Final author comments on "Polar dimethylsulfide (DMS) production insensitive to ocean acidification during shipboard microcosm experiments: a meta-analysis of 18 experiments from temperate to polar waters." by F.E. Hopkins et al., manuscript number bg-2018-55.

We are grateful to the reviewer for their positive view of our manuscript and their thorough assessment, which will bring great improvements. The reviewers comments are shown in italics, with our responses shown **in bold**. *Line numbers in our response refer to the revised version. The marked-up version of the manuscript comes after the response (starting at pg 10), and line numbers refer to this version.*

1. Response to Anonymous Referee #1

1.1 The paper describes the results of microcosm experiments 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 primary results are the absence of an effect of high CO2 on DMS/DMSP in polar waters, and the contrasting significant effect of high CO2 in decreasing DMSP concentration/DMSP production & increasing DMS production in temperate waters. The authors relate the difference in regional DMS response to variability of the carbonate system of each region; other factors (phytoplankton community, nutrients etc) are rejected due to the absence of significant relationships. The paper makes some interesting points regarding regional variation in response to acidification, which should be considered in models.

We thank the reviewer for their supportive comments on our paper. Our primary target audience includes climate modellers, and we agree that the DMS data we present should be considered in models where information on future DMS fluxes from polar regions is currently minimal.

1.2 I have two "medium" concerns with paper, the first being that the DMSP response to High CO2 is a little overstated; a significant DMSP response to High CO2 is limited to the first 48 hours in the polar experiments, after which there is no significant difference from the control. My other concern is that the interpretation, and proof of their hypothesis, rests on differences in regional variability of pH & the carbonate system, yet the data presented to support this are somewhat limited. I appreciate there are limited pH datasets available, but the data discussed are primarily large-scale spatial variability, and not the temporal variability that the phytoplankton experience.

We thank the reviewer for their considered comments and appreciate the improvements that they will make to our manuscript. We have endeavoured to address all their comments and concerns in our point-by-point response below.

Specific comments
1.3 Title doesn't scan as written ("IS insensitive") and is a little confusing with reference to the polar results, & then then the metanalysis of polar AND temperate results. A better title might be:
"DMS sensitivity to ocean acidification as determined in a meta-analysis of temperate to polar microcosm experiments"
Or, to highlight the polar results:
"A metanalysis of microcosm experiments shows that DMS production in polar waters is insensitive to ocean acidification"

We tend to agree with the reviewer with regards to the confusing title – the result of multiple reviews! So we thank this reviewer for pointing this out and making some nice suggestions for the title. We have decided to go with:

"A metanalysis of microcosm experiments shows that DMS production in polar waters is insensitive to ocean acidification"

1.4 Abstract Line 26 "resulting in an INCREASE in DMS emissions to the atmosphere….."

Text altered accordingly.

1.5 Discussion Line 443-445; The text implies there is a significant positive effect on DMSP of high CO2 at the 2nd time point, but this does seem apparent in Fig. 7D

The reviewer refers to:

"In contrast, at temperate stations, DMSP concentrations displayed a clear negative treatment effect, whilst at polar stations a positive effect was evident under high CO_2 and particularly at the first time point (48 – 96 h) (Fig. 7 C and D)".

We don't use the term 'significant' in this part of the text. We feel it is fair to say "a positive effect was evident", as the majority of data points fall above 1, indicating a positive treatment effect of high CO_2.

1.6 Line 450 "This data suggests that DMSP concentrations in polar waters may be upregulated…" again this is only for the first 48 hours; Fig 7D doesn't show a significant mean effect at 96 hours for polar waters. This could be a "shock" response to the dramatic alteration of pH and the carbonate system, before the phytoplankton community acclimate, which should be mentioned. Also, perhaps more accurate to say the results reflect a downregulation of DMSP in temperate waters (relative to polar waters), as the mean DMSP effect is significant for both experimental time periods temperate waters in Figs 7C&D (unlike in polar waters where there is only a significant difference in the first 24 hours in Fig 7C).

This paragraph has been re-written to take the reviewer's comments into consideration. Now reads (from L475):

"Our data imply that DMSP concentrations in temperate waters were downregulated in response to OA, attributed to the adverse effects of rapid OA on the growth of DMSP producers which led to reductions in the abundance of these types of phytoplankton (Richier et al. 2014, Hopkins and Archer 2014). By comparison, a more muted, but generally positive, DMSP response was seen in polar waters at the first time point, whilst these treatment effects were more or less undetectable by the second time point. There is some evidence that the enhanced DMSP concentrations in polar waters were accompanied by increased DMSP production rates (Figure 8), although data is not available for all experiments. However, these changes may reflect a short term 'shock' physiological protective response to the experimental OA, similar to that seen in response to other short term stressors such as high irradiance that result in an increase in DMSP concentrations (Sunda et al., 2002;Galindo et al., 2016). The lack of treatment effect in DMSP concentrations by the second time point may be indicative that the community had, to some extent, acclimated to the change, allowing DMSP production/concentrations to return to baseline levels. This may reflect a higher degree of

tolerance to rapid changes in carbonate chemistry amongst polar communities - species which are already adapted to highly variable irradiance/carbonate chemistry regimes (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015). Further experiments with polar communities would help to unravel the potential importance of such mechanisms and whether they facilitated the ability of polar phytoplankton communities to resist the high CO_2 treatments".

1.7 Line 459 "rapid OA on DMSP producers…" more detail required here. Is this an algal physiological response or change in phytoplankton community composition?

We have rewritten this section so this sentence is no longer included in its original form. See response to 1.6 above.

This new sentence, starting at L475 replaces the previous:

"Our data imply that DMSP concentrations in temperate waters were downregulated in response to OA, attributed to the adverse effects of rapid OA on the growth of DMSP producers which led to reductions in the abundance of these types of phytoplankton (Richier et al. 2014, Hopkins and Archer 2014)".

1.8 Line 460 This paragraph is a little contradictory; starts by saying DMSP production is upregulated in polar relative to temperate, and finishes with "the lesser response seen in polar waters"

Again, we have rewritten this section to make our point more clearly (See response to 1.6 above), so it is no longer included in its original form. The underlined sentence below addresses the reviewers specific comment:

"Our data imply that DMSP concentrations in temperate waters were downregulated in response to OA, attributed to the adverse effects of rapid OA on the growth of DMSP producers which led to reductions in the abundance of these types of phytoplankton (Richier et al. 2014, Hopkins and Archer 2014). By comparison, a more muted, but generally positive, DMSP response was seen in polar waters at the first time point, whilst these treatment effects were more or less undetectable by the second time point".

1.9 Line 466. "In an assessment across..."; this sentence should be rewritten for clarity

We have rewritten this sentence and broken the information down into two sentences. It now reads (starts L513):

"In an assessment across all experiments, Richier et al. (2018) showed that the magnitude of biological responses to short term CO_2 changes reflected the buffer capacity of the sampled waters. A consistent suppression of net growth rates in small phytoplankton (<10 µm) and total Chl *a* concentrations was observed under high CO_2 within experiments performed in temperate waters with higher buffer capacity".

1.10 Line 533-540. "The polar waters sampled during our study were characterised by pronounced gradients in carbonate chemistry over small spatial scales". Where is this shown? And what are the "small spatial scales"? The pH range of the whole voyage ("along each cruise track") is mentioned but theres no information provided on the length of these transects which

makes its difficult to compare the pH gradient between regions, or assess how significant the pH spatial gradients are. Phytoplankton won't experience the total pH range measured on a voyage, as their exposure will be limited by physical constraints such as currents and water masses. Furthermore, the sites sampled within each voyage will experience different pH variability. The information on the drivers of spatial gradients (in paragraph Line 541-554) is interesting, but theres no indication of the spatial scale associated with this to relate spatial pH gradients to phytoplankton. The authors have provided some examples of the temporal pH variation at certain sites (Paragraph Line 555-564), but these do not consider all pH data available (for example, Beare et al (2013) show large variation (7.8-8.5) in the central North Sea). The authors supply supporting evidence from other experiments that polar phytoplankton are relatively insensitive to variation in pH, but to support their hypothesis that the regional variation in pH is the primary factor driving differences in DMSP response, more evidence and analysis of differences in regional pH variability are required.

Beare, D., McQuatters-Gollop, A., van der Hammen, T., Machiels, M., Teoh, S. J., & Hall-Spencer, J. M. (2013). Long-term trends in calcifying plankton and pH in the North Sea. PLoS One, 8(5), e61175.

We thank the reviewer for highlighting this section, which has been subject to the scrutiny of several reviewers and had perhaps lost it way somewhat. Unfortunately, we do not have data on the pH variability at each sampling station so necessarily we must make our point using what data we have available, and that is the underway measurements along the cruise track. We realised an important point was missing from this section: that the OA response in polar vs temperate waters relates to the Revelle Factor (buffering capacity) of the sampled waters – it is this then that contributes to the greater level of variability in carbonate chemistry seen in polar waters. Thus, the point we wish to make is that the polar communities are already adapted to a variable carbonate chemistry environment, and this is the result of lowered buffering capacity in polar waters, and is also accentuated by other processes that occur in polar waters which create fluctuations in carbonate chemistry.

We thank the reviewer for flagging Beare et al. (2013) who do indeed show a wide range in pH in the North Sea. However, the sampling locations (Figure 1) are biased towards the German Bight, a region heavily influenced by the outflow of regional rivers which results in strong alkalinity driven pH fluctuations (see Artioli et al. 2012, 2014). The unique riverine-influenced, shallow characteristics of this region make it challenging to compare this data to the open ocean sampling locations that we are presenting.

Artioli, Y., Blackford, J. C., Butenschön, M., Holt, J. T., Wakelin, S. L., Thomas, H., ... & Allen, J. I. (2012). The carbonate system in the North Sea: Sensitivity and model validation. *Journal of Marine Systems*, *102*, 1-13.

Artioli, Y., Blackford, J. C., Nondal, G., Bellerby, R. G. J., Wakelin, S. L., Holt, J. T., ... & Allen, J. I. (2014). Heterogeneity of impacts of high CO 2 on the North Western European Shelf. *Biogeosciences*, *11*(3), 601-612.

We have added some additional text to section 4.4 and we hope this satisfies the reviewer's concerns. The section now reads (starts L582):

"4.3 Adaptation to a variable carbonate chemistry environment

Given that DMS production by polar phytoplankton communities appeared to be insensitive to experimental OA compared to significant sensitivity in temperate communities, we hypothesise

that polar communities are adapted to greater natural variability in carbonate chemistry over spatial and seasonal scales. This greater variability is partly the result of the lower buffering capacity (Revelle Factor) of polar waters compared to lower latitude waters, and partly due to specific processes that occur in the polar regions that strongly alter DIC concentrations (e.g. sea ice formation and melt, enhanced CO_2 dissolution into cold polar waters, upwelling of CO_2 rich water). Therefore, polar plankton communities are not only subject to geophysical processes that strongly alter in situ carbonate chemistry on both spatial and seasonal scales, but such changes are accompanied by larger pH changes than would occur in more strongly buffered temperate waters. Therefore, polar surface ocean communities are perhaps more likely to experience fluctuations between high pH and low pH over relatively smaller time/space scales (Tynan et al., 2016). Thus below, we discuss our findings in the context of the spatial pH variability we observed for each cruise track, and explore some of the processes that drive this variability in polar waters. Information on the pH variability at each sampling station is not available, so we cannot be certain of the exact carbonate chemistry variability to which each of the sampled communities may have been exposed and adapted. However, we can consider the overall variability in carbonate chemistry over the spatial scales of the cruise tracks to demonstrate the characteristics of each study area.

The polar waters sampled during our study were characterised by pronounced gradients in carbonate chemistry over relatively small spatial scales. In underway samples taken along each cruise track (Arctic Ocean 3500 nm, Southern Ocean 4000 nm), pH varied by 0.45 units (8.00 – 8.45) in the Arctic, and 0.40 units (8.30 - 7.90) in the Southern Ocean (Tynan et al. 2016). In some cases this range in variability was seen over relatively small distances: Figure 4 in Tynan et al. (2016) shows that pH fluctuated from 8.45 and 8.0 over a distance of 50 – 100 miles in the sea-ice influenced Fram Strait. By comparison, pH varied by a total of 0.2 units (8.22 - 8.02) in underway samples from the NW European shelf sea cruise (Rerolle et al. 2014). The observed horizontal gradients in polar waters were driven by different physical and biogeochemical processes in each ocean. In the Arctic Ocean, this variability in carbonate chemistry was partly driven by physical processes that controlled water mass composition, temperate and salinity, particularly in areas such as the Fram Strait and Greenland Sea. Along the ice-edge and into the Barents Sea, biological processes exerted a strong control, as abundant iron resulted in high chlorophyll concentrations, low DIC and elevated pH. By contrast, variations in temperature and salinity had only a small influence on carbonate chemistry in the Southern Ocean in areas with iron limitation, and larger changes were driven by a combination of calcification, advection and upwelling. Where iron was replete, e.g. near South Georgia, biological DIC drawdown had a large impact on carbonate chemistry (Tynan et al. 2016). A further set of processes was in play in sea ice influenced regions. At the Arctic ice edge, abundant iron drove strong bloom development along the ice edge, whilst sea ice retreat in the Southern Ocean was not always accompanied by iron release (Tynan et al. 2016).”

1.11 Line 634 Section 4.4. This section should highly other benefits of mesocosms (inclusion of larger components of the foodweb and physical factors (mixing, stratification, particle export) that are excluded from microcosms, and note that their longer duration & more holistic/inclusive framework makes mesocosm results more relevant for Earth System models. This section should also consider the shock effect of sharply altering pH in microcosms

> **We completely agree with the reviewer’s comments on this and agree that it would be useful to include such information in the paper. However, the specific section that they refer to does not seem to be the best part of the paper for this. We feel that it would fit better in the introduction, in the section beginning “Mesocosm experiments have been a critical tool…” where we already touch upon such issues. Therefore, we have added the following text to this section (starts L124):**

"The pseudo-natural conditions of mesocosm experiments offer the benefit of the inclusion of community dynamics of three or more trophic levels, providing the opportunity to investigate the influence of ecosystem dynamics on biogeochemical processes under experimental conditions (Riebesell et al., 2013b). Furthermore, physical processes such as particle export (Bach et al., 2016), which would be excluded by smaller scale experiments, can be considered within the holistic mesocosm framework, and make the results relevant for use within Earth system models (Six et al. 2013). However, the size, construction and associated costs of 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".

With regards to the reviewer's comment on the shock effect of altering pH in microcosms: we do not include specific discussion in this regard because we did not see any evidence of a shock response in the polar experiments. However, we do allude to our previous findings (Hopkins and Archer 2014) as possibly being driven by an acute 'shock' response to sudden pH change (e.g. L157-159). We have added some additional text to the introduction to show consideration for the potential shock effect (starts L149):

"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, and the potential to induce a 'shock' response to the sudden alteration of carbonate chemistry should be considered, particularly when working at the smaller microcosm scale".

1.12 Line 722. "Our findings contrast with two previous studies….." this sentence (the reasons for differences in previous polar microcosm responses) should be expanded on in the Discussion section

The "two previous studies…" to which this sentence refers to are Archer et al. (2013) and Hussherr et al. (2017). The whole of section 4.4 is dedicated to discussing the reasons why our findings contrast with the Arctic mesocosm experiment of Archer et al., whilst L774-786 discusses the differences with the polar microcosm experiment of Hussherr et al. The line which has been highlighted by the reviewer is simply a summary of the previous discussion. We feel no further discussion is required.

Technical corrections/Minor comments

Introduction
1.13 Line 52-66; why does this paragraph focus on pack ice & associated climate-related changes?

The reviewer refers to the section which starts "The biologically-rich seas surrounding the Arctic pack ice…". The intention of this paragraph was to explain the importance of the Arctic Ocean for DMS production – our motivation for investigating the effects of OA from this region. Perhaps use of the phrase 'pack-ice' in unnecessary and we can simply refer to the Arctic Ocean ice-edge and open waters. Therefore we have reworded as (L55)

"The biologically-rich ice-edge regions and open seas of the Arctic are a strong source of DMS to the Arctic atmosphere (Levasseur, 2013)".

We finish this paragraph by describing how sea ice loss may impact future DMS emission from

the Arctic. Given the reviewer's comment, we feel it would be better to end this paragraph by mentioning the potential effect of OA in the Arctic on DMS emissions. Thus we have added:

"The influence that OA will have on the production and flux of DMS, and how this may further influence the Arctic radiative balance, is poorly understood and requires further experimental and modelling efforts".

1.14 Line 113 "'winners vs loser' dynamic": this requires some explanation

Now reads (L116 – 121):

"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). <u>This is sufficient time to allow a 'winners vs loser' dynamic to develop, whereby the succession of the phytoplankton community is altered due to the differing sensitivities of different taxonomic groups to changes in carbonate chemistry (Bach et al., 2017)"</u>.

1.15 Line 137 "Polar" not required in this sentence as the paper presents experiments from temperate waters as well as polar

"polar" deleted from sentence.

Methods
1.16 Line 183. For the Drake Passage and Weddell Sea experiments suggest the Fe experiments are not mentioned (as their results aren't discussed), and the same notation is used as for the other experiments (High CO2, High CO2 +, etc)

We have removed mention of the Fe experiments and the section now reads:

"For Southern Ocean experiments, two experiments (*Drake Passage* and *Weddell Sea*) considered one CO_2 treatments (High). Three CO_2 treatments (High, High+, High++) were tested in the last two experiments (*South Georgia* and *South Sandwich*)".

1.17 Line 215-219. A 48-hour experiment seems very short; however, as pointed out growth rates are faster in temperate waters than polar incubations. The authors may want to use these differential growth rates to justify the comparison of response of shorter duration temperate experiments & longer duration polar experiments.

To make this point clearer to the reader, we have modified a line in this section (L233):

"The differential growth/metabolic rates between temperate and polar waters justify the comparison of response of shorter duration temperate experiments and longer duration polar experiments".

1.18 Line 211. IF the high frequency results are not discussed them exclude this from the Methods

The sentence referring to the high time frequency sampling has been deleted.

Results
1.19 Fig 2. As DMS & DMSP results (G-I) are only presented to depths of 100m, the non-DMS/P

parameters (A-F) should be only shown for this depth range, particularly as only the surface values for non-DMS/P variables are discussed in the Results section. Currently details of the depth profiles in A-F are not visible due to the extended vertical axis used.

Figure 2 has been altered so all parameters are plotted to 100m.

1.20 Fig 2. The depth profiles on DMS/P are not really discussed; the maxima is not always at the surface and these sub-surface maxima appear to be associated chl-a subsurface maxima

We have altered the text starting at L351 to take the reviewer's comments into consideration:

"In temperate waters, maximum DMS concentrations were generally seen in near surface measurements, ranging from 1.0 nmol L^{-1} for *E04* to 21.1 nmol L^{-1} for *E06*, with rapidly decreasing concentrations with depth (Figure 2 G). As an exception to this, DMS concentrations at *South Sandwich* showed a sub-surface maximum of 15 nM at 32 m, coincident with a subsurface Chl *a* maximum of 5.4 µg L^{-1}. DMSP generally ranged from 12 – 20 nmol L^{-1}, except *Barents Sea* where surface concentrations exceeded 60 nmol L^{-1} (Figure 2 H). DMSP tended to peak in the near surface waters, ranging from 12.0 nmol L^{-1} for E04 to 72.5 nmol L^{-1} for *E06*, although in some cases a subsurface maximum in overall DMSP concentrations was seen, as observed for *E05b* (89.8 nmol L^{-1} 20 m), and again coincident with a subsurface Chl a peak of >2 µg L^{-1} (Figure 2 F and 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), and resulted in high DMS:DMSP of 0.6 – 0.9 in the surface layer (Figure 2 I). DMS:DMSP did not exceed 0.5 at any other sampling stations".

1.21 Line 344. This description is misleading; both the 48-hr and 96-hr samples were collected within the incubation period

Text altered accordingly and now reads (L369):

"Initial concentrations of 1 – 2 nmol L^{-1} remained relatively constant over the first 48 h and then showed small increases of 1 - 4 nmol L^{-1} over the remainder of the incubation period."

1.22 Line 351 Fig 5 is DMSP data, not Fig 4

Corrected.

1.23 Line 372 The unpublished temperate data are an important component of this paper and so the Suppl. Table 2 data should instead be a Figure in the main paper (possibly including comparison with the publ. data from Hopkins& Archer (2014)).

We don't feel it would be useful to add another figure to the main paper – Figure 7, 8 and 9 include the data from the previously unpublished experiments in a useful visual meta-analysis. However, we have added a table to the main paper showing the DMS and DMSPt data from the four small-scale experiments to make the information easily accessible to the reader (moved from the supplementary info).

1.24 Line 388. "effect" missing

Sentence now reads: "No consistent effect of high CO_2…"

Discussion
1.25 Line 487 "For all Arctic stations …"; Drake Passage & the Weddell sea are not in the Arctic

The text has been altered and so now reads (L540):

"For all Arctic stations, as well as Southern Ocean stations *Drake Passage* and *Weddell Sea*, no response to high CO_2 was observed".

1.26 Line 698-702. These two sentences don't seem to address the topic of Section 4.4, or this paragraph and should perhaps be moved elsewhere in the text

These two sentences have been removed from this section, and we have altered the text at L682-686:

"Adaptation to such natural variability may induce the ability to resist abrupt changes within the polar biological community (Kapsenberg et al., 2015). This is manifested here as negligible impacts on rates of *de novo* DMSP synthesis and net DMS production in the microbial communities of the polar open oceans to short term changes in carbonate chemistry".

A metanalysis of microcosm experiments shows that dimethyl sulfide (DMS) production in polar waters is insensitive to ocean acidification

~~Polar dimethylsulfide (DMS) production insensitive to ocean acidification during shipboard microcosm experiments: a meta-analysis of 18 experiments from temperate to polar waters.~~

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Abstract. Emissions of dimethylsulfide (DMS) from the polar oceans play a key role in atmospheric processes and climate. Therefore, it is important to increase our understanding of how DMS production in these regions may respond to 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 similar 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, 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. If so, future temperate oceans could be more sensitive to OA resulting in an ~~change~~ increase 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., 2008a), and the atmospheric oxidation pathways of other key climate gases, including isoprene, ammonia and organohalogens (Chen and Jang, 2012; von Glasow and Crutzen, 2004; Johnson and Bell, 2008). Thus, our ability to predict the climate into the future requires an understanding of how marine DMS production

53 may respond to global change (Carpenter et al., 2012; Woodhouse et al., 2013; Menzo et al.,
54 2018).

55 The biologically-rich ice-edge regions and open seas surrounding theof the Arctic Arctic pack
56 ice are a strong source of DMS to the Arctic atmosphere (Levasseur, 2013). A seasonal cycle
57 in CCN numbers can be related to seasonality in the Arctic DMS flux (Chang et al., 2011).
58 Indeed, observations confirm that DMS oxidation products promote the growth of particles to
59 produce aerosols that may influence cloud processes and atmospheric albedo (Bigg and Leck,
60 2001; Rempillo et al., 2011; Korhonen et al., 2008b; Chang et al., 2011). Arctic new particle
61 formation events and peaks in aerosol optical depth (AOD) occur during summertime clean
62 air periods (when levels of anthropogenic black carbon diminish), and have been linked to
63 chlorophyll *a* maxima in surface waters and the presence of aerosols formed from DMS
64 oxidation products such as methanesulfonate (MSA). The atmospheric oxidation products of
65 DMS - SO_2 and H_2SO_4 - contribute to both the growth of existing particles and new particle
66 formation (NPF) in the Arctic atmosphere (Leaitch et al., 2013; Gabric et al., 2014; Sharma et
67 al., 2012). Thus, the ongoing and projected rapid loss of seasonal Arctic sea ice may
68 influence the Arctic radiation budget via changes to both the DMS flux and the associated
69 formation and growth of cloud-influencing particles (Sharma et al., 2012). The influence that
70 OA will have on the production and flux of DMS, and how this may further influence the
71 Arctic radiative balance, is poorly understood and requires further experimental and
72 modelling efforts.

73 During its short but highly productive summer season, the Southern Ocean is a hotspot of
74 DMS flux to the atmosphere, influenced by the prevalence of intense blooms of DMSP-rich
75 *Phaeocystis antarctica* (Schoemann et al., 2005) and the presence of persistent high winds
76 particularly in regions north of the sub-Antarctic front (Jarníková and Tortell, 2016). Around
77 3.4 Tg of sulfur is released from the Southern Ocean to the atmosphere between December

78 and February, a flux that represents ~15 % of global annual emissions of DMS (Jarníková
79 and Tortell, 2016). Elevated CCN numbers are seen in the most biologically active regions of
80 the Southern Ocean, with a significant contribution from DMS-driven secondary aerosol
81 formation processes (McCoy et al., 2015; Korhonen et al., 2008a). DMS-derived aerosols
82 from this region are estimated to contribute 6 to 10 W m^{-2} to reflected short wavelength
83 radiation, similar to the influence of anthropogenic aerosols in the polluted Northern
84 Hemisphere (McCoy et al., 2015). Given this important influence of polar DMS emissions on
85 atmospheric processes and climate, it is vital we increase our understanding of the influence
86 of future ocean acidification on DMS production.

87 The polar oceans are characterised by high dissolved inorganic carbon (C_T) concentrations
88 and a low carbonate system buffering capacity, mainly due to the increased solubility of CO_2
89 in cold waters (Sabine et al., 2004; Orr et al., 2005). This makes these regions particularly
90 susceptible to the impacts of ocean acidification (OA). For example, extensive carbonate
91 mineral undersaturation is expected to occur in Arctic waters within the next 20 – 80 years
92 (McNeil and Matear, 2008; Steinacher et al., 2009). OA has already led to a 0.1 unit decrease
93 in global surface ocean pH, with a further fall of ~0.4 units expected by the end of the century
94 (Orr et al., 2005). The greatest declines in pH are likely in the Arctic Ocean with a predicted
95 fall of 0.45 units by 2100 (Steinacher et al., 2009), with a fall of ~0.3 units predicted for the
96 Southern Ocean (McNeil and Matear, 2008; Hauri et al., 2016). OA is occurring at a rate not
97 seen on Earth for 300 Ma, and so the potential effects on marine organisms, communities and
98 ecosystems could be wide-ranging and severe (Raven et al., 2005; Hönisch et al., 2012).
99 Despite the imminent threat to polar ecosystems and the importance of DMS emissions to
100 atmospheric processes, our knowledge of the response of polar DMS production to OA is
101 limited to a single mesocosm experiment performed in a coastal fjord in Svalbard (Riebesell
102 et al., 2013a; Archer et al., 2013) and one shipboard microcosm experiment with seawater

103 collected from Baffin Bay (Hussherr et al., 2017). Both studies reported significant

104 reductions in DMS concentrations with increasing levels of pCO_2 during seasonal

105 phytoplankton blooms. Hussherr et al. (2017) also saw reductions in total DMSP whilst

106 Archer et al. (2013) observed a significant increase in this compound, driven by CO_2-induced

107 increases in growth and abundance of dinoflagellates. However, these two single studies

108 provide limited information on the wider response of the open Arctic or Southern Oceans.

109 Mesocosm experiments have been a critical tool for assessing OA effects on surface ocean

110 communities (Engel et al., 2005; Engel et al., 2008; Schulz et al., 2008; Hopkins et al., 2010;

111 Schulz et al., 2013; Webb et al., 2015; Kim et al., 2006; Kim et al., 2010; Crawfurd et al.,

112 2016; Webb et al., 2016). The response of DMS to OA has been examined several times,

113 predominantly at the same site in Norwegian coastal waters (Vogt et al., 2008; Hopkins et al.,

114 2010; Webb et al., 2015; Avgoustidi et al., 2012), twice in Korean coastal waters (Kim et al.,

115 2010; Park et al., 2014), and a single study in the coastal Arctic waters of Svalbard (Archer et

116 al., 2013). Mesocosm enclosures, ranging in volume from ~11,000 – 50,000 L, allow the

117 response of surface ocean communities to a range of CO_2 treatments to be monitored under

118 near-natural light and temperature conditions over time scales (weeks - months). This is

119 sufficient time to ~~that~~ allow a 'winners vs loser' dynamic to develop, whereby the succession

120 of the phytoplankton community is altered due to the differing sensitivities of different

121 taxonomic groups to changes in carbonate chemistry (Bach et al., 2017). The response of

122 DMS cycling to elevated CO_2 is generally driven by changes to the microbial community

123 structure (Brussaard et al., 2013; Archer et al., 2013; Hopkins et al., 2010; Engel et al., 2008).

124 The pseudo-natural conditions of mesocosm experiments offer the benefit of the inclusion of

125 community dynamics of three or more trophic levels, providing the opportunity to investigate

126 the influence of ecosystem dynamics on biogeochemical processes under experimental

127 conditions (Riebesell et al., 2013b). Furthermore, physical processes such as particle export

(Bach et al., 2016), which would be excluded by smaller scale experiments, can be considered within the holistic mesocosm framework, and make the results relevant for use within Earth system models (Six et al. 2013). However, the size, construction and associated costs of 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 presenting data from four previously unpublished experiments from the NW European shelf cruise, and 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 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. 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, and the potential to induce a ‘shock’ response to the sudden alteration of carbonate chemistry should be considered, particularly when working at

153 the smaller microcosm scale. Nevertheless, our approach can provide insight into the
154 physiological response and level of sensitivity to future OA of a variety of polar surface
155 ocean communities adapted to different in situ carbonate chemistry environments (Stillman
156 and Paganini, 2015), alongside the implications this may have for DMS production.

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

165 2 Material and Methods

166 2.1 Sampling stations

167 This study presents new data from two sets of field experiments carried out as a part of the
168 UK Ocean Acidification Research Programme (UKOA) aboard the RRS James Clark Ross in
169 the sub-Arctic and Arctic in June-July 2012 (JR271) and in the Southern Ocean in January-
170 February 2013 (JR274). Data are combined with the results from an earlier study on board the
171 RRS Discovery (D366) described in Hopkins & Archer (2014) performed in the temperate
172 waters of the NW European shelf. Additionally, four previously unpublished experiments
173 from D366 are also included (E02b, E04b, E05b, E06) as well as two temperate experiments
174 from JR271 (NS and IB) (see Table 1). In total, 18 incubations were performed; 11 in
175 temperate and sub-Arctic waters of the NW European shelf and North Atlantic, 3 in Arctic
176 waters and 4 in the Southern Ocean. Figure 1 shows the cruise tracks, surface concentrations

177 of DMS and total DMSP (DMSPt) at CTD sampling stations as well as the locations of
178 sampling for shipboard microcosms (See Table 1 for further details).

179 **2.2 Shipboard microcosm experiments**

180 The general design and implementation of the experimental microcosms for JR271 and
181 JR274 was essentially the same as for D366 and described in Richier et al. (2014), (2018) and
182 Hopkins & Archer (2014), but with the additional adoption of trace metal clean sampling and
183 incubation techniques in the low trace metal open ocean waters (see Richier et al. (2018)). At
184 each station, pre-dawn vertical profiles of temperature, salinity, oxygen, fluorescence,
185 turbidity and irradiance were used to choose and characterise the depth of experimental water
186 collection. Subsequently, water was collected within the mixed layer from three successive
187 separate casts of a trace-metal clean titanium CTD rosette comprising twenty-four 10 L
188 Niskin bottles. Depth profiles of auxiliary measurements are shown in Figure 2. Each cast
189 was used to fill one of a triplicated set of experimental bottles (locations and sample depths,
190 Table 1). Bottles were sampled within a class-100 filtered air environment within a trace
191 metal clean container to avoid contamination during the set up. The water was directly
192 transferred into acid-cleaned 4.5 L polycarbonate bottles using acid-cleaned silicon tubing,
193 with no screening or filtration.

194 The carbonate chemistry within the experimental bottles was manipulated by addition of
195 equimolar HCl and $NaHCO_3^-$ (1 mol L^{-1}) to achieve a range of CO_2 treatments: Mid CO_2
196 (Target: 550 µatm), High CO_2 (Target: 750 µatm), High+ CO_2 (Target: 1000 µatm) and
197 High++ CO_2 (Target: 2000 µatm) () (Gattuso et al., 2010). Three treatment levels were used
198 during the sub-Arctic/Arctic microcosms (Mid, High, High+). For Southern Ocean
199 experiments, two experiments (*Drake Passage* and *Weddell Sea*) underwent
200 combinedconsidered one CO_2 treatments CO_2 and Fe additions (ambient, Fe (2 nM), High
201 CO_2), Fe (2 nM) & High CO_2 (only high CO_2 treatments will be examined here; no response

202 ~~to Fe was detected in DMS or DMSP concentrations)~~. Three CO_2 treatments (High, High+,

203 High++) were tested in the last two experiments (*South Georgia* and *South Sandwich*). Full

204 details of the carbonate chemistry manipulations can be found in Richier et al. (2014) and

205 Richier et al. (2018). Broadly, achieved pCO_2 levels were well-matched to target values at the

206 start of the experiments (0 h), although differences in pCO_2 between target and initial values

207 were greater in the higher pCO_2 treatments, due to lowered carbonate system buffer capacity

208 at higher pCO_2. For all 18 experiments, actual pCO_2 values at 0 h were on average around

209 89% ± 12% (± 1 SD) of target values. The attained pCO_2 values, and pCO_2 at each

210 experimental time point, are presented in Figures 3 and 4. After first ensuring the absence of

211 bubbles or headspace, the bottles were sealed with high density polyethylene (HDPE) lids

212 with silicone/ polytetrafluoroethylene (PTFE) septa and placed in the incubation container.

213 Bottles were incubated inside a custom-designed temperature- and light-controlled shipping

214 container, set to match (±<1°C) the *in situ* water temperature at the time of water collection

215 (shown in Table 1) (see Richier et al. 2018). A constant light level (100 µE m^{-2} s^{-1}) was

216 provided by daylight simulating LED panels (Powerpax, UK). The light period within the

217 microcosms was representative of *in situ* conditions. For the sub-Arctic/Arctic Ocean

218 stations, experimental bottles were subjected to continuous light representative of the 24 h

219 daylight of the Arctic summer. For Southern Ocean and all temperate water stations, an 18:6

220 light: dark cycle was used. Each bottle belonged to a set of triplicates, and sacrificial

221 sampling of bottles was performed at two time points (see Table 1 for exact times). Use of

222 three sets of triplicates for each time point allowed for the sample requirements of the entire

223 scientific party (3 x 3 bottles, x 2 time points (see Table 1 for specific times for each

224 experiment), x 4 CO_2 treatments = 72 bottles in total). Experiments were run for between 4

225 and 7 days (96 h – 168 h) (15 out of 18 experiments), with initial sampling proceeded by two

226 further time points. For three temperate experiments (E02b, E04b, E05b see Table 1 and

Table 2) shorter two day incubations were performed, with a single sampling point at the end. E06 was run for 96 h (Table 1 and 2). ~~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.~~ Incubation times were extended for Southern Ocean stations *Weddell Sea*, *South Georgia* and *South Sandwich* (see Table 1) as minimal CO_2 response, attributed to slower microbial metabolism at low water temperatures, was observed for Arctic stations and the first Southern Ocean station *Drake Passage*. The differential growth/metabolic rates between temperate and polar waters justify the comparison of response of shorter duration temperate experiments and longer duration polar experiments. 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). Samples for carbonate chemistry measurements were taken first, followed by sampling for DMS, DMSP and related parameters.

2.3 Standing stocks of DMS and DMSP

Methods for the determination of seawater concentrations of DMS and DMSP are identical to those described in Hopkins & Archer (2014) and will therefore be described in brief here. Seawater DMS concentrations were determined by cryogenic purge and trap, with gas chromatography and pulsed flame photometric detection (GC-PFPD) (Archer et al., 2013). DMSP concentrations were measured as DMS following alkaline hydrolysis. Samples for total DMSP concentrations from temperate waters were fixed by addition of 35 µl of 50 % H_2SO_4 to 7 mL of seawater (Kiene and Slezak, 2006), and analysed following hydrolysis within 2 months of collection (Archer et al., 2013). Samples of DMSP that were collected in

251 polar waters were hydrolysed within 1 h of sample collection and analysed 6 – 12 h later. The
252 H_2SO_4 fixation method was not used for samples from polar waters given the likely
253 occurrence of *Phaeocystis sp*. which can result in the overestimation of DMSP concentrations
254 (del Valle et al., 2009). Similarly, concentrations of DMSPp were determined at each time
255 point by gravity filtering 7 ml of sample onto a 25 mm GF/F filter and preserving the filter in
256 7 ml of 35 mM H_2SO_4 in MQ-water (temperate samples) or immediately hydrolysing (polar
257 samples) and analysing by GC-PFPD. DMS calibrations were performed using alkaline cold-
258 hydrolysis (1 M NaOH) of DMSP sequentially diluted three times in MilliQ water to give
259 working standards in the range 0.03 – 3.3 ng S mL^{-1}. Five point calibrations were performed
260 every 2 – 4 days throughout the cruise.

261 **2.4 *De novo* DMSP synthesis**

262 *De novo* DMSP synthesis and gross production rates were determined for all microcosm
263 experiments, except *Barents Sea* and *South Sandwich*, at each experimental time point, using
264 methods based on the approach of Stefels et al. (2009) and described in detail in Archer et al.
265 (2013) and Hopkins and Archer (2014). Triplicate rate measurements were determined for
266 each CO_2 level. For each rate measurement three x 500 mL polycarbonate bottles were filled
267 by gently siphoning water from each replicate microcosm bottle. Trace amounts of
268 $NaH^{13}CO_3$, equivalent to ~6 % of *in situ* dissolved inorganic carbon (C_T), were added to each
269 500 mL bottle. The bottles were incubated in the microcosm incubation container with
270 temperature and light levels as described earlier. Samples were taken at 0 h, then at two
271 further time points over a 6 - 9 h period. At each time point, 250 mL was gravity filtered in
272 the dark through a 47 mm GF/F filter, the filter gently folded and placed in a 20 mL serum
273 vial with 10 mL of Milli-Q and one NaOH pellet, and the vial was crimp-sealed. Samples

274 were stored at -20°C until analysis by proton transfer reaction-mass spectrometer (PTR-MS)

275 (Stefels et al. 2009).

276 The specific growth rate of DMSP (μDMSP) was calculated assuming exponential growth

277 from:

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

278

279 (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

280 DMSP relative to total DMSP at time t, at the preceding time point (t-1) and at the subsequent

281 time point (t+1), respectively. Values of ^{64}MP were calculated from the protonated masses of

282 DMS as: mass 64/(mass63 + mass64 + mass65), determined by PTR-MS. $^{64}MP_{eq}$ is the

283 theoretical equilibrium proportion of 1 x ^{13}C based on a binomial distribution and the

284 proportion of tracer addition. An isotope fractionation factor α_k of 1.06 is included, based on

285 laboratory culture experiments using *Emiliania huxleyi* (Stefels et al. 2009). In vivo DMSP

286 gross production rates during the incubations (nmol L^{-1} h^{-1}) were calculated from μDMSP

287 and the initial particulate DMSP (DMSPp) concentration of the incubations (Hopkins &

288 Archer 2014, Stefels et al. 2009). These rates provide important information on how the

289 physiological status of DMSP-producing cells may be affected by OA within the bioassays.

290 **2.5 Seawater carbonate chemistry analysis**

291 The techniques and methods used to determine both the *in situ* and experimental carbonate

292 chemistry parameters, and to manipulate seawater carbonate chemistry within the

293 microcosms, are described in Richier et al. (2014) and will be only given in brief here.

294 Experimental T_0 measurements were taken directly from CTD bottles, and immediately

295 measured for total alkalinity (A_T) (Apollo SciTech AS-Alk2 Alkalinity Titrator) and

296 dissolved inorganic carbon (C_T) (Apollo SciTech C_T analyser (AS-C3) with LICOR 7000).

297 The CO2SYS programme (version 1.05) (Lewis and Wallace, 1998) was used to calculate the

298 remaining carbonate chemistry parameters including pCO_2.

299 Measurements of T_A and C_T were made from each bottle at each experimental time point and

300 again used to calculate the corresponding values for pCO_2 and pH_T. The carbonate chemistry

301 data for each sampling time point for each experiment are summarised in Supplementary

302 Table S1, S2 and S3 (Experimental starting conditions are given in Table 1).

303 **2.6 Chlorophyll a (Chl *a*) determinations**

304 Concentrations of Chl *a* were determined as described in Richier et al. (2014). Briefly, 100

305 mL aliquots of seawater from the incubation bottles were filtered through either 25 mm GF/F

306 (Whatman, 0.7 µm pore size) or polycarbonate filters (Whatman, 10 µm pore size) to yield

307 total and >10 µm size fractions, with the <10 µm fraction calculated by difference. Filters

308 were extracted in 6 mL HPLC-grade acetone (90%) overnight in a dark refrigerator.

309 Fluorescence was measured using a Turner Designs Trilogy fluorometer, which was regularly

310 calibrated with dilutions of pure Chl *a* (Sigma, UK) in acetone (90%).

311 **2.8 Community composition**

312 Small phytoplankton community composition was assessed by flow cytometry. For details of

313 methodology, see Richier et al. (2014).

314 **2.9 Data handling and statistical analyses**

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

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

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

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

319 Experiment location nested within Cruise location (see Table 1 for station IDs) and (iii) CO_2
320 level: 385, 550, 750, 1000 and 2000 µatm. Main effects and pairwise comparisons of the
321 different factors were analysed through unrestricted permutations of raw data. If a low
322 number of permutations were generated then the *p*-value was obtained through random
323 sampling of the asymptotic permutation distribution, using Monte Carlo tests.

324 One-way analysis of variance was used to identify differences in ratio of >10 µm Chl *a* to
325 total Chl *a* ($chl_{>10um}$: chl_{tot} , see Discussion). Initially, tests of normality were applied ($p<0.05$
326 = not normal), and if data failed to fit the assumptions of the test, linearity transformations of
327 the data were performed (logarithmic or square root), and the ANOVA proceeded from this
328 point. The results of ANOVA are given as follows: F = ratio of mean squares, df = degrees of
329 freedom, p = level of confidence. For those data still failing to display normality following
330 transformation, a rank-based Kruskal-Wallis test was applied (H = test statistic, df = degrees
331 of freedom, p = level of confidence).

332 **3 Results**

333 **3.1 Sampling stations**

334 At temperate sampling stations, sea surface temperatures ranged from 10.7°C for *Iceland*
335 *Basin*, to 15.3°C for *Bay of Biscay*, with surface salinity in the range 34.1 – 35.2, with the
336 exception of station E05b which had a relatively low salinity of 30.5 (Figure 2 and Table 1).
337 Seawater temperatures at the polar microcosm sampling stations ranged from -1.5°C at sea-
338 ice influenced stations (*Greenland Ice-edge* and *Weddell Sea*) up to 6.5°C for *Barents Sea*
339 (Fig. 2 A). Salinity values at all the Southern Ocean stations were <34, whilst they were ~35
340 at all the Arctic stations with the exception of *Greenland Ice-edge* which had the lowest
341 salinity of 32.5 (Fig. 2 B). Phototrophic nanoflagellate abundances were variable, with >3 x
342 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}

343 for all other stations (Fig. 2 D). Total bacterial abundances ranged from 3 x 10^5 cells mL^{-1} at
344 *Greenland Ice-edge* up to 3 x 10^6 cells mL^{-1} at *Barents Sea* (Fig. 2 E).

345 Chl *a* concentrations in temperate waters ranged from 0.3 µg L^{-1} for two North Sea stations
346 (*E05* and *North Sea*) up to 3.5 µg L^{-1} for *Irish Sea* (Figure 2 and Table 1). Chl a was also
347 variable in polar waters, exceeding 4 µg L^{-1} at *South Sandwich* and 2 µg L^{-1} at *Greenland Ice-*
348 *edge*, whilst the remaining stations ranged from 0.2 µg L^{-1} (*Weddell Sea*) to 1.5 µg L^{-1}
349 (*Barents Sea*) (Figure 2). The high Chl *a* concentrations at *South Sandwich* correspond to low
350 in-water irradiance levels at this station (Fig. 2 C).

351 In temperate waters, maximum DMS concentrations were generally seen in near surface
352 measurements, ranging from 1.0 nmol L^{-1} for *E04* to 21.1 nmol L^{-1} for *E06*, with rapidly
353 decreasing concentrations with depth (Figure 2 G). As an exception to this, DMS
354 concentrations at *South Sandwich* showed a sub-surface maximum of 15 nM at 32 m,
355 coincident with a subsurface Chl *a* maximum of 5.4 µg L^{-1}. ~~-~~DMSP generally ranged from 12
356 – 20 nmol L^{-1}, except *Barents Sea* where surface concentrations exceeded 60 nmol L^{-1}
357 (Figure 2 H). DMSP ~~also generally~~tended to peak~~ed~~ in the near surface waters, ranging from
358 12.0 nmol L^{-1} for E04 to 72.5 nmol L^{-1} for *E06*, although in some cases~~but the~~ a subsurface
359 maximum in overall DMSP concentrations was seen, as observed for *E05b* ~~of~~ (89.8 nmol L^{-1}
360 ~~was observed at~~ ~20 m), and again coincident with a subsurface Chl a peak of >2 µg L^{-1} ~~for~~
361 ~~*E05b*~~ (Figure 2 F and H). Surface DMS concentrations in polar waters were generally lower
362 than temperate waters, ranging from 1 – 3 nmol L^{-1}, with the exception of *South Sandwich*
363 where concentrations of ~12 nmol L^{-1} were observed (Figure 2 G), and resulted in high
364 DMS:DMSP of 0.6 – 0.9 in the surface layer (Figure 2 I). DMS:DMSP did not exceed 0.5 at
365 any other sampling stations.~~.~~ ~~DMSP generally ranged from 12 – 20 nmol L^{-1}, except *Barents*~~
366 ~~*Sea* where surface concentrations exceeded 60 nmol L^{-1} (Figure 2 H).~~

3.2 Response of DMS and DMSP to OA

The temporal trend in DMS concentrations showed a similar pattern for the three Arctic Ocean experiments. Initial concentrations of 1 – 2 nmol L^{-1} remained relatively constant over the first 48 h and then showed small increases of 1 - 4 nmol L^{-1} over the remainder of the incubation period (Figure 3). 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. Initial DMSP concentrations were more variable, from 6 nmol L^{-1} at *Greenland Ice-edge* to 12 nmol L^{-1} at *Barents Sea*, and either decreased slightly (net loss 1 – 2 nmol L^{-1} GG), or increased slightly (net increase ~4 nmol L^{-1} *Greenland Ice-edge*, ~3 nmol L^{-1} *Barents Sea*) (Figure 5 A – C). DMSP concentrations were found to decrease significantly in response to elevated CO_2 after 48 h for *Barents Sea* (Fig. ~~4~~ 5 C, t = 2.05, p = 0.025), whist no significant differences were seen after 96 h. No other 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 4). 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. 4 D). 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 5 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.

392 Concentrations were not generally pCO_2-treatment dependent with the exception of the final
393 time point at *South Georgia* (144 h) when a significantly lower DMSP with increasing CO_2
394 was observed (PERMANOVA, t = -5.685, p<0.001).

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

400 **3.3 Response of de novo DMSP synthesis and production to OA**

401 Rates of *de novo* DMSP synthesis (μDMSP) at initial time points ranged from 0.13 d^{-1}
402 (*Weddell Sea*, Fig. 6 G) to 0.23 d^{-1} (*Greenland Ice-edge*, Fig. 6 C), whilst DMSP production
403 ranged from 0.4 nmol L^{-1} d^{-1} (*Greenland Gyre*, Fig. 6 B) to 2.27 nmol L^{-1} d^{-1} (*Drake Passage*,
404 Fig. 6 F). Maximum rates of μDMSP of 0.37 -0.38 d^{-1} were observed at *Greenland Ice-edge*
405 after 48 h of incubation in all CO_2 treatments (Fig. 6 C). The highest rates of DMSP
406 production were observed at *South Georgia* after 96 h of incubation, and ranged from 4.1 –
407 6.9 nmol L^{-1} d^{-1} across CO_2 treatments (Fig. 6 J). Rates of DMSP synthesis and production
408 were generally lower than those measured in temperate waters (Hopkins and Archer, 2014)
409 (Initial rates: μDMSP 0.33 – 0.96 d^{-1}, 7.1 – 37.3 nmol L^{-1} d^{-1}), but were comparable to
410 measurements made during an Arctic mesocosm experiment (Archer et al., 2013) (0.1 – 0.25
411 d^{-1}, 3 – 5 nmol L^{-1} d^{-1} in non-bloom conditions). The lower rates in cold polar waters likely
412 reflect slower metabolic processes and are reflected by standing stock DMSP concentrations
413 which were also lower than in temperate waters (5 – 40 nmol L^{-1} polar, 8 – 60 nmol L^{-1}
414 temperate (Hopkins and Archer, 2014)). No consistent effect of high CO_2 were observed for
415 either DMSP synthesis or production in polar waters, similar to findings for DMSP standing

416 stocks. However, some notable but contrasting differences between CO_2 treatments were
417 observed. There was a 36% and 37% increase in μDMSP and DMSP production respectively
418 at 750 μatm for the *Drake Passage* after 96 h (Figure 6 E, F), and a 38% and 44% decrease in
419 both at 750 μatm after 144 h for *Weddell Sea* (Figure 5 G, H). For *Drake Passage*, the
420 difference between treatments at 96 h coincided with significantly higher nitrate
421 concentrations in the High CO_2 treatment (Nitrate/nitrite at 96 h: Ambient = 18.9 ± 0.2 μmol
422 L^{-1}, +CO_2 = 20.2 ± 0.1 μmol L^{-1}, ANOVA $F = 62.619$, $df = 1$, $p = 0.001$). However, it is
423 uncertain whether the difference in nutrient availability between treatments (approximately 5
424 %) would be significant enough to strongly influence the rate of DMSP production.

425 The differences in DMSP production rates did not correspond to any other measured
426 parameter. It is possible that changes in phytoplankton community composition may have led
427 to differences in DMSP production rates for *Drake Passage* and *Weddell Sea*, but no
428 quantification of large cells (diatoms, dinoflagellates) was undertaken for these experiments.

429 4 Discussion

430 4.1 Regional differences in the response of DMS(P) to OA

431 We combine our findings from the polar oceans with those from temperate waters into a
432 meta-analysis in order to assess the regional variability and drivers in the DMS(P) response to
433 OA. Figures 7 and 8 provide an overview of the results discussed so far in this current study,
434 together with the results from Hopkins & Archer (2014) as well as the results from 4
435 previously unpublished microcosm experiments from the NW European shelf cruise and a
436 further 2 temperate water microcosm experiments from the Arctic cruise (*North Sea* and
437 *Iceland Basin*, Table 1). This gives a total of 18 microcosm experiments, each with between 1
438 and 3 high CO_2 treatments.

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

446 The relative treatment effects ($[x]_{highCO2}/[x]_{ambientCO2}$) for DMS and DMSP (Figure 7), DMSP
447 synthesis and production (Figure 8), and Chl *a* and phototrophic nanoflagellate abundance
448 (Figure 9) are plotted against the Revelle Factor of the sampled waters. The Revelle Factor
449 (*R*), calculated here with CO2Sys using measurements of carbonate chemistry parameters (R
450 $= (\Delta pCO_2/\Delta TCO_2)/(pCO_2/TCO_2)$, Lewis and Wallace, 1998), describes how the partial
451 pressure of CO_2 in seawater (PCO_2) changes for a given change in DIC (Sabine et al., 2004;
452 Revelle and Suess, 1957). Its magnitude varies latitudinally, with lower values (9 – 12) from
453 the tropics to temperate waters, and the highest values in cold high latitude waters (13 – 15).
454 Thus polar waters can be considered poorly buffered with respect to changes in DIC.
455 Therefore, biologically-driven seasonal changes in seawater pCO_2 would result in larger
456 changes in pH than would be experienced in temperate waters (Egleston et al., 2010).
457 Furthermore, the seasonal sea ice cycle strongly influences carbonate chemistry, such that sea
458 ice regions exhibit wide fluctuations in carbonate chemistry (Revelle and Suess, 1957; Sabine
459 et al., 2004). Sampling stations with a *R* above ~12 represent the seven polar stations (right of
460 red dashed line Fig. 7, 8, 9). The surface waters of the polar oceans have naturally higher
461 levels of DIC and a reduced buffering capacity, driven by higher CO_2 solubility in colder
462 waters (Sabine et al., 2004). Thus, the relationship between experimental response and *R* is a
463 simple way of demonstrating the differences in response to OA between temperate and polar

464 waters and provides some insight into how the CO_2 sensitivity of different surface ocean

465 communities may relate to the *in situ* carbonate chemistry. The effect of elevated CO_2 on

466 DMS concentrations at polar stations, relative to ambient controls, was minimal at both

467 sampling points, and is in strong contrast to the results from experiments performed in waters

468 with lower values of R on the NW European shelf. In contrast, at temperate stations, DMSP

469 concentrations displayed a clear negative treatment effect, whilst at polar stations a positive

470 effect was evident under high CO_2 and particularly at the first time point (48 – 96 h) (Fig. 7 C

471 and D). *De novo* DMSP synthesis and DMSP production rates show a less consistent

472 response in either environment (Fig. 8 A and B), although a significant suppression of

473 DMSP production rates in temperate waters compared to polar waters was seen (Fig. 8 B,

474 Kruskal-Wallis One Way ANOVA $H = 8.711$, $df = 1$, $p = 0.003$). A similar but not significant

475 response was seen for *de novo* DMSP synthesis (Fig. 8A).

476 Our data imply that DMSP concentrations in temperate waters were downregulated in

477 response to OA, attributed to the adverse effects of rapid OA on the growth of DMSP

478 producers which led to reductions in the abundance of these types of phytoplankton (Richier

479 et al. 2014, Hopkins and Archer 2014). By comparison, a more muted, but generally positive,

480 DMSP response was seen in polar waters at the first time point, whilst these treatment effects

481 were more or less undetectable by the second time point. There is some evidence that the

482 enhanced DMSP concentrations in polar waters were accompanied by increased DMSP

483 production rates (Figure 8), although data is not available for all experiments. However, these

484 changes may reflect a short term 'shock' physiological protective response to the

485 experimental OA, similar to that seen in response to other short term stressors such as high

486 irradiance that result in an increase in DMSP concentrations (Sunda et al., 2002;Galindo et

487 al., 2016). The lack of treatment effect in DMSP concentrations by the second time point may

488 be indicative that the community had, to some extent, acclimated to the change, allowing

489 DMSP production/concentrations to return to baseline levels. This may reflect a higher
490 degree of tolerance to rapid changes in carbonate chemistry amongst polar communities -
491 species which are already adapted to highly variable irradiance/carbonate chemistry regimes
492 (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015). Further
493 experiments with polar communities would help to unravel the potential importance of such
494 mechanisms and whether they facilitated the ability of polar phytoplankton communities to
495 resist the high CO_2 treatments.

496 This data suggests that DMSP concentrations in polar waters may be upregulated in response
497 to OA compared to temperate waters. Given the potential photoprotective and antioxidant
498 role that DMSP plays, and which may be particularly relevant in the highly variable polar
499 sea-ice environment (e.g. irradiance, carbonate chemistry), these changes may reflect a
500 physiological protective response to the experimental OA (Sunda et al., 2002;Galindo et al.,
501 2016). An increase in DMSP concentrations could have either resulted from a physiological
502 up-regulation of DMSP synthesis or a reduction in bacterial DMSP consumption processes.
503 However, DMSP synthesis rates did not provide any conclusive evidence of upregulation in
504 polar waters. Instead, we observed a suppression of rates in temperate waters which may
505 reflect the adverse effects of rapid OA on the growth of DMSP producers which led to
506 reductions in the abundance of these types of phytoplankton (Richier et al. 2014, Hopkins and
507 Archer 2014). In contrast, the lesser positive but less pronounced response seen in polar
508 waters may reflect a higher degree of higher acclimative tolerance to rapid changes in
509 carbonate chemistry amongst polar communities. Further experiments with polar
510 communities would help to further unravel the potential importance of such mechanisms, and
511 whether they facilitated the ability of polar phytoplankton communities to resist the high CO_2
512 treatments.

The responses to OA observed for DMS and DMSP production are likely to be reflected in the dynamics of the DMSP-producing phytoplankton. In an assessment across all experiments, Richier et al. (2018) showed that the magnitude of biological responses to short term CO_2 changes reflected the buffer capacity of the sampled waters. A consistent suppression of net growth rates in small phytoplankton (<10 µm) and total Chl *a* concentrations was observed under high CO_2 within experiments performed in temperate waters with higher buffer capacity. ~~In an assessment across all experiments, Richier et al. (2018) showed that the maximal response to OA of total Chl *a* and net growth rates of small phytoplankton (<10 µm) observed during each experiment, declined the most in relation to increased buffering capacity and temperature of the initial water.~~ Generally, less significant relationships were found between the phytoplankton response and the other wide range of physical, chemical or biological variables that were examined (Richier et al. 2018).

In correspondence with the analyses carried out by Richier et al (2018), at 48 – 96 h (see Table 1), a statistically significant difference in response was seen between temperate and polar waters for Chl *a* (Kruskal-Wallis One Way ANOVA $H = 20.577$, $df = 1$, $p<0.001$). In general, at polar stations phytoplankton showed minimal response to elevated CO_2, in contrast to a strong negative response in temperate waters (Fig. 9A). By the second time point (96 – 144 h, see Table 1), no significant difference in response of Chl *a* between temperate and polar waters was apparent (Fig. 9B). As shown in Richier et al. (2014), phototrophic nanoflagellates responded to high CO_2 with large decreases in abundance in temperate waters and increases in abundance in polar waters (Fig. 9 C and D), with some exceptions: *North Sea* and *South Sandwich* gave the opposite response. The responses had lessened by the second time point (96 – 168 h, see Table 1).

537 In contrast, bacterial abundance did not show the same regional differences in response to
538 high CO_2 (see Hopkins and Archer (2014) for temperate waters, and Figure S1,
539 supplementary information, for polar waters). Bacterial abundance in temperate waters gave
540 variable and inconsistent responses to high CO_2. For all Arctic stations, as well as Southern
541 Ocean stations *Drake Passage* and *Weddell Sea*, no response to high CO_2 was observed. For
542 *South Georgia* and *South Sandwich*, bacterial abundance increased at 1000 and 2000 µatm,
543 with significant increases for *South Georgia* after 144 h of incubation (ANOVA $F = 137.936$,
544 $p<0.001$). Additionally, at Arctic stations *Greenland Gyre* and *Greenland Ice-edge*, no
545 overall effect of increased CO_2 on rates of DOC release, total carbon fixation or POC : DOC
546 was observed (Poulton et al. 2016).

547 Overall, the observed differences in the regional response of DMSP and DMS to carbonate
548 chemistry manipulation could not be attributed to any other measured factor that varied
549 systematically between temperate and polar waters. These include ambient nutrient
550 concentrations, which varied considerably but where direct manipulation had no influence on
551 the response, and initial community structure, which was not a significant predictor of the
552 phytoplankton response (Richier et al. 2018).

553 **4.2 Influence of community cell-size composition on DMS response**

554 It has been proposed that variability in the concentrations of carbonate species (e.g. pCO_2,
555 HCO_3^-, CO_3^{2-}) experienced by phytoplankton is related to cell size, such that smaller-celled
556 taxa (<10 µm) with a reduced diffusive boundary layer are naturally exposed to relatively less
557 variability compared to larger cells (Flynn et al., 2012). Thus, short-term and rapid changes in
558 carbonate chemistry, such as the kind imposed during our microcosm experiments, may have
559 a disproportionate effect on the physiology and growth of smaller celled species. Larger cells
560 may be better able to cope with variability as normal cellular metabolism results in significant

561 cell surface changes in carbonate chemistry parameters (Richier et al., 2014). Indeed, the
562 marked response in DMS concentrations to short term OA in temperate waters has been
563 attributed to this enhanced sensitivity of small phytoplankton (Hopkins and Archer, 2014).
564 Was the lack of DMS response to OA in polar waters therefore a result of the target
565 communities being dominated by larger-celled, less carbonate-sensitive species?

566 Size-fractionated Chl *a* measurements give an indication of the relative contribution of large
567 and small phytoplankton cells to the community. For experiments in temperate waters, the
568 mean ratio of >10 µm Chl *a* to total Chl *a* (hereafter *>10 µm : total*) of 0.32 ± 0.08 was lower
569 than the ratio for polar stations of 0.54 ± 0.13 (Table 2). Although the difference was not
570 statistically significant, this might imply a tendency towards communities dominated by
571 larger cells in the polar oceans, which may partially explain the apparent lack of DMS
572 response to elevated CO_2. However, this is not a consistent explanation for the observed
573 responses. For example, the Arctic *Barents Sea* station had the lowest observed *>10 µm :*
574 *total* of 0.04 ± 0.01, suggesting a community comprised almost entirely of <10 µm cells; yet
575 the response to short term OA differed to the response seen in temperate waters. No
576 significant CO_2 effects on DMS or DMSP concentrations or production rates were observed
577 at this station, whilst total Chl *a* significantly increased under the highest CO_2 treatments
578 after 96 h (PERMANOVA $F = 33.239$, $p<0.001$). Thus, our cell size theory does not hold for
579 all polar waters, suggesting that regardless of the dominant cell size, polar communities are
580 more resilient to OA. In the following section, we explore the causes of this apparent
581 insensitivity to OA in terms of the environmental conditions to which the communities have
582 presumably adapted.

583 **4.3 Adaptation to a variable carbonate chemistry environment**

584 Given that DMS production by polar phytoplankton communities appeared to be insensitive
585 to experimental OA compared to significant sensitivity in temperate communities, we
586 hypothesise that polar communities are adapted to greater natural variability in carbonate
587 chemistry over spatial and seasonal scales. This greater variability is partly the result of the
588 lower buffering capacity (Revelle Factor) of polar waters compared to lower latitude waters,
589 and partly due to specific processes that occur in the polar regions that strongly alter DIC
590 concentrations (e.g. sea ice formation and melt, enhanced CO_2 dissolution into cold polar
591 waters, upwelling of CO_2 rich water). Therefore, polar plankton communities are not only
592 subject to geophysical processes that strongly alter in situ carbonate chemistry on both spatial
593 and seasonal scales, but such changes are accompanied by larger pH changes than would
594 occur in more strongly buffered temperate waters. ~~such that~~Therefore, polar surface ocean
595 communities are perhaps more likely to ~~have~~ experience~~d~~ fluctuations between high pH and
596 low pH over relatively smaller ~~short~~ time/space scales (Tynan et al., 2016). Thus below, we
597 discuss our findings in the context of the spatial pH variability we observed for each cruise
598 track, and explore some of the processes that drive this variability in polar waters.
599 Information on the pH variability at each sampling station is not available, so we cannot be
600 certain of the exact carbonate chemistry variability to which each of the sampled
601 communities may have been exposed and adapted. However, we can consider the overall
602 variability in carbonate chemistry over the spatial scales of the cruise tracks to demonstrate
603 the characteristics of each study area.
604 The polar waters sampled during our study were characterised by pronounced gradients in
605 carbonate chemistry over relatively small spatial scales. ~~,~~ ~~such that surface ocean~~
606 ~~communities are more likely to have experienced fluctuations between high pH and low pH~~
607 ~~over short time scales (Tynan et al., 2016). For example, I~~in underway samples taken along
608 each cruise track (Arctic Ocean 3500 nm, Southern Ocean 4000 nm), pH varied by 0.45 units

609 (8.00 – 8.45) in the Arctic, and 0.40 units (8.30 - 7.90) in the Southern Ocean (Tynan et al.
610 2016). In some cases this range in variability was seen over relatively small distances: Figure
611 4 in Tynan et al. (2016) shows that pH fluctuated from 8.45 and 8.0 over a distance of 50 –
612 100 miles in the sea-ice influenced Fram Strait. By comparison, pH varied by a total of 0.2
613 units (8.22 - 8.02) in underway samples from the NW European shelf sea cruise (Rerolle et
614 al. 2014). The observed horizontal gradients in polar waters were driven by different
615 physical and biogeochemical processes in each ocean. In the Arctic Ocean, this variability in
616 carbonate chemistry was partly driven by physical processes that controlled water mass
617 composition, temperate and salinity, particularly in areas such as the Fram Strait and
618 Greenland Sea. Along the ice-edge and into the Barents Sea, biological processes exerted a
619 strong control, as abundant iron resulted in high chlorophyll concentrations, low DIC and
620 elevated pH. By contrast, variations in temperature and salinity had only a small influence on
621 carbonate chemistry in the Southern Ocean in areas with iron limitation, and larger changes
622 were driven by a combination of calcification, advection and upwelling. Where iron was
623 replete, e.g. near South Georgia, biological DIC drawdown had a large impact on carbonate
624 chemistry (Tynan et al. 2016). A further set of processes was in play in sea ice influenced
625 regions. At the Arctic ice edge, abundant iron drove strong bloom development along the ice
626 edge, whilst sea ice retreat in the Southern Ocean was not always accompanied by iron
627 release (Tynan et al. 2016).
628 For comparison with Arctic stations, Hagens and Middelburg (2016) report a seasonal pH
629 variability of up to 0.25 units from a single site in the open ocean surface waters in the
630 Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability of 0.3 – 0.4 units in
631 the McMurdo Sound, Antarctica. This implies that both open ocean and sea ice-influenced
632 polar waters experience large variations in carbonate chemistry over seasonal cycles. By
633 contrast, monthly averaged surface $p\mathrm{CO_2}$ data collected from station L4 in the Western

634 English Channel over the period 2007 – 2011 provides an example of typical carbonate
635 chemistry dynamics in NW European shelf sea waters. Over this period, pH had an annual
636 range of 0.15 units (8.05 – 8.20), accompanied by a range in pCO_2 of 302 – 412 μatm (Kitidis
637 et al., 2012).

638 The sea ice environment in particular is characterised by strong spatial and seasonal
639 variability in carbonate chemistry. Sea ice is inhabited by a specialised microbial community
640 with a complex set of metabolic and physiological adaptations allowing these organisms to
641 withstand wide fluctuations in pH up to as high as 9.9 in brine channels to as low as 7.5 in the
642 under-ice water (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015).
643 The open waters associated with the ice edge also experience strong gradients in pH and
644 other carbonate chemistry parameters. This can be attributed to two processes: 1. The strong
645 seasonal drawdown of DIC due to rapid biological uptake by phytoplankton blooms at the
646 productive ice edge which drives up pH. On the Arctic cruise, increases of up to 0.33 pH
647 units were attributed to such processes in this region (Tynan et al., 2016). The effect was less
648 dramatic in the Fe-limited and less productive Weddell Sea with gradients in pH ranging
649 from 8.20 – 8.10 (Tynan et al., 2016). 2. The drawdown of DIC is countered by the release
650 and accumulation of respired DIC under sea ice due to the degradation of organic matter.
651 However, this accumulation occurs in subsurface/bottom waters, which are isolated from the
652 productive surface mixed layer by strong physical stratification and hence, of less relevance
653 to the current study.

654 The influence of sea ice on carbonate chemistry combined with the strong biological
655 drawdown of DIC in polar waters may have influenced the ability of some of the
656 communities we sampled during our study to withstand the short term changes to carbonate
657 chemistry they experienced within the bioassays. Two of our sampling stations were 'sea-ice
658 influenced': *Greenland Ice Edge* and *Weddell Sea*. Both were in a state of sea ice retreat as

659 our sampling occurred in the summer months. Sampling for the *Greenland Ice Edge* station
660 was performed in open, deep water, near to an area of thick sea ice, with low fluorescence but
661 reasonable numbers of diatoms (Leakey, 2012). Similarly, the *Weddell Sea* station was
662 located near the edge of thick pack ice but in an area of open water that allowed sampling to
663 occur without hindrance by brash ice (Tarling, 2013). At both stations we saw little or no
664 response in DMS or DMSP to experimental acidification, which may imply that the *in situ*
665 communities were more or less adapted to fluctuations in pH. Our experimental OA resulted
666 in pH decreases of between 0.4 and 0.7 units. However, it is unclear whether the communities
667 we sampled were able to withstand the artificial pH perturbation because they were adapted
668 to living in sea ice, or whether they had adapted to cope with other fluctuations in carbonate
669 chemistry that occur in polar waters.

670 In summary, this demonstrates the high variability in carbonate chemistry, including pH,
671 which polar communities may experience relative to their temperate counterparts, and which
672 is partly driven by the lowered buffer capacity of polar waters to changes in DIC, relative to
673 the more well-buffered temperate waters. This may have resulted in ~~adapted~~ polar
674 communities that have adapted to and are more resilient to experimentally-induced OA. Of
675 course, it is important to recognise that this data represent only a snapshot (4 – 6 weeks) of a
676 year, and thus does not contain information on the range in variability over daily and seasonal
677 cycles, timescales which might be considered most important in terms of the carbonate
678 system variability experienced by the cells and how this drives CO_2 sensitivity (Flynn et al.
679 2012; Richier et al. 2018). Nevertheless, this inherent carbonate chemistry variability
680 experienced by organisms living in polar waters may equip them with the resilience to cope
681 with both experimental and future OA.

682 Adaptation to such natural variability may induce the ability to resist abrupt changes within
683 the polar biological community (Kapsenberg et al., 2015). This is manifested here as

684 negligible impacts on rates of *de novo* DMSP synthesis and net DMS production in the
685 microbial communities of the polar open oceans to short term changes in carbonate
686 chemistry. A number of previous studies in polar waters have reported similar findings.
687 Phytoplankton communities were able to tolerate a pCO_2 range of 84 – 643 µatm in ~12 d
688 minicosm experiments (650 L) in Antarctic coastal waters, with no effects on
689 nanophytoplankton abundance, and enhanced abundance of picophytoplankton and
690 prokaryotes (Davidson et al., 2016; Thomson et al., 2016). In experiments under the Arctic
691 ice, microbial communities demonstrated the capacity to respond either by selection or
692 physiological plasticity to elevated CO_2 during short term experiments (Monier et al., 2014).
693 Subarctic phytoplankton populations demonstrated a high level of resilience to OA in short
694 term experiments, suggesting a high level of physiological plasticity that was attributed to the
695 prevailing strong gradients in pCO_2 levels experienced in the sample region (Hoppe et al.,
696 2017). Furthermore, a more recent study describing ten CO_2 manipulation experiments in
697 Arctic waters found that primary production was largely insensitive to OA over a large range
698 of light and temperature levels (Hoppe et al., 2018). This supports our hypothesis that,
699 relative to temperate communities, polar microbial communities may have a high capacity to
700 compensate for environmental variability (Hoppe et al., 2018), and are thus already adapted
701 to, and are able to tolerate, large variations in carbonate chemistry. Thus by performing
702 multiple, replicated experiments over a broad geographic range, the findings of this study
703 imply that the DMS response may be both a reflection of: (i) the level of sensitivity of the
704 community to changes in the mean state of carbonate chemistry, and (ii) the regional
705 variability in carbonate chemistry experienced by different communities. This highlights the
706 limitations associated with simple extrapolation of results from a small number of
707 geographically-limited experiments e.g. Six et al. (2013). Such an approach lacks a

708 mechanistic understanding that would allow a model to capture the regional variability in
709 response that is apparent from the microcosms experiments presented here.

710 **4.4 Comparison to an Arctic mesocosm experiment**

711 Experimental data clearly provide useful information on the potential future DMS response to
712 OA, but these data become most powerful when incorporated in Earth System Models (ESM)
713 to facilitate predictions of future climate. To date, two modelling studies have used ESM to
714 assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al.,
715 2013;Schwinger et al., 2017), and both have used results from mesocosm experiments.
716 However, the DMS responses to OA within our short term microcosm experiments contrast
717 with the results of most previous mesocosm experiments, and of particular relevance to this
718 study, an earlier Arctic mesocosm experiment (Archer et al., 2013). Whilst no response in
719 DMS concentrations to OA was generally seen in the polar microcosm experiments discussed
720 here, a significant decrease in DMS with increasing levels of CO_2 in the earlier mesocosm
721 study was seen. Therefore, it is useful to consider how the differences in experimental design,
722 and other factors, between microcosms and mesocosms may result in contrasting DMS
723 responses to OA.

724 The short duration of the microcosm experiments (4 – 7 d) allows the physiological
725 (phenotypic) capacity of the community to changes in carbonate chemistry to be assessed. In
726 other words, how well is the community adapted to variable carbonate chemistry and how
727 does this influence its ability to acclimate to change? Although the mesocosm experiment
728 considered a longer time period (4 weeks), the first few days can be compared to the
729 microcosms. No differences in DMS or DMSP concentrations were detected for the first
730 week of the mesocosm experiment, implying a certain level of insensitivity of DMS
731 production to the rapid changes in carbonate chemistry. In fact, when taking all previous
732 mesocosm experiments into consideration, differences in DMS concentrations have

733 consistently been undetectable during the first 5 – 10 days, implying there is a limited short-
734 term physiological response by the in situ communities (Hopkins et al., 2010; Avgoustidi et
735 al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014). This is in contrast to the
736 strong response in the temperate microcosms from the NW European shelf (Hopkins and
737 Archer, 2014). However, all earlier mesocosm experiments have been performed in coastal
738 waters, which like polar waters, can experience a large natural range in carbonate chemistry.
739 In the case of coastal waters this is driven to a large extent by the influence of riverine
740 discharge and biological activity (Fassbender et al., 2016). Thus coastal communities may
741 also possess a higher level of adaptation to variable carbonate chemistry compared to the
742 open ocean communities of the temperate microcosms (Fassbender et al., 2016).

743 The later stages of mesocosm experiments address a different set of hypotheses, and are less
744 comparable to the microcosms reported here. With time, an increase in number of generations
745 leads to community structure changes and taxonomic shifts, driven by selection on the
746 standing genetic variation in response to the altered conditions. Moreover, the coastal Arctic
747 mesocosms were enriched with nutrients after 10 days, affording relief from nutrient
748 limitation and allowing differences between $p\mathrm{CO_2}$ treatments to be exposed, including a
749 strong DMS(P) response.(Archer et al., 2013; Schulz et al., 2013). During this period of
750 increased growth and productivity, CO_2 increases drove changes which reflected both the
751 physiological and genetic potential within the community, and resulted in taxonomic shifts.
752 The resultant population structure was changed, with an increase in abundance of
753 dinoflagellates, particularly *Heterocapsa rotundata*. Increases in DMSP concentrations and
754 DMSP synthesis rates were attributed to the population shift towards dinoflagellates. The
755 drivers of the reduced DMS concentrations were less clear, but may have been linked to
756 reduced DMSP-lyase capacity within the dominant phytoplankton, a reduction in bacterial
757 DMSP lysis, or an increase in bacterial DMS consumption rates (Archer et al., 2013). Again,

758 this is comparable to all other mesocosm experiments, wherein changes to DMS
759 concentrations can be associated with CO_2-driven shifts in community structure (Hopkins et
760 al., 2010; Avgoustidi et al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014; Webb
761 et al., 2015). However, given the lack of further experiments of a similar location, design and
762 duration to the Arctic mesocosm, it is unclear how representative the mesocosm result is of
763 the general community-driven response to OA in high latitude waters.

764 We did not generally see any broad-scale CO_2-effects on community structure in polar
765 waters. This can be demonstrated by a lack of significant differences in the mean ratio of >10
766 µm Chl *a* to total Chl *a* (*>10 µm : total*) between CO_2 treatments*,* implying there were no
767 broad changes in community composition (Table 2). *South Sandwich* was an exception to
768 this, where large and significant increases in the mean ratio of *>10 µm : total* were observed
769 at 750 µatm and 2000 µatm CO_2 relative to ambient CO_2 (ANOVA, $F = 207.144$, $p<0.001$, df
770 $= 3$), demonstrating that~~ed at~~ even at the short timescale of the microcosm experiments~~,~~ it is
771 possible for some changes to community composition to occur. Interestingly, this was also
772 the only polar station that exhibited any significant effects on DMS after 96 h of incubation
773 (Figure 4 D). However, given the lack of similar response at 1000 µatm, it remains equivocal
774 whether this was driven by a CO_2-effect or some other factor.

775 In contrast to our findings, a recent single 9 day microcosm experiment (Hussherr et al.,
776 2017) performed in Baffin Bay (Canadian Arctic) saw a linear 80% decrease in DMS
777 concentrations during spring bloom-like conditions. It should be noted that this response was
778 seen over a range of pCO_2 from 500 - 3000 µatm, far beyond the levels used in the present
779 study. Nevertheless, this implies that polar DMS production may be sensitive to OA at certain
780 times of the year, such as during the highly productive spring bloom, but less sensitive during
781 periods of low and stable productivity, such as the summer months sampled during this study.

782 Furthermore, a number of other studies from both the Arctic e.g. (Coello-Camba et al., 2014;
783 Holding et al., 2015; Thoisen et al., 2015) and the Southern Ocean e.g. (Trimborn et al.,
784 2017; Tortell et al., 2008; Hoppe et al., 2013) suggest that polar phytoplankton communities
785 can demonstrate sensitivity to OA, in contrast to our findings. This emphasises the need to
786 gain a more detailed understanding of both the spatial and seasonal variability in the polar
787 phytoplankton community and associated DMS response to changing ocean acidity.

788 **5 Conclusions**

789 We have shown that net DMS production by summertime polar open ocean microbial
790 communities is insensitive to OA during multiple, highly replicated short term microcosm
791 experiments. We provide evidence that, in contrast to temperate communities (Hopkins and
792 Archer, 2014), the polar communities we sampled were relatively insensitive to variations in
793 carbonate chemistry (Richier et al., 2018), manifested here as a minimal effect on net DMS
794 production. Our findings contrast with two previous studies performed in Arctic waters
795 (Archer et al. 2013; Hussherr et al. 2017) which showed significant decreases in DMS in
796 response to OA. These discrepancies may be driven by differences in experimental design,
797 variable sensitivity of microbial communities to changing carbonate chemistry between
798 different areas, or by variability in the response to OA depending on the time of year, nutrient
799 availability, and ambient levels of growth and productivity. This serves to highlight the
800 complex spatial and temporal variability in DMS response to OA which warrants further
801 investigation to improve model predictions.

802 Our results imply that the phytoplankton communities of the temperate microcosms initially
803 responded to the rapid increase in pCO_2 via a stress-induced response, resulting in large and
804 significant increases in DMS concentrations occurring over the shortest timescales (2 days),
805 with a lessening of the treatment effect with an increase in incubation time (Hopkins and

806 Archer 2014). The dominance of short response timescales in well-buffered temperate waters
807 may also indicate rapid acclimation of the phytoplankton populations following the initial
808 stress response, which forced the small-sized phytoplankton beyond their range of
809 acclimative tolerance and lead to increased DMS (Richier et al. 2018, Hopkins and Archer
810 2014). This supports the hypothesis that populations from higher latitude, less well-buffered
811 waters, already possess a certain degree of acclimative tolerance to variations in carbonate
812 chemistry environment. Although initial community size structure was not a significant
813 predictor of the response to high CO_2, it is possible that a combination of both community
814 composition and the natural range in variability in carbonate chemistry – as a function of
815 buffer capacity – may influence the DMS/P response to OA over a range of timescales
816 (Richier et al. 2018).

817 Our findings should be considered in the context of timescales of change (experimental vs
818 real world OA) and the potential of microbial communities to adapt to a gradually changing
819 environment. Microcosm experiments focus on the physiological response of microbial
820 communities to short term OA. Mesocosm experiments consider a timescale that allows the
821 response to be driven by community composition shifts, but are not long enough in duration
822 to incorporate an adaptive response. Neither approach is likely to accurately simulate the
823 response to the gradual changes in surface ocean pH that will occur over the next 50 – 100
824 years, nor the resulting changes in microbial community structure and distribution. However,
825 we hypothesise that the DMS response to OA should be considered not only in relation to
826 experimental perturbations to carbonate chemistry, but also in relation to the magnitude of
827 background variability in carbonate chemistry experienced by the DMS-producing organisms
828 and communities. Our findings suggest a strong link between the DMS response to OA and
829 background regional variability in the carbonate chemistry.

830 Models suggest the climate may be sensitive to changes in the spatial distribution of DMS
831 emissions over global scales (Woodhouse et al., 2013; Menzo et al., 2018). Such changes
832 could be driven by both physiological and adaptive responses to environmental change.
833 Accepting the limitations of experimental approaches, our findings suggest that net DMS
834 production from polar oceans may be resilient to OA in the context of its short term effects
835 on microbial communities. The oceans face a multitude of CO_2-driven changes in the coming
836 decades, including OA, warming, deoxygenation and loss of sea ice (Gattuso et al., 2015).
837 Our study addresses only one aspect of these future ocean stressors, but contributes to our
838 understanding of how DMS emissions from the polar oceans may alter, facilitating a better
839 understanding of Earth's future climate.

840 **Data availability**

841 All data has been deposited in and is accessible from the British Oceanographic Data Centre**.**

842 **Author contributions**

843 CMM, SR, FH, PDN and SDA designed the experiments. FH and JAS conducted the
844 measurements, FH and GLC analysed the data. FH prepared the paper with assistance and
845 contributions from all co-authors.

846 **Competing interests**

847 The authors declare that they have no conflict of interest.

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1229 phytoplankton community, Biogeosciences, 13, 4595-4613, 10.5194/bg-13-4595-2016, 2016.

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1231 Woodhouse, M. T., Mann, G. W., Carslaw, K. S., and Boucher, O.: Sensitivity of cloud
1232 condensation nuclei to regional changes in dimethyl-sulphide emissions, Atmos. Chem.
1233 Phys., 13, 2723-2733, 10.5194/acp-13-2723-2013, 2013.

1234 Table 1. Summary of the station locations and characteristic of the water sampled for the 18 microcosm experiments performed in temperate,
1235 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$_{total}$	*p*CO_2 (μatm) T_0	pH (total) T_0	Experimental timepoints T_1, T_2 (hours)	Reference
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*

1236 Table 2. Mean (± SD) ratio of >10µm Chl *a* to total Chl *a* ($chl_{>10µm}$:chl_{total}) for polar
1237 microcosm sampling stations. * indicates significant difference from the response to ambient
1238 CO_2. Exact CO2 treatments are down in Figure 3 and 4.

Station	Time	Ambient	Mid CO_2	High CO_2	High+ CO_2	High++ CO_2
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*

1239

1240 Table 3. DMS and DMSPt response (mean ± SD, *n* = 3) to high CO_2 treatments during
1241 previously unpublished small-scale experiments from the NW European shelf cruise D366.
1242 For details of sampling stations, see Table 1.

	0 h Ambient	**48 h Ambient**	**48 h Mid CO_2**	**48 h High CO_2**	**96 h Ambient**	**96 h Mid CO_2**	**96 h High CO_2**
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	18.1	24.2	25.3
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	20.4	30.7	32.0

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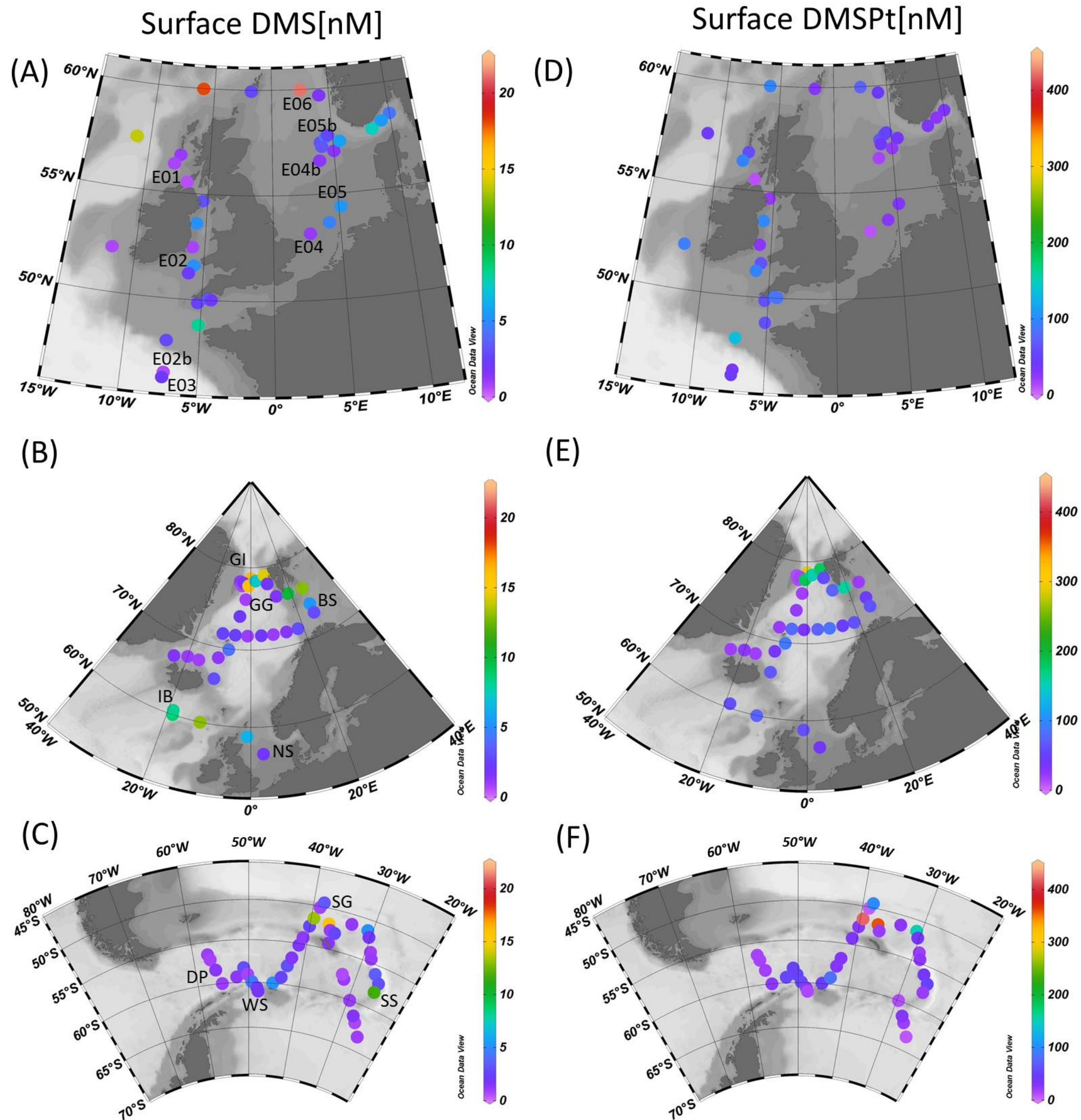
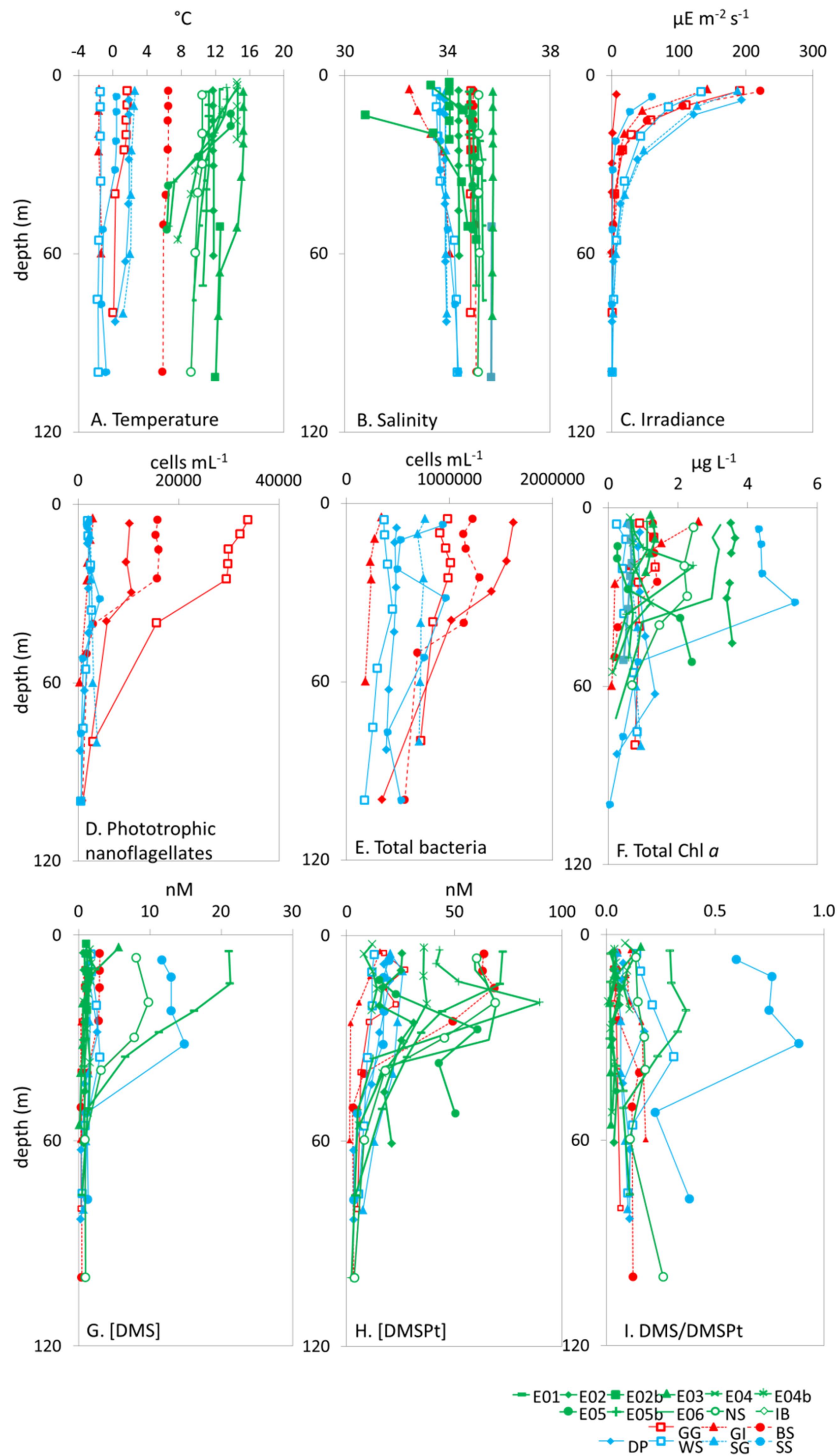


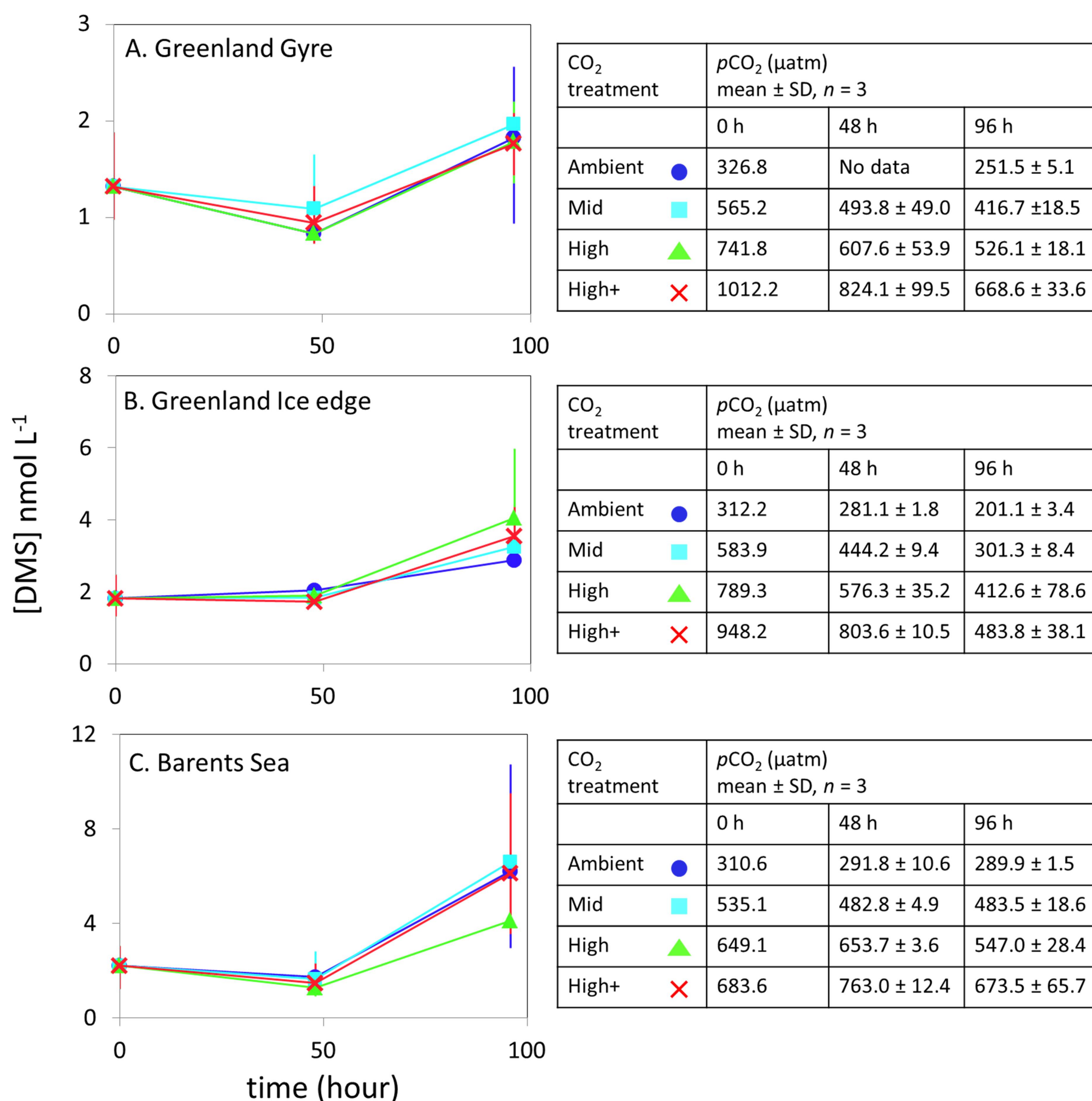
1247 Figure 1. Surface (<5 m) concentrations (nM) of DMS (A-C) and total DMSP (D-F) for
1248 cruises in the NW European shelf (D366) (A,D), the sub-Arctic and Arctic Ocean (JR271)
1249 (B,E) and the Southern Ocean (JR274) (C,F). Locations of sampling stations for microcosm
1250 experiments shown in letters/numbers. E01 – E05: see Hopkins & Archer 2014. NS = *North*
1251 *Sea*, IB = *Iceland Basin*, GI = *Greenland Ice-edge*, GG = *Greenland Gyre*, BS = *Barents Sea*,
1252 DP = *Drake Passage*, WS = *Weddell Sea*, SG = *South Georgia*, SS = *South Sandwich*.



1253

1254 Figure 2. Depth profiles down to 100 m depth for all 18 sampling stations showing A.
1255 Temperature (°C), B. Salinity, C. Irradiance (µE m^{-2} s^{-1}), D. phototrophic nanoflagellate
1256 abundance (cells mL^{-1}), E. total bacteria abundance (cells mL^{-1}), F. total Chl a (µg L^{-1}), G.
1257 [DMS] (nM), H. total [DMSP] (nM) and I. DMS/DMSPt from CTD casts at sampling
1258 stations for microcosm experiments in temperate (green), Arctic (red) and Southern Ocean
1259 (blue) waters. See Table 1 for station details. Data for irrandiance, phototrophic
1260 nanoflagellates and total bacteria were not collected for temperate stations.

1261



A. Greenland Gyre

CO_2 treatment	pCO_2 (µatm) mean ± SD, n = 3		
	0 h	48 h	96 h
Ambient ●	326.8	No data	251.5 ± 5.1
Mid ■	565.2	493.8 ± 49.0	416.7 ±18.5
High ▲	741.8	607.6 ± 53.9	526.1 ± 18.1
High+ ×	1012.2	824.1 ± 99.5	668.6 ± 33.6

B. Greenland Ice edge

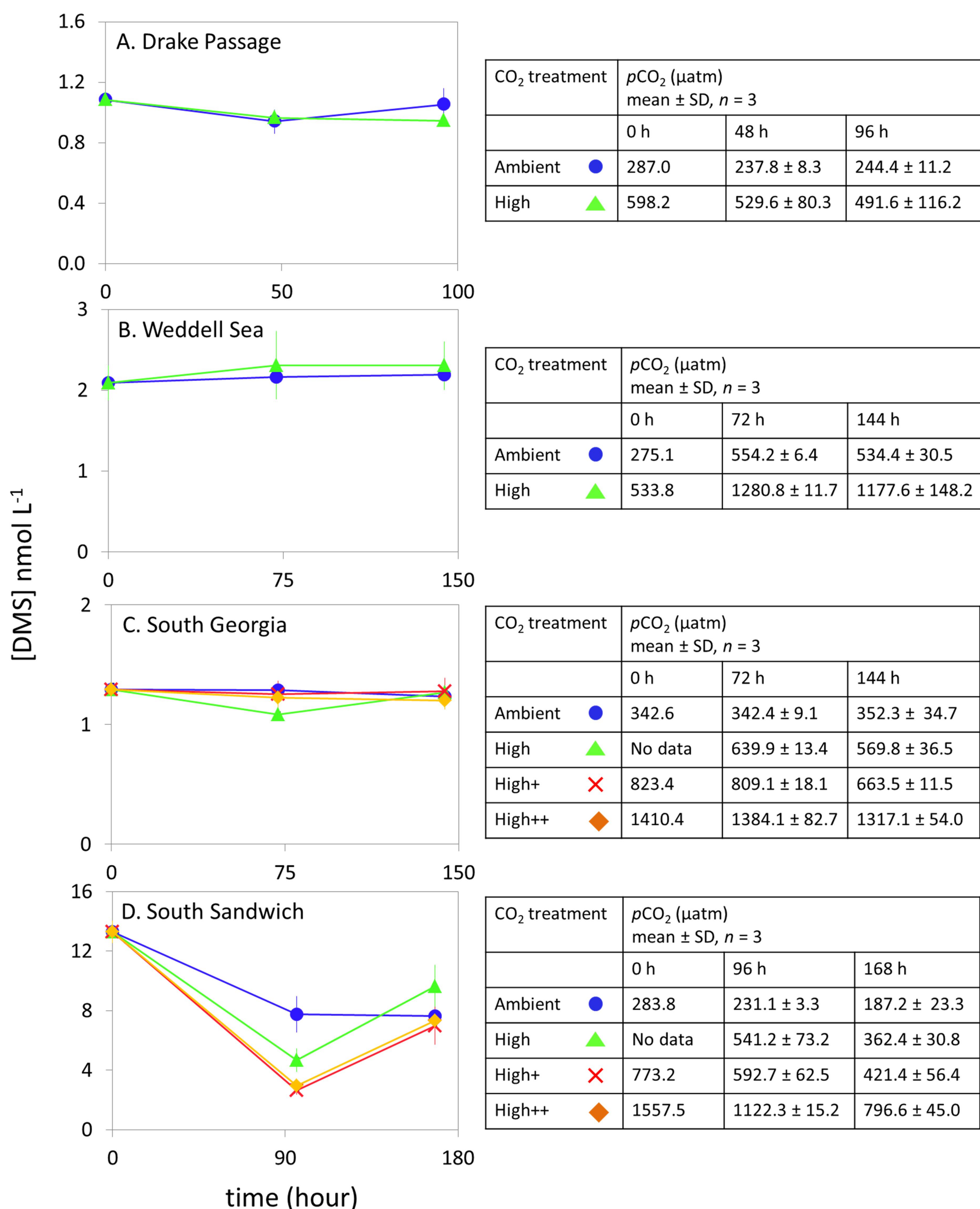
CO_2 treatment	pCO_2 (µatm) mean ± SD, n = 3		
	0 h	48 h	96 h
Ambient ●	312.2	281.1 ± 1.8	201.1 ± 3.4
Mid ■	583.9	444.2 ± 9.4	301.3 ± 8.4
High ▲	789.3	576.3 ± 35.2	412.6 ± 78.6
High+ ×	948.2	803.6 ± 10.5	483.8 ± 38.1

C. Barents Sea

CO_2 treatment	pCO_2 (µatm) mean ± SD, n = 3		
	0 h	48 h	96 h
Ambient ●	310.6	291.8 ± 10.6	289.9 ± 1.5
Mid ■	535.1	482.8 ± 4.9	483.5 ± 18.6
High ▲	649.1	653.7 ± 3.6	547.0 ± 28.4
High+ ×	683.6	763.0 ± 12.4	673.5 ± 65.7

1262

1263 Figure 3. DMS concentrations (nmol L^{-1}) during experimental microcosms performed in
1264 Arctic waters. Data shown is mean of triplicate incubations, and error bars show standard
1265 error on the mean. Tables show measurements of pCO_2 (µatm) for each treatment at each
1266 sampling time point. Initial measurements (0 h) were from a single sample, whilst
1267 measurements at 48 h and 96 h show mean ± SD of triplicate experimental bottles. Locations
1268 of water collection for microcosms shown in Figure 1 C – F.



CO_2 treatment	pCO_2 (µatm) mean ± SD, *n* = 3		
	0 h	48 h	96 h
Ambient ●	287.0	237.8 ± 8.3	244.4 ± 11.2
High ▲	598.2	529.6 ± 80.3	491.6 ± 116.2

CO_2 treatment	pCO_2 (µatm) mean ± SD, *n* = 3		
	0 h	72 h	144 h
Ambient ●	275.1	554.2 ± 6.4	534.4 ± 30.5
High ▲	533.8	1280.8 ± 11.7	1177.6 ± 148.2

CO_2 treatment	pCO_2 (µatm) mean ± SD, *n* = 3		
	0 h	72 h	144 h
Ambient ●	342.6	342.4 ± 9.1	352.3 ± 34.7
High ▲	No data	639.9 ± 13.4	569.8 ± 36.5
High+ ×	823.4	809.1 ± 18.1	663.5 ± 11.5
High++ ◆	1410.4	1384.1 ± 82.7	1317.1 ± 54.0

CO_2 treatment	pCO_2 (µatm) mean ± SD, *n* = 3		
	0 h	96 h	168 h
Ambient ●	283.8	231.1 ± 3.3	187.2 ± 23.3
High ▲	No data	541.2 ± 73.2	362.4 ± 30.8
High+ ×	773.2	592.7 ± 62.5	421.4 ± 56.4
High++ ◆	1557.5	1122.3 ± 15.2	796.6 ± 45.0

1269

1270 Figure 4. DMS concentrations (nmol L^{-1}) during experimental microcosms performed in
1271 Southern Ocean waters. Data shown is mean of triplicate incubations, and error bars show
1272 standard error on the mean. Tables show measurements of pCO_2 (µatm) for each treatment at
1273 each sampling time point. Initial measurements (0 h) were from a single sample, whilst
1274 measurements at 48 h and 96 h show mean ± SD of triplicate experimental bottles. Locations
1275 of water collection for microcosms shown in Figure 1 C – F.

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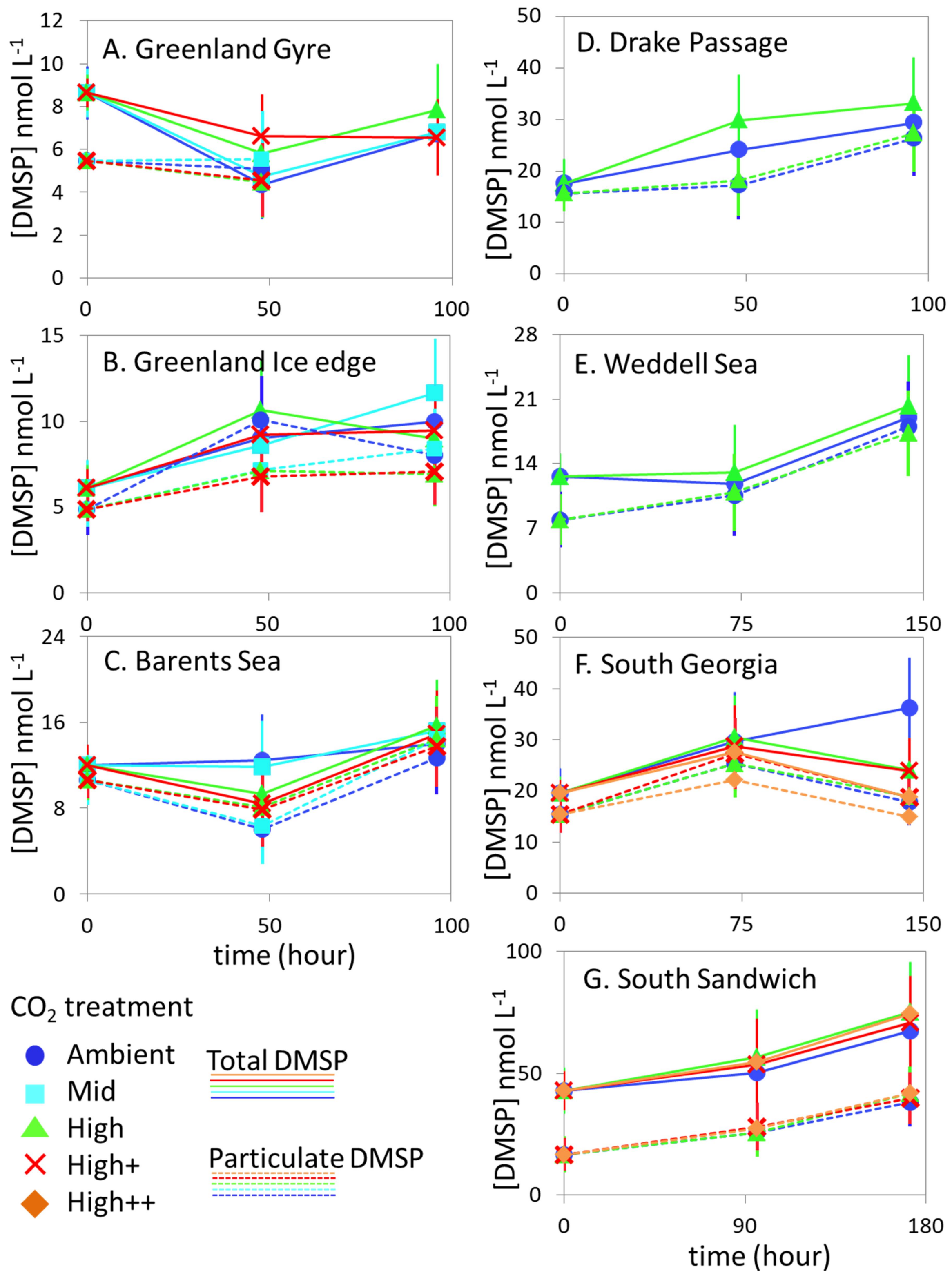
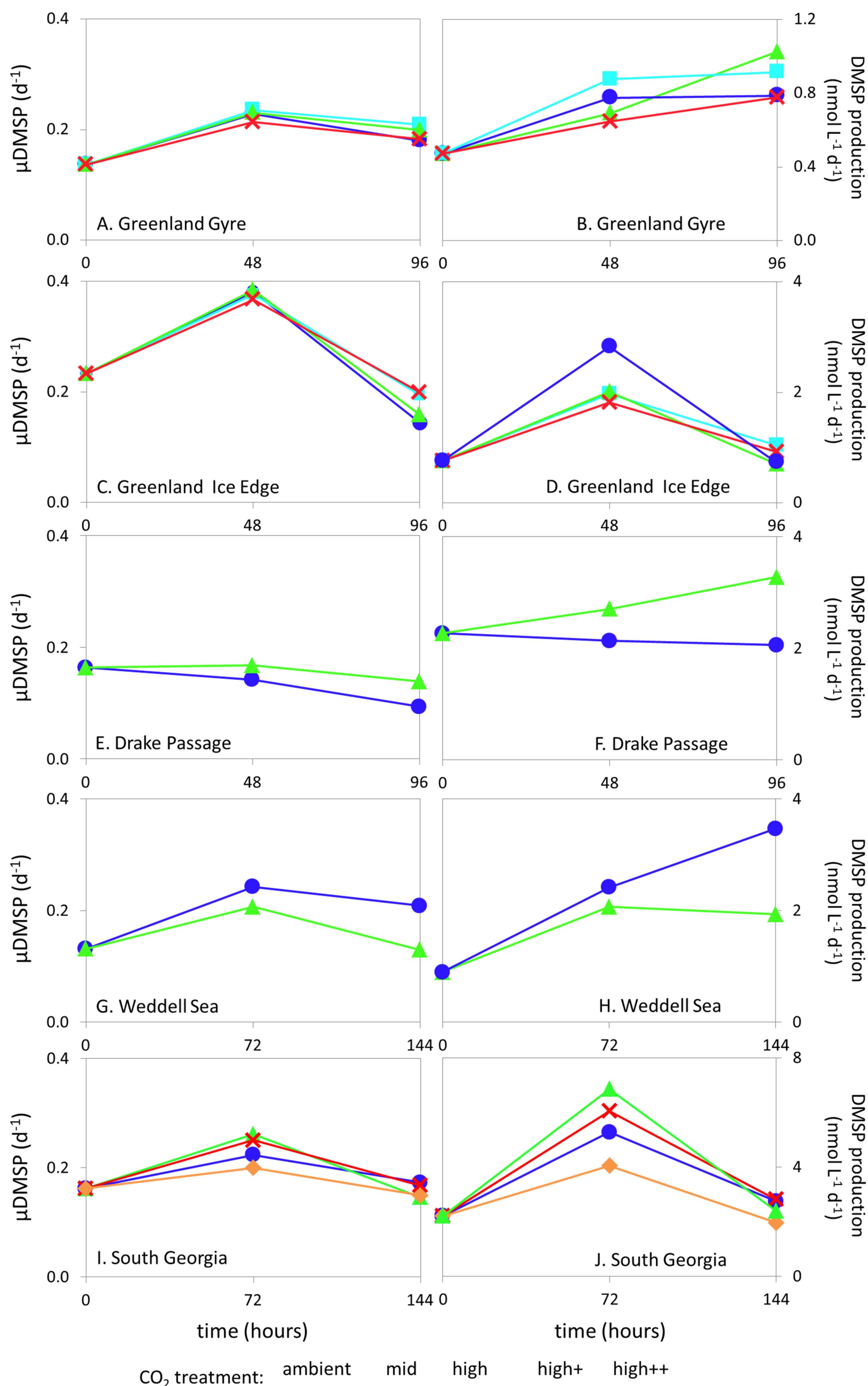


1277

1278 Figure 5. Total DMSP (solid lines) and particulate DMSP (dashed lines) concentrations (
1279 nmol L^{-1}) during experimental microcosms performed in Arctic waters (A - C) and in
1280 Southern Ocean waters (D – G). Data shown is mean of triplicate incubations, and error bars
1281 show standard error on the mean. Locations of water collection for microcosms shown in
1282 Figure 1 C – F. Particulate DMSP concentrations were used in calculations of DMSP
1283 production rates (Figure 6).

1284



1285

1286 Figure 6. De novo synthesis of DMSP (µDMSP, d^{-1}) (left column) and DMSP production
1287 rates (nmol L^{-1} d^{-1}) (right column) for Arctic Ocean stations *Greenland Gyre* (A,B),
1288 *Greenland Ice-edge* (C, D) and Southern Ocean stations *Drake Passage* (E, F), *Weddell Sea*
1289 (G, H) and *South Georgia* (I, J). No data is available for *Barents Sea* (Arctic Ocean) or *South*
1290 *Sandwich* (Southern Ocean).

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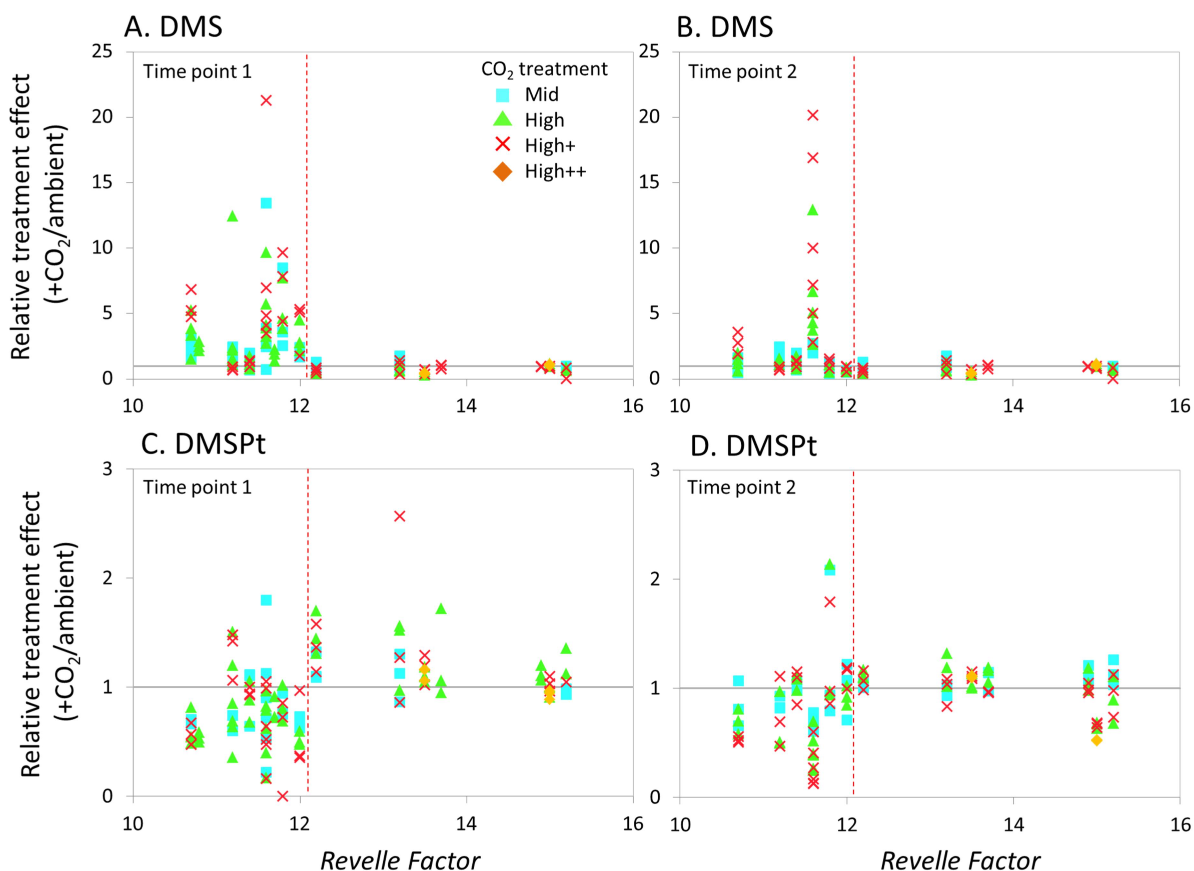

1292

1293 Figure 7. Relationship between Revelle Factor of the sampled water and the relative CO_2
1294 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for concentrations of DMS at T_1 (A) and T_2 (B),
1295 and for total DMSP concentrations at T_1 (C) and T_2 (D) for all microcosm experiments
1296 performed in NW European waters, sub-Arctic and Arctic waters, and the Southern Ocean.
1297 Grey solid line (= 1) indicates no effect of elevated CO_2. Revelle Factor > 12 = polar waters
1298 (indicated by red dashed line). T_1 = 48 h, except for WS and SG (72 h) and SS (96 h). For
1299 detailed analyses of the NW European shelf data, see Hopkins & Archer (2014).

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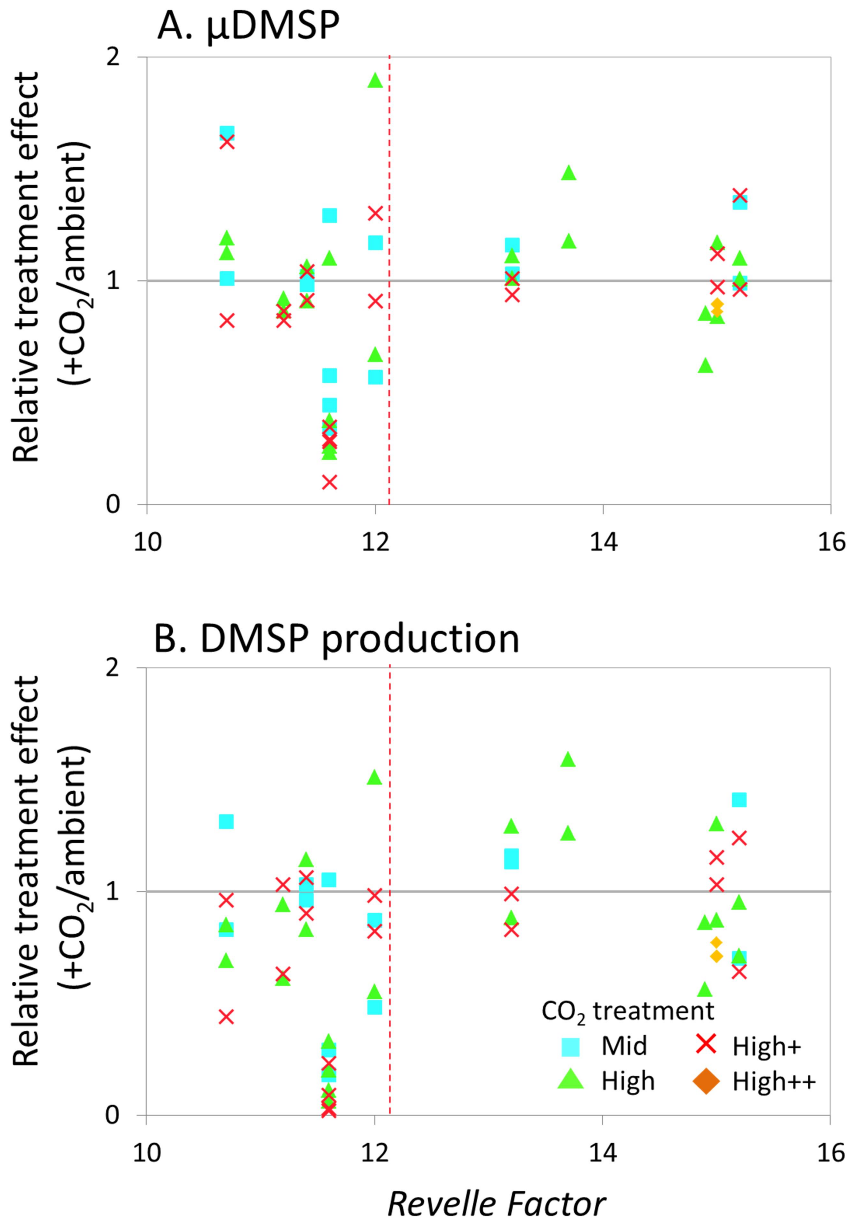
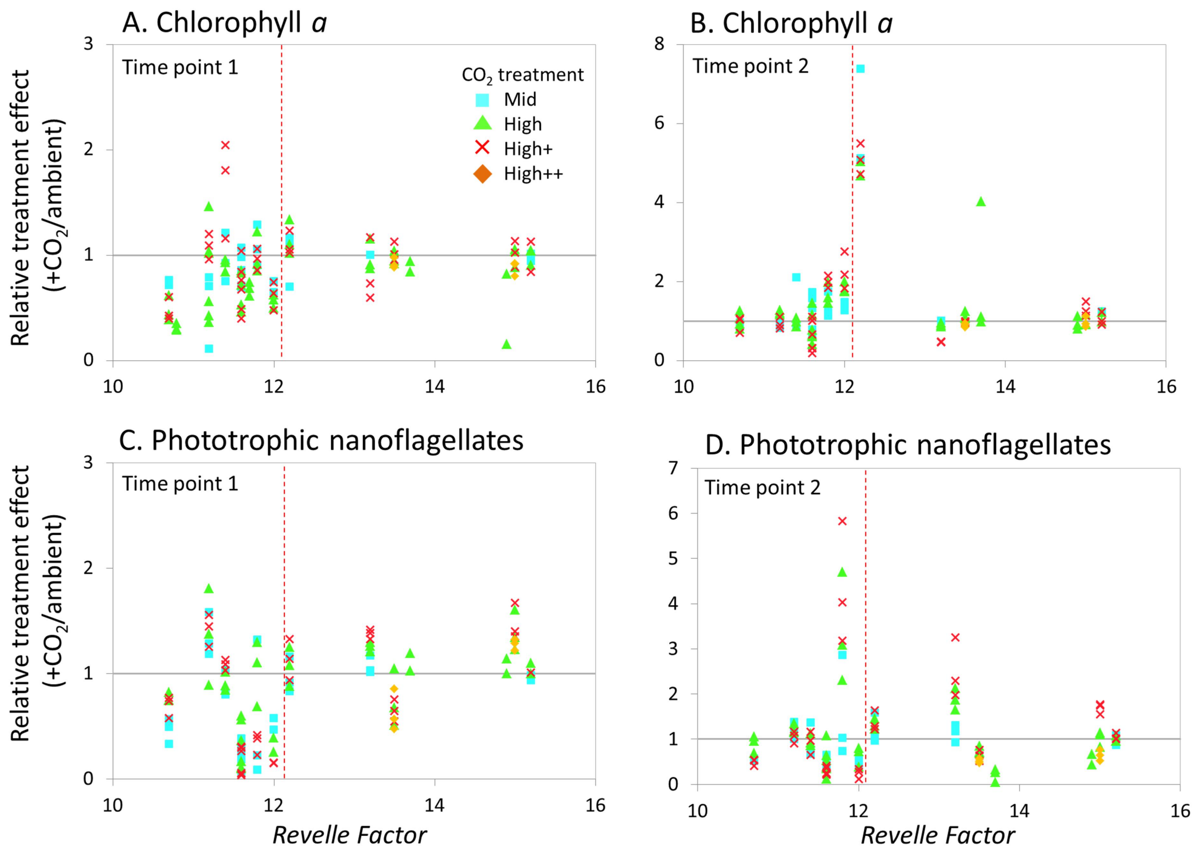


1301

1302 Figure 8. Relationship between the Revelle Factor of the sampled water and the relative CO_2
1303 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for de novo DMSP synthesis (µDMSp, d^{-1}) at T_1
1304 (A) and T_2 (B), and DMSP production rate (nmol L^{-1} d^{-1}) at T_1 (C) and T_2 (D) for microcosm
1305 experiments performed in NW European waters, sub-Arctic and Arctic waters, and the
1306 Southern Ocean. Grey solid line (= 1) indicates no effect of elevated CO_2. Revelle Factor >12
1307 = polar waters (indicated by red dashed line). T_1 = 48 h, T2 = 96 h, except for *Weddell Sea*
1308 and *South Georgia* (72 h, 144 h). For discussion of the NW European shelf data, see Hopkins
1309 & Archer (2014).



1310

1311 Figure 9. Relationship between the Revelle Factor of the sampled water and the relative CO_2
1312 treatment effect ($[x]_{highCO2}/[x]_{ambientCO2}$) for chlorophyll *a* concentrations at T_1 (A) and T_2 (B)
1313 and phototrophic nanoflagellate abundance at T1 (C) and T2 (D) for all microcosm
1314 experiments performed in NW European waters, sub-Arctic and Arctic waters, and the
1315 Southern Ocean. Grey solid line (= 1) indicates no effect of elevated CO_2. Revelle Factor >12
1316 = polar waters (indicated by red dashed line). T_1 = 48 h, T_2 = 96 h, except for *Weddell Sea*
1317 and *South Georgia* (72 h, 144 h) and *South Sandwich* (96 h, 168 h).

1318

1319