spots! and this DMSP did not seem to be available for algal or bacterial lyases, according to the low DMS concentrations found (1 nM). A: We discussed on P8601 L 5-14 the grazer and senescence effect on the DMS(P) pool. And it is right that the contribution

C4297

of unknown phytoplankton cannot exclude. However, we cannot say how big the effect is.

R1: P 8601: References to grazing are incomplete, and none refers to the impact of grazers at the ecosystem level. Check, for instance, Archer et al. (2002, 2010), Saló et al. (2010), Simó et al. (2002), etc. A: We thank the referee for the suggested papers. We added the references.

R1: P 8600, L20-22: Quoting Stefels et al. (2007), "haptophytes are the only group where all the species tested were observed to produce DMSP". Correlations should be used with caution before making too strong statements. A: We changed the statement in the ms.

R1: P 8601, section 3.4.2: I suggest rewriting the whole section for the following reasons: Values of MLD, subsurface or above-surface mean daily irradiance, vertical light attenuation coefficients ( $K_d$  of PAR, at least), and resulting SRDs should be reported, as done for other environmental variables. In this regard, it is critical the criterion used to define MLD (see Brainerd and Gregg, 1995; or de Boyer Montégut et al., 2004). To assess the importance of these factors relative to others, they should be treated in the same way: binned, smoothed, etc. as done with N:P ratios. Phytoplankton pigment composition could be treated similarly. A: We think that the finding from Simó, Dachs and Vallina is an interesting approach to predict DMS. However, we could not predict DMS with this approach; thus, we did not want to show data like the MLD, SRD,  $k$  or other parameters when we could not make a positive conclusion. We think we complicate the paper with showing results which are not meaningful and which are not improving our findings. We wanted to focus on the nutrient dependence. In the third paragraph above we explained that we could not bin the data as we have done for the nutrients because the binning was dependent on the N/P ratio and SRD, MLD and other parameters could not be linked to nutrients. We could also not find other criteria to group the data.

C4298

R1: L24-28: The argumentation is misleading. I cannot recall a marine epipelagic ecosystem where "biological effects are small" regarding DMS production, since significant DMS production pathways are all biological (which is clearly explained by the authors in the Introduction). Vallina and Simó's (2007) paper acknowledges that DMS production is the result of complex food web dynamics, which are embedded and modulated by the physical framework, including solar radiation, at various timescales. Accordingly, they just state that the DMS-SRD relationship is 1) a necessary condition for the CLAW hypothesis to hold, and 2) a useful shortcut for predicting surface DMS concentration. A: The referee is right that DMS production pathways are biological but the SRD approach is mainly based on physical parameters, chl *a* is the only biological parameter. The SRD algorithm is based on the DMS summer paradox which explains the high DMS concentrations in a low chl *a* environment. We argued in our paper that the upwelling area cannot compare to oligotrophic open ocean regions where the SRD algorithm can be used. Also other groups (references were given in the ms) could show that the SRD algorithm is not working in high biologically active regions.

R1: P 8602, section 3.4.3: Please refer also to Bucciarelli and Sunda's (2003) paper, which is relevant to the author's argumentation, even though a diatom strain was used in that study. A: done

R1: P 8603, section 3.4.4: The discussion of the potential spatial variability in DMS photolysis is slightly confusing and speculative, since only nitrate concentrations were actually measured. Toole et al. (2004) showed that not only nitrate is important, but also the variability in CDOM optical and chemical characteristics, which might be very different in freshly upwelled waters compared to "aged" surface waters. The impact of Br<sup>-</sup> and DIC has yet to be demonstrated in natural waters with little Br<sup>-</sup> and pH (DIC speciation) variability. A: Unfortunately, we did not measure CDOM during the cruise. Thus, we have no idea about the CDOM distribution and influence on the DMS concentration. We also did not measure Br<sup>-</sup>. However, the Br<sup>-</sup> concentration in seawater is high enough in general to have an effect on the DMS concentration as we

C4299

discussed in our ms. The photolysis of DMS is only a one reasonable explanation for our findings of low DMS concentrations with higher N:P ratios and, without evidence, it is speculative.

R1: P 8604 and 8605: I suggest that the authors modify this section according to the following comments: It is inconsistent to say, first, that “the increasing N limitation in combination with the high UV radiation...” were important, and then that “other factors such as MLD and SRD have not influenced the DMS surface distributions off Mauritania”. SRD is actually the MLD-integrated daily irradiance, so it has a lot to do with the amount of light available for photosynthesis and photochemistry, as well as phytoplankton and bacterioplankton stress. In other words: MLD and SRD are proxies of main ecosystem drivers, so they must play a role. Still, this does not imply that they are good predictors in that particular system. A: We replaced the sentence: “other factors such as MLD and SRD...”; to clarify the apparent inconsistency.

R1: The conclusions about the nutrient-induced switch seem feasible, but other hypotheses should be considered besides nitrogen availability. In particular, the role of DMS- and DMSP-consuming bacteria is hardly mentioned in the paper. A: We did not measure bacteria composition, uptake or consumption rates. Thus, we could not say anything about the influence of bacteria on DMS(P) in this region. However, we said that bacteria could have had a big influence on the sulfur cycle (P 8604 L25).

R1: Tables and figures Table 1: This literature data compilation is useful, but additional parameters would make it more valuable, e.g. DMS(P):Chla ratios. The concentration ranges reported may be misleading, because there is no clear indication of the depth horizon considered. Very low DMS(P) concentrations are most likely from below the mixed layer (e.g., DMS < 0.5 nM and DMSPp < 2 nM). A: additional information are given in the table

R1: Fig. 2: Is it possible to improve the appearance of the spatial interpolation? Filling better the gaps (without modifying the value of the actual sampling points) would make

C4300

it easier to understand the figure at a glance. A simpler color scale might help as well. A: The sampling frequency was not high enough in the Mauritanian region to interpolate the whole region which is shown on the map. When we fill the gaps single data points will present to big regions which is not reflecting the real distribution. To keep the gaps was a compromise between realistic data presentation and filling the map. We think that the color distribution highlighted best the strong gradients we wanted to show.

R1: Fig. 5 and 6: In the current presentation it is very difficult to see any patterns, only a few concurrent peaks and a maze of symbols and lines in some areas of the plot. In addition, the two figures are highly redundant. A graphical legend would be much appreciated, as well as a clearer use of symbols, lines and colors. Why not presenting the data in temperature bins, like in Fig. 7, or in any easier-to-digest graphic? A: We have changed the graphs.

R1: Fig. 7: this is the more interesting figure of the paper (together with Fig. 8). Some comments: Gray triangles are actually diamonds. A: done

R1: I suggest that standard deviation bars are added to the bins, and that average bin concentrations are shown without smoothing. A smoothed line could be overlaid. I also suggest adding at the background the DMS:DMSPt ratio in bars, the shape will look beautiful. This will be very illustrative of the N:P bin(s) where highest DMSPt to DMS conversion efficiencies occur. Why not making similar figures with DMS(P) concentrations and DMS:DMSPt ratios sorted according to MLD bins, SRD bins, % dinoflagellate biomass bins, etc... A: We added the DMS:DMSPt ratio in the background of the figure. The figure is much easier to read without showing the average concentrations because some points are too high.

R1: Technical corrections P 8592 (Abstract), L8 and L10: “the” seems unnecessary. P 8593 (Introduction), L8: “has been” instead of “was”? L18 and L25: “descriptive” instead of “process”. P 8595, L8-9: “Were” instead of “was”? “1-4L...” is plural (liters). P 8598, L11: “Haptophytes” instead of “haphthophytes”. P 8602, L24: perhaps an

C4301

hyphen missing in “N specific”? Might depend on the journal’s style guide. L26: “may only BE applicable”. A: all done

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C4302