Biogeosciences Discuss., 9, C7599–C7608, 2013
www.biogeosciences-discuss.net/9/C7599/2013/

Biogeosciences Discussions

Interactive comment on "Sulphur compounds, methane, and phytoplankton: interactions along a north-south transit in the western Pacific Ocean" *by* C. Zindler et al.

C. Zindler et al.

czindler@geomar.de

Received and published: 23 January 2013

Response to referee #2 for manuscript bgd-9-C5919-2012

We thank the referee #2 for working on our ms and providing helpful comments. The methods and discussion sections were condensed and focused. We also toned down the some speculative conclusion statements.

R2: However, I have some major concerns with the manuscript that I think need to be addressed if it is to make a significant contribution to the field. The authors should reassess what the important findings are of their study and how they can best concisely and clearly present these. Specific major concerns: 1. The study relies too heavily

on correlation as evidence of a causal link; this disregards all the information now available on the relatively rapid turnover rates of the reduced sulphur compounds in the surface ocean and the many mechanistic models on DMS cycling that have now been published. For instance, low DMSPd concentrations do not necessarily mean low DMSPd production rates; but may be controlled by rapid catabolism. Similarly, when it suits their argument the authors invoke rapid turnover as a cause of low DMS concentrations (P15021 L5+), for example, but without direct evidence this is simply speculation. Authors: We shortened parts of the results and discussion section and tried to focus on the main results, especially in the sections of the MLRM. We changed some interpretations of the results to have an overall conclusive discussion, which addresses the fast cycling of the marine sulphur species and the findings of the recent literature. In addition, we added a paragraph to the beginning of section 3.3 stating that we realize that correlation does not necessarily mean causation. We hope that this statement is clear and shows that we are simply trying to understand the interactions of certain variables in the sulphur cycle.

R2: 2. Interpretation of correlative and regression analyses seems highly 'elastic' and variable e.g. P15023 L13 an r2 = 0.19 means 'slight influenced'; while P15024 L14 an r2 = 0.29 is a 'weak linear positive correlation' ; in contrast P15022 L20 an r2 = 0.32 allows one to 'roughly estimate' DMS from DMSPp and DMSOp. These values stem from similar numbers of observations with highly significant F-statistic. A more consistent interpretation is required, otherwise it appears like the arguments/conclusions are pre-conceived and the data made to fit around them. This is clearly illustrated by the case of CH4 where a highly significant r2 = 0.69 with TChl is discounted (P15029 L8+) as a causal link. Authors: We describe the correlations now in the ms without reference to qualitativevalue (e.g. weak or strong), with the exception of the discussion regarding chl and sulphur compounds. This is still described as a relatively weak correlation because we want to make the point that marker pigments should be better indicators than chl.

BGD

9, C7599–C7608, 2013

Interactive Comment

R2: 3. While determination of the pigment composition and allocation to different phytoplankton cluster has undoubtedly been carried out in considerable depth, the information that it generates in relation to the sulphur compounds and methane is really inconclusive and throws little light on the taxonomic composition of the key producers of DMSP or DMSO in these waters. The authors summarise (P15032, L3+) "Several algal groups were identified as contributors to the DMSP and DMSO pool, mostly haptophytes, chrysophytes and dinoflagellates. Diatoms were also identified although they are not known to be significant sulphur producers". This does not seem very insightful given the amount of emphasis placed on pigment-based characterization of phytoplankton clusters and size classes in the manuscript and the subsequent multiple regression approach applied to it. Authors: It is relatively new to have a comprehensive dataset consisting of sulphur measurements and in situ pigment measurements. We have tried to tease apart the interactions using multiple regressions. However, because no mechanistic work was performed it is difficult to fully understand the complex cycle of the sulphur species and the influence of the phytoplankton on this cycle. We therefore tried to highlight the most significant results of the regressions to keep the ms understandable. The point of this exercise is twofold: 1) most of the information regarding the taxa influential in the sulphur cycle is laboratory based. It is useful to look at the natural world and corroborate or refute these findings. 2) Hopefully it will be become more routine to use marker pigments determined from satellite to pinpoint areas that should be important for the sulphur cycle in the future. Therefore, initial steps with in situ measurements need to be taken. This analysis is a first step.

R2: 4.The manuscript is over repetitive and could usefully be condensed. Separating the results from the discussion would help. At present the discussion sections interspersed amongst the lengthy description of the results add little to the manuscript and are often repeated. For instance, the authors base much of their explanation of DMSP, DMS and DMSO concentrations on the potential anti-oxidant role introduced by Sunda et al. (2002); with the structure as is, this particular point is repeated four times (P15012 L10; 15022 L7; 15030 L5; L15032 L5). A Discussion that was structured along the lines

BGD

9, C7599–C7608, 2013

of: i) the measurements in relationship to previous studies in the region; ii) the measurements in relation to other similar studies along meridional transects (of which there are several in the Atlantic, for instance) iii) the sources of DMSP, DMSO and DMS and their relationship to phytoplankton functional types and model development, including the use of remote sensing information; iv) the DMSO measurements in particular and their significance to the sulphur cycle; v) the methane concentrations in relation to other regions and previous measurements and their potential sources; or something similar, would be considerably more useful. Authors: We shortened parts of the results and discussion section and brought together results which had the same interpretation to avoid repetition. We think it is too difficult to understand the interpretation when the results are separated from the discussion because of the many correlations which were found (this was attempted). It seems that no matter how we group the section(s), there will be repetition (just to remind the readers). We thank the referee for the suggested structure of the discussion which showed detailed examination of the ms. We think that we addressed point i) and v.) sufficiently in the original text (see section 3.2 and 3.7, respectively). There are several studies already published discussing meridional transects in the Atlantic. We think that point ii) will unnecessarily enlarge the ms. We wanted to keep the focus on the Pacific Ocean. We also think that data analysis for use with models or remote sensing will overload the ms and will make it even more difficult to understand. We discussed the DMSO measurements more than the other sulphur species and we think that we gave new insight into the DMSO cycle and its influence on the sulphur cycle in general in the Pacific Ocean. Further on, we think that an additional discussion of CH4 data from the Atlantic is beyond the scope of our ms and could only be addressed in a comprehensive review ms, which was not our intention to write.

Other concerns / comments: R2: 1. Figure 2 is difficult to interpret in its current form, the bars are too narrow and contain too many divisions to easily be read. Plus, as the focus of the manuscript is the sulphur and methane story, then this figure could be omitted. Authors: We now merged the information of Fig.2 and Fig.3 in one figure

BGD

9, C7599–C7608, 2013

(new Figure 2) with two panels as recommended by the reviewers. The upper panel shows the total chl concentration in correspondence to the latitude sampled, the lower panel shows the ratio of phytoplankton group divided by the total chl-a concentration in correspondence to the latitude sampled.

R2: 2. The correct citation for Vogt and Liss 2009 is: Vogt, M., and P. S. Liss (2009), Dimethylsulfide and climate, in Surface OceanLower Atmosphere Processes, Geophys. Monogr. Ser., vol. 187, edited by C. Le Quéré and E. S. Saltzman, pp. 197–232, AGU, Washington, D. C., doi:10.1029/2008GM000790. Authors: Thank the referee for the right citation, we corrected it.

R2: 3. P15015 L10+ clarify whether this means three replicate sub-samples from one sample bottle or three separate sample bottles from which one sub-sample each was taken? Authors: For the sulphur compounds, we measured three replicate sub-samples (10 ml each) taken out of one 250 ml sample bottle (originally sampled from the pump system). For methane, we took three discreet samples and performed the same measurements on each. We clarified this in the text.

R2: 4. P15015 L10+ Although Zindler et al. 2012 is cited in reference to the analytical method, it should be made clear how DMSPp and DMSPd samples were separated (the same applies to the DMSOp and DMSPd) samples. In addition, how were DMSPt and DMSOt determined? This is important given the real potential to generate artifacts due to filtration when analyzing these compounds, particularly the dissolved components (Kiene and Slezak 2006). Authors: We described in more detail the whole analytical procedure. Short description: triplicate sub-samples were filtered and analysed first for DMS, than alkalized and measured for DMSPd. These sub-samples were stored afterwards and analysed later in the home laboratory for DMSOd. Additional unfiltered sub-samples taken from the same sample bottle, in the same manner as the dissolved fraction were alkalized and analysed for DMSPt. The same sample was used for the measurement of DMSOt. The particulate fraction of DMSP and DMSO was calculated by subtracting the dissolved fraction from the total fraction.

BGD

9, C7599–C7608, 2013

Interactive Comment

R2: 5. P15015 L20+ DMSO analysis needs to be clarified, if DMSOp and DMSOd 'were analysed out of the same samples used for DMSPp and DMSPd' why was the final DMSOp value calculated 'by subtracting DMSOd from the total DMSO concentration'. Authors: see the answer to point 4 above. We had to calculate the particulate fraction because we used unfiltered samples for the analysis of total DMSP and DMSO. To obtain DMSPp and DMSOp we had to subtract the dissolved fraction from the total because we did not measure directly the particulate fraction. We tried to clarify this in the ms.

R2: 6. P15015 L24. What was the analytical error based on and why 'mean analytical error'? Authors: We removed the word analytical from the text. The error is based on the standard deviation of the triplicate samples calculated according to David (1951). The mean error indicates the average standard deviation for all measurements performed during the cruise (e.g. for DMS we report that the average standard deviation for triplicate measurements is 20% of the measured concentration). We added the information in the text. For the full reference see the ms and the answers for referee #1.

R2: 7. P15016 L5 Sentence beginning 'No blanks. . .' needs to be clarified. Authors: We tested the analytical system for blanks in a systematic way: 1) with carrier gas only, 2) with ultra-pure water which was used for cleaning and preparing the standards, 3) with ultra-pure water mixed with the chemicals used in our analysis, such as NaOH and NaBH4 . It is known that the analysis of DMSO encounters the most difficulties due to easy contamination with atmospheric DMSO or DMSO which is attached on the material during analysis. With our test measurements we could exclude contamination. We revised this section of the text.

R2: 8. P15016 L9 CH4 sampling and analysis: what is meant by 'the same underway seawater supply' were the DMS(P)(O) analyses not from bottle samples? Authors: The methane samples were also taken from thepump system that is mentioned in the text for the sulphur samples (described on page 15015 L6-9) but in three separate vials not

BGD

9, C7599–C7608, 2013

in the same 250ml sample bottle like the sulphur compounds.

R2: Does 'in parallel to' mean at the same time? Authors: yes (described on page 15015 L6-9)

R2: What was the depth of the underway seawater supply? Authors: approximately 5 m depth (described on page 15015 L9)

R2: Were tests undertaken to confirm bottle and underway samples gave the same results for the CH4 analyses? Authors: All samples for sulphur, methane and pigments were taken from the same underway pump system installed in a hydrographic shaft. Is the reviewer referring to Niskin bottles? In that case, unfortunately, no tests were conducted because no CTD cast were driven. The comparison between the pumping system and CTD casts in general is an important point and will hopefully be addressed in the future onboard research vessels.

R2: 9. P15016 L17. Sentence 'According to...' requires rephrasing. Authors: We changed the sentence.

R2: 10. P15017 L2 'pico' is missing. Authors: We added the 'pico'.

R2: 11. P15019 L3. The description of the location of Cluster 2 type communities and Fig 1, do not match. Authors: The exact location of cluster 2 is shown in figure 3. We added the reference in the text. In figure 1 only the approximate locations of cluster 2 is shown. This is also mentioned in the figure caption. We only highlighted the regions where most of the stations of cluster 2 were found.

R2: 12. 15020 L18+. It is not made clear why the n values differ between regression analyses for the different compounds. Authors: The n values differed because, unfortunately, the analytical system did not always perform perfectly. There were cases where DMS was measured but the dissolved or total DMSP or DMSO could not be measured (and vice versa).

R2: 13. L15021 L7. Is there any evidence that the phytoplankton experienced oxidative

BGD

9, C7599–C7608, 2013

stress due to UV exposure or nutrient limitation? Otherwise this is too speculative, especially in terms of DMS turnover times. Presumably if the antioxidant system as proposed by Sunda et al. 2002 was occurring, oxidation of DMS to DMSO would occur within the cell and therefore that DMS would not appear in the dissolved phase; nor would DMSO if that was part of the cascade? Authors: We have no evidence for oxidative stress because the data we collected give no information about this point. Therefore, we can only speculate about the turnover times of DMS. However, it is most likely that oxidative stress occurred in the phytoplankton of this sampling region (oligotrophic, subtropical to tropical, sampling depth of around 5 m). We do wish to offer some hypotheses regarding our findings and hope to convey them cautiously.

R2: 14. P15021 L25, Fig. 6. The positive DMSO to SST trend is driven by 2 points only. It would be useful to illustrate where these points were obtained and why they differ so markedly from the other data. The significance of both regressions should also be provided. Authors: The one data point is from a study in the northern Baffin Bay (SST: $\sim 0^{\circ}$C, DMSPp: DMSOp ratio: 0.22, Bouillon et al., 2002) and the other data point is calculated according to data taken in the Antarctic published in Simó and Vila-Costa (2006a). Both data sets which were presented by these data points exhibited extremely low water temperature compared to the other studies. DMSO concentrations in the study of Boullion et al., (2002) were high compared to other sulphur compounds. The concentrations of DMSP and DMSO in the study of Simó and Vila-Costa's were in the range of other studies; however, the water temperature was important for this data point. These data points were from previously published data that are referenced (not our own) and it would be too lengthy to describe each point in detail. The significances of both regressions were given in the caption of figure 6. We also added this information in the text.

R2: 15. P15022 L19. Is there value in estimating DMS from DMSPp or DMSOp if they explain only 30 % of the variability in the DMS concentration? Authors: Yes, this is a meaningful value. The test was significant and also other multiple regressions showed

BGD

9, C7599–C7608, 2013

only this low R2. The sulphur cycle is too complex to obtain high values of variability but 30% is quite a lot for such a system.

R2: 16. One potentially important aspect of the transformations between sulphur species is the reduction of DMSO to DMS by eukaryotic phytoplankton (Spiese et al. 2009). This should at the least, be discussed. Authors: Thanks to the referee for this reference. We added this reference in the text and discussed it in the DMS section.

R2: 17. P15024 L22 Inconsistent argument. The antioxidant role of the sulphur species is cited several times as an explanation but here we are told the low TChl indicates enhanced radical production most likely did not occur. Authors: The referee is right. Our argumentation was not consistent. We changed our interpretation: The weak correlations may result from a dependency on certain algae taxon and not on phytoplankton in general for both DMSP and DMSO. In contrast, Lee et al.(1999b) found a negative correlation between DMSOp and Chl-a in a Canadian Fjord. They explained this observation with an increase in photosynthetic activity and, therefore, an increase in free radicals which reacted with DMSO. However, the correlations found in the Fjord were dependent on temporal variability and on the nano- to picoplankton fraction. Thus, more detailed correlations between phytoplankton and DMSO in western Pacific Ocean might gain more insight into their relationship (see section 3.6.3).

R2: 18. P15024 L23 Units should be nmol-1 mg-1. Authors: We had given the units nmol mg-1 in our ms. However, the conversion into the BG format changed the units by accident. Thanks the referee for the careful reading.

R2: 19. P15025 L6+ The diagnostic pigments used needs further explanation: for instance, diatoxanthin and diadinoxanthin are not exclusively diatom pigment by any means. Authors: The referee is right with their argument that diatoxanthin and diadinoxanthin are unspecific. However, these pigments are contained mainly in diatoms, thus we included it in our models. We were carefully in the interpretation of these pigments and used fucoxanthin as main indicator for diatoms. We refer to it in the ms.

BGD

9, C7599–C7608, 2013

Interactive Comment

R2: 20. P15025 L16. Why 'triggered' Authors: We changed to "caused".

R2: 21. Sections 3.6.1.; 3.6.2; 3.6.3. are too long and repetitious and could very usefully be reduced and focused. Authors: We shortened and focused these sections for clarity.

R2: 22. P15028 L10. Unclear sentence 'Interesting...' Authors: We rewrote the sentence: "Interestingly, only a few correlations were found in cluster 4 compared to cluster 2 and the entire transit."

R2: 23. P15028 L16. This seems a sweeping statement without any real basis; if it's going to be made it needs much more justification/explanation. Authors: The referee is right. This statement is too general based on the one data set. We rewrote the sentence:" Thus, large regions in the subtropical and tropical western North Pacific Ocean showed only a low dynamic of the sulphur cycle in the surface ocean during the transit in October 2009."

R2: 24. P15030 L7 DMSP should be DMSPd. Authors: That's right. We changed it in the text.

R2: 25. P15030 L12 Why 'remarkable' . Again, this section is highly speculative and poorly presented. Authors: We change the wording in the ms from "...it is remarkable..." to "...it should be noted...". We think it is important to mention the contrast between the two datasets. However, the referee is right that we were speculative in this section. We rewrote parts of the section to be more careful with our interpretations.

Interactive comment on Biogeosciences Discuss., 9, 15011, 2012.