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Contrasted sensitivity of DMSP production to high light exposure in two Arctic under-ice blooms

Virginie Galindo ^{a,b,*}, Maurice Levasseur ^a, Christopher John Mundy ^b, Michel Gosselin ^c, Michael Scarratt ^d, Tim Papakyriakou ^b, Jacqueline Stefels ^e, Matthew A. Gale ^b, Jean-Éric Tremblay ^a, Martine Lizotte ^a

^a Département de biologie, Québec-Océan, Université Laval, Québec, Québec G1V 0A6, Canada

^b Centre for Earth Observation Science (CEOS), Faculty of Environment, Earth and Resources, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

^c Institut des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski, Rimouski, Québec G5L 3A1, Canada

^d Maurice Lamontagne Institute, Fisheries and Oceans Canada, Mont-Joli, Québec G5H 3Z4, Canada

^e University of Groningen, Groningen Institute for Evolutionary Life Sciences, Plant Ecophysiology, P.O. Box 11103, 9700 CC Groningen, The Netherlands

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ABSTRACT

In polar regions, low-light acclimated phytoplankton thriving under sea ice may be suddenly exposed to high irradiance when ice pack breaks or surface currents carry them into adjacent ice-free areas. Here we experimentally determined how rapid shifts in light regime affect the phytoplankton and the production of dimethylsulfoniopropionate (DMSP), an algal compound with antioxidant properties. Springtime experiments were carried out on under-ice phytoplankton blooms that exhibited different taxonomic assemblages in 2010 and 2011 within the Canadian Arctic Archipelago. Phytoplankton samples collected under-ice were incubated for 24 h or less on the ice at irradiances mimicking what they would experience in an ice-free upper mixed layer. We observed contrasting responses between the two years. In 2010, exposure of the under-ice centric diatom bloom to high irradiance consistently resulted in a rapid chlorophyll *a* decrease accompanied by a quasi-total release of the intracellular DMSP. In 2011, only the first experiment conducted with a low biomass flagellate-dominated assemblage resulted in a similar response. During the subsequent under-ice pennate diatom bloom, neither a chlorophyll *a* decrease nor a consistent increase in dissolved DMSP concentrations were observed during the experiments. The results demonstrate that the response of under-ice phytoplankton to the irradiance prevailing in ice-free water may vary depending on the developmental stage and taxonomic composition of the under-ice bloom. The rapid chlorophyll *a* decrease during the centric diatom bloom in 2010 and the associated DMSP exudation may potentially lead to a significant increase in DMS production via the microbial pathway at the ice edge.

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1. Introduction

The light environment experienced by Arctic phytoplankton is undergoing important changes due to global warming. The warming of the Arctic has resulted in the decline of the snow cover, sea-ice thickness, and extent (Screen et al., 2011; Stroeve et al., 2012), and in an earlier melt onset (Markus et al., 2009). Since the late 1970's, the summer snow cover has decreased by 17.6% per decade (Derksen and Brown, 2012), while sea-ice extent reached a minimum record in September 2012, with 3.41 million km² (Parkinson and Comiso, 2013). Compounding factors also associated with warming in the Arctic include the replacement of multi-year ice by first-year ice, the latter exhibiting a lower albedo (e.g., Cavalieri and Parkinson, 2012; Derksen and Brown, 2012; Stroeve et al., 2012) and hence greater light

transmission (Nicolaus et al., 2012), as well as an increase in rain events (Screen and Simmonds, 2012). In addition to these changes in snow and ice conditions, ozone depletion in the Arctic (Manney et al., 2011) has been considerably greater than at mid-latitudes during the last two decades (Stamnes et al., 1990; Waibel et al., 1999). The combined effects of snow-ice decline and enhanced stratospheric ozone depletion result in an increase of irradiance reaching the surface of the Arctic Ocean, including ultraviolet radiation (UVR, 320–400 nm) that can penetrate sea ice (Belzile et al., 2000). Alternatively, the potential increase in irradiance could be attenuated by an increase in cloud cover due to enhanced local evaporation following the reduction of sea ice (Vavrus et al., 2011a,b).

To limit the damage caused by high UVR, phytoplankton have developed different photoprotective mechanisms (Brunet et al., 2011; Lavaud, 2007; Lepetit et al., 2012). These strategies include an increase in pigmentation (Dionisio-Sese, 2010; Goiris et al., 2012; Sinha et al., 1998), in UV-absorbing sunscreens, such as mycosporine-like amino-acid (MAA) (Garcia-Pichel, 1994; Llewellyn and Ains, 2010; Elliott

* Corresponding author at: Département de biologie, Québec-Océan, Université Laval, Québec, Québec G1V 0A6, Canada.

E-mail address: virginie.galindo@umanitoba.ca (V. Galindo).

et al., in press), and the use of antioxidants including MAA (Dunlap and Yamamoto, 1995), ascorbate, glutathione (Lohrmann et al., 2004), and dimethylsulfoniopropionate (DMSP) (Sunda et al., 2002, 2007). DMSP is the biological precursor of the climate-active gas dimethylsulfide (DMS) and has many functions. It can serve as a compatible solute (Stefels, 2000; Vairavamurthy et al., 1985) and a cryoprotectant (Karsten et al., 1996). DMSP is also involved in distinct physiological adaptations of phytoplankton related to environmental stresses such as nutrient limitation and high irradiance levels (Archer et al., 2009; Stefels, 2000; Sunda et al., 2002, 2007). Stefels (2000) suggested that DMSP exudation could also represent an overflow mechanism for excess intracellular carbon under unbalanced growth conditions. A few years later, Sunda et al. (2002) suggested that DMSP and its breakdown products (DMS, acrylate, dimethylsulfoxide (DMSO), and methanesulfonic acid (MSA)) could act as efficient antioxidants due to their capacity to scavenge hydroxyl radicals and other reactive oxygen species (ROS). The proposed antioxidant hypothesis led to numerous investigations on the influence of light on DMSP and DMS microbial transformations, notably DMSP synthesis and its conversion into DMS (Galí et al., 2011, 2013; Ruiz-González et al., 2012a; Toole et al., 2006).

Photoprotective mechanisms may be particularly important in seasonally ice-covered regions where under-ice phytoplankton can experience abrupt increases in irradiance upon the loss of protective ice cover. In the Arctic, microalgal blooms develop underneath the ice in spring and summer when snow and ice melt, as well as the development of melt ponds, promote light penetration through the ice (Arrigo et al., 2012; Mundy et al., 2014; Palmer et al., 2014). These low-light acclimated under-ice communities may be suddenly exposed to high light intensity when advective currents and/or sea-ice displacement transfer them towards open waters in leads, polynyas or at the ice edge. Photosynthesis of low-light acclimated algal cells can be saturated by irradiances as low as $20 \mu\text{mol photons m}^{-2} \text{s}^{-1}$. Hence, phytoplankton thriving under the ice may be sensitive to small increases in solar radiation (Beeler

SooHoo et al., 1987; Raven et al., 2000). A recent study in Antarctic waters by Vance et al. (2013) showed that a sudden increase in light may stimulate DMSP production in low light acclimated under-ice phytoplankton. Hence, the production of DMS(P) could be up-regulated following a rapid increase in photosynthetically active radiation (PAR, 400–700 nm) and, or UVR.

The objective of this study was to experimentally assess the influence of an abrupt increase in irradiance (PAR and UVR) on the chlorophyll *a* (Chl *a*) concentrations and DMSP production of under-ice phytoplankton during spring in the Arctic.

2. Materials and methods

2.1. Water collection and incubation protocol

Experiments were carried out on four occasions between 26 May and 19 June 2010 in Resolute Passage and on five occasions between 2 and 22 June 2011 in Allen Bay, Nunavut, Canada (Fig. 1). The field stations (ice camps) were located on first-year landfast sea ice with a thickness of ca. 140 cm during both years (Galindo et al., 2014).

To collect water from underneath the ice (ca. 2 m below the sea level), a hole was drilled in the sea-ice and the water was sampled at ca. 9:30 AM CDT in 2010 and 7:00 AM CDT in 2011 with a small electric submersible pump (12 V Cyclone®) tethered to an under-ice arm. The water inlet of the submersible pump was covered by a 200 μm Nitex mesh to remove large grazers. Water was pooled into one or two acid-cleaned 70 L isothermal containers (Coleman Xtreme) and kept in the dark. Water was gently mixed before being transferred by gravity and under dim light conditions to the incubation bags (i.e. 5 L Hyclone Labtainer® collapsible bags in 2010 and 10 L Coleman polyethylene collapsible bags in 2011). All manipulations were conducted at the ice camp, the treatments were done in triplicate, and the incubation began approximately one hour after the sampling. Transmittance

Fig. 1. Map showing the location of the ice camp in Resolute Passage in 2010 (74° 42.6'N; 95° 15'W) and in Allen Bay in 2011 (74° 43'N 95° 09'W). Locations of the Resolute hamlet and of the Polar Continental Shelf Program (PCSP) Facility are also indicated. Isobaths are in meters. Modified from Galindo et al. (2014).

through the two incubation bag types was measured from 280 to 700 nm at 1 nm intervals using a PerkinElmer LAMBDA 850 UV/Vis Spectrophotometer. Transmittances of the PAR and ultraviolet A radiation (UVA; 315–400 nm) were similar for both bag types, whereas ultraviolet B radiation (UVB; 290–315 nm) transmittance was up to 2 times higher in the incubation bags used in 2011 (Table 1).

In 2010, two light treatments were performed during each experimental day: (1) in situ (IS) light conditions (bags incubated in the water just below the ice using a custom built under-ice arm), and (2) high light (HL) conditions (bags placed in a black plastic incubator, located on the ice and continuously cooled with running seawater pumped from 1 m below the bottom surface of the ice using a small electric submersible pump (Pondmaster magnetic drive utility pump, Model 5500 GPH)). The light conditions experienced by phytoplankton cells in the HL treatment corresponded approximately to those observed by cells in ice-free waters with a surface mixed layer of 7 m, as estimated following the equation of Riley (1957):

$$I = \frac{I_0 (1 - e^{-kz})}{kz}$$

where I is the daily PAR averaged over the surface mixed layer ($\mu\text{mol photons m}^{-2} \text{ s}^{-1}$), I_0 is the daily averaged PAR at the surface ($\mu\text{mol photons m}^{-2} \text{ s}^{-1}$), k is the PAR diffuse attenuation coefficient assumed to be 0.092 m^{-1} (unpublished data from Barrow Strait area; M. Gosselin), and z is the surface mixed layer depth (m). At the start of the experiment, a single sample was collected to determine the initial taxonomic composition of the protist community. Subsamples for the determination of chlorophyll a (Chl a), particulate DMSP (DMSPp), dissolved DMSP (DMSPd), and nutrients were collected every 2 h.

In 2011, two treatments were added to the 2010 protocol: (1) medium light (ML, bags covered with a 300 μm Nitex mesh netting) and (2) low light (LL, bags covered with two overlapping 300 μm Nitex mesh netting). The incubators were located on the sea ice and continuously cooled, as in 2010. The light regime experienced by the cells in the ML and LL treatments corresponded approximately to those observed in ice-free waters with a surface mixed layer of ca. 12 and 22 m, respectively. The incubation period was extended to 24 h to assess the capacity of the phytoplankton to recover from the initial light shock. Since no recovery was observed, and in order to facilitate the comparison with the results from 2010, only data from the first 8 or 16 h are presented. Samples for the determination of the taxonomic composition of the protists were only collected at the beginning of the experiments. Subsamples were collected every 4 h for Chl a , DMSPp and DMSPd and every 8 h for nutrients, except for the experiments conducted on 10 and 18 June 2011 when all variables were sampled every 8 h.

Table 1
Percentage of transmittance of incident photosynthetically active radiation (PAR), ultraviolet A (UVA) and ultraviolet B (UVB) in incubation bags under in situ (IS), high (HL), medium (ML), and low (LL) light conditions in 2010 and 2011.

	PAR transmittance (%)	UVA transmittance (%)	UVB transmittance (%)
2010			
IS treatment	0.1–18		
HL treatment	69.6	51.5	16.7
2011			
IS treatment	0.2–18*		
LL treatment	42.3	31.5	19.7
ML treatment	60.8	35.5	26.6
HL treatment	72.5	50.2	34.3

* Time-series of PAR transmittance underneath the ice is detailed in Campbell et al. (2014).

2.2. Incident irradiance and under-ice PAR

Incident photosynthetically active radiation (PAR) was monitored with a Kipp & Zonen™ PAR-Lite sensor (1.3 m height) at a micrometeorological tower deployed at 0.5 and 2 km of the ice camp in 2010 and 2011, respectively. Incident UVA (315–325 nm) and UVB (290–315 nm) radiations were measured every second using a Brewer MKII spectrophotometer installed by Environment Canada at their meteorological station located 7–10 km east of the ice camps. Spectral UV data were integrated across each spectral band and saved as 10 min averages. Radiation (PAR and UV) was subsequently averaged daily for each experimental day and corrected for transmittance through the incubation bags. PAR underneath the ice (ca. 2 m below the sea level) was measured with a scalar PAR sensor (Biospherical QSP-2300) mounted on a Sea-Bird SBE 19plus V2 conductivity-temperature-depth (CTD) probe. Details of the data are available in Gale (2014). Cumulative under-ice PAR at 2 m below the sea level was calculated by integrating under-ice PAR values for the 3 days prior to the experiment date.

2.3. Nutrients

The water collected for nutrient analysis was filtered through a pre-combusted (5 h at 450 °C) Whatman GF/F glass-fiber filter inserted in a 25 mm filter holder. The filtrate was collected into 15 mL acid-cleaned polyethylene tubes after thorough rinsing. Samples were immediately stored in a –20 °C freezer until analysis. Concentrations of nutrients including nitrate plus nitrite ($\text{NO}_3^- + \text{NO}_2^-$), phosphate (PO_4^{3-}) and silicic acid ($\text{Si}(\text{OH})_4$) were measured with an Autoanalyzer 3 (SEAL Analytical) using the standard colorimetric methods of Grasshoff et al. (1999) and adapted by Martin et al. (2010). The detection limits were $0.03 \mu\text{mol L}^{-1}$ for total $\text{NO}_3^- + \text{NO}_2^-$ (which will be abbreviated hereafter as NO_x^-), $0.02 \mu\text{mol L}^{-1}$ for PO_4^{3-} and $0.2 \mu\text{mol L}^{-1}$ for $\text{Si}(\text{OH})_4$.

2.4. Chlorophyll a and taxonomic composition

To determine Chl a concentrations, samples were filtered onto Whatman GF/F 25 mm filters. Pigments were extracted from the filters after a minimum of 18 h (maximum 24 h) in 90% acetone at 4 °C in the dark (Parsons et al., 1984). Fluorescence of the extracted pigments was measured using a 10-005R Turner Designs fluorometer before and after acidification with 5% HCl. Chl a concentrations were calculated using the equation described by Holm-Hansen et al. (1965).

Before the beginning of experiments, samples for the identification and enumeration of protists ($>2 \mu\text{m}$) were preserved with acidic Lugol's solution (Parsons et al., 1984) and stored in the dark at 4 °C until analysis. In the laboratory, at least 400 cells were enumerated in each 10 mL settling chamber, using the inverted microscopy method (Lund et al., 1958).

2.5. Dimethylated sulfur compounds

In each incubation bag, samples were collected for the determination of total DMSP ($\text{DMSPt} = \text{DMSPp} + \text{DMSPd}$) and DMSPd. DMSPp concentrations were obtained by subtracting DMSPd from DMSPt concentrations. For DMSPt samples, 3.5 mL of seawater was collected into a 5 mL Falcon™ tube, while DMSPd was quantified using the less disruptive Small-Volume gravity Drip Filtration (SVDF) method (Kiene and Slezak, 2006). DMSP samples were preserved with 50 μL of 50% sulfuric acid (H_2SO_4) to prevent the production of DMS. DMS concentrations could not be determined for logistical limitations. Samples were analyzed using a purge and trap system coupled to a Varian 3800 gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD) (Levasseur et al., 2006). The analytical detection limit was 0.01 nmol L^{-1} for all sulfur compounds.

2.6. DMSP-specific production rate

To assess the impact of a sudden increase in incident irradiance on DMSP synthesis, DMSP-specific production rates were measured on 10 and 18 June 2011 using a stable isotopic method (Stefels et al., 2009). To do so, 120 L of seawater collected at 2 m was split in two coolers and inoculated with trace addition of $\text{NaH}^{13}\text{CO}_3$ (final concentration of $121 \mu\text{mol L}^{-1}$). The inoculated seawater was kept in the dark until transfer by gravity to triplicate incubation bags per treatment under dim light conditions in the field laboratory. ^{13}C is incorporated into DMSP through photosynthesis. The incubation bags were exposed to the same light treatments as described in Section 2.1 for 2011. At the beginning of the experiment, seawater was withdrawn from the incubation bags for the determination of dissolved inorganic carbon (DIC) following the method described in Miller et al. (2011). The incubations started at ca. 9:00 AM CDT for a 24 h duration and subsamples of seawater (ca. 500 mL) were collected every 4 h, and filtered onto Whatman GF/F 25 mm filters. The filters were placed into 25 mL serum bottles containing 10 mL of milliQ water and two pellets of NaOH to obtain a pH of 13.4–13.7, which converts particulate DMSP into DMS. The bottles were immediately sealed with butyl rubber septa and aluminum crimps, and stored at -20°C . At the home laboratory, the samples were carefully thawed and analyzed with a Proton-Transfer-Reaction Mass Spectrometry (PTR-MS, Ionicon, Innsbruck, Austria). The PTR-MS directly measures DMS from converted DMSP. DMSP-specific production rates were calculated with the Mass-Ratio-Progress method (Stefels et al., 2009).

2.7. Statistical analysis

Normality of the data was determined using the Shapiro–Wilk test with a 0.05 significance level. Statistical differences between the two sampling years were tested using Student's *t*-test. Relationships between variables were determined with Pearson's linear correlations (*r*). Loss rates of Chl *a* and exudation rates of DMSP were estimated from the slope of change in the concentrations of these variables over the incubation period (Model I linear regression). Statistical tests were carried out using JMP® 10.0 Software, and the graphics were produced using SigmaPlot 12.5 (Systat Software Inc.).

3. Results

3.1. Irradiance and initial chemical and biological conditions during the incubations

Prevailing environmental and biological conditions at the beginning of the experiments are presented in Table 2. During the four

experiments conducted in 2010, daily averages of incident PAR, UVA and UVB, were corrected for transmittance through the incubation bags, and hereafter referred to as “incubation PAR and UV”. The results were relatively similar with mean values of $492 \mu\text{mol photons m}^{-2} \text{s}^{-1}$, 0.41 W m^{-2} and 0.04 W m^{-2} , respectively. Daily corrected irradiance was more variable during the five experiments conducted in 2011. However, the mean daily averages of incubation PAR ($442 \mu\text{mol photons m}^{-2} \text{s}^{-1}$) and UVA (0.38 W m^{-2}) during the 2011 experiments were not significantly different from those observed in 2010 ($p = 0.45$ and $p = 0.59$, respectively; Student's *t*-tests). Despite the discrepancies in variability and incubation UVB, the range of the relative increase in light experienced by the algae during the experiments (expressed as the ratio of incident incubation to under-ice PAR at 2 m) was comparable during both years. Incubation under-ice PAR increased progressively from 6 to $40 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ in 2010, while in 2011, it was below $10 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ during the first two experiments and increased to ca. $80 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ during the last three. These trends could also be seen in the 3-day averaged incubation under-ice PAR values. Cumulative under-ice PAR at 2 m was below $10 \text{ mol photons m}^{-2}$ during the three first experiments in 2010 and increased to $43 \text{ mol photons m}^{-2}$ during the last one. In 2011, the first two experiments were conducted when cumulative under-ice PAR was below $1 \text{ mol photons m}^{-2}$, while during the last three experiments it remained above $17 \text{ mol photons m}^{-2}$.

The taxonomic composition of the under-ice protist assemblages showed important intra- and inter-annual variations (Fig. 2). In 2010, the first two experiments were characterized by low Chl *a* concentrations ($<0.25 \mu\text{g L}^{-1}$) and an algal assemblage numerically dominated by DMSP-rich flagellates as showed by the high DMSP/Chl *a* ratios (Fig. 2a; Table 3). These first two experiments were also characterized by pre-bloom nutrient conditions, i.e., high concentrations of NO_3^- ($>7.2 \mu\text{mol L}^{-1}$), Si(OH)_4 concentrations ($>13 \mu\text{mol L}^{-1}$), and PO_4^{3-} ($>1.04 \mu\text{mol L}^{-1}$) (Table 3). The two following experiments were conducted during the development of an under-ice bloom as indicated by the increase in Chl *a* concentrations from 2.23 to $7.54 \mu\text{g L}^{-1}$, an increase in centric diatom relative abundance from 0 to 76%, and the sharp decreases in both NO_3^- , from 6.4 to $0.6 \mu\text{mol L}^{-1}$, and in Si(OH)_4 , from 12.8 to $4.6 \mu\text{mol L}^{-1}$ (Fig. 2a; Table 3). In 2011, we captured the developing (first experiment), peak (second to fourth experiments), and declining (fifth experiment) phases of the pennate diatom bloom (Fig. 2b). The DMSP/Chl *a* ratios were low during the first two experiments and increased as the pennate diatom bloom developed (Table 3). Similarly in 2011, NO_3^- , Si(OH)_4 and PO_4^{3-} concentrations reached very low levels (<1.2 , <1.8 and $<0.92 \mu\text{mol L}^{-1}$, respectively), especially for NO_3^- during the last three experiments. Details on the dynamics of these two under-ice blooms are given in Galindo et al. (2014).

Table 2

Daily averaged photosynthetically active radiation (PAR), ultraviolet A radiation (UVA) and ultraviolet B radiation (UVB) in the incubation bags, average under-ice PAR during the 3 days prior to incubation, incubation under-ice PAR, 3-day cumulative under-ice PAR and relative PAR (ratio of incubation PAR to under-ice PAR) measured during the experiments in Resolute Passage in 2010 and in Allen Bay in 2011. The prefix “incubation” indicates that the irradiance values were corrected for the transmission through the incubation bags.

	Incubation PAR ($\mu\text{mol photons m}^{-2} \text{s}^{-1}$)	Incubation UVA (W m^{-2})	Incubation UVB (W m^{-2})	3-day average incubation under-ice PAR ^a ($\mu\text{mol photons m}^{-2} \text{s}^{-1}$)	Incubation under-ice PAR ($\mu\text{mol photons m}^{-2} \text{s}^{-1}$)	Cumulative under-ice PAR (mol photons m^{-2})	Relative PAR ^b
2010							
26 May	427	0.32	0.02	2.92 ± 0.93	6	2	71
01 June	464	0.38	0.03	1.44 ± 0.98	1	1	464
14 June	532	0.48	0.04	22.04 ± 17.35	21	10	25
19 June	543	0.47	0.04	93.86 ± 41.84	40	43	14
2011							
02 June	522	0.49	0.08	2.21 ± 1.71	1	1	522
10 June	374	0.31	0.05	2.40 ± 0.66	9	1	41
14 June	368	0.25	0.04	34.08 ± 25.56	75	17	5
18 June	599	0.46	0.09	72.35 ± 16.35	57	34	13
22 June	349	0.38	0.07	154.86 ± 50.10	85	64	4.1

^a Averaged concentrations $\pm$ standard deviation calculated from triplicate samples.

^b Ratio of incubation PAR to incubation under-ice PAR at 2 m.

Fig. 2. Time series of relative (bar plot) cell abundance of five groups of protists under the sea ice (ca. 2 m below the sea level) and algal biomass (circles) at the beginning of the experiments (a) in Resolute Passage in 2010 and (b) in Allen Bay in 2011. The group “Others” includes heterotrophic flagellates, ciliates, choanoflagellates and unidentified cells. Bars represent standard deviation (SD) calculated from triplicate samples. Modified from Galindo et al. (2014).

3.2. Variations in Chl *a* and DMSP during the experiments

Exposure of the under-ice algal assemblages to high irradiance resulted in a variety of responses, but two main types emerged: rapid decreases in Chl *a* and DMSP or no consistent changes in Chl *a* and DMSP. An example of these two main responses is presented in Fig. 3, while the results obtained during the nine incubations are summarized in Table 4.

In 2010, the responses were highly consistent across experiments: Chl *a* concentrations remained stable in the IS treatments but decreased over time in the HL treatments (Table 4). The loss of Chl *a* in the HL treatments was accompanied by a parallel decrease in DMSP concentrations. DMSP concentrations increased linearly during the four experiments, an increase corresponding to 66 to 100% of the loss in DMSP (Table 4).

In 2011, only the first experiment (2 June) exhibited a linear decrease in Chl *a* concentrations when the cells were exposed to higher irradiances (Table 4). The decrease in Chl *a* was observed in both the HL and ML treatments and the slopes of the regressions were not

significantly different between the two light treatments ($p = 0.32$, Student's *t*-test). DMSP concentrations decreased in these two treatments, but in contrast with 2010 where the decrease was immediate after light exposure, it took place after a lag of 4 h in 2011. A slight increase in DMSP accompanied the loss of DMSP, but the changes were not statistically different from the IS treatment. For the following four experiments which corresponded to the development of the pennate bloom, the exposure of the under-ice algae to an increasing gradient in irradiance had no significant effect on Chl *a*, DMSP and DMSP, except on 14 June when a net increase in DMSP was measured over time in all treatments (Table 4).

3.3. Influence of irradiance on DMSP-specific production rate

DMSP-specific production rates as a function of daily averaged incubation PAR during the 10 and 18 June 2011 experiments remained approximately constant over the day: the slope of the hourly specific

Table 3

Chemical and biological variables measured in the incubation bags at the beginning of the incubations during the experiments in Resolute Passage in 2010 and in Allen Bay in 2011. NOx^- = nitrate plus nitrite; PO_4^{3-} = phosphate; $\text{Si}(\text{OH})_4$ = silicic acid; Chl *a* = chlorophyll *a*; DMSPp = particulate dimethylsulfoniopropionate; DMSPd = dissolved DMSP; DMSPp/Chl *a* = particulate dimethylsulfoniopropionate/chlorophyll *a*.

	NOx^- ^a ($\mu\text{mol L}^{-1}$)	$\text{Si}(\text{OH})_4$ ^a ($\mu\text{mol L}^{-1}$)	PO_4^{3-} ^a ($\mu\text{mol L}^{-1}$)	DMSPd ^a (nmol L^{-1})	DMSPp ^a (nmol L^{-1})	Chl <i>a</i> ^a ($\mu\text{g L}^{-1}$)	DMSPp/Chl <i>a</i> (nmol μg^{-1})
2010							
26 May	7.2 ± 0.2	13.1 ± 0.5	1.04 ± 0.02	0.1 ± 0.2	3.7	0.24 ± 0.03	15.42
01 June	8.3 ± 0.1	15.0 ± 0.3	1.13 ± 0.03	0.2 ± 0.4	2.9 ± 1.0	0.20 ± 0.01	14.5
14 June	6.4 ± 0.5	12.8 ± 0.6	1.01 ± 0.03	2.0 ± 0.4	10.4 ± 1.6	2.23 ± 0.16	4.66
19 June	0.6 ± 0.0	4.6 ± 0.4	0.61 ± 0.03	4.0 ± 0.1	33.7 ± 5.7	7.54 ± 0.20	4.47
2011							
02 June	6.9 ± 0.1	13.1 ± 0.2	0.99 ± 0.01	0.1 ± 0.2	5.7 ± 1.3	0.87 ± 0.06	6.55
10 June	3.6 ± 0.1	8.2 ± 0.2	0.84 ± 0.01	1.5 ± 1.8	18.1 ± 3.0	4.55 ± 0.57	3.98
14 June	0.8 ± 0.3	1.8 ± 0.0	0.72 ± 0.00	20.8 ± 0.8	34.3 ± 4.1	5.02 ± 0.27	6.83
18 June	0.5 ± 0.3	1.4 ± 0.2	0.67 ± 0.01	2.1 ± 0.8	58.4 ± 5.2	5.42 ± 0.74	10.77
22 June	1.2 ± 0.0	na	0.92 ± 0.00	3.2 ± 0.5	33.5 ± 3.4	3.00 ± 0.30	11.17

na: Not available.

^a Averaged concentrations ± standard deviation calculated from triplicate samples.

production rates versus time, as derived from each time-point measurement over the 24-h incubation period, was not significantly different from zero (data not shown). Therefore, only average daily production rates are presented (Fig. 4). On 10 June 2011, the average DMSP-specific production rate was 0.20 d^{-1} at the very low light level underneath the ice. The production rate then decreased from 0.17 to 0.08 d^{-1} as PAR increased from 220 to 374 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ in the

incubation bags (Fig. 4a). On 18 June 2011, the average DMSP-specific production rate was 0.08 d^{-1} under the sea ice, and again decreased regularly from 0.08 down to 0.02 d^{-1} as PAR increased from 350 to 600 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ in the incubation bags (Fig. 4b). Variations in DMSP-specific production rates exhibited a similar pattern as with PAR when presented as a function of daily averaged UVA and UVB (data not shown).

Fig. 3. Variations of (a, d) chlorophyll *a*, (b, e) DMSPp, and (c, f) DMSPd during the experiments on 19 June 2010 in Resolute Passage and on 22 June 2011 in Allen Bay, respectively. The incubation bags were submitted to in situ (IS), high (HL), medium (ML), and low (LL) light conditions. Bars represent standard deviation (SD) calculated from triplicate samples.

Table 4

Net changes in chlorophyll *a* (Chl *a*), DMSPp and DMSPd over 6–16 h under in situ (IS), high (HL), medium (ML), and low (LL) light conditions in Resolute Passage in 2010 and in Allen Bay in 2011. Linear regression slope $\pm$ SE and regression coefficient (in parentheses) are shown. *: $p < 0.05$.

		Duration	Variations Chl <i>a</i> ($\mu\text{g L}^{-1} \text{h}^{-1}$)	Variations DMSPp ($\text{nmol L}^{-1} \text{h}^{-1}$)	Variations DMSPd ($\text{nmol L}^{-1} \text{h}^{-1}$)
2010					
26 May	IS	6 h	No trend	No trend	No trend
	HL	6 h	-0.04 ± 0.01 ($r = -0.94^*$)	-0.40 ± 0.20 ($r = -0.80^*$)	0.39 ± 0.18 ($r = 0.84^*$)
01 June	IS	6 h	No trend	No trend	No trend
	HL	6 h	-0.03 ± 0.01 ($r = -0.92^*$)	-0.46 ± 0.33 ($r = -0.66^*$)	0.18 ± 0.14 ($r = 0.67^*$)
14 June	IS	6 h	No trend	No trend	No trend
	HL	6 h	-0.34 ± 0.05 ($r = -0.97^*$)	-1.55 ± 0.17 ($r = -0.98^*$)	1.11 ± 0.18 ($r = 0.97^*$)
19 June	IS	8 h	No trend	No trend	No trend
	HL	8 h	-0.86 ± 0.15 ($r = -0.95^*$)	-3.10 ± 0.70 ($r = -0.93^*$)	2.26 ± 0.14 ($r = 0.99^*$)
2011 ^a					
02 June	IS	8 h	No trend	0.83 ± 0.14 ($r = 0.98$)	No trend
	HL	8 h	-0.07 ± 0.009 ($r = -0.99^*$)	-0.44 ± 7.87^b ($r = -0.27$)	0.09 ± 0.09 ($r = 0.71$)
	ML	8 h	-0.05 ± 0.01 ($r = -0.97^*$)	-0.26 ± 8.07^b ($r = -0.13$)	0.08 ± 0.04 ($r = 0.90$)
10 June	IS	16 h ^c	No trend	No trend	No trend
	HL	16 h ^c	No trend	No trend	No trend
	ML	16 h ^c	No trend	No trend	No trend
	LL	16 h ^c	No trend	No trend	No trend
14 June	IS	8 h	No trend	0.54 ± 0.07 ($r = 0.99$)	No trend
	HL	8 h	No trend	1.24 ± 0.18 ($r = 0.99$)	No trend
	ML	8 h	No trend	1.37 ± 0.19 ($r = 0.99$)	No trend
	LL	8 h	No trend	0.49 ± 0.14 ($r = 0.96$)	No trend
18 June	IS	16 h ^c	No trend	No trend	No trend
	HL	16 h ^c	No trend	No trend	No trend
	ML	16 h ^c	No trend	No trend	No trend
	LL	16 h ^c	No trend	No trend	No trend
22 June	IS	8 h	No trend	No trend	-0.10 ± 0.02 ($r = -0.92$)
	HL	8 h	No trend	No trend	No trend
	ML	8 h	No trend	No trend	No trend
	LL	8 h	No trend	No trend	No trend

^a For the sake of comparison with year 2010, only data from the first 8 h are presented for 2011.

^b Difference calculated between 4 and 8 h since the relationship was not linear during this incubation.

^c For these dates, the trends were determined for the first 16 h, since subsampling occurred every 8 h.

* Trend in light treatment significantly different than in situ treatment.

4. Discussion

Our results showed two contrasting responses of under-ice algae to a rapid increase in light. In 2010, all experiments exhibited a sharp decrease in chlorophyll *a*, indicating a high sensitivity of the under-ice phytoplankton to light, while in 2011, four experiments out of five showed no effect of light on chlorophyll *a*. The strong correlation observed between DMSPp concentrations and the abundance of diatoms ($r = 0.88$, $p < 0.01$) suggests that the diatoms exerted a marked influence on DMSPp variations. Although flagellates are known to be high DMSP producers, a significant relationship between their abundance and the reservoirs of DMSPp could not have been established here, likely owing their overall subordinate abundance in most of the experiments. Thus, as discussed below, the diversity in responses may be explained by the stage of the bloom (pre-bloom versus bloom) and on the taxonomic composition of the algal assemblage (centric versus pennate diatoms).

4.1. Chlorophyll *a* decrease and associated variations in DMSP under light stress in 2010

Results from the 2010 experiments revealed a very high sensitivity of the under-ice algae to the abrupt increases in irradiance. The response was highly consistent: exposure of the under-ice algae to the light levels they would experience near the surface under ice-free conditions resulted in a rapid (<8 h) chlorophyll *a* decrease, most probably due to cell lysis. In 2010, the chlorophyll *a* decrease took place irrespective of the developmental stage of the under-ice bloom (Chl *a* concentrations ranging from 0.20 to 7.54 $\mu\text{g L}^{-1}$), taxonomic dominance (flagellates versus centric diatoms) of algal assemblages, and nitrogen availability (NO_x declining from 8.3 to 0.6 $\mu\text{mol L}^{-1}$) (Table 3). During

the first two experiments that were dominated by flagellates, part of the transfer of particulate DMSP to the dissolved pool could be due to a loss of cell membrane integrity induced by light stresses, making the cells more prone to realizing DMSP upon filtration (Kiene and Slezak, 2006). During the two subsequent experiments, the assemblage was dominated by diatoms, which are known to be more resistant to cell breakage during filtration (Goldman and Dennett, 1985). Flagellates, which were also abundant during these experiments and known to be richer in DMSP than diatoms (Keller et al., 1989; Malin and Kirst, 1997), may also have been responsible for the high DMSP release. Assuming no DMSPp production during the experiments and no DMSPp loss during the filtration, we calculated that the phytoplankton lost more than 60% of their DMSP content during the first 6–8 h of exposure to high irradiance, probably through exudation and cellular lysis. In support of this explanation, DMSPd concentrations increased linearly during the incubation period, with 66 to 100% of the lost DMSPp recovered as DMSPd. Since no DMS was measured, we can only speculate on the fate of the remainder of the lost DMSPp. Part of it may have been transferred to the DMS pool after enzymatic conversion by bacteria or by algal exoenzymes or endoenzymes released during cell lysis (Stefels et al., 1995). Photo-oxidation of intracellular DMSP and intracellular or aqueous DMS into DMSO (Husband et al., 2012; Stefels et al., 2007), as well as demethylation of dissolved DMSP may have also taken place during the incubations. In the same study region, Galindo et al. (2015) showed that bacteria in the water column underneath the ice may consume DMSPd at an average rate of 5 $\text{nmol L}^{-1} \text{d}^{-1}$ with exceptional peak values reaching 44 $\text{nmol L}^{-1} \text{d}^{-1}$. At this average rate, bacteria could have consumed 1.7 nmol L^{-1} of DMSP during the 8 h experiment, i.e., 37 to 90% of the missing DMSP. Assuming DMS bacterial yields of 2 to 10% as measured in the under-ice water by Galindo et al. (2015) in the same region, we calculate that the DMSPd released

Fig. 4. Averaged DMSP-specific production rates as a function of daily average incubation photosynthetically active radiation (PAR) in the different treatments (in situ (IS), low (LL), medium (ML) and high (HL) light conditions) during the experiments conducted on (a) 10 June 2011 and (b) 18 June 2011 in Allen Bay. Bars represent standard deviation (SD) calculated from triplicate samples.

during the 2010 incubations could be biologically converted into DMS at a rate of 0.04 to 18 nmol L⁻¹ d⁻¹. These calculations should however be considered with caution, since they do not take into account the likely negative impact of high irradiance on bacterial DMSP consumption as demonstrated at lower latitudes (Ruiz-González et al., 2012b; Slezak et al., 2001, 2007) and the potential release of algal enzymes upon cell lysis. The high but realistic irradiance to which the cells were exposed in 2010 might have caused cell death, overcoming any antioxidant protection provided by intracellular DMSP. Under these harsh light conditions, the DMSP may be mostly photo-oxidized into DMSO following its reaction with OH radicals and O₂⁻ in chloroplasts or mitochondria (Mopper et al., 2015). Intracellular DMSP can also be cleaved to DMS, while DMSPd in the medium can be demethylated or cleaved into DMS by bacteria. Overall, our results from 2010 show that the sudden exposure of under-ice blooms to high irradiance at the ice edge may abruptly stop the growth of cells trapped close to the surface, and lead to significant increases in DMSPd concentrations and potentially DMS production through the microbial pathway.

4.2. Resistance of the under-ice pennate diatoms to high irradiance in 2011

In 2011, except for the first experiment on 2 June, the sudden exposure of the cells to irradiance levels mostly similar or higher than in 2010 (LL, ML and HL treatments) did not result in a decrease of chlorophyll *a* (Table 4). As discussed in this section, intra- and inter-annual variations in algal species dominance may explain these observations.

As observed in 2010, the under-ice algal assemblage was highly sensitive to an increase in light early in the season, on 2 June 2011. During this particular experiment, the high sensitivity of the under-ice algae to the increase in irradiance was demonstrated by the decrease of Chl *a* observed during this experiment, even with a moderate increase in light (ML treatment), as experienced by the algal cells in ice-free waters with a surface mixed layer of 12 m (Table 4). Algal biomass was still very low at that time (pre-bloom conditions) and the assemblage was dominated by flagellates (Fig. 2b). DMSPp concentrations also decreased during the first 8 h of this experiment, but in contrast with 2010, when the decrease was immediate upon light exposure treatment, DMSPp concentrations started to decrease only after 4 h (Table 4). These results confirm observations from the previous year showing that, early in the season, low-light acclimated under-ice algal assemblages dominated by flagellates were highly sensitive to strong light conditions. Although substantial, the loss of DMSPp (71%) measured during the 2 June 2011 experiment was not accompanied by an important increase in DMSPd (Table 4). The small increase in DMSPd measured in the medium in combination with the bacterial DMSP consumption rates reported by Galindo et al. (2015) for the study area can only explain 27% of the DMSP loss. This suggests that a part of the DMSPp was either intracellularly photo-oxidized into DMSO or cleaved to DMS, or that the released DMSPd was demethylated or cleaved to DMS in the medium by bacteria. UVB radiation was twice as high during this incubation than during the 2010 incubations, but in contrast to DMS (Slezak et al., 2001; Steiner and Denman, 2008; Toole et al., 2004) the direct influence of UVB radiation on DMSP photo-oxidation has not yet been demonstrated. Thus, the loss of DMSP cannot be firmly attributed to a higher DMSP photo-oxidation rate associated with higher UVB conditions.

During all four subsequent experiments, the exposure of phytoplankton to higher irradiances (i.e., LL, ML and HL treatments) did not result in a loss of chlorophyll *a*. The most plausible causes for this striking discrepancy with our previous observations are differences in the light history of the cells and/or in the developmental stage and taxonomic composition of the under-ice pennate diatom bloom, hence their physiological photo-acclimation. As mentioned in Galindo et al. (2014), more light generally penetrated the sea ice and reached the water column in 2011 than in 2010 due to a thinner snow cover and its fast, rain-induced disappearance in mid-June. However, the comparison between pairs of experiments showing contrasting responses to light (Chl *a* loss versus no Chl *a* loss) but similar light history (cumulative under-ice PAR; see Table 2), excludes light history as a main cause for the different responses. For example, the under-ice assemblages were exposed to comparable incubation PAR and experienced similar cumulative under-ice PAR (43 versus 34 mol photons m⁻²) during the 19 June 2010 and 18 June 2011 experiments, but showed Chl *a* loss and non-Chl *a* loss responses (Table 4), respectively. Similarly, although cumulative under-ice PAR was similar for the experiments conducted on 2 and 10 June 2011, chlorophyll *a* loss was only observed during the first one. This leaves a more advanced stage of bloom development and/or dominance by pennate diatoms as the most likely explanations for the lack of sensitivity to high light in some experiments.

Ice-associated pennate diatoms, which dominated the algal under-ice bloom in 2011 (Galindo et al., 2014), are known for their high photoacclimative capability and photoprotective pigment contents (Alou-Font et al., 2013). In a study in Antarctica, Petrou et al. (2011a) showed during onboard incubation experiments, that the resilience and photoacclimative capabilities of ice-associated pennate diatoms resulted in minimal photoinhibition under increased light conditions. The same authors also demonstrated, in the laboratory, that ice-associated pennate diatoms were more effective at regulating the allocation of light energy through non-photochemical quenching than planktonic pennate and centric diatoms (Petrou et al., 2011b). These results suggest that the striking difference in the light resistance demonstrated by the 2010 and 2011 under-ice blooms reflected mostly differences

in their taxonomic composition which Galindo et al. (2014) attributed to a speedier flushing of the ice algae in 2011 than in 2010 and their seeding of the under-ice bloom.

4.3. Responses of net and gross DMSP production to light

Among the 9 experiments conducted during this study, an increase in net DMSP production in response to exposure to high irradiance was observed on 14 June 2011 only (Table 4). During this experiment, net DMSP production was more than 2 times higher under the ML and HL treatments than under the IS and LL treatments. It is noteworthy that these increases in DMSPp were not accompanied by increases in Chl *a* biomass. The relatively mild UV conditions prevailing during that particular experiment ($<0.3 \text{ W m}^{-2}$ UVA, 0.04 W m^{-2} UVB) may explain this unique response. Unfortunately, no gross DMSP production measurements were conducted during this experiment (see below), nor do we have independent cellular growth rates, so we cannot attribute this increase to an up-regulation of DMSP synthesis in response to light or to an overall increase in growth.

Measurements of DMSP gross production during the experiments conducted four days before and after 14 June 2011 show that the same microalgal assemblage dominated by ice-associated pennate diatoms, down-regulated DMSP gross production when exposed to light levels above 210 and $350 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$, respectively, resulting in the absence of a relationship between the light intensity and spectrum and the net change in DMSPp concentrations. For the two experiments conducted on 10 and 18 June 2011, when gross DMSP production estimates were available, the comparison between net and gross DMSPp production allowed us the determination of the loss of newly synthesized DMSPp. In other words, the calculated DMSPp loss rate represents the minimal contribution of the newly synthesized DMSPp to the increase in DMSPd measured in the medium during the same period. To do so, DMSPp net production was calculated as the difference between DMSPp concentrations at the beginning and at the end of the 24 h incubation period. The high light treatment on 10 June was discarded from the analysis since the net DMSPp production exceeded the gross DMSPp production for unknown reasons. In the other treatments, gross DMSPp productions varied between 1.38 and $5.14 \text{ nmol L}^{-1} \text{ d}^{-1}$, while net DMSPp productions varied between 0.06 and $3.76 \text{ nmol L}^{-1} \text{ d}^{-1}$ (data not shown). These rates are in the same range for both experimental days and the net DMSPp production shows no consistent trend with the light treatments. The net DMSPp production accounted for 2–30% and 5–60% of the gross DMSPp production on 10 and 18 June, respectively. Assuming no loss of DMSPd in the medium during the incubations, our calculations suggest that 12 to 100% of the DMSP gross production may have been released by cells in the medium during the 24 h incubations. The remaining DMSPp may have been lost through other pathways (e.g., via microzooplankton grazing, or transformed into DMSO or DMS).

Under in situ irradiance (IS), the gross DMSP-specific production rates of ca. 0.20 d^{-1} measured on 10 June 2011 fell in the range of previously measured rates in Arctic waters (0.20 to 0.24 d^{-1} ; Archer et al., 2013) and in the Sargasso Sea (0.06 to 0.22 d^{-1} ; Stefels et al., 2009) (Fig. 4a). The lower rate of 0.07 d^{-1} measured in the IS treatment on 18 June could reflect the more advanced developmental stage of the under-ice bloom (Fig. 4b). As mentioned above, NO_x^- concentrations were low and Chl *a* biomass was high on 18 June, suggesting that the bloom had likely reached its peak concentration and that algal growth was nutrient-limited. As predicted by the antioxidant hypothesis (Sunda et al., 2002), the sharp increase in light would result in the production of ROS which in turn would up-regulate DMSP synthesis. However, our results do not support this hypothesis. The relatively high UVB/UV ratio of 0.14 measured in 2011 as compared to 0.07 in 2010 (data not shown) could have resulted in a down regulation of DMSP synthesis. The carbon overflow hypothesis (Stefels, 2000) predicts that algal DMSP gross production is not affected by environmental

stresses, such as nutrient limitation, as long as these do not impair carbon fixation. However, when overall growth is down regulated, an accompanied down regulation of DMSP production is also expected. On 18 June 2011, nutrient concentrations were low, likely limiting for algal growth considering the important biomass present (Table 3). In support of this interpretation, algal abundance and Chl *a* biomass decreased by the next sampling date of 22 June (Fig. 2b; Table 3). The low in situ gross DMSP-specific production rates measured on 18 June and the negative impact of light on this rate could thus reflect nutrient limitation of the under-ice algal assemblage. In the 10 June 2011 experiment, when nutrients were likely not limiting during this earlier time period (Table 3), DMSP production was approximately 3 times higher. These two experimental datasets show that sharp increases in UV irradiance may decrease gross DMSP-specific production rates, irrespective of nutrient availability to the autotrophic assemblage.

5. Conclusion

In polar regions, low-light acclimated algae growing under the sea ice in late spring/early summer and forming large blooms (the so-called under-ice blooms) can be exposed to strong and rapid increases in irradiance during ice break-up, sea-ice retreat, or displacement of the under-ice cells by advective currents towards leads and ice-edge zones. With the predicted climate warming-induced thinning of the ice cover and earlier formation of melt ponds, these under-ice blooms are expected to become more prevalent in the near future (Spall et al., 2014), possibly replacing ice-edge blooms in some circumstances. Our results show that exposure of these under-ice blooms to increases in irradiance as they would experience in ice-free waters may have widely different impacts on their physiology and DMSP dynamics, depending on their taxonomic composition. During the two successive years covered by this study, the initial under-ice low-biomass flagellate-dominated assemblage present early in the season (pre-bloom) was highly sensitive to a sudden light enhancement of 50 to 300 times the ambient value. Exposure to high irradiance resulted in loss of chlorophyll *a* and DMSP, which was partially retrieved in the dissolved pool and hence suggestive of lysis of algal cells. Light sensitivity of the subsequent under-ice diatom blooms depended on their taxonomic composition, with centric and pennate diatoms showing strong and weak sensitivity, respectively. This difference could have important consequences for the fate of these blooms once exposed to light. On the one hand, as observed for the flagellate-dominated assemblage early in the season, centric diatom cells could burst with most of their cellular content being transferred to the dissolved pool where it becomes available to heterotrophic bacteria, considerably modifying the flows of carbon and sulfur in surface waters. On the other hand, our results suggest that under-ice assemblages dominated by pennate diatoms can continue their development in the ice-free waters owing to their greater resistance to high irradiance. Finally, our experiments failed to show an up-regulation of DMSP-specific production rates following exposure to high irradiance, especially high UV radiations. The rapid lysis of algal cells, as observed during the 2010 under-ice centric diatom bloom, and the associated release of their DMSP content may potentially lead to a significant increase in DMS production through the microbial pathway in leads and at the ice edge. In order to test this hypothesis, future experiments should quantify the fate of this new pool of dissolved DMSP, either through its oxidation or consumption by bacteria and possible transformation into DMS.

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