

# **Impact of ocean acidification on Arctic phytoplankton blooms and dimethylsulfide concentration under simulated ice-free and under-ice conditions**

5    **Hussherr, Rachel<sup>1</sup>; Levasseur, Maurice<sup>1</sup>; Lizotte, Martine<sup>1</sup>; Tremblay, Jean-Éric<sup>1</sup>; Mol, Jacoba<sup>2</sup>; Thomas, Helmuth<sup>2</sup>; Gosselin, Michel<sup>3</sup>; Starr, Michel<sup>4</sup>; Miller, Lisa A.<sup>5</sup>; Jarníková, Tereza<sup>6</sup>; Schuback, Nina<sup>6</sup>; Mucci, Alfonso<sup>7</sup>**

[1] Québec-Océan and Takuvik joint UL-CNRS laboratory, Département de biologie, Université Laval, Québec, Québec G1V 0A6, Canada

10    [2] Department of Oceanography, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada

[3] Institut des sciences de la mer de Rimouski, Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada

[4] Maurice Lamontagne Institute, Fisheries and Oceans Canada, Mont-Joli, Québec G5H 3Z4, Canada

15    [5] Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, British Columbia V8L 4B2, Canada

[6] Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

20    [7] GEOTOP and Department of Earth and Planetary Sciences, McGill University, Montréal, Québec H3A 0E8, Canada

*Correspondence to:* Rachel Hussherr (rachel.hussherr@gmail.com)

**Abstract.** In an experimental assessment of the potential impact of Arctic Ocean acidification on seasonal phytoplankton blooms and associated dimethylsulfide (DMS) dynamics, we incubated water from Baffin Bay under conditions representing an acidified Arctic Ocean. Using two light regimes simulating under-ice/ subsurface chlorophyll maxima (low light; Low PAR and no UVB) and ice-free (high light; High PAR + UVA + UVB) conditions, water collected at 38 m was exposed over 9 days to 6 levels of decreasing pH from 8.1 to 7.2. A phytoplankton bloom dominated by the centric diatoms *Chaetoceros* spp. reaching up to  $7.5 \mu\text{g}$  chlorophyll *a*  $\text{L}^{-1}$  took place in all experimental bags. Total dimethylsulfoniopropionate (DMSP<sub>T</sub>) and DMS concentrations reached  $155 \text{ nmol L}^{-1}$  and  $19 \text{ nmol L}^{-1}$ , respectively. The sharp increase in DMSP<sub>T</sub> and DMS concentrations coincided with the exhaustion of  $\text{NO}_3^-$  in most microcosms, suggesting that nutrient stress stimulated DMS(P) synthesis by the diatom community. Under both light regimes, chlorophyll *a* and DMS concentrations decreased linearly with increasing proton concentration at all pH tested. Concentrations of DMSP<sub>T</sub> also decreased but only under high light and over a smaller pH range (from 8.1 to 7.6). In contrast to nanophytoplankton ( $2\text{--}20 \mu\text{m}$ ), picophytoplankton ( $\leq 2 \mu\text{m}$ ) was stimulated by the decreasing pH. We furthermore observed no significant difference between the two light regimes tested in term of chlorophyll *a*, phytoplankton abundance/ taxonomy, and DMSP/ DMS net concentrations. These results show that OA could significantly decrease the algal biomass and inhibit DMS production during the seasonal phytoplankton bloom in the Arctic, with possible consequences for the regional climate.

# 1 Introduction

As a result of anthropogenic emissions of carbon dioxide (CO<sub>2</sub>) to the atmosphere, important transformations are observed in the global ocean, including a rise in water temperature, a decrease in ocean pH, modifications of water circulation patterns and nutrient distributions, and a loss of sea-ice in the Arctic (ACIA, 2005; Fabry et al., 2009; Macdonald et al., 2015). Due to various feedback processes, the atmospheric temperature in the Arctic region above 64°N has warmed by 1.9°C between 1981 and 2012, a rate three times higher than the global average (ACIA, 2005; Ford et al., 2015). This phenomenon, known as the Arctic amplification (Cohen et al., 2014), is leading to the greatest regional transformations observed in the recent decades (ACIA, 2005). Given that the reduction in the extent and thickness of the sea ice cover and the acidification of surface waters are two factors that can potentially affect Arctic primary productivity, it is important to consider the associated effects on the production of biogenic climate-active gases such as dimethylsulfide (DMS).

Since the pre-industrial era, the ocean has absorbed more than one quarter of the anthropogenic CO<sub>2</sub> emitted to the atmosphere (Feely et al., 2009, and references therein). This phenomenon alters the chemistry of seawater and results in a decrease in pH. The dissolution of anthropogenic CO<sub>2</sub> has already led to an estimated 0.1 unit decrease of pH in the global ocean surface waters (Feely et al., 2009). An additional decrease of 0.2 pH unit is anticipated by the end of the century and as much as 0.8 by 2300, depending on future net CO<sub>2</sub> emissions (Caldeira and Wickett, 2003; Raven et al., 2005; Doney et al., 2009; Feely et al., 2009). Owing to the lower buffer capacity and greater solubility of CO<sub>2</sub> in cold waters and the dilution of total alkalinity (TA) by freshwater due to sea-ice melt and river run-off, a more rapid decline of 0.45 unit is predicted by 2100 for Arctic waters under IPCC SRES emission scenario A2 (Steinacher et al., 2009).

During the last two decades, many studies have attempted to quantify the sensitivity of marine ecosystems to ocean acidification (OA). Since the dissolution of atmospheric CO<sub>2</sub> increases its concentration in seawater, low pH-high *p*CO<sub>2</sub> could enhance phytoplankton growth rate by facilitating CO<sub>2</sub> uptake and reducing the energy cost of the Carbon Concentrating Mechanism (CCM, cellular processes used by algae to overcome CO<sub>2</sub> limitation in water) in some phytoplankton species (Gao and Campbell, 2014 and references therein). Accordingly, a decrease in pH has been reported to stimulate carbon fixation by phytoplankton (Doney et al., 2009; Gao

and Campbell, 2014; Wu et al., 2014; Mackey et al., 2015; Thoisen et al., 2015), but negative  
75 impacts of decreasing pH on phytoplankton growth have also been reported and attributed to pH-  
induced alterations in algal cell physiology, acid-base chemistry, trace metal availability, ion  
transport, protein functions, and nutrient uptake (Doney et al., 2009; Gao and Campbell, 2014;  
Richier et al., 2014; Mackay et al., 2015; Thoisen et al., 2015). Due to these potential antagonist  
effects, it is still difficult to predict how a specific bloom in a given area will respond to the  
80 projected decrease of ocean pH.

A ubiquitous, biogenic trace gas produced in the ocean (Keller et al., 1989; Townsend and Keller,  
1996; Kiene et al., 2000), DMS, accounts for 80% of the biogenic sulfur emitted from the ocean  
to the atmosphere (Kettle and Andreae, 2000). Once released to the atmosphere, DMS undergoes  
a rapid photochemical transformation into sulfate, which may result in an increase in the  
85 concentration of sulfate aerosols and cloud condensation nuclei. Emissions of DMS thus can  
increase cloud albedo and potentially cool the climate (Ferek et al., 1995; Quinn et al., 2002). The  
effect of DMS on climate is particularly important in regions of low aerosol burden, such as the  
summer Arctic atmosphere (Mungall et al., 2016). This gas is mostly produced by the  
degradation of dimethylsulfoniopropionate (DMSP), a cellular compound present in the majority  
90 of phytoplankton species where it fulfils several physiological functions, including  
osmoregulation (Dickson et al., 1980; Kirst, 1996; Van Bergeijk et al., 2003), cryoprotection  
(Kirst et al., 1991), and protection against reactive oxygen species (Sunda et al., 2002). A  
significant fraction of algal DMSP is released to the water column by exudation or from grazing;  
constituting a dissolved pool that is rapidly consumed by heterotrophic bacteria, which can cleave  
95 it into DMS (the “cleavage pathway”) or metabolize it via the demethylation/ demethiolation  
pathway (Kiene et al., 2000). Both unicellular algae and bacteria can thus convert DMSP to  
DMS, their relative contribution being governed by the taxonomic composition of the  
phytoplankton community, as well as the abundance and physiological state of the bacteria  
(Stefels et al., 2007). Oceanic DMS production is thus closely linked to phytoplankton bloom  
100 development, which makes it also potentially sensitive to OA.

Several studies have already highlighted the sensitivity of DMS production to decreases in  
seawater pH. The majority of these experimental studies revealed a negative impact of decreasing  
pH on DMS production (Hopkins et al., 2010; Avgoustidi et al., 2012; Archer et al., 2013; Webb

et al., 2016), but some have reported either no effect or a positive effect (Vogt et al., 2008; Hopkins and Archer, 2014). Several hypotheses have been proposed to explain these contrasting results. Some authors attribute the pH-induced variation in DMS production to an alteration of the physiological properties of the phytoplankton cells or of the bacterial DMSP metabolism (Vogt et al., 2008; Hopkins et al., 2010, Avgoustidi et al., 2012; Archer et al., 2013; Hopkins and Archer, 2014; Webb et al., 2015, 2016), whereas others evoke an interaction between the DMSP producers and their grazers (Kim et al., 2010; Park et al., 2014). So far, only one study has looked at the impact of OA on DMS dynamics in the Arctic (Archer et al., 2013). The results of this mesocosm study, conducted near Svalbard, show a decrease in DMS concentrations at low pH, suggesting that OA may significantly reduce DMS emissions to the atmosphere in the Arctic.

The main objective of this study was to experimentally assess the impact of decreasing pH on the DMS produced by an Arctic phytoplankton seasonal bloom. Furthermore, we investigated how light conditions corresponding to those experienced by a marginal ice phytoplankton bloom and an under-ice or subsurface phytoplankton bloom could modulate the effects of pH on phytoplankton and DMS variations. The latter was motivated by the strong contribution of subsurface phytoplankton layers to annual productivity in several sectors of the Arctic as well as the apparent increasing occurrence of under-ice blooms, attributed to the thinning of sea ice and the replacement of the multiyear ice by first-year ice (Martin et al., 2010; Frey et al., 2011; Palmer et al., 2014 and references therein).

## 2 Methods

### 2.1 Initial water collection and experimental setting

The incubation experiment was conducted on board of the Canadian research icebreaker *CCGS Amundsen* between 6 and 15 August 2015. The water was collected near the nitracline at 38 m depth at station BB-3 in Baffin Bay (see Fig. 1) using 12-L Niskin-type bottles deployed on a CTD rosette system. Since the cruise took place after the summer bloom in this part of the Arctic, we collected the water between the subsurface chlorophyll maximum (SCM) and the nitracline in order to have sufficient nutrient to support a bloom during our incubation. *In situ* temperature and salinity were respectively -1.35°C and 32.67 at the sampling depth. All water manipulations were done under dim light conditions in order to protect the cells from potential light shock. After the initial collection, water was gravity filtered through a 200  $\mu$ m Nitex mesh, in order to remove large grazers, and transferred to 12 gas-tight 10-L bags (HyClone Labtainer©, Thermo Scientific) using a Teflon tube installed between the Niskin bottle and the luer-valve of each bag. All 12 bags were placed in an incubator on the ship's foredeck, through which surface water was circulated to maintain the incubation bags close to sea surface temperature. Since our deck incubator was cooled with circulating surface water, we had no control over the temperature during the incubation (mean temperature of  $4.3 \pm 1.6^\circ\text{C}$  over the 9-day experiment). However, all bags were in the same incubator, hence submitted to the same temperature. An insulated box (a "cooler") was used to transport the samples whenever they had to be carried between the incubator and the ship-board laboratory. Water temperature was monitored every 15 minutes during the entire experiment using a RBR TR-1060 temperature recorder. Incident photosynthetically active radiation (PAR, 400-700 nm) was monitored continuously using a LI-1000 Data logger combined with a LI-190SA cosine sensor (LICOR) located near the incubator. Incident UVA (SED033 detector/UVA filter/W diffuser) and UVB (SED240 detector/UVB filter/W diffuser) radiation was measured daily (day 5 to 9 only due to instrument dysfunction during the first four days) around midday with an IL1700 radiometer (International Light).

## 2.2 Treatments and acidification protocol

### *Acidification protocol*

For this experiment, the phytoplankton communities were exposed to a pH gradient and two light regimes. Twelve incubation bags were separated into 2 groups of six bags to produce two similar sets of pH gradients (control + 5 acidified bags; Table 1). The pH gradient method has been successfully applied by Schulz et al. (2013) and Paul et al. (2016) and is suitable when the possibility of replication is limited (see Cottingham et al., 2005, and Havenhand et al., 2010, for more details).

After equilibrating at incubator temperature, the “non-control” samples were taken to the lab and acidified (at time T0, 6 August) by addition of strong acid and bicarbonate (HCl, 0.02 N; NaHCO<sub>3</sub>, 0.3 N) following procedures described by Riebesell et al. (2010). By keeping the alkalinity constant, this procedure mimics the natural acidification process as observed in global ocean waters. The volumes needed to reach each targeted pH value on the total hydrogen ion scale (mol kg<sup>-1</sup> SW) were determined with the help of the MS Excel macro CO<sub>2</sub>SYS (Pierrot et al. 2006) (using the carbonic acid dissociation constants (K<sub>1</sub> and K<sub>2</sub>) of Luecker et al., 2000 and the bisulfate dissociation constant (K<sub>H<sub>2</sub>SO<sub>4</sub></sub>) of Dickson, 1990). The acid and bicarbonate solutions were added in appropriate proportions to each bag using a syringe connected to the Luer-lock port of the bag. After acidification, each bag was gently inverted around 10 times before being returned to the incubator. The entire process of the bags acidification was completed within 4 hours. The incubator was then covered with a white canvas sheet until sunset and bags remained overnight in the incubator without further manipulation. After the initial acidification, the carbonate chemistry was not manipulated and the only changes in pH that occurred during the experiment were due to biological activity. Subsampling began the next day in the morning (T1, 7 August, around 7:00 am).

### *Light treatments*

Once acidified, each set of incubation bags covering the initial pH values between 8.1 and 7.2 was assigned to a light treatment (Tables 1 and 2): “low light” (LL, 6 bags), and “high light” (HL, 6 bags). The transmittance through the incubation bags of both LL and HL treatments was determined in the laboratory using a Perkin Elmer LAMBDA 850 Spectrophotometer. We based our experimental “low light” conditions (PAR, UVA and UVB transmittance of 32.6%, 20.6%

and 0%, respectively) on a model of the minimal light conditions required to trigger an under-ice bloom (Palmer et al., 2014) and available data from measurements of UV and PAR under ponded ice (Trodahl and Buckel, 1990; Perovich et al., 1998; Belzile et al., 2000; Frey et al., 2011; Palmer et al., 2014). As UVB is strongly attenuated by sea ice and thus likely negligible at 5 m depth under the ice (Frey et al., 2011; Palmer et al., 2014), those short wavelengths were eliminated. The LL treatment transmittances were achieved by covering the 6 LL bags with 2 layers of Nitex mesh (300  $\mu\text{m}$ ) and one layer of Mylar D film (0.13 mm thick; Demers et al., 1998). The Nitex mesh attenuated the entire light spectrum equally whereas the Mylar D film specifically removed the leftover UVB radiation (Demers et al., 1998; Roux et al., 2002). The resulting transmittance measured through the incubation bags under LL treatment was similar to light conditions encountered at 5 m depth under the ice in early summer (Frey et al., 2011) or at subsurface chlorophyll maxima, which are widespread in the Arctic Ocean (Martin et al. 2010, 2013).

The incubation bags dedicated to the HL treatment (PAR, UVA and UVB transmittance of 77.5%, 61.5% and 32.6%, respectively) were exposed to light conditions representing a typical Arctic upper mixed layer of approximately 5 m depth, based on the equation of Riley (1957):

$$E_z = E_0 \cdot \frac{1 - e^{-K_d \cdot Z}}{K_d \cdot Z}$$

where  $E_z$  ( $\mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ ) is the daily PAR averaged over the surface mixed layer,  $E_0$  ( $\mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ ) is the daily averaged PAR at the surface,  $K_d$  is the PAR diffuse attenuation coefficient (assumed to be  $0.123 \text{ m}^{-1}$ ; unpublished data from Baffin Bay, M. Gosselin), and  $Z$  (m) is the surface mixed layer depth. The attenuation of incident light for the HL treatment was only due to the bag itself.

### 2.3 Microcosm subsampling for chemical and biological variables

The 12 incubation bags (microcosms) were monitored over 9 days after the initial acidification (T0). Subsampling took place at 9:00 am the first day (T0), before the initial acidification, and between 6:00 and 10:00 a.m. for the 9 following days (T1-T9). Not all the variables were sampled every day. Water for pH, total alkalinity (TA), dissolved inorganic carbon (DIC), and DMS analyses was collected directly from the microcosms to minimise outgassing, whereas



water for the measurement of chlorophyll *a* (Chl *a*), nutrients, flow cytometry, and taxonomy was first collected in a brown bottle (Nalgene<sup>®</sup>, 1L) and kept at 4°C in the refrigerator until subsampling, generally 2 h after initial water sampling. Water for salinity determination was taken at T0 before the acidification process and at T9 in each incubation bag. Samples for salinity were stored in the dark in 250 mL plastic bottles until analysis in May 2016 using a Guidelines 8400B salinometer. At least half of the initial volume of the microcosms (5L) remained in the bags at the end of the experiment.

### *Carbonate system*

The pH was measured on T1, T2, T4, T6, T8, and T9 using an Agilent 8453 UV/Vis Spectrophotometer on the total hydrogen ion scale (pH<sub>T</sub>). Water was directly subsampled from the incubation bags to the spectrophotometric cells in order to minimise gas exchange with ambient air. The spectrophotometer cells (10 cm path length, V = 33 mL) were brought up to 25°C in an aluminum block before readings on the spectrophotometer (approximately 1 hour after sampling). Absorbance was measured at 434, 578, and 730 nm before and after addition of 50 µL of a *m*-cresol purple indicator dye solution (Clayton and Byrne, 1993). A second addition of 50 µL of *m*-cresol purple indicator dye solution was made to the sample in order to determine the extent of the dye perturbation on pH<sub>T</sub> values. Duplicates were analysed for each incubation bag, and pH<sub>T</sub> subsequently calculated according to Dickson et al. (2007, see their section SOP 6b). Data were then converted to mean incubation temperature using CO<sub>2</sub>SYS and the TA measurements (Pierrot et al., 2006). The *p*CO<sub>2</sub> values corresponding to each pH<sub>T</sub> measurement were also calculated using CO<sub>2</sub>SYS software. Concentrations in protons for each microcosm were calculated using the pH<sub>T</sub> measurements.

Water for TA and DIC analyses was subsampled early in the morning on days T1, T4 and T9. Water was gently collected from the incubation bags in pre-rinsed 250 mL glass bottles. Samples were analysed on board within 4 hours by coulometric and potentiometric titration for DIC and TA, respectively (more details are given for example in Johnson et al., 1993, or Dickson et al., 2007), using a VINDTA 3C (Versatile Instrument for the Determination of Titration Alkalinity, Marianda). Both the DIC and TA measurements were calibrated against Certified Reference Materials (CRMs, Andrew Dickson, Scripps Institution of Oceanography, USA) and the

reproducibility was better than 1 and 2  $\mu\text{mol kg}^{-1}$  SW, respectively, for the DIC and TA measurements.

### *Nutrients*

240 Water for nutrient analysis was filtered through Luer-lock syringe acrodisc filters (GMF, porosity of 0.7  $\mu\text{m}$ ) into 15 mL acid-washed polyethylene tubes. After collection, samples were stored at 4°C in the dark and analysed within 1 hour for nitrate ( $\text{NO}_3^-$ ) plus nitrite, nitrite ( $\text{NO}_2^-$ ), silicic acid ( $\text{Si(OH)}_4$ ), and soluble reactive phosphate (SRP) on a Bran and Luebbe Autoanalyser III using a colorimetric method adapted from Hansen and Koroleff (2007) (detection limits for;  $\text{NO}_3^-$  : 0.03  $\mu\text{mol L}^{-1}$ ;  $\text{NO}_2^-$  : 0.02  $\mu\text{mol L}^{-1}$ ;  $\text{Si(OH)}_4$ : 0.1  $\mu\text{mol L}^{-1}$ ; SRP: 0.05  $\mu\text{mol L}^{-1}$ ).

### *Plankton biomass and enumeration*

Water for Chl *a* concentration analysis was subsampled from each incubation bag every day using 1 L brown polyethylene bottles. The bottles were stored at 4°C in the dark for 2 hours before filtration onto 25 mm Whatman GF/F filters (0.7  $\mu\text{m}$  nominal pore size). Phytoplankton 250 pigments were extracted in 90% acetone and stored at 4°C in the dark for 20 hours. The fluorescence of the extracted pigments was then measured using a Turner Designs fluorometer 10-AU after acidification according to the method described by Parsons et al. (1984). Chl *a* concentrations were calculated from the equation published in Holm-Hansen et al. (1965).

For the enumeration of phytoplankton ( $\leq 20 \mu\text{m}$ ) and bacteria, sterile cryogenic polypropylene 255 vials were filled with 4 mL of water to which 20  $\mu\text{L}$  of glutaraldehyde (Grade I, 25% in water, Sigma Aldrich; Marie et al., 2005) were added. Duplicate samples were flash frozen in liquid nitrogen after standing 15 min at room temperature in dark. These samples were then stored at -80°C for 5 months until flow cytometry analysis. After defrosting to ambient air temperature, samples were analysed using a FASC Calibur FCB3 flow cytometer (Becton Dickinson). One of 260 the duplicate samples was used to determine the abundance of picophytoplankton (0.2-2  $\mu\text{m}$ ), which include picoeukaryotes and picocyanobacteria, and nanophytoplankton (2-20  $\mu\text{m}$ ) based on their autofluorescence characteristics and size (Marie et al., 2005). The other tube was used for bacterial counts (Marie et al., 1999).

On days T0, T5 and T9, water samples (between 100 and 250 mL depending on the biomass) 265 were taken for identification and counting of eukaryotic cells (protists) larger than 2  $\mu\text{m}$ . Samples

were preserved in acidic Lugol's solution (Parsons et al., 1984) and stored in the dark for 7 months until enumeration with an inverted microscope (WILD Heerbrugg) equipped with phase contrast optics (Lund et al., 1958). Thirteen selected samples collected under both light treatments and representing the whole range of pH amendments (i.e. pH<sub>T</sub> 8.1 (control), 7.6 and 7.2) were counted.

#### *Fast Repetition Rate Fluorometry (FRRF) measurements*

For FRRF measurements, 20 mL of seawater were taken directly from the microcosms at pH<sub>T</sub> 8.1, 7.8, and 7.2 for both HL and LL treatments on days T2, T4, T6, T7 and T9. Water was subsampled early in the morning in order to avoid photoinhibition (Schuback et al., 2015). The FRRF measurements were conducted on a bench top FRRF instrument (Soliense Inc.), as described in Schuback et al. (2015). For each sample, background fluorescence blanks were prepared by syringe filtering a small amount of water through a Whatman GF/F filter. Samples were kept at very low light (approx. 5  $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ ) at *in situ* temperature for 45 minutes before the measurements. A single turnover (ST) excitation protocol was applied to derive minimum ( $F_o$ ) and maximum ( $F_m$ ) chlorophyll *a* fluorescence yields by applying an iterative non-linear fitting procedure to a mean of 20 consecutive ST flashlet sequences using custom software (Kolber et al., 1998). The  $F_o$  and  $F_m$  were used to calculate  $F_v/F_m$  as  $(F_m - F_o)/F_m$ . In the absence of iron limitation, this ratio can be used as a sensitive indicator of algal photosynthetic efficiency (Maxwell and Johnson, 2000; Schuback et al., 2016).

#### *DMSP and DMS concentrations*

For the quantification of dissolved DMSP (DMSP<sub>d</sub>), 20 mL of the water sample were gravity-filtered through 47 mm Whatman GF/F filters and the first 3.5 mL of filtrate were stored in 5 mL polyethylene tubes using the less disruptive Small-Volume gravity Drip Filtration (SVDF) method described by Kiene and Slezak (2006). Tubes for total DMSP (DMSP<sub>T</sub>) samples were directly filled with 3.5 mL of unfiltered water. Samples of both DMSP<sub>d</sub> and DMSP<sub>T</sub> were preserved by adding 50  $\mu\text{L}$  of a 50% sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution to the 5 mL tubes, which were then stored at 4°C in the dark until analysis in laboratory. DMSP concentrations were determined as DMS through hydrolysis with a 5 N solution of NaOH, purging and cryotrapping in liquid nitrogen, followed by analysis on a Varian 3800 Gas Chromatograph equipped with a Pulsed Flame Photometric Detector (Varian 3800) with a detection limit of 0.1 nmol L<sup>-1</sup> (Scarratt

et al., 2000; Lizotte et al., 2012; Galindo et al., 2016). All DMSP samples were calibrated against multiple micro-injections of a 100 nmol L<sup>-1</sup> solution of standardized dimethyl-B-propiothetin (DMPT from Research Plus) hydrolyzed with a 5 N solution of NaOH.

Water samples for DMS concentration analysis were withdrawn on days T0, T2, T4 and every day for the remainder of the incubation period. DMS concentrations were determined onboard the ship using purging, trapping and S-specific gas chromatography, as described by Asher et al. (2015). The custom-built system described by Asher et al. (2015) was used here in manual mode by directly injecting 10 mL of each incubation sample into a sparge vessel. Water for DMS analysis was subsampled directly from each bag using a Luer-lock syringe and injected into the custom-built system at most 40 minutes after sampling. Ultra-high purity N<sub>2</sub> was used to extract the volatile DMS from solution at a flow rate of 100 mL min<sup>-1</sup>. The sparged DMS was adsorbed onto Carboxen-100 packed in a stainless steel trap. After trapping was completed, a series of high current pulses heated the trap to 250°C to desorb the DMS onto the capillary column prior to elution and detection by a Pulsed Flame Photometric Detector (PFPD, OI Analytical, Model 5380). Light emitted during combustion in the PFPD was converted to a voltage (using a PMT – photomultiplier tube) and recorded by the LabView software. Raw data outputs (peak voltages) were processed using Matlab by calculating the area under each curve and by comparing them to standard curves to give final DMS concentrations. Known DMS concentrations of 0, 3, 6, 9, 12, and 15 nmol L<sup>-1</sup> were processed for calibration purpose before each sampling day in order to obtain the standard curves. Area under each standard curve was calculated using Matlab and associated with its known DMS concentration.

## 2.4 Statistical analysis

All statistical analyses were run using RStudio (<http://www.rstudio.com/>). Normality of the data was determined using a Shapiro-Wilk test at the 0.05 significance level and data were transformed (log or square root) when the normality was rejected ( $p < 0.05$ ). To test for differences between pH and light treatments for the variables measured during the experiment (time-series of nutrient and Chl *a* concentrations, phytoplankton, bacteria abundances, and dimethylated compound concentrations), we used a generalized least square model that corrected for data autocorrelation due to time repetition (gls command in R studio, package nlme; also see the method described by Paul et al., 2016). In the model, time and pH were taken as two

continuous factors; the light was included as a categorical factor (2 levels: “Low Light”, “High Light”). As the inclusion of the interaction between light and pH in our gls model did not yield significant results, it was not included in our statistical analysis. Relationships between the average values of all response variables and the set of  $\text{pH}_T$  were evaluated using the Pearson’s

330 linear regression ( $r^2$ ).

### 3 Results

#### 3.1 Irradiance conditions

Daily mean incident PAR varied between 189 and 492  $\mu\text{mol m}^{-2}\text{quanta s}^{-1}$  during the 9 days of the incubation. Accordingly, daily mean PAR in the HL and LL treatment varied between 146 and 312  $\mu\text{mol m}^{-2}\text{quanta s}^{-1}$  and between 61 and 131  $\mu\text{mol m}^{-2}\text{quanta s}^{-1}$ , respectively (Table 2). Incident UVA and UVB levels varied respectively between 4 and 13  $\text{W m}^{-2}$ , and between 0.1 to 0.3  $\text{W m}^{-2}$  during the last 5 days of the experiment.

#### 3.2 State of the carbonate system

Table 1 summarizes values of four carbonate system parameters and associated protons concentrations ( $\text{pH}_T$ ,  $[\text{H}^+]$ , DIC, TA,  $p\text{CO}_2$ ) for each light and pH treatment at T0, T1, T4, and T9. At T1, the mean TA in the acidified bags was  $2221 \pm 16 \mu\text{mol kg}^{-1} \text{SW}$ , approximately 1% lower than the value of  $2243 \mu\text{mol kg}^{-1} \text{SW}$  measured in the original sample recovered from 38 m depth at station BB-3. At the beginning of the experiment (T1), the mean  $\text{pH}_T$  at  $4.27^\circ\text{C}$  (mean incubator temperature during the experiment) between HL and LL controls was  $7.939 \pm 0.003$  (see Table 1 and Fig. 2). Values for the following decreasing pH levels were  $7.779 \pm 0.012$ ,  $7.641 \pm 0.007$ ,  $7.460 \pm 0.001$ ,  $7.323 \pm 0.030$ , and  $7.159 \pm 0.004$ . As expected, the  $\text{pH}_T$  in all bags increased during the incubation period due to photosynthesis (Rost et al., 2008; Paul et al., 2016) (mean protons change per bag of  $-1.52 \times 10^{-8} \pm 6.67 \times 10^{-9} \text{mol L}^{-1}$  over the 9-day experiment; Fig. 2). A difference in  $\text{pH}_T$  (corresponding to an average proton difference of  $-8.87 \times 10^{-9} \pm 8.59 \times 10^{-9} \text{mol L}^{-1}$ ) was still observed at T9 between bags in both the LL and HL treatments (Fig. 2). The  $\text{pH}_T$  gradients between the two light treatments were thus very similar, allowing us to clearly discriminate between  $\text{pH}_T$  and light effects. Hereafter, we refer to the pH treatments by their mean  $\text{pH}_T$  values measured over the 9 incubation days: 8.1 (control) and decreasing mean  $\text{pH}_T$  values of 7.9, 7.8, 7.6, 7.4 and 7.2.

#### 3.3 Dissolved inorganic nutrient concentrations

At T1,  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$ , and SRP concentrations varied between 5.07-5.83, 8.87-10.45, and 0.94-1.00  $\mu\text{mol L}^{-1}$ , respectively (Fig. 3). All three nutrients displayed the same general temporal pattern during the incubation, irrespective of the light treatment. Their concentrations remained constant or increased slightly during the first three days and then decreased rapidly with the onset

of the bloom to very low or undetectable concentrations between T6 and T8 for  $\text{NO}_3^-$  (all  $\text{pH}_T$ ) and at T8 for  $\text{Si(OH)}_4$  (highest  $\text{pH}_T$  only). Likewise, SRP concentrations decreased in parallel with  $\text{NO}_3^-$  and  $\text{Si(OH)}_4$ , but remained higher than  $0.3 \mu\text{mol L}^{-1}$  during the whole experiment. The impact of pH on nutrient consumption was apparent under both light treatments, with nutrients being generally consumed more rapidly at high  $\text{pH}_T$  than at low  $\text{pH}_T$  (Fig. 3, Table 3). The  $\text{NO}_3^-$  depletion was temporally delayed in the most acidified treatments, reaching below detection values one day after the other treatments for microcosms at  $\text{pH}_T$  7.4 (T7) and two days after the others for microcosms at  $\text{pH}_T$  7.2 (T8). With the exception of microcosms at  $\text{pH}_T$  8.1 under LL, and at  $\text{pH}_T$  7.8 under both light treatments,  $\text{Si(OH)}_4$  remained at relatively high concentrations in all treatments after the peak of the bloom (Figs. 3c, d and 4a, b). While the ratio of  $\text{NO}_3^-$  to SRP uptake ( $\Delta\text{NO}_3^-:\Delta\text{SRP}$ ) during the incubation showed no statistical difference between the six  $\text{pH}_T$  treatments tested, the ratio  $\Delta\text{Si(OH)}_4:\Delta\text{NO}_3^-$  decreased linearly with increasing proton concentration for both light regimes ( $r^2 = 0.72$ ,  $p < 0.001$ ; data not shown). This change was driven mostly by a reduction in  $\text{Si(OH)}_4$  uptake, which exhibited a ca. 3-fold difference between experimental pH extremes compared to a ca. 1.7-fold difference for  $\Delta\text{NO}_3^-$  uptake (not shown).

### 3.4 Phytoplankton biomass

The mean Chl *a* concentration before the beginning of the experiment (T0) was  $0.686 \pm 0.004 \mu\text{g L}^{-1}$ , and increased exponentially from T1 to T5-T8, depending on the  $\text{pH}_T$  treatment, to reach maximum values varying between  $4.5$  and  $7.5 \mu\text{g L}^{-1}$  (Fig. 4a, b). The bloom period was followed by either a plateau or a small decrease in Chl *a* biomass. The temporal changes in Chl *a* concentrations were not affected by the light regimes but we observed a significant difference in Chl *a* concentrations between  $\text{pH}_T$  treatments (Table 3). Figure 5a shows the relationship between the mean Chl *a* concentrations and the corresponding mean proton concentrations over the entire experimental period. For both light regimes (data pooled), the mean Chl *a* concentration decreased linearly with increasing proton concentration (Fig. 5a, Table 4).

### 3.5 Phytoplankton abundance and taxonomy of the protist community > 2 $\mu\text{m}$

Nanophytoplankton (algal cells between  $2$  and  $20 \mu\text{m}$ ) abundance varied during the incubation from  $0.81 \times 10^3 \text{ cells mL}^{-1}$  on day T1 to  $19 \times 10^3 \text{ cells mL}^{-1}$ , a maximal value reached at  $\text{pH}_T$  7.61 on day T8 under LL conditions (Fig. 4c,d). For both light treatments, nanophytoplankton abundance increased steadily from T1 to T6-T8 and decreased or remained stable thereafter. This

trend is comparable with the trend observed for Chl *a* (Fig. 4a,b) but with the slight difference that the nanophytoplankton generally reached their maximal abundance 1-2 days after the Chl *a* concentration maxima. The lag probably reflects a decrease in Chl *a* synthesis (and thus Chl *a* cell quota) as the dividing cells were becoming nitrogen limited. Variations in nanophytoplankton abundance were significantly correlated with Chl *a* during the growth phase ( $r^2 = 0.78$ ,  $p < 0.001$ ), suggesting that nanophytoplankton were responsible for most of the biomass build-up during the bloom. Like Chl *a*, only the pH<sub>T</sub> gradient (not light treatment) appeared to have affected nanophytoplankton dynamics as we observed significant differences between nanophytoplankton abundances between all pH<sub>T</sub> tested (Table 3). As shown in Figure 5b, the mean nanophytoplankton abundances decreased as the proton concentration increased (data pooled, Table 4).

The initial protist community  $> 2 \mu\text{m}$  was dominated by centric diatoms (33% of total protist abundance), followed by cryptophyceae (22%), unidentified flagellates (17%), and prasinophyceae (12%) (Fig. 6). Pennate diatoms, dinophyceae and chrysophyceae were also present in smaller proportions (4, 3 and 2% respectively; included in the group named “others” in Fig. 6, given their low abundance). Among the protists  $> 2 \mu\text{m}$ , centric diatoms were dominant in most treatments at T5 and T9, accounting for between 72% and 89% of total cells, while the other groups initially present decreased in abundance or became undetectable. More than 90% of the centric diatoms belonged to the genus *Chaetoceros*. Although the dominant species of *Chaetoceros* could not be identified (the biomass of this genus was dominated by unidentified *Chaetoceros* comprised between 2 and 5  $\mu\text{m}$ ), *Chaetoceros gelidus*, *Chaetoceros wighamii*, *Chaetoceros cf. karianus* and *teniussimus* also contributed to the bloom. All microcosms subsampled during the experiment showed very similar taxonomic compositions, with *Chaetoceros* spp. dominating the community and accounting for more than 65% of cell abundance. The sole exception was the LL control microcosm (pH<sub>T</sub> of 8.1), in which the species composition on day T9 was more evenly distributed, with 58% of cell abundance attributed to groups other than centric diatoms. Within this fraction, flagellates accounted for 24% of the total abundance, choanoflagellidea for 12%, prasinophyceae for 10%, cryptophyceae for 2%, and minority protist groups (“others”) for 11%. Due to the low number of samples analyzed by inverted microscopy, it was not possible to statistically confirm whether the difference observed on day T9 between the control microcosm and the two other microcosms analyzed was related to



the pH gradient or resulted from inter-microcosm variability. Nevertheless, the general trends visible in Figure 6 suggest that the relative abundance of each protist group was not influenced by the light regime or the pH gradient. Centric diatoms, and especially *Chaetoceros* spp., remained the dominant taxa throughout the incubation period in every microcosm. Dinophyceae, which initially contributed up to 3% of the protist abundance, became undetectable in all microcosms, including the controls, suggesting a negative effect of bag manipulation and the incubation process on this taxon during the experiment.

During the present experiment, picophytoplankton (algal cells between 0.2 and 2  $\mu\text{m}$ ) accounted for more than 90% of total phytoplankton cells  $\leq 20 \mu\text{m}$ . Photosynthetic picocyanobacteria made up  $\leq 2\%$  of total abundance of picophytoplankton (i.e. picocyanobacteria + photosynthetic picoeukaryotes). Picophytoplankton cell abundance was low at the start of the experiment ( $< 5 \times 10^3 \text{ cells mL}^{-1}$ ) and remained at this low level until T3 when it began to increase to reach maximum concentrations ( $200\text{-}300 \times 10^3 \text{ cells mL}^{-1}$ ) between T7 and T8, depending on the  $\text{pH}_T$  (Fig. 4e, f). Exceptions to this trend are the two microcosms at the lowest  $\text{pH}_T$  under both light regimes, in which picophytoplankton abundance continued to increase linearly until the end of the experiment. Of the two stressors tested (light and pH), only  $\text{pH}_T$  had a weak but significant effect on picophytoplankton abundances (Table 3). As shown in Figure 5c, mean picophytoplankton abundance increased with increasing proton concentration for both light treatments although this relation does not appear to be linear (data pooled, Table 4).

### 3.6 Photosynthetic performance

The  $F_v/F_m$  ratio, a parameter widely used to indicate the photosynthetic performance of primary producers, was very similar between the two light treatments at each sampling day (Table 4). On days T2 and T4, the  $F_v/F_m$  ratios were higher than 0.5 under both light treatments and  $\text{pH}_T$  values of 8.1, 7.8, and 7.2, suggesting that the blooming algal cells were in good physiological condition. The ratios then decreased to ca. 0.3-0.4 between days T6-T9, when  $\text{NO}_3^-$  started to be exhausted in most microcosms and the increase in Chl *a* biomass and phytoplankton cell abundance had stopped (Figs. 3a, b and 4a-f). These results show low photosynthetic performance in the microcosms at the end of the experiment.

### 3.7 Bacteria

Bacterial abundances under both light treatments showed a moderate increase during the experiment (Fig. 4g,h). Although it is not evident on Figure 4 (g, h), the bacterial abundances were significantly different between both light and pH treatments, in contrast with the other variables presented above (Table 3). As shown in Figure 5d, the mean bacterial abundance decreased with increasing proton concentrations under HL but showed no proton/pH related effect under LL (Table 4).

### 3.8 DMSP and DMS concentrations

The DMSP<sub>T</sub> concentrations showed the same general temporal pattern in all microcosms (Fig. 7a,b). Initial average DMSP<sub>T</sub> concentration was  $7 \pm 3$  nmol L<sup>-1</sup>, and remained at this low level during the first five days of the experiment, increased sharply between T5 and T6 to reach values of 80 nmol L<sup>-1</sup> (under HL) and 120 nmol L<sup>-1</sup> (under LL), and remained high but variable for the rest of the experiment. Of the two stressors tested, only the pH gradient significantly influenced the DMSP<sub>T</sub> concentrations (Table 3). As shown in Figure 8a, the mean DMSP<sub>T</sub> concentration decreased with increasing proton concentration, but only under the HL treatment between pH<sub>T</sub> 8.1 – 7.6 (Table 4).

The DMSP<sub>d</sub> concentrations started at 0.5-1.8 nmol L<sup>-1</sup>, decreased slightly until T5 and then tended to increase, again slightly, to reach maximum values between 2 and 3 nmol L<sup>-1</sup> near the end of the experiment (Fig. 7c,d). Neither the light nor the pH<sub>T</sub> treatments significantly affected the DMSP<sub>d</sub> concentrations over the period of incubation (Table 3).

In most of the microcosms, temporal changes in DMS concentrations were very similar to those in DMSP<sub>T</sub> and were characterised by a gradual increase from 0.54 to ca. 4 nmol L<sup>-1</sup> between T1 and T5, a sudden increase to 10-20 nmol L<sup>-1</sup> between T5 and T7, followed by either a plateau or a decrease in concentrations until the end of the experiment (Fig. 7e,f). The sharp increase in DMS was not observed at the two lowest levels of pH<sub>T</sub> (i.e. 7.4 and 7.2). At these low pH<sub>T</sub> values, DMS concentrations did not exceed 6 nmol L<sup>-1</sup> during the phytoplankton growth phase. Of the two stressors tested, only the pH gradient had a significant effect on the DMS concentrations over time (Table 3). As shown in Figure 8b, the mean DMS concentration decreased with increasing proton concentration (Table 4). The average DMS:DMSP<sub>d</sub> ratio followed the same trend as for

DMS concentrations, showing a linear decrease over the whole range of proton concentration,  
480 irrespective of the light treatment (Fig. 8c, Table 4).

## 4 Discussion

In this study, a natural Arctic plankton community in a pre-bloom stage (initial high nutrient-low Chl *a* concentrations) was exposed over 9 days to reduced pH conditions under two contrasting light regimes. The two light regimes were designed to simulate the mean irradiance in an ice-free 5-m thick surface mixed layer (HL, marginal ice bloom conditions) and the mean irradiance at 5 m depth under a melting ponded ice pack (LL, under-ice bloom/ subsurface chlorophyll maximum conditions). The pH<sub>T</sub> gradient comprised 6 levels covering the range of pH expected between the present and the year 2300. We recognize that the rapid change in pH to which the plankton assemblage was exposed at the beginning of our study is not representative of the more gradual acidification that is taking place in the ocean. For this reason, negative impacts should be interpreted as potential extreme responses, and the planktonic community could be more adaptable than is implied by our results.

### 4.1 General bloom characteristics and associated variations in DMSP and DMS

During this experiment, a phytoplankton bloom numerically dominated by the centric diatom *Chaetoceros* spp. and by photosynthetic picoeukaryotes occurred almost simultaneously in all microcosms (Figs. 4c-f). The exponential growth phase lasted 6-7 days, a period during which the concentration of all three monitored nutrients decreased, with NO<sub>3</sub><sup>-</sup> reaching near-zero values. The F<sub>v</sub>/F<sub>m</sub> ratios around 0.5 characterised the period of exponential growth in all microcosms, including the controls (Table 5). The peak of the bloom and NO<sub>3</sub><sup>-</sup> depletion were followed by a decrease of F<sub>v</sub>/F<sub>m</sub> ratios and a stabilization or slight decrease in phytoplankton abundances (Figs. 3 and 4c-f). As the initial concentrations of nutrients in the incubation bags were similar to the concentrations found in the upper mixed layer before the spring bloom in Baffin Bay, we are confident that the bloom that took place in our bags is comparable to the spring bloom naturally developing in these waters (Tremblay et al., 2002, 2006). Furthermore, the dominance of diatoms during our experiment was expected as blooms of this phytoplankton group are commonly found at the marginal ice zone in the Arctic, and in Baffin Bay in particular (Poulin et al., 2011), and tend to dominate spring primary production when nutrients are non-limiting in this region (Heimdal, 1989; Matrai and Vernet, 1997; Wolfe et al., 1999; Von Quillfeldt, 2000).

Picophytoplankton were numerically more abundant than nanophytoplankton during our experiment, representing between 54% (during the diatom bloom) and up to 96% (post bloom

period) of total phytoplankton abundance. High picophytoplankton abundances (64% of total photosynthetic cell abundance  $\leq 20 \mu\text{m}$ ) have been reported by Tremblay et al. (2009) in the Canadian Arctic where, due to their small size, they accounted for only 16% of total Chl *a*.

515 During the growth phase of this study, concentrations of Chl *a* displayed a stronger correlation with nanophytoplankton abundances ( $r^2 = 0.78$ ,  $p < 0.001$ ) than they did with picophytoplankton ( $r^2 = 0.48$ ,  $p < 0.001$ ) despite the latter's numerical dominance. The taxonomy of the picophytoplankton was not determined during our study, but *Micromonas*-like species are known to be a major component of the photosynthetic picoeukaryotes in the Arctic (Lovejoy et al., 2007; Tremblay et al., 2009).

The DMSP<sub>T</sub> concentrations measured during the development of the diatom bloom correspond to a DMSP<sub>T</sub>:Chl *a* ratio ranging from 3 to 15 nmol  $\mu\text{g}^{-1}$  (data not shown), as expected for this phytoplankton group (Stefels et al., 2007). The sharp increase in DMSP<sub>T</sub> measured between T5 and T6 under both light regimes and at all pH<sub>T</sub> values investigated was however unexpected (Fig. 7a,b), as it contrasts with results from previous mesocosms experiments that showed a more gradual increase in DMSP along with algal biomass (Vogt et al., 2008; Archer et al., 2013; Park et al., 2014). During our experiment, this sharp increase in DMSP<sub>T</sub> and DMS coincided with the exhaustion of NO<sub>3</sub><sup>-</sup>, with the exception of the microcosms at pH<sub>T</sub> 7.4 and 7.2 under both light regimes (Fig. 3a, b). At the two latter pH the increase of DMSP<sub>T</sub> between T5 and T6 was of lower magnitude compared to the other microcosms and the remaining NO<sub>3</sub><sup>-</sup> concentrations varied from 0.9 to 2.6  $\mu\text{mol L}^{-1}$  in these bags at T6 (Fig. 7a, b). Previous laboratory experiments have shown that NO<sub>3</sub><sup>-</sup> limitation could induce a 25-fold increase in diatoms DMSP<sub>T</sub> cellular quotas (Keller et al., 1999; Bucciarelli and Sunda, 2003; Sunda et al., 2007). Our results show a ca. 9-fold increase of DMSP<sub>T</sub> between T5 and T6, which corresponds well with the values found in the literature (Sunda et al., 2007). Unicellular algae are known to synthesize DMSP during episodes of stress or senescence as an overflow mechanism to evacuate excess energy, sulfur, and carbon, while allowing the cell to function (Stefels et al., 2000; Hopkins and Archer, 2014). In response to NO<sub>3</sub><sup>-</sup> limitation, diatoms could have switched from the synthesis of glycine betaine (GBT), a nitrogen-containing osmolyte, to its sulfur analog DMSP (Andrea, 1986; Keller et al., 1999). Altogether, 540 these results suggest a relationship between the intensity of nitrate depletion and the magnitude of DMSP synthesis by the diatom community during our experiment. These results also suggest that diatoms could have more difficulty in efficiently taking up/assimilating NO<sub>3</sub><sup>-</sup> at lower pH.

## 4.2 Phytoplankton community and nutrient uptake response to the pH gradient

Lowering the pH had a negative impact on the mean concentration of Chl *a*, as well as on the mean abundance of nanophytoplankton during the 9-day experiment (Fig. 5a,b, Table 4). Considering that *Chaetoceros* diatoms accounted for more than 65% of the total abundance of the large phytoplankton ( $> 2 \mu\text{m}$ ) and most of the Chl *a* build-up, these results suggest that net carbon fixation by diatoms was negatively impacted by the decrease in pH, as observed in other studies (Gao and Campbell, 2014, and references therein). Altered seawater carbonate chemistry could perturb the energy requirements of diatom cells, leading to changes in respiration, cell surface and intracellular pH stability (Gao and Campbell, 2014 and reference therein). Such energy re-allocation could force diatoms to assign more energy to repair mechanisms and ion transport to remedy the acid-base perturbation, thus impairing their growth.

The relative uptake of nutrients was also impacted by the  $\text{pH}_T$  treatments in diatoms. The observed linear decrease of the  $\text{Si(OH)}_4$ :  $\text{NO}_3^-$  concentration ratio with increasing proton concentration, which was mostly driven by a reduction in  $\text{Si(OH)}_4$  consumption, either suggests that, at low  $\text{pH}_T$ , diatoms cells were less silicified or that non-diatom phytoplankton made a larger contribution to nutrient drawdown. The former is the most likely explanation since diatom abundance increased in all experimental treatments and numerically dominated the cells community  $> 2\mu\text{m}$  at T5 and T9, irrespective of the  $\text{pH}_T$  level tested. This explanation is also consistent with laboratory studies that previously reported an impairment of  $\text{Si(OH)}_4$  uptake in diatom cultures grown at low pH (Milligan et al., 2004; Hervé et al., 2012; Mejía et al., 2013). In Hervé et al. (2012), the cells exhibited similar growth rates at high and low pH, implying that the negative impact of a low pH on silification does not preclude bloom development in nature.

The picophytoplankton were also impacted by the decrease in  $\text{pH}_T$  (i.e. the augmentation of proton concentration), albeit differently from the nanophytoplankton. As shown in Figure 5c, their mean abundance increased as the proton concentration increased from  $0.1$  to  $2.0 \times 10^{-8} \text{ mol L}^{-1}$  and then tends to stabilise at  $\text{pH}_T$  below 7.6 (see Table 1 for the corresponding proton concentration). In contrast to our study, Richier et al. (2014) reported a negative impact of ocean acidification not only on nanophytoplankton but on picophytoplankton as well during a microcosm experiment using a similar methodology. In this study conducted with water from the northwest European shelf, lowering the pH resulted in a decrease in the abundance (cell number)

and biomass (Chl *a*) of phytoplankton < 10  $\mu\text{m}$ . These contrasting results could reflect differences in the initial picophytoplankton community composition and possible species-specific physiological response to OA. By contrast, a positive influence of a decreasing  $\text{pH}_\text{T}$  on picophytoplankton abundance, and particularly *Micromonas*-like phylotypes, has been previously reported by Hama et al. (2016) for a coastal planktonic community near Japan, as well as by others based on mesocosm experiments (Paulino et al., 2008; Brussaard et al., 2013). This response could be explained by an adjustment of the CCM (Carbon Concentrating mechanism) used by these small cells at low pH. Indeed, picophytoplankton may rely more on  $\text{CO}_2$  diffusion at lower pH than on investing energy in active  $\text{CO}_2$  and  $\text{HCO}_3^-$  uptake (Brussaard et al., 2013). The energy saved that way could translate into higher growth. Moreover, small picophytoplankton species are known to possess less effective CCM than diatoms (Mackey et al., 2015). If the picophytoplankton thriving in our experiment were not saturated with  $\text{CO}_2$  at *in situ* levels, an increase in  $p\text{CO}_2$  could have stimulated photosynthesis and growth of this size group (Brussaard et al., 2013).

In summary, during our experiment, OA stimulated picophytoplankton net growth over the whole range of  $\text{pH}_\text{T}$  investigated while impairing the development of nanophytoplankton, especially at the lowest  $\text{pH}_\text{T}$  tested. This implies that OA will most probably maintain or increase the numerical dominance of picophytoplankton over the nanophytoplankton in the Arctic Ocean (Newbold et al., 2012; Davidson et al., 2016). Tremblay et al. (2012) suggested that climate warming and the associated increase in surface water stratification could also favour the growth of small cells relative to larger diatoms, thus favouring the diminution of primary producers biomass. Our results suggest that OA could accentuate this community response caused by warming and stratification.

#### 4.3 Effect of the pH gradient on dimethylated compounds

During our experiment,  $\text{DMSP}_\text{T}$  and DMS responded differently to decreasing  $\text{pH}_\text{T}$ . While  $\text{DMSP}_\text{T}$  concentrations decreased between  $\text{pH}_\text{T}$  of 8.1 and 7.6 (see Table 1 for corresponding proton concentration values) only under HL conditions, DMS concentrations decreased linearly over the full range of  $\text{pH}_\text{T}$  investigated and under both light regimes (Fig. 8, Table 4).

Although not linear over the full range of  $\text{pH}_T$  investigated, the decrease in  $\text{DMSP}_T$  concentrations measured under HL conditions was, nevertheless, important (50%) over the range of  $\text{pH}_T$  predicted for ocean surface waters by 2100 (8.1 to 7.6, approximately corresponding to proton concentration between  $0.1$  and  $3.0 \times 10^{-8} \text{ mol L}^{-1}$  on Fig. 8a). The mean abundance of nanophytoplankton varied little within this  $\text{pH}_T$  range, while the abundance of picophytoplankton increased (Fig. 5b,c). The pH-induced decrease in  $\text{DMSP}_T$  under HL conditions could thus be related to a decrease in algal cellular DMSP quota. The more ambiguous response of  $\text{DMSP}_T$  to the  $\text{pH}_T$  decrease, compared to DMS, is in line with previous experiments that have also observed similar responses to OA for those two sulfur compounds (Vogt et al., 2008; Hopkins et al., 2010; Archer et al., 2013; Hopkins and Archer, 2014; Webb et al., 2015). Together, these results suggest that ongoing OA will have a stronger impact on the algal and bacterial DMSP transformation into DMS than on the synthesis of DMSP by algae (Vogt et al., 2008; Hopkins et al., 2010; Webb et al. 2016).

As in this study, several OA experiments conducted in mesocosms or with monospecific phytoplankton cultures have revealed a consistent decrease in DMS concentration under the influence of decreasing pH (Avgoustidi et al., 2012; Arnold et al., 2013; see Table 6 for a summary of past meso- and microcosm experiments). The percent decreases observed during our microcosm experiment over the full range of  $\text{pH}_T$  investigated are consistent with the results from other studies that also found decreases ranging from -34 to -82% (Table 6). Keeping in mind the limitations of the experimental protocols, the consistency of the DMS response to pH at different latitudes and with different planktonic assemblages suggests that the potential for DMS net production during the seasonal bloom is likely to decrease in the Arctic during the next centuries. However, it is important to also keep in mind that our short-term experiment precludes any acclimation of the algae to their new environment, something that is likely to take place in response to a more gradual change in pH. In that regard, two studies have highlighted the acclimation capacity/evolutionary adaptation of the strong DMS(P) producer *Emiliana Huxleyi* to decreases in pH (Lohbeck et al., 2012; 2014). More studies are needed to fully assess how the acclimation capacity of phytoplankton will combine with short-term physiological responses to environmental stressors to shape future DMS emissions and climate.



630 Multiple interrelated processes interact in the global ocean to regulate DMS dynamics. Hence, several hypotheses have been proposed to explain the observed attenuation of DMS concentrations at low pH. Whereas some authors suggest a physiological response of phytoplankton under conditions of acidification (Avgoustidi et al., 2012; Hopkins and Archer, 2014), others propose a pH-induced impact on bacterial activity (Archer et al., 2013; Webb et al., 635 2015) or on zooplankton grazing (Kim et al., 2010; Park et al., 2014). In our study, the absence of DMSP and DMS gross rate measurements limits our interpretation of the observed decreasing DMS trend. Results from the few previous studies where gross rate measurements were performed do not show a consistent effect of a decrease in pH on neither DMSP synthesis nor DMS consumption (Archer et al. 2013, Hopkins and Archer 2014). Despite the unavailability of 640 rate measurements in our study, the dominance of diatoms, an algal group lacking DMSP lyase enzymes, suggests that bacteria may have played a critical role in the observed DMS dynamics. Low pH conditions have been reported to stimulate the productivity, and hence the carbon demand, of bacteria (Maas et al., 2013; Piontek et al., 2013; Endres et al., 2014). This increase in bacterial productivity could in turn have resulted in an increase in sulfur demand leading to a 645 decrease in bacterial DMS yield (% of the DMSP taken up by the bacteria and cleaved into DMS). This interpretation is supported by the linear decrease in the DMS:DMSP<sub>d</sub> ratio observed over the full range of pH<sub>T</sub> investigated (Fig. 8c, Table 4), which suggests that at lower pH bacteria increasingly favoured the demethylation over the cleavage pathways of DMSP degradation. Although the decrease of this ratio could also result from an increase in 650 microzooplankton grazing on diatoms (Jones et al., 1998), we found no significant relationship between the micrograzers and phytoplankton, pH or DMS. Archer et al. (2013) also proposed that the pH-induced decrease in DMS observed during their experiments could partly be explained by a decrease in bacterial DMS yield related to the increase in phytoplankton biomass and net primary production at lower pH, as well as the associated increase in bacterial protein production 655 and sulfur demand. In contrast with their observations, however, phytoplankton biomass did not increase but decreased with pH<sub>T</sub> during our study. Nevertheless, this does not preclude the possibility of an increase in dissolved organic carbon (DOC) release by phytoplankton at low pH as previously reported (Riebesell et al., 2013). Whether the productivity and sulfur demand of DMS-consuming bacteria are also stimulated at low pH is unknown. If so, they may also have 660 contributed to the pH-induced decrease in DMS reported here and in other studies.

Finally, it is unlikely that grazing played a major role in the pH-associated reduction in DMS concentrations we observed. Although removing large grazers before the incubation may have affected the relative importance of microzooplankton grazing on phytoplankton during our experiment, no relationships between protist abundance and  $H^+$  or DMS were found.

Modifications in micrograzing activity at low pH have been reported to either stimulate (Kim et al., 2010) or decrease net DMS production (Park et al., 2014). Park et al. (2014) attributed the reduction in grazing to a pH-induced shift in the phytoplankton species composition, with larger diatoms outcompeting smaller DMSP-rich dinoflagellates in acidified treatments, resulting in a weaker grazing pressure on the small DMSP-rich phytoplankton species and therefore less release of DMSP and DMS. In our study, small DMSP-rich producers were not abundant and diatoms dominated the community biomass over the full range of  $pH_T$  investigated. It is important to note that dinophyceae did not survive in our incubation bags, so no conclusion can be drawn as to how they could have responded to a decrease in pH and influenced DMS net production.

#### 4.4 Response to the contrasting light regimes

The two experimental light treatments applied in this study had no significant effects on the temporal evolution, magnitude and taxonomic composition of the phytoplankton bloom (Table 3). These results show that both nanophytoplankton and picophytoplankton achieved optimal growth in the range of PAR used in our treatments. During a laboratory experiment, Gilstad and Sakshaug (1990) found that 10 Arctic diatom species exhibited negligible variations in growth rate at PAR levels ranging from 50 to 500  $\mu\text{mol quanta m}^{-2}\text{s}^{-1}$ , while their growth rate increased linearly with increased PAR from 0 to 50  $\mu\text{mol quanta m}^{-2}\text{s}^{-1}$ . During our experiment, PAR ranged from 61 to 402  $\mu\text{mol quanta m}^{-2}\text{s}^{-1}$  (Table 2), and these values fall within the tolerance range reported by Gilstad and Sakshaug (1990). Moreover, the phytoplankton community in our incubation was initially taken at 38 m depth where PAR irradiance was as low as 7  $\mu\text{mol quanta m}^{-2}\text{s}^{-1}$ . Thus, diatoms in our experience were already very well adapted for growing at very low light levels. As they were then capable of growing as efficiently in both the HL and LL treatment, we could assess that diatoms during our experiment were capable of adapting themselves to higher irradiances very quickly. This is supported by the high and similar  $F_v/F_m$  ratios recorded during the growth phase in both light treatments (Table 5), suggesting that photosynthesis was

equally efficient at HL and LL exposure. These results suggest that phytoplankton exiting the ice pack would not necessarily experience a light shock as severe as previously noted by others (Vance et al., 2013, Galindo et al., 2016).

Among the biological variables measured, only bacteria showed a significant response to the different light treatments, with higher abundances at LL than at HL exposure (Table 3, Fig. 5d). This may reflect the known sensitivity of bacteria to UVB radiation (Herndl et al., 1993), which was absent in our LL treatment.

We found no difference in the DMSP and DMS concentrations between the two light regimes tested, as the DMSP<sub>T</sub> and DMS variations were very similar under both LL and HL conditions (Table 3). This result was unexpected considering that several processes associated with the DMS cycle are either directly (e.g., DMS photo-oxidation) or indirectly (e.g., DMS bacterial production under high UV-R) light-sensitive (Sunda et al., 2002; Slezak et al., 2007; Galí et al., 2011). Previous studies demonstrated a strong positive correlation between the solar radiation dose (SRD) received by the plankton community in the upper mixed layer and the DMS concentrations measured in surface waters (Toole et al., 2004; Vallina and Simó, 2007). Hence, our working hypothesis was that light conditions under the ice pack (low PAR and quasi-absence of UV-R) would result in lower DMS concentrations than under open water light conditions (high PAR and high UV-R). The absence of such light response may suggest that our LL treatment, as it was already light saturating for diatoms, was not different enough from our HL treatment to trigger a different photo-induced response of diatoms. Hence, the differences in PAR and UV radiation between a 5 m mixed layer depth in ice-free water and under ponded first-year ice (or a subsurface chlorophyll layer) in summer may not be sufficient to significantly affect the net production of DMSP and DMS.

## 5 Conclusion

During this study, we demonstrated that a rapid decrease in surface water pH could negatively impact the net production of algal biomass as well as DMS concentrations in Baffin Bay waters. Irrespective of the treatment, a nanophytoplankton (diatoms mostly) and picophytoplankton bloom developed within 5 to 7 days in each of our microcosms. The growth of picophytoplankton was stimulated at low pH<sub>T</sub>, whereas the diatoms, which dominated the algal community in term

of biomass at all  $\text{pH}_T$  levels investigated, had their abundance negatively affected by the acidification, especially at the lowest  $\text{pH}_T$  level tested when compared to the controls. These results show that OA can potentially affect the magnitude of diatoms biomass in Arctic waters and enhance the already observed shift towards smaller autotrophic cells due to increased stratification (Li et al., 2009; Tremblay et al., 2012), although our results do not account for the acclimation/evolutionary adaptation potential of natural microbial communities.

Concurrent with the response of phytoplankton to OA, the DMS dynamics were strongly affected by decreasing the  $\text{pH}_T$ , with a 80% reduction in average DMS concentrations between the control and the lowest  $\text{pH}_T$  investigated (from  $\text{pH}_T$  8.1 to 7.2). This result adds to conclusions found in 70% of published studies that have focused on pH-DMS dynamics and showed a decrease in DMS concentrations as pH decreases. In contrast, the pH-induced decrease in  $\text{DMSP}_T$  concentration was less pronounced, as it only decreased under the HL treatment at relatively high  $\text{pH}_T$  (8.1 to 7.6). The synthesis of DMSP by unicellular algae appears to be less sensitive to OA than processes responsible for its conversion into DMS, as previously hypothesized by other authors (Vogt et al., 2008; Hopkins et al., 2010; Webb et al., 2016). The lack of rate measurements during our study precludes a definitive explanation for this trend, but a decrease in bacterial DMS yield seems to be the most probable candidate.

Our data highlighted a remarkable similarity in responses of the phytoplankton community and DMS-related processes to experimental variations in light (LL versus HL treatment). Indeed, neither the phytoplankton community nor the dimethylated sulfur compounds exhibited significantly different signatures between the two light treatments, which were designed to simulate contrasting light conditions, experienced by a marginal ice blooms (ice-free surface mixed layer) versus under-ice blooms (irradiance under a melting pondered ice pack) or subsurface chlorophyll maxima. Although further studies are needed to fully assess the importance of light in the context of climate change in the Arctic, our results show that Arctic diatoms may bloom under light conditions much lower than the one tested here. This apparent capacity of Arctic diatoms to grow under extremely low light conditions should be explored in future studies. As short-term impacts of OA on the DMS cycle become clearer, future studies should focus on assessing the potential susceptibility and adaptive mechanisms of microbial DMS(P) producers, processes that likely develop on a time scale closer to the natural OA rate.

**Acknowledgements.** The authors wish to thank commander Alain Gariépy, the officers, and crew of the Canadian ice-breaker NGCC Amundsen for their support during the project. We also want to thank Glenn Cooper and Kyle Simpson of the Institute of Ocean Sciences in Sidney, BC, for providing advice and the material and equipment needed for pH measurements; Isabelle Courchesne and Gabrièle Deslongchamps for the nutrients analysis, Marjolaine Blais for the flow cytometry analyses; and Jean-Bruno Nadalini for the taxonomic analyses. This study was funded by the NSERC Discovery Grant Program and Northern Research Supplement Program (M. Levasseur, M. Gosselin), as well as by the NETCARE network (funded under the NSERC Climate Change and Atmospheric Research program), ArcticNet (The Network of Centres of Excellence of Canada), and Fisheries and Oceans Canada. This is a contribution to the research programs of NETCARE, ArcticNet and Québec-Océan.

**Authors' contribution:** R. Husherr was responsible of the elaboration of the experimental design, the sampling process, the data analysis and processing and the redaction of this manuscript. Several co-authors provided specific data included in the manuscript and all co-authors contributed to the final edition of the paper.

The authors declare that they have no conflict of interest.

## References

- ACIA: Arctic Climate Impact Assessment, Cambridge University Press, Cambridge, 1042 pp, 2005.
- Andrea, M.O.: The ocean as a source of atmospheric sulfur compounds, in Buat-Menard, P. (Ed.), The Role of Sea-Air Exchange in Geochemical Cycling, Reidel, Dordrecht, 331-362, doi: 10.1007/978-94-009-4738-2\_14, 1986.
- 775 Archer, S.D., Kimmance, S.A., Stephens, J.A., Hopkins, F.E., Bellerby, R.G.J., Schulz, K.G., Piontek, J., and Engel, A.: Contrasting responses of DMS and DMSP to ocean acidification in Arctic waters, Biogeosciences, 10, 1893-1908, doi: 10.5194/bg-10-1893-2013, 2013.
- Arnold, H.E., Kerrison P., Steinke, M.: Interacting effects of ocean acidification and warming on growth and DMS-production in the haptophyte coccolithophore *Emiliania huxleyi*, Glob. Change Biol., 19, 1007-1016, doi: 10.1111/gcb.12105, 2013.
- 780 Asher, E.C., Dacey J.W.H., Jarniková, T., and Tortell, P.D.: Measurement of DMS, DMSO, and DMSP in natural waters by automated sequential chemical analysis, Limnol. Oceanogr.-Meth., 13, 451-462, doi: 10.1002/lom3.10039, 2015.
- 785 Avgoustidi, V., Nightingale, P.D., Joint, I., Steinke, M., Turner, S.M., Hopkins, F.E., and Liss, P.S.: Decreased marine dimethyl sulfide production under elevated CO<sub>2</sub> levels in mesocosm and in vitro studies. Environ. Chem., 9, 399-404, doi: 10.1017/EN11125, 2012.
- Belzile, C., Johannessen, S.C., Gosselin, M., Demers, S., and Miller, W.L.: Ultraviolet attenuation by dissolved and particulate constituents of first-year ice during late spring in an Arctic polynya, Limnol. Oceanogr., 45(6), 1265-1273, doi: 10.4319/lo.2000.45.6.1265, 2000.
- 790 Brussaard, C.P.D., Noordeloos, A.A.M., Witte, H., Collenteur, M.C.J., Schluz, K., Ludwig, A., and Riebesell, U.: Arctic microbial community dynamics influenced by elevated CO<sub>2</sub> levels, Biogeosciences, 10, 719-731, doi: 10.5194/bg-10-719-2013, 2013.
- Bucciarelli, E., and Sunda, W.G.: Influence of CO<sub>2</sub>, nitrate, phosphate, and silicate limitation on intracellular dimethylsulfoniopropionate in batch cultures of the coastal diatom *Thalassiosira pseudonana*, Limnol. Oceanogr., 48(6), 2256-2265, doi: 10.4319/lo.2003.48.6.2256, 2003.
- 795 Caldeira, K., and Wickett, M.E.: Anthropogenic carbon and ocean pH, Nature, 425, 365, doi: 10.1038/425365a, 2003.
- Clayton, T.D., and Byrne, R.H.: Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, Deep-Sea Res. I, 40 (10), 2115-2129, doi: 10.1016/0967-0637(93)90048-8, 1993.
- 800 Cohen, J., Screen, J.A., Furtado, J.C., Barlow, M., Whittleston, D., Coumou, D., Francis, J., Dethloff, K., Entkhabi, D., Overland, J., and Jones, J.: Recent Arctic amplification and extreme mid-latitude weather, Nat. Geosci., 7, 627-637, doi: 10.1038/NGEO2234, 2014.

- 805 Cottingham, K.L., Lennon, J.T., and Brown, B.L.: Knowing when to draw the line: designing more  
informative ecological experiments, *Front. Ecol. Environ.*, 3(3), 145-152, doi: 10.1890/1540-  
9295(2005)003[0145:KWTDTL]2.0.CO;2, 2005.
- Davidson, A.T., McKinlay, J., Westwood, K., Thomson, P.G., van den Enden, R., de Salas, M., Wright,  
S., Johnson, R., and Berry, K.: Enhanced CO<sub>2</sub> concentrations change the structure of Antarctic  
810 marine microbial communities, *Marine Ecol.-Prog. Ser.*, 552, 93-113, doi: 10.3354/meps11742,  
2016.
- Demers, S., Belzile, C., Lean, D.R.S, Mostajir, B., Roy, S., de Mora, S., Bird, D., Gosselin, M., Chanut,  
J.-P., and Levasseur, M.: An experimental tool to study the effects of ultraviolet radiation on  
planktonic communities: a mesocosm approach, *Environ. Tech.*, 19, 667-682, doi:  
815 10.1080/09593331908616723, 1998.
- Dickson, A.G.: Standard potential of the reaction: AgCl(s) + H<sub>2</sub> (g) = Ag(s) + HCl(aq), and the standard  
acidity constant of the ion HSO<sub>4</sub><sup>-</sup> in synthetic sea water from 273.15 to 318.15 K, *J. Chem.*  
*Thermodyn.*, 22, 113–127, doi: 10.1016/0021-9614(90)90074-z, 1990.
- Dickson, A.G., Sabine, C.L., and Christian, J.R.: Guide to best practices for ocean CO<sub>2</sub> measurements,  
820 PICES Special publication, 3, 191 pp, 2007.
- Dickson, D.M.G., Wyn Jones, R.G., and Davenport, J.: Steady state osmotic adaptation in *Ulva lactuca*,  
*Planta*, 150, 158-165, doi: 10.1007/BF00582360, 1980.
- Doney, S.C., Balch, W.M., Fabry, V.J., and Feely, R.A.: Ocean acidification, a critical emerging problem  
for the ocean sciences, *Oceanography*, 22(4), 16-25, 10.5670/oceanog.2009.93, 2009.
- 825 Endres, S., Galgani, L., Riebesell, U., Schulz, K.-G., and Engel, A.: Stimulated bacterial growth under  
elevated pCO<sub>2</sub>: results from an off-shore mesocosm study, *PLoS ONE*, 9(6), e99228, doi:  
10.1371/journal.pone.0099228, 2014.
- Fabry, V.J., Macclintock, J.B., Mathis, J.T., and Grebmeier, J.M.: Ocean acidification at high latitudes: the  
bellwether, *Oceanography*, 22(4), 160-171, doi: 10.5670/oceanog.2009.105, 2009.
- 830 Feely, R.A., Doney, S.C., and Cooley, S.R.: Ocean acidification, present conditions and future changes in  
a high-CO<sub>2</sub> world, *Oceanography*, 22(4), 36-47, doi: 10.5670/oceanog.2009.95, 2009.
- Ferek, R.J., Hobbs, P.V., Radke, L.F., Herring, J.A., Sturges, W.T., and Cota, F.C.: Dimethyl sulphide in  
the arctic atmosphere, *J. Geophys. Res.*, 100 (D12), 26093-26104, doi: 10.1029/95JD02374, 1995.
- Ford, J.D., McDowell, G., and Pearce, T.: The adaptation challenge in the Arctic, *Nat. Clim. Change*, 5,  
835 1046-1053, doi: 10.1038/ncimate2723, 2015.
- Frey, K.E., Perovich, D.K., and Light, B.: The spatial distribution of solar radiation under a melting Arctic  
sea ice cover, *Geophys. Res. Lett.*, 38, L22501, doi: 10.1029/2011GL049421, 2011.

- Galí, M., Saló, V., Almeda, R., Calbet, A., and Simó, R.: Stimulation of gross dimethylsulfide (DMS) production by solar radiation, *Geophys. Res. Lett.*, 38, L15612, doi: 10.1029/2011GL048051, 2011.
- Galindo, V., Levasseur, M., Mundy, C.J., Gosselin, M., Scaratt, M., Papakyriakou, T., Stefels, J., Gale, M.A., Tremblay, J.-E., and Lizotte M.: Contrasted sensitivity of DMSP production to high light exposure in two Arctic under-ice blooms, *J. Exp. Mar. Biol. Ecol.*, 475, 38-48, doi: 10.1016/j.jembe.2015.11.009, 2016.
- Gao, K., and Campbell, D.A.: Photophysiological responses of marine diatoms to elevated CO<sub>2</sub> and decreased pH: a review, *Funct. Plant Biol.*, 41, 449-459, doi: 10.1071/FP13247, 2014.
- Gilstad, M., Saksaug, E.: Growth rates of ten diatom species from the Barents Sea at different irradiances and day lengths, *Mar Ecol-Prog. Ser.*, 64, 169-173, 1990.
- Hama, T., Inoue, T., Suzuki, R., Kashiwazaki, H., Wada, S., Sasano, D., Kosugi, N., and Ishii, M.: Response of a phytoplankton community to nutrient addition under different CO<sub>2</sub> and pH conditions, *J. Oceanogr.*, 72, 207-223, doi: 10.1007/s10872-015-0322-4, 2016.
- Hansen, H.P., and Koroleff, F.: Determination of nutrients, in Grasshoff, K., Kremling, K., Ehrhardt, M. (Eds.), *Methods of seawater analysis*, Wiley-VCH, Weinheim, 159-228, doi: 10.1002/9783527613984, 2007.
- Havenhand, J., Dupont, S., and Quinn, G.P.: Designing ocean acidification experiments to maximise inference, in: Riebesell, U., Fabry, V.J., Gattuso, J.-P. (Eds.). *Guide to Best Practices in Ocean Acidification Research and Data Reporting*. Publications Office of the European Union, Luxembourg, 67-80, 2010.
- Heimdal, B.R.: Arctic Ocean Phytoplankton, in Herman Y. (Ed.), *The Arctic Seas. Climatology, Oceanography, Geology, and Biology*, Van Nostrand Reinhold Company, New-York, 193-222, 1989.
- Herndl, G.J., Müller-Niklas, G., and Frick, J.: Major role of ultraviolet-B in controlling bacterioplankton growth in the surface layer of the ocean, *Nature*, 361, 717-719, doi: 10.1038/361717a0, 1993.
- Hervé, V., Derr, J., Douady, S., Quinet, M., Moisan, L., and Lopez, P.J.: Multiparametric analyses reveal the pH-dependence of silicon biomineralization in diatoms, *PLoS ONE*, 7(10), e46722, doi: 10.1371/journal.pone.0046722, 2012.
- Holm-Hansen, O., Lorenzen, C.J., Holmes, R.W., and Strickland, J.D.H.: Fluorometric determination of chlorophyll, *Journal du Conseil International pour l'Exploration de la Mer*, 30, 3-15, doi: 10.1093/icesjms/30.1.3, 1965.
- Hopkins, F.E., Turner, S.M., Nightingale P.D., Steinke, M., Bakker, D., and Liss P.S.: Ocean acidification and marine trace gas emissions, *P. Natl. Acad. Sci. USA*, 107(2), 760-765, doi: 10.1073/pnas.0907163107, 2010.



- 875 Hopkins, F.E., Archer, S.D.: Consistent increase in dimethyl sulphide (DMS) in response to high CO<sub>2</sub> in five shipboard bioassays from contrasting NW European waters, *Biogeosciences*, 11, 4925-4940, doi: 10.5194/bg-11-4925-2014, 2014.
- Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K., and Wong, C.S.: Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector, *Mar. Chem.*, 44, 167-187, doi: 10.1016/0304-4203(93)90201-X, 1993.
- 880 Jones, G.B., Curran, M.A.J., Swan, H.B., Greene, R.M., Griffiths, F.B., and Clementson, L.A.: Influence of different water masses and biological activity on dimethylsulphide and dimethylsulphonioacetate in the subantarctic zone of the Southern Ocean during ACE 1, *J. Geophys. Res.*, 103(D13), 16691-16701, doi: 10.1029/98JD01200, 1998.
- 885 Keller, M.D., Bellows, W.K., and Guillard R.R.L.: Dimethyl sulfide production in marine phytoplankton, in Saltzman, E. and al. ACS symposium series (Ed.), *Biogenic sulfur in the environment*, American Chemical Society, Washington DC, 167-182, 1989.
- Keller, M.D., Kiene, R.P., Matrai, P.A., and Bellows, W.K.: Production of glycine betaine and dimethylsulfonylacetate in marine phytoplankton. II. N-limited chemostat cultures, *Mar. Biol.*, 135, 249-257, doi: 10.1007/s002270050622, 1999
- 890 Kettle, A.J., and Andreae, M.O.: Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models, *J. Geophys. Res.*, 105(D22), 26793-26808, doi: 10.1029/2000JD900252, 2000.
- Kiene, R.P., Linn, L.J., and Bruton, J.A.: The fate of dissolved dimethylsulfonylacetate (DMSP) in seawater: tracer studies using S-35-DMSP, *Geochim. Cosmochim. Acta.*, 64(16), 2797-2810, doi: 10.1016/S0016-7037(00)00399-9, 2000.
- 895 Kiene, R.P., and Slezak, D.: Low dissolved DMSP concentrations in seawater revealed by small-volume gravity filtration and dialysis sampling, *Limnol. Oceanogr.-Meth.*, 4, 80-85, doi: 10.4319/lom.2006.4.80, 2006.
- 900 Kim, J.-M., Lee, K., Yang, E.J., Shin, K., Noh, J.H., Park, K.-T., Hyun, B., Jeong, H.-J., Kim, J.-H., Kim, K.Y., Kim, M., Kim, H.-C., Jang, P.-G., and Jang, M.-C.: Enhanced production of oceanic dimethylsulfide resulting from CO<sub>2</sub>-induced grazing activity in a high CO<sub>2</sub> world, *Environ. Sci. Tech.*, 44(21), 8140-8143, doi: 10.1021/es102028k, 2010.
- 905 Kirst, G.O., Thiel, C., Wolff, H., Nothnagel, J., Wanzek, M., and Ulmke, R.: Dimethylsulfonylacetate (DMSP) in ice-algae and its possible biological role, *Mar. Chem.*, 35, 381-388, doi: 10.1016/S0304-4203(09)90030-5, 1991.
- Kirst, G.O.: Osmotic adjustment in phytoplankton and macroalgae: the use of dimethylsulfonylacetate (DMSP), in Kiene, R.P., Visscher, P., Keller, M., Kirst, G.O. (Eds.), *Biological and Environ. Chem. of DMSP and related compounds*, Plenum, New-York, 121-129, 1996.

- 910 Kolber, Z., Prášil, O., and Falkowski, P.G.: Measurements of variable chlorophyll fluorescence using fast repetition rate techniques: defining methodology and experimental protocols, *Biochim. Biophys. Acta*, 1367, 88-106, doi: 10.1016/S0005-2728(98)00135-2, 1998.
- Li, W.K.W., McLaughlin, F.A., Lovejoy, C., and Carmack, E.C.: Smallest algae thrive as the Arctic Ocean freshens, *Science*, 326, 539, doi: 10.1126/science.1179798, 2009.
- 915 Lizotte, M., Levasseur, M., Michaud, S., Scarratt, M.G., Merzouk, A., Gosselin, M., Pommier, J., Rivkin, R.B., and Kiene, R.P.: Macroscale patterns of the biological cycling of dimethylsulfonopropionate (DMSP) and dimethylsulfide (DMS) in the Northwest Atlantic, *Biogeochemistry*, 110, 183-200, doi: 10.1007/s10533-011-9698-4, 2012.
- Lohbeck, K.T., Riebesell, U., and Reusch, T.B.H.: Adaptive evolution of a key phytoplankton species to ocean acidification, *Nat. Geosci.*, 5, 346-351, doi: 10.1038/ngeo1441, 2012.
- 920 Lohbeck, K.T., Riebesell, U., and Reusch, T.B.H.: Gene expression changes in the coccolithophore *Emiliana Huxleyi* after 500 generations of selection to ocean acidification, *Proc. R. Soc. B.*, 281, 20140003, doi: 10.1098/rspb.2014.0003, 2014.
- Lovejoy, C., Vincent, W.F., Bonilla, S., Roy, S., Martineau, M.-J., Terrado, R., Potvin, M., Massana, R., and Pedrós-Alió, C.: Distribution, phylogeny, and growth of cold-adapted picoprasinophytes in arctic seas, *J. Phycol.*, 43(1), 78-89, doi: 10.1111/j.1529-8817.2006.00310.x, 2007.
- 925 Lueker, T.J., Dickson, A.G., and Keeling, C.D.: Ocean  $p\text{CO}_2$  calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of  $\text{CO}_2$  in gas and seawater at equilibrium, *Mar. Chem.*, 70, 105-119, doi: 10.1016/s0304-4203(00)00022-0, 2000.
- 930 Lund, J.W.G., Kipling, C., and Le Cren, E.D.: The inverted microscope method of estimating algal number and the statistical basis of estimations by counting, *Hydrobiologia*, 11, 143-170, doi: 10.1007/BF00007865, 1958.
- Maas, E.W., Law, C.S., Hall, J.A., Pickmere, S., Currie, K.I., Chang, F.H., Voyles, K.M., and Caird, D.: Effect of ocean acidification on bacterial abundance, activity and diversity in the Ross Sea, Antarctica, *Aquat. Microb. Ecol.*, 70, 1-15, doi: 10.3354/ame01663, 2013.
- 935 Macdonald, R.W., Kuzyk, Z.A., and Johannessen, S.C.: It is not just about the ice: a geochemical perspective on the changing Arctic Ocean, *Journal of Environmental Studies and Sciences*, 5(3), 288-301, doi: 10.1007/s13412-015-0302-4, 2015.
- Mackey, K.R.M., Morris, J.J., Morel, F.M.M., and Kranz, S.A.: Response of photosynthesis to ocean acidification, *Oceanography*, 28(2), 74-91, doi: 10.5670/oceanog.2015.33, 2015.
- 940 Matrai, P.A., and Vernet, M.: Dynamics of the vernal bloom in the marginal ice zone of the Barents Sea: Dimethyl sulfide and dimethylsulfoniopropionate budgets, *J. Geophys. Res.*, 102(C10), 22965-22979, doi: 10.1029/96JC03870, 1997.

- 945 Marie, D., Brussaard, C.P.D., Thyrraug R., Bratbak, G., and Vaultot, D.: Enumeration of marine viruses in culture and natural samples by flow cytometry, *Appl. Environ. Microb.*, 65(1), 45-52, 1999.
- Marie, D., Simon, N., and Vaultot, D.: Phytoplankton cell counting by flow cytometry, in: Andersen, R.A. (Ed.), *Algal Culturing Techniques*, Elsevier Academic Press, Burlington, MA, 253–268, 2005.
- 950 Martin, J., Tremblay, J.-É., Gagnon, J., Tremblay, G., Lapoussière, A., Jose, C., Poulin, M., Gosselin, M., Gratton, Y., and Michel, C.: Prevalence, structure and properties of subsurface chlorophyll maxima in Canadian Arctic waters, *Mar. Ecol.-Prog. Ser.*, 412, 69-84, doi: 10.3354/meps08666, 2010.
- Martin, J., Dumont, D., and Tremblay, J.-É.: Contribution of subsurface chlorophyll maxima to primary production in the coastal Beaufort Sea (Canadian Arctic): A model assessment, *J. Geophys. Res.-Oceans*, 118, 5873-5886, doi: 10.1002/2013JC008843, 2013
- 955 Maxwell, K., and Johnson, G.N.: Chlorophyll fluorescence- a practical guide, *J. Exp. Bot.*, 51(345), 659-668, doi: 10.1093/jexbot/51.345.659, 2000.
- Mejía, L.M., Isensee, K., Méndez-Vicente, A., Pisonero, J., Shimizu, N., González, C., Monteleone, B., and Stoll, H.: B content and Si/C ratios from cultured diatoms (*Thalassiosira pseudonana* and *Thalassiosira weissflogii*): relationship to seawater pH and diatom carbon acquisition, *Geochim. Cosmochim. Ac.*, 123, 322-337, doi: 10.1016/j.gca.2013.06.011, 2013.
- 960 Milligan, A.J., Varela, D.E., Brzezinski, M.A., and Morel, F.M.M.: Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of  $p\text{CO}_2$ , *Limnol. Oceanogr.*, 49(2), 322-329, doi: 10.4319/lo.2004.49.2.0322, 2004.
- 965 Mungall, E.L., Croft, B., Lizotte, M., Thomas, J.L., Murphy, J.G., Levasseur, M., Martin, R.V., Wentzell, J.J.B., Liggio, J., and Abatt, J.P.D.: Dimethyl sulphide in the summertime Arctic atmosphere: measurements and source sensitivity simulations, *Atmos. Chem. Phys.*, 16, 6665-6680, doi: 10.5194/acp-16-6665-2016, 2016.
- 970 Newbold, L.K., Olivier, A.E., Booth, T., Tiwari, B., DeSantis, T., Maguire, M., Andersen, G., van der Gast, C.J., and Whiteley, A.S.: The response of marine picoplankton to ocean acidification, *Environ. Microbiol.*, 14(9), 2293-2307, doi: 10.1111/j.1462-2920.2012.02762.x, 2012.
- Palmer, M.A., Saenz, B.T., and Arrigo, K.R.: Impacts of sea ice retreat, thinning, and melt-pond proliferation on the summer phytoplankton bloom in the Chukchi Sea, Arctic Ocean, *Deep-Sea Res. II*, 105, 85-104, doi: 10.1016/j.dsr.2.2014.03.016, 2014.
- 975 Park, K.-T., Lee, K., Shin, K., Yang, E.J., Hyun B., Kim, J.-M., Noh, J.H., Kim, M., Kong, B., Choi, D.H., Choi, S.-J., Jang, P.-G., and Jeong, H.J.: Direct linkage between Dimethyl Sulfide Production and Microzooplankton Grazing, Resulting from Prey Composition Change under High Partial Pressure of Carbon Dioxide Conditions, *Environ. Sci. Tech.*, 48, 4750-4756, doi: 10.1021/es403351h, 2014.

- 980 Parsons, T.R., Maita, Y., and Lalli, C.M.: A Manual of Chemical and Biological Methods for Seawater Analysis, Pergamon, New York, 1984.
- Paul, C., Sommer, U., Garzke, J., Moustaka-Gouni, M., Paul, A., and Matthiessen, B.: Effects of increased CO<sub>2</sub> concentration on nutrient limited coastal summer plankton depend on temperature, *Limnol. Oceanogr.*, 61, 853-868, doi: 10.1002/lno.10256, 2016.
- 985 Paulino, A.I., Egge, J.K., and Larsen, A.: Effects of increased atmospheric CO<sub>2</sub> on small and intermediate sized osmotrophs during a nutrient induced phytoplankton bloom, *Biogeosciences*, 5, 739–748, doi: 10.5194/bg-5-739-2008, 2008.
- Perovich, D.K., Roesler, C.S., and Pegau, W.S.: Variability in Arctic sea ice optical properties, *J. Geophys. Res.*, 103(C1), 1193-1208, doi: 10.1029/97JC01614, 1998.
- 990 Pierrot, D.E., Lewis, E., and Wallace, D.W.R.: MS Excel program developed for CO<sub>2</sub> system calculations, Carbon Dioxide Information Analysis Center, ONRL/CDIAC-105a, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 2006.
- Piontek, J., Borchard, C., Sperling, M., Schulz, K.G., Riebesell, U., and Engel A.: Response of bacterioplankton activity in an Arctic fjord system to elevated *p*CO<sub>2</sub>: results from a mesocosm perturbation study, *Biogeosciences*, 10, 297-314, doi: 10.5194/bg-10-297-2013, 2013.
- 995 Poulin, M., Daugbjerg, N., Gradinger, R., Ilyash, L., Ratkova, T., and von Quillfeldt, C.: The pan-Arctic biodiversity of marine pelagic and sea-ice unicellular eukaryotes: a first-attempt assessment, *Marine Biodiversity*, 41, 13-28, doi: 10.1007/s12526-010-0058-8, 2011.
- 1000 Quinn, P.K., Miller, T.L., Bates, T.S., Ogren, J.A., Andrews, E., and Shaw, G.E.: A 3-year record of simultaneously measured aerosol chemical and optical properties at Barrow, Alaska, *J. Geophys. Res.*, 170 (D11), 4130, doi: 10.1029/2001JD001248, 2002.
- Raven, J.R., Caldeira, K., Elderfield, H., Hoegh-Guldberg, O., Liss, P.S., Riebesell, U., Shepherd, J., Turley, C., and Watson, A.: Ocean acidification due to increasing atmospheric carbon dioxide, The Royal Society Policy document 12/05, 2005.
- 1005 Richier, S., Achterberg, E.P., Dumousseaud, C., Poulton, A.J., Suggett, D.J., Tyrell, T., Zubkov, M.V., and Moore, C.M.: Phytoplankton responses and associated carbon cycling during shipboard carbonate chemistry manipulation experiments conducted around Northwest European shelf seas, *Biogeosciences*, 11, 4733-4752, doi: 10.5194/bg-11-4733-2014, 2014
- Riebesell, U., Fabry, V.J., Hansson, L., and Gattuso, J.-P. (Eds.): Guide to best practices for ocean acidification research and data reporting, European commission, Belgium, 2010.
- 1010 Riebesell, U., Gattuso, J.-P., Thingstad, T.F., and Middelburg, J.J.: Preface “Arctic ocean acidification: pelagic ecosystem and biogeochemical responses during a mesocosm study”, *Biogeosciences*, 10, 5619-5626, doi: 10.5194/bg-10-5619-2013, 2013.

- Riley, G.A.: Phytoplankton of the North Central Sargasso Sea 1950-52, *Limnol. Oceanogr.*, 2, 252-270, doi: 10.1002/lno.1957.2.3.0252, 1957.
- 1015 Rost, B., Zondervan, D., and Wolf-Gladrow, D.: Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: Current knowledge, contradictions and research directions, *Mar. Ecol.-Prog. Ser.*, 373, 227–237, doi:10.3354/meps07776, 2008.
- Roux, R., Gosselin, M., Desrosiers, G., and Nozais, C.: Effects of reduced UV radiation on a microbenthic community during a microcosm experiment, *Mar. Ecol.-Prog. Ser.*, 229, 29-43, doi: 10.3354/meps225029, 2002.
- 1020 Scarratt, M.G., Levasseur, M., Schultes, S., Michaud, S., Cantin, G., Vézina, A., Gosselin, M., and de Mora, S.J.: Production and consumption of dimethylsulfide (DMS) in North Atlantic waters, *Mar. Ecol.-Prog. Ser.*, 204, 13-26, doi: 10.3354/meps204013, 2000.
- Schuback, N., Schallenberg, C., Duckham, C., Maldonado, M.T., and Tortell, P.D.: Interacting effects of light and iron availability on the coupling of photosynthetic electron transport and CO<sub>2</sub> assimilation in marine phytoplankton, *PLoS ONE*, 10, e0133235, doi: 10.1371/journal.pone.0133235, 2015.
- 1025 Schuback, N., Flecken, M., Maldonado, M.T., and Tortell, P.D.: Diurnal variation in the coupling of photosynthetic electron transport and carbon fixation in iron-limited phytoplankton in the NE subarctic Pacific, *Biogeosciences*, 13, 1019-1035, doi: 10.5194/bg-13-1019-2016, 2016.
- 1030 Schulz, K.G., Bellerby, R.G.J., Brussaard, C.P.D., Büdenbender, J., Czerny, J., Fischer, M., Koch-Klavnsen, S., Krug, S.A., Lischka, S., Ludwig, A., Meyerhöfer, M., Nondal, G., Silyakova, A., Stühr, A., and Riebesell, U.: Temporal biomass dynamics of an Arctic plankton bloom in response to increasing levels of atmospheric carbon dioxide, *Biogeosciences*, 10, 161-180, doi: 10.5194/bg-10-161-2013, 2013.
- 1035 Slezak, D., Kiene, R.P., Toole, D.A., Simó, R., and Kieber, D.: Effects of solar radiation on the fate of dissolved DMSP and conversion to DMS in seawater, *Aquat. Sci.*, 69, 377-393, doi: 10.1007/s00027-007-0896-z, 2007.
- Stefels, J.: Physiological aspects of the production and conversion of DMSP in marine algae and higher plants, *J. Sea Res.*, 43, 183-197, doi: 10.1016/S1385-1101(00)00030-7, 2000.
- 1040 Stefels, J., Steinke, M., Turner, S., Malin, G., and Belviso, S.: Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling, *Biogeochemistry*, 83, 245-275, doi: 10.1007/978-1-4020-6214-8\_18, 2007.
- 1045 Steinacher, M., Joos, F., Frölicher, T.L., Plattner, G.-K., and Doney, S.C.: Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model, *Biogeosciences*, 6, 515-533, doi: 10.5194/bg-6-515-2009, 2009.

- Sunda, W., Kieber, D.J., Kiene, R.P., and Huntsman, S.: An antioxidant function for DMSP and DMS in marine algae, *Nature*, 418, 317-320, doi: 10.1038/nature00851, 2002.
- 1050 Sunda, W., Hardison, R., Kiene, R.P., Bucciarelli, E., and Harada, H.: The effect of nitrogen limitation on cellular DMSP and DMS release in marine phytoplankton: climate feedback implication, *Aquat. Sci.*, 69, 341-351, doi: 10.1007/s00027-007-0887-0, 2007.
- Thoisen, C., Riisgaard, K., Lundholm, N., Nielsen, T.G., and Hansen, P.J.: Effect of acidification on an Arctic phytoplankton community from Disko Bay, West Greenland, *Mar. Ecol.-Prog. Ser.*, 520, 21-34, doi: 10.334/meps11123, 2015.
- 1055 Toole, D.A., and Siegel A.D.: Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: closing the loop, *Geophys. Res. Lett.*, 31, L09308, doi: 10.1029/2004GL019581, 2004.
- Townsend, D.W., and Keller, M.D.: Dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in relation to phytoplankton in the Gulf of Maine, *Mar. Ecol.-Prog. Ser.*, 137, 229-241, doi: 10.3354/meps137229, 1996.
- 1060 Tremblay, G., Belzile, C., Gosselin, M., Poulin, M., Roy, Suzanne, and Tremblay, J.-É.: Late summer phytoplankton distribution along 3500 km transect in Canadian Arctic waters: strong numerical dominance by picoeukaryotes, *Aquat. Microb. Ecol.*, 54, 55-70, doi: 10.3354/ame01257, 2009.
- Tremblay, J-E., Robert D., Varela, D. E., Lovejoy, C., Darnis , G., Nelson, R. J., and Sastri, A. R.: Current State and trends in Canadian Arctic marine ecosystems : I. Primary production, *Climatic Change*, 115 (1), 161-178, doi : 10.1007/s10584-012-0496-3, 2012.
- 1065 Tremblay, J-E., Michel, C., Hobson, K.A., Gosselin, M., and Price, N.P.: Bloom dynamics in early opening waters of the Arctic Ocean, *Limnol. Oceanogr.*, 51(2), 900-912, doi: 10.4319/lo.2006.51.2.0900, 2006.
- 1070 Tremblay, J-E., Gratton, Y., Carmack, E.C., Payne, C.D., and Price, N.M.: Impact of the large-scale Arctic circulation and the North Water Polynia on nutrient inventories in Baffin Bay, *J. Geophys. Res.*, 107(C8), 3112, doi: 10.1029/2000JC000595, 2002.
- Trodahl, H.J., and Buckley, R.G.: Enhanced ultraviolet transmission of Antarctic sea ice during the austral spring, *Geophys. Res. Lett.*, 17 (12), 2177-2179, doi: 10.1029/GL017i012p02177, 1990.
- 1075 Vallina, S.M., and Simó, R.: Strong relationship between DMS and the solar radiation dose over the global surface ocean. *Science*, 315, 506-508, doi: 10.1126/science.1133680, 2007.
- Vance, T.R., Davidson, A.T., Thomson, P.G., Levasseur, M., Lizotte, M., Curran, M.A.J., and Jones, G.B: Rapide DMSP production by an Antarctic phytoplankton community exposed to natural surface irradiances in late spring. *Aquat. Microb. Ecol.*, 71, 117-129, doi: 10.3354/ame01670, 2013.

- 1080 Van Bergeijk, S., Van Der Zee, C., and Stal, L.J.: Uptake and excretion of dimethylsulphoniopropionate is driven by salinity changes in the marine benthic diatom *Cylindrotheca closterium*, European J. Phycol., 38(4), 341-349, doi: 10.1080/096702603100011612600, 2003.
- Vogt, M., Steinke, M., Turner, S., Paulino, A., Meyerhöfer, M., Riebesell, U., LeQuéré, C., and Liss, P.: Dynamics of dimethylsulphoniopropionate and dimethylsulfide under different CO<sub>2</sub> concentrations during a mesocosm experiment, Biogeosciences, 5, 407-419, doi: 10.5194/bg-5-407-2008, 2008.
- 1085 Von Quillfeldt, C.H.: Common diatom species in arctic spring blooms: their distribution and abundance, Bot. Mar., 43, 499-516, doi: 10.1515/BOT.2000.050, 2000.
- Webb, A.L., Malin, G., Hopkins, F.E., Ho, K.L., Riebesell, U., Schulz, K.G., Larsen, A., and Liss, P.S.: Ocean acidification has different effects on the production of dimethylsulfide and dimethylsulphoniopropionate measured in cultures of *Emiliana huxleyi* and a mesocosm study: a comparison of laboratory monocultures and community interactions, Environ. Chem., 13, 314-329, doi: 10.1071/EN14268, 2015.
- 1090 Webb, A.L., Leedham-Elvidge, E., Hughes, C., Hopkins, F.E., Malin, G., Bach, L.T., Schulz, K., Crawford, K., Brussaard, C.P.D., Stühr, A., Riebesell, U., and Liss, P.S.: Effect of ocean acidification and elevated *f*CO<sub>2</sub> on trace gas production by a Baltic Sea summer phytoplankton community, Biogeosciences, 13, 4595-4613, doi:10.5194/bg-13-4595-2016, 2016.
- 1095 Wolfe, G.V., Levasseur, M., Cantin G., and Michaud, S.: Microbial consumption and production of dimethyl sulphide (DMS) in the Labrador Sea, Aquat. Microb. Ecol., 18, 197-205, doi: 10.3354/ame018197, 1999.
- 1100 Wu, Y., Campbell, D.A., Irwin A.J., Suggett, D.J., and Finkel, Z.V.: Ocean acidification enhances the growth rate of larger diatoms, Limnol. Oceanogr., 59(3), 1027-1034, doi: 10.4319/lo.2014.59.3.1027, 2014.

1105

**Table 1.** Values of pH<sub>T</sub> (total hydrogen ion scale), the associated proton concentration [H<sup>+</sup>] dissolved inorganic carbon (DIC), total alkalinity (TA), and *p*CO<sub>2</sub> in the microcosms under low light (LL) and high light (HL) treatments on days T0, T1, T4, and T9. Values of *p*CO<sub>2</sub> were calculated using CO<sub>2</sub>SYS software, values of proton concentrations were calculated after the pH<sub>T</sub> measurements. 1L and 1H are the control microcosms.

|           |    | pH <sub>T</sub>            |      |      | [H <sup>+</sup> ]                         |      |      | DIC                        |      |      | TA                         |      |      | <i>p</i> CO <sub>2</sub> |      |      |
|-----------|----|----------------------------|------|------|---|------|------|----------------------------|------|------|----------------------------|------|------|--------------------------|------|------|
|           |    | (total hydrogen ion scale) |      |      | (x 10 <sup>-8</sup> mol L <sup>-1</sup> ) |      |      | (μmol kg <sup>-1</sup> SW) |      |      | (μmol kg <sup>-1</sup> SW) |      |      | (μatm)                   |      |      |
|           |    | T0                         |      |      | T0  |      |      | T0                         |      |      | T0                         |      |      | T0                       |      |      |
|           |    | 7.94                       |      |      | 1.15                                      |      |      | 2137                       |      |      | 2243                       |      |      | 492                      |      |      |
|           |    | T1                         | T4   | T9   | T1  | T4   | T9   | T1                         | T4   | T9   | T1                         | T4   | T9   | T1                       | T4   | T9   |
| Microcosm | 1L | 7.94                       | 7.99 | 8.22 | 1.15                                      | 1.03 | 0.60 | 2142                       | 2129 | 2041 | 2238                       | 2243 | 2247 | 509                      | 451  | 247  |
|           | 2L | 7.79                       | 7.84 | 8.11 | 1.62                                      | 1.46 | 0.77 | 2186                       | 2178 | 2083 | 2237                       | 2243 | 2243 | 738                      | 658  | 326  |
|           | 3L | 7.65                       | 7.70 | 8.06 | 2.24                                      | 1.99 | 0.87 | 2221                       | 2222 | 2099 | 2231                       | 2248 | 2238 | 1040                     | 917  | 375  |
|           | 4L | 7.46                       | 7.49 | 7.83 | 3.47                                      | 3.24 | 1.47 | 2261                       | 2255 | 2163 | 2217                       | 2220 | 2226 | 1618                     | 1508 | 660  |
|           | 5L | 7.34                       | 7.36 | 7.65 | 4.57                                      | 4.37 | 2.23 | 2293                       | 2293 | 2210 | 2212                       | 2217 | 2222 | 2116                     | 2046 | 1022 |
|           | 6L | 7.16                       | 7.17 | 7.33 | 6.92                                      | 6.73 | 4.68 | 2366                       | 2340 | 2283 | 2210                       | 2192 | 2198 | 3296                     | 3149 | 2179 |
|           | 1H | 7.94                       | 8.00 | 8.22 | 1.15                                      | 1.01 | 0.61 | 2144                       | 2129 | 2041 | 2242                       | 2246 | 2245 | 505                      | 442  | 249  |
|           | 2H | 7.77                       | 7.85 | 8.12 | 1.70                                      | 1.42 | 0.76 | 2184                       | 2169 | 2075 | 2229                       | 2237 | 2237 | 768                      | 638  | 322  |
|           | 3H | 7.64                       | 7.69 | 8.02 | 2.29                                      | 2.06 | 0.96 | 2218                       | 2210 | 2109 | 2225                       | 2231 | 2233 | 1063                     | 946  | 415  |
|           | 4H | 7.46                       | 7.49 | 7.85 | 3.47                                      | 3.27 | 1.42 | 2260                       | 2257 | 2157 | 2217                       | 2222 | 2225 | 1610                     | 1521 | 636  |
|           | 5H | 7.30                       | 7.32 | 7.53 | 5.01                                      | 4.82 | 2.92 | 2304                       | 2302 | 2236 | 2208                       | 2211 | 2214 | 2337                     | 2259 | 1349 |
|           | 6H | 7.16                       | 7.17 | 7.30 | 6.92                                      | 6.73 | 5.00 | 2330                       | 2326 | 2281 | 2178                       | 2178 | 2185 | 3208                     | 3134 | 2318 |



1110

**Table 2.** Photosynthetically active radiation (PAR), ultraviolet A radiation (UVA) and ultraviolet B radiation (UVB) measured during the 9-day microcosm experiment. Values are shown for the incident irradiance and the estimated irradiance under the high light (HL) and low light (LL) treatments (i.e. values corrected for the transmission through the incubation bags). PAR values were averaged over a day whereas UVA and UVB were measured each day around noon between T5 and T9 only due to instrument dysfunction during the 4 first days.

|      |       | PAR ( $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$ ) |     |     | UV-A ( $\text{W m}^{-2}$ ) |     |      | UV-B ( $\text{W m}^{-2}$ ) |      |    |
|------|-------|---|-----|-----|----------------------------|-----|------|----------------------------|------|----|
|      |       | Incident  | HL  | LL  | Incident                   | HL  | LL   | Incident                   | HL   | LL |
| Time | (day) |   |     |     |                            |     |      |                            |      |    |
|      | T1    | 189   | 146 | 61  |                            |     |      |                            |      |    |
|      | T2    | 216   | 168 | 70  |                            |     |      |                            |      |    |
|      | T3    | 333   | 258 | 109 |                            |     |      |                            |      |    |
|      | T4    | 402   | 312 | 131 |                            |     |      |                            |      |    |
|      | T5    | 394   | 306 | 129 | 13                         | 7.8 | 2.6  | 0.37                       | 0.12 | -  |
|      | T6    | 381   | 270 | 124 | 4.6                        | 2.8 | 0.94 | 0.2                        | 0.07 |    |
|      | T7    | 348   | 304 | 113 | 12                         | 7.6 | 2.5  | 0.37                       | 0.12 |    |
|      | T8    | 392   | 304 | 128 | 10                         | 6.2 | 2.1  | 0.36                       | 0.12 |    |
|      | T9    | 272   | 211 | 89  | 4.9                        | 3   | 1    | 0.17                       | 0.06 |    |

1115 **Table 3.** Overview of the results of generalized least square models testing for the effects of time,  
light, and pH<sub>T</sub> over the duration of the incubation on nitrate, silicic acid, soluble reactive  
phosphate (SRP), chlorophyll *a*, dissolved DMSP, total DMSP, and DMS concentrations, as well  
as nanophytoplankton, picophytoplankton, and bacterial abundances. Type of transformations  
1120 applied to data when necessary are indicated in parentheses, significant results are indicated in  
bold, df are the degrees of freedom, p is the significance of the t-value.

| Response variable                                     | Factor | df  | t-value | p                 |
|---|--------|-----|---------|-------------------|
| Nitrate ( $\mu\text{mol L}^{-1}$ )                    | Time   | 77  | -7.853  | <b>&lt; 0.001</b> |
|   | Light  | 77  | -0.395  | 0.693             |
|   | pH     | 77  | -5.156  | <b>&lt; 0.001</b> |
| Silicic acid ( $\mu\text{mol L}^{-1}$ )               | Time   | 108 | -8.308  | <b>&lt; 0.001</b> |
|   | Light  | 108 | 0.123   | 0.903             |
|   | pH     | 108 | -6.608  | <b>&lt; 0.001</b> |
| (sqrt) SRP ( $\mu\text{mol L}^{-1}$ )                 | Time   | 108 | -8.487  | <b>&lt; 0.001</b> |
|   | Light  | 108 | -1.826  | 0.071             |
|   | pH     | 108 | -6.915  | <b>&lt; 0.001</b> |
| (sqrt) Chlorophyll <i>a</i> ( $\mu\text{g L}^{-1}$ )  | Time   | 108 | 7.456   | <b>&lt; 0.001</b> |
|   | Light  | 108 | 0.151   | 0.880             |
|   | pH     | 108 | 4.862   | <b>&lt; 0.001</b> |
| (sqrt) Nanophytoplankton<br>(cells $\text{mL}^{-1}$ ) | Time   | 107 | 17.614  | <b>&lt; 0.001</b> |
|   | Light  | 107 | -0.346  | 0.608             |
|   | pH     | 107 | 6.513   | <b>&lt; 0.001</b> |
| (sqrt) Picophytoplankton<br>(cells $\text{mL}^{-1}$ ) | Time   | 107 | 26.926  | <b>&lt; 0.001</b> |
|   | Light  | 107 | 1.388   | 0.185             |
|   | pH     | 107 | 2.043   | <b>0.035</b>      |

|  |       |     |        |                   |
|--|-------|-----|--------|-------------------|
| (2 outliers removed) Bacteria<br>(cells mL <sup>-1</sup> ) | Time  | 104 | 4.300  | <b>&lt; 0.001</b> |
|  | Light | 104 | 2.604  | <b>0.011</b>      |
|  | pH    | 104 | 3.167  | <b>&lt; 0.01</b>  |
| Total DMSP (nmol L <sup>-1</sup> )                         | Time  | 108 | 1.562  | 0.121             |
|  | Light | 108 | 0.950  | 0.344             |
|  | pH    | 108 | 2.070  | <b>0.041</b>      |
| (log) Dissolved DMSP<br>(nmol L <sup>-1</sup> )            | Time  | 60  | 2.529  | <b>0.014</b>      |
|  | Light | 60  | -0.753 | 0.454             |
|  | pH    | 60  | 0.362  | 0.718             |
| (sqrt) DMS (nmol L <sup>-1</sup> )                         | Time  | 77  | 2.478  | <b>0.015</b>      |
|  | Light | 77  | 0.387  | 0.700             |
|  | pH    | 77  | 6.635  | <b>&lt; 0.001</b> |

---

1125

**Table 4.** Empirical relationships of various biological or chemical (response) variables with proton concentration ( $\text{mol L}^{-1}$ ). Values are the means of all the microcosms. Linear regressions were performed on both light treatments when light had significant effect on the response variable (see Table 3). Significant results are in bold, df are the degrees of liberty,  $r^2$  is the squared Pearson correlation coefficient between proton concentration and the response variable, and p is the significance of each parameters of the regression.

| Response variable                                  | df | $r^2$ | Parameters |                       | p                 |
|--|----|-------|------------|-----------------------|-------------------|
| Mean Chlorophyll <i>a</i> ( $\mu\text{g L}^{-1}$ ) | 10 | 0.86  | slope      | $-2.70 \cdot 10^7$    | <b>&lt; 0.001</b> |
|  |    |       | intercept  | 3.95                  | <b>&lt; 0.001</b> |
| Mean nanophytoplankton ( $\text{cells mL}^{-1}$ )  | 10 | 0.73  | slope      | $-4.37 \cdot 10^{10}$ | <b>&lt; 0.001</b> |
|  |    |       | intercept  | $6.74 \cdot 10^3$     | <b>&lt; 0.001</b> |
| Mean picophytoplankton ( $\text{cells mL}^{-1}$ )  | 10 | 0.32  | slope      | $6.52 \cdot 10^{11}$  | <b>0.056</b>      |
|  |    |       | intercept  | $6.73 \cdot 10^4$     | <b>&lt; 0.001</b> |
| Mean bacteria ( $\text{cells mL}^{-1}$ )           |    |       |            |                       |                   |
| <i>High Light</i>                                  | 4  | 0.84  | slope      | $-2.54 \cdot 10^{12}$ | <b>&lt; 0.01</b>  |
|  |    |       | intercept  | $9.77 \cdot 10^5$     | <b>&lt; 0.001</b> |
| <i>Low Light</i>                                   | 4  | 0.33  | slope      | $-8.04 \cdot 10^{11}$ | 0.23              |
|  |    |       | intercept  | $1.01 \cdot 10^6$     | <b>&lt; 0.001</b> |
| Mean DMSP <sub>T</sub> ( $\text{nmol L}^{-1}$ )    | 10 | 0.04  | slope      | $-6.90 \cdot 10^7$    | 0.55              |
|  |    |       | intercept  | $3.81 \cdot 10^1$     | <b>&lt; 0.001</b> |
| Mean DMS ( $\text{nmol L}^{-1}$ )                  | 10 | 0.9   | slope      | $-1.19 \cdot 10^8$    | <b>&lt; 0.001</b> |
|  |    |       | intercept  | 8.37                  | <b>&lt; 0.001</b> |
| Mean DMS:DMSPd ratio                               | 10 | 0.57  | slope      | $-1.02 \cdot 10^8$    | <b>&lt; 0.01</b>  |
|  |    |       | intercept  | 8.45                  | <b>&lt; 0.001</b> |

1130

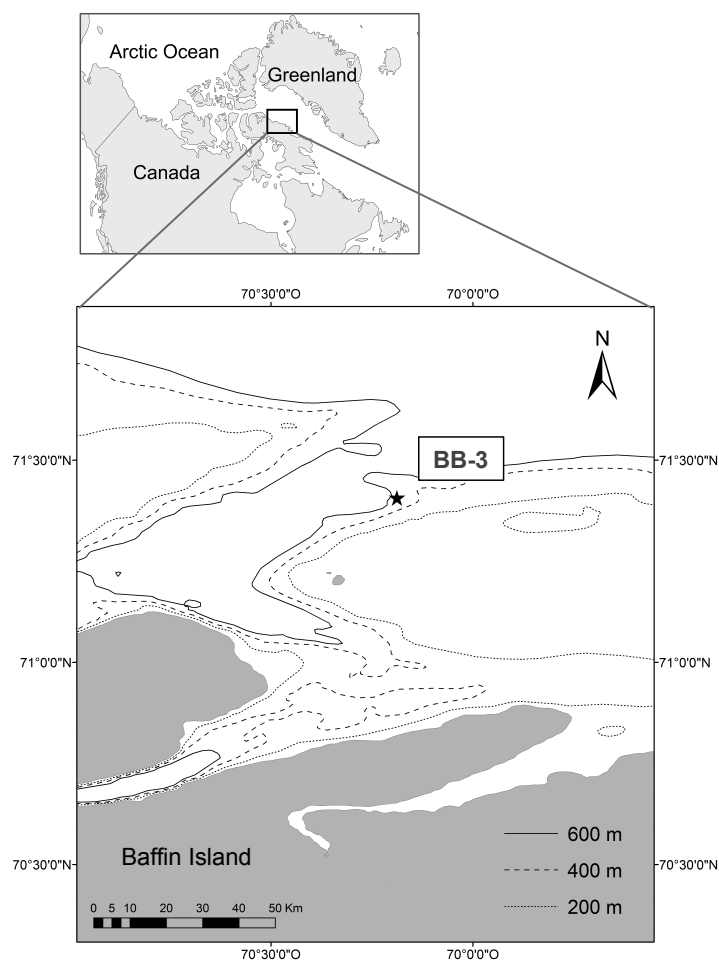
**Table 5.**  $F_v/F_m$  ratios for three different  $pH_T$  measured on days T2, T4, T6, T7 and T9 under high light (HL) and low light (LL) conditions.

|       |    | pH |  | 8.07 |      | 7.81 |      | 7.22 |      |
|-------|----|----|--|------|------|------|------|------|------|
|       |    |    |  | HL   | LL   | HL   | LL   | HL   | LL   |
| Time  |    |    |  |      |      |      |      |      |      |
| (day) |    |    |  |      |      |      |      |      |      |
|       | T2 |    |  | 0.52 | 0.55 | 0.51 | 0.53 | 0.44 | 0.46 |
|       | T4 |    |  | 0.59 | 0.58 | 0.58 | 0.59 | 0.5  | 0.5  |
|       | T6 |    |  | 0.49 | 0.47 | 0.44 | 0.51 | 0.5  | 0.5  |
|       | T7 |    |  | 0.4  | 0.4  | 0.41 | 0.42 | 0.5  | 0.52 |
|       | T9 |    |  | 0.31 | 0.32 | 0.33 | 0.36 | 0.36 | 0.37 |

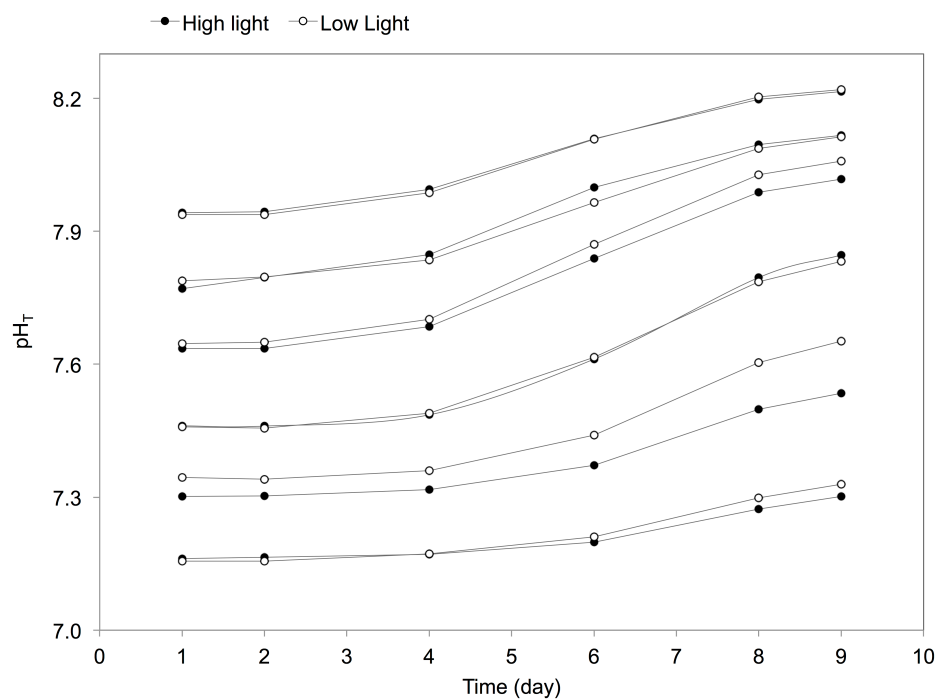
**Table 6.** Changes in dimethylsulfide (DMS) concentrations reported in previous CO<sub>2</sub> perturbation experiments in mesocosms or microcosms.  $\Delta$ pH represents the change in pH<sub>T</sub> applied in each experiment. In our study, pH<sub>T</sub> ranged from 7.94 to 7.16 at day T1. ND: No data

| Location               | $\Delta$ pH | $p$ CO <sub>2</sub> range ( $\mu$ atm) | Change in DMS (%) | Reference              |
|------------------------|-------------|--|-------------------|------------------------|
| Baffin Bay, Arctic     | -0.75       | 500 - 3000                             | -80               | This study             |
| Baltic Sea             | -0.4        | 350 - 1500                             | -34               | Webb et al. 2016       |
| Raunesfjorden, Norway  | -0.6        | 280 - 3000                             | -60               | Webb et al. 2015       |
| Jangmok, Korea         | -0.5        | 160 - 830                              | -82               | Park et al. 2014       |
| Kongsfjorden, Svalbard | -0.8        | 180 - 1420                             | -60               | Archer et al. 2013     |
| Raunesfjorden, Norway  | -0.2        | 300 - 750                              | -40               | Avgoustidi et al. 2013 |
| Raunesfjorden, Norway  | -0.3        | 300 - 750                              | -57               | Hopkins et al. 2010    |
| Raunesfjorden, Norway  | -0.5        | 300 - 750                              | 0                 | Vogt et al. 2008       |
| NW European Shelf      | -0.4        | 340 - 1000                             | 225               | Hopkins et Archer 2014 |
| Jangmok, Korea         | ND          | 400 - 900                              | 80                | Kim et al. 2010        |

## Figures

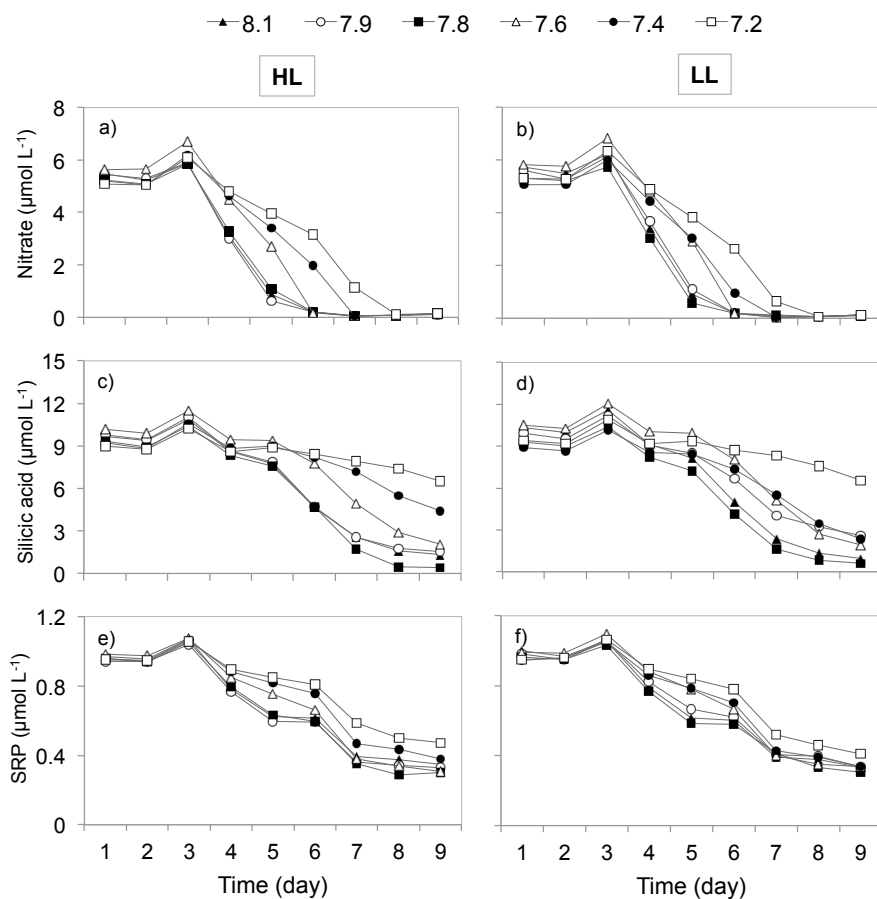


**Fig. 1.** Map showing the location of station BB-3 (71°24.373'N; 70°11.269'W) where seawater was collected for the incubation experiment.



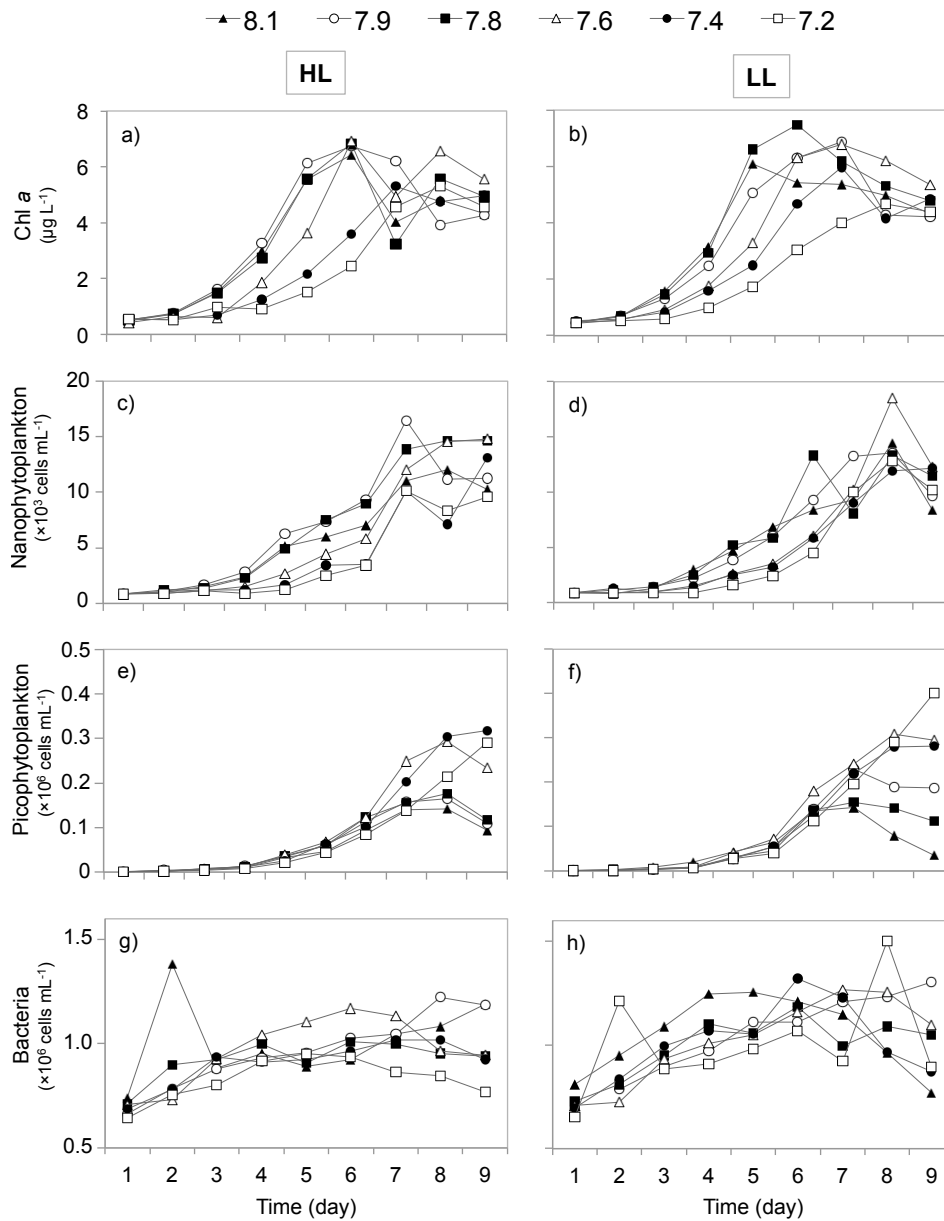
**Fig. 2.** Temporal variations in pH<sub>T</sub> (total hydrogen ion scale) during the microcosm experiment. Black and white circles represent the pH gradient in the high light (HL) and low light (LL) treatments, respectively.



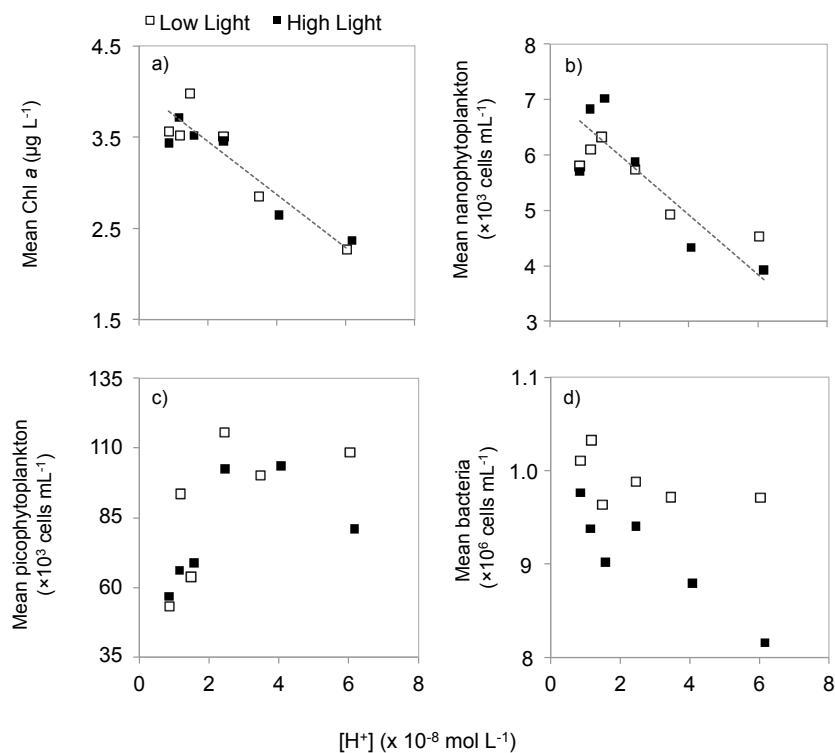


**Fig. 3.** Temporal variations in (a,b) nitrate, (c,d) silicic acid, and (e,f) soluble reactive phosphate (SRP) concentrations during the experiment. Left and right panels show variations under the high light (HL) and low light (LL) treatments, respectively. Each curve represents a microcosm identified by its mean  $pH_T$  value.

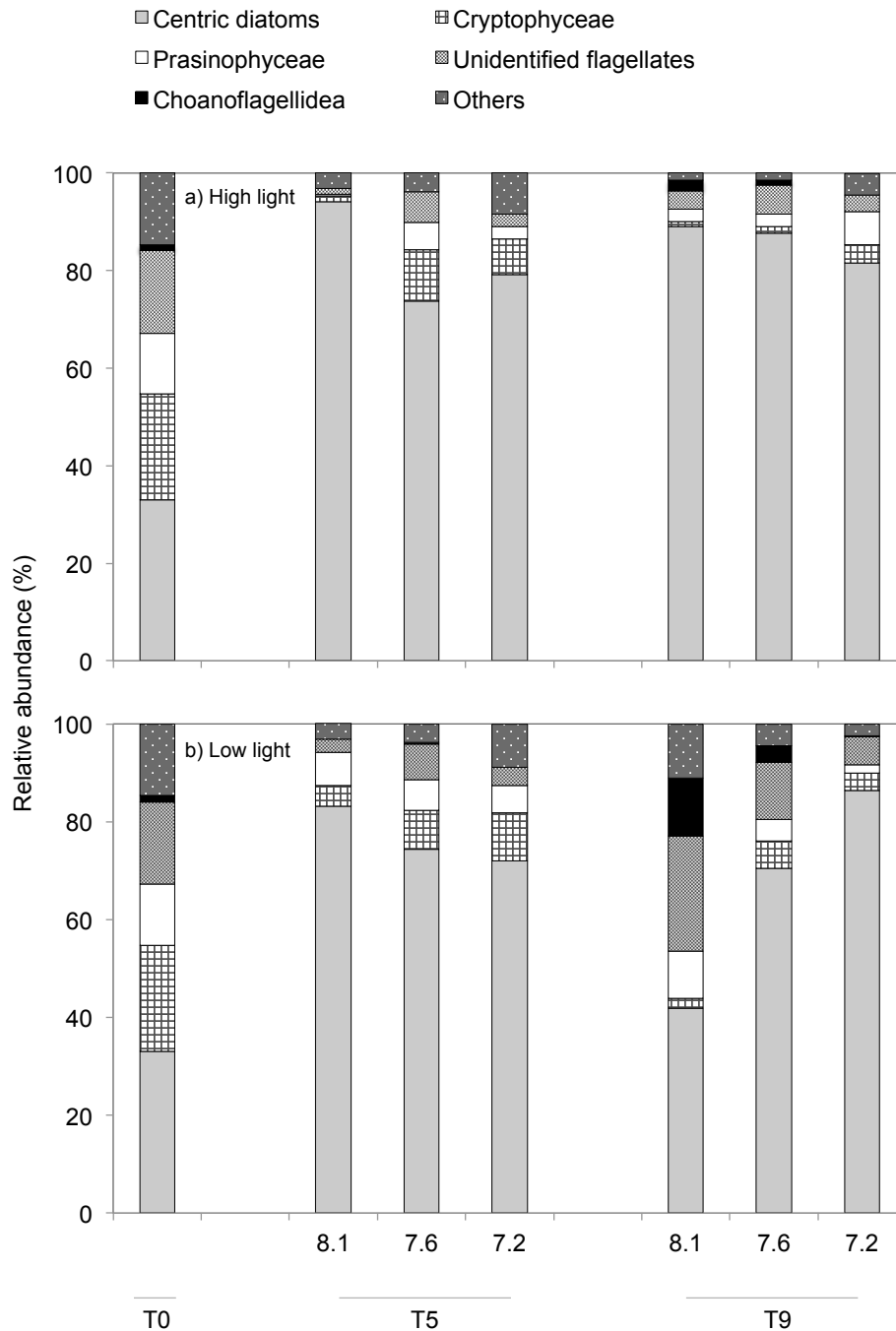
1155



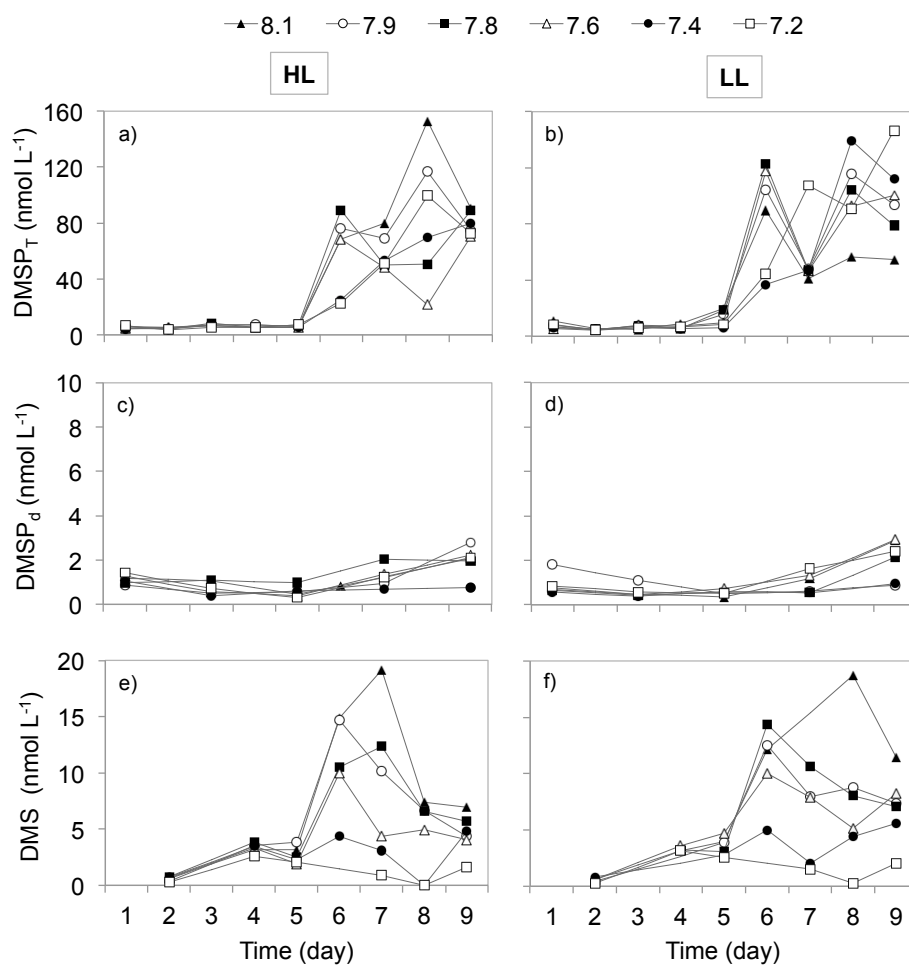
**Fig. 4.** Temporal variations in (a,b) chlorophyll *a* (Chl *a*) concentration, (c,d) nanophytoplankton, (e,f) picophytoplankton, and (g,h) bacteria during the microcosm experiment. Left and right panels show variations under the high light (HL) and low light (LL) treatments, respectively. Each curve represents a microcosm identified by its mean pH<sub>T</sub> value.



**Fig. 5.** Relationships between the mean proton concentration values ( $[H^+]$ ) and a) mean Chlorophyll *a* (Chl *a*), b) mean nanophytoplankton abundance, c) mean picophytoplankton abundance, and d) mean bacteria abundance. Values are the means over the duration of the incubation in each microcosm. Significant regressions are shown with dashed lines; details of which are given in Table 4. Regressions were based on the full dataset when no significant difference between the light treatments was detected (see also Table 3 for more details).

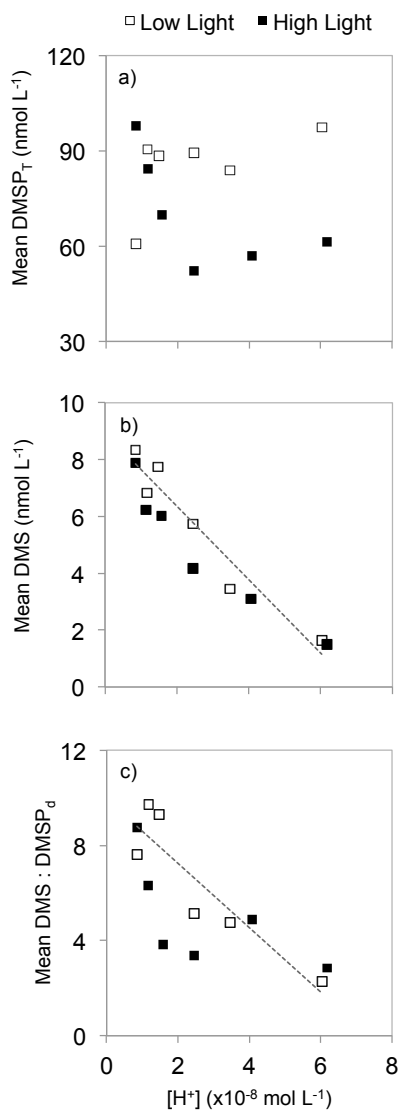


**Fig. 6.** Relative abundance of 6 groups of protists at the beginning (T0), the middle (T5) and the end (T9) of the microcosm experiment for (a) high light (HL) and (b) low light (LL) treatments. The group “Others” includes pennate diatoms, dinophyceae, chrysophyceae, dictyophyceae, euglenophyceae, ciliates and unidentified cells. Each barplot represents a pH treatment. The barplot at T0 represents the initial community assemblage before pH manipulations, and is therefore the same for both light treatments.



**Fig. 7.** Temporal variations in (a,b) total DMSP ( $\text{DMSP}_T$ ), (c,d) dissolved DMSP ( $\text{DMSP}_d$ ), and (e,f) DMS concentrations during the microcosm experiment. Left and right panels show variations under the high light (HL) and low light (LL) treatments, respectively. Each curve represents a microcosm identified by its mean  $\text{pH}_T$  value.

1185



**Fig. 8.** Relationships between the mean proton concentration values ( $[H^+]$ ) and (a) mean total DMSP concentration, (b) mean DMS concentration, and (c) mean DMS:DMSP<sub>d</sub> ratio. Values are the mean over the duration of the incubation in each microcosm. Significant regressions are shown as dashed lines, details of which are given in Table 4.

1190