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

Anonymous Referee #1

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General comments

Zindler’s et al. paper assesses the spatial variability of dimethylated sulfur compounds off Mauritania, as related to the upwelling activity. DMS and DMSP concentrations in surface waters are compared to biotic and abiotic drivers of marine sulfur cycling. A salient finding of this work is the switch from low to high DMS:DMSPt ratios as a function of nitrate scarcity, which they interpret in the light of the nutrient- and radiation-induced oxidative stress hypothesis.

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

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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 confusion 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 cooccur (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).

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.). 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.

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.

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

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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 non-parametric tests. I suggest summarizing the most relevant statistical results in a table.

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.

Specific comments

P 8592 (Abstract): I suggest rewriting the whole abstract, according to the general comments and to the specific comments listed below.

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).

L11-12: Please tone down: “presumably” instead of “most likely”.

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:DMSPt ratios” is even more appropriate.

P 8593 (Introduction)

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

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authors meant haptophytes (including non-calcifiers), instead of coccolithophorids.

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. 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.

P 8594 (Methods)

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.

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.

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.

L1-5: Please add some punctuation marks.

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

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neighbor transects.

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.

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.

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. $6 \mu\text{mol } \mu\text{g}^{-1}$ (that is, 6000 nmol μg^{-1} or 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

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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).

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.

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.

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.

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.

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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.

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- and DIC has yet to be demonstrated in natural waters with little Br- and pH (DIC speciation) variability.

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.

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.

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

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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., $\text{DMS} < 0.5 \text{ nM}$ and $\text{DMSPP} < 2 \text{ nM}$).

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 it easier to understand the figure at a glance. A simpler color scale might help as well.

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?

Fig. 7: this is the more interesting figure of the paper (together with Fig. 8). Some comments:

Gray triangles are actually diamonds.

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...

Technical corrections

P 8592 (Abstract), L8 and L10: “the” seems unnecessary.

P 8593 (Introduction), L8: “has been” instead of “was”?

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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 “haphophytes”.

P 8602, L24: perhaps an hyphen missing in “N specific”? Might depend on the journal’s style guide.

L26: “may only BE applicable”.

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