Final author comments on "Dimethylsulfide (DMS) production in polar ocean may be resilient to ocean acidification" by F.E. Hopkins et al., manuscript number bg-2018-55

We thank both anonymous reviewers for their detailed, constructive, and positive reviews of our manuscript – we greatly appreciate the care and detail that has gone into its assessment. Below we respond to their comments point-by-point. It is worth noting that the related paper by Richier et al. (2018) has now been accepted for publication in Global Change Biology (doi: 10.1111/gcb.14324), providing further substantiation of many of the discussion points in this manuscript. The reviewers comments are shown in italics, with our responses shown in bold. Line numbers in our response refer to the revised version.

1. **Response to Anonymous Referee #1**

General comments

1.1 The paper describes experimental results examining the response of DMS and DMSP concentration, synthesis & production rates to acidification in Southern Ocean & Arctic waters and compares them with previously published results from the NW European shelves. The authors report regional trends in responses, which they attribute to the variability in the carbonate system and its influence on the plasticity of the phytoplankton community and DMS/DMSP response. The analysis is somewhat limited to the carbonate system & phytoplankton size class without consideration of other factors. The paper is clear and well-written, and makes important points including regional variation in response to acidification, and also that different processes occurring at different scales are responsible for the variable responses reported over different timescales (as exemplified by comparison of microcosm versus mesocosm responses). The paper is of publication standard if the points below relating to interpretation & analysis can be addressed.

We thank the reviewer for their positive view of our paper, and we are confident that we have addressed their concerns.

Specific comments

1.2 Title The comparison with the NW European Shelf results is an important part of this paper and merits mention in the title

The title has been changed to:

"Dimethylsulfide (DMS) production in polar oceans may be insensitive to ocean acidification: a meta-analysis of 18 microcosm experiments from temperate to polar waters".

'resilient' has been replaced with 'insensitive' at the suggestion of reviewer #2, see point 2.8 below.

1.3 Introduction Line 122–these microcosm experiments are not long enough to test adaptation. Results from experiments on timescales of < 1 week may give insight into plasticity and acclimation, but not "adaptive capacity"

We acknowledge this point while further noting that a key point we emphasise is that we interpret the variable sensitivity to short term experimental conditions observed as potentially corresponding to pre-existing adaptation to prevailing conditions across sampled populations/systems. Text has been altered accordingly in three places (line numbers correspond to revised version):

L124: "The focus is then on the effect of short-term CO_2 exposure on physiological processes, as well as the extent of the variability in acclimation between communities".

L126: "The capacity of organisms to acclimate to changing environmental conditions contributes to the level of resilience of key ecosystem functions, such as DMS production".

L132: "…our approach can provide insight into the physiological response of a variety of polar surface ocean communities, as well as their potential level of sensitivity to future OA when compared between environments that differ in carbonate chemistry…".

1.4 *Results Fig. 3 Error bars are relatively large at 96 hours in Arctic waters – this should be noted and discussed*

We feel that this observation does not add any additional insights to the results or discussion so we have simply added into the results text:

L331: "Increased variability between triplicate incubations became apparent in all three Arctic experiments by 96 h but no significant effects of elevated CO_2 on DMS concentrations were observed".

1.5 *Line 304-305; Fig 4c Error - "DMSP concentrations were found to DEcrease significantly in response to elevated CO2 AT 48 h for Barents Sea (Fig. 4 C)". Also note that DMSP was not significantly different at 96 hours.*

Text has been altered accordingly.

1.6 *Discussion 4.1 Regional differences in the response of DMS(P) to OA The interpretation of the treatment effects would benefit from statistical analysis to support the interpretation in:*

Line 375-376 "De novo DMSP synthesis and DMSP production rates show a similar relationship with DIC/Alk (Fig. 7 A and B)" - is the difference between 0.91 > and < 0.91 significant? With the exclusion of one station (DIC/Alk ~0.901) there looks to be no difference in Figure 7. Statistical confirmation required.

Statistics have been confirmed and the text now reads:

"*De novo* DMSP synthesis and DMSP production rates show a similar relationship with C_T/A_T (Fig. 7 A and B), with a significant suppression of DMSP production rates in temperate waters compared to polar waters (Fig. 7B, Kruskal-Wallis One Way ANOVA $H = 8.711$, $df = 1$, $p = 0.003$). Although a similar trend was seen for *de novo* DMSP synthesis, the difference between temperate and polar waters was not statistically significant (Fig. 7A)".

Line 379-380. "At T1, Chl a showed little response to elevated CO2 at polar stations, whereas a strong negative response was seen in temperate waters (Fig. 8A)" – again this description does not really match the data in the figure. The polar stations show a smaller range of treatment effect than temperate stations which show both larger positive and negative effects. Statistical confirmation required

Line 380-382. "A slight positive response in Chl a was seen at most temperate stations by T2, with generally little response at polar stations (Fig. 8 B)." Aren't the highest treatment effects at the polar stations? Statistical confirmation required

Statistics have been confirmed and the text now reads:

"At T_1, a statistically significant difference in response was seen between temperate and polar waters for Chl *a* (Kruskal-Wallis One Way ANOVA $H = 20.577$, $df = 1$, $p<0.001$), with minimal response to elevated CO_2 at polar stations, and in general a strong negative response was seen in temperate waters (Fig. 8A). By T_2, no significant difference in response of Chl *a* between temperate and polar waters was detectable (Fig. 8B), although a slight positive response in Chl *a* was seen at some temperate stations, and polar stations showed a minimal response, with the exception of *Barents Sea* which saw strongly enhanced Chl *a* at T_2 (Fig. 8 B)".

1.7 *The analysis is limited to considering the carbonate system & phytoplankton size class as the factors determining regional response. Other factors will have differed between the polar waters and NW European shelf and may have influenced DMS/DMSP response to ocean acidification such as temperature, light, nutrients and phytoplankton community composition. For example, the authors mention "slower microbial metabolism at low water temperatures", so could this explain the observed difference in regional response? Datasets for these variables are most likely available, and a more comprehensive analysis that considers these would benefit the paper and interpretation. This may have already been carried out by the authors, in which case it should be noted that there are no relationships between response and these other variables.*

Richier et al. (2018) provide a detailed overview of the role of other potential environmental drivers for the differences in response between temperate and polar waters. This paper has now been accepted for publication in Global Change Biology, so we will refer the reader to it for more detailed analysis of this issue. To address the reviewers concerns, we have also added an appropriate amount of discussion relating to this to the current manuscript.

Firstly, to address the reviewers comment on "slower microbial metabolism at low temperature waters": we failed to observe strong responses to high CO_2 in experiments performed in Arctic waters (cruise JR271), therefore incubation times during the Southern Ocean experiments (cruise JR274) were increased from 4 to 6 to 8 days, whilst including a higher CO_2 treatment (2000 µatm). However, the magnitudes of the responses were found to be independent of overall experimental duration. As Richier et al. (2018) explain, net growth rates may be expected to be 2- to 3 –fold higher in the warmest compared to the coldest waters (Eppley, 1972), and indeed maximum Chl a-normalised photosynthesis rates were indeed 2- to 3-fold higher in polar waters – but the response to experimentally-induced OA in polar waters remained insignificant despite the length of incubation being up to twice the duration of temperate experiments, and up to 4x longer, than the 48 h time point where strong responses were typically observed in temperate waters.

We have added the following to the methods section at L210:

"The magnitude of response was not related to incubation times, and expected differences in net growth rates (2- to 3-fold higher in temperate compared to polar waters (Eppley 1972)) did not account for the differences in response magnitude despite the increased incubation time in polar waters (see Richier et al. (2018) for detailed discussion)".

Secondly, to address the reviewers concerns regarding "other factors [that] will have differed between polar waters and NW European shelf…" that may have influenced the response, we have added the following to the Discussion:

L440: "Across all experiments, the response of net total community Chl *a* and net growth rates of small phytoplankton (<10 µm) scaled with pCO_2 treatment, and strongly correlated with in situ carbonate chemistry, whilst no relationships were found with any of the other wide range of initial physical, chemical or biological variables (Richier et al. 2018). Overall, the observed differences in regional response to carbonate chemistry manipulation could not be attributed to any other measured factor that varied systematically between temperate and polar waters. These include ambient nutrient concentrations, which varied considerably but where direct manipulation had no influence on the response, and initial community structure, which was not a significant predictor of the response (Richier et al. 2018)".

1.8 A minor point here is that methodological differences should also be considering when assessing response. For example, different light cycles were used on different voyages.

Different light cycles were used on different voyages to simulate the *in situ* light conditions/light:dark cycles for the time of year of sampling. We don't expect this to have affected the response to OA, and it would have been inappropriate to have used the same light cycle on all cruises.

1.9 They should also consider the degree to which the experimental manipulations alter the carbonate system relative to the ambient mean. The magnitude of change upon acid/base addition from the mean state of the carbonate system may be a more important factor than the regional range. For example, a proportionally larger shift in pH or carbonate upon acid/base addition may initiate a greater stress response and so DMS/DMSP production.

Ambient pCO_2 and pH for each sampling station are shown in Table 1. A large range of ambient carbonate chemistry was observed across all waters, with no consistent relationship with location (e.g. pCO_2: NW Euro shelf 287 – 400 uatm, Arctic 289 – 304 uatm, Southern Ocean 272 – 510 uatm). Experimental manipulation of carbonate chemistry was accurately calculated and implemented using the CO_2SYS programme (see Richier et al. 2018 for methods, and Richier et al. 2014 Figure 3 for a comparison of target vs actual pCO_2 following experimental manipulation for NW European shelf experiments). Our experiments provided no apparent evidence of a relationship between the proportional shift in pH/carbonate chemistry and the magnitude of the response as a function of the initial state of the carbonate system, rather, as emphasised, the presence or absence of any observable response broadly correlated with the initial state of the carbonate system (see also Richier et al. 2018), with subsequent response strength then scaling with magnitude of manipulation in those experiments where any response could be observed.

1.10 Lines 431-434: "In the following section, we explore the causes of this apparent resilience in terms of the environmental conditions to which the communities have presumably adapted." It should be noted that the variation in DIC/Alk reflects regional scale variation in single point measurements at each station (Line 362 "...the sampled waters"), and not the DIC/Alk variation at a particular site. Phytoplankton may experience greater or less variation at a single location on a temporal basis, which may be a more important factor determining response. The role of temporal variation in determining response should be discussed.

We agree with the reviewer that variation of carbonate chemistry on a temporal basis may be important in determining the response to experimental OA, although, as discussed in Richier et al. (2018), we also note that it is the range of variability experienced at the cellular level over generation timescales (i.e. days) which is likely to be the most important. However, given the lack of temporal data for each sampling station we acknowledge that we cannot make definitive statements in this regard. We have acknowledged in the text that the amount of variation in carbonate chemistry experienced by plankton communities at a single location on a temporal basis should also be considered:

L495 onwards: "Although it might be expected that carbonate system variability on the level 'experienced' by the cells, i.e. ~daily cellular level variability, might be the most important factor driving sensitivity (Flynn et al. 2012; Richier et al. 2018), our data represent only a snapshot (4 – 6 weeks) of a year, and thus do not contain information on the range in variability over seasonal cycles. For comparison with Arctic stations, Hagens and Middelburg (2016) report a seasonal pH variability of up to 0.25 units from a single site in the open ocean surface waters in the Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability of 0.3 – 0.4 units in the McMurdo Sound, Antarctica. This implies that both polar open ocean and coastal/sea ice locations experience equally large variations in carbonate chemistry over seasonal cycles. In open ocean waters this is driven by enhanced drawdown of DIC and CO_2 during the productive spring and summer months, countered by lower productivity and strong mixing in the winter (Hagens and Middelburg 2016). In coastal and sea-ice affected regions, seasonal pH variability may be enhanced further by tidal exchanges, and by dilution of T_C/T_A caused by sea-ice melt (Kapsenberg et al. 2015)."

1.11 Lines 451-457. The examples cited to support the authors contention that variability induces plasticity are from coastal waters and under ice, where greater variability would be expected. Would the variability be equally as large at the open ocean stations in this study?

The carbonate chemistry/pH variability may be as large in the open waters of the polar oceans, as in coastal/sea-ice waters. The open waters of the polar oceans experience high levels of productivity during the spring and summer, and given that these waters are less well-buffered with respect to CO_2 uptake, this will lead to a greater range of both short-term cellular scale variability (Flynn et al. 2012; Richier et al. 2018) and seasonal carbonate chemistry characteristics in these waters (Sabine et al. 2004, Orr et al. 2005). Hagen and Middleburg (2016) assess the factors that control seasonal pH variability in surface waters, using a station in the open waters of the Iceland Sea as one of their examples. At this site, pH is shown to vary by up to 0.25 pH units over a seasonal cycle. This is due to a strong drawdown of DIC and pCO_2 during the productive spring months, and a rise in DIC and pCO_2 in winter as a result of reduced productivity and strong

mixing. This is of a similar magnitude to seasonal pH variability at a coastal, sea-ice dominated site in the Antarctic (McMurdo Sound, Kapsenberg et al. 2015) where pH variability of 0.3 – 0.4 units is observed – and this range is among the greatest observed in the ocean. Therefore, it is reasonable to assume that the seasonal variability at open ocean polar stations may be of a similar order to the variability observed in coastal/sea-ice stations.

The text has been edited and extended to take into account the information detailed above as for point 1.10.

Line 462-463 The authors mention the mean state here. Although the inclusion of the Tynan et al (2016) data is useful, this regional variation gives no indication of the local spatial & temporal variation that phytoplankton would experience at each station. The argument would be stronger if the responses were compared with mean local values for the carbonate system (from Tynan et al) for each station, which will to some extent, integrate temporal & spatial variability, rather than using just the values for the water sampled for the experiment (which I assume is what was done).

The DIC/Alk values used for comparison of the response magnitude are representative of the "mean local values" for each station, and are also "the water sampled for the experiment". We are unclear what the reviewer would like to see here. Table 1 shows the pCO_2 and pH for each sampling station and the DIC/Alk was derived from the other measurements of the carbonate system made from these same samples. We do not believe these values integrate temporal and spatial variability as they are discrete measurements made on the water sampled for the incubations. Furthermore community composition is also transient, such that the phytoplankton that were present in the sampled water would not necessarily have been present all the time/everywhere. As emphasised above, our overall hypothesis is that cellular level variability is likely to be the most significant driver of local adaption of communities and hence sensitivity to manipulative forcing (Flynn et al. 2012; Richier et al. 2018).

<u>Technical corrections</u>

1.12 Line 55 chlorophyll-a maxima IN SURFACE WATERS

Text changed accordingly, now reads "…and have been linked to chlorophyll *a* maxima <u>in surface waters</u> and the presence of aerosols formed from DMS oxidation products such as methanesulfonate (MSA)".

1.13 Line 87 Sentence is a bit clunky

Sentence has been re-worded and now reads: "OA is occurring at a rate not seen on Earth for 300 Ma, and so the potential effects on marine organisms, communities and ecosystems could be wide-ranging and severe".

1.14 Line 130-133 Shorten sentence

The sentence has been shortened and now reads: "Nevertheless, our approach can provide insight into the physiological response and level of acclimation to future OA of a variety of polar surface ocean communities adapted to different in situ carbonate chemistry environments (Stillman and Paganini 2015), alongside the implications this may have for DMS production".

1.15 Line 145 – Clarify that the Hopkins & Archer (2014) is from the NW European Shelf

Text changed accordingly, now reads: "Data are combined with the results from an earlier study on board the RRS Discovery (D366) described in Hopkins & Archer (2014) <u>performed in the temperate waters of the NW European shelf</u>".

1.16 Line 256 – What does E1E4/E5 refer to?

We assume the reviewer is referring to Line 265. E1-E4/E5 describes the experiment identifiers for the polar cruises - but incorrectly - so thank you for pointing this out. The text now refers the reader to Table 1 for station identifiers.

1.17 Line 315 "Initial DMSP concentrations were higher AT THE SOUTHERN OCEAN STATIONS than for Arctic stations..."

Text changed accordingly, now reads: "Initial DMSP concentrations were higher <u>at the Southern Ocean stations</u> than for Arctic stations,…"

1.18 Line 317 "Net increases in DMSP occurred throughout, EXCEPT AT SOUTH GEORGIA..."

Text changed accordingly, now reads: "Net increases in DMSP occurred throughout, <u>except at South Georgia</u>, and were on the order of between <10 nmol L^{-1} - >30 nmol L^{-1} over the course of the incubations".

1.19 Line 320 "the final time point at South Georgia (144 h) when a significantly LOWER DMSP with increasing CO2 was observed"

Text changed accordingly, now reads: "Concentrations were not generally $p$$CO_2$-treatment dependent with the exception of the final time point at *South Georgia* (144 h) when a <u>significantly lower DMSP</u> with increasing CO_2 was observed…"

1.20 Line 350. As the results from the 4 unpublished NW European microcosm experiments are not presented in this paper, they should be identified as unpublished in Table 1

As stated in the text that the reviewer refers to, the data from the 4 previously unpublished NW European microcosm experiments are included in the meta-analysis in this paper (Figures 6, 7, 8), so it is reasonable to identify them as "*This study*" in Table 1.

Line 365; Table 1 legend should identify that the polar stations are the two JR voyages excluding Station NS & IB.

Text added to Table 1 legend: "All polar stations were sampled for JR271 and JR274, with the exception of NS and IB".

1. **Response to Anonymous Referee #2**

<u>**General comments**</u>

2.1 Hopkins et al. Present a large dataset on DMS(P) production by phytoplankton in short term OA experiments from the Arctic, the Southern Ocean and the North Atlantic. This is an interesting

and important dataset. I especially acknowledge the importance to publish 'negative results', i.e. absence of significant effects of experimental treatments, which is often neglected in OA research but should receive a lot more attention.

We thank the reviewer for their positive view of our work, and also agree that it is important to publish 'negative results' to give the full picture on the effects of ocean acidification.

2.2 I find the hypothesis that then environmental history of organisms will determine their sensitivity to environmental change very convincing. Currently, the data (or its presentation) is not really suited to convincingly convey this message though. This does not mean that the hypothesis should not be mentioned, but it should be clearly marked as a hypothesis rather than a finding.

We have changed "suggest" to "hypothesise" on L24.

We have changed "Our findings support the notion that,.." to "This supports our hypothesis that…" on L524.

We have changed "However, results from our study indicate that the DMS response to OA…", to "However, we hypothesise that the DMS response to OA…" on L657.

2.3 Furthermore, I would argue that the significant OA effects observed in the two cited coastal communities really question the validity of this hypothesis, as the degree of carbonate chemistry variability is much more pronounced in coastal vs. open ocean compared to temperate vs. polar. Therefore, your conclusions need to be more specific to the current study, and not towards polar systems in general.

We would argue that pH variability over seasonal time scales in the open ocean polar waters is comparable to coastal/sea ice dominated areas. Additionally, as noted elsewhere in our responses, we hypothesise that cellular scale variations are likely to be the most relevant (Flynn et al. 2012; Richier et al. 2018).

See response to reviewer #1, point 1.13.

2.4 One of my general methodological concerns that need to be addressed in the discussion is the fact that especially in short-term experiments, 50% variation in the experiment duration can have a huge impact on the outcome, especially if the phytoplankton initially show a lag phase as often observed in such experiments with natural communities. It makes a huge difference if OA effects are compared after 48h or 4d or 7d. While after 2 days, physiology most likely is not fully acclimated to the treatment conditions yet, 4d or 7d duration most likely show acclimated responses but potentially also reflect shifts in the composition of the communities. Also the differences in the number of hours at T1 and T2 should be accounted for by always referring to the number of hours rather than the time point throughout the manuscript.

For the NW European shelf cruise and the Arctic Cruise, all experiments were 96 h in duration, with samples taken at 0 h, 48 h and 96 h. As we failed to observe strong responses within experiments performed in the Arctic, incubation times were increased for a subset of experiments on the Southern Ocean cruise. This was to investigate whether the lack of strong response in Artic waters was related to slower microbial metabolism in the low temperature waters. To address

this, three experiments of increasingly longer duration from 96 h to 144 h to 168 h were performed (Weddell Sea, South Georgia, South Sandwich), and with the inclusion of a higher target pCO2 of 2000 µatm. However, the magnitude of the response in both biological and DMS-related variables were found to be independent of the experimental duration. See also Richier et al. (2018). This is evidenced by the effect of CO_2 treatment on net growth rates. Net growth rates may be expected to be 2- to 3 –fold higher in the warmest compared to the coldest waters (Eppley, 1972), and indeed maximum Chl a-normalised photosynthesis rates were 2- to 3-fold higher in polar waters – but the response to experimentally-induced OA in polar waters remained insignificant despite the length of incubation being up to twice the duration of temperate experiments, and up to 4x longer, than the 48 h time point where strong responses were typically observed in temperate waters.

The following has been added at L210:

"The magnitude of response was not related to incubation times, and expected differences in net growth rates (2- to 3-fold higher in temperate compared to polar waters (Eppley 1972)) did not account for the differences in response magnitude despite the increased incubation time in polar waters (see Richier et al. (2018) for detailed discussion)".

2.5 *It should also be included into the discussion that the significant impacts that Hussherr et al (2017) observed were measured over a much larger pCO2 range (up to 3000 µatm).*

We have added to the text at L606:

"It should be noted that this response was seen over a range of pCO_2 from 500 - 3000 µatm, far beyond the levels used in the present study".

We do not feel this warrants any further discussion, as using a gradient of CO_2 treatment levels is an accepted and useful technique in ocean acidification experiments. It allows the use of regression statistics for assessment of possible CO_2 effects, and increases the chances of detecting any threshold level for CO_2/pH sensitive processes (Riebesell et al., 2013, Biogeosciences, 10, 1835–1847).

2.6 *One major problem with this dataset is that the experimental carbonate chemistry was not well controlled. For example, at the 1000µatm pCO2 level, T2 pCO2 levels vary between approx. 400 and 1000µatm (Table S2). Therefore, the data should be represented using the real carbonate chemistry instead of the assigned values. I understand that this implies replotting and reanalysing most of the data, but currently the levels that are tested against each other are actually not separated when it comes to carbonate chemistry.*

Although we acknowledge that our approach of allowing the carbonate system to vary as a result of biological activity necessitated that some drift occurred following initial imposed conditions, we would argue that our plotting/presentation of the data remains appropriate – and would not agree that this is a "major problem". In Figures 3, 4, 5, 6, 7 and 8 the legend clearly states the CO_2 values shown are "nominal", meaning they are representative of the initial target CO_2 treatments used for each experiment. This is simpler and clearer than showing a complicated range of values for each individual plot and experiment. However, we do concede that we could have presented

the actual treatment levels somewhere in the original submission, and we have now done so, with the addition of a table to the supplementary information (see below).

For the NW European shelf cruise, a comprehensive comparison of the accuracy and precision of the carbonate chemistry manipulation method, as well as an analysis of 'actual' vs 'target' *p*CO_2 values and the variability in the former over the experimental duration has already been presented in Figure 3, Richier et al. (2014), demonstrating that the achieved pCO_2 levels were well matched to target values at T_0 for E01 – E05, whilst acknowledging that differences in pCO_2 between target and initial values were more pronounced in the higher-pCO_2 treatments, a reflection of the lower buffer capacity of the carbonate system at higher pCO_2.

We have added the following to the methods section (L181 onwards):

"Full details of the carbonate chemistry manipulations can be found in Richier et al. (2014) and Richier et al. (2018). Broadly, achieved pCO_2 levels were well-matched to target values at T_0, although differences in pCO_2 between target and initial values were greater in the higher pCO_2 treatments, due to lowered carbonate system buffer capacity at higher pCO_2. For all 18 experiments, actual attained pCO_2 values were on average around 89% ± 12% (± 1 SD) of target values. The attained pCO_2 values are presented in Table S1 on the Supplementary Information. For simplicity, experimental data is presented against its target ('nominal') pCO_2 treatment throughout the paper".

And we have added this table to the Supplementary Information:

Table S1. Summary of *p*CO_2 (µatm) and pH_T (total scale) measured immediately following carbonate chemistry manipulation of experimental bioassays (Time point 0, T_0).

		pCO_2 (µatm) at T_0					pH_T at T_0				
Cruise ID	**Expt ID**	**ambient**	**550 (nominal)**	**750 (nominal)**	**1000 (nominal)**	**2000 (nominal)**	**ambient**	**550 (nominal)**	**750 (nominal)**	**1000 (nominal)**	**2000 (nominal)**
D366	E01	342.3	564.1	746.4	969.6		8.1	7.9	7.8	7.7	
	E02	n.d.	533.4	n.d.	862.7		n.d.	7.9	n.d.	7.8	
	E02b	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	
	E03	345.4	531.2	673.9	877.8		8.1	7.9	7.9	7.8	
	E04	395.4	533.4	691.4	936.6		8.1	7.9	7.8	7.7	
	E04b	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	
	E05	374.7	528.9	730.5	917.5		8.1	7.9	7.8	7.7	
	E05b	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	
	E06	n.d.	n.d.	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	
JR271	NS	286.5	524.7	n.d.	620.1		8.2	7.9	n.d.	7.9	
	IB	280.4	434.3	583.3	673.1		8.2	8.0	7.9	7.9	
	GG	326.8	565.2	741.8	1012.2		8.1	7.9	7.8	7.7	
	GI	312.2	583.9	789.3	948.2		8.1	7.9	7.7	7.7	
	BS	310.6	535.1	649.1	683.6		8.1	7.9	7.9	7.8	
JR274	DP	287.0		598.2			8.2		7.9		
	WS	275.1		533.8			8.2		7.9		
	SG	342.6		n.d.	823.4	1410.4	8.1		n.d.	7.7	7.5
	SS	283.8		n.d.	773.2	1557.5	8.2		n.d.	7.8	7.5

For figure 6, 7 and 8, the data is plotted against the carbonate chemistry (*C_T/A_T*) of the sampled waters (i.e. measurements made before carbonate chemistry manipulation), not from the incubations, so again the data does not require replotting.

2.7 In conclusion, I get the impression that the authors really try to tell a story that does not fit their data. I think that the hypothesis (more variable carbonate chemistry causes organisms to be less

sensitive) presented here makes a lot of sense, but for various reasons the data set is not suited to prove or disprove it.

We hope that, given the changes we have now made to the manuscript and the clarification we have provided on all the reviewers points, alongside the related analysis within Richier et al. (2018), that the reviewer will now be satisfied that the dataset appropriately addresses the hypothesis posed.

Specific comments

2.8 Title and throughout: To my knowledge, the term "resilience" refers to the ability of a system to return to the initial state after disturbance. Therefore, I do not think that the experimental setup and the response pattern (or its absence) in your study allows for statements on resilience. I suggest to use "insensitivity", "resistance" or something along these lines instead.

L481: "resilience" replaced with "insensitivity"

L507: "resilience" replaced with "the ability to resist"

L589: now reads: "The results of our microcosm experiments suggest insensitivity of *de novo* DMSP production and net DMS production in the microbial communities of the polar open oceans to short term changes in carbonate chemistry".

2.9 L22-27: As you refer to the other studies conducted in the Arctic, you also need to include their results in your statement, or be more specific that you only refer to the presented dataset and not the polar evidence in general.

We have altered the text at L23-28 to take the reviewers comment into account, and emphasise we are specifically referring to the presented dataset:

"Based on our findings, we hypothesise that the differences in DMS response between temperate and polar waters reflect the natural variability in carbonate chemistry to which the respective communities of each region may already be adapted. This implies that future temperate oceans could be more sensitive to OA resulting in a change in DMS emissions to the atmosphere, whilst perhaps surprisingly DMS emissions from the polar oceans may remain relatively unchanged".

2.10 L24-31: In the discussion, you do not refer to "geographical" or "regional" differences but compare temperate vs. polar systems. I would try to be more consistent here.

L23 – 25 now reads: "Based on our findings, we hypothesise that the differences in DMS response between temperate and polar waters reflect the natural variability in carbonate chemistry to which the respective communities of each region may already be adapted".

At L32 we use "geographically distinct regions" and "regionally distinct" in reference to the temperate vs polar waters, which we believe is appropriate.

2.11 Introduction: The introduction is quite long, especially DMS(P) biogeochemistry is described in a lot of detail, even though most of this is not referred to in the discussion. I would suggest to

shorten it. If your discussion does not focus at all on biogeochemistry, do you really need all this detail here?

We disagree with the reviewer. It is important to set the scene, to convince the reader of the importance of DMS, and justify why we are interested in the response of DMS to OA, both in general biogeochemical terms, and specifically with regard to the polar regions of this study.

2.12 L92-95: This is correct, but one shouldn't forget that it is the coastal areas that are the most productive and therefore important ones. In my opinion you do not even have to somehow restrict the importance of these two previous studies, your study is a valuable contribution even though two other ones exist.

We have re-worded the sentence at L96-97 at the reviewer's recommendation:

"However, these two single studies provide limited information on the wider response of the open Arctic or Southern Oceans".

2.13 L118: Here and in a few other instances you refer to your incubations as being "identical", but in the methods you state that the day length was adapted to the respective in situ conditions. Therefore, I would not use the term "identical".

L20: "identical" has been replaced with "similar"

L120: "identical" changed to "near-identical"

L411: "identical" has been deleted

2.14 L119-120: I think the differences in nutrients and incubation temperatures play a big role in understanding the results, so they need to be shown in one of the tables. Referring to a paper under review is not sufficient for such important information. Generally, the authors should provide all relevant information (at least in the supplement) if the other manuscript is not publically available yet.

As indicated above, the paper of Richier et al. (2018) has now been accepted for publication.

In situ temperatures at the time of sample collection are already shown in Table 1. Incubation temperatures were maintained (±1°C) at the in situ value.

Methods text has been adjusted so now reads:

L190: "Bottles were incubated inside a custom-designed temperature- and light-controlled shipping container, set to match (±<1°C) the *in situ* water temperature at the time of water collection (shown in Table 1) (see Richier et al. 2018)".

The nutrients and incubation temperatures did not play a role in understanding the results. We refer to Richier et al. (2018) for more detailed discussion of this, and have added the following to the current manuscript:

L440: "Across all experiments, the response of net total community Chl *a* and net growth rates of small phytoplankton (<10 µm) scaled with pCO_2 treatment, and strongly correlated with in situ carbonate chemistry, whilst no relationships were found with any of the other wide range of initial physical, chemical or biological variables (Richier et al. 2018). Overall, the observed differences in regional response to carbonate chemistry manipulation could not be attributed to any other measured factor that varied between temperate and polar waters. These include ambient nutrient concentrations, which varied considerably but had no influence on the response, and initial community structure, which was not a significant predictor of the response (Richier et al. 2018)".

2.15 L122-125, L130: While I do agree that differences in environmental variability most likely have an impact on the adaptive capacity of communities, you cannot estimate this adaptive capacity in short-term incubation experiments that run for several days only.

See response 1.3 to reviewer #1. Text has been altered accordingly.

2.16 L229-231: I am wondering if it wouldn't make more sense to normalize DMSP concentrations to biomass? This is especially the case if you want to test for "stress-induced algal processes" (L135-136) rather than biomass-dependent effects.

We feel this is not necessary, as we present specific rates of DMSP synthesis. In vivo DMSP synthesis is closely associated with photosynthesis within the cell, so determination of the rate of this process gives an indication of the effects of stress-induced algal processes on DMSP production. This is a much more useful parameter than biomass-normalised DMSP standing stocks, as the DMSP pool is the net results of various and varying processes (see Stefels et al. 2009), with variable contributions to DMSP production by different groups of phytoplankton.

2.17 L252-259: I do not think that you can infer growth rates from the Chla measurements, given that there was probably strong photoacclimatory processes happening in response to the change in light fields (naturally varying to constantly high). You do not really need these rates for your story, so I suggest to omit this parameter all together, i.e. also from results and discussion.

At the reviewer's suggestion we have removed relative growth rates from the paper.

2.18 L278: The results from the Atlantic experiments are used a lot in the discussion, they should therefore also be included in the results (and methods), especially but not exclusively the previously unpublished ones.

We have now described the methods and results from the 6 previously unpublished experiments in temperate waters.

Some minor adjustments have been made to the methods text to account for the temperate experiments, but the reader is generally referred to the related studies for the full details (Hopkins and Archer 2014, Richier et al. 2014, Richier et al. 2018):

L151: "Additionally, four previously unpublished experiments from D366 are also included (E02b, E04b, E05b, E06) as well as two temperate experiments from JR271 (NS and IB) (see Table 1)".

L197: "For Southern Ocean and all temperate water stations, an 18:6 light: dark cycle was used".

L202: "Experiments were generally run for ≥4 days (15 out of 18 experiments), with initial sampling proceeded by two further time points. For three temperate experiments (E02b, E04b, E05b, see Table 1) a shorter 2 day incubation was performed, with a single sampling point at the end. For E06 (see Table 1) high time frequency sampling was performed (0, 1, 4, 14, 24, 48, 72, 96 h) although only the data at 48 h and 96 h is considered in this analysis".

Figure 2 now includes depth profile data from all 18 sampling stations, and the results text now includes full description of the data for all 18 stations:

L301: "At temperate sampling stations, sea surface temperatures ranged from 10.7°C for *Iceland Basin*, to 15.3°C for *Bay of Biscay*, with surface salinity in the range 34.1 – 35.2, with the exception of station E05b which had a relatively low salinity of 30.5 (Figure 2 and Table 1)".

L312: "Chl *a* concentrations in temperate waters ranged from 0.3 µg L^{-1} for two North Sea stations (*E05* and *North Sea*) up to 3.5 µg L^{-1} for *Irish Sea* (Figure 2 and Table 1). Chl a was also variable in polar waters, exceeding 4 µg L^{-1} at *South Sandwich* and 2 µg L^{-1} at *Greenland Ice-edge*, whilst the remaining stations ranged from 0.2 µg L^{-1} (*Weddell Sea*) to 1.5 µg L^{-1} (Figure 2)".

L318: "In temperate waters, maximum DMS concentrations were generally seen in near surface measurements, ranging from 1.0 nM for *E04* to 21.1 nM for *E06*, with rapidly decreasing concentrations with depth (Figure 2 G). DMSP also generally peaked in the near surface waters, ranging from 12.0 nM for E04 to 72.5 nM for *E06*, but the maximum overall DMSP concentration of 89.8 nM was observed at ~20 m for *E05b* (Figure 2 H). Surface DMS concentrations in polar waters were generally lower than temperate waters, ranging from 1 – 3 nmol L^{-1}, with the exception of *South Sandwich* where concentrations of ~12 nmol L^{-1} were observed (Figure 2 G)".

The DMS and DMSP results from the 6 previously unpublished temperate microcosm experiments are now shown in the Supplementary Information, in Table S4 (E02b, E04b, E05b, E06 from D366) and Figure S2 (*North Sea* and *Iceland Basin* from JR271), and described in brief in the results section:

L355: "Results from the previously unpublished experiments from temperate waters are in strong agreement with the five experiments presented in Hopkins and Archer (2014), with consistently decreased DMS concentrations and enhanced DMSP under elevated CO_2. The data is presented in the Supplementary Information, Table S4 and Figure S2, and included in the meta-analysis in section 4.1 of this paper".

Table S4. DMS and DMSPt response (mean ± SD, n = 3) to high CO_2 treatments during previously unpublished small-scale experiments from the NW European shelf cruise D366. For details of stations, see Table 1 in the main paper.

	0 h ambient	**48 h ambient**	**48 h 550 µatm**	**48 h 750 µatm**
DMS (nM)				
E02b	2.4 ± 0.3	2.1 ± 0.6		2.7 ± 0.6
E04b		6.4 ± 1.4		14.7 ± 8.1
E05b		3.3 ± 0.1		4.5 ± 0.6
E06	18.7 ± 0.5	18.1	24.2	25.2
DMSPt (nM)				
E02b		49.5 ± 2.0		26.4 ± 2.9
E04b		68.2 ± 10.3		36.8 ± 7.5
E05b		48.7 ± 11.2		37.4 ± 4.8
E06	76.7 ± 5.7	114.6	98.43	108.5

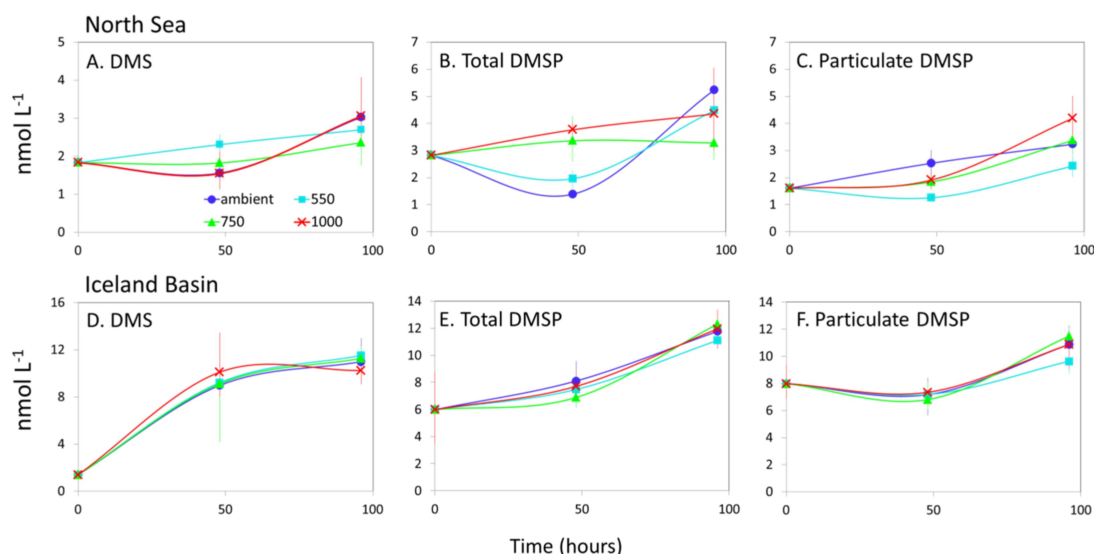


Figure S2. DMS, total DMSP and particulate DMSP concentrations (nmol L^{-1}) during experimental microcosms performed in temperate waters at stations *North Sea* and *Iceland Basin* from cruise JR271. Data shown is mean of triplicate incubations, and error bars show standard error on the mean. Locations of water collection for microcosms are given in Table 1.

2.19 L284-287: Methods are missing for the nanoflagellate and bacteria abundances data,

The following has been added to the methods section (L278):

"2.8 Community composition

Composition of small phytoplankton and bacteria community composition was assessed by flow cytometry. For details of methodology, see Richier et al. (2014)".

2.20 L291: Methods for irradiance measurements are missing

Text has been added to the methods at L162:

"At each station, pre-dawn vertical profiles of temperature, salinity, oxygen, fluorescence, turbidity and irradiance were used to choose and characterise the depth of experimental water collection".

2.21 L314: This is important information that really helps your line of argument, I would therefore put stronger emphasis on this in the discussion.

It is slightly unclear but does the reviewer refer to the statement: "Significant differences ceased to be detectable by the end of the incubations (168 h)"?

The section referred to describes the DMS response within the *South Sandwich* experiment which showed a significant CO_2 treatment effect after 96 h of incubation, which then ceased to be detectable by the end of the experiment (172 h). This single time point measurement out of the 7 polar experiments is an exception to the general overall trend of no DMS response – it was also accompanied by almost identical mean DMSP concentrations under all CO_2 treatments (Figure 4 G). Therefore it is difficult to gauge the significance of this result. Once this data is combined into the meta-analysis, it is clear this DMS response at *South Sandwich* is negligible compared to the magnitude of responses we saw in temperate waters (Figure 6 A).

2.22 L328-335: This comparison of standing stocks is highly dependent on the time of sampling. You therefore need to include information about and discussion on the timing of sampling relative to bloom phenology. I.e. if the Arctic and Southern Ocean samples were taken in (macro and/or micro) nutrient depleted waters after a bloom, can you really make such general statements on polar vs. temperate waters? Was the temperate sampling also conducted in similar phases of biomass dynamics? If not, you have a problematic bias towards low productivity in the polar samples that needs to be taken into account.

Coherent responses to OA occurred regardless of initial conditions, in terms of both the general biological response, and the DMS/P response. See Richier et al. (2018) for an assessment of the observed responses in comparison to a range of initial environmental. Importantly, differences in net phytoplankton growth rates as a function of pCO_2 treatment showed no correlation with any of the other wide range of initial physical, chemical and biological variables tested, including nutrient concentrations. Initial community structure was not an important factor in determining responses to pCO2 treatment (Richier et al. 2018). Thus although it is likely that we sampled waters that were at different stages of bloom phenology, this did not appear have an influence on our findings. Indeed, we note that a wide range of initial chlorophyll standing stocks was sampled on both high latitude cruises (Table 1). Overall, the most important factor influencing the biological, and DMS/P response to elevated pCO_2, was the carbonate chemistry characteristics of the sampled waters. Thus, our findings suggest that both the organism and ecosystem level response to OA is related to variability in the mean state of the carbonate chemistry system, alongside the associated natural range of variability in carbonate chemistry experienced by organisms (Flynn et al. 2012; Richier et al. 2018). Both these factors are likely linked to regional variability in the buffering capacity of ocean waters.

The lower rates of DMSP synthesis in polar waters compared to temperate waters is not necessarily due to lower levels of productivity but rather 'slower metabolic processes' as we state in this section. We compare our results to 'non-bloom conditions' from the Archer et al. (2013) paper because although higher rates were observed during this study (10 – 15 nmol L^{-1} d^{-1}), they occurred following artificial addition of inorganic nutrients to the mesocosms, which is not comparable to open ocean rates measured during the OA microcosm experiments.

We addressed the issue of 'slower metabolic rates' in colder polar waters in response 1.7 to reviewer #1.

2.23 L340-342: This in a strong indication for the importance of other drivers (nutrients, species composition, ...). You need to show these and check whether there are significant effects here.

Whilst we agree it would be interesting to attempt to unravel what is driving any differences in DMSP production in polar waters, we feel that it is outside of the scope of this paper.

2.24 L360ff: I really like this way of presenting the data. You should, however, also show the same plot with pCO2 instead of TA/DIC for comparison because I do not agree with you that this ratio gives a full overview of the in situ carbonate chemistry.

We feel it would not be a useful exercise to replot all the data against pCO_2, based on single discrete measurements. The relevance of this value is unclear, as it can be so variable in space and time.

We use DIC/Alk as it is the simplest way of representing the buffer capacity of the sampled waters. We could also have plotted against the Revelle factor of the sampled waters, and the relationship would have looked almost identical, as the Revelle factor is indeed a function of DIC/Alk, and quantified the ocean's sensitivity to an increase in CO_2. Therefore we believe that DIC/Alk is the simplest and more appropriate way of visualising our data in terms of its geographical location.

2.25 L372 and throughout the entire manuscript: Report the time points in days or hours instead of T1, T2 etc. because this is not consistently the same time point as well as for better readability and consistency throughout the text.

Reporting the time points in hours throughout the manuscript would make the results text clunky and confusing to read, as there is some variability. Therefore, we will keep the T_1/T_2 notation, but refer to the times broadly and refer the reader to Table 1 which outlines all the specific sampling times.

Added at L201: "(T_1, $T_{2,}$ see Table 1 for specific times for each experiment)"..,

L410 now reads: "…was minimal at all sampling points…"

L413 now reads: "…particularly at T_1 (48 – 96 h)…"

Figure 7 legend text has been altered: "T_1 = 48 h, T2 = 96 h, except for *Weddell Sea* and *South Georgia* (72 h, 144 h)".

Figure 8 legend text has been altered: "T_1 = 48 h, T_2 = 96 h, except for *Weddell Sea* and *South Georgia* (72 h, 144 h) and *South Sandwich* (96 h, 168 h)".

2.26 L377-282: This strongly suggests that, due to temperature-driven differences in metabolic rates and their effects on how fast the communities can acclimate to changed conditions, the experiments emerge out of measurement noise at different times.

If the differences were driven by temperature, rates would be expected to be higher in warmer temperate waters and lower in cold polar waters – but this is not the case. Also see response 1.6 to reviewer 1.

To make our point more clearly, the text now reads (L413):

"*De novo* DMSP synthesis and DMSP production rates show a similar relationship with C_T/A_T (Fig. 7 A and B), with a significant suppression of DMSP production rates in temperate waters compared to polar waters (Fig. 7B, Kruskal-Wallis One Way ANOVA H = 8.711, df = 1, p = 0.003). Although a similar trend was seen for *de novo* DMSP synthesis, the difference between temperate and polar waters was not statistically significant (Fig. 7A)".

Therefore, this suppression of rates in temperate waters is likely related to the relative decreases in net growth (Chl a accumulations, phytoplankton cell counts, community biomass) seen in temperate waters (see also Richier et al. 2018).

2.27 Discussion: A discussion of stress vs. acclimated response is missing

The following text has been added to the discussion at L631:

"Our results imply that the phytoplankton communities of the temperate microcosms initially responded to the rapid increase in pCO_2 via a stress-induced response, resulting in large and significant increases in DMS concentrations occurring over the shortest timescales (2 days), with a lessening of the treatment effect with an increase in incubation time (Hopkins and Archer 2014). Within non-nutrient amended treatments such a reduction in response with time may also have been driven by nutrient exhaustion, which could have lead the system to a similar state across all CO_2 treatments, although we note that carbonate chemistry manipulation induced responses were also similar within nutrient amended treatments (Richier et al. 2014, 2018). The dominance of short response timescales in well-buffered temperate waters may also indicate rapid acclimation of the phytoplankton populations following the initial stress response, which forced the small-sized phytoplankton beyond their range of acclimative tolerance and lead to increased DMS (Richier et al. 2018, Hopkins and Archer 2014).

This supports the hypothesis that populations from higher latitude, less well-buffered waters, already possess a certain degree of physiological tolerance to variations in carbonate chemistry environment. Although initial community size structure was not a significant predictor of the response to high CO_2, it is possible that a combination of both community composition and the natural range in variability in carbonate chemistry – as a function of buffer capacity – may influence the DMS/P response to OA over a range of timescales (Richier et al. 2018)".

2.28 L399: Everything until here reads more like results than like a discussion section. Please consider rearranging.

The section the reviewer refers to describes the meta-analysis of all the data from the 3 cruises – we believe this can be considered suitable content for the discussion and have left it unchanged. It should be viewed as a synthesis rather than a simple description of results.

2.29 L410-412: The authors seem to imply that CO2 sensitivity is only occurring in form of negative effects, even though there are many studies that show beneficial effects of increased substrate availability for photosynthesis, which is particularly true for picoeukaryotes (e.g. Schulz et al. 2017). Please take this aspect into account.

The section the reviewer refers to does not imply this. Rather, here we provide an explanation for our observations.

2.30 L436-439: I do not agree that your data really shows this: Figure 9 indicates the Arctic Ocean carbonate chemistry to be actually more similar to the Atlantic than to the Southern Ocean.

We disagree. The data show that the variability in carbonate chemistry in the polar oceans is much larger than in temperate waters – as described in the text the reviewer refers to.

2.31 L444-448: Such a comparison only makes sense if the same geographical and temporal ranges, and phases of biomass cycle (pre-bloom/ bloom/post-bloom, before/after winter convection etc.) were covered in the different study areas. Please clarify if this was the case.

See response 1.12 to reviewer #1 with regard to accounting for the possible variability in pH over seasonal scales.

2.32 L451-455: In the Southern Ocean, several studies have shown strong OA-effects on species composition (e.g. Tortell et al. 2008, Feng et al. 2010, Hoppe et al. 2013, Trimborn et al. 2017). L455-457: Similarly, you are missing previous work done in the Arctic (Coello-Camba et al. 2014, Holding et al. 2015, Thoisen et al. 2015, Hoppe et al. 2017a,b) that need to be considered.

We have re-worded the suggested line so that it no longer implies that this is all the available data.

L512:"A number of previous studies in polar waters have reported similar findings". However, we believe it would over-complicate this part of the discussion, and disrupt the flow, if we were to bring in the other suggested references at this point in the paper.

L519: We have added in two recently published study which provides further substantiation for our hypothesis, "Subarctic phytoplankton populations demonstrated a high level of resilience to OA in short term experiments, suggesting a high level of physiological plasticity that was attributed to the prevailing strong gradients in pCO_2 levels experienced in the sample region (Hoppe et al. 2017). Furthermore, a recent study describing ten CO_2 manipulation experiments in Arctic waters found that primary production was largely insensitive to OA over a large range of light and temperature levels (Hoppe et al. 2018). This supports our hypothesis that, relative to temperate communities, polar microbial communities may have a high capacity to compensate for

environmental variability (Hoppe et al. 2018), and are thus already adapted to, and are able to tolerate, large variations in carbonate chemistry".

Therefore, we have made reference to these studies later in the paper at the end of section 4.4, where we already provide evidence that the DMS response is likely to be variable over temporal and spatial scales:

L611: "Furthermore, a number of other studies from both the Arctic e.g. (Coello-Camba et al. 2014; Holding et al. 2015; Thoisen et al. 2015) and the Southern Ocean e.g. (Tortell et al. 2008; Hoppe et al. 2013; Trimborn et al. 2017) suggest that polar phytoplankton communities can demonstrate sensitivity to OA, in contrast to our findings. This emphasises the need to gain a more detailed understanding of both the spatial and seasonal variability in the polar phytoplankton community and associated DMS response to changing ocean acidity".

2.33 L460: n=3 is not "highly" replicated

"Highly" has been omitted.

2.34 L469: Why are you comparing your data in detail with Archer et al. (2013) but not Hussherr et al. (2017)?

We use this section to highlight the differences between experimental approaches, as it is useful for the reader to understand why we might see such different results between microcosm experiments and mesocosm experiments. We have altered the text to make this point come across more clearly to the reader:

"Experimental data clearly provide useful information on the potential future DMS response to OA, but these data become most powerful when incorporated in Earth System Models (ESM) to facilitate predictions of future climate. To date, two modelling studies have used ESM to assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al. 2013; Schwinger et al. 2017), and both have used results from mesocosm experiments. However, the DMS responses to OA within our short term microcosm experiments contrast with the results of most previous mesocosm experiments, and of particular relevance to this study, an earlier Arctic mesocosm experiment (Archer et al. 2013). Whilst no response in DMS concentrations to OA was generally seen in the microcosm experiments discussed here, a significant decrease in DMS with increasing levels of CO_2 in the earlier mesocosm study was seen. Therefore, it is useful to consider how the differences in experimental design between microcosms and mesocosms may result in contrasting DMS responses to OA".

As Hussherr et al. also used a microcosm approach, we include a short comparison at the end of this section (L594 onwards) to emphasise that discrepancies can also occur even when using similar experimental techniques.

2.35 L475: I would rather refer to the most common not the maximum duration.

"maximum of…" has been omitted.

2.36 L482-488: Is this difference really due to different sensitivities, or differences in biological rates, that lead to the fact that small physiological changes are detectable at different time points?

It is unlikely that biological rates will vary significantly between mesocosms and microcosms, as each experimental system should be a reasonable representation of the natural system which was sampled. Although there is not total certainty that it is due to differences in sensitivities, this is a hypothesis we put forward to help explain the differences in response to OA that we observe between these experimental approaches.

2.37 L515-521: You first imply that the short duration of the experiments would render changes in species composition rather unlikely, but then you report one case where you indeed observed changes. I would say that this indicates that the timescales in general would have allowed for changes in composition also in the other experiments.

Text has been altered and now reads (L589): "We did not generally see any broad-scale CO_2-effects on community structure in polar waters. This can be demonstrated by a lack of significant differences in the mean ratio of >10 µm Chl *a* to total Chl *a* (*>10 µm : total*) between CO_2 treatments*,* implying there were no broad changes in community composition (Table 2). *South Sandwich* was an exception to this, where large and significant increases in the mean ratio of *>10 µm : total* were observed at 750 µatm and 2000 µatm CO_2 relative to ambient CO_2 (ANOVA, F = 207.144, p<0.001, df = 3), demonstrated at even the short timescale of the microcosm experiments, it is possible for some changes to community composition to occur".

2.38 L543-550: I agree that it is an interesting finding that coastal DMS production seems to be more sensitive to OA than that from the open ocean. This finding does, however, really hint against the proposed mechanisms of insensitivity, because coastal systems are a lot more variable in carbonate chemistry compared to the open ocean (e.g. Thoisen et al. 2015). Thus, the interpretation of and conclusions from the dataset have to be reassessed.

Given the reviewers comments on this issue, we believe that the comparison between 'coastal' and 'open ocean' waters complicates this part of our discussion, so we have removed mention of this comparison. We instead discuss the possibility that there is likely to be regional variability in the response of DMS to OA. The key point is that the DMS response to OA in polar regions is complex and likely to be influenced by a number of temporal and spatial factors. The main users of our data are climate modellers, and we wish to emphasise that when trying to model the future flux of DMS, it is important to take this variability into account. The section now reads (L623):

"Our findings contrast with two previous studies performed in Arctic waters (Archer et al. 2013, Hussherr et al. 2017) which showed significant decreases in DMS in response to OA. These discrepancies may be driven by differences in the sensitivity of microbial communities to changing carbonate chemistry between different areas, or by variability in the response to OA depending on the time of year, nutrient availability, and ambient levels of growth and productivity. This serves to highlight the complex spatial and temporal variability in DMS response to OA which warrants further investigation to improve model predictions".

2.39 Figures 3, 4, 5, 7, 8, S3: Given the lack of control in carbonate chemistry in many experiments (Table S2), this representation is misleading. The data needs to be presented accounted for the real carbonate chemistry in the incubations.

We have addressed this above in point 2.6.

Technical Corrections

2.40 L11: I suggest replacing "we increase" by "to increase"

Text changed accordingly.

2.41 L12: I suggest referring explicitly to climate change instead of environmental change. Otherwise, the step to OA is kind of abrupt.

Done.

2.42 L28: Do you really mean "region may vary in response to OA" or rather "region may vary in their response to OA"?

Text changed accordingly, now reads: "By demonstrating that DMS emissions from geographically distinct regions may vary in their response to OA,…"

2.43 L190: replace "made" by "taken"

Done.

2.44 L207: omit "all" as in the caption of figure 5 you state that these data are not available for two of the stations.

Text changed accordingly, now reads: "*De novo* DMSP synthesis and gross production rates were determined for all microcosm experiments, except *Barents Sea* and *South Sandwich*,…".

2.45 L237-238: According to the Journal style, it would be A_T and C_T for total alkalinity and total dissolved inorganic carbon, respectively

We have changed T_A to A_T and DIC to C_T throughout.

2.46 L372: Omit "identical" as irradiances and temperatures were not the same

Done.

2.47 L497-500: Something does not see correct in this sentence, please rephrase

This sentence has been rephrased (L571): "Moreover, the coastal Arctic mesocosms were enriched with nutrients after 10 days, affording relief from nutrient limitation and allowing differences between pCO_2 treatments to be exposed, including a strong DMS(P) response".

2.48 L532: Insert "low and" between "periods of" and "stable productivity"

Done.

2.49 L539: "is insensitive to OA during multiple short term microcosm" instead of "is resilient to OA during multiple, highly replicated short term microcosm"

Done.

2.50 L542: add additional references mentioned above

We have instead removed reference to Davidson et al. (2016) as this was incorrectly cited here, and only refer to the results from our own study (which was the intention).

2.51 L559: Replace "results from our study indicate" by a more honest "we hypothesise" or something similar.

Done.

2.52 Table 1: Add macro nutrient (at least NO3) levels and incubation temperatures (will be more variable than in situ). Also "Comment" should read "Reference". Shouldn't "Sample depth" read "Sampling depth"?

The temperate of the incubation container was maintained at the in situ sampling temperature (±<1°C) (see methods in Richier et al. 2014, Biogeosciences, doi:10.5194/bg-11-4733-2014). Methods text (L191) has been altered to confirm this:

"Bottles were incubated inside a custom-designed temperature- and light-controlled shipping container, set to match the *in situ* water temperature at the time of water collection (±<1°C, see Richier et al. 2018)".

Nitrate concentrations have been added to the Table as suggested. And other suggested changes have been made.

2.53 All Figures: Please indicate number of replicates and type of error estimate in the caption

Now included in figure captions for Figure 3 and Figure 4:

"Data shown is mean of triplicate incubations, and error bars show standard error on the mean".

2.54 Figure 2: Replace "µE m-2 s-1" by "µmol photons m-2 s-1" or "µmol quanta m-2 s-1" in figure and caption. Also, the panels are so close together that the top and bottom axis descriptions get messy, please move them apart a bit.

Done.

References

Archer, S. D., S. A. Kimmance, J. A. Stephens, F. E. Hopkins, R. G. J. Bellerby, K. G. Schulz, J. Piontek and A. Engel (2013). "Contrasting responses of DMS and DMSP to ocean acidification in Arctic waters." Biogeosciences **10**(3): 1893-1908.

Coello-Camba, A., S. Agustí, J. Holding, J. M. Arrieta and C. M. Duarte (2014). "Interactive effect of temperature and CO2 increase in Arctic phytoplankton." Frontiers in Marine Science **1**: 49.

Eppley, R. W. (1972). "Temperature and phytoplankton growth in the sea." Fish. bull **70**(4): 1063-1085.

Flynn, K. J., J. C. Blackford, M. E. Baird, J. A. Raven, D. R. Clark, J. Beardall, C. Brownlee, H. Fabian and G. L. Wheeler (2012). "Changes in pH at the exterior surface of plankton with ocean acidification." Nature Climate Change **2**(7): 510-513.

Hagens, M. and J. J. Middelburg (2016). "Attributing seasonal pH variability in surface ocean waters to governing factors." Geophysical Research Letters **43**(24): 12,528-512,537.

Holding, J. M., C. M. Duarte, M. Sanz-Martin, E. Mesa, J. M. Arrieta, M. Chierici, I. E. Hendriks, L. S. Garcia-Corral, A. Regaudie-de-Gioux, A. Delgado, M. Reigstad, P. Wassmann and S. Agusti (2015). "Temperature dependence of CO2-enhanced primary production in the European Arctic Ocean." Nature Clim. Change **advance online publication**.

Hoppe, C. J., N. Schuback, D. M. Semeniuk, M. T. Maldonado and B. Rost (2017). "Functional Redundancy Facilitates Resilience of Subarctic Phytoplankton Assemblages toward Ocean Acidification and High Irradiance." Frontiers in Marine Science **4**: 229.

Hoppe, C. J. M., C. S. Hassler, C. D. Payne, P. D. Tortell, B. Rost and S. Trimborn (2013). "Iron Limitation Modulates Ocean Acidification Effects on Southern Ocean Phytoplankton Communities." PLOS ONE **8**(11): e79890.

Hoppe, C. J. M., K. K. E. Wolf, N. Schuback, P. D. Tortell and B. Rost (2018). "Compensation of ocean acidification effects in Arctic phytoplankton assemblages." Nature Climate Change **8**(6): 529-533.

Kapsenberg, L., A. L. Kelley, E. C. Shaw, T. R. Martz and G. E. Hofmann (2015). "Near-shore Antarctic pH variability has implications for the design of ocean acidification experiments." Scientific Reports **5**: 9638.

Richier, S., E. P. Achterberg, M. P. Humphreys, A. J. Poulton, D. J. Suggett, T. Tyrrell and C. M. Moore (2018). "Geographical CO_2 sensitivity of phytoplankton correlates with ocean buffer capacity." Global Change Biology.

Schwinger, J., J. Tjiputra, N. Goris, K. D. Six, A. Kirkevåg, Ø. Seland, C. Heinze and T. Ilyina (2017). "Amplification of global warming through pH-dependence of DMS-production simulated with a fully coupled Earth system model (under review in Biogeosciences, doi: 10.5194/bg-2017-33)." Biogeosciences.

Six, K. D., S. Kloster, T. Ilyina, S. D. Archer, K. Zhang and E. Maier-Reimer (2013). "Global warming amplified by reduced sulphur fluxes as a result of ocean acidification." Nature Climate Change **3**(11): 975.

Stillman, J. H. and A. W. Paganini (2015). "Biochemical adaptation to ocean acidification." Journal of Experimental Biology **218**(12): 1946-1955.

Thoisen, C., K. Riisgaard, N. Lundholm, T. G. Nielsen and P. J. Hansen (2015). "Effect of acidification on an Arctic phytoplankton community from Disko Bay, West Greenland." Marine Ecology Progress Series **520**: 21-34.

Tortell, P. D., C. D. Payne, Y. Li, S. Trimborn, B. Rost, W. O. Smith, C. Riesselman, R. B. Dunbar, P. Sedwick and G. R. DiTullio (2008). "CO_2 sensitivity of Southern Ocean phytoplankton." Geophysical Research Letters **35**.

Trimborn, S., T. Brenneis, C. J. M. Hoppe, L. M. Laglera, L. Norman, J. Santos-Echeandía, C. Völkner, D. Wolf-Gladrow and C. S. Hassler (2017). "Iron sources alter the response of Southern Ocean phytoplankton to ocean acidification." Marine Ecology Progress Series **578**: 35-50.

Dimethylsulfide (DMS) production in polar oceans may be ~~resilient~~ insensitive to ocean acidification: a meta-analysis of 18 ~~short-term~~ microcosm experiments from temperate to polar waters.

Frances E. Hopkins[1], Philip D. Nightingale[1], John A. Stephens[1], C. Mark Moore[2], Sophie Richier[2], Gemma L. Cripps[2], Stephen D. Archer[3]

[1]Plymouth Marine Laboratory, Plymouth, PL1 3DH, U.K.

[2]Ocean and Earth Science, National Oceanography Centre, University of Southampton, Southampton, U.K.

[3]Bigelow Laboratory for Ocean Sciences, Maine, U.S.A.

Correspondence to: Frances E. Hopkins (fhop@pml.ac.uk)

Abstract. Emissions of dimethylsulfide (DMS) from the polar oceans play a key role in atmospheric processes and climate. Therefore, it is important ~~we~~ to increase our understanding of how DMS production in these regions may respond to ~~environmental~~ climate change. The polar oceans are particularly vulnerable to ocean acidification (OA). However, our understanding of the polar DMS response is limited to two studies conducted in Arctic waters, where in both cases DMS concentrations decreased with increasing acidity. Here, we report on our findings from seven summertime shipboard microcosm experiments undertaken in a variety of locations in the Arctic Ocean and Southern Ocean. These experiments reveal no significant effects of short term OA on the net production of DMS by planktonic communities. This is in contrast to ~~identical~~ experiments from temperate NW European shelf waters where surface ocean communities responded to OA with significant increases in dissolved DMS concentrations. A meta-analysis of the findings from both temperate and polar waters (n = 18 experiments) reveals clear regional differences in the DMS response to OA. Based on our findings, ~~W~~we ~~suggest~~ hypothesise that ~~these regional~~the differences in DMS response between temperate and polar waters reflect the natural variability in carbonate chemistry to which the respective communities of each region

Formatted

may already be adapted. This implies that ~~F~~future temperate oceans could be more sensitive to OA resulting in a change in DMS emissions to the atmosphere, whilst perhaps surprisingly DMS emissions from the polar oceans may remain relatively unchanged. By demonstrating that DMS emissions from geographically distinct regions may vary in their response to OA, our results may facilitate a better understanding of Earth's future climate. Our study suggests that the way in which processes that generate DMS respond to OA may be regionally distinct and this should be taken into account in predicting future DMS emissions and their influence on Earth's climate.

1 Introduction

The trace gas dimethylsulfide (DMS) is a key ingredient in a cocktail of gases that exchange between the ocean and atmosphere. Dissolved DMS is produced via the enzymatic breakdown of dimethylsulfoniopropionate (DMSP), a secondary algal metabolite implicated in a number of cellular roles, including the regulation of carbon and sulfur metabolism via an overflow mechanism (Stefels 2000) and protection against oxidative stress (Sunda et al. 2002). Oceanic DMS emissions amount to 17 - 34 Tg S y^{-1}, representing 80 - 90% of all marine biogenic S emissions, and up to 50% of global biogenic emissions (Lana et al. 2011). DMS and its oxidation products play vital roles in atmospheric chemistry and climate processes. These processes include aerosol formation pathways that influence the concentration of cloud condensation nuclei (CCN) with implications for Earth's albedo and climate (Charlson et al. 1987; Korhonen et al. 2008), and the atmospheric oxidation pathways of other key climate gases, including isoprene, ammonia and organohalogens (von Glasow and Crutzen 2004; Johnson and Bell 2008; Chen and Jang 2012). Thus, our ability to predict the climate into the future requires an understanding of how marine DMS production may respond to global change (Carpenter et al. 2012; Woodhouse et al. 2013).

The biologically-rich seas surrounding the Arctic pack ice are a strong source of DMS to the Arctic atmosphere (Levasseur 2013). A seasonal cycle in CCN numbers can be related to seasonality in the Arctic DMS flux (Chang et al. 2011). Indeed, observations confirm that DMS oxidation products promote the growth of particles to produce aerosols that may influence cloud processes and atmospheric albedo (Bigg and Leck 2001; Korhonen et al. 2008; Chang et al. 2011; Rempillo et al. 2011). Arctic new particle formation events and peaks in aerosol optical depth (AOD) occur during summertime clean air periods (when levels of anthropogenic black carbon diminish), and have been linked to chlorophyll *a* maxima in surface waters and the presence of ~~biogenic~~ aerosols formed from DMS oxidation products such as methanesulfonate (MSA). The atmospheric oxidation products of DMS - SO_2 and H_2SO_4 - contribute to both the growth of existing particles and new particle formation (NPF) in the Arctic atmosphere (Sharma et al. 2012; Leaitch et al. 2013; Gabric et al. 2014). Thus, the ongoing and projected rapid loss of seasonal Arctic sea ice may influence the Arctic radiation budget via changes to both the DMS flux and the associated formation and growth of cloud-influencing particles (Sharma et al. 2012).

During its short but highly productive summer season, the Southern Ocean is a hotspot of DMS flux to the atmosphere, influenced by the prevalence of intense blooms of DMSP-rich *Phaeocystis antarctica* (Schoemann et al. 2005) and the presence of persistent high winds particularly in regions north of the sub-Antarctic front (Jarníková and Tortell 2016). Around 3.4 Tg of sulfur is released to the atmosphere between December and February, a flux that represents ~15 % of global annual emissions of DMS (Jarníková and Tortell 2016). Elevated CCN numbers are seen in the most biologically active regions of the Southern Ocean, with a significant contribution from DMS-driven secondary aerosol formation processes (Korhonen et al. 2008; McCoy et al. 2015). DMS-derived aerosols from this region are estimated to contribute 6 to 10 W m^{-2} to reflected short wavelength radiation, similar to the influence of

77 anthropogenic aerosols in the polluted Northern Hemisphere (McCoy et al. 2015). Given this

78 important influence of polar DMS emissions on atmospheric processes and climate, it is vital

79 we increase our understanding of the influence of future ocean acidification on DMS

80 production.

81 The polar oceans are characterised by high dissolved inorganic carbon (~~*DIC*~~C_T)

82 concentrations and a low carbonate system buffering capacity, mainly due to the increased

83 solubility of CO_2 in cold waters (Sabine et al. 2004; Orr et al. 2005). This makes these

84 regions particularly susceptible to the impacts of ocean acidification (OA). For example,

85 extensive carbonate mineral undersaturation is expected to occur in Arctic waters within the

86 next 20 – 80 years (McNeil and Matear 2008; Steinacher et al. 2009). OA has already led to a

87 0.1 unit decrease in global surface ocean pH, with a further fall of ~0.4 units expected by the

88 end of the century (Orr et al. 2005). The greatest declines in pH are likely in the Arctic Ocean

89 with a predicted fall of 0.45 units by 2100 (Steinacher et al. 2009). OA is occurring at a rate

90 not seen on Earth for 300 Ma, and so the potential effects on marine organisms, communities

91 and ecosystems could be wide-ranging and severe ~~The potential effects of OA on marine~~

92 ~~organisms, communities and ecosystems could be wide-ranging and severe, due in part to the~~

93 ~~speed and extent of a change not seen on Earth for at least 300 Ma~~ (Raven et al. 2005;

94 Hönisch et al. 2012). Despite the imminent threat to polar ecosystems and the importance of

95 DMS emissions to atmospheric processes, our knowledge of the response of polar DMS

96 production to OA is limited to a single mesocosm experiment performed in a coastal fjord in

97 Svalbard (Archer et al. 2013; Riebesell et al. 2013) and one shipboard microcosm experiment

98 with seawater collected from Baffin Bay (Hussherr et al. 2017). Both studies reported

99 significant reductions in DMS concentrations with increasing levels of pCO_2 during seasonal

100 phytoplankton blooms. However, -these two single studies provide limited information on the

Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Formatted: Not Highlight
Field Code Changed
Comment [FH1]: A bit clunky?
Formatted: Not Highlight
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

~~may not be fully representative of the~~ wider response of the open Arctic or Southern Oceans ~~due to their coastal locations~~.

Mesocosm experiments are a critical tool for assessing OA effects on surface ocean communities. Initial studies focused on the growth and decline of blooms with (Engel et al. 2005; Kim et al. 2006; Engel et al. 2008; Schulz et al. 2008; Hopkins et al. 2010; Kim et al. 2010; Schulz et al. 2013; Webb et al. 2015), or without (Crawfurd et al. 2016; Webb et al. 2016) the addition of inorganic nutrients. The response of DMS to OA has been examined several times, predominantly at the same site in Norwegian coastal waters (Vogt et al. 2008; Hopkins et al. 2010; Avgoustidi et al. 2012; Webb et al. 2015). There have also been two studies in Korean coastal waters (Kim et al. 2010; Park et al. 2014), as well as the single mesocosm study in the coastal (sub) Arctic waters of Svalbard (Archer et al. 2013). Mesocosm enclosures, ranging in volume from ~11,000 – 50,000 L, allow the response of surface ocean communities to a range of CO_2 treatments to be monitored under near-natural light and temperature conditions over time scales (weeks - months) that allow a 'winners vs loser' dynamic to develop. The response of DMS cycling to elevated CO_2 is generally driven by changes to the microbial community structure (Engel et al. 2008; Hopkins et al. 2010; Archer et al. 2013; Brussaard et al. 2013). The size and construction of the mesocosms has limited their deployment to coastal/sheltered waters, resulting in minimal geographical coverage, and leaving large gaps in our understanding of the response of open ocean phytoplankton communities to OA.

Here, we adopt an alternative but complementary approach to explore the effects of OA on the cycling of DMS with the use of short-term shipboard microcosm experiments. We build on the previous temperate NW European shelf studies of Hopkins & Archer (2014) by extending our experimental approach to the Arctic and Southern Oceans. Vessel-based research enables multiple short term (days) near-identical incubations to be performed over

extensive spatial scales, that encompass natural gradients in carbonate chemistry, temperature and nutrients (Richier et al. 2014; Richier et al. 2018). This allows an assessment to be made of how a range of surface ocean communities, adapted to a variety of environmental conditions, respond to the same driver. The focus is then on the effect of short-term CO_2 exposure on physiological processes, as well as the extent of the variability in ~~adaptive capacity~~acclimation between communities. The capacity of organisms to acclimate to changing environmental conditions contributes to the resilience of key ecosystem functions, such as DMS production. ~~level of adaptive capacity within an ecosystem determines the level of resilience to changing environmental conditions~~. Therefore, do spatially-diverse communities respond differently to short term OA, and can this be explained by the range of environmental conditions to which each is presumably already adapted? The rapid CO_2 changes implemented in this study, and during mesocosm studies, are far from representative of the predicted rate of change to seawater chemistry over the coming decades. Nevertheless, our approach can provide insight into the physiological response and level of ~~acclimation~~sensitivity to future OA of a variety of polar surface ocean communities adapted to different in situ carbonate chemistry environments, ~~as well as their potential level of acclimationadaptive capacity to future OA when compared between environments that differ in carbonate chemistry~~ (Stillman and Paganini 2015), alongside the implications this may have for DMS production.

Communities of the NW European shelf consistently responded to acute OA with significant increases in net DMS production, likely a result of an increase in stress-induced algal processes (Hopkins and Archer 2014). Do polar phytoplankton communities, which are potentially adapted to contrasting biogeochemical environments, respond in the same way? By expanding our approach to encompass both polar oceans, we can assess regional contrasts in response. To this end, we combine our findings for temperate waters with those for the

Field Code Changed
Field Code Changed
Field Code Changed
Comment [FH2]: Shorten sentence?
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Formatted: Not Highlight
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

151 polar oceans into a meta-analysis to advance our understanding of the regional variability and
152 drivers in the DMS response to OA.

153 **2 Material and Methods**

154 **2.1 Sampling stations**

155 This study presents new data from two sets of field experiments carried out as a part of the
156 UK Ocean Acidification Research Programme (UKOA) aboard the RRS James Clark Ross in
157 the sub-Arctic and Arctic in June-July 2012 (JR271) and in the Southern Ocean in January-
158 February 2013 (JR274). Data are combined with the results from an earlier study on board the
159 RRS Discovery (D366) described in Hopkins & Archer (2014) performed in the temperate
160 waters of the NW European shelf. Additionally, four previously unpublished experiments
161 from D366 are also included (E02b, E04b, E05b, E06) as well as two temperate experiments
162 from JR271 (NS and IB) (see Table 1). In total, 18 incubations were performed; 11 in
163 temperate and sub-Arctic waters of the NW European shelf and North Atlantic, 3 in Arctic
164 waters and 4 in the Southern Ocean. Figure 1 shows the cruise tracks, surface concentrations
165 of DMS and total DMSP (DMSPt) at CTD sampling stations as well as the locations of
166 sampling for shipboard microcosms (See Table 1 for further details).

167 **2.2 Shipboard microcosm experiments**

168 The general design and implementation of the experimental microcosms for JR271 and
169 JR274 was essentially the same as for D366 and described in Richier et al. (2014), (2018) and
170 Hopkins & Archer (2014), but with the additional adoption of trace metal clean sampling and
171 incubation techniques in the low trace metal open ocean waters (see Richier et al. (2018)). At
172 each station, pre-dawn vertical profiles of temperature, salinity, oxygen, fluorescence,
173 turbidity and irradiance were used to choose and characterise the depth of experimental water
174 collection. ~~At each station w~~Subsequently, water was collected ~~pre-dawn~~ within the mixed

Field Code Changed

175 layer from three successive separate casts of a trace-metal clean titanium CTD rosette
176 comprising twenty-four 10 L Niskin bottles. Each cast was used to fill one of a triplicated set
177 of experimental bottles (locations and sample depths, Table 1). Bottles were sampled within a
178 class-100 filtered air environment within a trace metal clean container to avoid contamination
179 during the set up. The water was directly transferred into acid-cleaned 4.5 L polycarbonate
180 bottles using acid-cleaned silicon tubing, with no screening or filtration.

181 The carbonate chemistry within the experimental bottles was manipulated by addition of
182 equimolar HCl and $NaHCO_3^-$ (1 mol L^{-1}) to achieve a range of target CO_2 values (550, 750,
183 1000, 2000 µatm) (Gattuso et al. 2010). For the sub-Arctic/Arctic microcosms, additions
184 were used to attain three target CO_2 levels (550 µatm, 750 µatm and 1000 µatm). For
185 Southern Ocean experiments, two experiments (*Drake Passage* and *Weddell Sea*) underwent
186 combined CO_2 and Fe additions (ambient, Fe (2 nM), high CO_2 (750 µatm), Fe (2 nM) + high
187 CO_2 (750µatm) (only high CO_2 treatments will be examined here; no response to Fe was
188 detected in DMS or DMSP concentrations). Three CO_2 treatments (750 µatm, 1000 µatm,
189 2000 µatm) were tested in the last two experiments (*South Georgia* and *South Sandwich*).
190 Full details of the carbonate chemistry manipulations can be found in Richier et al. (2014)
191 and Richier et al. (2018). Broadly, achieved pCO_2 levels were well-matched to target values
192 at T_0, although differences in pCO_2 between target and initial values were greater in the
193 higher pCO_2 treatments, due to lowered carbonate system buffer capacity at higher pCO_2. For
194 all 18 experiments, actual attained pCO_2 values were on average within 89% ± 12% (± 1 SD)
195 of target values. The attained pCO_2 values are presented in Table S1 on the Supplementary
196 Information. For simplicity, experimental data is presented against its target ('nominal')
197 pCO_2 treatment throughout the paper. After first ensuring the absence of bubbles or
198 headspace, the bottles were sealed with high density polyethylene (HDPE) lids with silicone/
199 polytetrafluoroethylene (PTFE) septa and placed in the incubation container. Bottles were

Field Code Changed
Field Code Changed
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript
Formatted: Subscript

200 incubated inside a custom-designed temperature- and light-controlled shipping container, set
201 to match (±<1°C) the *in situ* water temperature at the time of water collection (shown in
202 Table 1) (±<1°C, see Richier et al. 2018). A constant light level (100 µE m^{-2} s^{-1}) was
203 provided by daylight simulating LED panels (Powerpax, UK). The light period within the
204 microcosms was representative of *in situ* conditions. For the sub-Arctic/Arctic Ocean
205 stations, experimental bottles were subjected to continuous light representative of the 24 h
206 daylight of the Arctic summer. For Southern Ocean and all temperate water stations, an 18:6
207 light: dark cycle was used.. Each bottle belonged to a set of triplicates, and sacrificial
208 sampling of bottles was performed (see Table 1 for chosen time points). Use of three sets of
209 triplicates for each time point allowed for the sample requirements of the entire scientific
210 party (3 x 3 bottles, x 2 time points (T_1, T_2, see Table 1 for specific times for each
211 experiment), x 4 CO_2 treatments = 72 bottles in total). Experiments were generally run for ≥4
212 days (15 out of 18 experiments), with initial sampling proceeded by two further time points.
213 For three temperate experiments (E02b, E04b, E05b, see Table 1) a shorter 2 day incubation
214 was performed, with a single sampling point at the end. For E06 (see Table 1) high time
215 frequency sampling was performed (0, 1, 4, 14, 24, 48, 72, 96 h) although only the data at 48
216 h and 96 h is considered in this analysis. Incubation times were extended for Southern Ocean
217 stations *Weddell Sea*, *South Georgia* and *South Sandwich* (see Table 1) as minimal CO_2
218 response, attributed to slower microbial metabolism at low water temperatures, was observed
219 for Arctic stations and the first Southern Ocean station *Drake Passage* over 96 h. The
220 magnitude of response was not related to incubation times, and expected differences in net
221 growth rates (2- to 3-fold higher in temperate compared to polar waters (Eppley 1972)) did
222 not account for the differences in response magnitude despite the increased incubation time in
223 polar waters (see also Richier et al. (2018) for detailed discussion). Samples for carbonate

Field Code Changed

Field Code Changed

Field Code Changed

224 chemistry measurements were ~~made~~ taken first, followed by sampling for DMS, DMSP and
225 related parameters.

226 **2.3 Standing stocks of DMS and DMSP**

227 Methods for the determination of seawater concentrations of DMS and DMSP are identical to
228 those described in Hopkins & Archer (2014) and will therefore be described in brief here.
229 Seawater DMS concentrations were determined by cryogenic purge and trap, with gas
230 chromatography and pulsed flame photometric detection (Archer et al., 2013). Samples for
231 total DMSP concentrations were fixed by addition of 35 µl of 50 % H_2SO_4 to 7 mL of
232 seawater (Kiene and Slezak 2006), and analysed within 2 months of collection (Archer et al.
233 2013). Concentrations of DMSPp were determined at each time point by gravity filtering 7
234 ml of sample onto a 25 mm GF/F filter and preserving the filter in 7 ml of 35 mM H_2SO_4 in
235 MQ-water. DMSP concentrations were subsequently measured as DMS following alkaline
236 hydrolysis. DMS calibrations were performed using alkaline cold-hydrolysis (1 M NaOH) of
237 DMSP sequentially diluted three times in MilliQ water to give working standards in the range
238 0.03 – 3.3 ng S mL^{-1}. Five point calibrations were performed every 2 – 4 days throughout the
239 cruise.

240 **2.4 *De novo* DMSP synthesis**

241 *De novo* DMSP synthesis and gross production rates were determined for all microcosm
242 experiments, except *Barents Sea* and *South Sandwich*, at each experimental time point, using
243 methods based on the approach of Stefels et al. (2009) and described in detail in Archer et al.
244 (2013) and Hopkins and Archer (2014). Triplicate rate measurements were determined for
245 each CO_2 level. For each rate measurement three x 500 mL polycarbonate bottles were filled
246 by gently siphoning water from each replicate microcosm bottle. Trace amounts of
247 $NaH^{13}CO_3$, equivalent to ~6 % of *in situ* dissolved inorganic carbon (~~*DIC*~~C_T), were added to

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript

248 each 500 mL bottle. The bottles were incubated in the microcosm incubation container with
249 temperature and light levels as described earlier. Samples were taken at 0 h, then at two
250 further time points over a 6 - 9 h period. At each time point, 250 mL was gravity filtered in
251 the dark through a 47 mm GF/F filter, the filter gently folded and placed in a 20 mL serum
252 vial with 10 mL of Milli-Q and one NaOH pellet, and the vial was crimp-sealed. Samples
253 were stored at -20°C until analysis by proton transfer reaction-mass spectrometer (PTR-MS)
254 (Stefels et al. 2009).

255 The specific growth rate of DMSP (μDMSP) was calculated assuming exponential growth
256 from:

257
$$\mu_t(\Delta t^{-1}) = \alpha_k \text{ x AVG}\left[\ln\left(\frac{^{64}MP_{eq} - {}^{64}MP_{t-1}}{^{64}MP_{eq} - {}^{64}MP_{t}}\right), \ln\left(\frac{^{64}MP_{eq} - {}^{64}MP_{t}}{^{64}MP_{eq} - {}^{64}MP_{t+1}}\right)\right] \quad 1$$

258 (Stefels et al. 2009) where $^{64}MP_t$, $^{64}MP_{t-1}$, $^{64}MP_{t+1}$ are the proportion of 1 x ^{13}C labelled
259 DMSP relative to total DMSP at time t, at the preceding time point (t-1) and at the subsequent
260 time point (t+1), respectively. Values of ^{64}MP were calculated from the protonated masses of
261 DMS as: mass 64/(mass63+mass64+mass65), determined by PTR-MS. $^{64}MP_{eq}$ is the
262 theoretical equilibrium proportion of 1 x ^{13}C based on a binomial distribution and the
263 proportion of tracer addition. An isotope fractionation factor α_k of 1.06 is included, based on
264 laboratory culture experiments using *Emiliania huxleyi* (Stefels et al. 2009). Gross DMSP
265 production rates during the incubations (nmol L^{-1} h^{-1}) were calculated from μDMSP and the
266 initial particulate DMSP (DMSPp) concentration of the incubations (shown in Figure 4).

267 **2.5 Seawater carbonate chemistry analysis**

268 The techniques and methods used to determine both the *in situ* and experimental carbonate
269 chemistry parameters, and to manipulate seawater carbonate chemistry within the

microcosms, are described in Richier et al. (2014) and will be only given in brief here. Experimental T_0 measurements were taken directly from CTD bottles, and immediately measured for total alkalinity (A_T~~T_A~~) (Apollo SciTech AS-Alk2 Alkalinity Titrator ~~Ct analyser (AS-C3) with LI-COR 7000~~) and dissolved inorganic carbon (C_T~~DIC~~) (Apollo SciTech C_T analyser (AS-C3) with LICOR 7000)~~AS-Alk2 Alkalinity Titrator)~~. The CO2SYS programme (version 1.05) (Lewis and Wallace 1998) was used to calculate the remaining carbonate chemistry parameters including $p\mathrm{CO_2}$.

Measurements of ~~T_A~~-T_A and C_T~~DIC~~ were made from each bottle at each experimental time point and again used to calculate the corresponding values for $p\mathrm{CO_2}$ and $\mathrm{pH_T}$. The carbonate chemistry data for each ~~at~~ sampling time point~~T_1 and T_2 of~~for each experiment ~~and each CO_2 treatment level~~ are summarised in Supplementary Table S1, S2 and S3 ~~and Supplementary Table S2~~ (~~T_0 data~~Experimental starting conditions are given in Table 1).

2.6 Chlorophyll a (Chl *a*) determinations

Concentrations of Chl *a* were determined as described in Richier et al. (2014). Briefly, 100 mL aliquots of seawater from the incubation bottles were filtered through either 25 mm GF/F (Whatman, 0.7 µm pore size) or polycarbonate filters (Whatman, 10 µm pore size) to yield total and >10 µm size fractions, with the <10 µm fraction calculated by difference. Filters were extracted in 6 mL HPLC-grade acetone (90%) overnight in a dark refrigerator. Fluorescence was measured using a Turner Designs Trilogy fluorometer, which was regularly calibrated with dilutions of pure Chl *a* (Sigma, UK) in acetone (90%).

~~**2.7 Relative growth rate (RGR)**~~

Formatted: Font: Italic, Not Superscript/ Subscript
Formatted: Font: Italic
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript

291 Relative growth rate (RGR), an indicator of the level of net autotrophy within the

292 experimental microcosms, was calculated as the change in Chl *a* concentrations between the

293 first two experimental time points:

294 $$RGR = \frac{(ln(C1)) - (ln(C0))}{T1 - T0} \quad 2$$

295 Where C_0 and C_1 are Chl *a* concentration at experimental time points T_0 and T_1, and T is time

296 in days.

297 **2.8 Community composition**

298 **Composition of small phytoplankton community compostion was assessed by flow**

299 **cytometry. For details of methodology, see Richier et al. (2014).**

300 **2.8 9 Data handling and statistical analyses**

301 Permutational analysis of variance (PERMANOVA) was used to analyse the difference in

302 response of DMS and DMSP concentrations to OA, both between and within the two polar

303 cruises in this study. Both dependant variables were analysed separately using a nested

304 factorial design with three factors; (i) Cruise Location: Arctic and Southern Ocean, (ii)

305 Experiment location nested within Cruise location: E1 - E4/E5, (see Table 1 for station IDs)

306 and (iii) CO_2 level: 385, 550, 750, 1000 and 2000 µatm. Main effects and pairwise

307 comparisons of the different factors were analysed through unrestricted permutations of raw

308 data. If a low number of permutations were generated then the *p*-value was obtained through

309 random sampling of the asymptotic permutation distribution, using Monte Carlo tests.

310 One-way analysis of variance was used to identify differences in ratio of >10 µm Chl *a* to

311 total Chl *a* ($chl_{>10um}$: chl_{tot} , see Discussion). Initially, tests of normality were applied (p<0.05

312 = not normal), and if data failed to fit the assumptions of the test, linearity transformations of

Formatted: Not Highlight

Formatted: Font: Bold

Formatted: Font: Bold

Comment [FH3]: What does this refer to?

the data were performed (logarithmic or square root), and the ANOVA proceeded from this point. The results of ANOVA are given as follows: *F* = ratio of mean squares, *df* = degrees of freedom, *p* = level of confidence. For those data still failing to display normality following transformation, a rank-based Kruskal-Wallis test was applied (*H* = test statistic, *df* = degrees of freedom, *p* = level of confidence).

3 Results

3.1 Sampling stations

At temperate sampling stations, sea surface temperatures ranged from 10.7°C for *Iceland Basin*, to 15.3°C for *Bay of Biscay*, with surface salinity in the range 34.1 – 35.2, with the exception of station E05b which had a relatively low salinity of 30.5 (Figure 2 and Table 1). Seawater temperatures at the polar microcosm sampling stations ranged from -1.5°C at sea-ice influenced stations (*Greenland Ice-edge* and *Weddell Sea*) up to 6.5°C for *Barents Sea* (Fig. 2 A). Salinity values at all the Southern Ocean stations were <34, whilst they were ~35 at all the Arctic stations with the exception of *Greenland Ice-edge* which had the lowest salinity of 32.5 (Fig. 2 B). Phototrophic nanoflagellate abundances were variable, with >3 x 10^4 cells mL^{-1} at *Greenland Gyre*, 1.5 x 10^4 cells mL^{-1} at *Barents Sea* and <3 x 10^3 cells mL^{-1} for all other stations (Fig. 2 D). Total bacterial abundances ranged from 3 x 10^5 cells mL^{-1} at *Greenland Ice-edge* up to 3 x 10^6 cells mL^{-1} at *Barents Sea* (Fig. 2 E).

Chl *a* concentrations in temperate waters ranged from 0.3 µg L^{-1} for two North Sea stations (*E05* and *North Sea*) up to 3.5 µg L^{-1} for *Irish Sea* (Figure 2 and Table 1). Chl a was also ~~were similarly~~ variable in polar waters, exceeding 4 µg L^{-1} at *South Sandwich* and 2 µg L^{-1} at *Greenland Ice-edge*, whilst the remaining stations ranged from 0.2 µg L^{-1} (*Weddell Sea*) to 1.5 µg L^{-1} (Figure~~.~~ 2 ~~F~~).

Formatted: Font: Italic
Formatted: Font: Italic
Formatted: Superscript
Formatted: Font: Italic
Formatted: Font: Italic
Formatted: Font: Italic
Formatted: Font: Not Italic

336 The high Chl *a* concentrations at *South Sandwich* are reflected in low in-water irradiance
337 levels at this station (Fig. 2 C).

338 In temperate waters, maximum DMS concentrations were generally seen in near surface
339 measurements, ranging from 1.0 nM for *E04* to 21.1 nM for *E06*, with rapidly decreasing
340 concentrations with depth (Figure 2 G). DMSP also generally peaked in the near surface
341 waters, ranging from 12.0 nM for E04 to 72.5 nM for *E06*, but the maximum overall DMSP
342 concentration of 89.8 nM was observed at ~20 m for *E05b* (Figure 2 H). Surface DMS
343 concentrations in polar waters were generally lower than temperate waters, ranginged from 1
344 – 3 ~~nmol L~~$^{-1}$nM, with the exception of *South Sandwich* where concentrations of ~12 ~~nmol~~
345 ~~L~~$^{-1}$nM were observed (Figure. 2 G). DMSP generally ranged from 12 – 20 ~~nmol L~~$^{-}$nM^{1},
346 except *Barents Sea* where surface concentrations exceeded 60 ~~nmol L~~$^{-1}$nM (Figure. 2 H).

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Italic

Formatted: Font: Not Bold, Not Italic

347 **3.2 Response of DMS and DMSP to OA**

348 The temporal trend in DMS concentrations showed a similar pattern for the three Arctic
349 Ocean experiments. Initial concentrations of 1 – 2 nmol L^{-1} remained relatively constant over
350 the first 48 h and then showed small increases of 1 - 4 nmol L^{-1} over the incubation period
351 (Figure 3 A – C). Increased variability between triplicate incubations became apparent in all
352 three Arctic experiments by 96 h, but no significant effects of elevated CO_2 on DMS
353 concentrations were observed. Initial DMSP concentrations were more variable, from 6 nmol
354 L^{-1} at *Greenland Ice-edge* to 12 nmol L^{-1} at *Barents Sea*, and either decreased slightly (net
355 loss 1 – 2 nmol L^{-1} GG), or increased slightly (net increase ~4 nmol L^{-1} *Greenland Ice-edge*,
356 ~3 nmol L^{-1} *Barents Sea*) (Figure 4 A – C). DMSP concentrations were found to ~~increase~~
357 decrease significantly in response to elevated CO_2 after 48 h for *Barents Sea* (Fig. 4 C, t =
358 2.05, p = 0.025), whist no significant differences were seen after 96 h. ~~but n~~No other
359 significant responses in DMSP were identified.

The range of initial DMS concentrations was greater at Southern Ocean sampling stations compared to the Arctic, from 1 nmol L^{-1} at *Drake Passage* up to 13 nmol L^{-1} at *South Sandwich* (Figure 3 D – G). DMS concentrations showed little change over the course of 96 – 168 h incubations and no effect of elevated CO_2, with the exception of *South Sandwich* (Fig. 3 G). Here, concentrations decreased sharply after 96 h by between 3 and 11 nmol L^{-1}. Concentrations at 96 h were CO_2-treatment dependent, with significant decreases in DMS concentration occurring with increasing levels of CO_2 (PERMANOVA, $t = 2.61$, $p = 0.028$). Significant differences ceased to be detectable by the end of the incubations (168 h).

Initial DMSP concentrations were higher at the Southern Ocean stations than for Arctic stations, ranging from 13 nmol L^{-1} for *Weddell Sea* to 40 nmol L^{-1} for *South Sandwich* (Figure 4 D – G). Net increases in DMSP occurred throughout, except at South Georgia, and were on the order of between <10 nmol L^{-1} - >30 nmol L^{-1} over the course of the incubations. Concentrations were not generally pCO_2-treatment dependent with the exception of the final time point at *South Georgia* (144 h) when a ~~significant decrease in~~significantly lower DMSP with increasing CO_2 was observed (PERMANOVA, $t = -5.685$, $p<0.001$).

Results from the previously unpublished experiments from temperate waters are in strong agreement with the five experiments presented in Hopkins and Archer (2014), with consistently decreased DMS concentrations and enhanced DMSP under elevated CO_2. The data is presented in the Supplementary Information, Table S4 and Figure S2, and included in the meta-analysis in section 4.1 of this paper.

3.3 Response of de novo DMSP synthesis and production to OA

Rates of *de novo* DMSP synthesis (µDMSP) at initial time points (T_0) ranged from 0.13 d^{-1} (*Weddell Sea*, Fig. 5 G) to 0.23 d^{-1} (*Greenland Ice-edge*, Fig. 5 C), whilst DMSP production ranged from 0.4 nmol L^{-1} d^{-1} (*Greenland Gyre*, Fig. 5 B) to 2.27 nmol L^{-1} d^{-1} (*Drake Passage*,

384 Fig. 5 F). Maximum rates of μDMSP of 0.37 -0.38 d^{-1} were observed at *Greenland Ice-edge*
385 after 48 h of incubation in all CO_2 treatments (Fig. 5 C). The highest rates of DMSP
386 production were observed at *South Georgia* after 96 h of incubation, and ranged from 4.1 –
387 6.9 nmol L^{-1} d^{-1} across CO_2 treatments (Fig. 5 J). Rates of DMSP synthesis and production
388 were generally lower than those measured in temperate waters (Hopkins and Archer 2014)
389 (Initial rates: μDMSP 0.33 – 0.96 d^{-1}, 7.1 – 37.3 nmol L^{-1} d^{-1}), but were comparable to
390 measurements made during an Arctic mesocosm experiment (Archer et al. 2013) (0.1 – 0.25
391 d^{-1}, 3 – 5 nmol L^{-1} d^{-1} in non-bloom conditions). The lower rates in cold polar waters likely
392 reflect slower metabolic processes and are reflected by standing stock DMSP concentrations
393 which were also lower than in temperate waters (5 – 40 nmol L^{-1} polar, 8 – 60 nmol L^{-1}
394 temperate (Hopkins and Archer 2014)). No consistent evidence of CO_2 sensitivity was seen in
395 either DMSP synthesis or production, similar to findings for DMSP standing stocks. Some
396 notable but conflicting differences between CO_2 treatments were observed. There was a 36%
397 and 37% increase in μDMSP and DMSP production respectively at 750 μatm for the *Drake*
398 *Passage* after 96 h (Figure 5 E, F), and a 38% and 44% decrease in both at 750 μatm after
399 144 h for *Weddell Sea* (Figure 5 G, H). Nevertheless, no consistent and significant effects of
400 high CO_2 were observed for rates of *de novo* DMSP synthesis or DMSP production in polar
401 waters.

402 **4 Discussion**

403 **4.1 Regional differences in the response of DMS(P) to OA**

404 We combine our findings from the polar oceans with those from temperate waters into a
405 meta-analysis in order to assess the regional variability and drivers in the DMS(P) response to
406 OA. Figures 6 and 7 provide an overview of the results discussed so far in this current study,
407 together with the results from Hopkins & Archer (2014) as well as the results from 4

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

408 previously unpublished microcosm experiments from the NW European shelf cruise and a
409 further 2 temperate water microcosm experiments from the Arctic cruise (*North Sea* and
410 *Iceland Basin*, Table 1). This gives a total of 18 microcosm experiments, each with between 1
411 and 3 high CO_2 treatments.

412 Hopkins & Archer (2014) reported consistent and significant increases in DMS concentration
413 in response to elevated CO_2 that were accompanied by significant decreases in DMSPt
414 concentrations. Bacterially-mediated DMS processes appeared to be insensitive to OA, with
415 no detectable effects on dark rates of DMS consumption and gross production, and no
416 consistent response seen in bacterial abundance (Hopkins and Archer 2014). In general, there
417 were large short-term decreases in Chl *a* concentrations and phototrophic nanoflagellate
418 abundance in response to elevated CO_2 in these experiments (Richier et al. 2014).

419 The relative treatment effects ($[x]_{highCO2}/[x]_{ambientCO2}$) for DMS and DMSP (Figure 6), Chl *a*
420 and~~,~~ phototrophic nanoflagellate abundance ~~and relative growth rates~~ (Figure ~~7~~8) are plotted
421 against the ratio of T_C ~~DIC~~ to ~~*total alkalinity*~~ T_A (~~*DIC/Alk*~~ T_C/T_A) of the sampled waters, in
422 order to place our findings in context of the total experimental data set. The value of C_T/A_T
423 ~~*DIC/Alk*~~ ranges from 0.84 – 0.95 within the mixed layer, and increases towards high latitude
424 waters (Egleston et al. 2010). Thus, stations with C_T/A_T ~~DIC/Alk~~ above ~0.91 represent the
425 seven polar stations (right of red dashed line Fig. 6 and 7). The surface waters of the polar
426 oceans have a reduced buffering capacity due to higher CO_2 solubility in colder waters, and
427 so are less resistant to local variations in C_T ~~DIC~~ and A_T ~~Alk~~ (Sabine et al. 2004). Thus, the
428 relationship between experimental response and C_T/A_T ~~DIC/Alk~~ is a simple way of
429 demonstrating how the CO_2 sensitivity of different surface ocean communities relates to the
430 *in situ* carbonate chemistry. The effect of elevated CO_2 on DMS concentrations at polar
431 stations, relative to ambient controls, was minimal at ~~both T_1 and T_2~~ all sampling points, and
432 is in strong contrast to the results from ~~identical~~ experiments performed on the NW European

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

433 shelf. At temperate stations, DMSP displayed a clear negative treatment effect, whilst at polar
434 stations a positive effect was evident under high CO_2, and particularly at T_1 (48 – 96 h) (Fig.
435 6 C and D). *De novo* DMSP synthesis and DMSP production rates show a similar relationship
436 with C_T/A_T ~~DIC/Alk~~ (Fig. 7 A and B), with a significant suppression of DMSP production
437 rates in temperate waters compared to polar waters (Fig. 7B, Kruskal-Wallis One Way
438 ANOVA $H = 8.711$, $df = 1$, $p = 0.003$). Although a similar trend was seen for *de novo* DMSP
439 synthesis, the difference between temperate and polar waters was not statistically significant
440 (Fig. 7A). ~~tendency towards suppression of these rates in temperate waters at elevated CO_2~~
441 ~~and a tendency towards a positive effect in polar waters. However, the smaller number of~~
442 ~~data makes the relationships less definitive.~~ At T_1 (48 – 96 h, see Table 1), a statistically
443 significant difference in response was seen between temperate and polar waters for Chl *a*
444 (Kruskal-Wallis One Way ANOVA $H = 20.577$, $df = 1$, $p<0.001$), with ~~showed little~~minimal
445 response to elevated CO_2 at polar stations, and in general ~~whereas~~ a strong negative response
446 was seen in temperate waters (Fig. 8A). By T_2 (96 – 144 h, see Table 1), no significant
447 difference in response of Chl *a* between temperate and polar waters was detectable (Fig. 8B),
448 although ~~A~~a slight positive response in Chl *a* was seen at ~~most~~ some temperate stations ~~by T_2~~,
449 and polar stations showed a minimal response, with the exception of *Barents Sea* which saw
450 strongly enhanced Chl *a* at T_2 (96 h) ~~with generally little response at polar stations~~ (Fig. 8 B).

451 In general, phototrophic nanoflagellates responded to high CO_2 with large decreases in
452 abundance in temperate waters (Richier et al. 2014), and increases in abundance in polar
453 waters (Fig. 8 C and D), with some exceptions: *North Sea* and *South Sandwich* gave the
454 opposite response. The impacts had lessened by T_2 (96 – 168 h, see Table 1). In contrast,
455 bacterial abundance did not show the same regional differences in response to high CO_2 (see
456 Hopkins and Archer (2014) for temperate waters, and Figure S1, supplementary information,
457 for polar waters). Bacterial abundance in temperate waters gave variable and inconsistent

Formatted: Not Superscript/ Subscript

Formatted: Font: Italic

Formatted: Font: Italic, Subscript

Formatted: Font: Italic

Formatted: Font: Italic, Subscript

458 responses to high CO_2. For all Arctic stations, *Drake Passage* and *Weddell Sea*, no response
459 to high CO_2 was observed. For *South Georgia* and *South Sandwich*, bacterial abundance
460 increased at 1000 and 2000 µatm, with significant increases for *South Georgia* after 144 h of
461 incubation (ANOVA $F = 137.936$, $p<0.001$). Additionally, at Arctic stations *Greenland Gyre*
462 and *Greenland Ice-edge*, no overall effect of increased CO_2 on rates of DOC release, total
463 carbon fixation or POC : DOC was observed (Poulton et al. 2016).

Field Code Changed
Field Code Changed

464 Across all experiments, the response of net total community Chl *a* and net growth rates of
465 small phytoplankton (<10 µm) scaled with pCO_2 treatment, and strongly correlated with in
466 situ carbonate chemistry, whilst no relationships were found with any of the other wide range
467 of initial physical, chemical or biological variables (Richier et al. 2018). Overall, the
468 observed differences in regional response to carbonate chemistry manipulation could not be
469 attributed to any other measured factor that varied between temperate and polar waters. These
470 include ambient nutrient concentrations, which varied considerably but had no influence on
471 the response, and initial community structure, which was not a significant predictor of the
472 response (Richier et al. 2018).

473

474 The treatment effect on relative growth rate (RGR) (Fig. 8 E and F) at T_1 (48 – 96 h, see
475 Table 1) was minimal across all stations, with the exception of some outliers. Treatment
476 effects were more discernible by T_2 (96 – 168 h, Table 1), with a strong negative impact in
477 temperate waters, contrasting with a minimal to positive effect at polar stations. Additionally,
478 at Arctic stations *Greenland Gyre* and *Greenland Ice-edge*, no overall effect of increased CO_2
479 on rates of DOC release, total carbon fixation or POC : DOC was observed (Poulton et al.
480 2016).

Field Code Changed
Field Code Changed

481 In summary, the relative response in both DMS(P) and a range of biological parameters

482 (Richier et al. 2018) to CO_2 treatment in polar waters follows a distinctly different pattern to

483 experiments performed in temperate waters. In the following sections we explore the

484 possible drivers of the regional variability in response to OA.

485 **4.2 Influence of community cell-size composition on DMS response**

486 It has been proposed that variability in the concentrations of carbonate species (e.g. pCO_2,

487 HCO_3^-, CO_3^{2-}) experienced by phytoplankton is related to cell size, such that smaller-celled

488 taxa (<10 µm) with a reduced diffusive boundary layer are naturally exposed to relatively less

489 variability compared to larger cells (Flynn et al. 2012). Thus, short-term and rapid changes in

490 carbonate chemistry, such as the kind imposed during our microcosm experiments, may have

491 a disproportionate effect on the physiology and growth of smaller celled species. Larger cells

492 may be better able to cope with variability as normal cellular metabolism results in significant

493 cell surface changes in carbonate chemistry parameters (Richier et al. 2014). Indeed, the

494 marked response in DMS concentrations to short term OA in temperate waters has been

495 attributed to this enhanced sensitivity of small phytoplankton (Hopkins and Archer 2014).

496 Was the lack of DMS response to OA in polar waters therefore a result of the target

497 communities being dominated by larger-celled, less carbonate-sensitive species?

498 Size-fractionated Chl *a* measurements give an indication of the relative contribution of large

499 and small phytoplankton cells to the community. For experiments in temperate waters, the

500 mean ratio of >10 µm Chl *a* to total Chl *a* (hereafter *>10 µm : total*) of 0.32 ± 0.08 was lower

501 than the ratio for polar stations of 0.54 ± 0.13 (Table 2). Although the difference was not

502 statistically significant, this might imply a tendency towards communities dominated by

503 larger cells in the polar oceans, which may partially explain the apparent lack of DMS

504 response to elevated CO_2. However, this is not a consistent explanation for the observed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

505 responses. For example, the Arctic *Barents Sea* station had the lowest observed *>10 µm : total* of 0.04 ± 0.01, suggesting a community comprised almost entirely of <10 µm cells; yet the response to short term OA differed to the response seen in temperate waters. No significant CO_2 effects on DMS or DMSP concentrations or production rates were observed at this station, whilst total Chl *a* significantly increased under the highest CO_2 treatments after 96 h (PERMANOVA F = 33.239, P<0.001). Thus, our cell size theory does not hold for all polar waters, suggesting that regardless of the dominant cell size, polar communities are more resilient to OA. In the following section, we explore the causes of this apparent ~~resilience~~ insensitivity to OA in terms of the environmental conditions to which the communities have presumably adapted.

515 **4.3 Adaptation to a variable carbonate chemistry environment**

516 The variation in *in situ* surface ocean carbonate chemistry parameters for all three cruises (see Tynan et al. 2016 for details), is summarised in Figure 9. These data demonstrate both the latitudinal differences in surface ocean carbonate chemistry between temperate and polar waters, as well as the within-region variability which is controlled by the respective buffer capacities. Thus, a narrow range of values for all carbonate parameters was observed in the NW European shelf waters relative to the less well-buffered Arctic and Southern Ocean waters. The polar waters sampled during our study were characterised by pronounced gradients in carbonate chemistry over small spatial scales, such that surface ocean communities are more likely to have experienced fluctuations between high pH/$\Omega_{aragonite}$ and low pH/$\Omega_{aragonite}$ over short time scales (Tynan et al. 2016). For example, pH_T varied by only 0.15 units (8.20 - 8.05) in NW European shelf waters, compared to 0.35 units (8.05 - 7.7) in the Arctic, and 0.40 units (8.25 - 7.85) in the Southern Ocean. Our data represent only a snapshot (4 – 6 weeks) of a year, ~~so the annual variability in carbonate chemistry is likely to~~

Field Code Changed

Field Code Changed

529 ~~be much greater~~with a lack of information on the range in variability over seasonal cycles.

530 ~~Blackford and Gilbert (2007)~~For comparison with Arctic stations, Hagens and Middelburg

531 (2016) report a seasonal pH variability of up to 0.25 units from a single site in the open ocean

532 surface waters in the Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability

533 of 0.3 – 0.4 units in the McMurdo Sound, Antarctica. This implies that both polar open ocean

534 and coastal/sea ice locations experience equally large variations in carbonate chemistry over

535 seasonal cycles. In open ocean waters this is driven by enhanced drawdown of C_T~~DIC~~ and

536 CO_2 during the productive spring and summer months, countered by lower productivity and

537 strong mixing in the winter (Hagens and Middelburg 2016). In coastal and sea-ice affected

538 regions, seasonal pH variability may be enhanced further by tidal exchanges, and by dilution

539 of C_T/A_T~~DIC/TA~~ caused by sea-ice melt (Kapsenberg et al. 2015). Adaptation to such natural

540 variability may induce the ability to resist ~~resilience to~~ abrupt changes within the polar

541 biological community (Kapsenberg et al. 2015). This ~~resilience~~ is manifested here as

542 negligible impacts on rates of *de novo* DMSP synthesis and net DMS production. ~~The few~~A

543 number of ~~published~~previous studies in polar waters have reported similar findings.

544 Phytoplankton communities were able to tolerate a $p$$CO_2$ range of 84 – 643 µatm in ~12 d

545 minicosm experiments (650 L) in Antarctic coastal waters, with no effects on

546 nanophytoplankton abundance, and enhanced abundance of picophytoplankton and

547 prokaryotes (Davidson et al. 2016; Thomson et al. 2016). In experiments under the Arctic ice,

548 microbial communities demonstrated the capacity to respond either by selection or

549 physiological plasticity to elevated CO_2 during short term experiments (Monier et al. 2014).

550 This supports our hypothesis that~~Our findings support the notion that~~, relative to temperate

551 communities, polar microbial communities are already adapted to, and are able to tolerate,

552 large variations in carbonate chemistry. Thus by performing multiple, ~~highly~~ replicated

553 experiments over a broad geographic range, the findings of this study imply that the DMS

Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Field Code Changed
Field Code Changed
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Formatted: Not Highlight
Formatted: Not Highlight
Field Code Changed
Formatted: Not Highlight
Formatted: Not Highlight
Field Code Changed
Formatted: Not Highlight

554 response may be both a reflection of: (i) the level of sensitivity of the community to changes
555 in the mean state of carbonate chemistry, and (ii) the levels of regional variability in
556 carbonate chemistry experienced by different communities. This highlights the limitations
557 associated with simple extrapolation of results from a small number of geographically-limited
558 experiments e.g. Six et al. (2013). Such an approach lacks a mechanistic understanding that
559 would allow a model to capture the regional variability in response that is apparent from the
560 microcosms experiments presented here.

561 **4.4 Comparison to an Arctic mesocosm experiment**

562 Experimental data clearly provide useful information on the potential future DMS response to
563 OA, but these data become most powerful when incorporated in Earth System Models (ESM)
564 to facilitate predictions of future climate. To date, two modelling studies have used ESM to
565 assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al.
566 2013; Schwinger et al. 2017), and both have used results from mesocosm experiments.
567 However, ~~T~~the DMS responses to OA within our short term microcosm experiments contrast
568 with the results of most previous mesocosm experiments, and of particular relevance to this
569 study, an earlier Arctic mesocosm experiment (Archer et al. 2013). Whilst no response in
570 DMS concentrations to OA was generally seen in the microcosm experiments discussed here,
571 ~~a significant~~a significant decrease in DMS with increasing levels of CO_2 in the earlier
572 mesocosm study was ~~reported~~seen. Therefore, it is useful to consider how the differences in
573 experimental design between microcosms and mesocosms may result in contrasting DMS
574 responses to OA. ~~We now explore and consider the reasons behind these differences.~~

575 The short duration of the microcosm experiments (~~maximum of~~ 4 – 7 d) allows the
576 physiological (phenotypic) capacity of the community to changes in carbonate chemistry to
577 be assessed. In other words, how well is the community adapted to variable carbonate
578 chemistry and how does this influence its ability to acclimate to change? Although the

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

mesocosm experiment considered a longer time period (4 weeks), the first few days can be compared to the microcosms. No differences in DMS or DMSP concentrations were detected for the first week of the mesocosm experiment, implying a certain level of insensitivity of DMS production to the rapid changes in carbonate chemistry. In fact, when taking all previous mesocosm experiments into consideration, differences in DMS concentrations have consistently been undetectable during the first 5 – 10 days, implying there is a limited short-term physiological response by the in situ communities (Vogt et al. 2008; Hopkins et al. 2010; Kim et al. 2010; Avgoustidi et al. 2012; Park et al. 2014). This is in contrast to the strong response in the temperate microcosms from the NW European shelf (Hopkins and Archer 2014). However, all earlier mesocosm experiments have been performed in coastal waters, which like polar waters, can experience a large natural range in carbonate chemistry. In the case of coastal waters this is driven to a large extent by the influence of riverine discharge and biological activity (Fassbender et al. 2016). Thus coastal communities may also possess a higher level of adaptation to variable carbonate chemistry compared to the open ocean communities of the temperate microcosms ~~reported here~~ (Fassbender et al. 2016).

The later stages of mesocosm experiments address a different set of hypotheses, and are less comparable to the microcosms reported here. With time, an increase in number of generations leads to community structure changes and taxonomic shifts, driven by selection on the standing genetic variation in response to the altered conditions. Moreover, the coastal Arctic mesocosms were enriched with nutrients after 10 days. This resulting in relief from nutrient limitation which allowed differences between pCO_2 treatments to be exposed, including a strong DMS(P) response.~~Moreover, the coastal Arctic mesocosms were enriched with nutrients after 10 days, and the resultant relief from nutrient limitation allowed differences between pCO_2 treatments to be exposed, including a strong DMS(P) response~~ (Archer et al. 2013; Schulz et al. 2013). During this period of increased growth and productivity, CO_2

Field Code Changed

Comment [FH4]: Rephrase?

604 increases drove changes which reflected both the physiological and genetic potential within
605 the community, and resulted in taxonomic shifts. The resultant population structure was
606 changed, with an increase in abundance of dinoflagellates, particularly *Heterocapsa*
607 *rotundata*. Increases in DMSP concentrations and DMSP synthesis rates were attributed to
608 the population shift towards dinoflagellates. The drivers of the reduced DMS concentrations
609 were less clear, but may have been linked to reduced DMSP-lyase capacity within the
610 dominant phytoplankton, a reduction in bacterial DMSP lysis, or an increase in bacterial
611 DMS consumption rates (Archer et al. 2013). Again, this is comparable to all other
612 mesocosm experiments, wherein changes to DMS concentrations can be associated with CO_2-
613 driven shifts in community structure (Vogt et al. 2008; Hopkins et al. 2010; Kim et al. 2010;
614 Avgoustidi et al. 2012; Park et al. 2014; Webb et al. 2015). However, given the lack of
615 further experiments of a similar location, design and duration to the Arctic mesocosm, it is
616 unclear how representative the mesocosm result is of the general community-driven response
617 to OA in high latitude waters.

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Field Code Changed

Formatted: Font: (Default) +Body (Calibri), 11 pt

618 ~~As expected, given the shorter duration of the microcosms, w~~We did not generally see any
619 broad-scale CO_2-effects on community structure in polar waters. This can be demonstrated by
620 a lack of significant differences in the mean ratio of >10 µm Chl *a* to total Chl *a* (*>10 µm :*
621 *total*) between CO_2 treatments, implying there were no broad changes in community
622 composition (Table 2). *South Sandwich* was an exception to this, where large and significant
623 increases in the mean ratio of *>10 µm : total* were observed at 750 µatm and 2000 µatm CO_2
624 relative to ambient CO_2 (ANOVA, $F = 207.144$, $p<0.001$, $df = 3$), demonstrated at even the
625 short timescale of the microcosm experiments, it is possible for some changes to community
626 composition to occur. Interestingly, this was also the only polar station that exhibited any
627 significant effects on DMS after 96 h of incubation (Figure 3G). However, given the lack of
628 similar response at 1000 µatm, it remains equivocal whether this was driven by a CO_2-effect

629 or some other factor. The results of our microcosm experiments suggest ~~resilience~~
630 insensitivity ~~in~~of *de novo* DMSP production and net DMS production in the microbial
631 communities of the polar open oceans ~~in response~~ to short term changes in carbonate
632 chemistry. This may be driven by a high level of adaptation within the targeted
633 phytoplankton communities to naturally varying carbonate chemistry.

634 In contrast to our findings, a recent single 9 day microcosm experiment (Hussherr et al.,
635 2017) performed in Baffin Bay (Canadian Arctic) saw a linear 80% decrease in DMS
636 concentrations during spring bloom-like conditions. It should be noted that this response was
637 seen over a range of pCO_2 from 500 - 3000 µatm, far beyond the levels used in the present
638 study. -Nevertheless, ~~T~~this implies that polar DMS production may be sensitive to OA at
639 certain times of the year, such as during the highly productive spring bloom, but less sensitive
640 during periods of low and stable productivity, such as the summer months sampled during
641 this study. Furthermore, a number of other studies from both the Arctic e.g. (Coello-Camba et
642 al. 2014; Holding et al. 2015; Thoisen et al. 2015) and the Southern Ocean e.g. (Tortell et al.
643 2008; Hoppe et al. 2013; Trimborn et al. 2017) suggest that polar phytoplankton communities
644 can demonstrate sensitivity to OA, in contrast to our findings. This emphasises the need to
645 gain a more detailed understanding of both the spatial and seasonal variability in the polar
646 phytoplankton community and associated DMS response to changing ocean acidity.

647 **5 Conclusions**

648 We have shown that net DMS production by summertime polar open ocean microbial
649 communities is ~~resilient~~ insensitive to OA during multiple, highly replicated short term
650 microcosm experiments. We provide ~~further~~ evidence that, in contrast to temperate
651 communities (Hopkins and Archer 2014), the polar communities we sampled were relatively
652 insensitive to variations in carbonate chemistry (Richier et al. 2018), manifested here as a

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

minimal effect on net DMS production. Our findings contrast with two previous studies performed in ~~coastal~~ Arctic waters (Archer et al. 2013, Hussherr et al. 2017) which showed significant decreases in DMS in response to OA. These discrepancies may be driven by differences in the sensitivity of microbial communities to changing carbonate chemistry between ~~coastal and open ocean waters~~different areas, or by variability in the response to OA depending on the time of year, nutrient availability, and ambient levels of growth and productivity. This serves to highlight the complex spatial and temporal variability in DMS response to OA which warrants further investigation to improve model predictions.

Our results imply that the phytoplankton communities of the temperate microcosms initially responded to the rapid increase in pCO_2 via a stress-induced response, resulting in large and significant increases in DMS concentrations occurring over the shortest timescales (2 days), with a lessening of the treatment effect with an increase in incubation time (Hopkins and Archer 2014). This reduction in response with time may also have been driven by nutrient exhaustion, given the lack of nutrient enrichment to the microcosms, which could have lead the system to a similar state across all CO2 treatments (Richier et al. 2014, 2018). The dominance of short response timescales in well-buffered temperate waters may also indicate rapid acclimation of the phytoplankton populations following the initial stress response, which forced the small-sized phytoplankton beyond their range of acclimative tolerance and lead to increased DMS (Richier et al. 2018, Hopkins and Archer 2014).

This supports the hypothesis that populations from higher latitude, less well-buffered waters, already possess a certain degree of acclimative tolerance to variations in carbonate chemistry environment. Although initial community size structure was not a significant predictor of the response to high CO_2, it is possible that a combination of both community composition and the natural range in variability in carbonate chemistry – as a function of buffer capacity – may influence the DMS/P response to OA over a range of timescales (Richier et al. 2018).

Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold

Formatted: Line spacing: Double

678 Our findings should be considered in the context of timescales of change (experimental vs
679 real world OA) and the potential of microbial communities to adapt to a gradually changing
680 environment. Microcosm experiments focus on the physiological response of microbial
681 communities to short term OA. Mesocosm experiments consider a timescale that allows the
682 response to be driven by community composition shifts, but are not long enough in duration
683 to incorporate an adaptive response. Neither approach is likely to accurately simulate the
684 response to the gradual changes in surface ocean pH that will occur over the next 50 – 100
685 years, nor the resulting changes in microbial community structure and distribution. However,
686 ~~results from our study indicate~~we hypothesise that the DMS response to OA should be
687 considered not only in relation to experimental perturbations to carbonate chemistry, but also
688 in relation to the magnitude of background variability in carbonate chemistry experienced by
689 the DMS-producing organisms and communities. Our findings suggest a strong link between
690 the DMS response to OA and background regional variability in the carbonate chemistry.

691 Models suggest the climate may be sensitive to changes in the spatial distribution of DMS
692 emissions over global scales (Woodhouse et al. 2013). Such changes could be driven by both
693 physiological and adaptive responses to environmental change. Accepting the limitations of
694 experimental approaches, our findings suggest that net DMS production from polar oceans
695 may be resilient to OA in the context of its short term effects on microbial communities. The
696 oceans face a multitude of CO_2-driven changes in the coming decades, including OA,
697 warming, deoxygenation and loss of sea ice (Gattuso et al. 2015). Our study addresses only
698 one aspect of these future ocean stressors, but contributes to our understanding of how DMS
699 emissions from the polar oceans may alter, facilitating a better understanding of Earth's
700 future climate.

Field Code Changed
Field Code Changed
Field Code Changed
Field Code Changed

701 **Acknowledgements**

This work was funded under the UK Ocean Acidification thematic programme (UKOA) via the UK Natural Environment Research Council (NERC) grants to PD Nightingale and SD Archer (NE/H017259/1) and to T Tyrell, EP Achterberg and CM Moore (NE/H017348/1). The UK Department for Environment, Food and Rural Affairs (Defra) and the UK Department of Energy and Climate Change (DECC) also contributed to funding UKOA. The National Science Foundation, United States, provided additional support to SD Archer ((NSF OCE-1316133). Our work and transit in the coastal waters of Greenland, Iceland and Svalbard was granted thanks to permissions provided by the Danish, Icelandic and Norwegian diplomatic authorities. We thank the captains and crew of the RRS Discovery (cruise D366) and RRS James Clark Ross (cruises JR271 and JR274), and the technical staff of the National Marine Facilities and the British Antarctic Survey. We are grateful to Mariana Ribas-Ribas and Eithne Tynan for carbonate chemistry data, Elaine Mitchell and Clement Georges for flow cytometry data, and Mariana Ribas-Ribas and Rob Thomas (BODC) for data management.

References

Archer, S. D., S. A. Kimmance, J. A. Stephens, F. E. Hopkins, R. G. J. Bellerby, K. G. Schulz, J. Piontek and A. Engel (2013). "Contrasting responses of DMS and DMSP to ocean acidification in Arctic waters." Biogeosciences **10**(3): 1893-1908.

Avgoustidi, V., P. D. Nightingale, I. R. Joint, M. Steinke, S. M. Turner, F. E. Hopkins and P. S. Liss (2012). "Decreased marine dimethyl sulfide production under elevated CO2 levels in mesocosm and in vitro studies." Environmental Chemistry **9**(4): 399-404.

Bigg, E. K. and C. Leck (2001). "Properties of the aerosol over the central Arctic Ocean." Journal of Geophysical Research: Atmospheres **106**(D23): 32101-32109.

Blackford, J. C. and F. J. Gilbert (2007). "pH variability and CO_2 induced acidification in the North Sea." Journal of Marine Systems **64**(1-4): 229-241.

731 Brussaard, C. P. D., A. A. M. Noordeloos, H. Witte, M. C. J. Collenteur, K. Schulz, A.
732 Ludwig and U. Riebesell (2013). "Arctic microbial community dynamics influenced by
733 elevated CO2 levels." Biogeosciences **10**(2): 719-731.

734

735 Carpenter, L. J., S. D. Archer and R. Beale (2012). "Ocean-atmosphere trace gas exchange."
736 Chemical Society Reviews **41**(19): 6473-6506.

737

738 Chang, R. Y. W., S. J. Sjostedt, J. R. Pierce, T. N. Papakyriakou, M. G. Scarratt, S. Michaud,
739 M. Levasseur, W. R. Leaitch and J. P. Abbatt (2011). "Relating atmospheric and oceanic
740 DMS levels to particle nucleation events in the Canadian Arctic." Journal of Geophysical
741 Research: Atmospheres **116**(D17).

742

743 Charlson, R. J., J. E. Lovelock, M. O. Andreae and S. G. Warren (1987). "Oceanic
744 phytoplankton, atmospheric sulphur, cloud albedo and climate." Nature **326**: 655-661.

745

746 Chen, T. and M. Jang (2012). "Secondary organic aerosol formation from photooxidation of a
747 mixture of dimethyl sulfide and isoprene." Atmospheric Environment **46**: 271-278.

748

749 Coello-Camba, A., S. Agustí, J. Holding, J. M. Arrieta and C. M. Duarte (2014). "Interactive
750 effect of temperature and CO2 increase in Arctic phytoplankton." Frontiers in Marine Science
751 **1**: 49.

752

753 Crawfurd, K. J., C. P. D. Brussaard and U. Riebesell (2016). "Shifts in the microbial
754 community in the Baltic Sea with increasing CO2." Biogeosciences Discuss. **2016**: 1-51.

755

756 Davidson, A. T., J. McKinlay, K. Westwood, P. Thompson, R. van den Enden, M. de Salas,
757 S. Wright, R. Johnson and K. Berry (2016). "Enhanced CO 2 concentrations change the
758 structure of Antarctic marine microbial communities." Mar Ecol Prog Ser. doi **10**: 3354.

759

760 Egleston, E. S., C. L. Sabine and F. M. M. Morel (2010). "Revelle revisited: Buffer factors
761 that quantify the response of ocean chemistry to changes in DIC and alkalinity." Global
762 Biogeochemical Cycles **24**(1): n/a-n/a.

763

764 Engel, A., K. Schulz, U. Riebesell, R. Bellerby, B. Delille and M. Schartau (2008). "Effects
765 of CO_2 on particle size distribution and phytoplankton abundance during a mesocosm bloom
766 experiment (PeECE II)." Biogeosciences **5**: 509-521.

767

768 Engel, A., I. Zondervan, K. Aerts, L. Beaufort, A. Benthien, L. Chou, B. Delille, J.-P.
769 Gattuso, J. Harlay, C. Heeman, L. Hoffman, S. Jacquet, J. Nejstgaard, M.-D. Pizay, E.
770 Rochelle-Newall, U. Schneider, A. Terbrueggen and U. Riebesell (2005). "Testing the direct
771 effect of CO_2 concentrations on a bloom of the coccolithophorid *Emiliania huxleyi* in
772 mesocosm experiments." Limnology and Oceanography **50**(2): 493-507.

773
774 Eppley, R. W. (1972). "Temperature and phytoplankton growth in the sea." Fish. bull **70**(4):
775 1063-1085.

776
777 Fassbender, A. J., C. L. Sabine and K. M. Feifel (2016). "Consideration of coastal carbonate
778 chemistry in understanding biological calcification." Geophysical Research Letters **43**(9):
779 4467-4476.

780
781 Flynn, K. J., J. C. Blackford, M. E. Baird, J. A. Raven, D. R. Clark, J. Beardall, C. Brownlee,
782 H. Fabian and G. L. Wheeler (2012). "Changes in pH at the exterior surface of plankton with
783 ocean acidification." Nature Climate Change **2**(7): 510-513.

784
785 Gabric, A. J., B. Qu, P. A. Matrai, C. Murphy, H. Lu, D. R. Lin, F. Qian and M. Zhao (2014).
786 "Investigating the coupling between phytoplankton biomass, aerosol optical depth and sea-ice
787 cover in the Greenland Sea." Dynamics of Atmospheres and Oceans **66**(0): 94-109.

788
789 Gattuso, J.-P., K. Lee, B. Rost and K. Schulz (2010). Approaches and tools to manipulate the
790 carbonate chemistry. Guide to Best Practices for Ocean Acidification Research and Data
791 Reporting. U. Riebesell, V. J. Fabry, L. Hansson and J. P. Gattuso. Pulblications Office of the
792 European Union, Luxembourg**:** 263.

793
794 Gattuso, J.-P., A. Magnan, R. Bille, W. Cheung, E. Howes, F. Joos, D. Allemand, L. Bopp, S.
795 Cooley and C. Eakin (2015). "Contrasting futures for ocean and society from different
796 anthropogenic CO2 emissions scenarios." Science **349**(6243): aac4722.

797
798 Hagens, M. and J. J. Middelburg (2016). "Attributing seasonal pH variability in surface ocean
799 waters to governing factors." Geophysical Research Letters **43**(24): 12,528-512,537.

800
801 Holding, J. M., C. M. Duarte, M. Sanz-Martin, E. Mesa, J. M. Arrieta, M. Chierici, I. E.
802 Hendriks, L. S. Garcia-Corral, A. Regaudie-de-Gioux, A. Delgado, M. Reigstad, P.
803 Wassmann and S. Agusti (2015). "Temperature dependence of CO2-enhanced primary
804 production in the European Arctic Ocean." Nature Clim. Change **advance online**
805 **publication**.

806
807 Hönisch, B., A. Ridgwell, D. N. Schmidt, E. Thomas, S. J. Gibbs, A. Sluijs, R. Zeebe, L.
808 Kump, R. C. Martindale, S. E. Greene, W. Kiessling, J. Ries, J. C. Zachos, D. L. Royer, S.
809 Barker, T. M. Marchitto, R. Moyer, C. Pelejero, P. Ziveri, G. L. Foster and B. Williams
810 (2012). "The Geological Record of Ocean Acidification." Science **335**(6072): 1058-1063.

811
812 Hopkins, F. E. and S. D. Archer (2014). "Consistent increase in dimethyl sulfide (DMS) in
813 response to high CO2 in five shipboard bioassays from contrasting NW European waters."
814 Biogeosciences **11**(18): 4925-4940.

815

Hopkins, F. E., S. M. Turner, P. D. Nightingale, M. Steinke, D. Bakker and P. S. Liss (2010). "Ocean acidification and marine trace gas emissions." Proceedings of the National Academy of Sciences **107**(2): 760-765.

Hopkins, F. E., S. M. Turner, P. D. Nightingale, M. Steinke and P. S. Liss (2010). "Ocean acidification and marine biogenic trace gas production." Proceedings of the National Academy of Sciences **107**(2): 760-765.

Hoppe, C. J. M., C. S. Hassler, C. D. Payne, P. D. Tortell, B. Rost and S. Trimborn (2013). "Iron Limitation Modulates Ocean Acidification Effects on Southern Ocean Phytoplankton Communities." PLOS ONE **8**(11): e79890.

Hussherr, R., M. Levasseur, M. Lizotte, J.-É. Tremblay, J. Mol, T. Helmuth, M. Gosselin, M. Starr, L. A. Miller and T. Jarniková (2017). "Impact of ocean acidification on Arctic phytoplankton blooms and dimethyl sulfide concentration under simulated ice-free and under-ice conditions." Biogeosciences **14**(9): 2407.

Jarníková, T. and P. D. Tortell (2016). "Towards a revised climatology of summertime dimethylsulfide concentrations and sea–air fluxes in the Southern Ocean." Environmental Chemistry **13**(2): 364-378.

Johnson, M. T. and T. G. Bell (2008). "Coupling between dimethylsulfide emissions and the ocean-atmosphere exchange of ammonia." Environmental Chemistry **5**(4): 259-267.

Kapsenberg, L., A. L. Kelley, E. C. Shaw, T. R. Martz and G. E. Hofmann (2015). "Near-shore Antarctic pH variability has implications for the design of ocean acidification experiments." Scientific Reports **5**: 9638.

Kiene, R. P. and D. Slezak (2006). "Low dissolved DMSP concentrations in seawater revealed by small-volume gravity filtration and dialysis sampling " Limnology and Oceanography Methods **4**: 80-95.

Kim, J. M., K. Lee, K. Shin, J. H. Kang, H. W. Lee, M. Kim, P. G. Jang and M. C. Jang (2006). "The effect of seawater CO2 concentration on growth of a natural phytoplankton assemblage in a controlled mesocosm experiment." Limnology and Oceanography **51**(4): 1629-1636.

Kim, J. M., K. Lee, E. J. Yang, K. Shin, J. H. Noh, K. T. Park, B. Hyun, H. J. Jeong, J. H. Kim, K. Y. Kim, M. Kim, H. C. Kim, P. G. Jang and M. C. Jang (2010). "Enhanced Production of Oceanic Dimethylsulfide Resulting from CO2-Induced Grazing Activity in a High CO2 World." Environmental Science & Technology **44**(21): 8140-8143.

858 Korhonen, H., K. S. Carslaw, D. V. Spracklen, G. W. Mann and M. T. Woodhouse (2008).
859 "Influence of oceanic dimethyl sulfide emissions on cloud condensation nuclei concentrations
860 and seasonality over the remote Southern Hemisphere oceans: A global model study." Journal
861 of Geophysical Research-Atmospheres **113**(D15): 16.
862
863 Korhonen, H., K. S. Carslaw, D. V. Spracklen, D. A. Ridley and J. Ström (2008). "A global
864 model study of processes controlling aerosol size distributions in the Arctic spring and
865 summer." Journal of Geophysical Research **113**(D8): D08211.
866
867 Lana, A., T. G. Bell, R. Simó, S. M. Vallina, J. Ballabrera-Poy, A. J. Kettle, J. Dachs, L.
868 Bopp, E. S. Saltzman, J. Stefels, J. E. Johnson and P. S. Liss (2011). "An updated
869 climatology of surface dimethlysulfide concentrations and emission fluxes in the global
870 ocean." Global Biogeochem. Cycles **25**(1): GB1004.
871
872 Leaitch, W. R., S. Sharma, L. Huang, D. Toom-Sauntry, A. Chivulescu, A. M. Macdonald, K.
873 von Salzen, J. R. Pierce, A. K. Bertram and J. C. Schroder (2013). "Dimethyl sulfide control
874 of the clean summertime Arctic aerosol and cloud." Elementa: Science of the Anthropocene
875 **1**(1): 000017.
876
877 Levasseur, M. (2013). "Impact of Arctic meltdown on the microbial cycling of sulphur."
878 Nature Geoscience **6**(9): 691-700.
879
880 Lewis, E. and D. W. R. Wallace (1998). Program Developed for CO2 System Calculations.
881 Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S.
882 Department of Energy, Oak Ridge, Tennessee.
883
884 McCoy, D. T., S. M. Burrows, R. Wood, D. P. Grosvenor, S. M. Elliott, P.-L. Ma, P. J. Rasch
885 and D. L. Hartmann (2015). "Natural aerosols explain seasonal and spatial patterns of
886 Southern Ocean cloud albedo." Science Advances **1**(6).
887
888 McNeil, B. I. and R. J. Matear (2008). "Southern Ocean acidification: A tipping point at 450-
889 ppm atmospheric CO2." Proceedings of the National Academy of Sciences **105**(48): 18860-
890 18864.
891
892 Monier, A., H. S. Findlay, S. Charvet and C. Lovejoy (2014). "Late winter under ice pelagic
893 microbial communities in the high Arctic Ocean and the impact of short-term exposure to
894 elevated CO2 levels." Name: Frontiers in Microbiology **5**: 490.
895
896 Orr, J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N.
897 Gruber, A. Ishida and F. Joos (2005). "Anthropogenic ocean acidification over the twenty-
898 first century and its impact on calcifying organisms." Nature **437**(7059): 681-686.
899

900 Park, K.-T., K. Lee, K. Shin, E. J. Yang, B. Hyun, J.-M. Kim, J. H. Noh, M. Kim, B. Kong,
901 D. H. Choi, S.-J. Choi, P.-G. Jang and H. J. Jeong (2014). "Direct Linkage between Dimethyl
902 Sulfide Production and Microzooplankton Grazing, Resulting from Prey Composition
903 Change under High Partial Pressure of Carbon Dioxide Conditions." Environmental Science
904 & Technology **48**(9): 4750-4756.
905
906 Poulton, A. J., C. J. Daniels, M. Esposito, M. P. Humphreys, E. Mitchell, M. Ribas-Ribas, B.
907 C. Russell, M. C. Stinchcombe, E. Tynan and S. Richier (2016). "Production of dissolved
908 organic carbon by Arctic plankton communities: Responses to elevated carbon dioxide and
909 the availability of light and nutrients." Deep Sea Research Part II: Topical Studies in
910 Oceanography **127**: 60-74.
911
912 Raven, J., K. Caldeira, H. Elderfield, O. Hoegh-Guldberg, P. Liss, U. Riebesell, J. Shepherd,
913 C. Turley and A. Watson (2005). "Ocean acidification due to increasing atmospheric carbon
914 dioxide." The Royal Society **Policy Document 12/05, London**.
915
916 Rempillo, O., A. M. Seguin, A. L. Norman, M. Scarratt, S. Michaud, R. Chang, S. Sjostedt, J.
917 Abbatt, B. Else and T. Papakyriakou (2011). "Dimethyl sulfide air-sea fluxes and biogenic
918 sulfur as a source of new aerosols in the Arctic fall." Journal of Geophysical Research:
919 Atmospheres **116**(D17).
920
921 Richier, S., E. P. Achterberg, C. Dumousseaud, A. J. Poulton, D. J. Suggett, T. Tyrrell, M. V.
922 Zubkov and C. M. Moore (2014). "Phytoplankton responses and associated carbon cycling
923 during shipboard carbonate chemistry manipulation experiments conducted around Northwest
924 European shelf seas." Biogeosciences **11**(17): 4733-4752.
925
926 Richier, S., E. P. Achterberg, M. P. Humphreys, A. J. Poulton, D. J. Suggett, T. Tyrrell and
927 C. M. Moore (2018). "Geographical CO_2 sensitivity of phytoplankton correlates with ocean
928 buffer capacity." Global Change Biology.
929
930 Riebesell, U., J. P. Gattuso, T. F. Thingstad and J. J. Middelburg (2013). "Preface "Arctic
931 ocean acidification: pelagic ecosystem and biogeochemical responses during a mesocosm
932 study"." Biogeosciences **10**(8): 5619-5626.
933
934 Sabine, C. L., R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C.
935 S. Wong, D. W. R. Wallace, B. Tilbrook, F. J. Millero, T.-H. Peng, A. Kozyr, T. Ono and A.
936 F. Rios (2004). "The oceanic sink for anthropogenic CO_2." Science **305**: 367-371.
937
938 Schoemann, V., S. Becquevort, J. Stefels, V. Rousseau and C. Lancelot (2005). "Phaeocystis
939 blooms in the global ocean and their controlling mechanisms: a review." Journal of Sea
940 Research **53**(1): 43-66.
941
942 Schulz, K. G., R. G. J. Bellerby, C. P. D. Brussaard, J. Büdenbender, J. Czerny, A. Engel, M.
943 Fischer, S. Koch-Klavsen, S. A. Krug, S. Lischka, A. Ludwig, M. Meyerhöfer, G. Nondal, A.

944 Silyakova, A. Stuhr and U. Riebesell (2013). "Temporal biomass dynamics of an Arctic
945 plankton bloom in response to increasing levels of atmospheric carbon dioxide."
946 Biogeosciences **10**(1): 161-180.
947
948 Schulz, K. G., U. Riebesell, R. G. J. Bellerby, H. Biswas, M. Meyerhofer, M. N. Muller, J. K.
949 Egge, J. C. Nejstgaard, C. Neill, J. Wohlers and E. Zollner (2008). "Build-up and decline of
950 organic matter during PeECE III." Biogeosciences **5**: 707-718.
951
952 Schwinger, J., J. Tjiputra, N. Goris, K. D. Six, A. Kirkevåg, Ø. Seland, C. Heinze and T.
953 Ilyina (2017). "Amplification of global warming through pH-dependence of DMS-production
954 simulated with a fully coupled Earth system model (under review in Biogeosciences, doi:
955 10.5194/bg-2017-33)." Biogeosciences.
956
957 Sharma, S., E. Chan, M. Ishizawa, D. Toom-Sauntry, S. Gong, S. Li, D. Tarasick, W.
958 Leaitch, A. Norman and P. Quinn (2012). "Influence of transport and ocean ice extent on
959 biogenic aerosol sulfur in the Arctic atmosphere." Journal of Geophysical Research:
960 Atmospheres **117**(D12).
961
962 Six, K. D., S. Kloster, T. Ilyina, S. D. Archer, K. Zhang and E. Maier-Reimer (2013). "Global
963 warming amplified by reduced sulphur fluxes as a result of ocean acidification." Nature
964 Climate Change **3**(11): 975.
965
966 Stefels, J. (2000). "Physiological aspects of the production and conversion of DMSP in
967 marine algae and higher plants." Journal of Sea Research **43**: 183-197.
968
969 Steinacher, M., F. Joos, T. L. Frolicher, G. K. Plattner and S. C. Doney (2009). "Imminent
970 ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-
971 climate model." Biogeosciences **6**(4): 515-533.
972
973 Stillman, J. H. and A. W. Paganini (2015). "Biochemical adaptation to ocean acidification."
974 Journal of Experimental Biology **218**(12): 1946-1955.
975
976 Sunda, W., D. J. Kieber, R. P. Kiene and S. Huntsman (2002). "An antioxidant function for
977 DMSP and DMS in marine algae." Nature **418**: 317-320.
978
979 Thoisen, C., K. Riisgaard, N. Lundholm, T. G. Nielsen and P. J. Hansen (2015). "Effect of
980 acidification on an Arctic phytoplankton community from Disko Bay, West Greenland."
981 Marine Ecology Progress Series **520**: 21-34.
982
983 Thomson, P. G., A. T. Davidson and L. Maher (2016). "Increasing CO2 changes community
984 composition of pico- and nano-sized protists and prokaryotes at a coastal Antarctic site."
985 Marine Ecology Progress Series **554**: 51-69.

986
987 Tortell, P. D., C. D. Payne, Y. Li, S. Trimborn, B. Rost, W. O. Smith, C. Riesselman, R. B.
988 Dunbar, P. Sedwick and G. R. DiTullio (2008). "CO_2 sensitivity of Southern Ocean
989 phytoplankton." Geophysical Research Letters **35**.

990
991 Trimborn, S., T. Brenneis, C. J. M. Hoppe, L. M. Laglera, L. Norman, J. Santos-Echeandía,
992 C. Völkner, D. Wolf-Gladrow and C. S. Hassler (2017). "Iron sources alter the response of
993 Southern Ocean phytoplankton to ocean acidification." Marine Ecology Progress Series **578**:
994 35-50.

995
996 Tynan, E., J. S. Clarke, M. P. Humphreys, M. Ribas-Ribas, M. Esposito, V. M. C. Rérolle, C.
997 Schlosser, S. E. Thorpe, T. Tyrrell and E. P. Achterberg (2016). "Physical and
998 biogeochemical controls on the variability in surface pH and calcium carbonate saturation
999 states in the Atlantic sectors of the Arctic and Southern Oceans." Deep Sea Research Part II:
1000 Topical Studies in Oceanography.

1001
1002 Vogt, M., M. Steinke, S. Turner, A. Paulino, M. Meyerhöfer, U. Riebesell, C. LeQuéré and P.
1003 Liss (2008). "Dynamics of dimethylsulphoniopropionate and dimethylsulphide under
1004 different CO_2 concentrations during a mesocosm experiment." Biogeosciences **5**: 407-419.

1005
1006 von Glasow, R. and P. J. Crutzen (2004). "Model study of multiphase DMS oxidation with a
1007 focus on halogens." Atmos. Chem. Phys. **4**(3): 589-608.

1008
1009 Webb, A. L., E. Leedham-Elvidge, C. Hughes, F. E. Hopkins, G. Malin, L. T. Bach, K.
1010 Schulz, K. Crawfurd, C. P. D. Brussaard, A. Stuhr, U. Riebesell and P. S. Liss (2016). "Effect
1011 of ocean acidification and elevated fCO2 on trace gas production by a Baltic Sea summer
1012 phytoplankton community." Biogeosciences Discuss. **2016**: 1-37.

1013
1014 Webb, A. L., G. Malin, F. E. Hopkins, K. L. Ho, U. Riebesell, K. G. Schulz, A. Larsen and P.
1015 S. Liss (2015). "Ocean acidification has different effects on the production of dimethylsulfide
1016 and dimethylsulfoniopropionate measured in cultures of Emiliania huxleyi and a mesocosm
1017 study: a comparison of laboratory monocultures and community interactions." Environmental
1018 Chemistry: -.

1019
1020 Woodhouse, M. T., G. W. Mann, K. S. Carslaw and O. Boucher (2013). "Sensitivity of cloud
1021 condensation nuclei to regional changes in dimethyl-sulphide emissions." Atmos. Chem.
1022 Phys. **13**(5): 2723-2733.

1023

1024

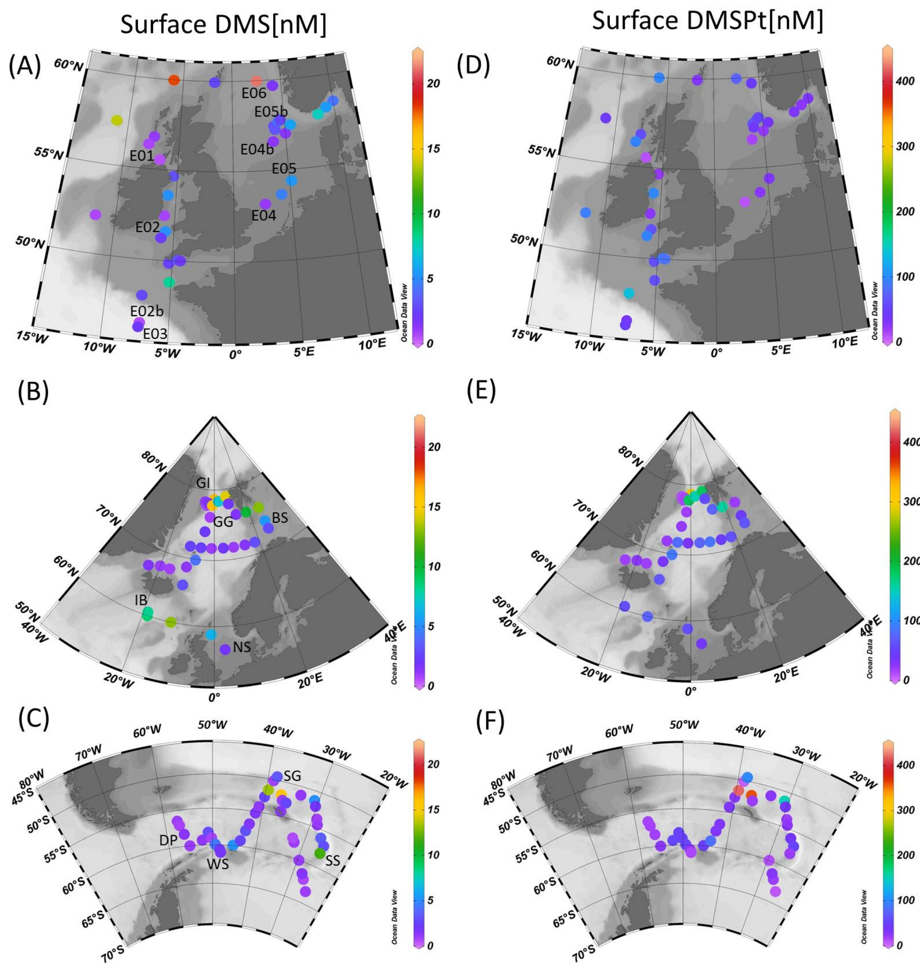
1025 Table 1. Summary of the station locations and characteristic of the water sampled for the 18 microcosm experiments performed in temperate,
1026 sub-polar and polar waters. All polar stations were sampled for JR271 and JR274, with the exception of NS and IB.

Cruise	Station ID	Location	Sampling location	Sampling date	Sampling depth (m)	SST (°C)	Salinity	Nitrate (uM)	Total Chl *a* (µg L^{-1})	$chl_{>10\ \mu m}$: chl_{total}	pCO_2 (µatm) T_0	pH (total) T_0	Experimental timepoints T_1, T_2 (hours)	Comment
D366	E01	Mingulay Reef	56°47.688N 7°24.300W	8 June 2011	6	11.3	34.8	1.1	3.3	no data	334.9	8.1	48, 96	*Hopkins & Archer (2014)*
	E02	Irish Sea	52°28.237N 5°54.052W	14 June 2011	5	11.8	34.4	0.3	3.5	0.80 ± 0.03	329.3	8.1	48, 96	*Hopkins & Archer (2014)*
	E02b	Bay of Biscay	46°29.794N 7°12.355W	19 June 2011	5	14.5	35.6	0.9	1.8	no data	340.3	8.1	48	*This study*
	E03	Bay of Biscay	46°12.137N 7°13.253W	21 June 2011	10	15.3	35.8	0.6	0.8	0.43 ± 0.03	323.9	8.1	48, 96	*Hopkins & Archer (2014)*
	E04	Southern North Sea	52°59.661N 2°29.841E	26 June 2011	5	14.6	34.1	0.9	1.3	0.19 ± 0.02	399.8	8.0	48, 96	*Hopkins & Archer (2014)*
	E04b	Mid North Sea	57°45.729N 4°35.434E	29 June 2011	5	13.2	34.8	No data	0.5	0.14 ± 0.003	327.3	8.1	48	*This study*
	E05	Mid North Sea	56°30.293N 3°39.506E	2 July 2011	12	14.0	35.0	0.2	0.3	0.23 ± 0.01	360.2	8.1	48, 96	*Hopkins & Archer (2014)*
	E05b	Atlantic Ocean	59°40.721N 4°07.633E	3 July 2011	4	13.4	30.7	0.3	0.7	0.12 ± 0.01	310.7	8.1	48	*This study*
	E06	Atlantic Ocean	59°59.011N 2°30.896E	3 July 2011	4	12.5	34.9	0.4	1.1	0.14 ± 0.01	287.1	8.2	48	*This study*
JR271	NS	Mid North Sea	56°15.59N 2°37.59E	3 June 2012	15	10.8	35.1	0.04	0.3	0.52 ± 0.05	300.5	8.2	48, 96	*This study*
	IB	Iceland Basin	60°35.39N 18°51.23W	8 June 2012	7	10.7	35.2	5.0	1.8	0.27 ± 0.02	309.7	8.1	48, 96	*This study*
	GG-AO	Greenland Gyre	76°10.52 N 2°32.96 W	13 June 2012	5	1.7	34.9	9.3	1.0	0.34 ± 0.001	289.3	8.2	48, 96	*This study*
	GI-AO	Greenland ice edge	78°21.15 N 3°39.85 W	18 June 2012	5	-1.6	32.6	4.2	2.7	0.78 ± 0.03	304.7	8.1	48, 96	*This study*
	BS-AO	Barents Sea	72°53.49 N 26°00.09 W	24 June 2012	5	6.6	35.0	5.4	1.3	0.04 ± 0.01	304.3	8.1	48, 96	*This study*
JR274	DP-SO	Drake Passage	58°22.00 S 56°15.12 W	13 Jan 2013	8	1.9	33.2	22.0	2.4	1.00 ± 0.06	279.3	8.2	48, 96	*This study*
	WS-SO	Weddell Sea	60°58.55 S 48°05.19 W	18 Jan 2013	6	-1.4	33.6	24.9	0.6	0.67 ± 0.06	510.5	7.9	72, 144	*This study*
	SG-SO	South Georgia	52°41.36 S 36°37.28 W	25 Jan 2013	5	2.2	33.9	24.1	0.7	0.35 ± 0.04	342.6	8.1	72, 144	*This study*
	SS-SO	South Sandwich	58°05.13 S 25°55.55 W	1 Feb 2013	7	0.5	33.7	18.5	4.6	0.57 ± 0.02	272.6	8.2	96, 168	*This study*

Formatted Table

1027 Table 2. Mean (± SD) ratio of >10µm Chl *a* to total Chl *a* ($chl_{>10\mu m}$:chl_{total}) for polar
1028 microcosm sampling stations. * indicates significant difference from the response to ambient
1029 CO_2.

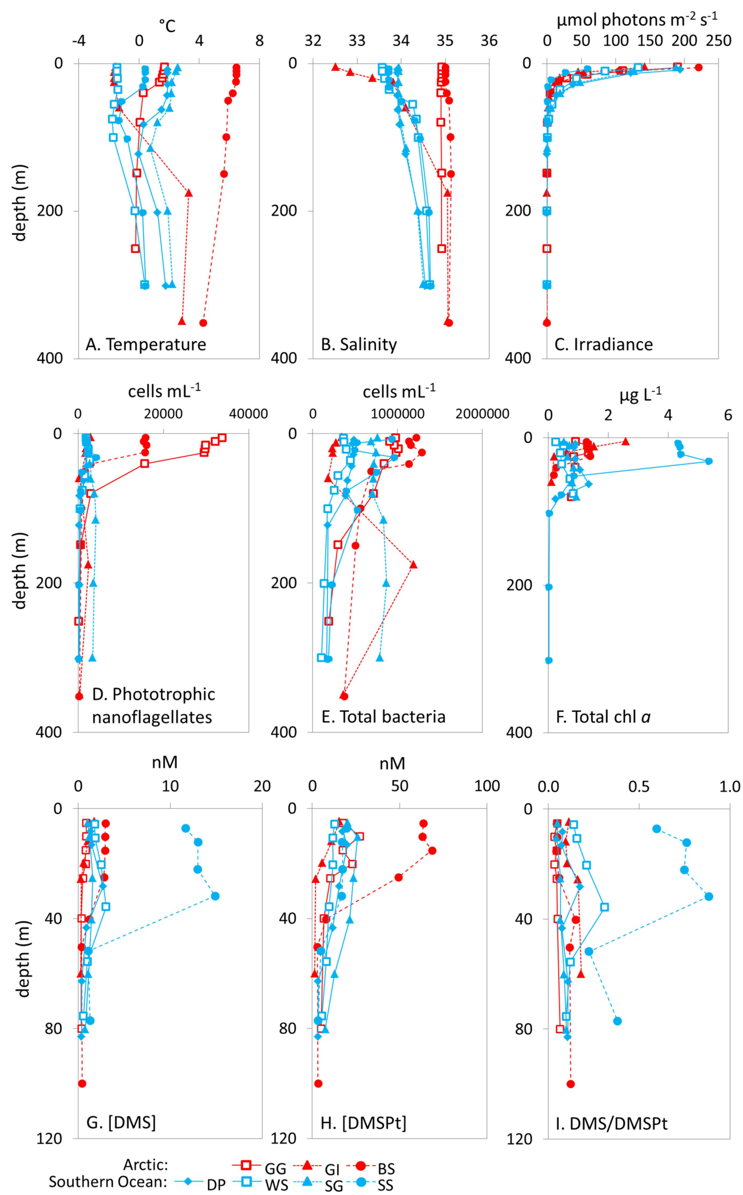
Station	Time	ambient	550 µatm	750 µatm	1000 µatm	2000 µatm
GG						
	48 h	0.3 ± 0.1	0.3 ± 0.03	0.4 ± 0.2	0.3 ± 0.1	N/A
	96 h	1.0 ± 0.02	0.9 ± 0.2	0.8 ± 0.1	0.7 ± 0.2	
GI						
	48 h	1.0 ± 0.1	1.0 ± 0.1	0.8 ± 0.1	1.0 ± 0.0	N/A
	96 h	1.0 ± 0.1	1.1 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	
BS						
	48 h	0.02 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	N/A
	96 h	0.04 ± 0.01	0.05 ± 0.04	0.05 ± 0.04	0.04 ± 0.04	
DP						
	48 h	1.0 ± 0.3	N/A	1.0 ± 0.1	N/A	N/A
	96 h	0.9 ± 0.1		1.0 ± 0.1		
WS						
	72 h	0.6 ± 0.1	N/A	0.7 ± 0.1	N/A	N/A
	144 h	0.7 ± 0.1		0.7 ± 0.1		
SG						
	72 h	0.3 ± 0.02	N/A	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.03
	144 h	0.5 ± 0.1		0.6 ± 0.04	0.5 ± 0.1	0.4 ± 0.03
SS						
	96 h	0.7 ± 0.04	N/A	1.5 ± 0.1*	0.7 ± 0.02	1.6 ± 0.1*
	168 h	0.9 ± 0.2		1.4 ± 0.02*	0.8 ± 0.004	1.4 ± 0.2*



1030

1031 Figure 1. Surface (<5 m) concentrations (nM) of DMS (A-C) and total DMSP (D-F) for
1032 cruises in the NW European shelf (D366) (A,D), the sub-Arctic and Arctic Ocean (JR271)
1033 (B,E) and the Southern Ocean (JR274) (C,F). Locations of sampling stations for microcosm
1034 experiments shown in letters/numbers. E01 – E05: see Hopkins & Archer 2014. NS = *North*
1035 *Sea*, IB = *Iceland Basin*, GI = *Greenland Ice-edge*, GG = *Greenland Gyre*, BS = *Barents Sea*,
1036 DP = *Drake Passage*, WS = *Weddell Sea*, SG = *South Georgia*, SS = *South Sandwich*.

1037



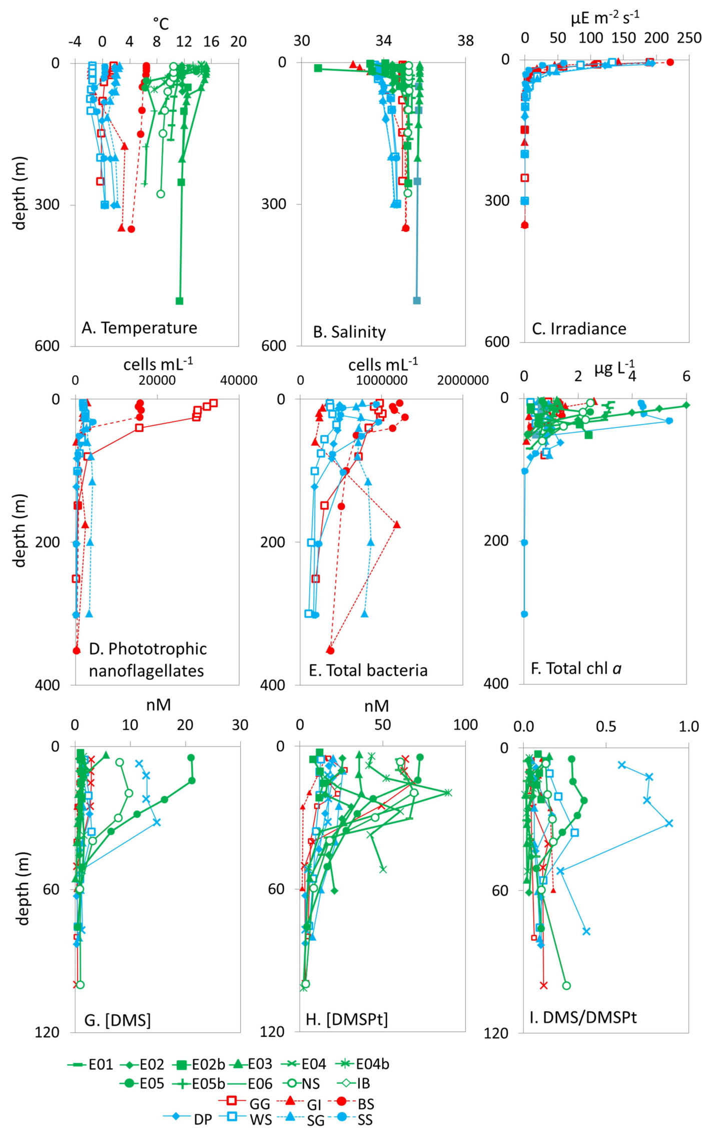
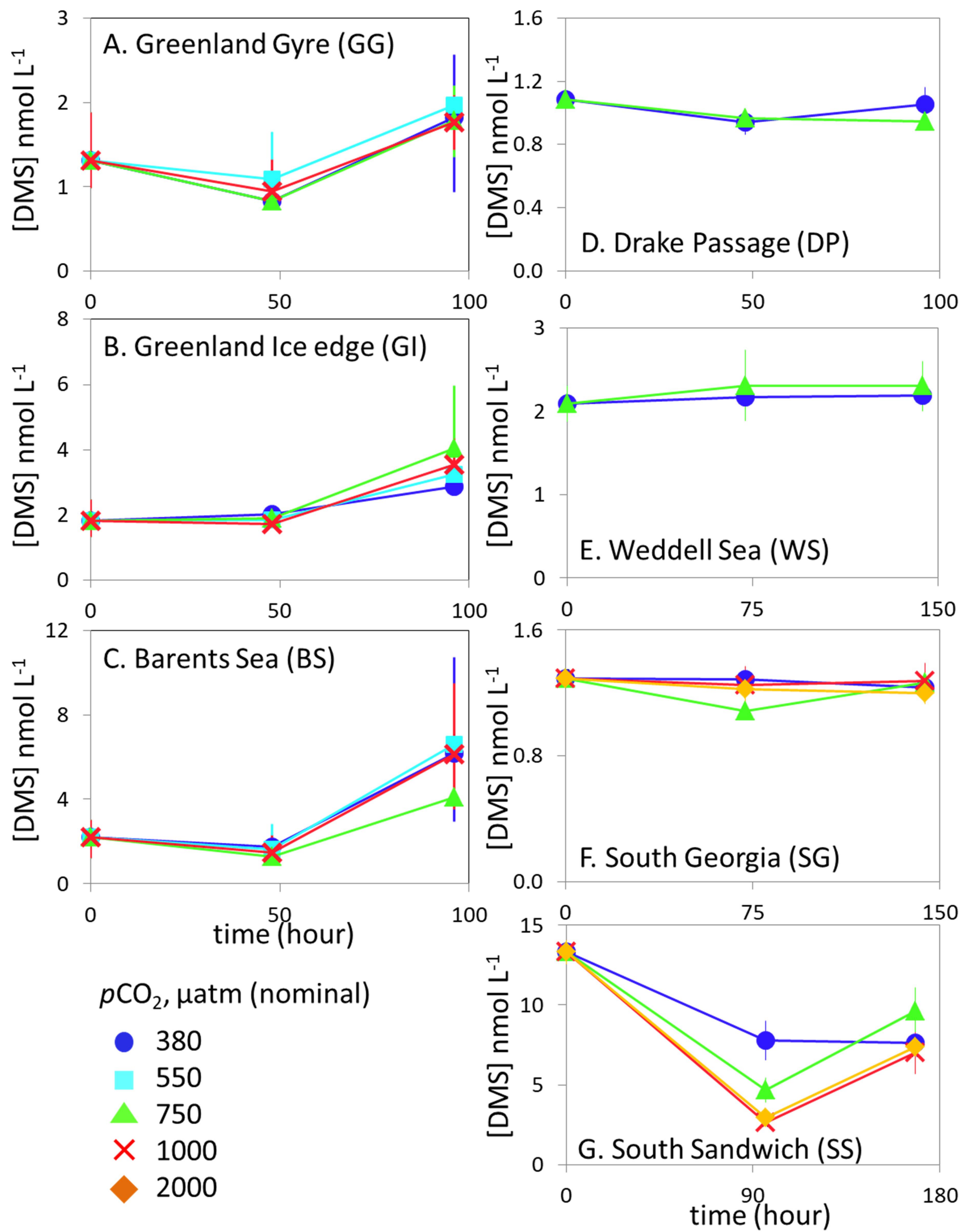


Figure 2. Depth profiles ~~at the seven polar~~for all 18 sampling ~~sampling~~ stations showing A. Temperature (°C), B. Salinity, C. Irradiance (μE m^{-2} s^{-1}), D. phototrophic nanoflagellate abundance (cells mL^{-1}), E. total bacteria abundance (cells mL^{-1}), F. total Chl a (μg L^{-1}), G. [DMS] (nM), H. total [DMSP] (nM) and I. DMS/DMSPt from CTD casts at sampling stations for microcosm experiments in temperate (green), Arctic (red) and Southern Ocean (blue) waters. See Table 1 for station details. Data for irrandiance, phototrophic nanoflagellates and total bacteria were not collected for temperate stations.~~GG = *Greenland Gyre*, GI = *Greenland Ice-edge*, BS = *Barents Sea*, DP = *Drake Passage*, WS = *Weddell Sea*, SG = *South Georgia*, SS = *South Sandwich*~~

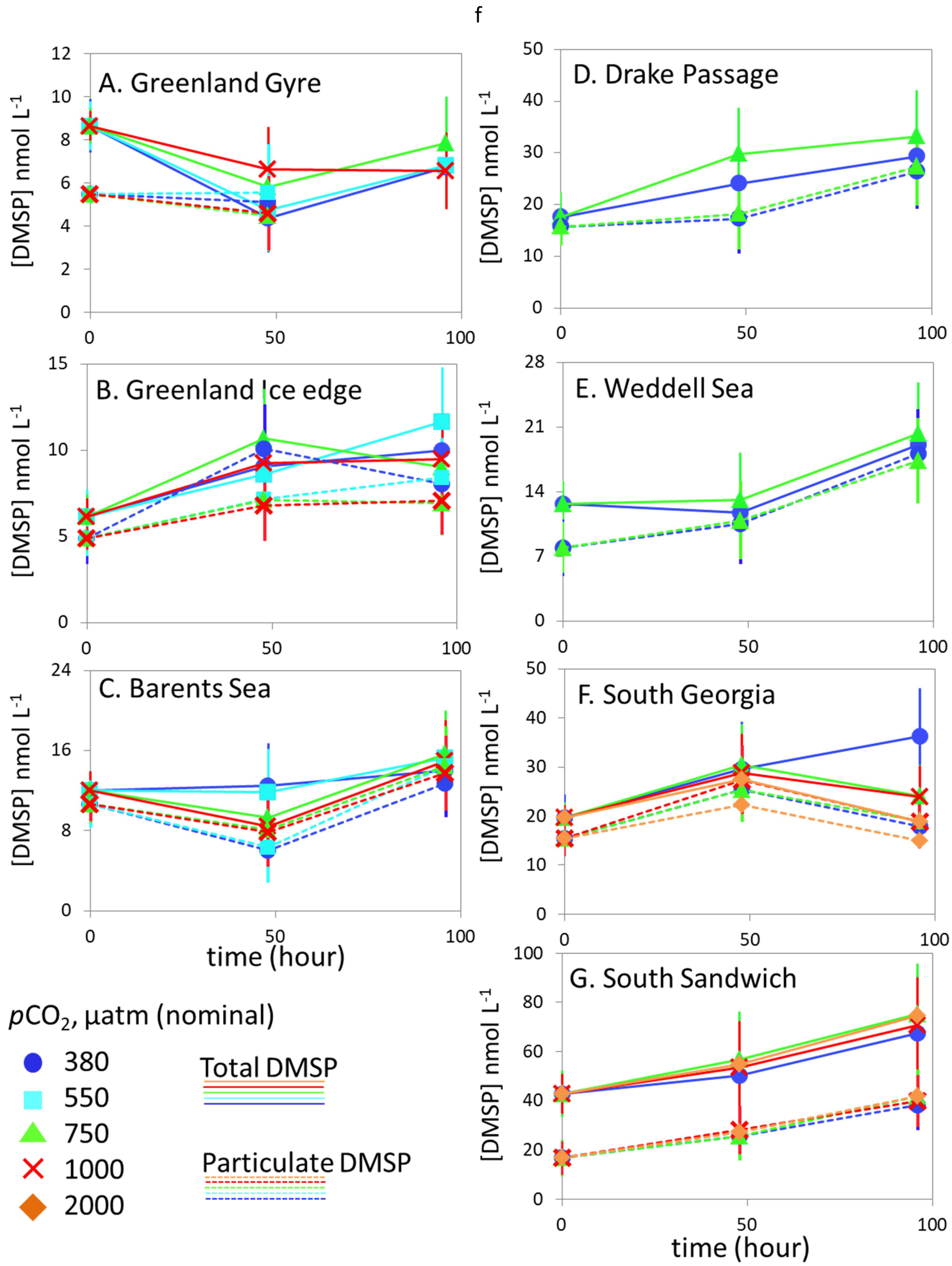


1048

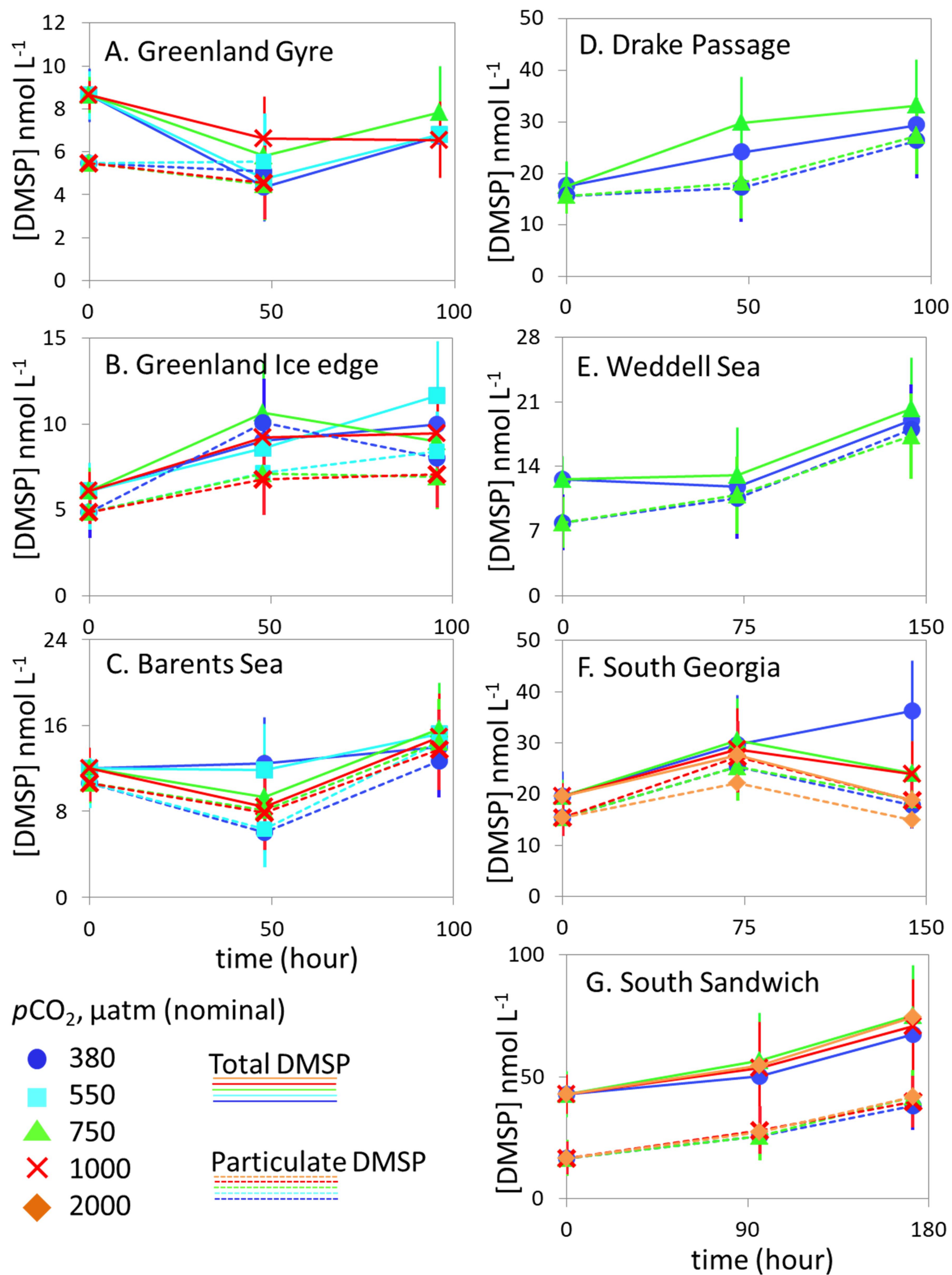
1049 Figure 3. DMS concentrations (nmol L^{-1}) during experimental microcosms performed in
1050 Arctic waters (A - C) and in Southern Ocean waters (D – G). Data shown is mean of triplicate
1051 incubations, and ~~E~~error bars show standard error on the mean. Locations of water collection
1052 for microcosms shown in Figure 1 C – F.

1053

f



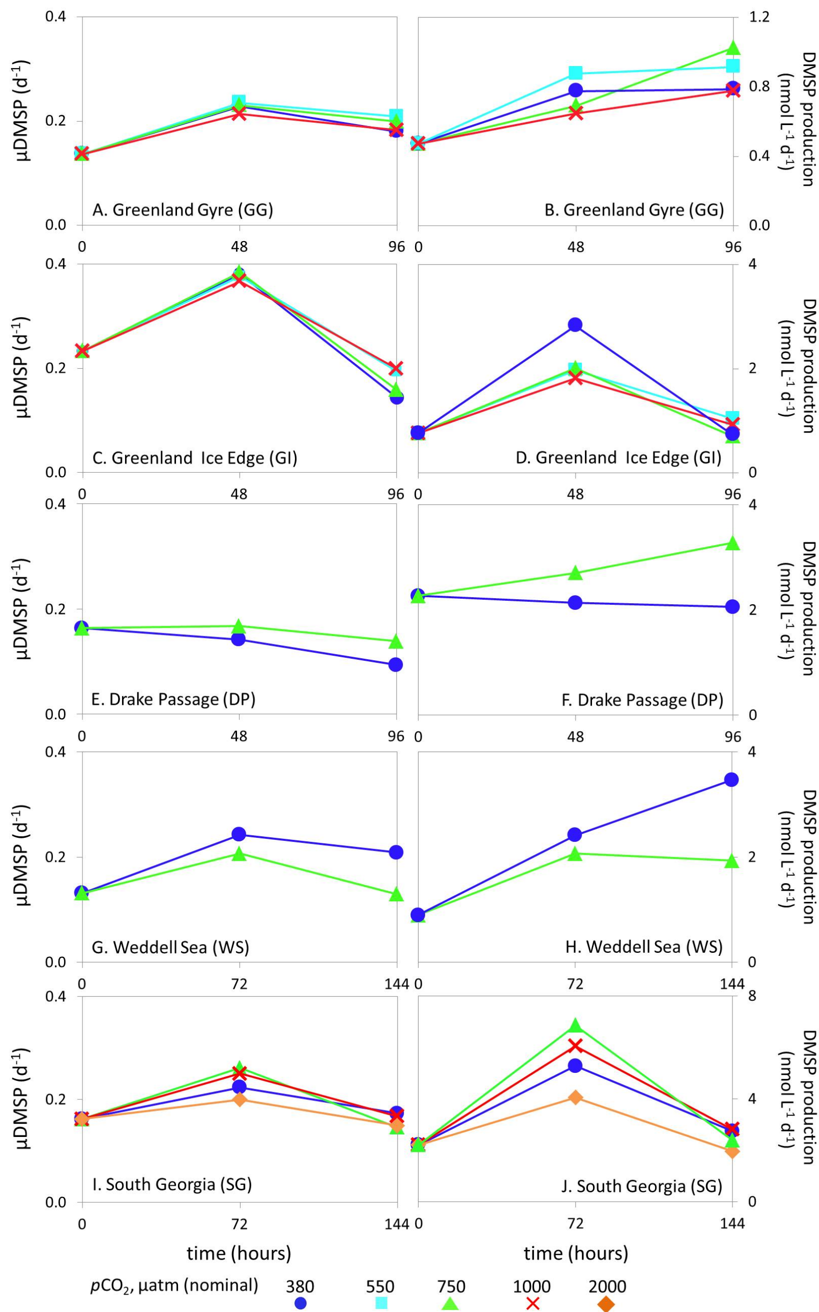
1054



1055

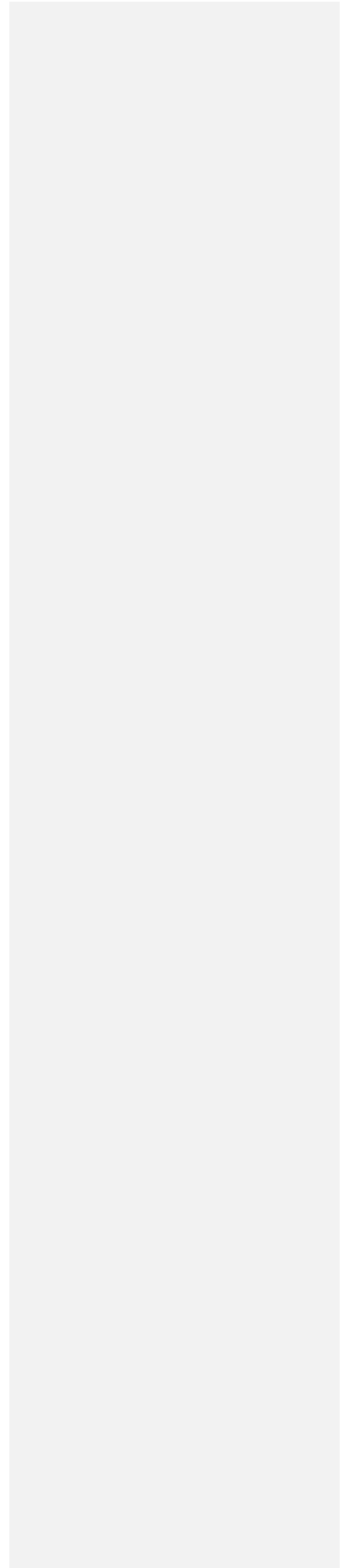
1056 Figure 4. Total DMSP (solid lines) and particulate DMSP (dashed lines) concentrations (
1057 nmol L^{-1}) during experimental microcosms performed in Arctic waters (A - C) and in
1058 Southern Ocean waters (D – G). Data shown is mean of triplicate incubations, and error bars
1059 show standard error on the mean. ~~Error bars show standard error.~~ Locations of water
1060 collection for microcosms shown in Figure 1 C – F. Particulate DMSP concentrations were
1061 used in calculations of DMSP production rates (Figure 5).

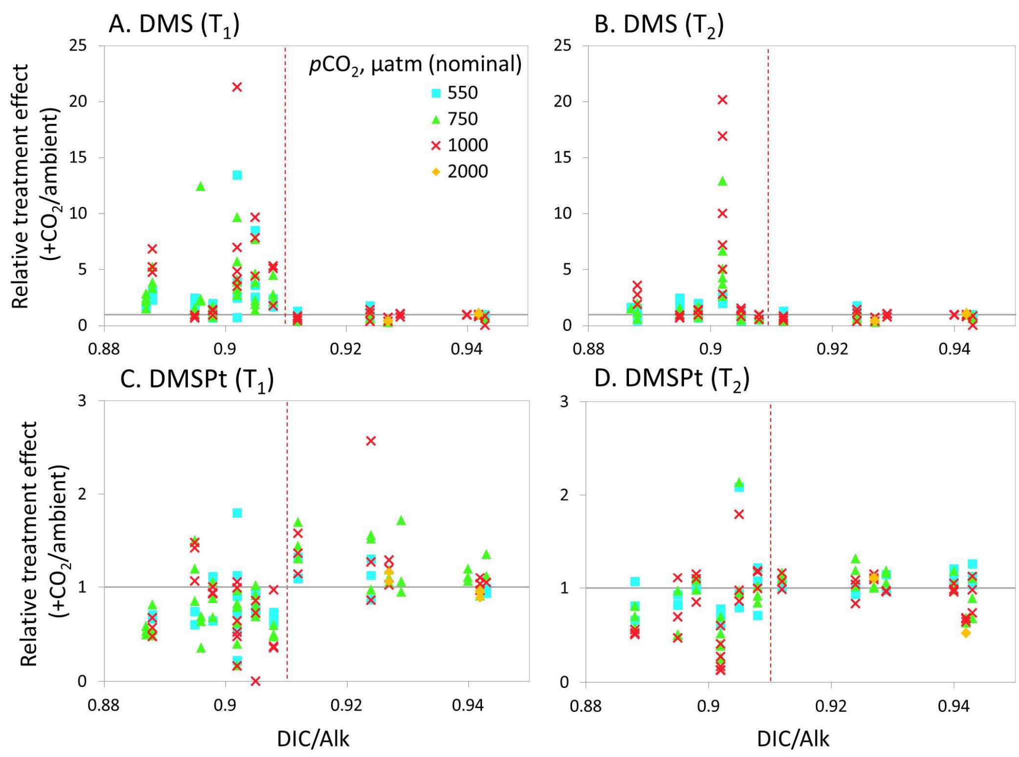
1062



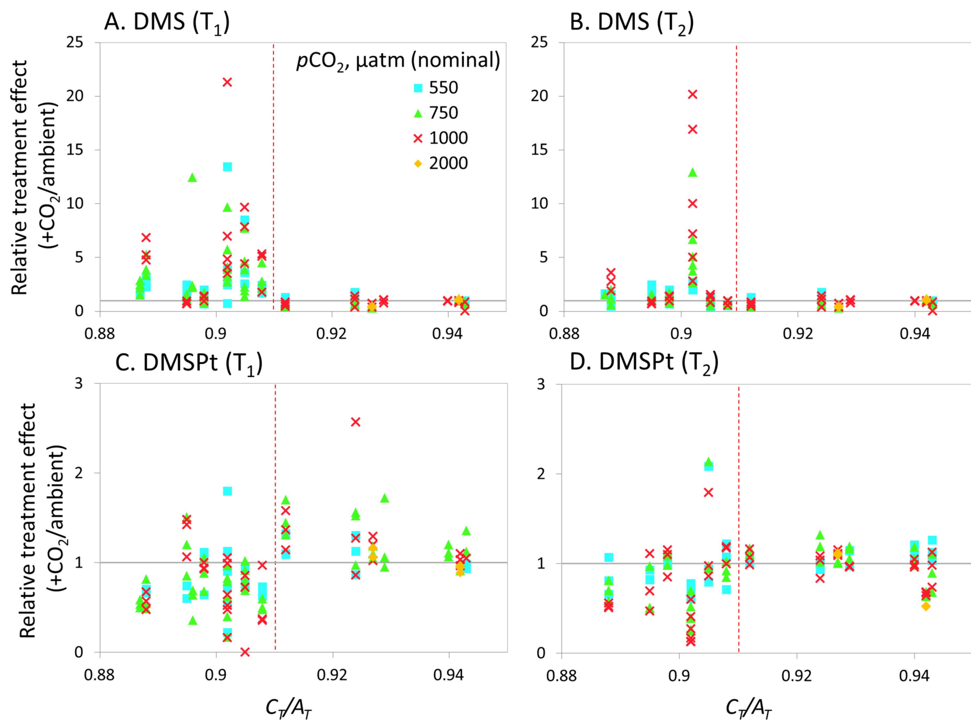
1063 Figure 5. De novo synthesis of DMSP (µDMSP, d^{-1}) (left column) and DMSP production
1064 rates (nmol L^{-1} d^{-1}) (right column) for Arctic Ocean stations *Greenland Gyre* (A,B),
1065 *Greenland Ice-edge* (C, D) and Southern Ocean stations *Drake Passage* (E, F), *Weddell Sea*
1066 (G, H) and *South Georgia* (I, J). No data is available for *Barents Sea* (Arctic Ocean) or *South*
1067 *Sandwich* (Southern Ocean).

1068





1069



1070

Figure 6. Relationship between the ratio of dissolved inorganic carbon ~~DIC~~ C_T to total alkalinity (~~*DIC/Alk*~~C_T/A_T) of the sampled water and the relative CO_2 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for concentrations of DMS at T_1 (A) and T_2 (B), and for total DMSP concentrations at T_1 (C) and T_2 (D) for all microcosm experiments performed in NW European waters, sub-Arctic and Arctic waters, and the Southern Ocean. Grey solid line (= 1) indicates no effect of elevated CO_2. C_T/A_T~~DIC/Alk~~ >0.91 = polar waters (indicated by red dashed line). T_1 = 48 h, except for WS and SG (72 h) and SS (96 h). For detailed analyses of the NW European shelf data, see Hopkins & Archer (2014).

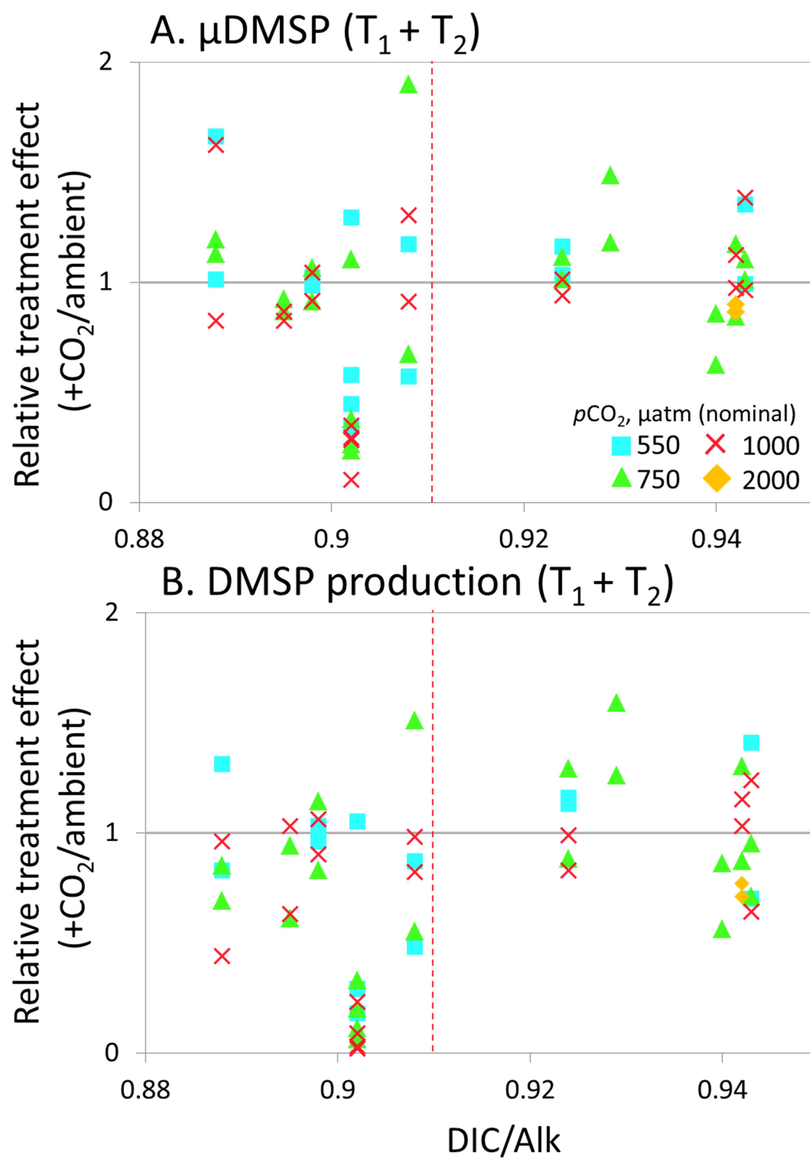
Formatted: Subscript

Formatted: Font: Italic

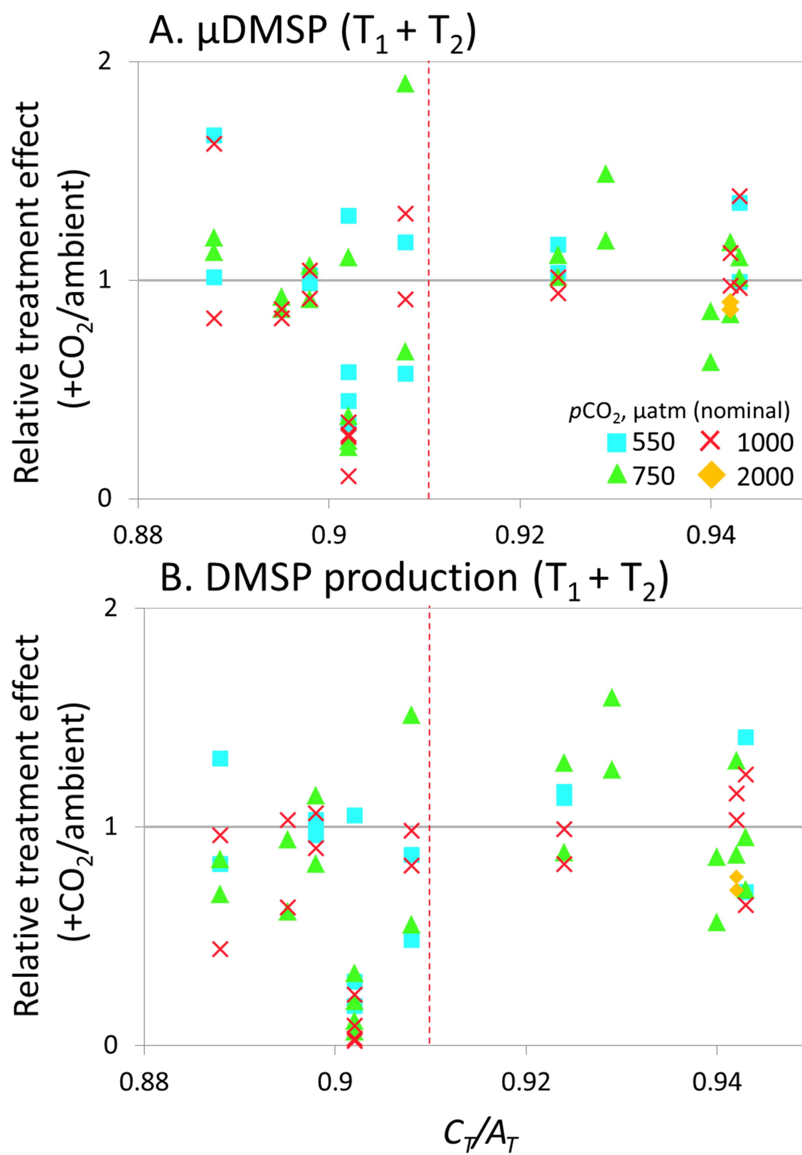
Formatted: Font: Italic, Subscript

Formatted: Font: Italic

Formatted: Font: Italic, Subscript



1079



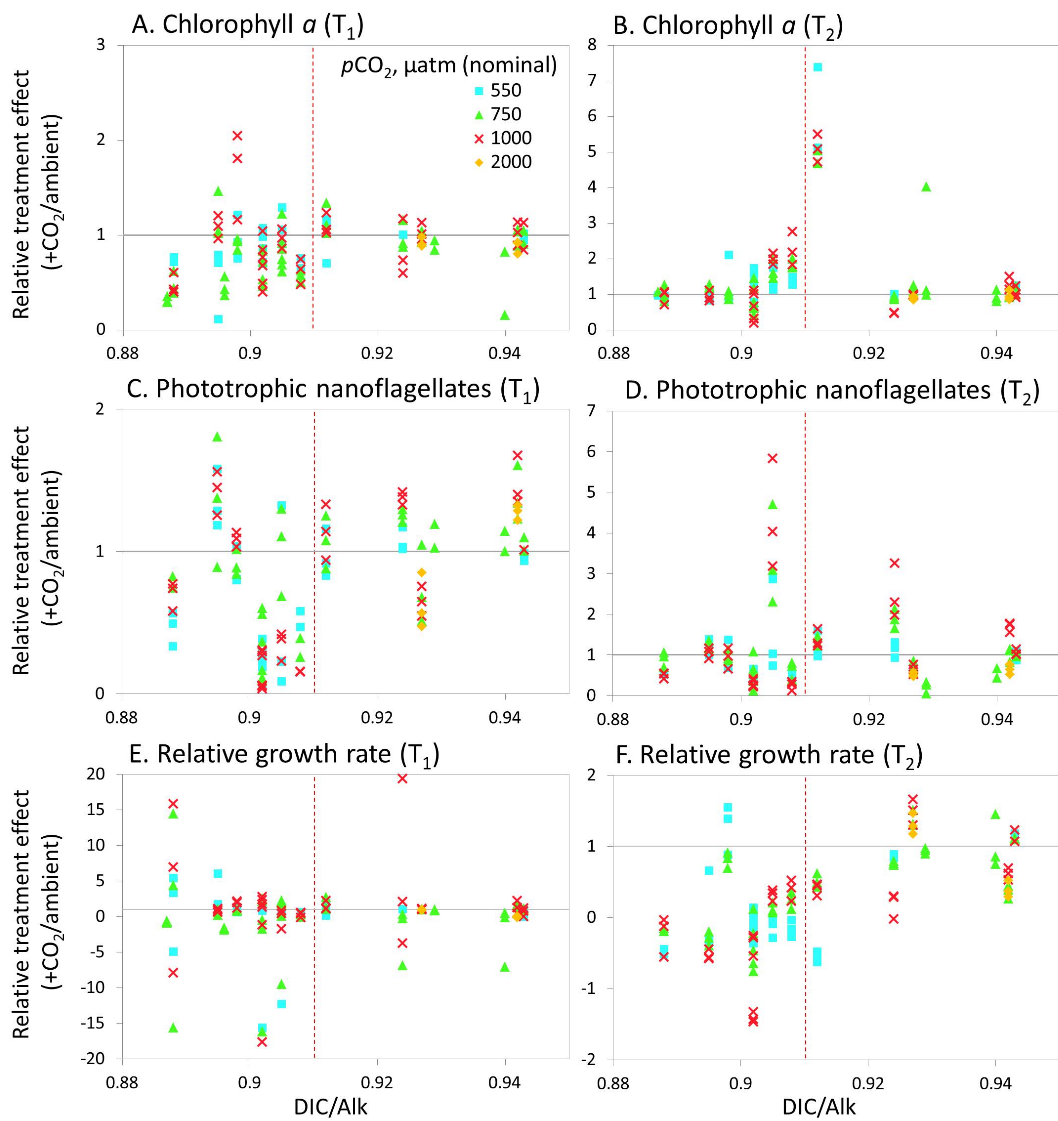
1080

1081 Figure 7. Relationship between the ratio of dissolved inorganic carbon C_TDIC to alkalinity
1082 (C_T/A_TDIC/Alk) of the sampled water and the relative CO_2 treatment effect at
1083 ($[x]_{highCO2}/[x]_{ambientCO2}$) for de novo DMSP synthesis (µDMSp, d^{-1}) at T_1 (A) and T_2 (B), and
1084 DMSP production rate (nmol L^{-1} d^{-1}) at T_1 (C) and T_2 (D) for microcosm experiments
1085 performed in NW European waters, sub-Arctic and Arctic waters, and the Southern Ocean.
1086 Grey solid line (= 1) indicates no effect of elevated CO_2. C_T/A_TDIC/Alk >0.91 = polar waters
1087 (indicated by red dashed line). T_1 = 48 h, T2 = 96 h, except for *Weddell Sea* and *South*

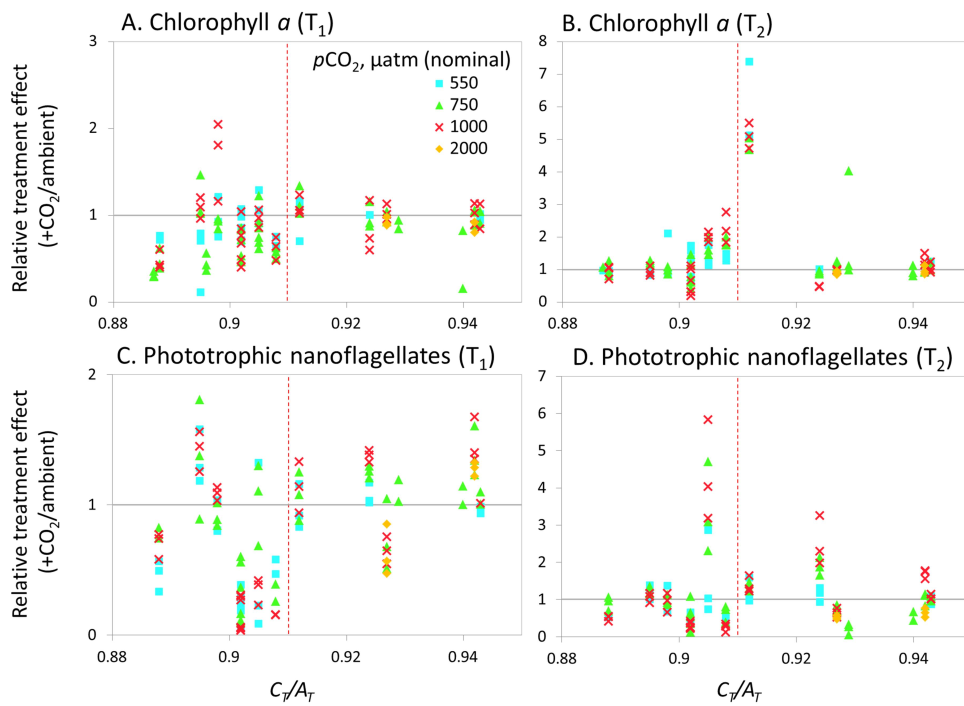
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic

1088 *Georgia* (72 h, 144 h). For discussion of the NW European shelf data, see Hopkins & Archer
1089 (2014).

1090

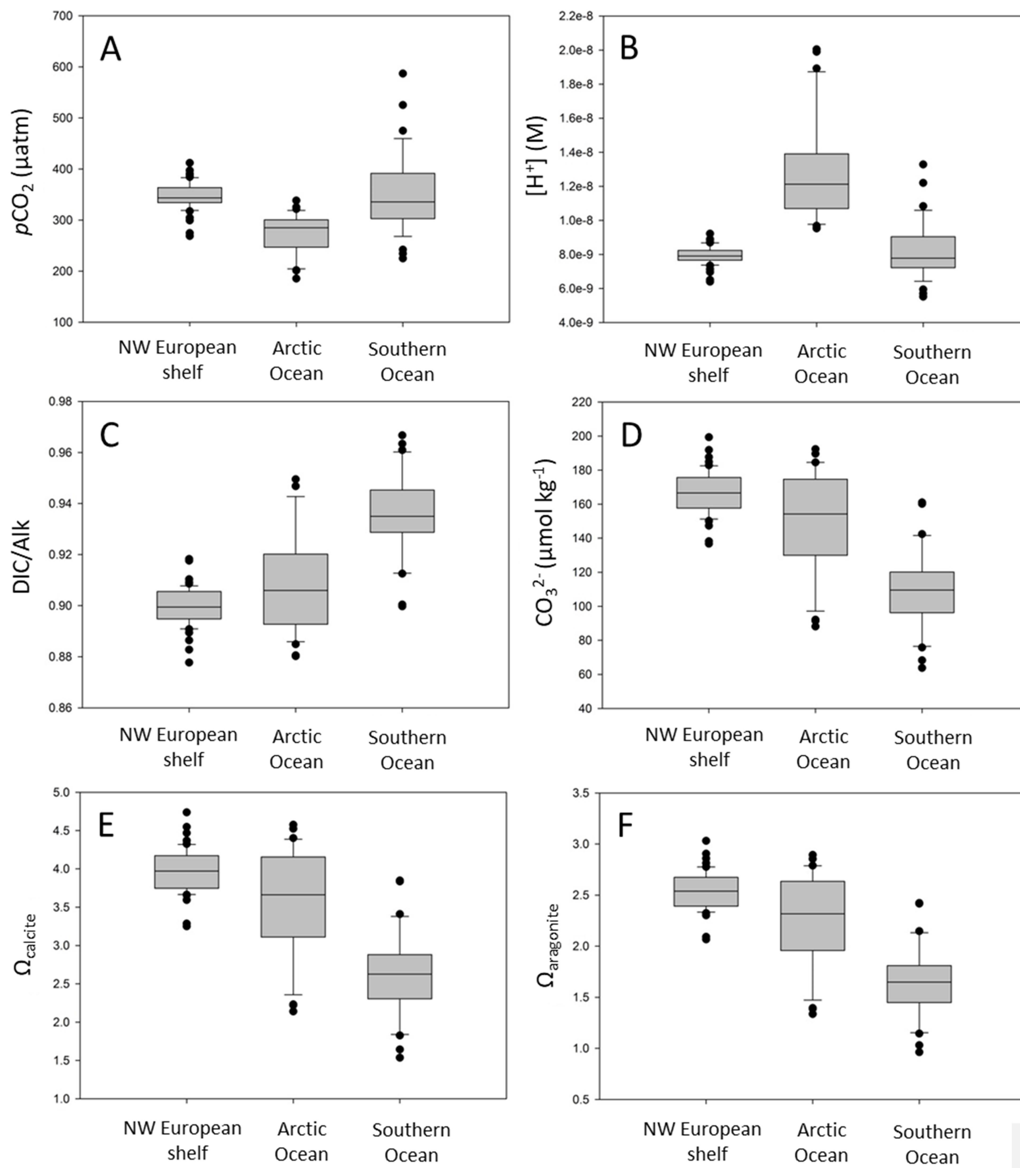


1091

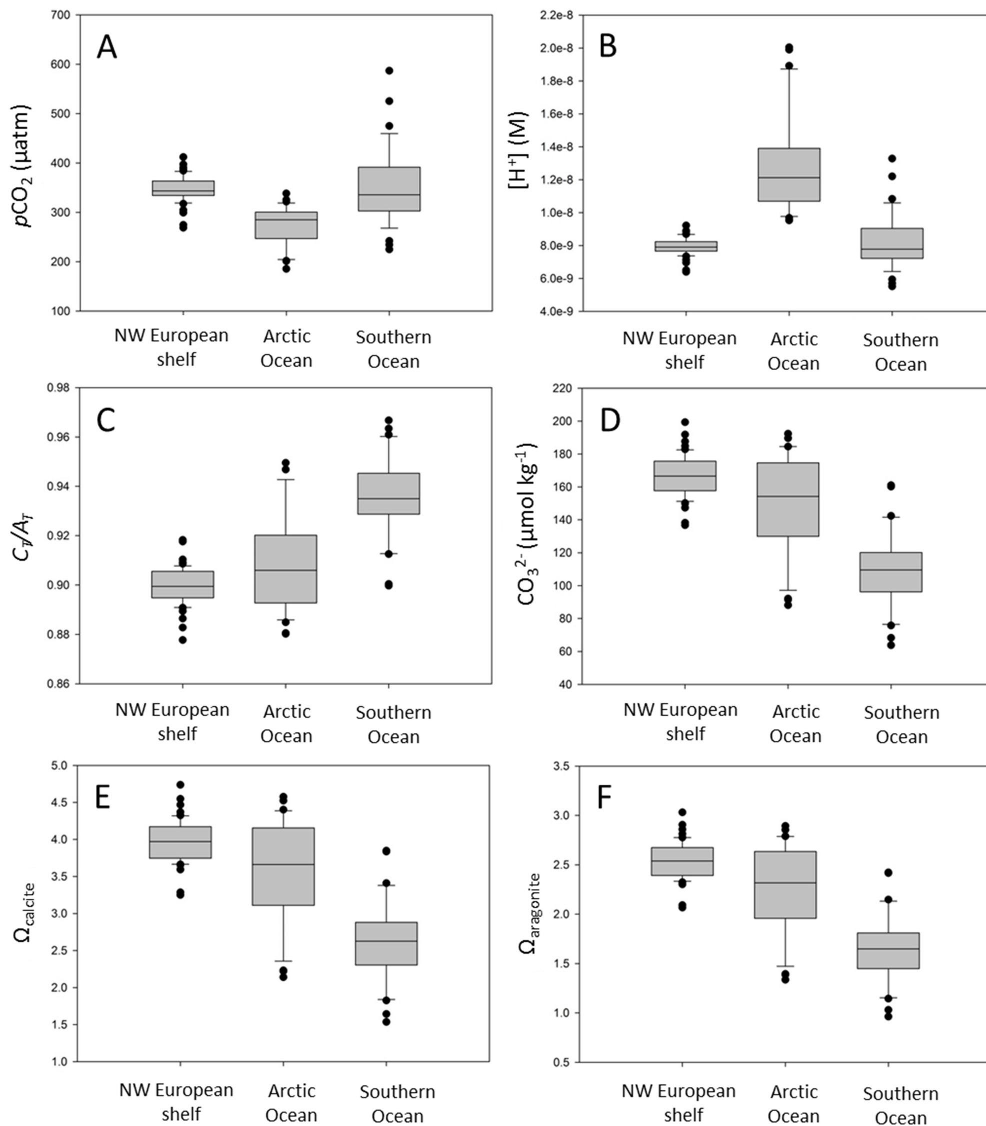


1092 Figure 8. Relationship between the ratio of dissolved inorganic carbon (C_T)~~DIC t~~ to total
1093 alkalinity (C_T/A_T~~DIC/Alk~~) of the sampled water and the relative CO_2 treatment effect
1094 ($[x]_{highCO2}/[x]_{ambientCO2}$) for chlorophyll *a* concentrations at T_1 (A) and T_2 (B) and ~~,~~
1095 phototrophic nanoflagellate abundance at T1 (C) and T2 (D)~~, and relative growth rate at T_1~~
1096 ~~(E) and T_2 (F)~~ for all microcosm experiments performed in NW European waters, sub-Arctic
1097 and Arctic waters, and the Southern Ocean. Grey solid line (= 1) indicates no effect of
1098 elevated CO_2. C_T/A_T~~DIC/Alk~~ >0.91 = polar waters (indicated by red dashed line). T_1 = 48 h,
1099 T_2 = 96 h, except for *Weddell Sea* and *South Georgia* (72 h, 144 h) and *South Sandwich* (96
1100 h, 168 h).

Formatted: Not Superscript/ Subscript



1101



1102

1103 Figure 9. Variation in underway surface ocean carbonate chemistry parameters across the
1104 NW European shelf, Arctic Ocean and Southern Ocean for each of the cruises in this study.
1105 A. Seawater pCO_2 (µatm), B. Seawater $[H^+]$ (M), C. dissolved inorganic carbon (C_T)~~DIC~~ to
1106 total alkalinity (A_T) ratio (~~DIC/Alk~~C_T/A_T), D. Carbonate ion concentration (CO_3^{2-}) (µmol kg^{-1}), E. Calcite saturation state ($\Omega_{calcite}$), F. Aragonite saturation state ($\Omega_{aragonite}$).
1107
1108

Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript
Formatted: Font: Italic
Formatted: Font: Italic, Subscript