# Interactive comment on "Impact of ocean acidification on Arctic phytoplankton blooms and dimethylsulfide production under simulated ice-free and under-ice conditions" by Rachel Hussherr et al.

# **Anonymous Referee #1**

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# Summary

Hussherr et al. present an interesting and timely study that addresses the lack of data we have on the response of DMS concentrations in Arctic waters to ocean acidification. Specifically, the paper presents the results of a 9 day experiment in which seawater was incubated in 10 L gas tight bags under a range of pH/pCO2 treatments, from pHT 7.9 - pHT 7.2, representing a range from 'present day' to end of century to extreme far future values. Furthermore, the authors investigated the role of light, dividing the bags into low light and high light treatments, in order to simulate ice free and under ice conditions. The pH gradient method is an established and wellused technique, most useful when the possibility of replication is limited. Acidification was performed using the addition of strong acid and base, again another established technique. Samples for a range of parameters were taken on a regular basis over the 9 day experiment. Within 3 days of the start of the incubation period, a bloom initiated in all bags, leading to an increase in phytoplankton biomass and DMS/DMSP concentrations – differences in the response were attributed to the pH treatments, with no clear observed effect of light. DMS concentrations significantly decreased with decreasing pH, which is in agreement with the one other previous study from Arctic waters (Archer et al. 2013), leading to the conclusion that DMS concentrations during Arctic blooms may be lower in the future, with possible implications for the Arctic climate. The paper is generally well written and logically structured. I have identified a number of minor issues that the authors should address, relating to the methods and the bloom dynamics. Assuming the authors make the suggested changes, this paper would be suitable for publication in Biogeosciences.

In the first place, the authors wish to thank the referee for the positive and constructive comments. Every comment made has been carefully considered and the manuscript has been amended/modified when necessary by addressing each point one-by-one.

### Key points

1. Methods: L128: the authors state they 'poured' seawater into the gas-tight bags. Through a luer valve? Some clarity is needed as to their exact methods. Pouring is not recommended when handling gas sensitive samples as the gas phase equilibrium may be altered. Notwithstanding the difficulty in pouring anything through a luer valve! Some more detailed explanation is required.

The water was transferred by gravity from the Niskin bottle to the gas-tight bags using a Teflon

tube connected between the output valve of the Niskin bottle and the luer-valve of the bag.

This information has been added to the text.

L137 - New sentence: "After initial collection, water was gravity filtered through a 200  $\mu$ m Nitex mesh, in order to remove large grazers, and transferred to 12 gas-tight 10-L bags (HyClone Labtainer©, Thermo Scientific) using a Teflon tube linking the output valve of the Niskin bottle and the luer-valve of the bag."

L131: Samples were incubated at  $4.3 \pm 1.6$  °C. This seems warm for experiments that are attempting to simulate 'under ice' conditions. Can the authors provide some justification/ further explanation?

This is a good point. We are aware that the experimental temperature did not perfectly reproduce the conditions prevailing under the ice. Our deck incubator was constantly flushed with surface water during the cruise and we had no control over the temperature of the water. However, all HL and LL bags were in the same incubator, hence submitted to the same temperature.

The following sentence was added to address this issue:

- L142 145: "Since our deck incubator was cooled with circulating surface water, we had no control on the temperature during the incubation (mean temperature of  $4.3 \pm 1.6$ °C over the 9-day experiment). However, all bags were in the same incubator, hence submitted to the same temperature."
- 2. What stimulated the bloom in the bags? Were the team expecting a bloom to occur in the way it did in the bags? Did a bloom also develop in the sampled water simultaneously (i.e. was this a natural or artificial bloom?)? Many questions. . .therefore some more discussion would be useful to the reader. After all, without such a nice bloom, it is unlikely a DMS(P) response would have been observed. L492: the authors talk about their findings in the context of the Arctic spring phytoplankton bloom but actually this experiment sampled waters in August, which must qualify as late summer for the Arctic. So how comparable were the starting conditions to the spring bloom?

This is also a very good point that we are now addressing in the revised version of the manuscript. Since the cruise took place after the summer bloom in this part of the Arctic, we collected the water just below the nitracline in order to have sufficient nutrients at the beginning of the incubation to support a bloom. The nutrient concentrations at the sampling depth (38 m) corresponded to the concentrations found in the upper mixed layer in Baffin Bay in spring before the seasonal bloom (Tremblay et al. 2002, 2006). The taxonomic composition of the bloom was also similar to the one taking place in spring in this area, with *Chaetoceros* species dominating the assemblage (Von Quillfeldt, 2000). We are thus confident that the bloom that took place in our bags is comparable to the 'natural' spring bloom. But we agree that this point should have been made clearer in the paper.

L 132 - 134, new sentence: "Since the cruise took place after the summer bloom in this part of the Arctic, we collected the water just below the nitracline in order to have sufficient nutrients to support a bloom during our incubation".

L 506 – 509, new sentence: "As the initial concentrations of nutrients measured in our incubation bags were similar to the concentrations found in upper mixed layer waters in early spring before the seasonal bloom in Baffin Bay, we are confident that the bloom that took place in our bags is comparable to the natural spring bloom taking place in these waters (Tremblay et al., 2002, 2006). Furthermore, the dominance of diatoms (...)"

3. Reference to Richier et al. (2014) (Phytoplankton responses and associated carbon cycling during shipboard carbonate chemistry manipulation experiments conducted around Northwest European shelf seas) is lacking and should be included in the discussions. The work of Richier et al. is the most similar to this study in terms of the experimental techniques used. The authors do cite Hopkins & Archer (2014) which was part of the same study, but only in a DMS(P) context. The shipboard incubations of Richier et al. and Hopkins & Archer also need to be addressed in the context of this study in terms of the phytoplankton response.

We are now directly referring to the paper by Richier et al. (2014) in the revised version of the manuscript (see the following responses to the specific comments L 79 - 81 and L 575 - 581).

# Specific comments and suggestions

Title: it would be more accurate to say 'DMS concentrations', as 'production' implies that the work include rate measurements.

As suggested, the title has been changed for "Impact of ocean acidification on Arctic phytoplankton blooms and dimethylsulfide concentrations under simulated ice-free and under-ice conditions".

- L45 49: These two sentences are somewhat ambiguous and need further explanation. Why is climate change 'faster and more important' in the Arctic? In what respect?
- L 50 53: The sentence has been modified as follows: "Due to various feedback processes, the air temperature in the Arctic above  $64^{\circ}N$  has warmed by  $1.9^{\circ}C$  between 1981 and 2012, a rate three times higher than the global average (ACIA, 2005, Ford et al., 2015). This phenomenon is known as the Arctic amplification (Cohen et al., 2014)."
- L50-52: this sentence seems detached and slightly out of context. I see what the authors intend by it. Perhaps they could re-phrase so it says something like: 'Given that the reduction in extent and thickness of sea ice cover and the acidification of surface waters can potentially impact primary productivity, it is important to consider the associated effects on the production of biogenic climate-active gases. . .' or similar, just to change the emphasis slightly, and provide an impetus for the work.
- L56 59: Thank you for the suggestion. The sentence has been changed for: "Given that the reduction in extent and thickness of sea ice cover and the acidification of surface waters can potentially impact primary productivity, it is important to consider the associated effects on the production of biogenic climate-active gases such as dimethysulfide (DMS) in the Arctic".

L70 - 75, and throughout: the authors make no mention of Richier et al (2014), a recent and relevant paper that should be cited.

L 79 – 81: Reference to Richier et al. has been added as follow: "(...) but negative impacts of decreasing pH on phytoplankton growth have also been reported and attributed to pH-induced alterations in algal cells physiology, acid-base chemistry, trace metal availability, ion transport, protein functions, and nutrient uptake (Doney et al., 2009; Gao and Campbell, 2014; Richier et al., 2014; Mackay et al., 2015; Thoisen et al., 2015)."

L80: re-word. Suggest: 'Emissions of DMS thus can...'L83: add 'atmosphere' at end of sentence (so reads 'summer Arctic atmosphere').

L 88: As suggested "The DMS emission" has been changed for "Emissions of DMS". L 91: "such as the summer Arctic" has been changed for "such as the summer Arctic atmosphere".

L97: Not necessary to cite Webb at this point as it is not a review paper. Fine to just cite the references as you specifically mention them later in the paragraph.

L 104: "Several studies have already highlighted the sensitivity of DMS production to decreases in seawater pH (Webb et al., 2015 and references therein)" has been changed for "Several studies have already highlighted the sensitivity of DMS production to decreases in seawater pH."

L99: although Archer et al. is mentioned later in the paragraph in an Arctic specific context, it would be appropriate to add it to the listed references here.

L 105 – 108: "The majority of these experimental studies revealed a negative impact of decreasing pH on DMS production (Hopkins et al., 2010; Avgoustidi et al., 2012; Webb et al., 2016)" has been changed for "The majority of these experimental studies revealed a negative impact of decreasing pH on DMS production (Hopkins et al., 2010; Avgoustidi et al., 2012; Archer et al., 2013; Webb et al., 2016)"

L142: 'submitted' would be better substituted for 'exposed'.

L156: "the phytoplankton communities were submitted to a pH gradient and two light regimes" has been changed for "the phytoplankton communities were exposed to a pH gradient and two light regimes."

L397: should read 'species'.

L 413: "specie" has been changed to "species"

L403: to improve readability, re-phrase: 'The sole exception was the LL control mesocosm...'

L 419 – 421: "The sole exception was the control microcosm (p $H_T$  of 8.1) exposed to LL conditions" has been changed to "The sole exception was the LL control microcosm (p $H_T$  of 8.1)".

L452: Rather than staying 'high pHT', it would be useful to state the range of pH over which the

response was observed.

L 467 – 469: "the mean DMSP<sub>T</sub> concentration decreased with increasing proton concentration, but only under the HL treatment at high pH<sub>T</sub>" has been changed to "the mean DMSP<sub>T</sub> concentration decreased with increasing proton concentration but only under the HL treatment between pH<sub>T</sub> 8.1 - 7.6".

L513 - 517: this long sentence needs some re-wording as it is currently hard to follow and the English is poor in places.

L 532 – 536:

Old sentence: "During our experiment, the sharp increase in DMSP<sub>T</sub> and DMS coincided with the exhaustion of  $NO_3^-$  in most of the microcosms (Fig. 3a, b). Despite  $NO_3^-$  concentration still ranged between 0.9 and 2.6  $\mu$ mol L<sup>-1</sup> at day T6 in the microscosms at lowest pH (i.e. 7.4 and 7.2), the observed peak in DMSP<sub>T</sub> concentration in those bags was of lower magnitude, reaching approximately 30 nmol L<sup>-1</sup> at T6 (in contrast with other microcosms, where DMSP<sub>T</sub> reached values around 100 nmol L<sup>-1</sup> that day)".

New sentence: "During our experiment, the sharp increase in DMSP<sub>T</sub> and DMS coincided with the exhaustion of  $NO_3^-$ , with the exception of the microcosms at pH<sub>T</sub> 7.4 and 7.2 under both light regimes (Fig. 3a, b). At those pH, the increase of DMSP<sub>T</sub> between T5 and T6 was of lower magnitude compared to the other microcosms and  $NO_3^-$  concentrations between 0.9 and 2.6  $\mu$ mol L<sup>-1</sup> were still measured in the bags at T6 (Fig. 7a, b)."

L524: should read 'switched'.

L 543: "switch" has been changed to "switched".

L527 – 528: needs re-wording. Suggest: 'These results also suggest that diatoms could have more difficulty in efficiently taking up/assimilating. . .'

L 546 - 547: "These results also suggest that diatoms could have more difficulty to efficiently take up/ assimilate NO<sub>3</sub> at lower pH" has been change to "These results also suggest that diatoms could have more difficulty in efficiently taking up/ assimilating NO<sub>3</sub> at lower pH".

Section 4.2: some discussion of the results in comparison to the findings of Richier et al. would be useful, as the two studies use very similar techniques – yet yield quite contrasting responses.

The following sentences were added in section 4.2:

L 575 - 581: "In contrast to our study, Richier et al. (2014) reported a negative impact of ocean acidification not only on nanophytoplankton but on picophytoplankton as well during a microcosm experiment using a similar methodology. In this study conducted with water from the northwest European shelf, lowering the pH resulted in a decrease in the abundance (cell number) and biomass (Chl a) of phytoplankton < 10  $\mu$ m. These contrasting results could reflect differences in the initial picophytoplankton community composition and possible species-specific physiological response to OA. By contrast, (...)"

L608 – 610: Archer et al (2013) and Hopkins and Archer (2014) report rate measurements – so this statement is not correct, and their findings should be included in the discussion.

L 640: The sentence "Unfortunately, these hypotheses remain to be confirmed, given the lack of DMS production and degradation rate measurements." was deleted.

L 642 - 646: Was added to the discussion: "Results from the few previous studies where gross rate measurements were performed show no consistent effect of a decrease in pH on neither DMSP synthesis nor DMS consumption (Archer et al. 2013, Hopkins and Archer 2014). Despite the lack of rate measurements in our study, the dominance of diatoms, an algal group lacking DMSP lyase enzymes, suggests that bacteria may have played a critical role in the observed DMS dynamics."

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