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

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

The biologically-rich ice-edge regions and open seas of the Arctic 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). 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.

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., 2013a; 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). 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). 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 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.

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 the smaller microcosm scale. Nevertheless, our approach can provide insight into the physiological response and level of sensitivity to future OA of a variety of 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

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 Additionally, four previously unpublished experiments from D366 are also included (E02b, E04b, E05b, E06) as well as two temperate experiments from JR271 (NS and IB) (see Table 1).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

2.2 Shipboard microcosm experiments

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

199 although differences in pCO_2 between target and initial values were greater in the higher
200 pCO_2 treatments, due to lowered carbonate system buffer capacity at higher pCO_2. For all 18
201 experiments, actual pCO_2 values at 0 h were on average around 89% ± 12% (± 1 SD) of
202 target values. The attained pCO_2 values, and pCO_2 at each experimental time point, are
203 presented in Figures 3 and 4. After first ensuring the absence of bubbles or headspace, the
204 bottles were sealed with high density polyethylene (HDPE) lids with silicone/
205 polytetrafluoroethylene (PTFE) septa and placed in the incubation container. Bottles were
206 incubated inside a custom-designed temperature- and light-controlled shipping container, set
207 to match (±<1°C) the *in situ* water temperature at the time of water collection (shown in
208 Table 1) (see Richier et al. 2018). A constant light level (100 µE m^{-2} s^{-1}) was provided by
209 daylight simulating LED panels (Powerpax, UK). The light period within the microcosms
210 was representative of *in situ* conditions. For the sub-Arctic/Arctic Ocean stations,
211 experimental bottles were subjected to continuous light representative of the 24 h daylight of
212 the Arctic summer. For Southern Ocean and all temperate water stations, an 18:6 light: dark
213 cycle was used. Each bottle belonged to a set of triplicates, and sacrificial sampling of bottles
214 was performed at two time points (see Table 1 for exact times). Use of three sets of triplicates
215 for each time point allowed for the sample requirements of the entire scientific party (3 x 3
216 bottles, x 2 time points (see Table 1 for specific times for each experiment), x 4 CO_2
217 treatments = 72 bottles in total). Experiments were run for between 4 and 7 days (96 h – 168
218 h) (15 out of 18 experiments), with initial sampling proceeded by two further time points. For
219 three temperate experiments (E02b, E04b, E05b see Table 1 and Table 2) shorter two day
220 incubations were performed, with a single sampling point at the end. E06 was run for 96 h
221 (Table 1 and 2). Incubation times were extended for Southern Ocean stations *Weddell Sea*,
222 *South Georgia* and *South Sandwich* (see Table 1) as minimal CO_2 response, attributed to
223 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 polar waters were hydrolysed within 1 h of sample collection and analysed 6 – 12 h later. The H_2SO_4 fixation method was not used for samples from polar waters given the likely occurrence of *Phaeocystis sp*. which can result in the overestimation of DMSP concentrations (del Valle et al., 2009). Similarly, concentrations of DMSPp were determined at each time point by gravity filtering 7 ml of sample onto a 25 mm GF/F filter and preserving the filter in 7 ml of 35 mM H_2SO_4 in MQ-water (temperate samples) or immediately hydrolysing (polar samples) and analysing by GC-PFPD. DMS calibrations were performed using alkaline cold-

248 hydrolysis (1 M NaOH) of DMSP sequentially diluted three times in MilliQ water to give
249 working standards in the range 0.03 – 3.3 ng S mL^{-1}. Five point calibrations were performed
250 every 2 – 4 days throughout the cruise.

251 **2.4 *De novo* DMSP synthesis**

252 *De novo* DMSP synthesis and gross production rates were determined for all microcosm
253 experiments, except *Barents Sea* and *South Sandwich*, at each experimental time point, using
254 methods based on the approach of Stefels et al. (2009) and described in detail in Archer et al.
255 (2013) and Hopkins and Archer (2014). Triplicate rate measurements were determined for
256 each CO_2 level. For each rate measurement three x 500 mL polycarbonate bottles were filled
257 by gently siphoning water from each replicate microcosm bottle. Trace amounts of
258 $NaH^{13}CO_3$, equivalent to ~6 % of *in situ* dissolved inorganic carbon (C_T), were added to each
259 500 mL bottle. The bottles were incubated in the microcosm incubation container with
260 temperature and light levels as described earlier. Samples were taken at 0 h, then at two
261 further time points over a 6 - 9 h period. At each time point, 250 mL was gravity filtered in
262 the dark through a 47 mm GF/F filter, the filter gently folded and placed in a 20 mL serum
263 vial with 10 mL of Milli-Q and one NaOH pellet, and the vial was crimp-sealed. Samples
264 were stored at -20°C until analysis by proton transfer reaction-mass spectrometer (PTR-MS)
265 (Stefels et al. 2009).

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

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

268

(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).

293 **2.6 Chlorophyll a (Chl *a*) determinations**

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

301 **2.8 Community composition**

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

304 **2.9 Data handling and statistical analyses**

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

314 One-way analysis of variance was used to identify differences in ratio of >10 µm Chl *a* to
315 total Chl *a* ($chl_{>10um}$: chl_{tot} , see Discussion). Initially, tests of normality were applied (p<0.05

316 = not normal), and if data failed to fit the assumptions of the test, linearity transformations of
317 the data were performed (logarithmic or square root), and the ANOVA proceeded from this
318 point. The results of ANOVA are given as follows: *F* = ratio of mean squares, *df* = degrees of
319 freedom, *p* = level of confidence. For those data still failing to display normality following
320 transformation, a rank-based Kruskal-Wallis test was applied (*H* = test statistic, *df* = degrees
321 of freedom, *p* = level of confidence).

322 **3 Results**

323 **3.1 Sampling stations**

324 At temperate sampling stations, sea surface temperatures ranged from 10.7°C for *Iceland*
325 *Basin*, to 15.3°C for *Bay of Biscay*, with surface salinity in the range 34.1 – 35.2, with the
326 exception of station E05b which had a relatively low salinity of 30.5 (Figure 2 and Table 1).
327 Seawater temperatures at the polar microcosm sampling stations ranged from -1.5°C at sea-
328 ice influenced stations (*Greenland Ice-edge* and *Weddell Sea*) up to 6.5°C for *Barents Sea*
329 (Fig. 2 A). Salinity values at all the Southern Ocean stations were <34, whilst they were ~35
330 at all the Arctic stations with the exception of *Greenland Ice-edge* which had the lowest
331 salinity of 32.5 (Fig. 2 B). Phototrophic nanoflagellate abundances were variable, with >3 x
332 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}
333 for all other stations (Fig. 2 D). Total bacterial abundances ranged from 3 x 10^5 cells mL^{-1} at
334 *Greenland Ice-edge* up to 3 x 10^6 cells mL^{-1} at *Barents Sea* (Fig. 2 E).

335 Chl *a* concentrations in temperate waters ranged from 0.3 µg L^{-1} for two North Sea stations
336 (*E05* and *North Sea*) up to 3.5 µg L^{-1} for *Irish Sea* (Figure 2 and Table 1). Chl a was also
337 variable in polar waters, exceeding 4 µg L^{-1} at *South Sandwich* and 2 µg L^{-1} at *Greenland Ice-*
338 *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). 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.

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

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

3.3 Response of de novo DMSP synthesis and production to OA

Rates of *de novo* DMSP synthesis (µDMSP) at initial time points ranged from 0.13 d^{-1} (*Weddell Sea*, Fig. 6 G) to 0.23 d^{-1} (*Greenland Ice-edge*, Fig. 6 C), whilst DMSP production ranged from 0.4 nmol L^{-1} d^{-1} (*Greenland Gyre*, Fig. 6 B) to 2.27 nmol L^{-1} d^{-1} (*Drake Passage*, Fig. 6 F). Maximum rates of µDMSP of 0.37 -0.38 d^{-1} were observed at *Greenland Ice-edge* after 48 h of incubation in all CO_2 treatments (Fig. 6 C). The highest rates of DMSP production were observed at *South Georgia* after 96 h of incubation, and ranged from 4.1 – 6.9 nmol L^{-1} d^{-1} across CO_2 treatments (Fig. 6 J). Rates of DMSP synthesis and production were generally lower than those measured in temperate waters (Hopkins and Archer, 2014) (Initial rates: µDMSP 0.33 – 0.96 d^{-1}, 7.1 – 37.3 nmol L^{-1} d^{-1}), but were comparable to measurements made during an Arctic mesocosm experiment (Archer et al., 2013) (0.1 – 0.25 d^{-1}, 3 – 5 nmol L^{-1} d^{-1} in non-bloom conditions). The lower rates in cold polar waters likely reflect slower metabolic processes and are reflected by standing stock DMSP concentrations which were also lower than in temperate waters (5 – 40 nmol L^{-1} polar, 8 – 60 nmol L^{-1} temperate (Hopkins and Archer, 2014)). No consistent effect of high CO_2 were observed for either DMSP synthesis or production in polar waters, similar to findings for DMSP standing stocks. However, some notable but contrasting differences between CO_2 treatments were observed. There was a 36% and 37% increase in µDMSP and DMSP production respectively at 750 µatm for the *Drake Passage* after 96 h (Figure 6 E, F), and a 38% and 44% decrease in both at 750 µatm after 144 h for *Weddell Sea* (Figure 5 G, H). For *Drake Passage*, the difference between treatments at 96 h coincided with significantly higher nitrate concentrations in the High CO_2 treatment (Nitrate/nitrite at 96 h: Ambient = 18.9 ± 0.2 µmol L^{-1}, +CO_2 = 20.2 ± 0.1 µmol L^{-1}, ANOVA $F = 62.619$, $df = 1$, $p = 0.001$). However, it is uncertain whether the difference in nutrient availability between treatments (approximately 5 %) would be significant enough to strongly influence the rate of DMSP production.

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

417 **4 Discussion**

418 **4.1 Regional differences in the response of DMS(P) to OA**

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

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

434 The relative treatment effects ($[x]_{highCO2}/[x]_{ambientCO2}$) for DMS and DMSP (Figure 7), DMSP
435 synthesis and production (Figure 8), and Chl *a* and phototrophic nanoflagellate abundance

436 (Figure 9) are plotted against the Revelle Factor of the sampled waters. The Revelle Factor
437 (R), calculated here with CO2Sys using measurements of carbonate chemistry parameters (R
438 = $(\Delta pCO_2/\Delta TCO_2)/(pCO_2/TCO_2)$, Lewis and Wallace, 1998), describes how the partial
439 pressure of CO_2 in seawater (PCO_2) changes for a given change in DIC (Sabine et al., 2004;
440 Revelle and Suess, 1957). Its magnitude varies latitudinally, with lower values (9 – 12) from
441 the tropics to temperate waters, and the highest values in cold high latitude waters (13 – 15).
442 Thus polar waters can be considered poorly buffered with respect to changes in DIC.
443 Therefore, biologically-driven seasonal changes in seawater pCO_2 would result in larger
444 changes in pH than would be experienced in temperate waters (Egleston et al., 2010).
445 Furthermore, the seasonal sea ice cycle strongly influences carbonate chemistry, such that sea
446 ice regions exhibit wide fluctuations in carbonate chemistry (Revelle and Suess, 1957; Sabine
447 et al., 2004). Sampling stations with a R above ~12 represent the seven polar stations (right of
448 red dashed line Fig. 7, 8, 9). The surface waters of the polar oceans have naturally higher
449 levels of DIC and a reduced buffering capacity, driven by higher CO_2 solubility in colder
450 waters (Sabine et al., 2004). Thus, the relationship between experimental response and R is a
451 simple way of demonstrating the differences in response to OA between temperate and polar
452 waters and provides some insight into how the CO_2 sensitivity of different surface ocean
453 communities may relate to the *in situ* carbonate chemistry. The effect of elevated CO_2 on
454 DMS concentrations at polar stations, relative to ambient controls, was minimal at both
455 sampling points, and is in strong contrast to the results from experiments performed in waters
456 with lower values of R on the NW European shelf. In contrast, at temperate stations, DMSP
457 concentrations displayed a clear negative treatment effect, whilst at polar stations a positive
458 effect was evident under high CO_2 and particularly at the first time point (48 – 96 h) (Fig. 7 C
459 and D). *De novo* DMSP synthesis and DMSP production rates show a less consistent
460 response in either environment (Fig. 8 A and B), although a significant suppression of

461 DMSP production rates in temperate waters compared to polar waters was seen (Fig. 8 B,
462 Kruskal-Wallis One Way ANOVA $H = 8.711$, $df = 1$, $p = 0.003$). A similar but not significant
463 response was seen for *de novo* DMSP synthesis (Fig. 8A).

464 Our data imply that DMSP concentrations in temperate waters were downregulated in
465 response to OA, attributed to the adverse effects of rapid OA on the growth of DMSP
466 producers which led to reductions in the abundance of these types of phytoplankton (Richier
467 et al. 2014, Hopkins and Archer 2014). By comparison, a more muted, but generally positive,
468 DMSP response was seen in polar waters at the first time point, whilst these treatment effects
469 were more or less undetectable by the second time point. There is some evidence that the
470 enhanced DMSP concentrations in polar waters were accompanied by increased DMSP
471 production rates (Figure 8), although data is not available for all experiments. However, these
472 changes may reflect a short term 'shock' physiological protective response to the
473 experimental OA, similar to that seen in response to other short term stressors such as high
474 irradiance that result in an increase in DMSP concentrations (Sunda et al., 2002;Galindo et
475 al., 2016). The lack of treatment effect in DMSP concentrations by the second time point may
476 be indicative that the community had, to some extent, acclimated to the change, allowing
477 DMSP production/concentrations to return to baseline levels. This may reflect a higher
478 degree of tolerance to rapid changes in carbonate chemistry amongst polar communities -
479 species which are already adapted to highly variable irradiance/carbonate chemistry regimes
480 (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015). Further
481 experiments with polar communities would help to unravel the potential importance of such
482 mechanisms and whether they facilitated the ability of polar phytoplankton communities to
483 resist the high CO_2 treatments.

484 The responses to OA observed for DMS and DMSP production are likely to be reflected in
485 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.

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).

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, as well as Southern Ocean 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,

511 with significant increases for *South Georgia* after 144 h of incubation (ANOVA $F = 137.936$,
512 $p<0.001$). Additionally, at Arctic stations *Greenland Gyre* and *Greenland Ice-edge*, no
513 overall effect of increased CO_2 on rates of DOC release, total carbon fixation or POC : DOC
514 was observed (Poulton et al. 2016).

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

521 **4.2 Influence of community cell-size composition on DMS response**

522 It has been proposed that variability in the concentrations of carbonate species (e.g. pCO_2,
523 HCO_3^-, CO_3^{2-}) experienced by phytoplankton is related to cell size, such that smaller-celled
524 taxa (<10 μm) with a reduced diffusive boundary layer are naturally exposed to relatively less
525 variability compared to larger cells (Flynn et al., 2012). Thus, short-term and rapid changes in
526 carbonate chemistry, such as the kind imposed during our microcosm experiments, may have
527 a disproportionate effect on the physiology and growth of smaller celled species. Larger cells
528 may be better able to cope with variability as normal cellular metabolism results in significant
529 cell surface changes in carbonate chemistry parameters (Richier et al., 2014). Indeed, the
530 marked response in DMS concentrations to short term OA in temperate waters has been
531 attributed to this enhanced sensitivity of small phytoplankton (Hopkins and Archer, 2014).
532 Was the lack of DMS response to OA in polar waters therefore a result of the target
533 communities being dominated by larger-celled, less carbonate-sensitive species?

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

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

558 concentrations (e.g. sea ice formation and melt, enhanced CO_2 dissolution into cold polar
559 waters, upwelling of CO_2 rich water). Therefore, polar plankton communities are not only
560 subject to geophysical processes that strongly alter in situ carbonate chemistry on both spatial
561 and seasonal scales, but such changes are accompanied by larger pH changes than would
562 occur in more strongly buffered temperate waters. Therefore, polar surface ocean
563 communities are perhaps more likely to experience fluctuations between high pH and low pH
564 over relatively smaller time/space scales (Tynan et al., 2016). Thus below, we discuss our
565 findings in the context of the spatial pH variability we observed for each cruise track, and
566 explore some of the processes that drive this variability in polar waters. Information on the
567 pH variability at each sampling station is not available, so we cannot be certain of the exact
568 carbonate chemistry variability to which each of the sampled communities may have been
569 exposed and adapted. However, we can consider the overall variability in carbonate
570 chemistry over the spatial scales of the cruise tracks to demonstrate the characteristics of each
571 study area.
572 The polar waters sampled during our study were characterised by pronounced gradients in
573 carbonate chemistry over relatively small spatial scales. In underway samples taken along
574 each cruise track (Arctic Ocean 3500 nm, Southern Ocean 4000 nm), pH varied by 0.45 units
575 (8.00 – 8.45) in the Arctic, and 0.40 units (8.30 - 7.90) in the Southern Ocean (Tynan et al.
576 2016). In some cases this range in variability was seen over relatively small distances: Figure
577 4 in Tynan et al. (2016) shows that pH fluctuated from 8.45 and 8.0 over a distance of 50 –
578 100 miles in the sea-ice influenced Fram Strait. By comparison, pH varied by a total of 0.2
579 units (8.22 - 8.02) in underway samples from the NW European shelf sea cruise (Rerolle et
580 al. 2014). The observed horizontal gradients in polar waters were driven by different
581 physical and biogeochemical processes in each ocean. In the Arctic Ocean, this variability in
582 carbonate chemistry was partly driven by physical processes that controlled water mass

583 composition, temperate and salinity, particularly in areas such as the Fram Strait and
584 Greenland Sea. Along the ice-edge and into the Barents Sea, biological processes exerted a
585 strong control, as abundant iron resulted in high chlorophyll concentrations, low DIC and
586 elevated pH. By contrast, variations in temperature and salinity had only a small influence on
587 carbonate chemistry in the Southern Ocean in areas with iron limitation, and larger changes
588 were driven by a combination of calcification, advection and upwelling. Where iron was
589 replete, e.g. near South Georgia, biological DIC drawdown had a large impact on carbonate
590 chemistry (Tynan et al. 2016). A further set of processes was in play in sea ice influenced
591 regions. At the Arctic ice edge, abundant iron drove strong bloom development along the ice
592 edge, whilst sea ice retreat in the Southern Ocean was not always accompanied by iron
593 release (Tynan et al. 2016).
594 For comparison with Arctic stations, Hagens and Middelburg (2016) report a seasonal pH
595 variability of up to 0.25 units from a single site in the open ocean surface waters in the
596 Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability of 0.3 – 0.4 units in
597 the McMurdo Sound, Antarctica. This implies that both open ocean and sea ice-influenced
598 polar waters experience large variations in carbonate chemistry over seasonal cycles. By
599 contrast, monthly averaged surface pCO_2 data collected from station L4 in the Western
600 English Channel over the period 2007 – 2011 provides an example of typical carbonate
601 chemistry dynamics in NW European shelf sea waters. Over this period, pH had an annual
602 range of 0.15 units (8.05 – 8.20), accompanied by a range in pCO_2 of 302 – 412 μatm (Kitidis
603 et al., 2012).
604 The sea ice environment in particular is characterised by strong spatial and seasonal
605 variability in carbonate chemistry. Sea ice is inhabited by a specialised microbial community
606 with a complex set of metabolic and physiological adaptations allowing these organisms to
607 withstand wide fluctuations in pH up to as high as 9.9 in brine channels to as low as 7.5 in the

608 under-ice water (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015).
609 The open waters associated with the ice edge also experience strong gradients in pH and
610 other carbonate chemistry parameters. This can be attributed to two processes: 1. The strong
611 seasonal drawdown of DIC due to rapid biological uptake by phytoplankton blooms at the
612 productive ice edge which drives up pH. On the Arctic cruise, increases of up to 0.33 pH
613 units were attributed to such processes in this region (Tynan et al., 2016). The effect was less
614 dramatic in the Fe-limited and less productive Weddell Sea with gradients in pH ranging
615 from 8.20 – 8.10 (Tynan et al., 2016). 2. The drawdown of DIC is countered by the release
616 and accumulation of respired DIC under sea ice due to the degradation of organic matter.
617 However, this accumulation occurs in subsurface/bottom waters, which are isolated from the
618 productive surface mixed layer by strong physical stratification and hence, of less relevance
619 to the current study.
620 The influence of sea ice on carbonate chemistry combined with the strong biological
621 drawdown of DIC in polar waters may have influenced the ability of some of the
622 communities we sampled during our study to withstand the short term changes to carbonate
623 chemistry they experienced within the bioassays. Two of our sampling stations were 'sea-ice
624 influenced': *Greenland Ice Edge* and *Weddell Sea*. Both were in a state of sea ice retreat as
625 our sampling occurred in the summer months. Sampling for the *Greenland Ice Edge* station
626 was performed in open, deep water, near to an area of thick sea ice, with low fluorescence but
627 reasonable numbers of diatoms (Leakey, 2012). Similarly, the *Weddell Sea* station was
628 located near the edge of thick pack ice but in an area of open water that allowed sampling to
629 occur without hindrance by brash ice (Tarling, 2013). At both stations we saw little or no
630 response in DMS or DMSP to experimental acidification, which may imply that the *in situ*
631 communities were more or less adapted to fluctuations in pH. Our experimental OA resulted
632 in pH decreases of between 0.4 and 0.7 units. However, it is unclear whether the communities

633 we sampled were able to withstand the artificial pH perturbation because they were adapted
634 to living in sea ice, or whether they had adapted to cope with other fluctuations in carbonate
635 chemistry that occur in polar waters.
636 In summary, this demonstrates the high variability in carbonate chemistry, including pH,
637 which polar communities may experience relative to their temperate counterparts, and which
638 is partly driven by the lowered buffer capacity of polar waters to changes in DIC, relative to
639 the more well-buffered temperate waters. This may have resulted in polar communities that
640 have adapted to and are more resilient to experimentally-induced OA. Of course, it is
641 important to recognise that this data represent only a snapshot (4 – 6 weeks) of a year, and
642 thus does not contain information on the range in variability over daily and seasonal cycles,
643 timescales which might be considered most important in terms of the carbonate system
644 variability experienced by the cells and how this drives CO_2 sensitivity (Flynn et al. 2012;
645 Richier et al. 2018). Nevertheless, this inherent carbonate chemistry variability experienced
646 by organisms living in polar waters may equip them with the resilience to cope with both
647 experimental and future OA.
648 Adaptation to such natural variability may induce the ability to resist abrupt changes within
649 the polar biological community (Kapsenberg et al., 2015). This is manifested here as
650 negligible impacts on rates of *de novo* DMSP synthesis and net DMS production in the
651 microbial communities of the polar open oceans to short term changes in carbonate
652 chemistry. A number of previous studies in polar waters have reported similar findings.
653 Phytoplankton communities were able to tolerate a pCO_2 range of 84 – 643 µatm in ~12 d
654 minicosm experiments (650 L) in Antarctic coastal waters, with no effects on
655 nanophytoplankton abundance, and enhanced abundance of picophytoplankton and
656 prokaryotes (Davidson et al., 2016; Thomson et al., 2016). In experiments under the Arctic
657 ice, microbial communities demonstrated the capacity to respond either by selection or

658 physiological plasticity to elevated CO_2 during short term experiments (Monier et al., 2014).
659 Subarctic phytoplankton populations demonstrated a high level of resilience to OA in short
660 term experiments, suggesting a high level of physiological plasticity that was attributed to the
661 prevailing strong gradients in pCO_2 levels experienced in the sample region (Hoppe et al.,
662 2017). Furthermore, a more recent study describing ten CO_2 manipulation experiments in
663 Arctic waters found that primary production was largely insensitive to OA over a large range
664 of light and temperature levels (Hoppe et al., 2018). This supports our hypothesis that,
665 relative to temperate communities, polar microbial communities may have a high capacity to
666 compensate for environmental variability (Hoppe et al., 2018), and are thus already adapted
667 to, and are able to tolerate, large variations in carbonate chemistry. Thus by performing
668 multiple, replicated experiments over a broad geographic range, the findings of this study
669 imply that the DMS response may be both a reflection of: (i) the level of sensitivity of the
670 community to changes in the mean state of carbonate chemistry, and (ii) the regional
671 variability in carbonate chemistry experienced by different communities. This highlights the
672 limitations associated with simple extrapolation of results from a small number of
673 geographically-limited experiments e.g. Six et al. (2013). Such an approach lacks a
674 mechanistic understanding that would allow a model to capture the regional variability in
675 response that is apparent from the microcosms experiments presented here.

676 **4.4 Comparison to an Arctic mesocosm experiment**

677 Experimental data clearly provide useful information on the potential future DMS response to
678 OA, but these data become most powerful when incorporated in Earth System Models (ESM)
679 to facilitate predictions of future climate. To date, two modelling studies have used ESM to
680 assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al.,
681 2013;Schwinger et al., 2017), and both have used results from mesocosm experiments.
682 However, the DMS responses to OA within our short term microcosm experiments contrast

683 with the results of most previous mesocosm experiments, and of particular relevance to this
684 study, an earlier Arctic mesocosm experiment (Archer et al., 2013). Whilst no response in
685 DMS concentrations to OA was generally seen in the polar microcosm experiments discussed
686 here, a significant decrease in DMS with increasing levels of CO_2 in the earlier mesocosm
687 study was seen. Therefore, it is useful to consider how the differences in experimental design,
688 and other factors, between microcosms and mesocosms may result in contrasting DMS
689 responses to OA.

690 The short duration of the microcosm experiments (4 – 7 d) allows the physiological
691 (phenotypic) capacity of the community to changes in carbonate chemistry to be assessed. In
692 other words, how well is the community adapted to variable carbonate chemistry and how
693 does this influence its ability to acclimate to change? Although the mesocosm experiment
694 considered a longer time period (4 weeks), the first few days can be compared to the
695 microcosms. No differences in DMS or DMSP concentrations were detected for the first
696 week of the mesocosm experiment, implying a certain level of insensitivity of DMS
697 production to the rapid changes in carbonate chemistry. In fact, when taking all previous
698 mesocosm experiments into consideration, differences in DMS concentrations have
699 consistently been undetectable during the first 5 – 10 days, implying there is a limited short-
700 term physiological response by the in situ communities (Hopkins et al., 2010; Avgoustidi et
701 al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014). This is in contrast to the
702 strong response in the temperate microcosms from the NW European shelf (Hopkins and
703 Archer, 2014). However, all earlier mesocosm experiments have been performed in coastal
704 waters, which like polar waters, can experience a large natural range in carbonate chemistry.
705 In the case of coastal waters this is driven to a large extent by the influence of riverine
706 discharge and biological activity (Fassbender et al., 2016). Thus coastal communities may

707 also possess a higher level of adaptation to variable carbonate chemistry compared to the
708 open ocean communities of the temperate microcosms (Fassbender et al., 2016).

709 The later stages of mesocosm experiments address a different set of hypotheses, and are less
710 comparable to the microcosms reported here. With time, an increase in number of generations
711 leads to community structure changes and taxonomic shifts, driven by selection on the
712 standing genetic variation in response to the altered conditions. Moreover, the coastal Arctic
713 mesocosms were enriched with nutrients after 10 days, affording relief from nutrient
714 limitation and allowing differences between pCO_2 treatments to be exposed, including a
715 strong DMS(P) response.(Archer et al., 2013; Schulz et al., 2013). During this period of
716 increased growth and productivity, CO_2 increases drove changes which reflected both the
717 physiological and genetic potential within the community, and resulted in taxonomic shifts.
718 The resultant population structure was changed, with an increase in abundance of
719 dinoflagellates, particularly *Heterocapsa rotundata*. Increases in DMSP concentrations and
720 DMSP synthesis rates were attributed to the population shift towards dinoflagellates. The
721 drivers of the reduced DMS concentrations were less clear, but may have been linked to
722 reduced DMSP-lyase capacity within the dominant phytoplankton, a reduction in bacterial
723 DMSP lysis, or an increase in bacterial DMS consumption rates (Archer et al., 2013). Again,
724 this is comparable to all other mesocosm experiments, wherein changes to DMS
725 concentrations can be associated with CO_2-driven shifts in community structure (Hopkins et
726 al., 2010; Avgoustidi et al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014; Webb
727 et al., 2015). However, given the lack of further experiments of a similar location, design and
728 duration to the Arctic mesocosm, it is unclear how representative the mesocosm result is of
729 the general community-driven response to OA in high latitude waters.

730 We did not generally see any broad-scale CO_2-effects on community structure in polar
731 waters. This can be demonstrated by a lack of significant differences in the mean ratio of >10

732 µm Chl *a* to total Chl *a* (*>10 µm : total*) between CO_2 treatments, implying there were no
733 broad changes in community composition (Table 2). *South Sandwich* was an exception to
734 this, where large and significant increases in the mean ratio of *>10 µm : total* were observed
735 at 750 µatm and 2000 µatm CO_2 relative to ambient CO_2 (ANOVA, $F = 207.144$, $p<0.001$, $df = 3$), demonstrating that even at the short timescale of the microcosm experiments it is
736 = 3), demonstrating that even at the short timescale of the microcosm experiments it is
737 possible for some changes to community composition to occur. Interestingly, this was also
738 the only polar station that exhibited any significant effects on DMS after 96 h of incubation
739 (Figure 4 D). However, given the lack of similar response at 1000 µatm, it remains equivocal
740 whether this was driven by a CO_2-effect or some other factor.

741 In contrast to our findings, a recent single 9 day microcosm experiment (Hussherr et al.,
742 2017) performed in Baffin Bay (Canadian Arctic) saw a linear 80% decrease in DMS
743 concentrations during spring bloom-like conditions. It should be noted that this response was
744 seen over a range of pCO_2 from 500 - 3000 µatm, far beyond the levels used in the present
745 study. Nevertheless, this implies that polar DMS production may be sensitive to OA at certain
746 times of the year, such as during the highly productive spring bloom, but less sensitive during
747 periods of low and stable productivity, such as the summer months sampled during this study.
748 Furthermore, a number of other studies from both the Arctic e.g. (Coello-Camba et al., 2014;
749 Holding et al., 2015; Thoisen et al., 2015) and the Southern Ocean e.g. (Trimborn et al.,
750 2017; Tortell et al., 2008; Hoppe et al., 2013) suggest that polar phytoplankton communities
751 can demonstrate sensitivity to OA, in contrast to our findings. This emphasises the need to
752 gain a more detailed understanding of both the spatial and seasonal variability in the polar
753 phytoplankton community and associated DMS response to changing ocean acidity.

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

Our results imply that the phytoplankton communities of the temperate microcosms initially responded to the rapid increase in pCO_2 via a stress-induced response, resulting in large and significant increases in DMS concentrations occurring over the shortest timescales (2 days), with a lessening of the treatment effect with an increase in incubation time (Hopkins and Archer 2014). The dominance of short response timescales in well-buffered temperate waters may also indicate rapid acclimation of the phytoplankton populations following the initial stress response, which forced the small-sized phytoplankton beyond their range of acclimative tolerance and lead to increased DMS (Richier et al. 2018, Hopkins and Archer 2014). This supports the hypothesis that populations from higher latitude, less well-buffered waters, already possess a certain degree of acclimative tolerance to variations in carbonate chemistry environment. Although initial community size structure was not a significant predictor of the response to high CO_2, it is possible that a combination of both community

780 composition and the natural range in variability in carbonate chemistry – as a function of
781 buffer capacity – may influence the DMS/P response to OA over a range of timescales
782 (Richier et al. 2018).

783 Our findings should be considered in the context of timescales of change (experimental vs
784 real world OA) and the potential of microbial communities to adapt to a gradually changing
785 environment. Microcosm experiments focus on the physiological response of microbial
786 communities to short term OA. Mesocosm experiments consider a timescale that allows the
787 response to be driven by community composition shifts, but are not long enough in duration
788 to incorporate an adaptive response. Neither approach is likely to accurately simulate the
789 response to the gradual changes in surface ocean pH that will occur over the next 50 – 100
790 years, nor the resulting changes in microbial community structure and distribution. However,
791 we hypothesise that the DMS response to OA should be considered not only in relation to
792 experimental perturbations to carbonate chemistry, but also in relation to the magnitude of
793 background variability in carbonate chemistry experienced by the DMS-producing organisms
794 and communities. Our findings suggest a strong link between the DMS response to OA and
795 background regional variability in the carbonate chemistry.

796 Models suggest the climate may be sensitive to changes in the spatial distribution of DMS
797 emissions over global scales (Woodhouse et al., 2013; Menzo et al., 2018). Such changes
798 could be driven by both physiological and adaptive responses to environmental change.
799 Accepting the limitations of experimental approaches, our findings suggest that net DMS
800 production from polar oceans may be resilient to OA in the context of its short term effects
801 on microbial communities. The oceans face a multitude of CO_2-driven changes in the coming
802 decades, including OA, warming, deoxygenation and loss of sea ice (Gattuso et al., 2015).
803 Our study addresses only one aspect of these future ocean stressors, but contributes to our

804 understanding of how DMS emissions from the polar oceans may alter, facilitating a better
805 understanding of Earth's future climate.

806 **Data availability**

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

808 **Author contributions**

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

812 **Competing interests**

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

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822 **Review statement**

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1198 Table 1. Summary of the station locations and characteristic of the water sampled for the 18 microcosm experiments performed in temperate,
1199 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. 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*

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

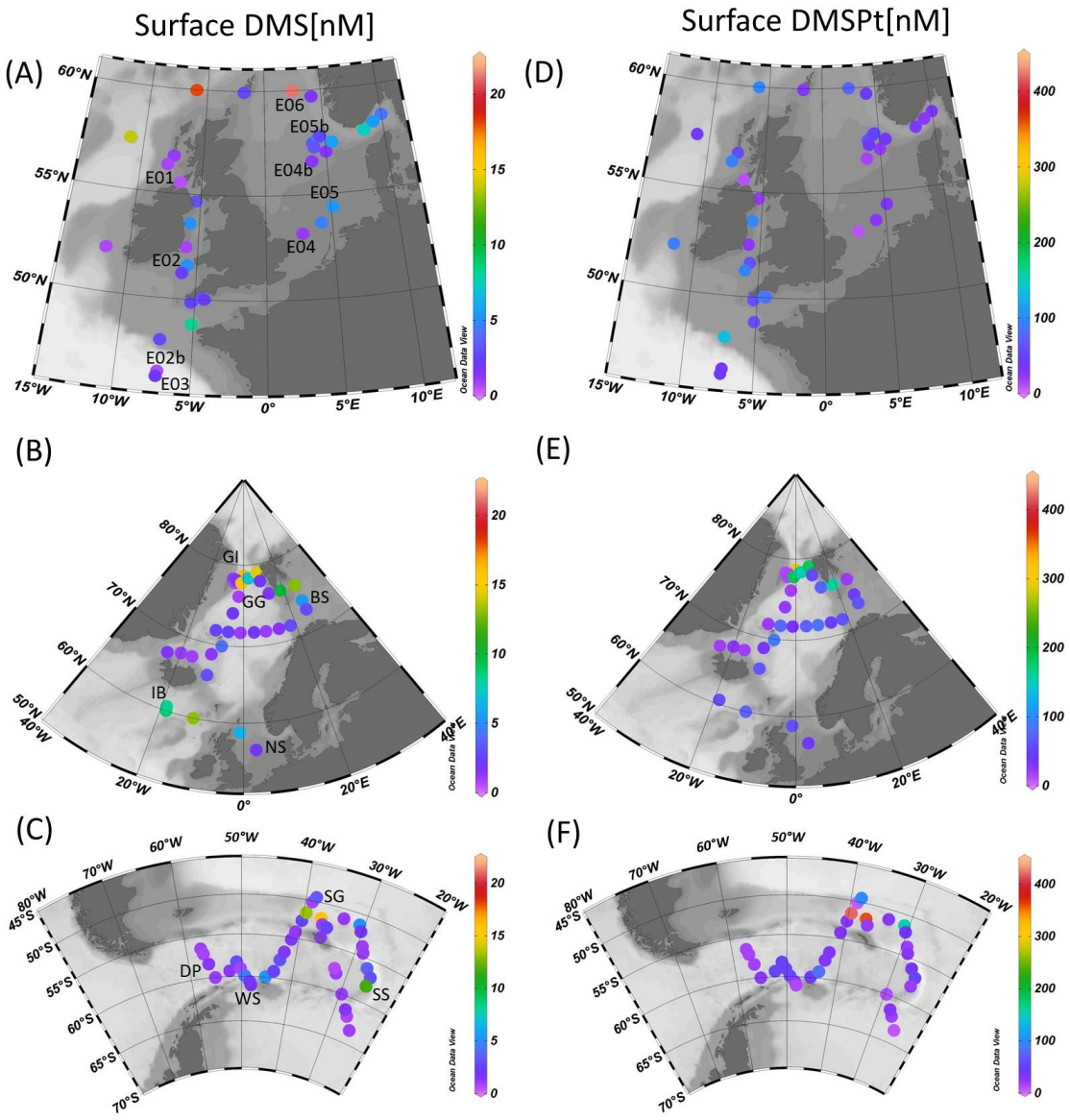


Figure 1. Surface (<5 m) concentrations (nM) of DMS (A-C) and total DMSP (D-F) for cruises in the NW European shelf (D366) (A,D), the sub-Arctic and Arctic Ocean (JR271) (B,E) and the Southern Ocean (JR274) (C,F). Locations of sampling stations for microcosm experiments shown in letters/numbers. E01 – 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*.

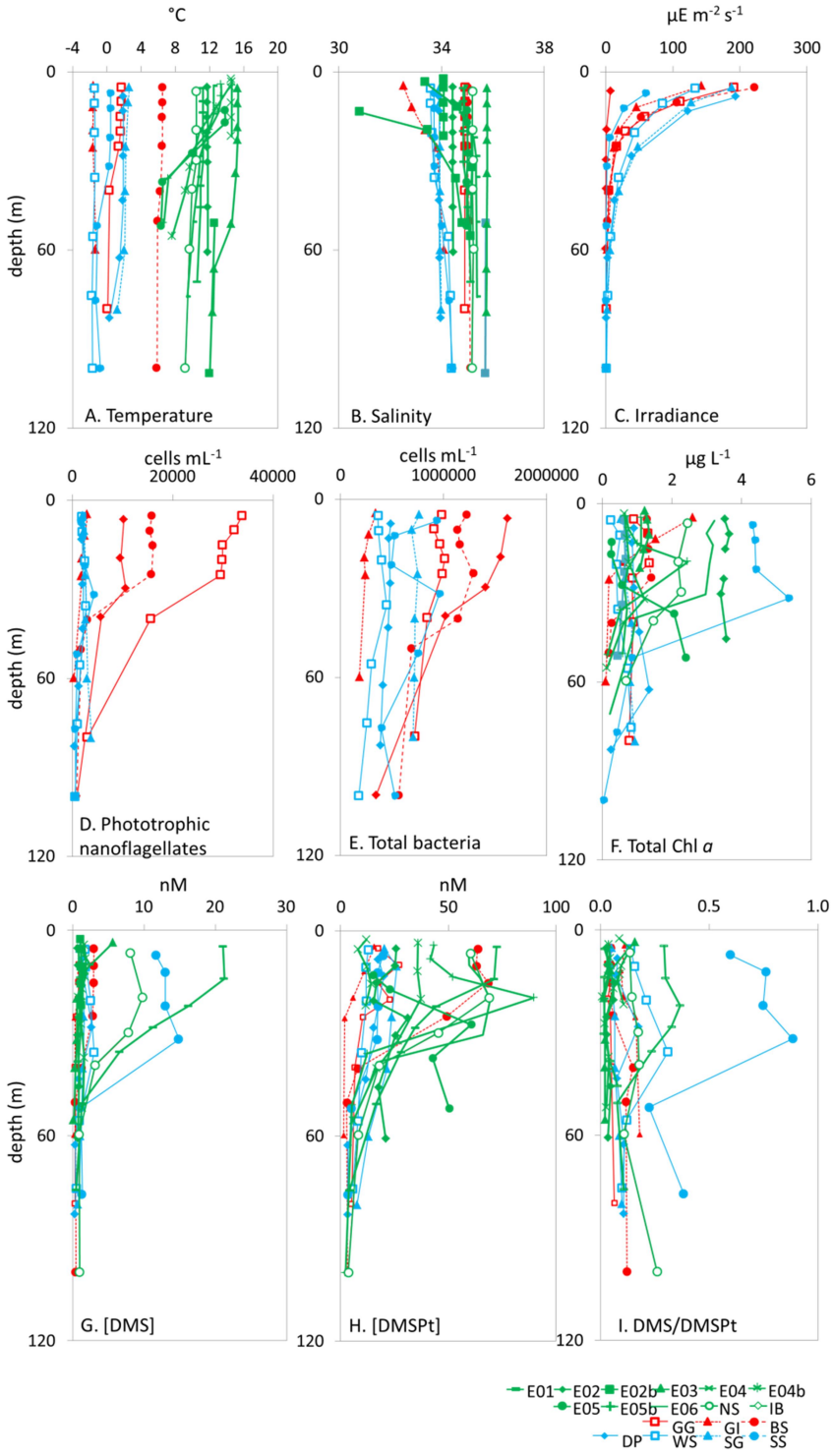
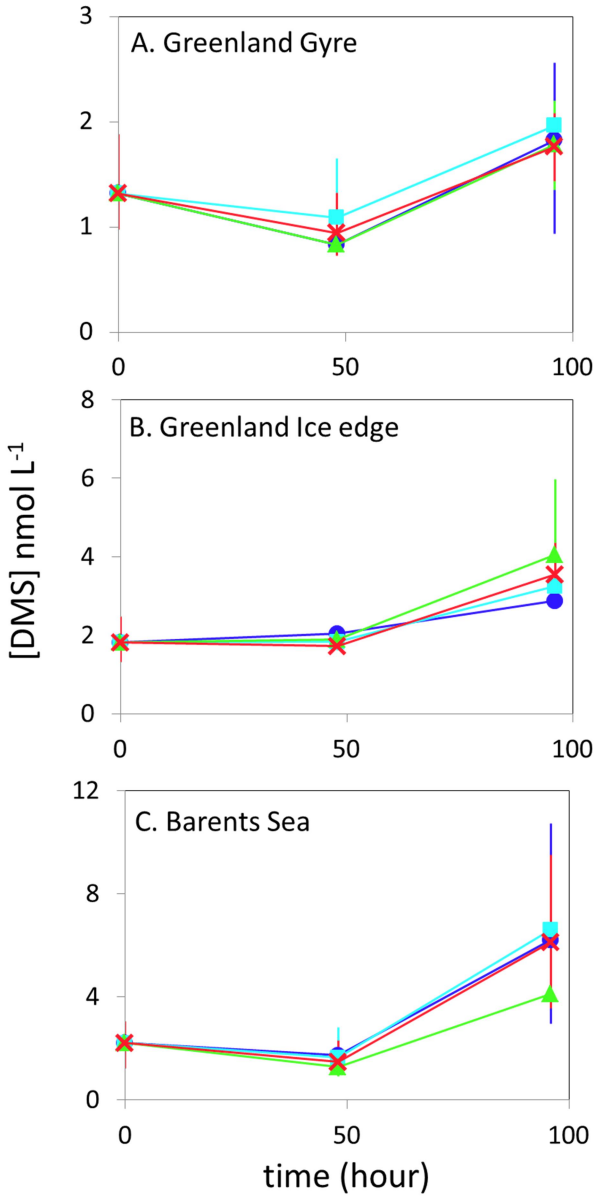


Figure 2. Depth profiles down to 100 m depth for all 18 sampling stations showing A. Temperature (°C), B. Salinity, C. Irradiance (µE m^{-2} s^{-1}), D. phototrophic nanoflagellate abundance (cells mL^{-1}), E. total bacteria abundance (cells mL^{-1}), F. total Chl a (µg L^{-1}), G. [DMS] (nM), H. total [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 irradiance, phototrophic nanoflagellates and total bacteria were not collected for temperate stations.

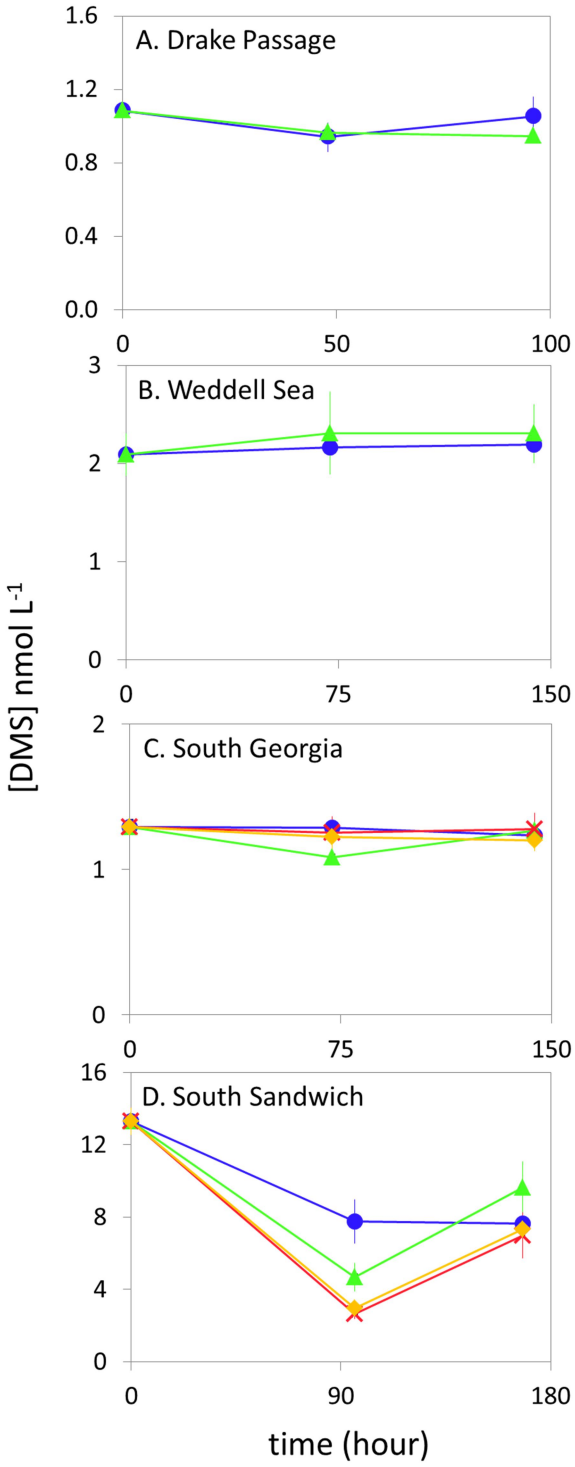


CO_2 treatment	pCO_2 (µatm) mean ± SD, n = 3		
	0 h	48 h	96 h
Ambient ●	326.8	No data	251.5 ± 5.1
Mid ■	565.2	493.8 ± 49.0	416.7 ±18.5
High ▲	741.8	607.6 ± 53.9	526.1 ± 18.1
High+ ×	1012.2	824.1 ± 99.5	668.6 ± 33.6

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.

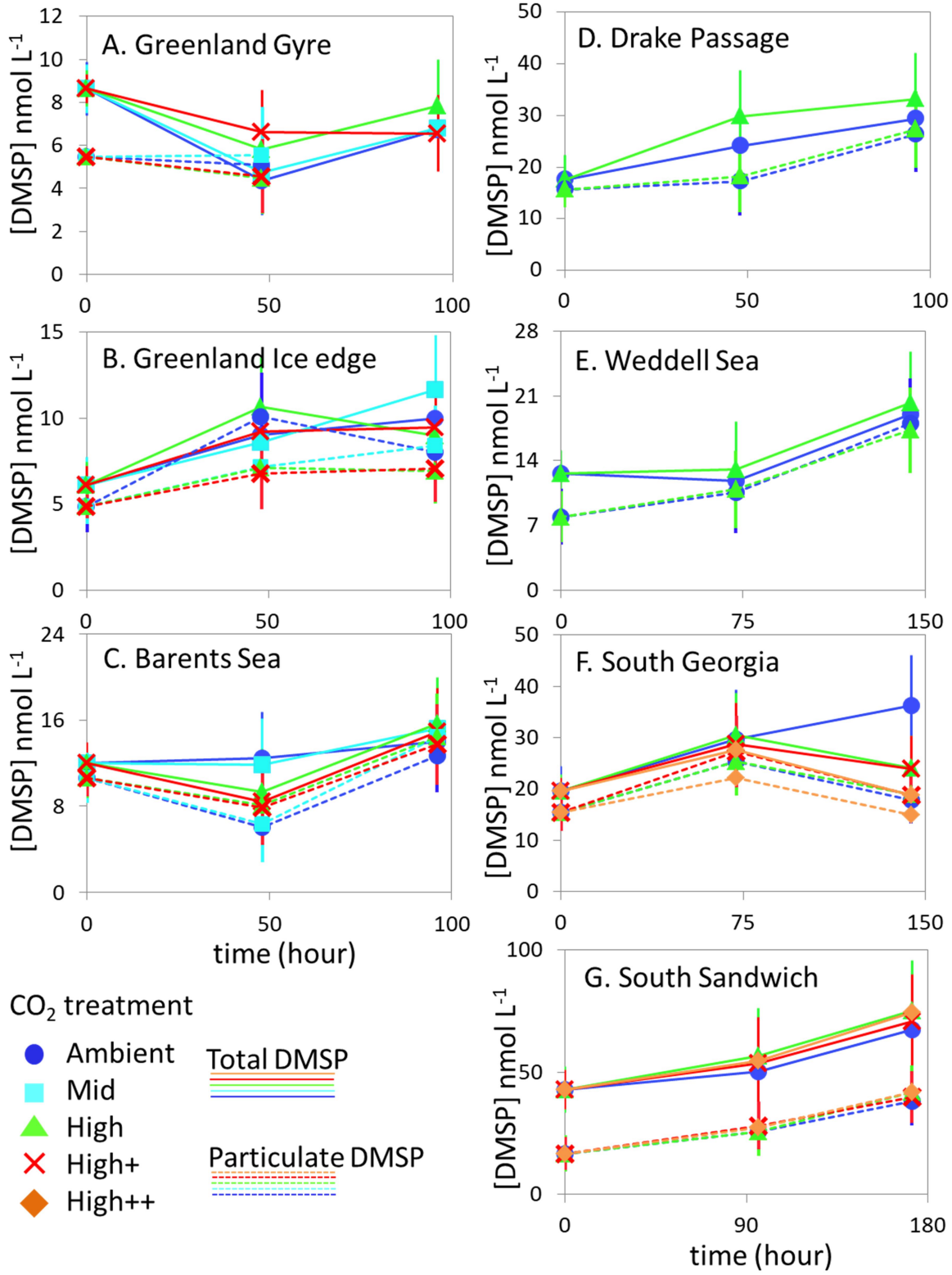


Figure 5. Total DMSP (solid lines) and particulate DMSP (dashed lines) concentrations (nmol L^{-1}) during experimental microcosms performed in Arctic waters (A - C) and in Southern Ocean waters (D – G). Data shown is mean of triplicate incubations, and error bars show standard error on the mean. Locations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

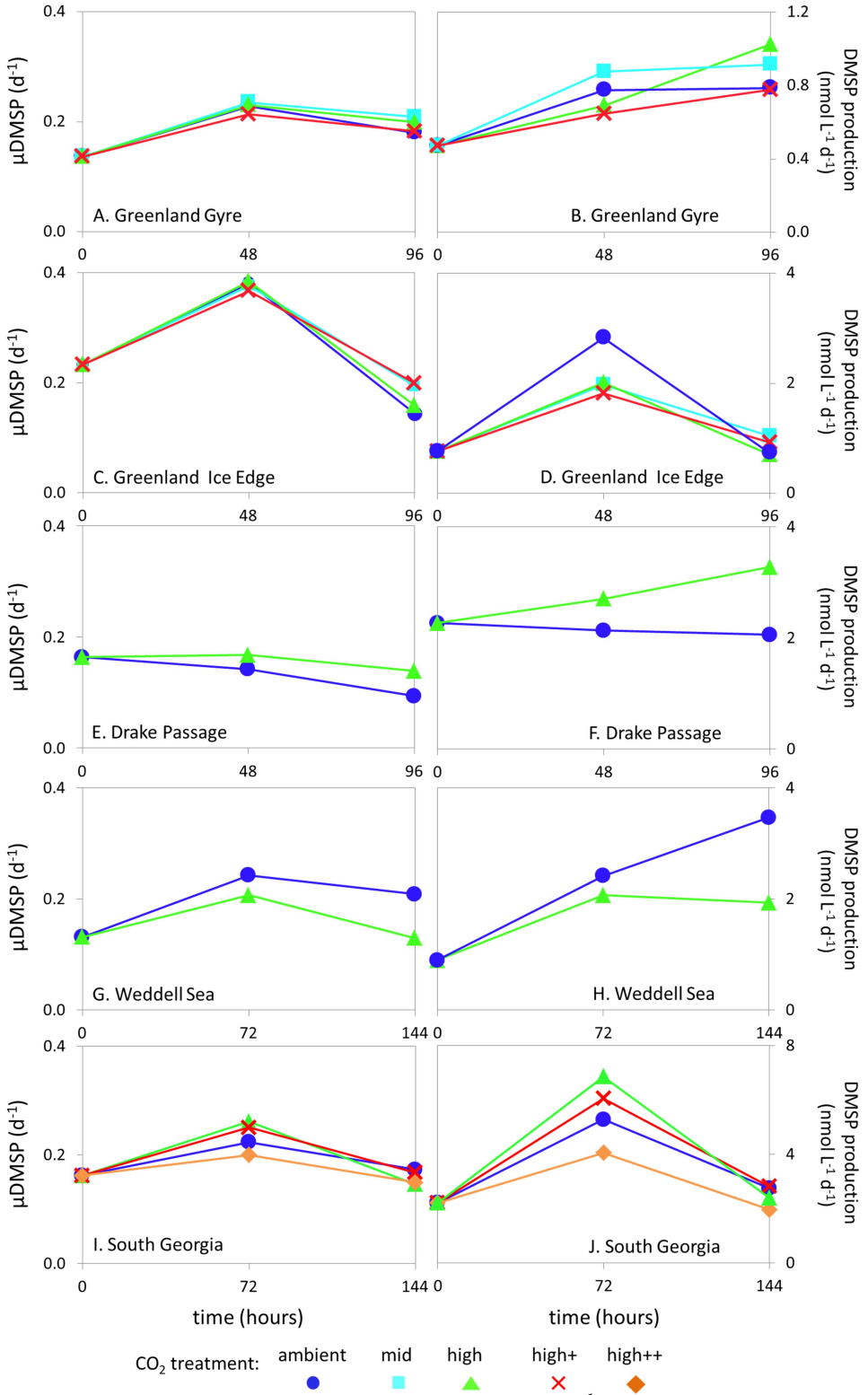


Figure 6. De novo synthesis of DMSP (µDMSP, d^{-1}) (left column) and DMSP production rates (nmol L^{-1} d^{-1}) (right column) for Arctic Ocean stations *Greenland Gyre* (A,B), *Greenland Ice-edge* (C, D) and Southern Ocean stations *Drake Passage* (E, F), *Weddell Sea* (G, H) and *South Georgia* (I,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

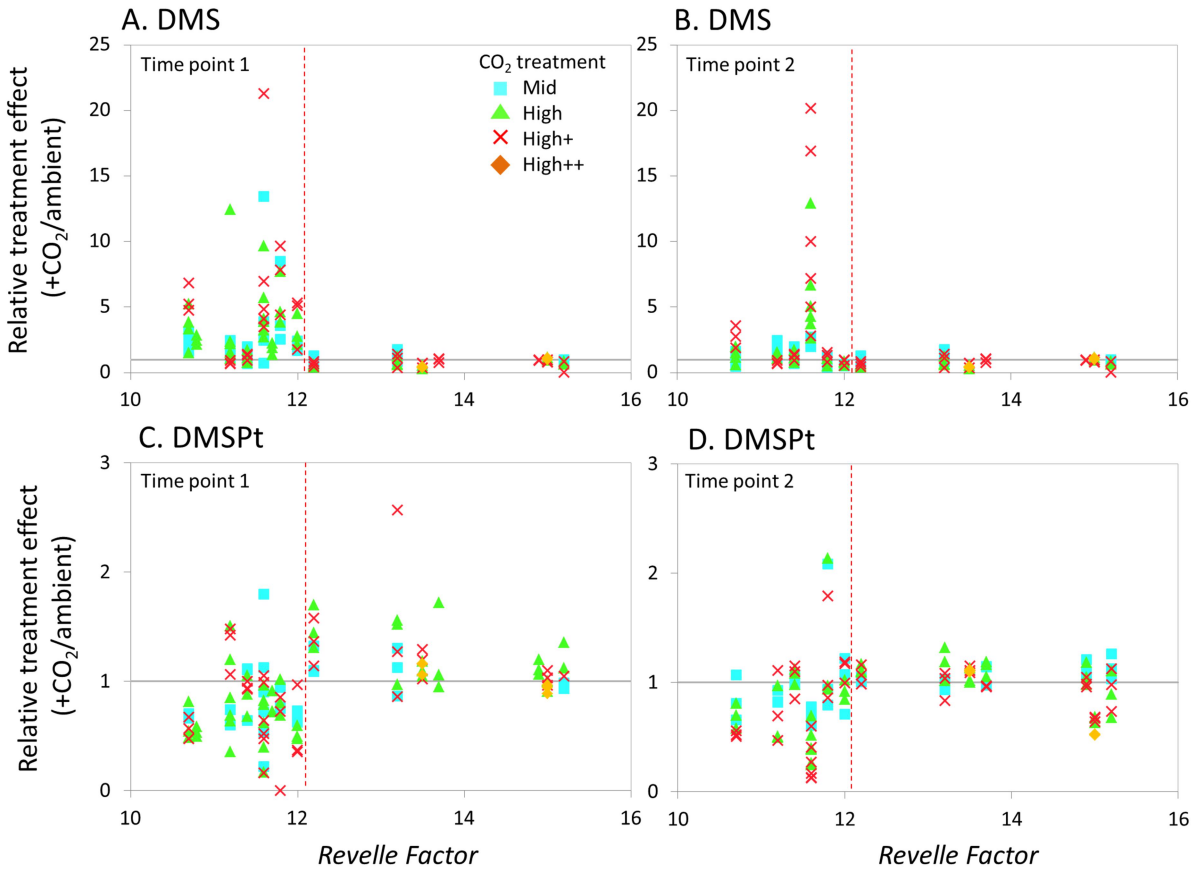


Figure 7. Relationship between Revelle Factor of the sampled water and the relative CO_2 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for concentrations of DMS at T_1 (A) and T_2 (B), and for total DMSP concentrations at T_1 (C) and T_2 (D) for all microcosm experiments performed in NW European 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).

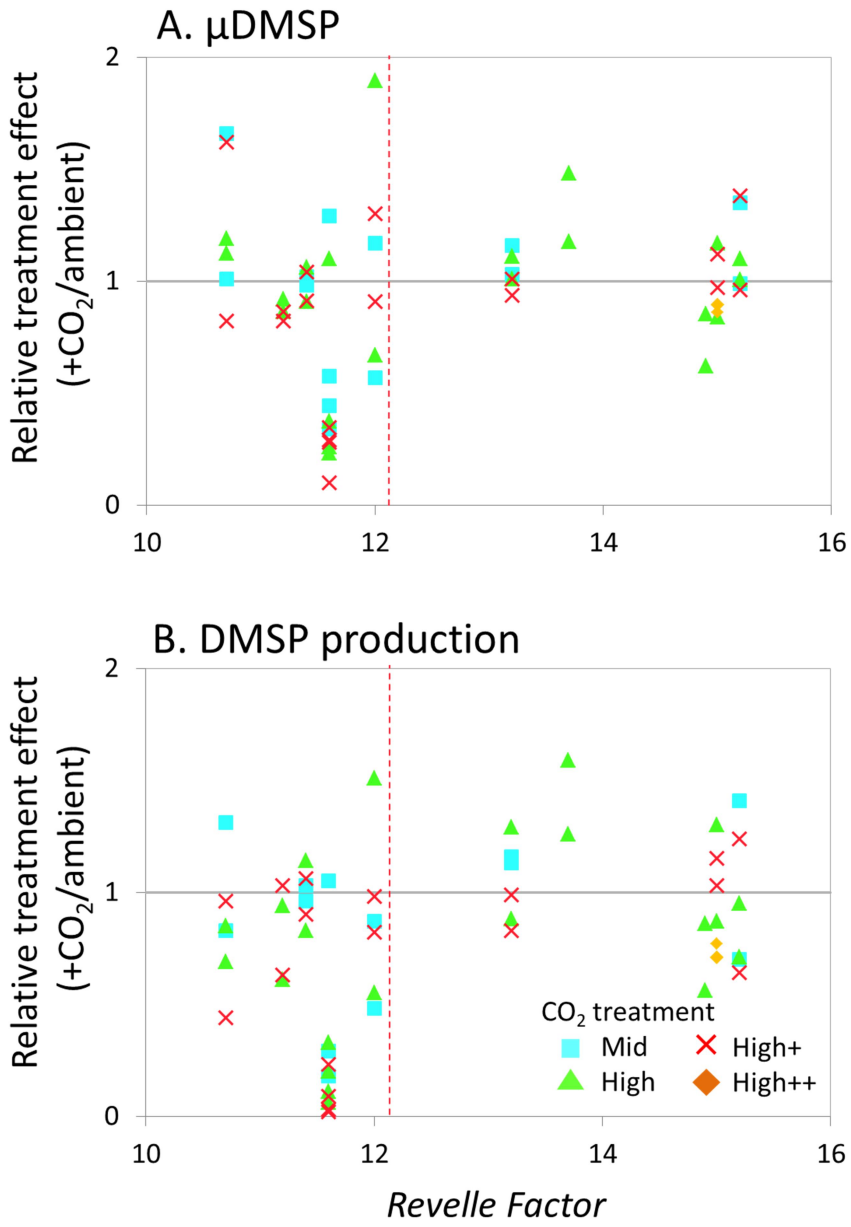
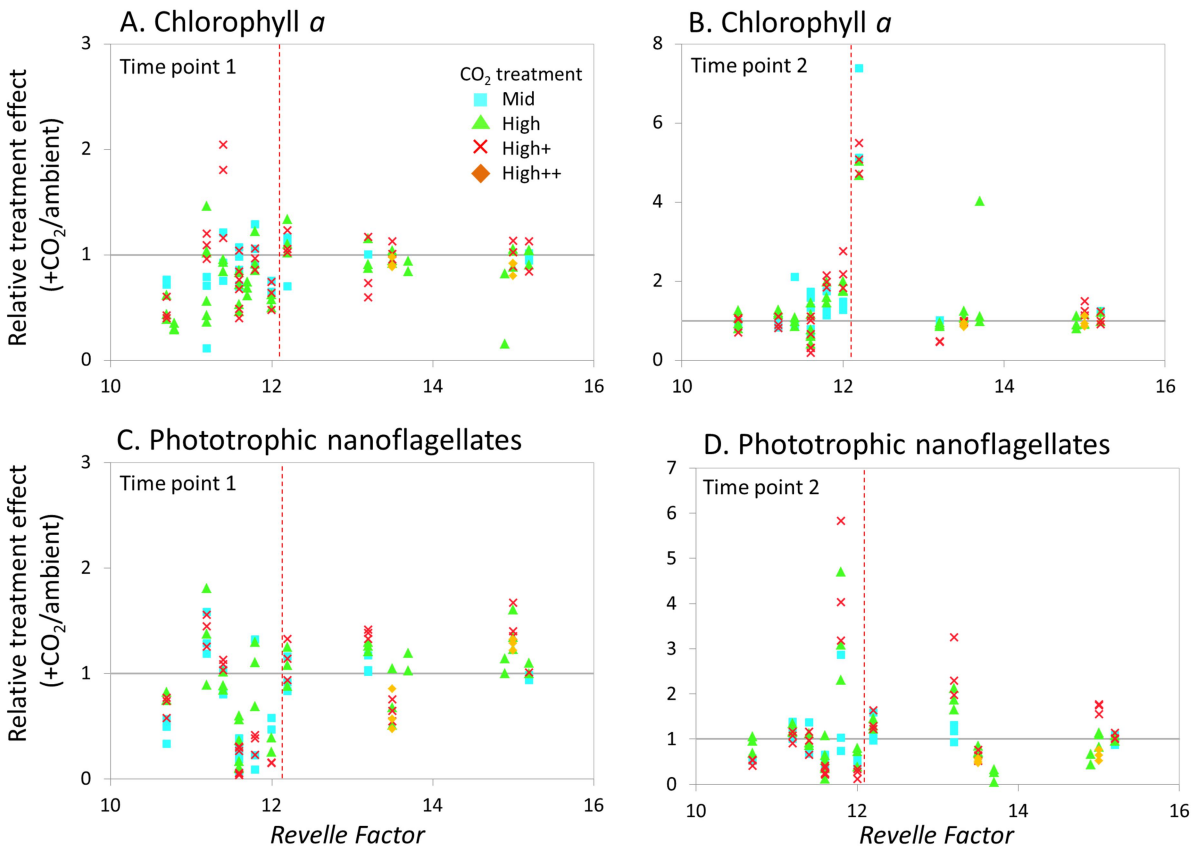


Figure 8. Relationship between the Revelle Factor of the sampled water and the relative CO_2 treatment effect at ($[x]_{highCO2}/[x]_{ambientCO2}$) for de novo DMSP synthesis (µDMSp, d^{-1}) at T_1 (A) and T_2 (B), and DMSP production rate (nmol L^{-1} d^{-1}) at T_1 (C) and T_2 (D) for microcosm experiments 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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1275 Figure 9. Relationship between the Revelle Factor of the sampled water and the relative CO_2
1276 treatment effect ($[x]_{highCO2}/[x]_{ambientCO2}$) for chlorophyll *a* concentrations at T_1 (A) and T_2 (B)
1277 and phototrophic nanoflagellate abundance at T1 (C) and T2 (D) for all microcosm
1278 experiments performed in NW European waters, sub-Arctic and Arctic waters, and the
1279 Southern Ocean. Grey solid line (= 1) indicates no effect of elevated CO_2. Revelle Factor >12
1280 = polar waters (indicated by red dashed line). T_1 = 48 h, T_2 = 96 h, except for *Weddell Sea*
1281 and *South Georgia* (72 h, 144 h) and *South Sandwich* (96 h, 168 h).

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