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

Frances E. Hopkins¹, Philip D. Nightingale¹, John A. Stephens¹, C. Mark Moore², Sophie Richier², Gemma L. Cripps², Stephen D. Archer³

¹Plymouth Marine Laboratory, Plymouth, PL1 3DH, U.K.
²Ocean and Earth Science, National Oceanography Centre, University of Southampton, Southampton, U.K.
³Bigelow Laboratory for Ocean Sciences, Maine, U.S.A.

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

Abstract. Emissions of dimethylsulfide (DMS) from the polar oceans play a key role in atmospheric processes and climate. Therefore, it is important 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 - \( \text{SO}_2 \) and \( \text{H}_2\text{SO}_4 \) - 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 \textit{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 \( \sim 15 \% \) 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 $p$CO$_2$ 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
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) 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 CO2 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 CO2 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
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$_2$SO$_4$ 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$_2$SO$_4$ 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$_2$SO$_4$ in MQ-water (temperate samples) or immediately hydrolysing (polar samples) and analysing by GC-PFPD. DMS calibrations were performed using alkaline cold-hydrolysis (1 M NaOH) of DMSP sequentially diluted three times in MilliQ water to give working standards in the range 0.03 – 3.3 ng S mL$^{-1}$. Five point calibrations were performed every 2 – 4 days throughout the cruise.

2.4 De novo DMSP synthesis

De novo DMSP synthesis and gross production rates were determined for all microcosm experiments, except Barents Sea and South Sandwich, at each experimental time point, using methods based on the approach of Stefels et al. (2009) and described in detail in Archer et al. (2013) and Hopkins and Archer (2014). Triplicate rate measurements were determined for 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 ($\mu_{DMSP}$) was calculated assuming exponential growth
from:

$$
\mu_t(\Delta t^{-1}) = \alpha_k \times AVG \left[ \ln \left( \frac{64 \text{MP}_{eq} - 64 \text{MP}_{t-1}}{64 \text{MP}_{eq} - 64 \text{MP}_t} \right) , \ln \left( \frac{64 \text{MP}_{eq} - 64 \text{MP}_{t+1}}{64 \text{MP}_{eq} - 64 \text{MP}_t} \right) \right]
$$

(Stefels et al. 2009) where $64 \text{MP}_t$, $64 \text{MP}_{t-1}$, $64 \text{MP}_{t+1}$ 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 $64 \text{MP}$ were calculated from the protonated masses of
DMS as: mass 64/(mass63 + mass64 + mass65), determined by PTR-MS. $64 \text{MP}_{eq}$ 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 $\alpha_k$ 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 $\mu_{DMSP}$
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<sub>0</sub> measurements were taken directly from CTD bottles, and immediately measured for total alkalinity (A<sub>T</sub>) (Apollo SciTech AS-Alk2 Alkalinity Titrator) and dissolved inorganic carbon (C<sub>T</sub>) (Apollo SciTech C<sub>T</sub>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<sub>2</sub>. Measurements of T<sub>A</sub> and C<sub>T</sub> were made from each bottle at each experimental time point and again used to calculate the corresponding values for pCO<sub>2</sub> and pH<sub>T</sub>. 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%).
2.8 Community composition

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

2.9 Data handling and statistical analyses

Permutational analysis of variance (PERMANOVA) was used to analyse the difference in response of DMS and DMSP concentrations to OA, both between and within the two polar cruises in this study. Both dependant variables were analysed separately using a nested factorial design with three factors; (i) Cruise Location: Arctic and Southern Ocean, (ii) Experiment location nested within Cruise location (see Table 1 for station IDs) and (iii) CO₂ level: 385, 550, 750, 1000 and 2000 µatm. Main effects and pairwise comparisons of the different factors were analysed through unrestricted permutations of raw data. If a low number of permutations were generated then the \( p \)-value was obtained through random sampling of the asymptotic permutation distribution, using Monte Carlo tests.

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

3 Results

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

Seawater temperatures at the polar microcosm sampling stations ranged from -1.5°C at sea-ice influenced stations (Greenland Ice-edge and Weddell Sea) up to 6.5°C for Barents Sea (Fig. 2 A). Salinity values at all the Southern Ocean stations were <34, whilst they were ~35 at all the Arctic stations with the exception of Greenland Ice-edge which had the lowest salinity of 32.5 (Fig. 2 B). Phototrophic nanoflagellate abundances were variable, with >3 x 10⁴ cells mL⁻¹ at Greenland Gyre, 1.5 x 10⁴ cells mL⁻¹ at Barents Sea and <3 x 10³ cells mL⁻¹ for all other stations (Fig. 2 D). Total bacterial abundances ranged from 3 x 10⁵ cells mL⁻¹ at Greenland Ice-edge up to 3 x 10⁶ 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
– 20 nmol L\(^{-1}\), except Barents Sea where surface concentrations exceeded 60 nmol L\(^{-1}\) (Figure 2 H).

### 3.2 Response of DMS and DMSP to OA

The temporal trend in DMS concentrations showed a similar pattern for the three Arctic Ocean experiments. Initial concentrations of 1 – 2 nmol L\(^{-1}\) remained relatively constant over the first 48 h and then showed small increases of 1 - 4 nmol L\(^{-1}\) over the incubation period (Figure 3). Increased variability between triplicate incubations became apparent in all three Arctic experiments by 96 h, but no significant effects of elevated CO\(_2\) on DMS concentrations were observed. Initial DMSP concentrations were more variable, from 6 nmol L\(^{-1}\) at Greenland Ice-edge to 12 nmol L\(^{-1}\) at Barents Sea, and either decreased slightly (net loss 1 – 2 nmol L\(^{-1}\) GG), or increased slightly (net increase ~4 nmol L\(^{-1}\)) Greenland Ice-edge, ~3 nmol L\(^{-1}\) Barents Sea) (Figure 5 A – C). DMSP concentrations were found to decrease significantly in response to elevated CO\(_2\) after 48 h for Barents Sea (Fig. 4 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 \(p\)CO\(_2\)-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 (\(\mu\)DMSP) 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 \(\mu\)DMSP 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: \(\mu\)DMSP 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 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 treatments 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. The differences in DMSP production rates did not correspond to any other measured parameter. It is possible that changes in phytoplankton community composition may have led to differences in DMSP production rates for Drake Passage and Weddell Sea, but no quantification of large cells (diatoms, dinoflagellates) was undertaken for these experiments.

4 Discussion

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

We combine our findings from the polar oceans with those from temperate waters into a meta-analysis in order to assess the regional variability and drivers in the DMS(P) response to OA. Figures 7 and 8 provide an overview of the results discussed so far in this current study, together with the results from Hopkins & Archer (2014) as well as the results from 4 previously unpublished microcosm experiments from the NW European shelf cruise and a further 2 temperate water microcosm experiments from the Arctic cruise (North Sea and
This gives a total of 18 microcosm experiments, each with between 1 and 3 high CO₂ treatments.

Hopkins & Archer (2014) reported consistent and significant increases in DMS concentration in response to elevated CO₂ that were accompanied by significant decreases in DMSPt concentrations. Bacterially-mediated DMS processes appeared to be insensitive to OA, with no detectable effects on dark rates of DMS consumption and gross production, and no consistent response seen in bacterial abundance (Hopkins and Archer, 2014). In general, there were large short-term decreases in Chl a concentrations and phototrophic nanoflagellate abundance in response to elevated CO₂ in these experiments (Richier et al., 2014).

The relative treatment effects ([x]_{highCO2}/[x]_{ambientCO2}) for DMS and DMSP (Figure 7), DMSP synthesis and production (Figure 8), and Chl a and phototrophic nanoflagellate abundance (Figure 9) are plotted against the Revelle Factor of the sampled waters. The Revelle Factor (R), calculated here with CO2Sys using measurements of carbonate chemistry parameters (R = (ΔpCO₂/ΔTCO₂)/(pCO₂/TCO₂), Lewis and Wallace, 1998), describes how the partial pressure of CO₂ in seawater (pCO₂) changes for a given change in DIC (Sabine et al., 2004; Revelle and Suess, 1957). Its magnitude varies latitudinally, with lower values (9 – 12) from the tropics to temperate waters, and the highest values in cold high latitude waters (13 – 15). Thus polar waters can be considered poorly buffered with respect to changes in DIC.

Therefore, biologically-driven seasonal changes in seawater pCO₂ would result in larger changes in pH than would be experienced in temperate waters. (Egleston et al., 2010). Furthermore, the seasonal sea ice cycle strongly influences carbonate chemistry, such that sea ice regions exhibit wide fluctuations in carbonate chemistry (Revelle and Suess, 1957; Sabine et al., 2004). Sampling stations with a R above ~12 represent the seven polar stations (right of red dashed line Fig. 7, 8, 9). The surface waters of the polar oceans have naturally higher levels of DIC and a reduced buffering capacity, driven by higher CO₂ solubility in colder
waters (Sabine et al., 2004). Thus, the relationship between experimental response and $R$ is a simple way of demonstrating the differences in response to OA between temperate and polar waters and provides some insight into how the CO$_2$ sensitivity of different surface ocean communities may relate to the *in situ* carbonate chemistry. The effect of elevated CO$_2$ on DMS concentrations at polar stations, relative to ambient controls, was minimal at both sampling points, and is in strong contrast to the results from experiments performed in waters with lower values of $R$ on the NW European shelf. In contrast, at temperate stations, DMSP concentrations displayed a clear negative treatment effect, whilst at polar stations a positive effect was evident under high CO$_2$, and particularly at the first time point (48 – 96 h) (Fig. 7 C and D). *De novo* DMSP synthesis and DMSP production rates show a less consistent response in either environment (Fig. 8 A and B), although a significant suppression of DMSP production rates in temperate waters compared to polar waters was seen (Fig. 8 B, Kruskal-Wallis One Way ANOVA $H = 8.711, df = 1, p = 0.003$). A similar but not significant response was seen for *de novo* DMSP synthesis (Fig. 8A).

This data suggests that DMSP concentrations in polar waters may be upregulated in response to OA compared to temperate waters. Given the potential photoprotective and antioxidant role that DMSP plays, and which may be particularly relevant in the highly variable polar sea-ice environment (e.g. irradiance, carbonate chemistry), these changes may reflect a physiological protective response to the experimental OA (Sunda et al., 2002; Galindo et al., 2016). An increase in DMSP concentrations could have either resulted from a physiological up-regulation of DMSP synthesis or a reduction in bacterial DMSP consumption processes. However, DMSP synthesis rates did not provide any conclusive evidence of upregulation in polar waters. Instead, we observed a suppression of rates in temperate waters which may reflect the adverse effects of rapid OA on DMSP producers (Richier et al. 2014, Hopkins and Archer 2014). In contrast, the lesser response seen in polar waters may reflect a higher
acclimative tolerance to rapid changes in carbonate chemistry amongst polar communities. Further experiments with polar communities would help to further unravel the potential importance of such mechanisms, and whether they facilitated the ability of polar phytoplankton communities to resist the high CO$_2$ treatments.

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

In correspondence with the analyses carried out by Richier et al (2018), at 48 – 96 h (see Table 1), a statistically significant difference in response was seen between temperate and polar waters for Chl $a$ (Kruskal-Wallis One Way ANOVA $H = 20.577$, $df = 1$, $p<0.001$). In general, at polar stations phytoplankton showed minimal response to elevated CO$_2$, in contrast to a strong negative response in temperate waters (Fig. 9A). By the second time point (96 – 144 h, see Table 1), no significant difference in response of Chl $a$ between temperate and polar waters was apparent (Fig. 9B). As shown in Richier et al. (2014), phototrophic nanoflagellates responded to high CO$_2$ with large decreases in abundance in temperate waters and increases in abundance in polar waters (Fig. 9 C and D), with some exceptions: North Sea and South Sandwich gave the opposite response. The responses had lessened by the second time point (96 – 168 h, see Table 1).
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. $p$CO$_2$, 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
marked response in DMS concentrations to short term OA in temperate waters has been attributed to this enhanced sensitivity of small phytoplankton (Hopkins and Archer, 2014). Was the lack of DMS response to OA in polar waters therefore a result of the target 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 $>10 \mu m$ Chl $a$ to total Chl $a$ (hereafter $>10 \mu m : total$) of $0.32 \pm 0.08$ was lower than the ratio for polar stations of $0.54 \pm 0.13$ (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 $>10 \mu m : total$ of $0.04 \pm 0.01$, suggesting a community comprised almost entirely of $<10 \mu m$ 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. 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
Iceland Sea, whilst Kapsenberg et al. (2015) report an annual variability of 0.3 – 0.4 units in
the McMurdo Sound, Antarctica. This implies that both open ocean and sea ice-influenced
polar waters experience large variations in carbonate chemistry over seasonal cycles. By
contrast, monthly averaged surface $p$CO$_2$ data collected from station L4 in the Western
English Channel over the period 2007 – 2011 provides an example of typical carbonate
chemistry dynamics in NW European shelf sea waters. Over this period, pH had an annual
range of 0.15 units (8.05 – 8.20), accompanied by a range in $p$CO$_2$ of 302 – 412 µatm (Kitidis
et al., 2012).

The sea ice environment in particular is characterised by strong spatial and seasonal
variability in carbonate chemistry. Sea ice is inhabited by a specialised microbial community
with a complex set of metabolic and physiological adaptations allowing these organisms to
withstand wide fluctuations in pH up to as high as 9.9 in brine channels to as low as 7.5 in the
under-ice water (Thomas and Dieckmann, 2002; Rysgaard et al., 2012; Thoisen et al., 2015).
The open waters associated with the ice edge also experience strong gradients in pH and
other carbonate chemistry parameters. This can be attributed to two processes: 1. The strong
seasonal drawdown of DIC due to rapid biological uptake by phytoplankton blooms at the
productive ice edge which drives up pH. On the Arctic cruise, increases of up to 0.33 pH
units were attributed to such processes in this region (Tynan et al., 2016). The effect was less
dramatic in the Fe-limited and less productive Weddell Sea with gradients in pH ranging
from 8.20 – 8.10 (Tynan et al., 2016). 2. The drawdown of DIC is countered by the release
and accumulation of respired DIC under sea ice due to the degradation of organic matter.
However, this accumulation occurs in subsurface/bottom waters, which are isolated from the
productive surface mixed layer by strong physical stratification and hence, of less relevance
to the current study.
The influence of sea ice on carbonate chemistry combined with the strong biological drawdown of DIC in polar waters may have influenced the ability of some of the communities we sampled during our study to withstand the short term changes to carbonate chemistry they experienced within the bioassays. Two of our sampling stations were ‘sea-ice influenced’: Greenland Ice Edge and Weddell Sea. Both were in a state of sea ice retreat as our sampling occurred in the summer months. Sampling for the Greenland Ice Edge station was performed in open, deep water, near to an area of thick sea ice, with low fluorescence but reasonable numbers of diatoms (Leakey, 2012). Similarly, the Weddell Sea station was located near the edge of thick pack ice but in an area of open water that allowed sampling to occur without hindrance by brash ice (Tarling, 2013). At both stations we saw little or no response in DMS or DMSP to experimental acidification, which may imply that the in situ communities were more or less adapted to fluctuations in pH. Our experimental OA resulted in pH decreases of between 0.4 and 0.7 units. However, it is unclear whether the communities we sampled were able to withstand the artificial pH perturbation because they were adapted to living in sea ice, or whether they had adapted to cope with other fluctuations in carbonate chemistry that occur in polar waters.

In summary, this demonstrates the high variability in carbonate chemistry, including pH, which polar communities may experience relative to their temperate counterparts. This may have resulted in adapted communities resilient to experimentally-induced OA. Of course, it is important to recognise that this data represent only a snapshot (4 – 6 weeks) of a year, and thus does not contain information on the range in variability over daily and seasonal cycles, timescales which might be considered most important in terms of the carbonate system variability experienced by the cells and how this drives CO₂ sensitivity (Flynn et al. 2012; 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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
with simple extrapolation of results from a small number of geographically-limited experiments e.g. Six et al. (2013). Such an approach lacks a mechanistic understanding that would allow a model to capture the regional variability in response that is apparent from the microcosms experiments presented here.

4.4 Comparison to an Arctic mesocosm experiment

Experimental data clearly provide useful information on the potential future DMS response to OA, but these data become most powerful when incorporated in Earth System Models (ESM) to facilitate predictions of future climate. To date, two modelling studies have used ESM to assess the potential climate feedback resulting from the DMS sensitivity to OA (Six et al., 2013; Schwinger et al., 2017), and both have used results from mesocosm experiments. However, the DMS responses to OA within our short term microcosm experiments contrast with the results of most previous mesocosm experiments, and of particular relevance to this study, an earlier Arctic mesocosm experiment (Archer et al., 2013). Whilst no response in DMS concentrations to OA was generally seen in the polar microcosm experiments discussed here, a significant decrease in DMS with increasing levels of CO$_2$ in the earlier mesocosm study was seen. Therefore, it is useful to consider how the differences in experimental design, and other factors, between microcosms and mesocosms may result in contrasting DMS responses to OA.

The short duration of the microcosm experiments (4 – 7 d) allows the physiological (phenotypic) capacity of the community to changes in carbonate chemistry to be assessed. In other words, how well is the community adapted to variable carbonate chemistry and how does this influence its ability to acclimate to change? Although the mesocosm experiment considered a longer time period (4 weeks), the first few days can be compared to the microcosms. No differences in DMS or DMSP concentrations were detected for the first week of the mesocosm experiment, implying a certain level of insensitivity of DMS
production to the rapid changes in carbonate chemistry. In fact, when taking all previous mesocosm experiments into consideration, differences in DMS concentrations have consistently been undetectable during the first 5 – 10 days, implying there is a limited short-term physiological response by the in situ communities (Hopkins et al., 2010; Avgoustidi et al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014). This is in contrast to the strong response in the temperate microcosms from the NW European shelf (Hopkins and Archer, 2014). However, all earlier mesocosm experiments have been performed in coastal waters, which like polar waters, can experience a large natural range in carbonate chemistry. In the case of coastal waters this is driven to a large extent by the influence of riverine discharge and biological activity (Fassbender et al., 2016). Thus coastal communities may also possess a higher level of adaptation to variable carbonate chemistry compared to the open ocean communities of the temperate microcosms (Fassbender et al., 2016). The later stages of mesocosm experiments address a different set of hypotheses, and are less comparable to the microcosms reported here. With time, an increase in number of generations leads to community structure changes and taxonomic shifts, driven by selection on the standing genetic variation in response to the altered conditions. Moreover, the coastal Arctic mesocosms were enriched with nutrients after 10 days, affording relief from nutrient limitation and allowing differences between pCO₂ treatments to be exposed, including a strong DMS(P) response (Archer et al., 2013; Schulz et al., 2013). During this period of increased growth and productivity, CO₂ increases drove changes which reflected both the physiological and genetic potential within the community, and resulted in taxonomic shifts. The resultant population structure was changed, with an increase in abundance of dinoflagellates, particularly Heterocapsa rotundata. Increases in DMSP concentrations and DMSP synthesis rates were attributed to the population shift towards dinoflagellates. The drivers of the reduced DMS concentrations were less clear, but may have been linked to
reduced DMSP-lyase capacity within the dominant phytoplankton, a reduction in bacterial
DMSP lysis, or an increase in bacterial DMS consumption rates (Archer et al., 2013). Again,
this is comparable to all other mesocosm experiments, wherein changes to DMS
concentrations can be associated with CO₂-driven shifts in community structure (Hopkins et
al., 2010; Avgoustidi et al., 2012; Vogt et al., 2008; Kim et al., 2010; Park et al., 2014; Webb
et al., 2015). However, given the lack of further experiments of a similar location, design and
duration to the Arctic mesocosm, it is unclear how representative the mesocosm result is of
the general community-driven response to OA in high latitude waters.

We did not generally see any broad-scale CO₂-effects on community structure in polar
waters. This can be demonstrated by a lack of significant differences in the mean ratio of >10
µm Chl a to total Chl a (>10 µm : total) between CO₂ treatments, implying there were no
broad changes in community composition (Table 2). South Sandwich was an exception to
this, where large and significant increases in the mean ratio of >10 µm : total were observed
at 750 µatm and 2000 µatm CO₂ relative to ambient CO₂ (ANOVA, F = 207.144, p<0.001, df
= 3), demonstrated at even the short timescale of the microcosm experiments, it is possible
for some changes to community composition to occur. Interestingly, this was also the only
polar station that exhibited any significant effects on DMS after 96 h of incubation (Figure 4
D). However, given the lack of similar response at 1000 µatm, it remains equivocal whether
this was driven by a CO₂-effect or some other factor. The results of our microcosm
experiments suggest insensitivity of de novo DMSP production and net DMS production in
the microbial communities of the polar open oceans to short term changes in carbonate
chemistry. This may be driven by a high level of adaptation within the targeted
phytoplankton communities to naturally varying carbonate chemistry.
In contrast to our findings, a recent single 9 day microcosm experiment (Huss err 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 $p$CO$_2$ 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; Husserr 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 composition and the natural range in variability in carbonate chemistry – as a function of buffer capacity – may influence the DMS/P response to OA over a range of timescales (Richier et al. 2018).

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

Models suggest the climate may be sensitive to changes in the spatial distribution of DMS emissions over global scales (Woodhouse et al., 2013; Menzo et al., 2018). Such changes could be driven by both physiological and adaptive responses to environmental change. Accepting the limitations of experimental approaches, our findings suggest that net DMS production from polar oceans may be resilient to OA in the context of its short term effects on microbial communities. The oceans face a multitude of CO$_2$-driven changes in the coming decades, including OA, warming, deoxygenation and loss of sea ice (Gattuso et al., 2015). Our study addresses only one aspect of these future ocean stressors, but contributes to our understanding of how DMS emissions from the polar oceans may alter, facilitating a better understanding of Earth’s future climate.

**Data availability**

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

**Author contributions**

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

**Competing interests**

The authors declare that they have no conflict of interest.
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Review statement

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

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Station ID</th>
<th>Location</th>
<th>Sampling location</th>
<th>Sampling date</th>
<th>Sampling depth (m)</th>
<th>SST (°C)</th>
<th>Salinity (uM)</th>
<th>Nitrate (µM)</th>
<th>Total Chl a (µg L⁻¹)</th>
<th>chl-10 µm : chl_total</th>
<th>pH (total)</th>
<th>Experimental timepoints</th>
<th>Reference</th>
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<td>D366</td>
<td>E01</td>
<td>Mingulay Reef</td>
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<td>8 June 2011</td>
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<td>34.8</td>
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<td>3.3</td>
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<td>334.9</td>
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<td>48, 96</td>
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<td>Irish Sea</td>
<td>52°28.237N 5°54.052W</td>
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<td>46°29.794N 7°12.355W</td>
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<td>E03</td>
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<td>46°12.137N 7°13.253W</td>
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<td>0.3</td>
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<td>59°40.721N 4°07.633E</td>
<td>3 July 2011</td>
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<td>59°59.011N 2°30.896E</td>
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<td>NS</td>
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<td>56°15.59N 2°37.59E</td>
<td>3 June 2012</td>
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<td>35.1</td>
<td>0.04</td>
<td>0.3</td>
<td>0.52 ± 0.05</td>
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<td>IB</td>
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<td>60°35.39N 18°51.23W</td>
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<td>7</td>
<td>10.7</td>
<td>35.2</td>
<td>5.0</td>
<td>1.8</td>
<td>0.27 ± 0.02</td>
<td>309.7</td>
<td>8.1</td>
<td>48, 96</td>
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<tr>
<td></td>
<td>GG-AO</td>
<td>Greenland Gyre</td>
<td>76°10.52 N 2°32.96 W</td>
<td>13 June 2012</td>
<td>5</td>
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<td>0.34 ± 0.001</td>
<td>289.3</td>
<td>8.2</td>
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<td>GI-AO</td>
<td>Greenland ice edge</td>
<td>78°21.15 N 3°39.85 W</td>
<td>18 June 2012</td>
<td>5</td>
<td>-1.6</td>
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<td>BS-AO</td>
<td>Barents Sea</td>
<td>72°53.49 N 26°00.09 W</td>
<td>24 June 2012</td>
<td>5</td>
<td>6.6</td>
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<td>JR274</td>
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<td>Drake Passage</td>
<td>58°22.00 S 56°15.12 W</td>
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<td>22.0</td>
<td>2.4</td>
<td>1.00 ± 0.06</td>
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<td>8.2</td>
<td>48, 96</td>
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<td>WS-SO</td>
<td>Weddell Sea</td>
<td>60°58.55 S 48°05.19 W</td>
<td>18 Jan 2013</td>
<td>6</td>
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<td>72, 144</td>
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<td>SG-SO</td>
<td>South Georgia</td>
<td>52°41.36 S 36°37.28 W</td>
<td>25 Jan 2013</td>
<td>5</td>
<td>2.2</td>
<td>33.9</td>
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<td>SS-SO</td>
<td>South Sandwich</td>
<td>58°05.13 S 25°55.55 W</td>
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<td>0.5</td>
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<td>0.57 ± 0.02</td>
<td>272.6</td>
<td>8.2</td>
<td>96, 168</td>
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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$_2$.

<table>
<thead>
<tr>
<th>Station</th>
<th>Time</th>
<th>ambient</th>
<th>550 µatm</th>
<th>750 µatm</th>
<th>1000 µatm</th>
<th>2000 µatm</th>
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<td>GG</td>
<td>48 h</td>
<td>0.3 ± 0.1</td>
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<td>0.4 ± 0.2</td>
<td>0.3 ± 0.1</td>
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<tr>
<td></td>
<td>96 h</td>
<td>1.0 ± 0.02</td>
<td>0.9 ± 0.2</td>
<td>0.8 ± 0.1</td>
<td>0.7 ± 0.2</td>
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</tr>
<tr>
<td>GI</td>
<td>48 h</td>
<td>1.0 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>1.0 ± 0.0</td>
<td>N/A</td>
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<tr>
<td></td>
<td>96 h</td>
<td>1.0 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>0.8 ± 1.0</td>
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<tr>
<td>BS</td>
<td>48 h</td>
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<td>96 h</td>
<td>0.04 ± 0.01</td>
<td>0.05 ± 0.04</td>
<td>0.05 ± 0.04</td>
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<td>DP</td>
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<td>1.0 ± 0.1</td>
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<tr>
<td></td>
<td>96 h</td>
<td>0.9 ± 0.1</td>
<td>N/A</td>
<td>1.0 ± 0.1</td>
<td>N/A</td>
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<td>WS</td>
<td>72 h</td>
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<td>N/A</td>
<td>0.7 ± 0.1</td>
<td>N/A</td>
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<td>144 h</td>
<td>0.7 ± 0.1</td>
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<td>0.7 ± 0.1</td>
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<tr>
<td>SG</td>
<td>72 h</td>
<td>0.3 ± 0.02</td>
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<td>0.4 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.03</td>
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<td></td>
<td>144 h</td>
<td>0.5 ± 0.1</td>
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<td>0.6 ± 0.04</td>
<td>0.5 ± 0.1</td>
<td>0.4 ± 0.03</td>
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<tr>
<td>SS</td>
<td>96 h</td>
<td>0.7 ± 0.04</td>
<td>N/A</td>
<td>1.5 ± 0.1*</td>
<td>0.7 ± 0.02</td>
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<td>168 h</td>
<td>0.9 ± 0.2</td>
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<td>1.4 ± 0.02*</td>
<td>0.8 ± 0.004</td>
<td>1.4 ± 0.2*</td>
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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 irradiance, phototrophic nanoflagellates and total bacteria were not collected for temperate stations.
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 $p$CO$_2$ (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 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 ($\mu$DMSP, 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]$_{\text{high CO}_2}$/[x]$_{\text{ambient CO}_2}$) 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, T$_2$ = 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).
Figure 9. Relationship between the Revelle Factor of the sampled water and the relative CO$_2$ treatment effect ([X]$_{\text{high CO}_2}$/[X]$_{\text{ambient CO}_2}$) for chlorophyll $a$ concentrations at T$_1$ (A) and T$_2$ (B) and phototrophic nanoflagellate abundance 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, T$_2 = 96$ h, except for Weddell Sea and South Georgia (72 h, 144 h) and South Sandwich (96 h, 168 h).