

Interactive comment on "Effect of ocean acidification and elevated fCO $_2$ on trace gas production by a Baltic Sea summer phytoplankton community" by A.L. Webb et al.

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The authors would like to thank the reviewer for their comments and discussions at all stages of the review process, which have improved the overall quality of the manuscript. I have addressed the reviewer's comments individually.

General comment This paper presents data from an acidification experiments conducted in large mesocosms in the Baltic Sea during the 2012 summer. The mesocosms system used here has been described in the past and used in previous successful ocean acidification experiments. This is considered as the state-of-the-art system for that type of experiments. As usual in multidisciplinary experiments, many different papers were produced, some of which are already published. This particular

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paper focuses on the impact of acidification on the production of biogenic trace gases (dimethylsulfide and a suite of halocarbons), but makes several references to other papers related to the same study.

Few general remarks: 1. The upwelling event that took place in the middle of the experiment (t16) certainly confused the issue by cooling the water of the mesocosms. For that reason, the changes in biogenic gases concentrations observed after this event result from both the cooling and the acidification of the water. This is recognized by the authors and properly discussed in this version of the paper.

- 2. Measurements made outside the mesocosms are interesting by themselves, and as they are in this version of the paper, should not be compared with the results from the mesocosms where the upwelling event only translated into a decrease in temperature, but no change in salinity and more importantly no change in plankton composition. These are two independent stories which need to be treated as such. In that regard, in situ data could be presented in a separate figure to emphasize this point. A reason to do so is that the Phases indicated in figures 1 and 2 are not relevant to the in situ measurements. This would also allow to rescale the Y-axis of figure 1c and 2a and make the changes in chl-a and DMS concentrations in the mesocosms more visible.
- AR. This has previously been discussed, however it doubled the number of figures in the manuscript, while not increasing the clarity of the information displayed to a huge degree. The differences in DMS concentration in the different mesocosms is clearly visible in the current figure 3 due to the scale of the difference.
- 3. The lack of detectable DMSP concentrations is obviously surprising. Although the authors offer possible solutions to this conundrum, the fact remains that they are able to detect a by-product of DMSP degradation but not DMSP itself, known to be, in many circumstances, orders of magnitude higher than DMS. It is difficult to believe that 30 days worth of samples within a diverse community of phytoplankton did not generate a single detectable nmol of DMSP. Some loss can be explained through the presence

of acid-sensitive species (colonial Phaeocystis etc.), but the authors rule this out themselves as an important process by specifying that this type of phytoplankton accounted for less than 10% of the community. In fact cryptophytes and chlorophytes dominated the community. Various species of these two groups are known to produce DMSP (Keller et al 1989) but not known to be sensitive to the acid treatment. As stated by the authors, a methodological problem can probably explain these results.

Specific comments P1, 25: . . .challenged Baltic Sea.

AR. Challenging is more appropriate as the sentence is talking about the challenges present and future in the Baltic Sea encountered by phytoplankton.

P2, 55: . . .the global ocean has absorbed. . .

AR. Changed

P2,41: Would it be possible to come up with a 'dilution' factor? Using salinity as a conservative parameter perhaps? This would allow to roughly estimate how much of the variability of the parameters measured at the surface needs to be explained by other factors (production/consumption).

AR. We do not know the salinity of the upwelling water, nor the percentage volume of the upwelled water injected into the surface system. This makes this very hard to quantify.

P4, 110: Suggestion: replace 'Post-spring bloom' by 'Following the spring bloom'.

AR. Changed

P4, 114: . . . 2012 summer post-bloom season. . .

AR. Changed

P5, 132: . . .such as fish. . .The removal of large zooplankton is probably more relevant here than fish.

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AR. Although it took a week to get 1 small fish out...

P6, 163: . . . with 100% absorbance of UV light. . .Later in the manuscript, it is mentioned that some UV light could affect the processes taking place close to the surface in the mesocosms. This seems to be in contradiction that 100% UV is removed.

AR. UV was still able to impact the very surface waters where it did not pass through the films. There is a 1m high gap in the mesocosm design between the top of the TPU bag and the PVC rain cover, where the samples are taken from. Light is able to pass through this gap in morning and evening and hit the surface waters.

P8, 230: . . .turnover of DMSPD. . .Replace by 'dissolved DMSP'.

AR. Changed

P8, 246: Measurements of carbonate chemistry and community dynamics.

AR. Changed

P10, 281: . . .decreased over Phase 1 in the . . .The phase numbers are not properly aligned in figure 1c (on my printed copy at least), and absent in figure 2, 3 and 4 (which are by the way wrongly numbered).

AR. Figures have been amended

P10. 287: . . .no variation with depth (data not shown). . .

AR. Added

P10, 297: . . .a significant effect on phytoplankton growth (and biogases production), explaining. . .

AR. Added

P11, 324: . . .that light availability and surface water temperatures. . .Delete 'environmental conditions of limited' and 'lower'.

AR. Agreed

P11, 330: A significant 34% reduction. . .These results could be better explained taking into account the temporal variability which is significant. Actually, DMS concentrations increased as Chl concentrations decreased, and the increase in DMS was less important at high PCO2. After day 21, DMS decreased gradually in all treatments until the end of the experiment.

AR. The DMS disconnect from Chl-a is a fairly common occurrence, and it would have been a lot more interesting to discuss if DMS had been connected to Chl-a concentrations! To a degree, it is interesting that DMS peaked after the Chl-a, but without any DMSP measurements, it is difficult to know to what degree this was connected. From previous mesocosm experiments and turnover rates of DMS, the temporal delay in DMS peak after Chl-a (if it exists) is usually only 2-3 days, not over a week.

P11, 333: (Fig. 3a) to be replaced by (Fig. 2a). P11, 336: (Fig. 3b) to be replaced by (Fig. 2b).

AR. Changed

P11, 337: Furthermore, increases in DMS. . .were delayed by three days. . .This 3-day delay is not obvious in Fig. 2a. Am I missing something?

AR. The increase in DMS in the highest CO2 mesocosms started three days after that in the ambient and mid-level CO2. As the DMS increased to such a small degree in the high CO2, it is not an obvious result, however it can be seen in Fig. 2.

P12, 348: Although the majority. . .This paragraph needs an introduction sentence. As in my previous review of this paper, I still think that there is too much emphasis on a rare pathway of DMS production considering that the problem is most probably a methodological one. This paragraph is important but could be shortened.

AR. The first sentence has been amended to be more of an introduction. This paragraph has been shortened significsantly from the original version, and to shorten it

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further would be to miss out the summary of where knowledge of the alternate pathway originates from and how it affects the results of this experiment.

P12, 358: Correlations between. . .Only one P value is presented. Should it be 'correlation' instead of 'correlations'? I am also wondering if all the data were pooled (all treatments) to compute this statistic.

AR. There was also correlation between the single celled cyanobacterial abundance, which has been included, and the colonial cyanobacterial abundance (data not shown as not finalised when preparing the manuscript). The statistics are also given in the supplemental file.

P12, 373: The peak in DMS concentrations is unlikely to be a delayed response. But the increase in DMS coincided with the decline in Chl-a concentrations (t15-t21), something frequently observed in nature in response to higher DOC production and bacterial activity during bloom decline. My point here is that the results should be presented and discussed in term of temporal changes, not only correlations.

AR. Comments have been included as to the temporal variation in DMS concentrations between the mesocosms, and as mentioned above, it is not uncommon for there to be a complete disconnect between Chl-a and DMS, and we have no DMSP concentrations to form a connection between the two. There was an increased in DOC on t15 shortly before the DMS peak, which has been referenced to Hornick et al 2016 (this issue).

P13, 379: . . . 2009). DMS and DMSP. . .

AR. Changed

P13, 398: This is relevant. . .I don't understand the logic here. In the absence of DMSP values, whatever the reason, I don't think that one can conclude that 'DMS concentrations were likely more affected by the change in ÆŠCO2 than the production of the precursors'.

AR. Final sentence deleted

P13, 405: and therefore lower DMS microbial yield from DMSP and/or greater consumption of DMS and conversion to DMSO. DMS yields may vary from 5 to 40% depending on the S and C demand of the bacteria and the quality of DOM. There are many references on variations in DMS yields. A good starting point is the paper by Kiene and Linn 2000 (Distribution and turnover of dissolved DMSP and its relationship with bacterial production and dimethylsulfide in the Gulf of Mexico. Limnol Oceanogr 45: 849-861).

AR. A comment has been included to the effect that bacterial consumption varies to a wide degree.

P15, 441: . . .where some UV light was able to pass. . .This seems to be in contradiction with the statement that 100% of UV radiation was absorbed by the cover (P6, 163). This requires clarification.

AR. See comment above

P15, 455: The peak of CH2I2 coincided with the decline of the bloom, as observed for DMS. I am not convinced that the positive correlations observed between these compounds and the abundance of the different taxa are relevant if the production of the compounds is related to processes linked to the decline of the bloom (ex. increase in DOC).

AR. There is no direct evidence of a link between the production of these compounds, but there is also no evidence that this link does not exist. This is why this is presented as a correlation, but does not equal causation, and was not described as such here.

P15, 466: The cleaning of the walls of the mesocosms and the associated apparent released of DOM as mentioned here seem to be an important potential artifact. As noted, this could be very important for photochemically and microbially driven processes. This potential problem, which could also be important for DMS production, should be discussed in more details in this paper. Would it be useful to indicate on the

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different figures when these cleanings took place? Overall, providing more details on the impact of these cleaning events would be of great value for colleagues planning to conduct similar long term mesocosms experiments.

AR. Cleaning during the experiments was not as regular as was hoped for, and only took place during the second part of the experiment. Because of this it is likely that the cleaning had a significant effect on DMS concentrations due to the input of DOC into the mesocosm. A comment to this effect has been included.

P16, 490: . . . indicators of algal biomass. PP was not measured here.

AR. Changed

P17/177, 503/504: . . .low net increase in total Chl-a. . .

AR. Added

P18, 550: Typo: Two dots before 'but peaked'.

AR. Removed

P18, 558: As the CO2 levels increased during Phase II. . . As mentioned by the authors at the beginning of this section, comparing the mesocosms results with the in situ ones is inappropriate. The different Phases (0, I, II) make only sense for the mesocosms experiment where they indicate either treatments or events. They are irrelevant to the in situ measurements. Keeping this comparison is confusing.

AR. A bit of the comparison is removed. The phase has been changed to the day no.

P18, 562: . . .this decrease in DMS may also be attributed to CO2 levels. . ..

AR. Section removed

P19, 577: . . .that production was probably not limited. . .

AR. Changed

P19, 598: . . .living and acclimated to. . .

AR. Changed

P20, 603-607: These two sentences would benefit from a rewording.

AR. Last sentence has been restructured.

P20, 615: For the concentrations of halocarbons, . . . of the Baltic Sea. I am not sure about this conclusion. This is very speculative since deep water upwelling and ocean acidification through air-sea CO2 exchange are two different processes. Upwelling brings nutrients, microbes, etc. . . in surface water in addition to high CO2.

AR. This section has been reworded.

P 35. This should be Figure 2 (instead of 3).

AR. Changed

P 36. This should be Figure 3 (instead of 4).

AR. Changed

P 37: This should be Figure 4 (instead of 5).

AR. changed

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