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Interactive comment on "Effect of ocean acidification and elevated $f\mathrm{CO}_2$ 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.

1-An initial paragraph or section evaluating the overall quality of the discussion paper ("general comments"), The manuscript is well structured and for the most parts easily readable. The results show a lack of response of gas concentrations to the experimental design and no linkage to the external conditions due to the outside undergoing its own "experiment", i.e., upwelling. No rates are reported; not clear any were measured. Hence, the entire manuscript must be clarified that the values represent "net" values and not production, nor consumption or degradation, nor emission. Hence, I strongly suggest removing most comments from the discussion that pertain to "climate change" and simply state that concentrations remained the same regardless and emphasize that we (and especially modelers) need to have rates of production, consumption, (photo/chem)-degradation or even "net" rates to include in our prognostic and predictive models.

AR. The mentions of climate change in the discussion section are quite limited, and although the change in halocarbons was limited, the change in DMS concentrations was high between the different treatments. The mention of the Six et al. paper was important, as this study was based on one mesocosm experiment and the results of the model output would have been more significant if the results of a number of mesocosm experiments had been included. A comment has been included to the effect that the reviewer says, that rates of consumption and production of halocarbons are needed to improve model output.

I recommend publishing pending changes. I also suggest shortening some of the longish speculative paragraphs; it's hard to explain why there is no apparent change! In general, I think the manuscript would profit if it was a bit more structured based on hypotheses, rather than being purely descriptive. You must have had some expectations when the experiment was started (and the proposal written!), especially since you had results from previous mesocosm experiments. Especially since no (?) rates were measured.

AR. No rates were measured as it was difficult given the sampling regime of the experiment, without performing additional incubation experiments. There were hypotheses prior to the experiment, mainly that halocarbon concentrations would show some really interesting and varied results under high CO2, as a diazotrophic cyanobacteria bloom occurred. As this bloom did not really occur in the mesocosms, these hypotheses did not apply, particularly since the majority of the 'interesting results' occurred in DMS (but no DMSP). It was therefore important to discuss the lack of DMSP for the community as a whole, to draw to light the issues with the DMSP acidification/ fixing method, and not to concentrate so hard on the lack of changes within the halocarbons.

2- section addressing individual scientific questions/issues ("specific comments"), The manuscript addresses the influence of ocean acidification on the production of dimethylsulfide (DMS) and 7 halocarbons in a Baltic Sea mesocosm experiment. The authors effectively found no differences in DMS and halocarbon concentrations over time among the various fCO2 treatments; and no obvious relationship to any other environmental (biological or chemical) variable measured. Difficult to explain without knowing whether turnover is fast. The authors found a decrease of DMS concentrations for highest fCO2 treatments vs. controls only in the last phase (when Chla declined) and none of the other detected differences in halocarbons were CO2 related. The outcome of this study is a relevant piece of information, indicating that most likely there will be no major changes to halocarbon concentrations in the Baltic Sea anytime soon, and the authors conclude that this might be due to the already well adapted community in the unstable Baltic Sea environment with regards to S, T, CO2 and many other factors. The results are interesting by themselves, and valuable for modelers, though modelers need rates. The DMS results again confirm results from a range of mesocosm studies.

3- compact listing of purely technical corrections at the very end ("technical corrections": typing errors, etc.). Line 247, 248: Inconsistent placing of units, 10m (no space) but 486 nm (space), e.g. line 247, 248 vs 261. You might wanna check if there are more.

AR. Units checked throughout manuscript

Line 70: "Both DMS and DMSP are major routes of sulphur and carbon flux through the marine microbial food web". I wouldn't call them a route, they could be called transporters, or they provide the basis for major routes. Or DMS and DMSP based metabolic pathways are the route... AR. Changed 'are' to 'provide the basis for'

Line 72: Where do they state that in this reference? I think Simo et al., 2009 should be the reference for phytoplanktonic demand (pages 50-51 e.g.), and Vila Costa et al., 2006a for bacteria (page 653)? Or you put them in as combined references for both (after sulphur demand)

AR. References have been combined at the end of the sentence

Line 142: That was the standard deviation at the beginning? ∼50%, ∼7%, and ∼75%? That's a lot to start with... Any thoughts on how that could potentially affect the outcome of the experiments on the bacterial metabolism side of halocarbon and DMS production?

AR. Certainly for the halocarbons, the difference in nutrients between mesocosms had no effect on the eventual concentrations measured throughout the experiment. A comment has been included in the DMS section as to how this could affect things. Since the differences in DMS were only identifiable during Phase 2, nutrient concentrations had by then showed much lower standard deviation between mesocosms.

Line 169: replace ; with a ,

AR. changed

Line 171: why no comparable pigment analysis, what's the rationale behind it?

AR. Pigment analysis was only carried out in the full 17m depth of the mesocosms. Many other parameters (not discussed in this manuscript) were analysed through the full water depth. In the previous mesocosm experiment, trace gas concentrations were significant in the surface 10m of the water column and diluted by the extra water, so during this experiment, concentrations were taken only from the surface 10m. Flow cytometry was performed both on the surface 10 m and the full 17m depth, but due to a large number of samples, HPLC pigment analysis was only performed on the full water depth.

Line 179: Is that shown anywhere? Otherwise please state what the precision was, and that it is not further shown.

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AR. Precision calculated as the percent deviation and inserted in manuscript.

Line 237: careful. The del Valle et al samples were DMSPd and DMSPt; not DMSPp. The Kiene group estimates DMSPp by difference between the total and dissolved pool.

AR. It is uncertain what the reviewer is highlighting here. The samples during the mesocosm experiment were DMSPt and DMSPp, but none of them showed any DMSP within. In the manuscript, there is no distinct emphasis on DMSPp over DMSPt, as the reviewer seems to be suggesting there was. This has been clarified in the manuscript by using DMSPt instead of just DMSP.

Line 247: 17mIWS space needed

AR. changed

Line 248: Chl-a the a is superscripted

AR. Could not find this error. Most likely corrected already.

Line 300: Mixing of the mesocosms after closure prior to t-3 did not trigger a notable increase in Chl-ÉŚ in Phase 1; in previous mesocosm experiments, mixing redistributed nutrients from the deeper stratified layers throughout the water column I get what you are saying, but I think you should add what redistributing nutrients did- I am assuming here that it lead to an increase in Chl-a?

AR. In previous mesocosm experiments, redistribution of the nutrients from below the stratified surface layers results in a significant bloom of Chl-a. However, this was not identified during this experiment, suggesting a limiting factor.

Line 282: "mainly through air-sea gas exchange" – isn't that usually considered to be limited by the small surface area / volume ratio? Please comment on why this should not be the same for your analyzed gases.

AR. The sea-air exchange will still exist during the mesocosm experiment, but it will be significantly decreased due to restrictions on wind interactions due to the mesocosm walls, reduced wave action and a very low SA: vol ratio for the water in the mesocosm. It is acknowledged that the trace gases will be lost to the atmosphere in the same way as CO_2, but at different rates for different compounds. This is commented on later on particularly for the bromocarbons which showed a steady decrease in concentration throughout the experiment. We know that there was a steep CO_2 gradient to the atmosphere, we do not know the concentration gradients for the halocarbons or DMS: if atmospheric halocarbon concentrations are equivalent to concentrations in the mesocosms (potentially possibly in the forests of finland), there would be a significantly lower rate of halocarbon loss than CO_2 loss from the mesocosms.

Line 302: no direct result of the CO_2 additions because there was no significant difference between controls and treatments?

AR. Sentence clarified with ‘as no difference was identified between enriched mesocosms and controls’

Line 309: chlorophytes (largest contributor to chl a) are not exactly known to be high DMSP or DMS producers; you may want to mention that given stated link to pico and nanoeukaryotes as possible sources. This is why bringing in the Fig, S3 as Fig 3c somewhere actually shows that there are differences among treatments.

AR. L 382, a statement was added to the DMS and community parameters section stating ‘Of the studied phytoplankton groupings, neither the cryptophyes or chlorophyes as the largest contributors of Chl-a have ever been identified as significant producers of DMSP.’ It was decided to keep figure S3 in the supplementary, as DMS is clearly disconnected from total Chl-a concentrations, during Phase 2. The statistics on the DMS: Chl-a ration are also insignificant due to the high standard deviation. This plot was therefore given for interest in the supplemental, but was not considered sufficiently rebust to include in the finished manuscript.

Line 311-312: so between the opposing trends for pico I and pico II, the next effect on DMS in the system is zero?

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AR. This section is discussing the differences seen in the mesocosms, and is not discussing the DMS concentrations. It is not implicitly stated that these groups are directly responsible for the DMS concentrations. There are many parameters acting on the DMS concentrations on top of the changes in these groups.

Line 331: Please explain F-test or at least the H0 you used in one sentence in the methods section.

AR. Null hypothesis added to the methods section

Line 348-369: Simply there was no relationship between patterns (or lack thereof) in DMS concentrations and any other measured variable. And no rate measurements available. Please say so. Too many possibilities, too many unknowns. This section reads a bit like "filler"; sorry.

AR. This section was significantly reduced prior to online discussion. It was decided that this section was necessary to discuss the alternate production pathways of DMS that could potentially be available in the Baltic Sea. A discussion occurred as to how this could be further investigated, and the authors felt it was important to keep this section relatively whole to allow for further research into these pathways, with this manuscript as a starting point.

Line 354: synthesis should be synthesise

AR. changed

Line 358: Correlations between DMS and the cyanobacterial equivalent Chl-ÉŚ 359 (p=0.42, p<0.01) indicate that the methylation pathway may be a potential source of DMS within the 360 Baltic Sea community. Reference? Data shown anywhere?

AR. The cyanobacterial equivalent Chl-a and the single celled cyanobacterial abundance are shown in Supplementary. They were previously included in the paper, but it was considered too much data for too little solid evidence. This sentence therefore keeps the idea that there MAY be a relationship between DMS and cyanobacterial activity, but does not outright state that there is. The authors feel this could be a significant area of research that needs further investigation.

Line 367: Stop! What rates of net DMS production? Did you measured or estimate them? If you did, please indicate and discuss!

AR. No rates of production were calculated, hence the 'net' DMS production (concentrations remain the same despite removal and addition processes). However, in this instance this has been changed to 'measured DMS concentrations'.

Line 371: but I thought that Syn does not make DMS?! There never is high DMS concentration reported along with it in subtrop regions (DiTullio et al., others). Didn't Vla-Costa et al. 2006 report uptake of DMSPd (not DMS) by Syn and other picoeukaryotes?

AR. Other literature has not identified Syn as a significant producer of DMS or DMSP. This statistics reported a significant correlation with cyanobacteria, which is reported here, both the single-celled and multi-celled variety (Data not shown). This section has been amended by the addition of 'predominantly' Synechococcus' as it is likely there are other single celled cyanobacteria within the population aside from Syn.

Line 372: Why is it unlikely?

AR. It has never been observed previously that a DMS peak occurs 5 days after a peak in Chl-a which has been directly linked to the Chla peak. DMS and Chla concentrations are rarely coupled, indeed even DMSP is rarely coupled to Chla, sot his result is not unexpected.

Line 379: just one period.

AR. removed

Line 386: "However, these experiments limit our ability to generalize"... I don't think it's the experiments limiting, but rather the varying responses, is that what you are saying?

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AR. Essentially, yes. The mesocosm experiments have been measuring DMS, DMSP and community parameters for a number of years now, and yet still no consensus appears as to the response to community changes. Mesocosm experiments also have their distinct disadvantages in their own right. This sentence has been amended to ‘the varying response within the mesocosm experiments’

Line 410-411: no data on consumption, no bacterial rates described, then what is the basis for this statement? Confusing.

AR. This statement has been amended to ‘it is not known if this loss pathway is stimulated at high CO2’

Line 412: “Synechococcus has been identified 412 as a DMS consumer in the open ocean“ Reference, please. Syn consumed labelled DMSPd, not DMS (Vila-Costa et al 2006)

AR. This reference to Syn has been removed, as it is a DMSP consumer, not DMS.

Line 431: Sections 3.3 and 3.4: No rates of anything for the halogenated compounds either? Just checking. AR. No, no rates were measured, due to the sampling limitations of the mesocosm experiment.

Lines 518-522: well, was the region isolated from the coastal environment or not? You can’t have it both ways. I understand that the mesocosm bags were closed so they wouldn’t have a macroalgal component. This will come back in the discussion

AR. The water within the bags was isolated from the outside environment, but this statement was to highlight that halocarbons were likely present in high concentrations in the water column prior to the mesocosm installation and closure. This would therefore have influenced halocarbon, particularly bromocarbon concentrations at the beginning of the experiment. This section has been reworded to make this clearer.

Line 548: I agree that the comparison between the mesocosms and the outside is inappropriate. The outside underwent its own and different “experiment”

Line 557: please delete sentence about DMSp as it implies that there was none because none detected when it is an analytical issue AR. removed

Line 558-569: given the statement in Line 548, please remove this paragraph as it mixes mesocosm conditions with outside conditions. It is pure speculation as a lot more changed with the injection of upwelled water than fCO2- i.e., particles, nutrients, DOM, etc, etc

AR. Paragraph deleted.

Line 576: Is CH2CII really polyiodinated?

AR. polyhalogenated

Line 584: Check your manuscript for Chl-ÉŚ, the ÉŚ is alternating between superscript and normal

AR. Checked – all changed to italic

Line 586-590: It is above indicated that macroalgal beds were not a source. Now, it is implied that those macroalgals beds were close? or far? in location w/r to the mesocosms. And the prevailing circulation was from the beds towards the mesocosms? And waht about vertical input? The entire DMS section is predicated on upwelling, ie, water injection from below NOT lateral advection. Can't have tvertical input for one gas and horizontal input for the other one.

AR. The mesocosms were approximately 500m from the shore, however the maximum depth of the seabed was 20-25m, so macroalgae growing there would have been within a few metres of the water taken from the Baltic. There was also free-floating macroalgae in the water column which could have contributed. The mesocosms were set up in a Fjard, which although had minimal tidal impact, had obvious signs of water movement in and out, with significant currents identified when mooring the boats to the mesocosms for sampling. A comment was included which stated that there was limited change in bromocarbons during the upwelling, likely that the upwelled water had

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similar concentrations to the surface waters.

Line 593-607: good

Line 599: I think you want to stress here, that the values are high enough to be considered an already adapted site, rather than stressing that they are lower than elsewhere, correct? “[. . .] at such a location with a relatively low fCO2 excursion compared to some sites [. . .]”, maybe rephrase to “[. . .] at such a location with a relatively high fCO2 excursion, however still relatively low when compared to some sites [. . .]”

AR. Agreed and changed.

Line 609-611: Not all the time, only after the decline of Chl-a, right? I wouldn’t stretch it out, then. AR. This statement was included as it was the most important finding of the mesocosm experiment, and compared to all the other mesocosm experiments.

Line 614: production was not measured, only concentrations. Please change production for cycling because the levels measured are a net result

AR. Changed

Line 615: since rates were not measured, you don’t know whether was a response (ie, prodn and/or cons), only that the measured concentrations did not change

AR. Changed to ‘the measured concentrations did not change’

Line 617: no change IF under similar meteorological conditions as during this sampling

AR. Added the proviso ‘without significant alteration top the meteorological conditions’

Line 617-621: NET production or availability. Again, same issue. Also, rather simplistic as meteorology must be considered.

AR. Added ‘net’

L621-625: This is a weak concluding paragraph. It says nothing at all. Keep it honest and simple by saying that no changes in concentrations were seen and that next time it would be best to measure rates so these rates can be included in models to have better predictions!! So sorry that you didn't see any changes nor anything "exciting".

AR. This paragraph has been amended to include the reviewers comments.

Figures in general: I find it very irritating how the units are given, e.g. fCO2/μatm. I read the "/" as 'per', which makes it confusing. I would very much prefer if you put fCO2 (μatm) or fCO2 [μatm]

AR. The figures have been amended to have the units in brackets

Fig 3: The Legend is misleading. It sounds as if you were showing an integration, but you are actually showing the mean from a water sample integrated from the top 10m. "Dashed lines show the Phases of the experiment as given in Fig. 2," should be moved to the a0 part of the legend, as it is not shown in 3b.

AR. Legend amended

Supplement Figures: Fig. S2: Top left y axis is formatted differently. Also t vs T as abbreviation for time between S1 and S2

AR. Figures have been amended.

There are two Tables 1 in the supplement.

AR. Table S2 renamed

There is a Fig. S3 that is never mentioned in the text which I suggest actually be moved into the main section as Fig 3c as it shows a difference of DMS/chl among mesocosms!

AR. The standard deviation during this figure is so high that it is a non-significant finding, and it has been established that there is no link between DMS and Chla. This figure was originally in the manuscript but was removed during the first round of reviewer comments prior to online discussion.

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