Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2018-338-AC3, 2018

Biogeosciences Discussions

Interactive comment on "Contrasting effects of acidification and warming on dimethylsulfide concentrations during a temperate estuarine fall bloom mesocosm experiment" *by* Robin Bénard et al.

Robin Bénard et al.

robin.benard.1@ulaval.ca

Received and published: 12 December 2018

Referee #3 comments: This manuscript describes the DMS/P results from a mesocosm experiment during which both CO2 levels and temperature were manipulated. The authors found that changes in CO2 and temperature did not influence DMSP values, but did impact DMS concentrations. DMS concentrations were linearly anti-correlated with CO2 levels and positively correlated with temperature. Their results indicate that changes in bacterial production are the cause for the changes in DMS between treatments. The scientific work reported is well done and is important contribution to our

understanding of DMS/P dynamics in the surface ocean under changing environmental conditions. It appears to be the first mesocosm paper to report the influence of multiple stressors on surface ocean DMS production. The authors also do a good job of outlining the limitations of the experiment. This manuscript should be published in Biogeosciences after the minor revisions stated below have been adequately addressed.

Author's response (AR) to general comments: We thank the reviewer for the thorough evaluation of the manuscript and the positive comments.

Specific Comments Abstract – not all acronyms are spelled out. AR: All acronyms appear to be spelled out.

Line 56 - Is Larouche the best reference here? Did someone do this work before? AR: As noted in Laroche et al. (1999), the release of DMSP in the dissolved fraction by phytoplankton is(was) usually attributed to cell autolysis prior to their study. Prior work on exudation of DMSP by phytoplankton is summarized in their Table 3 (Vairavamurthy et al., 1985; Dacey & Wakeham 1986; Gabric et al., 1993; Lawrence et al., 1993; van den Berg et al., 1993). However, as noted in Stefels et al. (2007), the modelling work by Laroche et al. (1999) was a defining study expanding on the earlier suggestions of active DMSP exudation clearly differentiating it from exudation during autolysis.

Lines 60-69 - Why is DMSO production not considered as part of the surface ocean cycling processes? AR: This part of the introduction focuses on the heterotrophic processes mediating most of the turnover of S-DMSPd relevant to the study. As we did not measure DMSO or DMSO-relevant processes we did not expand on this aspect of the sulfur cycle in order to be more concise and not overburden the reader with a part of the sulfur cycle that is not directly included in the study.

Addition (74): Additionally, the biological and photochemical oxidation of dimethylsulfoxide (DMSO) is an important sink for DMS, while DMSO reduction can also represent a DMS source (Stefels et al. 2007; Spiese et al., 2009; Asher et al., 2011).

Line 138 – Typo, are should be is AR: Fixed.

Lines 147-149 - Why did the pH adjustment procedure stop working after the bloom? AR: This system allows the addition of CO2-saturated water, effectively keeping the pH constant when the bloom develops (automatically adding CO2 while it is being consumed by phytoplankton during photosynthesis), but it cannot withdraw CO2 from the mesocosm when the bloom becomes nitrate-limited and respiration surpasses photosynthesis (effectively releasing CO2 in the mesocosm). Thus we observe a slight decrease in pH (increase in pCO2) towards the end of the experiment.

Line 167 - Typo, should say saturated AR: Fixed.

Section 2.3.3 - Were the samples sparged before measuring cleaving the DMSP to DMS? AR: For added clarity, the section has been modified. Old section: The DMSP samples were injected into a purge and trap (PnT) system before being completely flushed using 1–5 mL Milli-QTM water into the helium purged chamber heated to 70 °C. DMSP concentrations were determined by a mole to mole conversion to DMS following hydrolysis with a 5 M NaOH solution injected in the chamber prior to the sample, and trapping the gas sample in a loop immersed in liquid nitrogen. The loop was then heated in a water bath to release the trapped sample and analyzed using a Varian 3800 Gas Chromatograph equipped with a pulsed flame photometric detector (PFPD, Varian 3800) and a detection limit of 0.9 nmol L-1 (Scarratt et al., 2000; Lizotte et al., 2012). Samples for the quantification of DMS were directly collected from the mesocosms into 20 mL glass vials with a butyl septa and aluminum crimp. The samples were kept in the dark at 4 °C until analysis was carried out within hours of collection using the PnT system described above.

New section: To quantify DMSPt, 1 mL of NaOH (5 M) was injected into a purge and trap (PnT) system prior to the 3.5 mL sample to hydrolyze DMSP into DMS following a mole-to-mole conversion. Ultrapure helium was used to bubble the heated chamber (70 °C; 50 $\pm$ 5 mL min-1; 4 min) trapping the gas sample in a loop immersed in liquid

nitrogen. The loop was then heated in a water bath to release the trapped sample and analyzed using a Varian 3800 Gas Chromatograph equipped with a pulsed flame photometric detector (PFPD, Varian 3800) and a detection limit of 0.9 nmol L-1 (Scarratt et al., 2000; Lizotte et al., 2012). DMSP concentrations were determined against a calibration curve using standardized DMSP samples prepared by diluting known concentrations of DMSP standard (Research Plus Inc.) into deionized water and analyzed following the same methodology. Samples for the quantification of DMS were directly collected from the mesocosms into 20 mL glass vials with a butyl septa and aluminum crimp. The samples were kept in the dark at 4 °C until analysis was carried out within hours of collection by injecting the 20 mL sample in the PnT system described above, without the prior addition of NaOH. DMS concentrations were calculated against microliter injections of DMS diluted with ultrapure helium using a permeation tube (Certified Calibration by Kin-Tek Laboratories Inc.; Lizotte et al., 2012).

Line 355 - What were the other PFTs? Were they significant DMSP producers, potentially leading to a lot of DMSP in the water despite their low abundance? Excerpt from Bénard et al. (2018) : "S. costatum was the dominant species in all mesocosms (70–90 % of the total number of eukaryotic cells), except for one mesocosm (M3, pH 7.6 at 10 °C) where a mixed dominance of Chrysochromulina spp. (a prymnesiophyte of 2–5 μm) and S. costatum was observed (Fig. 3.6a). S. costatum accounted for 80–90 % of the total eukaryotic cell counts in all mesocosms at the end of the experiment carried out at 10 °C. At 15 °C, the composition of the assemblage had shifted toward a dominance of unidentified flagellates and choanoflagellates (2–20 μm) in all mesocosms with these two groups accounting for 55–80 % of the total cell counts while diatoms showed signs of loss of viability as indicated by the presence of empty frustules (Fig. 6b)." Prymnesiophytes are known to be high DMSP producers and could have represented a sizeable fraction despite their low abundance. However, as can be seen in Figure 6 of Bénard et al. (2018), the mesocosm m3 presented the highest prymnesiophyte proportion, but had one of the lowest DMSP content. Dinoflagellates, another high-DMSP producing group, did not contribute to the community. Therefore,

without denying the possible contribution of other PFTs to the overall DMSP pool, it is plausible that most DMSP stemmed from the dominant diatom community.

Section 4.3.1 - Were there contrasting studies? Why are they not discussed? AR: The following has been modified (L376): Old sentence: Several earlier mesocosm experiments have shown similar decreasing trends of DMS concentrations with increasing pCO2 (Hopkins et al., 2010; Archer et al., 2013; Park et al., 2014; Webb et al., 2015, 2016). In these studies, the pCO2-induced decreases in DMS . . .

New sentence: Few studies have shown a neutral of positive effect of increasing pCO2 on DMS concentrations, stemming from altered phytoplankton taxonomy, microzooplankton grazing, or diverging bacterial activity promoting DMS production (Vogt et al.,2008; Kim et al., 2010; Hopkins and Archer, 2014). However, the majority of studies have shown a decreasing trend of DMS concentrations with increasing pCO2 similar to our results (Hopkins et al., 2010; Archer et al., 2013; Park et al., 2014; Webb et al., 2015, 2016). In these studies, the pCO2-induced decreases in DMS . . .

Line 431 – Doesn't this mean that lowered conversion rates (from DMSP to DMS) are not responsible for the lower DMS concentrations? See also the comment to the conclusion section below. AR: The gross estimations we calculated are within the normal range of DMSP-to-DMS conversions. However, what we suggest is that the conversion rate is lowered by an increase in pCO2 although it stays within the "expected" range present in the literature (passing from 32% in the low pCO2 treatments to 0.5% in the high pCO2 treatments).

Lines 434-439 – I think these sentences should be saved for the conclusions to avoid summary/redundancy. AR: While we agree on the need for clarity and avoidance of redundancy, we believe it is imperative to conclude this section with these statements, which delve into speculative aspects and references that are not fit for the general conclusion.

Line 482 – Why is it stated that the lower DMS concentrations are likely caused by less

conversion from DMSP when the calculated conversion rates are within the normal range (see comment for line 431)? AR: As stated regarding the L431 comment, the gross DMSP-to-DMS conversion rates estimations are within the normal range present in the literature. However, what can be extrapolated from our results is that the conversion rates (which were at the high-end of the range under the lowest pCO2 treatments) decreased to the low-end of the range under high pCO2. Thus, the lower DMS concentrations are likely caused by less conversion of DMSP to DMS, although the calculated conversion rates stays within the "natural" range

Conclusions - I would have liked to see more discussion about what the authors would like to test next (e.g. pathways that cause lower DMS under high CO2, longer experiments to see if the community adapts to the changed environmental conditions). AR: Future research suggestions are intrinsically part of the limitations section. However, the following has been added to the conclusion.

New sentence (L489): Further studies should focus on the relationship between bacterial conversion of DMSP to DMS and pCO2, to mechanistically verify the suggested cause of the DMS reduction observed in this experiment. Moreover, an extended range of temperature should also be considered for future multiple stressors experiment as warming had, more often than not, a stronger effect on the community than acidification.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-338, 2018.