

Interactive comment on “Spatial and temporal variability of the dimethylsulfide to chlorophyll ratio in the surface ocean: an assessment in the light of phytoplankton composition determined from space” by I. Masotti et al.

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We thank the referee 2 for what we see as a fair and considered review. We are grateful that the referee thinks that this paper is relevant to BG, includes new ideas and an in depth analysis of an important data set, that the question addressed is important and the methodological approach unique, and that this community paper represents an important contribution to the field.

Answer to all comments from referee 2 (referee (R), author (A)).

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R. Few years ago, Alvain and colleagues developed an algorithm (PHYSAT) allowing determining the distribution of six key Phytoplankton Functional Types (PFT) from space where and when one PFT is dominating the assemblage and biomass is not exceeding 4 mg m^{-3} . This was an important contribution to ‘space’ oceanography given that several ocean processes are heavily influenced by phytoplankton types. One of these processes is the production of DMS, a biogenic gas contributing to the global climate regulation. As mentioned by the authors, DMS distribution at the surface of the ocean is generally not correlated with total algal biomass indices such as chlorophyll a. The production of DMS is dependent on the presence of strong DMSP (the algal precursor of DMS) or DMS producers in the community, and of algal DMSP-lyase, the enzyme responsible for the cleavage of DMSP into DMS. High intracellular DMSP concentrations and DMSP-lyases are found mostly in prymnesiophytes and dinoflagellates, with diatom being poor DMSP producers and having no DMSP-lyase. In addition, several abiotic and other biotic processes contribute to the net DMS production. For these reasons, attends to related DMS levels to the chlorophyll a signal from space have not been successful so far.

In this paper, the authors assessed the influence of phytoplankton speciation on the variability of the DMS:Chl ratio at the global scale. Different data sets were used by the authors in order to explore the existence of linear relationship between DMS and Chl in water masses with different PFTs. To do so, they used satellite imagery for Chl and PHYSAT, and DMS values from the PMLE global data base (plus some unpublished cruises data). In their analysis, there are thus three widely different data sets: 1) 10-year climatology for PHYSAT, 2) space measurements for Chl, and 3) in situ measurements for DMS. It is difficult to appreciate how combining these three different data sets may have impacted on the conclusions. Nevertheless, it is important for the reader to keep this limitation in mind when going through the results and discussion.

A. In fact, we use monthly composites both for ocean color and for the phytoplankton group dominance patterns and monthly climatologies (1998-2006).

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R. The major conclusion of the manuscript is that large scale variations in DMS:Chl ratios are not consistent within phytoplankton group. The authors should be prudent here since PHYSAT only identifies dominant groups. As mentioned several times in the discussion, non-dominant PFTs may be responsible for most of the DMS signal in many instances. I am thus concerned by their conclusion stating: 'Our results suggest that the species composition is not a first order controller of the global DMS dynamics' (page 3633, line 2). That could be true, but the results presented in this paper do not support this conclusion. They also found a particularly clear decoupling between DMS and Chl in the Equatorial Divergence. The decoupling between DMS and Chl has been reported before and called the 'Sumer DMS Paradox' by Simó and Pedrós-Alió (1999). I was surprised to find no reference to this previous study here.

A. We have modified the abstract and conclusion where we refer to phytoplankton group dominance (PGD) and no more to species composition.

Copied from revised abstract: "Hence, in a majority of cases PGD is not of primary importance in controlling DMS:Chl variations. We therefore conclude that water-leaving radiance spectra obtained simultaneously from ocean color sensor measurements of Chl concentrations and dominant phytoplankton groups can not be used to predict global fields of DMS."

Copied from revised conclusion: "We therefore conclude that ocean color sensor measurements of Chl concentrations and dominant phytoplankton groups can not be used to predict global fields of DMS."

Simó and Pedrós-Alió (1999) is quoted in the revised reference list.

R. With that said, this paper is relevant to BG and includes new ideas and an in depth analysis of an important data set. The question addressed is important and their methodological approach unique. Such analysis was never attempted at this scale. I thus consider that this community paper represents an important contribution to the field and should be published following some revisions.

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A. Thank you.

R. ABSTRACT The DMS:Chl ratio varies widely in the surface ocean also because DMS is ventilated and Chl is not.

A. The referee is right but it is laborious to reconstruct the history of DMS ventilation along cruise track. That is why we have neglected the role of ventilation. We will readdress this point below.

R. INTRODUCTION Page 3608, line 20: The authors should acknowledge that Chl and DMS vary on different time scales, days and hours respectively. This also contributes to the poor correlation between the two variables. As mentioned previously, ventilation which only affects DMS levels should also be mentioned.

A. We agree. We have modified two sentences in the revised Introduction.

"Attempts to correlate DMS concentrations to chlorophyll (Chl) have not proven robust likely because (1) Chl and DMS vary on different time scales, days and hours respectively, and (2) the cycle of DMS in seawater is controlled by a number of complex physical, chemical and biological processes (Kettle et al., 1999; Stefels et al., 2007; Vogt and Liss, 2009)."

"Also, by comparing DMS:Chl with the PHYSAT products we implicitly underestimate the role that the physical (ventilation, vertical mixing and the mixed layer depth, Simó and Pedrós-Alió, 1999), chemical (e.g. photooxidation, Bouillon and Miller, 2004) and biological removal processes (e.g. bacterial consumption, Kiene et al., 2000) play on DMS."

R. Page 3610, line 11: It is important to specify that PHYSAT detects the main dominant phytoplankton group since this dominant group may not be responsible for most of the DMS signal under certain circumstances. This is done here, but this limitation is somewhat lost in the discussion. I suspect that Chl have been measured along DMS during most of the cruises cited. I am wondering why the authors did not attempt to

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compare in situ DMS:Chl ratios with DMS:Chl ratios estimated from space?

A. Phytoplankton group dominance is now used throughout the revised manuscript.

Because the PHYSAT method was applied to SeaWiFS data, it was logical to use SeaWiFS data also to assess the Chl concentrations. The other reasons for which SeaWiFS data were used instead of in situ Chl measurements are (1) Chl measurements were not available along each cruise track and (2), when available, the chlorophyll fluorescence sensors were not always calibrated. Moreover, diurnal fluorescence values exhibit light-dependent depressions resulting from non-photochemical quenching processes, so fluorescence-based chlorophyll estimates are restricted to nighttime data. This was especially true in the eastern equatorial Pacific during the 2003 cruise (Behrenfeld and Boss, 2006). Hence, we have used the best satellite products available at the time of the study and applied no temporal and spatial regriding procedure and matched SeaWiFS data with DMS measurements according to the month and the geographical coordinates.

R. METHODS Page 3610, line 18: Information regarding the effect of the pump on DMSP should be removed since not relevant to this work.

A. We have removed DMSPp and DMSPd data but we think that it is informative to show that total DMSP concentration is less affected by the pump than DMS.

R. Page 3614, line 1: . . . According to this validation. . . are validated. What to you mean?

A. We mean: "according to the results of the validation exercise carried out by Alvain et al. (2008)." In the revised manuscript we summarize the results of this validation exercise (Methods section, sub-section 2.2.2).

R. Page 3614, line 8: The poor performance of PHYSAT to detect dominance of Phaeocystis and coccolithophores is certainly not good news in the context of the present study.

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A. Dr. S. Alvain is presently working on this specific aspect using data collected during the CROZEX experiment (Seeyave et al., 2007).

R. RESULTS Page 3616, line 19: These results are interesting by their own, but are not all relevant with the study. As done in the previous paragraph, I would terminate this paragraph (and the other similar ones of the results section) by a short sentence stating where the DMS surveys have been done. In that case, something like: The DMS survey covered the NANO and mixed SYN-PRO zones. This will help the reader to keep in mind the information relevant to this study.

A. Acknowledged and addressed.

R. Page 3616, line 26: Idem – I would add the following sentence: 'The DMS survey was carried out mostly in the mixed SYN-PRO zone'.

A. Acknowledged and addressed.

R. Page 3616, line 9: Need a sentence here describing where the DMS surveys took place.

A. Acknowledged and addressed.

R. Page 3616, line 9: As for the Pacific section, I suggest to begin a new paragraph for each survey (In summer. . .). The match between Chl and PHYSAT is obviously poor here, Fig. 3c showing more productive zones than PHYSAT. This is not clearly discussed. I am also concerned by the poor representation of the coccolithophores and a potential overestimation of the contribution of diatoms in the assemblage. Reference to the papers by Scarratt et al. (2002, 2007) which include DMS:Chl a ratios and phytoplankton composition over extended transects in the North-western Atlantic will be relevant to the discussion of these data.

A. Acknowledged and addressed. The referee is right, the match between Chl and PHYSAT is obviously poor here. In fact, DIAT dominance is almost absent west of 40°W and in the Labrador Sea. There are NANO blooms west of 40°W and DIAT

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blooms east of 40°W. Although the Scarratt and Marandino cruises took place during different months and years (Sep. 99 and July 07, respectively), it is worth noting that diatoms were rare in the center of the Labrador Sea in late summer 2009 (see Fig. 5a, panel 6 in Scarratt et al. 2007) as in the summer PHYSAT climatology (July). However, since HPLC pigment samples were not collected during the Sep. 99 survey, it is impossible to repeat the validation exercise of Alvain et al. (2008) in the area surveyed by Scarratt et al. (2007). The paper by Scarratt et al. (2007) reports DMS:Chl a ratios in the North-western Atlantic in September 1999. Unfortunately, the Sep. 99 and the July 07 cruises followed very different routes across the North-western Atlantic. It is also unfortunate that Scarratt et al. (2002) and Marandino et al. (2008) both surveyed the Northwest Atlantic Continental Shelves (NWCS) but during different months (May and July, respectively). Therefore, it is not possible to compare DMS:Chl a ratios calculated from in situ Chl (Scarratt et al., 2002) and satellite Chl concentrations (this work). Reference to the paper by Scarratt et al. (2002) is relevant to the discussion of the Sargasso Sea data. Scarratt et al. (2002) is quoted in the revised reference list.

R. Fig. 4: CN-198 (as in Fig. 1) or CN-128 (as in Table 1)?

A. CN-198

R. Page 3616, line 24: This area seems to be too broad to be representative of the ice edge. The authors should be more specific.

A. "near the ice edge" removed in revised MS.

R. Page 3620, line 18: Obviously, the authors worked hard to find a way to present their data. However, I still find the interpretation of Figures 5, 6, 7 and 8 difficult (the small size of the panels as well as their poor resolution – on my computer at least – make their visual analysis very laborious. Each figure should occupy the full width of the page (ex. Fig. 7 and 8?). That would help. As expected, there is a lot of variability in DMS levels and DMS:Chl ratios and in some instance this variability if not properly acknowledge by the authors (see below for an example).

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A. The original figures occupied the full width of the page. They were reprocessed automatically during on-line submission.

R. Page 3618, line 11: 'DMS concentrations were systematically higher'. This is not so evident in Fig. 5e.

A. The yellow vertical bands correspond to the convergent equatorial front (CEF) where DMS accumulates.

R. Page 3610, line 15: 'This is apparently in contradiction. . .'. If so, what is the value of the rest of the data presented? I am a bit harsh here, but given the complexity of the data set presented and the wide variations observed; this is an honest but certainly not reinsuring sentence.

A. This should have been part of the discussion section. We copy here the paragraph of the revised discussion section where we address this "apparent contradiction". "Second, the survey in the North Atlantic between the US coast and Iceland (CN-233) provides another illustration of the role of non-dominant phytoplankton in DMS production. Marandino et al. (2008) showed that the variability in seawater DMS levels was related to the satellite-derived distributions of coccoliths and, to a lesser extent, chlorophyll. However, PHYSAT did not detect COC dominance along the cruise track except in the vicinity of Iceland where, unfortunately, DMS was not measured (Fig. 8f). In the absence of other field measurements (e.g. cell enumeration), it is impossible to assess the relative contribution of coccolithophores to phytoplankton biomass during CN-233. Nevertheless, the distribution of calcifying and silicifying phytoplankton in relation to environmental and biogeochemical parameters during the late stages of the 2005 north Atlantic spring bloom was investigated by Leblanc et al. (2009). The spatial distributions of fucoxanthin, biogenic silica, 19'-hexanoyloxyfucoxanthin, particulate inorganic carbon (calcite) and peridinin concentrations, showed that diatoms dominated the phytoplankton community over prymnesiophytes, coccolithophores and autotrophic dinoflagellates in the Icelandic basin and shelf in early July. Hence, satellite products

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and ship-based observations in the western North Atlantic in summer suggest that coccolithophores account for a non-dominant fraction of phytoplankton. Thus, the mean DMS:Chl in DIAT dominated areas (4.8 ± 1.5 mmol g⁻¹, Table 2) could result from the production of DMS by coccolithophores (DMS vs.calcite relationship of Marandino et al. (2008) which supports earlier findings of Matrai and Keller (1993)) with diatoms responsible for the high chlorophyll levels.”

R. Page 3623, line 1-30: It is not clear why the data from Tortell and Long are only presented in the supplemental materials. This does not make the paper easier to work through.

A. The data from Tortell and Long are now presented in the main text (new Figure 6).

R. DISCUSSION

The beginning of the discussion does not provide a complete and up to date view of the DMS literature. The authors referred to either old (albeit good) papers (ex. Turner et al. 1988) or their own recent papers (Marandino et al. 2008). Although ignored here, information on how the DMS:Chl ratios vary with species in the field can be found in the literature. By the way, the paper by Matrai and Vernet (1997) provides a very nice example of a diatom and a *Phaeocystis* assemblages producing similar amount of DMS. As mentioned before, the authors never mentioned the potential role of DMS ventilation on the DMS:Chl ratio. If they consider this abiotic DMS loss term not important, they should explain why.

The ‘caveats’ described in the first part of the Discussion section were predictable and are not a result of this study.

A. Acknowledged and addressed.

Copied from the revised Discussion section: “There, DMS:Chl were lower than 1 mmol g⁻¹ because the DMS precursor (DMSP) was associated with a non-dominant fraction of phytoplankton made of small sized eucaryotes and single cells of *Phaeocystis*

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antarctica. In ice-free waters of the Barents Sea (station IV) where diatoms accounted for about 80% of phytoplanktonic carbon biomass, the sea surface DMS:Chl was ca. 3.5 mmol g⁻¹ (Matrai and Vernet, 1997). Consequently, a mean DMS:Chl equal to 4.9 ± 2.2 mmol g⁻¹ measured during CN-233 (Table 3) is a relatively high number for an area dominated by low DMSP producers.”

The ‘caveats’ described in the first part of the Discussion section are now part of the Introduction. “However, there are limitations to this approach. The well known physiological adaptation of the Chl content of phytoplankton cells to environmental growth conditions could be responsible for part of the changes in DMS:Chl. DMS production could derive from the sub-fraction of marine organisms classified as non-dominant by PHYSAT. Also, by comparing DMS:Chl with the PHYSAT products we implicitly underestimate the role that the physical (ventilation, vertical mixing and the mixed layer depth, Simó and Pedrós-Alió, 1999), chemical (e.g. photooxidation, Bouillon and Miller, 2004) and biological removal processes (e.g. bacterial consumption, Kiene et al., 2000) play on DMS. This can not be assessed directly from satellite measurements at this time. Therefore, many important biotic and abiotic DMS loss terms can not be considered in our study. Nevertheless, PHYSAT is an important tool which enables us to evaluate the importance of phytoplankton group dominance in marine DMS dynamics at a large scale.”

“Also, by comparing DMS:Chl with the PHYSAT products we implicitly underestimate the role that the physical (ventilation, vertical mixing and the mixed layer depth, Simó and Pedrós-Alió, 1999), chemical (e.g. photooxidation, Bouillon and Miller, 2004) and biological removal processes (e.g. bacterial consumption, Kiene et al., 2000) play on DMS.”

R. Other specific comments Page 3608, line 10: Replace ‘affect’ by ‘effect’. Page 3608, line 27: . . . from space by PHYSAT. Page 3610, line 21: . . . the effect. . . Page 3624, line 23: It seems that ‘laborious’ or ‘tedious’ would be more appropriate than ‘difficult’. Page 3626, line 9: ‘With these. . .’ Page 3626, line 11: ‘way than Colomb et al’. This is

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the first mention of this study, which seems very important in the context of the present one. If so, this study should be presented in the Introduction section.

A. Acknowledged and addressed. Copied from the revised Introduction section: "The detection of the dominant phytoplankton groups in marine surface waters from space is now possible using the PHYSAT algorithm (Alvain et al., 2005). PHYSAT was applied for the first time by Colomb et al. (2009) to a survey of atmospheric DMS concentrations carried out across the frontal systems that separate warm waters of the Indian Ocean south subtropical gyre from cool waters of the Indian sector of the Southern Ocean. The highest atmospheric levels of DMS were restricted to a zone rich in Chl where the dominant phytoplankton was DIAT. Based on phytoplankton culture work, one would have expected to find high DMS:Chl associated with a dominance of NANO, PHAEO or COC, and low ratios when SYN, PRO or DIAT dominate."

R. Page 3628, line 6: 'Clearly, DMS accumulated there too. . . ' The authors do not provide explanation for the observed increase in DMS concentration. The reference to bird foraging is speculative and does not contribute to the interpretation of the data.

A. We think that reference to bird foraging is informative. It is interesting to mention that the CEF accumulates DMS (this work) and buoyant organic material that can be seen from space and attracts foraging seabirds and other trophic level species (Pennington et al., 2006 and references therein).

R. Page 3629, line 7+: Could be interesting to refer to the paper by Wong et al. (2006) which also explores some potential DMS ENSO cycle in the NE Pacific.

A. Acknowledged and addressed. Copied from the revised Discussion section: "These results provide after Wong et al. (2006) a new example of how climate fluctuations, through altering the physical properties of the upper ocean, may influence the DMS concentrations in the open ocean."

R. Page 3632, line 9: 'would trace that of the oligotrophy. . . ' Not clear what the authors

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mean here. Needs to be reworded.

A. Acknowledged and addressed. Copied from the revised Discussion section: "Thus, it is likely that the seasonal expansion towards the north of the PRO signature, as observed by Alvain et al. (2008) in the North Atlantic basin, traces that of oligotrophic systems and the well known associated relative accumulation of DMS that characterizes them (summer DMS paradox, Simó and Pedrós-Alió, 1999)."

R. Page 3632, line 14: 'from space of several phytoplankton functional. . . '. Should read: 'from space of the dominance of several. . . '

A. Acknowledged and addressed.

R. Page 3632, line 21: About the high and low DMS-producing phytoplankton. Given the complexity of the abiotic and biotic mechanisms responsible for DMS net production, it will be more accurate to mention the 'high and low DMSP-producing phytoplankton'. Similarly, few if any DMS researcher would expect to see variations in DMS:Chl ratios as large as variations in DMSP:Chl ratios as mentioned in Page 3631, line 13. It is misleading to not make a clear distinction between DMSP and the gas DMS given their widely different dynamics.

A. Acknowledged and addressed.

R. Page 3632, line 26: 'is not consistent within DOMINANT phytoplankton group'.

A. Acknowledged and addressed.

R. Figures General comment: Many figures as small and busy. They should be all scale up to the full journal page width. Fig. 2. Indicate in the legend what panels a and b, b and c, and c and d mean. Fig. 10. Y-axis should be the same for the two panels.

A. Acknowledged and addressed.

Reference cited in this answer to comments from referee 2:

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