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

1 Introduction

The trace gas dimethylsulfide (DMS) is a key ingredient in a cocktail of gases that exchange between the ocean and atmosphere. Dissolved DMS is produced via the enzymatic breakdown of dimethylsulfoniopropionate (DMSP), a secondary algal metabolite implicated in a number of cellular roles, including the regulation of carbon and sulfur metabolism via an overflow mechanism (Stefels, 2000) and protection against oxidative stress (Sunda et al., 2002). Oceanic DMS emissions amount to 17 - 34 Tg S y^{-1}, representing 80 - 90% of all marine biogenic S emissions, and up to 50% of global biogenic emissions (Lana et al., 2011). DMS and its oxidation products play vital roles in atmospheric chemistry and climate processes. These processes include aerosol formation pathways that influence the concentration of cloud condensation nuclei (CCN) with implications for Earth's albedo and climate (Charlson et al., 1987; Korhonen et al., 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 may respond to global change (Carpenter et al., 2012; Woodhouse et al., 2013; Menzo et al., 2018).

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

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

radiation, similar to the influence of anthropogenic aerosols in the polluted Northern Hemisphere (McCoy et al., 2015). Given this important influence of polar DMS emissions on atmospheric processes and climate, it is vital we increase our understanding of the influence of future ocean acidification on DMS production.

The polar oceans are characterised by high dissolved inorganic carbon (C_T) concentrations and a low carbonate system buffering capacity, mainly due to the increased solubility of CO_2 in cold waters (Sabine et al., 2004; Orr et al., 2005). This makes these regions particularly susceptible to the impacts of ocean acidification (OA). For example, extensive carbonate mineral undersaturation is expected to occur in Arctic waters within the next 20 – 80 years (McNeil and Matear, 2008; Steinacher et al., 2009). OA has already led to a 0.1 unit decrease in global surface ocean pH, with a further fall of ~0.4 units expected by the end of the century (Orr et al., 2005). The greatest declines in pH are likely in the Arctic Ocean with a predicted fall of 0.45 units by 2100 (Steinacher et al., 2009), with a fall of ~0.3 units predicted for the Southern Ocean (McNeil and Matear, 2008; Hauri et al., 2016). OA is occurring at a rate not seen on Earth for 300 Ma, and so the potential effects on marine organisms, communities and ecosystems could be wide-ranging and severe (Raven et al., 2005; Hönisch et al., 2012). Despite the imminent threat to polar ecosystems and the importance of DMS emissions to atmospheric processes, our knowledge of the response of polar DMS production to OA is limited to a single mesocosm experiment performed in a coastal fjord in Svalbard (Riebesell et al., 2013; Archer et al., 2013) and one shipboard microcosm experiment with seawater collected from Baffin Bay (Hussherr et al., 2017). Both studies reported significant reductions in DMS concentrations with increasing levels of pCO_2 during seasonal phytoplankton blooms. Hussherr et al. (2017) also saw reductions in total DMSP whilst Archer et al. (2013) observed a significant increase in this compound, driven by CO_2-induced

increases in growth and abundance of dinoflagellates. However, these two single studies provide limited information on the wider response of the open Arctic or Southern Oceans.

Mesocosm experiments have been a critical tool for assessing OA effects on surface ocean communities (Engel et al., 2005; Engel et al., 2008; Schulz et al., 2008; Hopkins et al., 2010; Schulz et al., 2013; Webb et al., 2015; Kim et al., 2006; Kim et al., 2010; Crawfurd et al., 2016; Webb et al., 2016). The response of DMS to OA has been examined several times, predominantly at the same site in Norwegian coastal waters (Vogt et al., 2008; Hopkins et al., 2010; Webb et al., 2015; Avgoustidi et al., 2012), twice in Korean coastal waters (Kim et al., 2010; Park et al., 2014), and a single study in the coastal Arctic waters of Svalbard (Archer et al., 2013). Mesocosm enclosures, ranging in volume from ~11,000 – 50,000 L, allow the response of surface ocean communities to a range of CO_2 treatments to be monitored under near-natural light and temperature conditions over time scales (weeks - months) that allow a 'winners vs loser' dynamic to develop. The response of DMS cycling to elevated CO_2 is generally driven by changes to the microbial community structure (Brussaard et al., 2013; Archer et al., 2013; Hopkins et al., 2010; Engel et al., 2008). 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. Nevertheless, our approach can provide insight into the physiological response and level of sensitivity to future OA of a variety of polar surface ocean communities adapted to different in situ carbonate chemistry environments (Stillman and Paganini, 2015), alongside the implications this may have for DMS production.

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

2 Material and Methods

2.1 Sampling stations

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

162 **2.2 Shipboard microcosm experiments**

163 The general design and implementation of the experimental microcosms for JR271 and
164 JR274 was essentially the same as for D366 and described in Richier et al. (2014), (2018) and
165 Hopkins & Archer (2014), but with the additional adoption of trace metal clean sampling and
166 incubation techniques in the low trace metal open ocean waters (see Richier et al. (2018)). At
167 each station, pre-dawn vertical profiles of temperature, salinity, oxygen, fluorescence,
168 turbidity and irradiance were used to choose and characterise the depth of experimental water
169 collection. Subsequently, water was collected within the mixed layer from three successive
170 separate casts of a trace-metal clean titanium CTD rosette comprising twenty-four 10 L
171 Niskin bottles. Depth profiles of auxiliary measurements are shown in Figure 2. Each cast
172 was used to fill one of a triplicated set of experimental bottles (locations and sample depths,
173 Table 1). Bottles were sampled within a class-100 filtered air environment within a trace
174 metal clean container to avoid contamination during the set up. The water was directly

transferred into acid-cleaned 4.5 L polycarbonate bottles using acid-cleaned silicon tubing, with no screening or filtration.

The carbonate chemistry within the experimental bottles was manipulated by addition of equimolar HCl and $NaHCO_3^-$ (1 mol L^{-1}) to achieve a range of CO_2 treatments: Mid CO_2 (Target: 550 µatm), High CO_2 (Target: 750 µatm), High+ CO_2 (Target: 1000 µatm) and High++ CO_2 (Target: 2000 µatm) (Gattuso et al., 2010). Three treatment levels were used during the sub-Arctic/Arctic microcosms (Mid, High, High+). For Southern Ocean experiments, two experiments (*Drake Passage* and *Weddell Sea*) underwent combined CO_2 and Fe additions (ambient, Fe (2 nM), High CO_2, Fe (2 nM) & High CO_2 (only high CO_2 treatments will be examined here; no response to Fe was detected in DMS or DMSP concentrations). Three CO_2 treatments (High, High+, High++) were tested in the last two experiments (*South Georgia* and *South Sandwich*). Full details of the carbonate chemistry manipulations can be found in Richier et al. (2014) and Richier et al. (2018). Broadly, achieved pCO_2 levels were well-matched to target values at the start of the experiments (0 h), although differences in pCO_2 between target and initial values were greater in the higher pCO_2 treatments, due to lowered carbonate system buffer capacity at higher pCO_2. For all 18 experiments, actual pCO_2 values at 0 h were on average around 89% ± 12% (± 1 SD) of target values. The attained pCO_2 values, and pCO_2 at each experimental time point, are presented in Figures 3 and 4. After first ensuring the absence of bubbles or headspace, the bottles were sealed with high density polyethylene (HDPE) lids with silicone/ polytetrafluoroethylene (PTFE) septa and placed in the incubation container. Bottles were incubated inside a custom-designed temperature- and light-controlled shipping container, set to match (±<1°C) the *in situ* water temperature at the time of water collection (shown in Table 1) (see Richier et al. 2018). A constant light level (100 µE m^{-2} s^{-1}) was provided by daylight simulating LED panels (Powerpax, UK). The light period within the microcosms

was representative of *in situ* conditions. For the sub-Arctic/Arctic Ocean stations, experimental bottles were subjected to continuous light representative of the 24 h daylight of the Arctic summer. For Southern Ocean and all temperate water stations, an 18:6 light: dark cycle was used. Each bottle belonged to a set of triplicates, and sacrificial sampling of bottles was performed at two time points (see Table 1 for exact times). Use of three sets of triplicates for each time point allowed for the sample requirements of the entire scientific party (3 x 3 bottles, x 2 time points (see Table 1 for specific times for each experiment), x 4 CO_2 treatments = 72 bottles in total). Experiments were run for between 4 and 7 days (96 h – 168 h) (15 out of 18 experiments), with initial sampling proceeded by two further time points. For three temperate experiments (E02b, E04b, E05b, see Table 1) a shorter 2 day incubation was performed, with a single sampling point at the end. For E06 (see Table 1) high time frequency sampling was performed (0, 1, 4, 14, 24, 48, 72, 96 h) although only the data at 48 h and 96 h is considered in this analysis. 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 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

223 Methods for the determination of seawater concentrations of DMS and DMSP are identical to
224 those described in Hopkins & Archer (2014) and will therefore be described in brief here.
225 Seawater DMS concentrations were determined by cryogenic purge and trap, with gas
226 chromatography and pulsed flame photometric detection (GC-PFPD) (Archer et al., 2013).
227 DMSP concentrations were measured as DMS following alkaline hydrolysis. Samples for
228 total DMSP concentrations from temperate waters were fixed by addition of 35 µl of 50 %
229 H_2SO_4 to 7 mL of seawater (Kiene and Slezak, 2006), and analysed following hydrolysis
230 within 2 months of collection (Archer et al., 2013). Samples of DMSP that were collected in
231 polar waters were hydrolysed within 1 h of sample collection and analysed 6 – 12 h later. The
232 H_2SO_4 fixation method was not used for samples from polar waters given the likely
233 occurrence of *Phaeocystis sp*. which can result in the overestimation of DMSP concentrations
234 (del Valle et al., 2009). Similarly, concentrations of DMSPp were determined at each time
235 point by gravity filtering 7 ml of sample onto a 25 mm GF/F filter and preserving the filter in
236 7 ml of 35 mM H_2SO_4 in MQ-water (temperate samples) or immediately hydrolysing (polar
237 samples) and analysing by GC-PFPD. DMS calibrations were performed using alkaline cold-
238 hydrolysis (1 M NaOH) of DMSP sequentially diluted three times in MilliQ water to give
239 working standards in the range 0.03 – 3.3 ng S mL^{-1}. Five point calibrations were performed
240 every 2 – 4 days throughout the cruise.

241 **2.4 *De novo* DMSP synthesis**

242 *De novo* DMSP synthesis and gross production rates were determined for all microcosm
243 experiments, except *Barents Sea* and *South Sandwich*, at each experimental time point, using
244 methods based on the approach of Stefels et al. (2009) and described in detail in Archer et al.
245 (2013) and Hopkins and Archer (2014). Triplicate rate measurements were determined for
246 each CO_2 level. For each rate measurement three x 500 mL polycarbonate bottles were filled

by gently siphoning water from each replicate microcosm bottle. Trace amounts of $NaH^{13}CO_3$, equivalent to ~6 % of *in situ* dissolved inorganic carbon (C_T), were added to each 500 mL bottle. The bottles were incubated in the microcosm incubation container with temperature and light levels as described earlier. Samples were taken at 0 h, then at two further time points over a 6 - 9 h period. At each time point, 250 mL was gravity filtered in the dark through a 47 mm GF/F filter, the filter gently folded and placed in a 20 mL serum vial with 10 mL of Milli-Q and one NaOH pellet, and the vial was crimp-sealed. Samples were stored at -20°C until analysis by proton transfer reaction-mass spectrometer (PTR-MS) (Stefels et al. 2009).

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

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

(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 DMSP relative to total DMSP at time t, at the preceding time point (t-1) and at the subsequent time point (t+1), respectively. Values of ^{64}MP were calculated from the protonated masses of DMS as: mass 64/(mass63 + mass64 + mass65), determined by PTR-MS. $^{64}MP_{eq}$ is the theoretical equilibrium proportion of 1 x ^{13}C based on a binomial distribution and the proportion of tracer addition. An isotope fractionation factor α_k of 1.06 is included, based on laboratory culture experiments using *Emiliania huxleyi* (Stefels et al. 2009). In vivo DMSP gross production rates during the incubations (nmol L^{-1} h^{-1}) were calculated from μDMSP and the initial particulate DMSP (DMSPp) concentration of the incubations (Hopkins &

Archer 2014, Stefels et al. 2009). These rates provide important information on how the physiological status of DMSP-producing cells may be affected by OA within the bioassays.

2.5 Seawater carbonate chemistry analysis

The techniques and methods used to determine both the *in situ* and experimental carbonate chemistry parameters, and to manipulate seawater carbonate chemistry within the microcosms, are described in Richier et al. (2014) and will be only given in brief here. Experimental T_0 measurements were taken directly from CTD bottles, and immediately measured for total alkalinity (A_T) (Apollo SciTech AS-Alk2 Alkalinity Titrator) and dissolved inorganic carbon (C_T) (Apollo SciTech C_T analyser (AS-C3) with LICOR 7000). The CO2SYS programme (version 1.05) (Lewis and Wallace, 1998) was used to calculate the remaining carbonate chemistry parameters including pCO_2.

Measurements of T_A and C_T were made from each bottle at each experimental time point and again used to calculate the corresponding values for pCO_2 and pH_T. The carbonate chemistry data for each sampling time point for each experiment are summarised in Supplementary Table S1, S2 and S3 (Experimental starting conditions are given in Table 1).

2.6 Chlorophyll a (Chl *a*) determinations

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

291 **2.8 Community composition**

292 Small phytoplankton community composition was assessed by flow cytometry. For details of
293 methodology, see Richier et al. (2014).

294 **2.9 Data handling and statistical analyses**

295 Permutational analysis of variance (PERMANOVA) was used to analyse the difference in
296 response of DMS and DMSP concentrations to OA, both between and within the two polar
297 cruises in this study. Both dependant variables were analysed separately using a nested
298 factorial design with three factors; (i) Cruise Location: Arctic and Southern Ocean, (ii)
299 Experiment location nested within Cruise location (see Table 1 for station IDs) and (iii) CO_2
300 level: 385, 550, 750, 1000 and 2000 µatm. Main effects and pairwise comparisons of the
301 different factors were analysed through unrestricted permutations of raw data. If a low
302 number of permutations were generated then the *p*-value was obtained through random
303 sampling of the asymptotic permutation distribution, using Monte Carlo tests.

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

312 **3 Results**

313 **3.1 Sampling stations**

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

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

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

339 – 20 nmol L^{-1}, except *Barents Sea* where surface concentrations exceeded 60 nmol L^{-1}
340 (Figure 2 H).

341 **3.2 Response of DMS and DMSP to OA**

342 The temporal trend in DMS concentrations showed a similar pattern for the three Arctic
343 Ocean experiments. Initial concentrations of 1 – 2 nmol L^{-1} remained relatively constant over
344 the first 48 h and then showed small increases of 1 - 4 nmol L^{-1} over the incubation period
345 (Figure 3). Increased variability between triplicate incubations became apparent in all three
346 Arctic experiments by 96 h, but no significant effects of elevated CO_2 on DMS
347 concentrations were observed. Initial DMSP concentrations were more variable, from 6 nmol
348 L^{-1} at *Greenland Ice-edge* to 12 nmol L^{-1} at *Barents Sea*, and either decreased slightly (net
349 loss 1 – 2 nmol L^{-1} GG), or increased slightly (net increase ~4 nmol L^{-1} *Greenland Ice-edge*,
350 ~3 nmol L^{-1} *Barents Sea*) (Figure 5 A – C). DMSP concentrations were found to decrease
351 significantly in response to elevated CO_2 after 48 h for *Barents Sea* (Fig. 4 C, $t = 2.05$, $p =$
352 0.025), whist no significant differences were seen after 96 h. No other significant responses
353 in DMSP were identified.

354 The range of initial DMS concentrations was greater at Southern Ocean sampling stations
355 compared to the Arctic, from 1 nmol L^{-1} at *Drake Passage* up to 13 nmol L^{-1} at *South*
356 *Sandwich* (Figure 4). DMS concentrations showed little change over the course of 96 – 168 h
357 incubations and no effect of elevated CO_2, with the exception of *South Sandwich* (Fig. 4 D).
358 Here, concentrations decreased sharply after 96 h by between 3 and 11 nmol L^{-1}.
359 Concentrations at 96 h were CO_2-treatment dependent, with significant decreases in DMS
360 concentration occurring with increasing levels of CO_2 (PERMANOVA, $t = 2.61$, $p = 0.028$).
361 Significant differences ceased to be detectable by the end of the incubations (168 h). Initial
362 DMSP concentrations were higher at the Southern Ocean stations than for Arctic stations,

363 ranging from 13 nmol L^{-1} for *Weddell Sea* to 40 nmol L^{-1} for *South Sandwich* (Figure 5 D –
364 G). Net increases in DMSP occurred throughout, except at South Georgia, and were on the
365 order of between <10 nmol L^{-1} - >30 nmol L^{-1} over the course of the incubations.
366 Concentrations were not generally pCO_2-treatment dependent with the exception of the final
367 time point at *South Georgia* (144 h) when a significantly lower DMSP with increasing CO_2
368 was observed (PERMANOVA, t = -5.685, p<0.001).

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

374 **3.3 Response of de novo DMSP synthesis and production to OA**

375 Rates of *de novo* DMSP synthesis (µDMSP) at initial time points ranged from 0.13 d^{-1}
376 (*Weddell Sea*, Fig. 6 G) to 0.23 d^{-1} (*Greenland Ice-edge*, Fig. 6 C), whilst DMSP production
377 ranged from 0.4 nmol L^{-1} d^{-1} (*Greenland Gyre*, Fig. 6 B) to 2.27 nmol L^{-1} d^{-1} (*Drake Passage*,
378 Fig. 6 F). Maximum rates of µDMSP of 0.37 -0.38 d^{-1} were observed at *Greenland Ice-edge*
379 after 48 h of incubation in all CO_2 treatments (Fig. 6 C). The highest rates of DMSP
380 production were observed at *South Georgia* after 96 h of incubation, and ranged from 4.1 –
381 6.9 nmol L^{-1} d^{-1} across CO_2 treatments (Fig. 6 J). Rates of DMSP synthesis and production
382 were generally lower than those measured in temperate waters (Hopkins and Archer, 2014)
383 (Initial rates: µDMSP 0.33 – 0.96 d^{-1}, 7.1 – 37.3 nmol L^{-1} d^{-1}), but were comparable to
384 measurements made during an Arctic mesocosm experiment (Archer et al., 2013) (0.1 – 0.25
385 d^{-1}, 3 – 5 nmol L^{-1} d^{-1} in non-bloom conditions). The lower rates in cold polar waters likely
386 reflect slower metabolic processes and are reflected by standing stock DMSP concentrations

387 which were also lower than in temperate waters (5 – 40 nmol L^{-1} polar, 8 – 60 nmol L^{-1}
388 temperate (Hopkins and Archer, 2014)). No consistent of high CO_2 were observed for either
389 DMSP synthesis or production in polar waters, similar to findings for DMSP standing stocks.
390 However, some notable but contrasting differences between CO_2 treatments were observed.
391 There was a 36% and 37% increase in µDMSP and DMSP production respectively at 750
392 µatm for the *Drake Passage* after 96 h (Figure 6 E, F), and a 38% and 44% decrease in both
393 at 750 µatm after 144 h for *Weddell Sea* (Figure 5 G, H). For *Drake Passage*, the difference
394 between treatments at 96 h coincided with significantly higher nitrate concentrations in the
395 High CO_2 treatment (Nitrate/nitrite at 96 h: Ambient = 18.9 ± 0.2 µmol L^{-1}, +CO_2 = 20.2 ±
396 0.1 µmol L^{-1}, ANOVA $F = 62.619$, $df = 1$, $p = 0.001$). However, it is uncertain whether the
397 difference in nutrient availability between treatments (approximately 5 %) would be
398 significant enough to strongly influence the rate of DMSP production.

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

403 **4 Discussion**

404 **4.1 Regional differences in the response of DMS(P) to OA**

405 We combine our findings from the polar oceans with those from temperate waters into a
406 meta-analysis in order to assess the regional variability and drivers in the DMS(P) response to
407 OA. Figures 7 and 8 provide an overview of the results discussed so far in this current study,
408 together with the results from Hopkins & Archer (2014) as well as the results from 4
409 previously unpublished microcosm experiments from the NW European shelf cruise and a
410 further 2 temperate water microcosm experiments from the Arctic cruise (*North Sea* and

411 *Iceland Basin*, Table 1). This gives a total of 18 microcosm experiments, each with between 1
412 and 3 high CO_2 treatments.

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

420 The relative treatment effects ($[x]_{highCO2}/[x]_{ambientCO2}$) for DMS and DMSP (Figure 7), DMSP
421 synthesis and production (Figure 8), and Chl *a* and phototrophic nanoflagellate abundance
422 (Figure 9) are plotted against the Revelle Factor of the sampled waters. The Revelle Factor
423 (*R*), calculated here with CO2Sys using measurements of carbonate chemistry parameters (*R*
424 = $(\Delta pCO_2/\Delta TCO_2)/(pCO_2/TCO_2)$, Lewis and Wallace, 1998), describes how the partial
425 pressure of CO_2 in seawater (PCO_2) changes for a given change in DIC (Sabine et al., 2004;
426 Revelle and Suess, 1957). Its magnitude varies latitudinally, with lower values (9 – 12) from
427 the tropics to temperate waters, and the highest values in cold high latitude waters (13 – 15).
428 Thus polar waters can be considered poorly buffered with respect to changes in DIC.
429 Therefore, biologically-driven seasonal changes in seawater pCO_2 would result in larger
430 changes in pH than would be experienced in temperate waters. (Egleston et al., 2010).
431 Furthermore, the seasonal sea ice cycle strongly influences carbonate chemistry, such that sea
432 ice regions exhibit wide fluctuations in carbonate chemistry (Revelle and Suess, 1957; Sabine
433 et al., 2004). Sampling stations with a *R* above ~12 represent the seven polar stations (right of
434 red dashed line Fig. 7, 8, 9). The surface waters of the polar oceans have naturally higher
435 levels of DIC and a reduced buffering capacity, driven by higher CO_2 solubility in colder

436 waters (Sabine et al., 2004). Thus, the relationship between experimental response and *R* is a
437 simple way of demonstrating the differences in response to OA between temperate and polar
438 waters and provides some insight into how the CO_2 sensitivity of different surface ocean
439 communities may relate to the *in situ* carbonate chemistry. The effect of elevated CO_2 on
440 DMS concentrations at polar stations, relative to ambient controls, was minimal at both
441 sampling points, and is in strong contrast to the results from experiments performed in waters
442 with lower values of *R* on the NW European shelf. In contrast, at temperate stations, DMSP
443 concentrations displayed a clear negative treatment effect, whilst at polar stations a positive
444 effect was evident under high CO_2, and particularly at the first time point (48 – 96 h) (Fig. 7
445 C and D). *De novo* DMSP synthesis and DMSP production rates show a less consistent
446 response in either environment (Fig. 8 A and B), although a significant suppression of
447 DMSP production rates in temperate waters compared to polar waters was seen (Fig. 8 B,
448 Kruskal-Wallis One Way ANOVA $H = 8.711$, $df = 1$, $p = 0.003$). A similar but not significant
449 response was seen for *de novo* DMSP synthesis (Fig. 8A).

450 This data suggests that DMSP concentrations in polar waters may be upregulated in response
451 to OA compared to temperate waters. Given the potential photoprotective and antioxidant
452 role that DMSP plays, and which may be particularly relevant in the highly variable polar
453 sea-ice environment (e.g. irradiance, carbonate chemistry), these changes may reflect a
454 physiological protective response to the experimental OA (Sunda et al., 2002;Galindo et al.,
455 2016). An increase in DMSP concentrations could have either resulted from a physiological
456 up-regulation of DMSP synthesis or a reduction in bacterial DMSP consumption processes.
457 However, DMSP synthesis rates did not provide any conclusive evidence of upregulation in
458 polar waters. Instead, we observed a suppression of rates in temperate waters which may
459 reflect the adverse effects of rapid OA on DMSP producers (Richier et al. 2014, Hopkins and
460 Archer 2014). In contrast, the lesser response seen in polar waters may reflect a higher

461 acclimative tolerance to rapid changes in carbonate chemistry amongst polar communities.
462 Further experiments with polar communities would help to further unravel the potential
463 importance of such mechanisms, and whether they facilitated the ability of polar
464 phytoplankton communities to resist the high CO_2 treatments.

465 The responses to OA observed for DMS and DMSP production are likely to be reflected in
466 the dynamics of the DMSP-producing phytoplankton. In an assessment across all
467 experiments, Richier et al. (2018) showed that the maximal response to OA of total Chl *a* and
468 net growth rates of small phytoplankton (<10 µm) observed during each experiment,
469 declined the most in relation to increased buffering capacity and temperature of the initial
470 water. Generally, less significant relationships were found between the phytoplankton
471 response and the other wide range of physical, chemical or biological variables that were
472 examined (Richier et al. 2018).

473 In correspondence with the analyses carried out by Richier et al (2018), at 48 – 96 h (see
474 Table 1), a statistically significant difference in response was seen between temperate and
475 polar waters for Chl *a* (Kruskal-Wallis One Way ANOVA $H = 20.577$, $df = 1$, $p<0.001$). In
476 general, at polar stations phytoplankton showed minimal response to elevated CO_2, in
477 contrast to a strong negative response in temperate waters (Fig. 9A). By the second time point
478 (96 – 144 h, see Table 1), no significant difference in response of Chl *a* between temperate
479 and polar waters was apparent (Fig. 9B). As shown in Richier et al. (2014), phototrophic
480 nanoflagellates responded to high CO_2 with large decreases in abundance in temperate waters
481 and increases in abundance in polar waters (Fig. 9 C and D), with some exceptions: *North*
482 *Sea* and *South Sandwich* gave the opposite response. The responses had lessened by the
483 second time point (96 – 168 h, see Table 1).

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

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

4.2 Influence of community cell-size composition on DMS response

It has been proposed that variability in the concentrations of carbonate species (e.g. pCO_2, HCO_3^-, CO_3^{2-}) experienced by phytoplankton is related to cell size, such that smaller-celled taxa (<10 µm) with a reduced diffusive boundary layer are naturally exposed to relatively less variability compared to larger cells (Flynn et al., 2012). Thus, short-term and rapid changes in carbonate chemistry, such as the kind imposed during our microcosm experiments, may have a disproportionate effect on the physiology and growth of smaller celled species. Larger cells may be better able to cope with variability as normal cellular metabolism results in significant cell surface changes in carbonate chemistry parameters (Richier et al., 2014). Indeed, the

508 marked response in DMS concentrations to short term OA in temperate waters has been
509 attributed to this enhanced sensitivity of small phytoplankton (Hopkins and Archer, 2014).
510 Was the lack of DMS response to OA in polar waters therefore a result of the target
511 communities being dominated by larger-celled, less carbonate-sensitive species?

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

529 **4.3 Adaptation to a variable carbonate chemistry environment**

530 Given that DMS production by polar phytoplankton communities appeared to be insensitive
531 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. The polar waters sampled during our study were characterised by pronounced gradients in carbonate chemistry over small spatial scales, such that surface ocean communities are more likely to have experienced fluctuations between high pH and low pH over short time scales (Tynan et al., 2016). For example, in underway samples taken along each cruise track, 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). By comparison, pH varied by 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).

For comparison with Arctic stations, Hagens and Middelburg (2016) report a seasonal pH variability of up to 0.25 units from a single site in the open ocean surface waters in the

557 Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability of 0.3 – 0.4 units in
558 the McMurdo Sound, Antarctica. This implies that both open ocean and sea ice-influenced
559 polar waters experience large variations in carbonate chemistry over seasonal cycles. By
560 contrast, monthly averaged surface pCO_2 data collected from station L4 in the Western
561 English Channel over the period 2007 – 2011 provides an example of typical carbonate
562 chemistry dynamics in NW European shelf sea waters. Over this period, pH had an annual
563 range of 0.15 units (8.05 – 8.20), accompanied by a range in pCO_2 of 302 – 412 µatm (Kitidis
564 et al., 2012).
565 The sea ice environment in particular is characterised by strong spatial and seasonal
566 variability in carbonate chemistry. Sea ice is inhabited by a specialised microbial community
567 with a complex set of metabolic and physiological adaptations allowing these organisms to
568 withstand wide fluctuations in pH up to as high as 9.9 in brine channels to as low as 7.5 in the
569 under-ice water (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015).
570 The open waters associated with the ice edge also experience strong gradients in pH and
571 other carbonate chemistry parameters. This can be attributed to two processes: 1. The strong
572 seasonal drawdown of DIC due to rapid biological uptake by phytoplankton blooms at the
573 productive ice edge which drives up pH. On the Arctic cruise, increases of up to 0.33 pH
574 units were attributed to such processes in this region (Tynan et al., 2016). The effect was less
575 dramatic in the Fe-limited and less productive Weddell Sea with gradients in pH ranging
576 from 8.20 – 8.10 (Tynan et al., 2016). 2. The drawdown of DIC is countered by the release
577 and accumulation of respired DIC under sea ice due to the degradation of organic matter.
578 However, this accumulation occurs in subsurface/bottom waters, which are isolated from the
579 productive surface mixed layer by strong physical stratification and hence, of less relevance
580 to the current study.

581 The influence of sea ice on carbonate chemistry combined with the strong biological
582 drawdown of DIC in polar waters may have influenced the ability of some of the
583 communities we sampled during our study to withstand the short term changes to carbonate
584 chemistry they experienced within the bioassays. Two of our sampling stations were 'sea-ice
585 influenced': *Greenland Ice Edge* and *Weddell Sea*. Both were in a state of sea ice retreat as
586 our sampling occurred in the summer months. Sampling for the *Greenland Ice Edge* station
587 was performed in open, deep water, near to an area of thick sea ice, with low fluorescence but
588 reasonable numbers of diatoms (Leakey, 2012). Similarly, the *Weddell Sea* station was
589 located near the edge of thick pack ice but in an area of open water that allowed sampling to
590 occur without hindrance by brash ice (Tarling, 2013). At both stations we saw little or no
591 response in DMS or DMSP to experimental acidification, which may imply that the *in situ*
592 communities were more or less adapted to fluctuations in pH. Our experimental OA resulted
593 in pH decreases of between 0.4 and 0.7 units. However, it is unclear whether the communities
594 we sampled were able to withstand the artificial pH perturbation because they were adapted
595 to living in sea ice, or whether they had adapted to cope with other fluctuations in carbonate
596 chemistry that occur in polar waters.
597 In summary, this demonstrates the high variability in carbonate chemistry, including pH,
598 which polar communities may experience relative to their temperate counterparts. This may
599 have resulted in adapted communities resilient to experimentally-induced OA. Of course, it is
600 important to recognise that this data represent only a snapshot (4 – 6 weeks) of a year, and
601 thus does not contain information on the range in variability over daily and seasonal cycles,
602 timescales which might be considered most important in terms of the carbonate system
603 variability experienced by the cells and how this drives CO_2 sensitivity (Flynn et al. 2012;
604 Richier et al. 2018). Nevertheless, this inherent carbonate chemistry variability experienced

by organisms living in polar waters may equip them with the resilience to cope with both experimental and future OA.

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. A number of previous studies in polar waters have reported similar findings. Phytoplankton communities were able to tolerate a pCO_2 range of 84 – 643 µatm in ~12 d minicosm experiments (650 L) in Antarctic coastal waters, with no effects on nanophytoplankton abundance, and enhanced abundance of picophytoplankton and prokaryotes (Davidson et al., 2016; Thomson et al., 2016). In experiments under the Arctic ice, microbial communities demonstrated the capacity to respond either by selection or physiological plasticity to elevated CO_2 during short term experiments (Monier et al., 2014). Subarctic phytoplankton populations demonstrated a high level of resilience to OA in short term experiments, suggesting a high level of physiological plasticity that was attributed to the prevailing strong gradients in pCO_2 levels experienced in the sample region (Hoppe et al., 2017). Furthermore, a more recent study describing ten CO_2 manipulation experiments in Arctic waters found that primary production was largely insensitive to OA over a large range of light and temperature levels (Hoppe et al., 2018). This supports our hypothesis that, relative to temperate communities, polar microbial communities may have a high capacity to compensate for environmental variability (Hoppe et al., 2018), and are thus already adapted to, and are able to tolerate, large variations in carbonate chemistry. Thus by performing multiple, replicated experiments over a broad geographic range, the findings of this study imply that the DMS response may be both a reflection of: (i) the level of sensitivity of the community to changes in the mean state of carbonate chemistry, and (ii) the regional variability in carbonate chemistry experienced by different communities. This highlights the limitations associated

630 with simple extrapolation of results from a small number of geographically-limited
631 experiments e.g. Six et al. (2013). Such an approach lacks a mechanistic understanding that
632 would allow a model to capture the regional variability in response that is apparent from the
633 microcosms experiments presented here.

634 **4.4 Comparison to an Arctic mesocosm experiment**

635 Experimental data clearly provide useful information on the potential future DMS response to
636 OA, but these data become most powerful when incorporated in Earth System Models (ESM)
637 to facilitate predictions of future climate. To date, two modelling studies have used ESM to
638 assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al.,
639 2013;Schwinger et al., 2017), and both have used results from mesocosm experiments.
640 However, the DMS responses to OA within our short term microcosm experiments contrast
641 with the results of most previous mesocosm experiments, and of particular relevance to this
642 study, an earlier Arctic mesocosm experiment (Archer et al., 2013). Whilst no response in
643 DMS concentrations to OA was generally seen in the polar microcosm experiments discussed
644 here, a significant decrease in DMS with increasing levels of CO_2 in the earlier mesocosm
645 study was seen. Therefore, it is useful to consider how the differences in experimental design,
646 and other factors, between microcosms and mesocosms may result in contrasting DMS
647 responses to OA.

648 The short duration of the microcosm experiments (4 – 7 d) allows the physiological
649 (phenotypic) capacity of the community to changes in carbonate chemistry to be assessed. In
650 other words, how well is the community adapted to variable carbonate chemistry and how
651 does this influence its ability to acclimate to change? Although the mesocosm experiment
652 considered a longer time period (4 weeks), the first few days can be compared to the
653 microcosms. No differences in DMS or DMSP concentrations were detected for the first
654 week of the mesocosm experiment, implying a certain level of insensitivity of DMS

655 production to the rapid changes in carbonate chemistry. In fact, when taking all previous
656 mesocosm experiments into consideration, differences in DMS concentrations have
657 consistently been undetectable during the first 5 – 10 days, implying there is a limited short-
658 term physiological response by the in situ communities (Hopkins et al., 2010; Avgoustidi et
659 al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014). This is in contrast to the
660 strong response in the temperate microcosms from the NW European shelf (Hopkins and
661 Archer, 2014). However, all earlier mesocosm experiments have been performed in coastal
662 waters, which like polar waters, can experience a large natural range in carbonate chemistry.
663 In the case of coastal waters this is driven to a large extent by the influence of riverine
664 discharge and biological activity (Fassbender et al., 2016). Thus coastal communities may
665 also possess a higher level of adaptation to variable carbonate chemistry compared to the
666 open ocean communities of the temperate microcosms (Fassbender et al., 2016).

667 The later stages of mesocosm experiments address a different set of hypotheses, and are less
668 comparable to the microcosms reported here. With time, an increase in number of generations
669 leads to community structure changes and taxonomic shifts, driven by selection on the
670 standing genetic variation in response to the altered conditions. Moreover, the coastal Arctic
671 mesocosms were enriched with nutrients after 10 days, affording relief from nutrient
672 limitation and allowing differences between pCO_2 treatments to be exposed, including a
673 strong DMS(P) response.(Archer et al., 2013; Schulz et al., 2013). During this period of
674 increased growth and productivity, CO_2 increases drove changes which reflected both the
675 physiological and genetic potential within the community, and resulted in taxonomic shifts.
676 The resultant population structure was changed, with an increase in abundance of
677 dinoflagellates, particularly *Heterocapsa rotundata*. Increases in DMSP concentrations and
678 DMSP synthesis rates were attributed to the population shift towards dinoflagellates. The
679 drivers of the reduced DMS concentrations were less clear, but may have been linked to

680 reduced DMSP-lyase capacity within the dominant phytoplankton, a reduction in bacterial
681 DMSP lysis, or an increase in bacterial DMS consumption rates (Archer et al., 2013). Again,
682 this is comparable to all other mesocosm experiments, wherein changes to DMS
683 concentrations can be associated with CO_2-driven shifts in community structure (Hopkins et
684 al., 2010; Avgoustidi et al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014; Webb
685 et al., 2015). However, given the lack of further experiments of a similar location, design and
686 duration to the Arctic mesocosm, it is unclear how representative the mesocosm result is of
687 the general community-driven response to OA in high latitude waters.

688 We did not generally see any broad-scale CO_2-effects on community structure in polar
689 waters. This can be demonstrated by a lack of significant differences in the mean ratio of >10
690 µm Chl *a* to total Chl *a* (*>10 µm : total*) between CO_2 treatments, implying there were no
691 broad changes in community composition (Table 2). *South Sandwich* was an exception to
692 this, where large and significant increases in the mean ratio of *>10 µm : total* were observed
693 at 750 µatm and 2000 µatm CO_2 relative to ambient CO_2 (ANOVA, $F = 207.144$, $p<0.001$, $df = 3$), demonstrated at even the short timescale of the microcosm experiments, it is possible
695 for some changes to community composition to occur. Interestingly, this was also the only
696 polar station that exhibited any significant effects on DMS after 96 h of incubation (Figure 4
697 D). However, given the lack of similar response at 1000 µatm, it remains equivocal whether
698 this was driven by a CO_2-effect or some other factor. The results of our microcosm
699 experiments suggest insensitivity of *de novo* DMSP production and net DMS production in
700 the microbial communities of the polar open oceans to short term changes in carbonate
701 chemistry. This may be driven by a high level of adaptation within the targeted
702 phytoplankton communities to naturally varying carbonate chemistry.

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

5 Conclusions

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

728 complex spatial and temporal variability in DMS response to OA which warrants further
729 investigation to improve model predictions.

730 Our results imply that the phytoplankton communities of the temperate microcosms initially
731 responded to the rapid increase in pCO_2 via a stress-induced response, resulting in large and
732 significant increases in DMS concentrations occurring over the shortest timescales (2 days),
733 with a lessening of the treatment effect with an increase in incubation time (Hopkins and
734 Archer 2014). The dominance of short response timescales in well-buffered temperate waters
735 may also indicate rapid acclimation of the phytoplankton populations following the initial
736 stress response, which forced the small-sized phytoplankton beyond their range of
737 acclimative tolerance and lead to increased DMS (Richier et al. 2018, Hopkins and Archer
738 2014). This supports the hypothesis that populations from higher latitude, less well-buffered
739 waters, already possess a certain degree of acclimative tolerance to variations in carbonate
740 chemistry environment. Although initial community size structure was not a significant
741 predictor of the response to high CO_2, it is possible that a combination of both community
742 composition and the natural range in variability in carbonate chemistry – as a function of
743 buffer capacity – may influence the DMS/P response to OA over a range of timescales
744 (Richier et al. 2018).

745 Our findings should be considered in the context of timescales of change (experimental vs
746 real world OA) and the potential of microbial communities to adapt to a gradually changing
747 environment. Microcosm experiments focus on the physiological response of microbial
748 communities to short term OA. Mesocosm experiments consider a timescale that allows the
749 response to be driven by community composition shifts, but are not long enough in duration
750 to incorporate an adaptive response. Neither approach is likely to accurately simulate the
751 response to the gradual changes in surface ocean pH that will occur over the next 50 – 100
752 years, nor the resulting changes in microbial community structure and distribution. However,

753 we hypothesise that the DMS response to OA should be considered not only in relation to
754 experimental perturbations to carbonate chemistry, but also in relation to the magnitude of
755 background variability in carbonate chemistry experienced by the DMS-producing organisms
756 and communities. Our findings suggest a strong link between the DMS response to OA and
757 background regional variability in the carbonate chemistry.

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

768 **Data availability**

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

770 **Author contributions**

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

774 **Competing interests**

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

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1150 Table 1. Summary of the station locations and characteristic of the water sampled for the 18 microcosm experiments performed in temperate,
1151 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* ($\mu g\ L^{-1}$)	$chl_{>10\ \mu m}$: chl_{total}	pCO_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 (2*
	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 (2*
	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 (2*
	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 (2*
	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 (2*
	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*

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

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

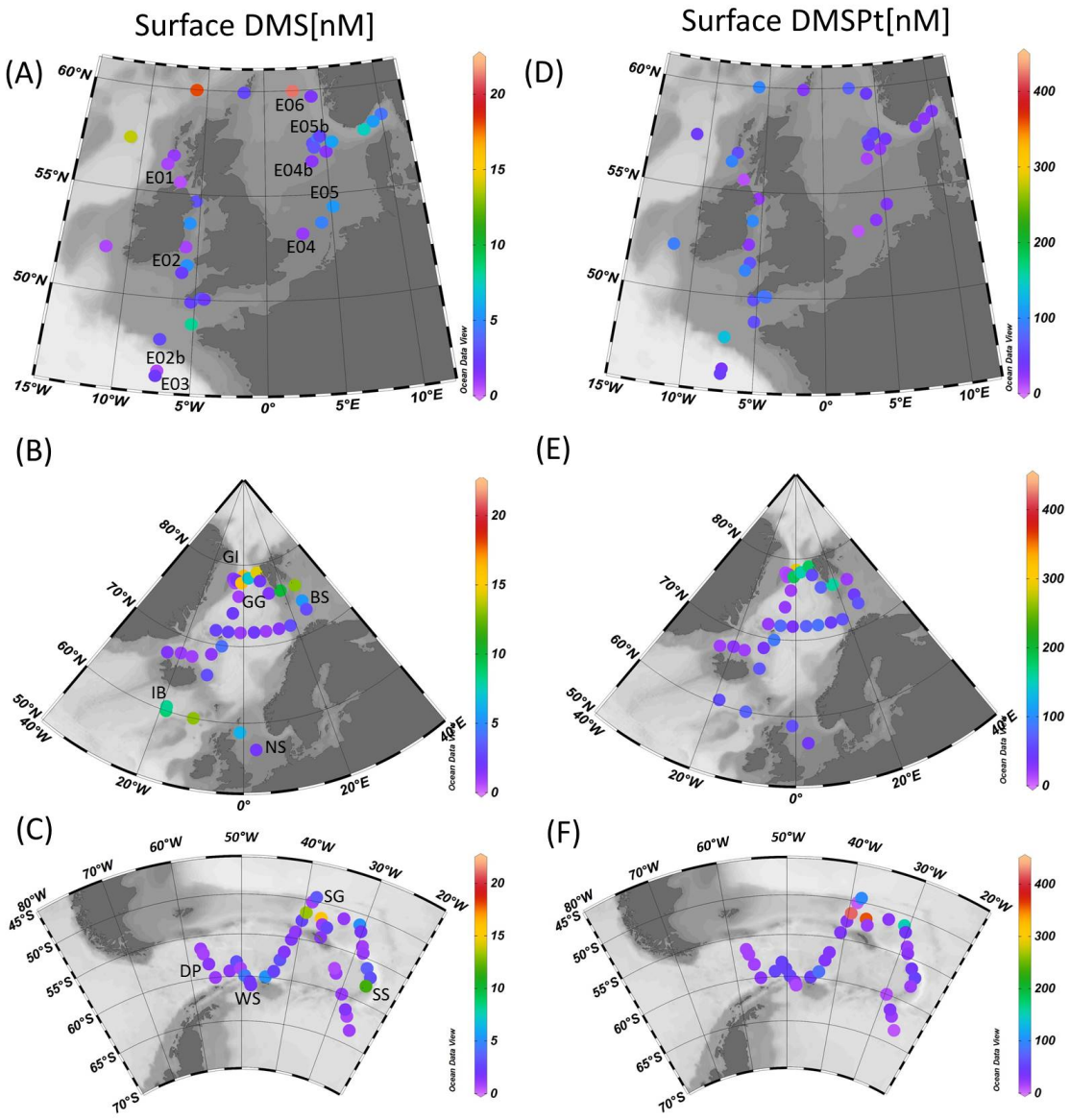


Figure 1. Surface (<5 m) concentrations (nM) of DMS (A-C) and total DMSP (D-F) for cruises in the NW European shelf (D366) (A,D), the sub-Arctic and Arctic Ocean (JR271) (B,E) and the Southern Ocean (JR274) (C,F). Locations of sampling stations for microcosm experiments shown in letters/numbers. E01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

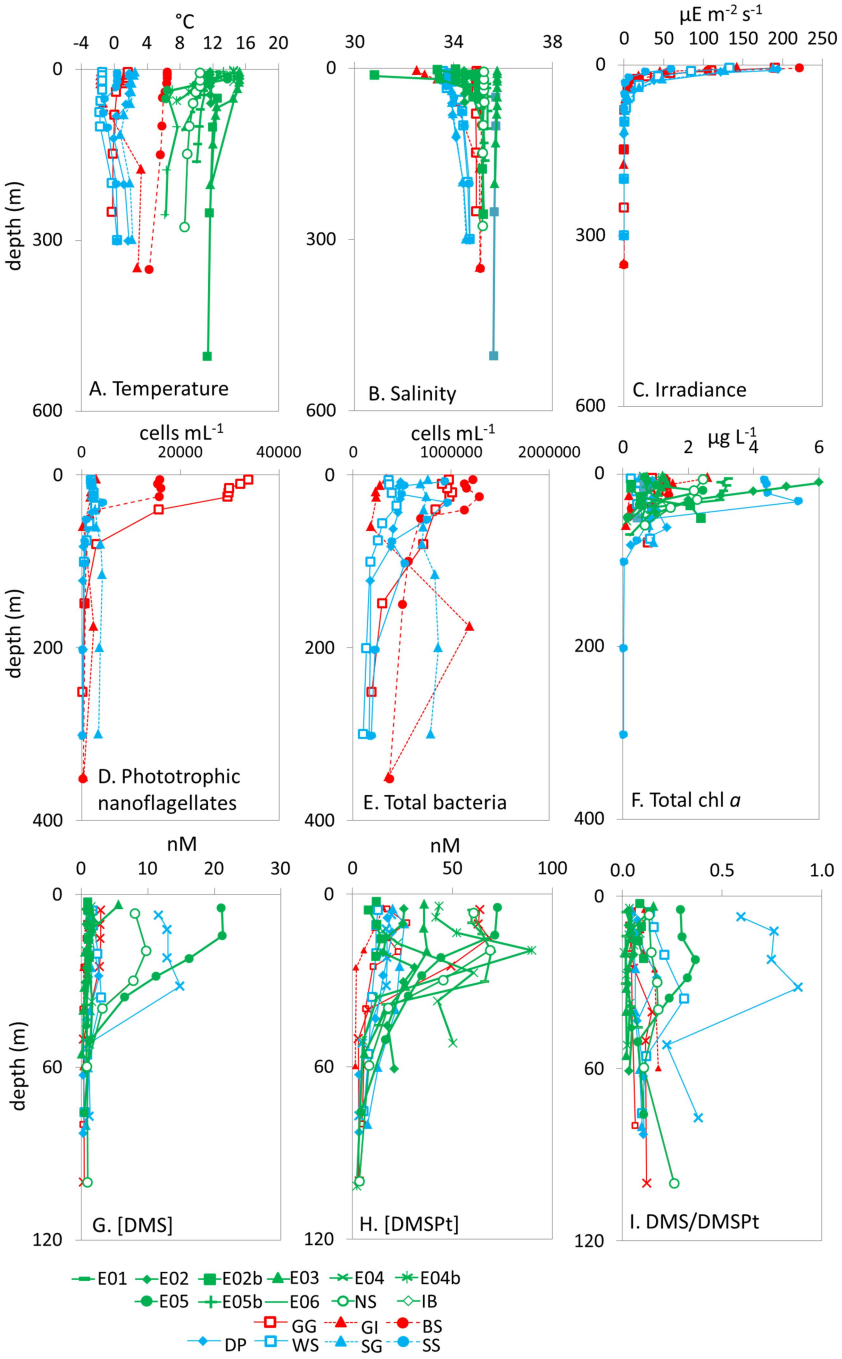
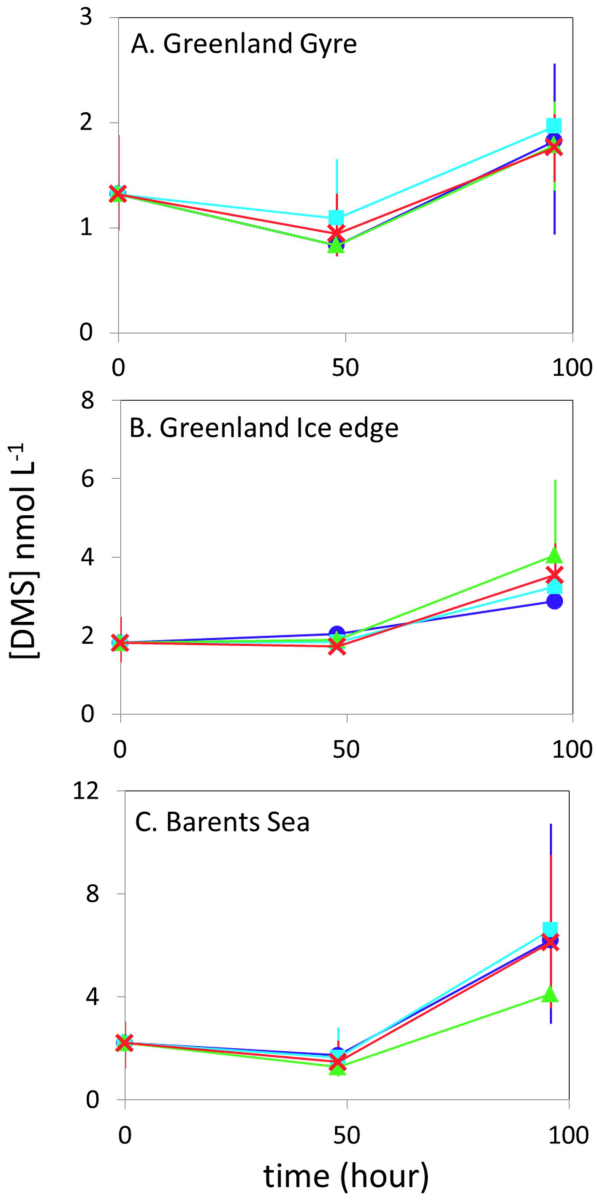


Figure 2. Depth profiles for all 18 sampling stations showing A. Temperature (°C), B. Salinity, C. Irradiance (µE m^{-2} s^{-1}), D. phototrophic nanoflagellate abundance (cells mL^{-1}), E. total bacteria abundance (cells mL^{-1}), F. total Chl a (µg L^{-1}), G. [DMS] (nM), H. total [DMSP] (nM) and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

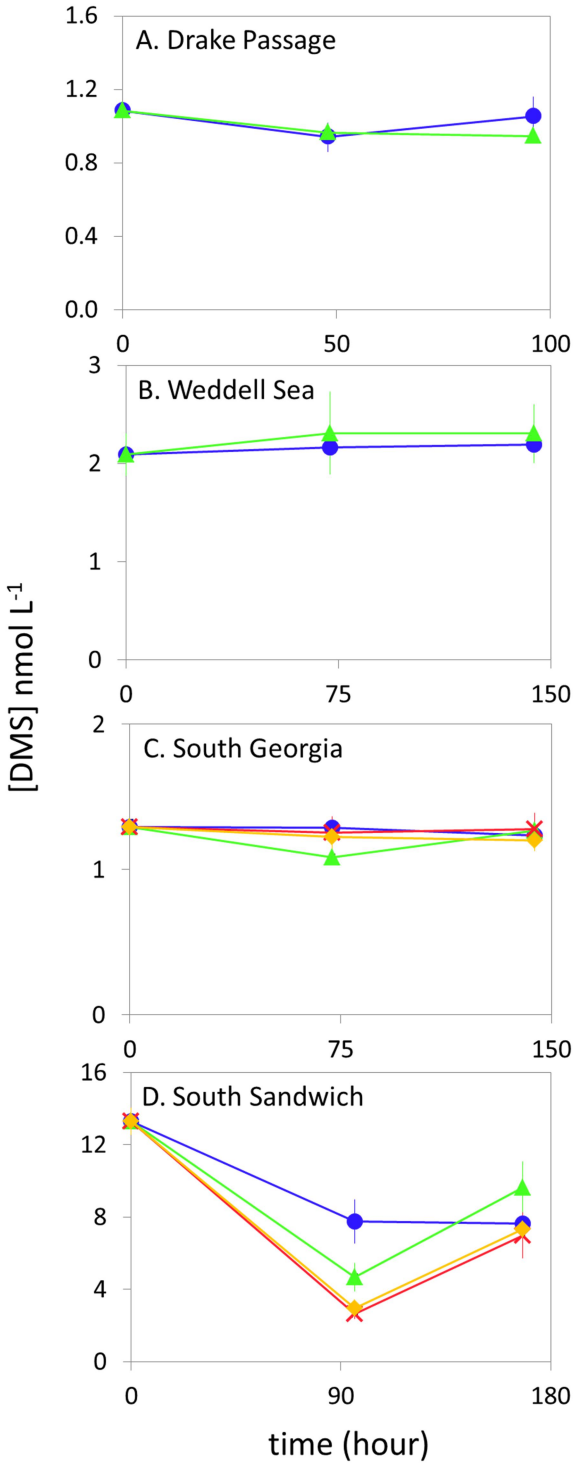


CO_2 treatment	pCO_2 (µatm) mean ± SD, n = 3		
	0 h	48 h	96 h
Ambient ●	326.8	No data	251.5 ± 5.1
Mid ■	565.2	493.8 ± 49.0	416.7 ±18.5
High ▲	741.8	607.6 ± 53.9	526.1 ± 18.1
High+ ×	1012.2	824.1 ± 99.5	668.6 ± 33.6

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

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

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

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

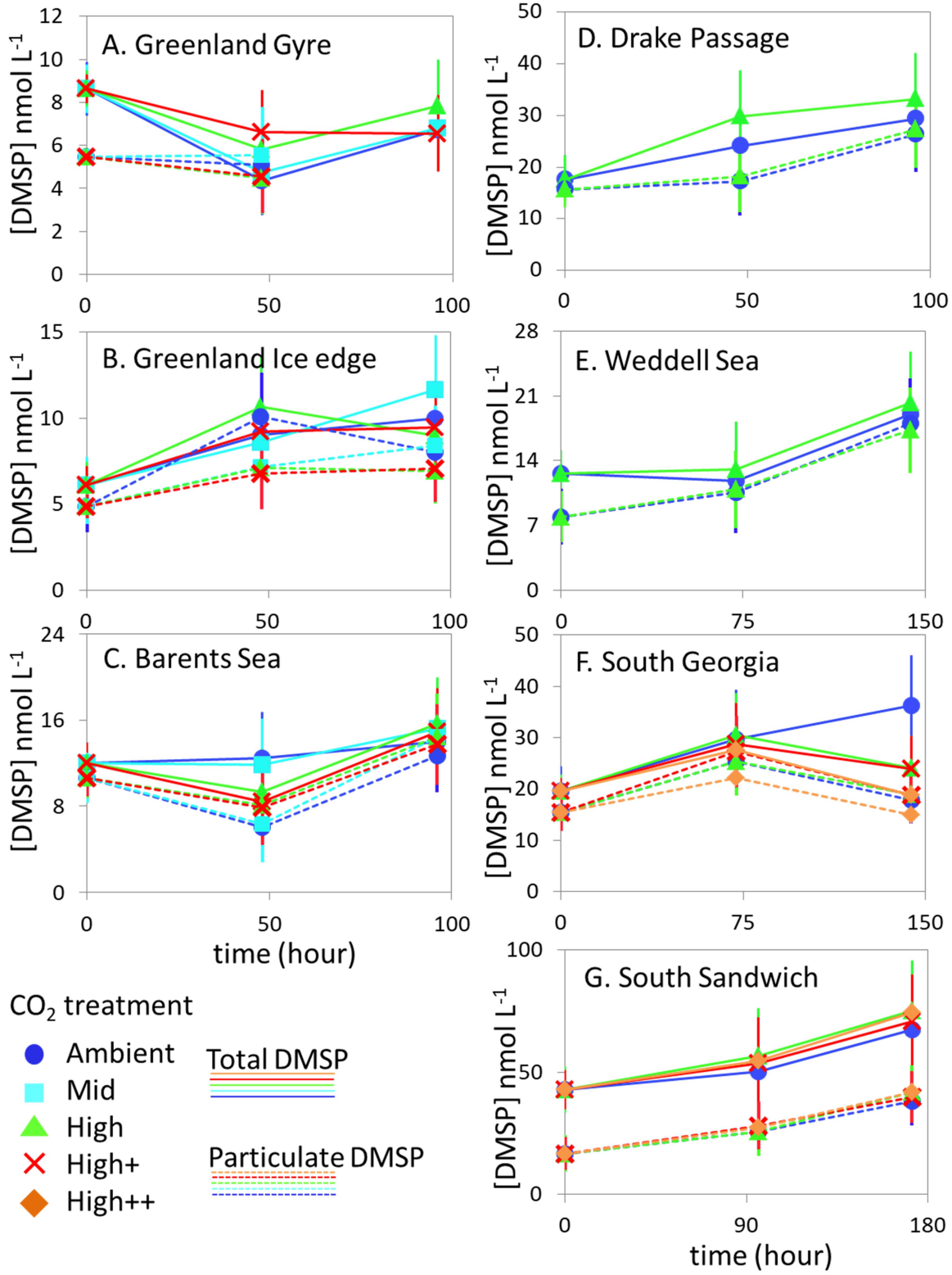


Figure 5. Total DMSP (solid lines) and particulate DMSP (dashed lines) concentrations (nmol L^{-1}) during experimental microcosms performed in Arctic waters (A - C) and in Southern Ocean waters (D – G). Data shown is mean of triplicate incubations, and error bars show standard error on the mean. Locations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

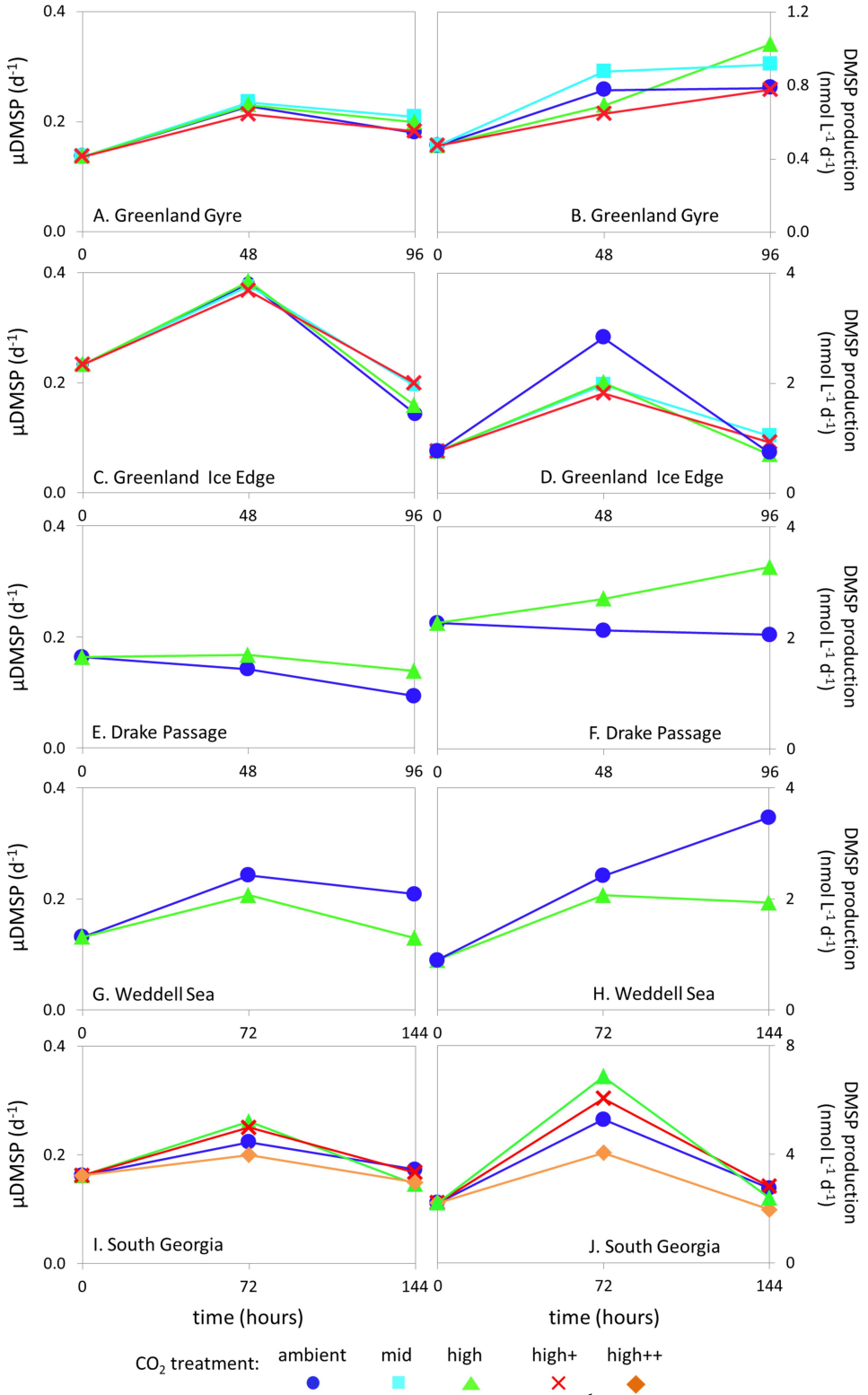


Figure 6. De novo synthesis of DMSP (µDMSP, d^{-1}) (left column) and DMSP production rates (nmol L^{-1} d^{-1}) (right column) for Arctic Ocean stations *Greenland Gyre* (A,B), *Greenland Ice-edge* (C, D) and Southern Ocean stations *Drake Passage* (E, F), *Weddell Sea* (G, H) and *South Georgia* (I,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

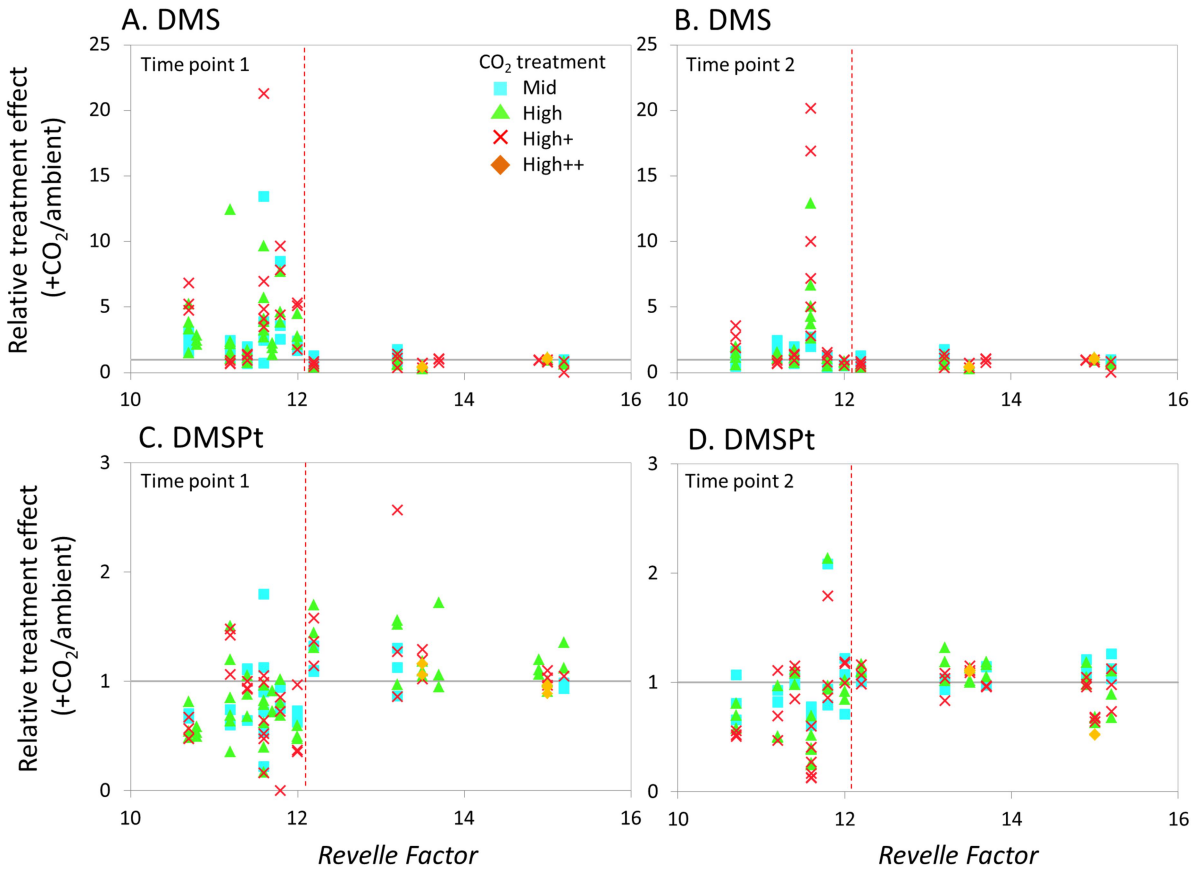


Figure 7. Relationship between Revelle Factor of the sampled water and the relative CO_2 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for concentrations of DMS at T_1 (A) and T_2 (B), and for total DMSP concentrations at T_1 (C) and T_2 (D) for all microcosm experiments performed in NW European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

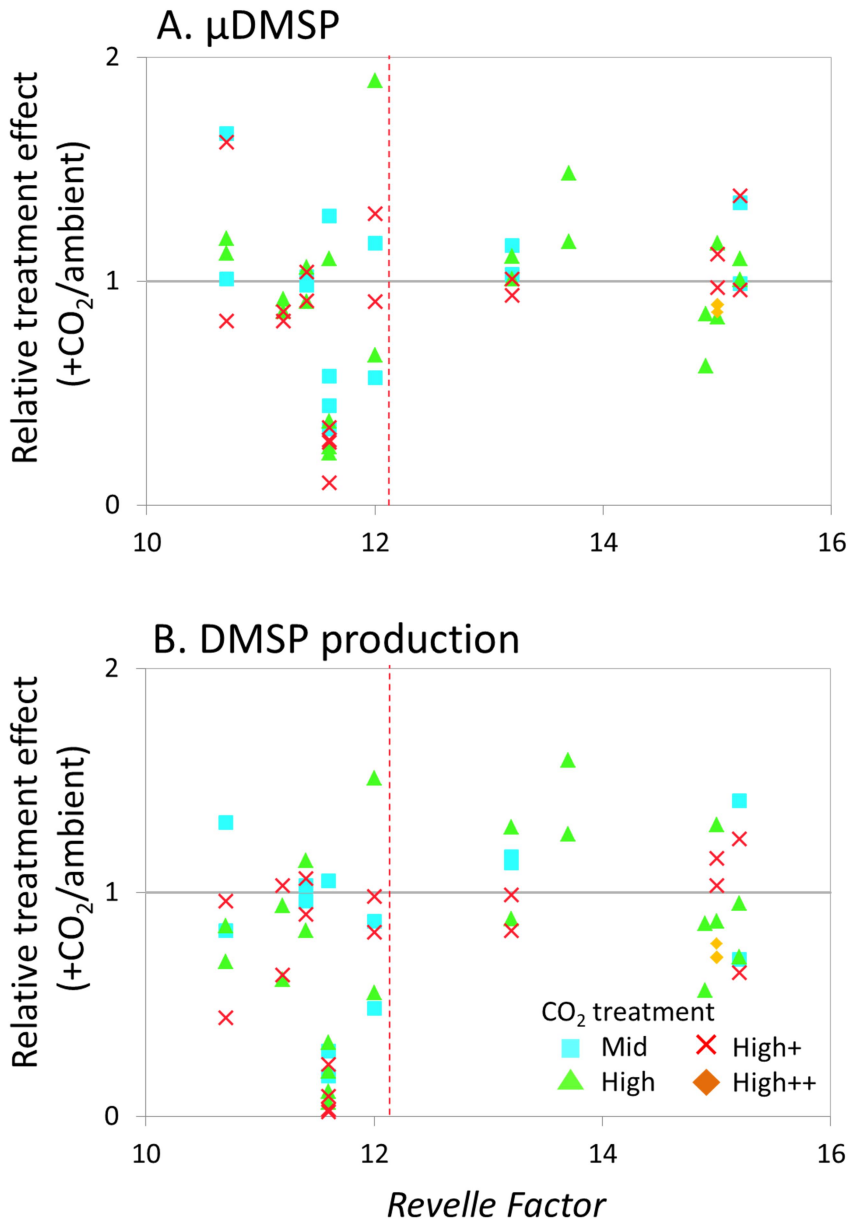
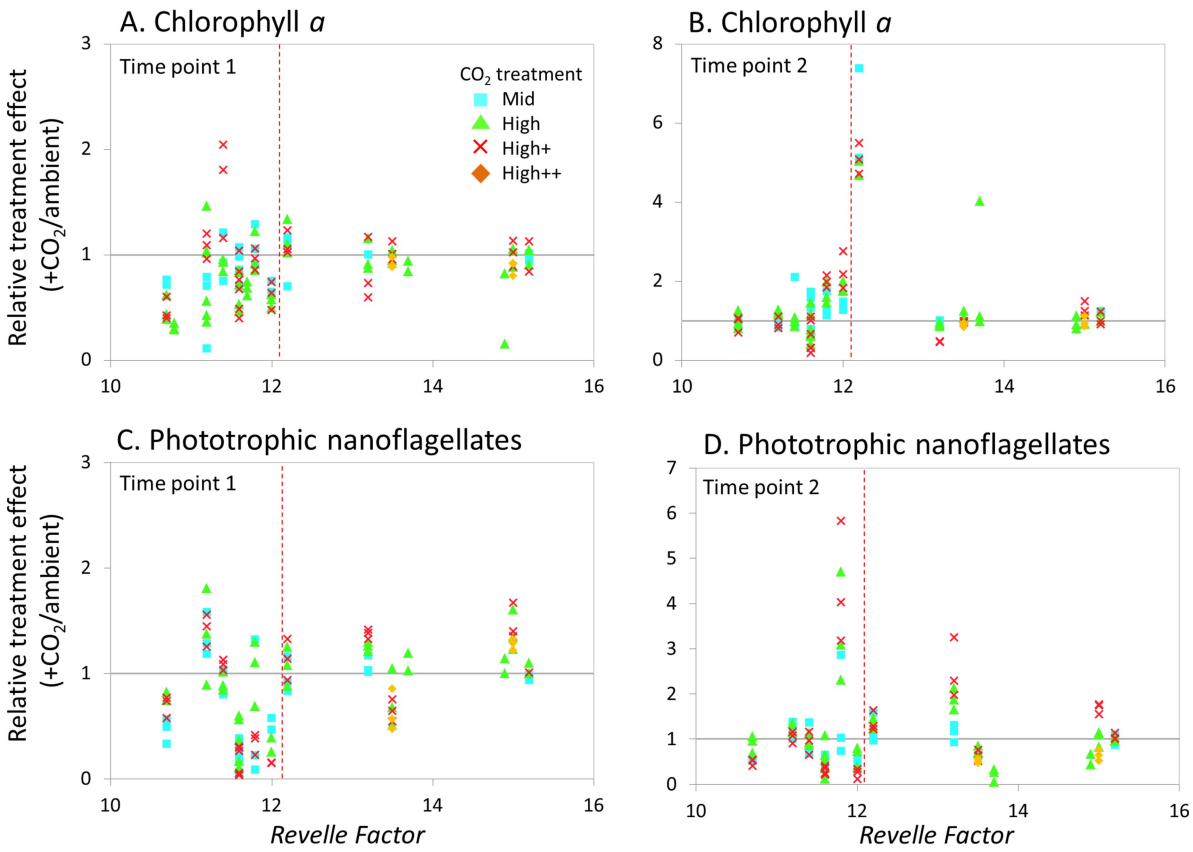


Figure 8. Relationship between the Revelle Factor of the sampled water and the relative CO_2 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for de novo DMSP synthesis (µDMSp, d^{-1}) at T_1 (A) and T_2 (B), and DMSP production rate (nmol L^{-1} d^{-1}) at T_1 (C) and T_2 (D) for microcosm experiments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



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1220 Figure 9. Relationship between the Revelle Factor of the sampled water and the relative CO_2
1221 treatment effect ($[x]_{highCO2}/[x]_{ambientCO2}$) for chlorophyll *a* concentrations at T_1 (A) and T_2 (B)
1222 and phototrophic nanoflagellate abundance at T1 (C) and T2 (D) for all microcosm
1223 experiments performed in NW European waters, sub-Arctic and Arctic waters, and the
1224 Southern Ocean. Grey solid line (= 1) indicates no effect of elevated CO_2. Revelle Factor >12
1225 = polar waters (indicated by red dashed line). T_1 = 48 h, T_2 = 96 h, except for *Weddell Sea*
1226 and *South Georgia* (72 h, 144 h) and *South Sandwich* (96 h, 168 h).

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