Review: "Patterns and drivers of dimethylsulfide concentration in the northeast Subarctic Pacific across multiple spatial and temporal scales"

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Reviewer: Martí Galí

General comments

DMS accounts for approximately 20% of global sulfur emissions and represents a major source of cloud-seeding aerosols in unpolluted marine atmospheres. Therefore, marine DMS emission plays a key climatic role by modulating the radiative properties of aerosols and clouds, as well as precipitation. However, our understanding of DMS drivers across multiple spatial and temporal scales remains limited, and thus our predictive capacity. Reliable high-resolution DMS datasets are essential to improve regional and global DMS climatologies, avoiding artifacts and biases that affect interpolated climatologies based on sparse data, and potentially providing sufficient observations to allow for the evaluation of interannual variability.

The paper by Alysia E. Herr and coauthors makes a valuable contribution to the understanding of DMS distribution patterns in the northeast Subarctic Pacific (NESAP) region. Particularly, it highlights the difficulty in finding unifying criteria across this region, characterized by sharp biogeochemical gradients. From a methodological standpoint, I appreciated the authors presenting traditional discrete GC-FPD measurements along with high-resolution MIMS data (Fig. 3). This comparison increases our confidence in high-resolution DMS surveys, which might be prone to measurement artifacts caused by cell breakage upon pumping and in-line filtration. (I also appreciated the new datasets being readily uploaded to the PMEL archive!). The paper is well written and structured, and the figures and tables are clear and informative. Yet, I suggest the authors to add several citations to give readers a broader perspective on the subject, while recognizing the relevance of previous studies. Below I list what are, in my opinion, the main shortcomings of the article, which I recommend addressing through the Results, Discussion and Conclusions sections:

1. Treatment of DMSPt and phytoplankton groups/size classes in the data analysis. "Dominance vs. abundance":

1.1. I strongly encourage the authors to show total DMSP (DMSPt) concentrations, not just DMSPt:Chl ratios, and analyze their relationship with DMS, simply because DMSPt is the precursor of DMS. DMSPt concentration should be displayed (Fig. 4, 6 and 7).

1.2. Correlations between [DMS] and the dominance (relative abundance) of certain phytoplankton groups, as reported in this paper, can be misleading (the same applies to DMS vs. the DMSPt:Chl ratios). For example, in transect T3 (Fig. 7), the authors report a negative correlation between DMS and relative prymnesiophyte abundance ($r = -0.75$). In the middle of T3, inshore of the front, Chl increases sharply from ~1 to 30 $\mu g\ L^{-1}$, whereas % prymnesiophytes decreases from ~20% to ~5%. Still, the abundance of prymnesiophytes increases by about 8-fold, while DMS increases "only" by ~3-fold (~5

to ~15 nM). Thus, the increase in prymnesiophytes might suffice to explain the increase in DMS, be it through direct DMS release by prymnesiophytes or through the activity of micrograzers and bacteria. It is well known that increases in microphytoplankton abundance (mostly diatoms) are generally accompanied by increases of other phytoplankton groups (Barber and Hiscock, 2006; Uitz et al., 2006), as in the current dataset.

1.3 Dinoflagellates: Why is their abundance not reported and their role not discussed, although they are quoted in the Introduction and beginning of the Discussion as important players (Steiner et al., 2012)? More generally, I wonder what phytoplankton groups made up the ~50% of the pigment biomass that is omitted in Fig. 4, 6 and 7. What about other high-DMSP nanophytoplankton like chrysophytes and pelagophytes?

2. Process measurements:

2.1. I was puzzled to see dissolved DMSP consumption rate constants (kDMSPd) ranging between ~30 and 100 d^{-1}, while kDMSPd values in the literature are generally lower than 10 d^{-1} (Galí and Simó, 2015). Highest kDMSPd reported so far are ~20 d^{-1} in the NE Pacific (Royer et al., 2010) and near South Zealand (Lizotte et al., 2017). Is there a mistake? Everything would look more consistent in terms of S and C cycling (Kiene and Linn, 2000) if the reported kDMSPd had units of h^{-1} instead of d^{-1}. Otherwise, the contribution of heterotrophic DMSPd conusmption to DMSPt cycling and bacterial S and C demand would be suspiciously high (as some quick calculations can show).

2.2. Although the data suggest distinct DMS(P) cycling regimes, I am not sure the amount of process measurements suffices to resolve DMS variability across fronts. In addition, important DMS production and loss terms were not measured. The finding that variations in biological DMS consumption (kDMS) drove [DMS] across regions seems robust (although DMS photolysis, a potentially important loss term, was not measured). Regarding DMS sources, DMS production from particulate DMSP cleavage was not assessed, and previous studies suggest it is important globally (Galí and Simó, 2015) and in this region (Asher et al., 2017). This fits well with prymnesiophyte and (dinoflagellate?) driven DMS production.
As DMS concentration is set by the dynamic balance between gross production rates (nM d^{-1}) and total DMS loss rate constants (d^{-1}) (Galí and Simó, 2015), conclusions based on a subset of production and loss processes are weak. Note also that the contribution of DMSPd turnover to DMS concentration is set by the product [DMSPd]*KDMSPd*Yd, where Yd is the DMS yield from dissolved DMSPd consumption. Thus, the relationship between kDMSPd and [DMS] tells little if Yd is not known (Yd can easily vary between 5 and 20%). The control of kDMS on [DMS] is comparatively more direct. I propose:

(i) displaying the relationship between kDMS, [DMS] and potentially other variables (T, S, Chl, ...) in a scatterplot-like graphic.

(ii) discussing more in depth the control of [DMS] by measured and non-measured DMS budget terms to give a more balanced view of the potential processes at play (see Galí and Simó, 2015).

3. Algorithm evaluation and regional tuning:

Several previous studies have shown that global-scale algorithms have poor skill at predicting regional DMS variability (e.g. Bell et al., 2006; Galí et al., 2018; Hind et al., 2011), not to talk about the mesoscale. The authors tried to tune pre-existing algorithms to their dataset using least squares fits, but they did not show the new coefficients, only the improved skill metrics. Consequently, the interpretation of this exercise remains vague and does not shed much light on the controlling factors, nor it helps designing better algorithms. I suggest either deleting this section (my choice) or reshaping and expanding it to make it more informative (making use of the supplemental information).

Specific comments

Introduction

P2 L17: please specify what zone of the "Southern Ocean". Iron-depleted regions of the subpolar Southern Ocean (approx. 40 to 60S) are relatively unproductive and typically have low [DMS]... (Jarníková and Tortell, 2016; Kiene et al., 2007; Lana et al., 2011).

P3 L1-7: These lines suggest that we do understand what causes high DMS concentrations in this area. I think we don't, for two main reasons:
(i) We do not understand interannual variability (Galí et al., 2018; Steiner et al., 2012).
(ii) We do not understand well enough the interplay between iron limitation, dominance of high DMSP producers (depicted by DMSPt:Chl) and DMS production pathways. The authors quote "the effects of mixed layer stratification and Fe-limitation, which may act to increase DMS/P production as a means to offset oxidative stress (Sunda et al. 2002)". However, Royer et al. (2010) found a positive correlation between iron concentration and DMSPt:Chl ratios in the HNLC area within the NESAP. This is contrary to what one would expect if Fe stress caused major increases in DMSPt:Chl ratios. It is possible that small Fe additions stimulate preferentially high DMSP producers (Levasseur et al., 2006; Steiner et al., 2012), which would result in a positive correlation between DMSPt:Chl and Fe as long as high DMSP producers are not outcompeted by diatoms. Regarding DMSP-to-DMS yields, although Royer et al. (2010) documented higher bacterial DMS yields in the Fe-depleted HNLC region, Steiner et al. (2012) pointed to dinoflagellates and micrograzers as key players in DMS production. The latter would imply a dominant role of DMS production from the particulate pool, involving phytoplanktonic DMSP lyases. These processes are poorly documented in the NESAP area.

P3 L12: I suggest citing here Simó et al. (2018) (The quantitative role of microzooplankton grazing in dimethylsulfide (DMS) production in the NW Mediterranean) to support the importance of grazing-mediated DMS production. A major

finding of that paper is that "throughout the year, grazing-mediated DMS production explained 73% of the variance in the DMS concentration".

P3 L18. I missed two relevant citations here:
1. Belviso et al. (2003) "Mesoscale features of surface water DMSP and DMS concentrations in the Atlantic Ocean off Morocco and in the Mediterranean Sea". A precursor study showing sharp changes in DMS:DMSPt:Chl across mesoscale features and fronts.
2. Royer et al. (2015) Small-scale variability patterns of DMS and phytoplankton in surface waters of the "tropical and subtropical Atlantic, Indian, and Pacific Oceans". A high-resolution DMS survey across 21000 km in the tropical oceans, showing that "much of the variability in DMS concentrations occurs at scales between 15 and 50 km, that is, at the lower edge of mesoscale dynamics, decreasing with latitude and productivity. DMS variability was found to be more commonly related to that of phytoplankton-related variables than to that of physical variables".

Methods

P5 L3: Please report more statistics (RMSE, mean bias, linear regression equation...) comparing MIMS and GC-FPD, either here or on the figure (which should be 3, not 2).

P6 L27: Phytoplankton biomass tends to peak in late summer in the oceanic sector of the NESAP. Regarding DMS, there seems to be more similarity between August and September than between August and June (Galí et al., 2018; Lana et al., 2011; Steiner et al., 2012), perhaps related to the dinoflagellate abundance in late summer (Steiner et al., 2012). I understand the authors' choice reflects data availability, but I suggest cautioning the reader that June, July and August can be very different.

P7 L14-15: Please add citations for all satellite products: PAR (Frouin et al., 2003), Chl-a (Hu et al., 2012; O'Reilly et al., 1998).

P7 L29: What fraction of your 1-degree bins is over bottom depths shallower than 2000 m, where MLD is not available? Could this bias the evaluation of empirical algorithms, given the distinct biogeochemical dynamics of shelf seas? What would be the impact of replacing time-resolved MLD data by a monthly climatology? Perhaps using climatological MLD would make a little difference in oceanic areas, while allowing testing of the algorithms in the entire NESAP domain. Also, how did data gaps caused by cloudiness affect algorithm evaluation? (as suggested by P9 L25 in Results, and Fig. 1 top panels).

P7 L30: Please specify what DMS and SST datasets were used in combination with daily 2.5-degree wind speed data to calculate DMS flux: non-binned data, 1-degree binned data retaining temporal variability, or the 1-degree summer climatology?

P8 L9: I would add "all observations within the JJA months for a given year were averaged" (to avoid confusion with the way monthly climatologies like L11 are calculated).

P8 L27: Did you try Spearman's rank correlations? This could help identifying nonlinear monotonic relationships.

P8 L32: If the section on algorithm evaluation is not dropped, the authors could also evaluate the two-step algorithm of Galí et al. (2018). We showed that it outperforms SD02 and VS07 in most oceanic areas, although it has difficulties to reproduce the DMS seasonal cycle at Ocean Station P. The global algorithm of Anderson et al. (2001) would also be an interesting choice here as it performed well across contrasting trophic regimes in the SE Pacific (Hind et al., 2011).

Results

P10 L10-15: How well compare the estimates of phytoplankton size classes derived from absorption (underway WetLabs instrument) to HPLC pigments?

P10 L18: The difference may be significant due to large N, but is it relevant when the ranges overlap so much? Note also that saying DMS concentrations were significantly different in different years downplays the utility of calculating a multiyear climatology.

P11 L12: Beyond the high SSHA-DMS coherence at the mesoscale, Fig. 5 shows there is a lot of unresolved submesoscale variability, probably due to biological heterogeneity, in agreement with (Royer et al., 2015).

P11 L20: Relative abundance or absolute? Also, I suggest specifying that these size classes were derived from underway absorption data, not HPLC, to avoid confusion.

P11 L30: How can significance be tested with n = 2 at each side of the front (Fig. 4)? I suggest reporting ranges. Qualitatively, I agree that k's were different at either side of the front.

P12 L1-2: This explanation is unclear. See general comment 2.2.

P12 L31-32: Same as above.

P13 L30: Can this be tested statistically somehow? See general comment 2.2.

P13 L33: Please check units (general comment 2.1).

P15 L15-26: See general comment 3. This section would be more interesting if the authors explained the rationale behind the original algorithms, reported the tuned coefficients, and explained in what sense they alter the performance of the original

algorithms. In particular, turning from negative to positive slope in VS07 completely alters the rationale behind this algorithm.

Discussion

P17 L13: could you please explain more explicitly the relationship between positive SSHA and high DMS? Eg, anticyclonic eddies detaching from a frontal area and transporting a certain water type, or whatever... This can help us understand why SSHA can show both positive and negative correlations to DMS (as explained at the bottom of the same page).

P17 L19: The unpublished meta-analysis should be cited as pers. comm., I guess.

P17 L23-27: The negative correlation between SRD and DMS in the whole region (Table 5, original VS07 algorithm) goes against this argument.

P18 L20: OK, but transient [DMS] and kDMS do not even need to be invoked. The relationship may also arise at nearly-steady state, where [DMS] = (gross production rate) / (total loss rate constant), where total loss is dominated by biological DMS consumption k, as explained by (Galí and Simó, 2015).

P18 L26: As the authors explain, DMS consumption rates will be positively correlated to [DMS] as long as [DMS] is more variable than kDMS, because cons. rate = [DMS]*kDMS. I suggest removing this sentence.: "In contrast to DMS rate constants (d-1), water column DMS consumption rates (nM d-1) showed a positive correlation with DMS concentrations ($r=0.65$, $p=0.01$). This result is not unexpected, as consumption rates are the product of rate constants and in situ concentrations".

P19 L4: I also suggest removing this: "In contrast to biological loss, turnover time due to sea-air flux showed no correlation to DMS concentrations".

P19 L13-23: I suggest refining the writing here: see general comment 2.2.

P19 section 4.4: Would it be possible to quantify interannual variability of DMS (see Fig. 3 of Steiner et al., 2012) using the merged dataset? Interannual variability has been overlooked (Galí et al., 2018), with so much emphasis on the mean (climatological) state... This part of the Discussion is currently a bit poor.

P20-21, section 4.6: The last two paragraphs of this section seem to contradict each other. Does elevated productivity (which usually follows elevated biomass) translate into high DMS, or not? If only in some places, why? What are the relevant scales for this comparison? It would be interesting to cite here the work of (Kameyama et al., 2013) "Strong relationship between dimethyl sulfide and net community production in the western subarctic Pacific", perhaps extracting more information from your own NCP vs. DMS data.

P21 L17-18: Data from tables 4 and 5 supports this idea, so I suggest citing the tables here (ie, the HNCL PSAE shows the highest negative correlations between DMS and bot NO3 and SRD).

Edits

P5 L5-6: I suggest removing "and rate measurements to examine potential drivers of spatial variation". Rates were not measured in underway samples...

P6 L12: "sampled" should be "samples".

Table 1: please replace "June" by "August" for cruise LPA07.

P12 L7-8: please remove "given no new production". DMS removal expressed as a daily % would also hold in the presence of DMS production (as it is usually the case).

P15 L1: Please correct "We also calculated and DMS:Chla..."

P20 L14: "distinction", rather than "measure"?

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