

## ***Interactive comment on “Contrasting responses of DMS and DMSP to ocean acidification in Arctic waters” by S. D. Archer et al.***

**Anonymous Referee #2**

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General comments:

This paper documents observed changes in DMS and DMSP during a CO<sub>2</sub> enrichment experiment in the Arctic Ocean. The paper is very well written, and the results seem thoroughly analysed and well illustrated. Thus, in my view the paper deserves a speedy publication in Biogeosciences. I have only a few suggestions for minor revisions that I would like to encourage the authors to consider.

Specific comments:

Introduction

At present, the introduction does not convince me entirely in terms of its structure. An extremely detailed and lengthy paragraph about the role of DMS in the atmosphere is

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followed by a very short and not very detailed paragraph on ocean acidification in the Arctic. This is followed by some discussion about what has previously been observed in CO<sub>2</sub> enrichment experiments, but the paragraph then turns into a review of the DMS cycle and its source and sink processes, mixed with a report of some relevant lab results. I suggest that the authors revise the logic of the introduction. In particular, I would focus more on what previous experiments have found, what their limitations were, and how the current study overcomes some of the limitations of previous publications and what its major strengths are.

p 12804, l 25: Although there remains... particularly... this... Who is 'this', and please simplify sentence.

P 12805, l 1-26: This is too detailed compared with the rest and the reader is lost as to why you mention isoprene and other biogenic primary organic aerosols. What do you want to convey? Revise and shorten.

P 12806, l 1: .... 0.1 pH units lower ... and 30% increase.. This sentence requires a reference.

P 12806, l 5: 'likely to impact on the physiology.. with implications' In which way and which implications? This paragraph remains very vague.

P 12806, l 12: 'conclusive identification of the mechanisms involved'... why has this not been achieved so far?

P 12806, l 16-22: 'If ocean acidification...' I am not so convinced about this argument. Changes in PP will only change DMSP production if the DMSP producers are affected. This would hold if the ecosystem was composed of the 'variety of DMS producers' you mention in the sentence above, but if your entire ecosystem consisted of, say, diatoms, and their PP decreased then we wouldn't expect to see large changes in DMSP production. In particular, in the sentence below you then stress the large range of intracellular concentrations for different taxa. And changes in PP may NOT amplify

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changes in DMPS production if shifts in composition do not affect the DMS producers. Clarify logic.

P 12806, I 26: Now you add some kind of review of the DMS sinks here. How does this fit here? Shouldn't you describe the DMS cycle somewhere as a whole, and then tell us which steps could be affected by ocean acidification, and for which processes we already have observational evidence? I get a little lost here.

Material and Methods:

P 12808, I 5: What is 't - 7'? Do you mean t-7?

P 12808, I 5: 'Nine large floating mesocosms...' Shape? And were they closed or open at the bottom?

P 12808, I 13: 'received varying amounts of CO<sub>2</sub>-saturated seawater' What does this mean? Was this added on top, or mixed with the rest of the water, did both untreated and treated seawater masses originate from the same location and how was the water CO<sub>2</sub>-saturated prior to its addition? In particular, what fraction of the 50m<sup>3</sup> is 'a varying amount'? A reference to a corresponding paper may help. I see that you point me at Riebesell, Bellerby and Schulz, but some info on how the CO<sub>2</sub> enrichment may or may not have affected the initial plankton composition would be helpful.

P 12808, I 14: t<sub>1</sub> - t<sub>4</sub> makes four days in my calculation, not five as you write here.

P 12808, I 17 and 12812, I 20: Why were nutrients added in the middle of the experiment?

p.12809, I 14: How often were both the DMS and the DMSP analysis system calibrated during and after the experiment, and what was the analytical uncertainty for triplicate analyses of the calibration samples, also ~10%?

p12809, I 20: Does the addition of NaHCO<sub>3</sub> affect the pH of the samples?

P 12809, I 22: Not sure I follow here:  $3 \times 12 \times 1.25 \text{ l} = 45 \text{ l}$ . But you took  $3 \times 20 \text{ l} = 60 \text{ l}$  of

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sample? What happened to the rest of the sample water?

P 12809, I 26: Why did you collect water from 6m depth and incubated it at ~2.3 m depth? Practical reasons?

P 12810, I 25: Why did you incubate the PP samples at a different location/under different conditions than those for the PP samples?

P 12811, I 9: Change brackets around Ragni et al. 2008.

Results

The analysis of the results in terms of statistical methods is based on linear regression and ANOVA-type factor analysis. What is a recurrent problem for this type of experiments is the temporal autocorrelation of the individual (daily) measurements. ANOVA and common regression analysis methods do not routinely correct for this, and significance levels of results tend to be over-estimated. Techniques in time-series analysis, however, are now using methods that include a correction of auto-correlation for the estimation of trends etc. While it is still unclear to me how this problem affects the analysis in studies such as this one, I think it would help future analyses if the authors of this study were to verify if autocorrelation is an issue here (see below), and to discuss their findings briefly in their text if necessary.

P 12812, I 15: Correct units of DMS concentrations. Why do you say that 1.5 nM is high? As far as I remember that is not that far from the global annual mean?

P 12813, I 12: 'by the varied levels of acidity', yes, and random fluctuations in the seed populations that may have caused chaotic and unpredictable biomass evolution in the different mesocosms?

P 12813, I 14: Wouldn't you have expected the diatoms and dinoflagellates to dominate during phase II, and the picos to succeed them during phase III?

P 12813, I 22: What do you mean by 'pervasive environmental forcing'?

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P 12814, I 9: 'this did not amount to a significant relationship' What do you mean here? If you take a linear regression to measure covariation, this will not be influenced by a fixed set-off? Please clarify.

P 12814, I 10: Please label 'a' and 'b' in your table 1. What are these? Also say how you use your data points: Do you fit all daily data for all 9 mesocosms and for each phase separately? Please explain where  $n=67$ ,  $n=80$  and  $n=61$  come from, and why they differ between DMSPt and DMS. Last but not least, all data from individual mesocosms is temporally autocorrelated, and you do not seem to correct for this here (at least you do not discuss it)? If you use ANOVA, this method usually tends to regard all measurements as independent, which is clearly not the case here. Do you think this will influence your significance levels? Please discuss the statistical techniques you use somewhere.

P 12815, I 12: I do not understand argument (1). Please expand.

P12816, I 5-6: I don't understand what you mean by 'is corroborated by...' since I really really do not see anything significant in the 'supposed decrease in Fv/Fm ratio'. How did the large error in each measurement enter your calculation of the regression, and the uncertainty of your slope and intercept? Since your method section does not contain any subsection where the statistical treatment of your data is discussed, this should be mentioned elsewhere.

P 12816: Figure 6c: Please specify here that you use daily match-ups between the two measured variables. I can see 9 dots, but the reader cannot remember if phase II was nine days long?

P 12817: Please correct 'tof' on line 11.

P 12819: Figure 8: Please label A and B.

Discussion:

P 12823, I 12: It seems to me that after several mesocosm experiments, the interpre-  
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tation of the DMS/DMSp related results still struggles with the same limitations. A full mechanistic understanding of what goes on in those mesocosms in terms of DMS cycling is not possible with the current set of measurements, and findings depend a lot on what the other people part of the experiment choose to measure, ie. which phytoplankton size fractions are being analysed etc. Like that, a lot of the conclusions still have to be drawn from indirect evidence, or excluding the least plausible alternatives. Could you please add a paragraph that explains what 'future studies' should comprise if they are to shed light on the mechanisms involved in the marine DMS cycle, from DMSp production to DMS consumption. And do you believe an 'optimal experiment' is feasible? If not, do you really think 'future studies' will allow a mechanistic understanding of the complex suite of processes involved? Do you think a mechanistic understanding is in fact necessary?

Conclusions:

P 12824, I 15ff: Modellers can only accurately model the DMS cycle if the rates (and not only the concentrations) of DMS production and consumption are known. Since your study does not give any DMS production or consumption rates, it will be tricky for modellers to follow your advice. Modellers certainly agree that the inclusion of a H+ sensitivity would be desirable, but we need to get present DMS concentrations right first. While I like your recommendation, and while I totally agree that your data is of great value, I would still be relieved if you were to caveat your recommendation with something like 'as soon as models are able to realistically simulate present DMS concentrations, they should parameterise the effects of ocean acidification....' or 'We still struggle to understand and hence model the marine DMS cycle, but once we understand the basics, we could...'. I think you know what I mean. If the pH effect on DMS is included by simply decreasing the production rates linearly as  $f(\text{pH})$  based on the available data, we'll once more end up with empirical and thus totally inflexible models that may not get the central mechanisms right. Observationalists would surely criticise modellers for such an approach.

P 12825: I fully agree to your last paragraph.

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