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Dimethylsulfide dynamics in first-year sea ice melt ponds in the Canadian Arctic Archipelago

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Abstract.

Melt pond formation is a natural seasonal pan-Arctic process. During the thawing season, melt ponds may cover up to 90% of the Arctic first year sea ice (FYI) and 15 to 25% of the multi-year sea ice (MYI). These pools of water lying at the surface of the sea-ice cover are habitats for microorganisms and represent a potential source of the biogenic gas dimethylsulfide (DMS) for the atmosphere. Here we report on the concentrations and dynamics of DMS in nine melt ponds sampled in July 2014 in the Eastern Canadian Arctic. DMS concentrations were under the detection limit (< 0.01 nmol l^{-1}) in freshwater melt ponds, and increased linearly with salinity up to ca. 6 nmol l^{-1} in brackish melt ponds ($r_s = 0.84$, $p < 0.05$). This relationship suggests that the intrusion of seawater in melt ponds is a key physical mechanism responsible for the presence of DMS. Results from experiments conducted with water from three melt ponds incubated for 24h with and without the addition of two stable isotope-labelled precursors of DMS (dimethylsulfoniopropionate (D6-DMSP) and dimethylsulfoxide (^{13}C-DMSO) show that de novo biological production of DMS can also take place within brackish melt ponds through bacterial DMSP uptake and cleavage. Our results suggest that FYI melt ponds could represent a reservoir of DMS ranging from ca. 6 to 11 tons of sulfur in the Arctic during July-August available for potential flux to the atmosphere. The importance of this ice-related source of DMS for the Arctic atmosphere is expected to increase as a response to the thinning of sea ice and the areal and temporal expansion of melt ponds on Arctic FYI.

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1 Introduction

Melt ponds represent an important but understudied component of the Arctic sea-ice system. Snow deposited at the surface of the sea ice progressively melts during the thawing season and may accumulate in depressions at the surface of the ice to form melt ponds (Lüthje et al., 2006), likely through a recently identified process of percolation blockage (Polashenski et al., 2017). In the Arctic, melt pond fraction over first-year sea ice (FYI) in late spring-summer usually ranges from 50% to 60%, locally reaching 90% (Fetterer and Untersteiner, 1998; Eicken et al., 2004; Lüthje et al., 2006; Perovich et al., 2011). Rösel et al. (2012) have reported a 15% increase in melt pond fraction for the month of June during the last decade in the Arctic, most likely attributed to global climate change. This partly reflects the progressive replacement of multi–year sea ice (MYI) by FYI observed since the 1980's (National Snow and Ice Data Center, NSIDC, http://nsidc.org), favouring the formation of shallow melt ponds that spread over increasingly large areas (Agarwal et al., 2011; Ehn et al., 2011). The importance of melt ponds in the Arctic, as a water-air interface involved in heat and gas exchanges, is thus expected to increase in the future.

Dimethylsulfide (DMS) is a climate-relevant compound potentially involved in a feedback loop known as the 'CLAW' hypothesis (Charlson et al., 1987) linking the biology and climate through the production of DMS-derived aerosols. Acting as cloud condensation nuclei, the aerosols could contribute to the genesis of longer-lived and higher-albedo clouds (Twomey, 1974; Albrecht, 1989), and thus influence the radiation balance of the Earth. The effect of DMS on cloud properties is particularly important over remote pristine marine areas (Carslaw et al., 2013). The summertime Arctic atmosphere displays low coagulation and condensation sinks related to increased wet deposition of particles, and reduced atmospheric aerosol particle loading from anthropogenic sources at lower latitudes (Browse et al., 2012; Croft et al., 2016). Shallow inversion layers that stabilize air masses above the Arctic also reduce the loss of newly formed fine particles. Hence, the Arctic is a favourable terrain for new particle formation from biogenic DMS (Chang et al., 2011; Collins et al., 2017; Giamarelou et al., 2016; Mungall et al., 2016; Willis et al., 2016).

DMS produced in the surface oceans represents 95% of the natural reduced sulfur emitted to the atmosphere (Stefels et al., 2007). This DMS mainly stems from the enzymatic cleavage of dimethylsulfoniopropionate (DMSP), a cellular compound found in several phytoplankton species (reviewed by Hughes et al., 2014). Between 1 and 40% of the DMSP produced by algae reaches the atmosphere as DMS (Simó and Pedrós-Alió, 1999a). The DMSP-lyase enzymes that mediate DMS production are present in members of the groups Haptophyceae and Dinophyceae, and to a lesser extent, Chrysophyceae (Niki et al., 2000). DMSP plays several roles in phytoplankton, including osmoregulation (Dickson et al., 1980; Kirst, 1996; Van Bergeijk et al., 2003), cryoprotection (Kirst et al., 1991), and prevention of cellular oxidation (Sunda et al., 2002). Two regimes of ocean DMS production are documented. A "bloom-driven" regime in eutrophic regions where the DMS concentrations are controlled by phytoplankton blooms (Stefels et al., 2007), and a "stress-driven" regime in oligotrophic open ocean regions, where DMS concentrations are highly correlated to UV radiation (Toole and Siegel, 2004), nutrient limitation (Stefels, 2000), in situ -temperatures (Karsten et al., 1996; van Rijssel and Gieskes, 2002), and -salinity (e.g. Kirst, 1996). Bacteria are also major contributors to DMS production. Part of the DMSP produced by algae is released

in the water where it is readily used by heterotrophic bacteria as carbon and sulfur sources (Kiene et al., 2000; Simó, 2001; Vila-Costa et al., 2006). The fraction of dissolved DMSP ($DMSP_d$) consumed by heterotrophic bacteria and cleaved into DMS (DMS yield) may vary depending on the microbial community composition, its sulfur requirements, and the availability of other reduced forms of sulfur (Kiene et al., 2000; Stefels et al., 2007). In addition to this pathway, a few studies have demonstrated the potential for reduction of dimethylsulfoxide (DMSO) by marine bacteria and phytoplankton as a source of DMS (e.g. Spiese et al., 2009; Asher et al., 2011). This metabolic pathway is however not ubiquitous among bacterial assemblages and may not be important quantitatively (Hatton et al., 2012; Hughes et al., 2014). Microbial consumption, photolysis and ventilation are the three sinks influencing the concentrations of DMS in surface mixed layers (Bates et al., 1994; Kieber et al., 1996; Simó and Pedrós-Alió, 1999b; del Valle et al. 2007, 2009).

Only two studies have specifically reported on DMS in melt ponds so far. They revealed concentrations ranging from 0.1 to 2.2 nmol l^{-1} in the high Arctic (Sharma et al., 1999), and as high as 250 nmol l^{-1} in Antarctic melt ponds (Asher et al., 2011). In the second study, bacterial DMSO reduction was identified as the main mechanism responsible for the high DMS concentrations. Although the key mechanisms responsible for the DMS measured in Arctic melt ponds has not been assessed so far, their reported colonization by micro-, nano- and pico-sized algae as well as bacteria (Bursa, 1963; Gradinger et al., 2005; Elliott et al., 2015) suggests that DMS in these melt ponds may also originate from algal and bacterial DMSP metabolism.

In this study, we report on the DMS concentrations in nine melt ponds located in the Eastern Canadian Arctic Archipelago (CAA), and on the prerequisites and processes responsible for the presence of this climate-active gas.

2 Materials and Methods

2.1 Study sites and environmental measurements

Nine melt ponds distributed between four stations located in Navy Board Inlet (Ice1 - MP1 and MP2 – 18 July), Barrow Strait (Ice2 - MP1 to MP3 – 20 July, and Ice3 - MP1 and MP2 – 21 July), and Resolute Passage (Ice4 - MP1 and MP2 – 23 July) were sampled during the joint NETCARE/ArcticNet research cruise conducted in 2014 on board the Canadian Coast Guard Ship (CCGS) *Amundsen* (Fig. 1). At each station, except Ice2, measurements of sea ice and snow thickness, along with sea-ice freeboard were conducted within a 3m distance of the melt ponds using a gauge (Kovacs Enterprise). Two ice cores for sea-ice temperature and salinity measurements were extracted using a 9cm core barrel (Kovacs Mark II) at every station where ice sampling was logistically possible. According to a widely used protocol (e.g. Rysgaard et al., 2007; Mundy et al., 2011; Galindo et al., 2015), sea-ice temperature was measured on site using a high-precision thermometer (Testo 720) in a hole drilled 5cm below the ice surface. For the determination of salinity of surface sea ice, a 10cm section was cut with a handsaw, stored in a plastic container, and allowed to melt at room temperature. A conductivity probe (Cond 330i, WTW) was used to determine the bulk salinity of melt water samples. Sea-ice porosity was constrained through the empirical

approach developed by Golden et al. (1998) where a threshold salinity of 5 psu typical of FYI corresponds to a critical temperature of approximately -5°C (known as the "rule of fives"). Due to logistical constraints, neither ice nor snow measurements were conducted at station Ice2.

Melt pond depth, length and width were determined using a graduated stick and a tape ruler. Melt pond water temperature was measured using a high precision thermometer (61220-601 digital data logger, VWR) and water salinity was measured using the conductivity probe mentioned above. For each sampling location, two to three members of the research team visually assessed the maximum pond fraction based on pictures taken from the bridge (see Fig. 1c for examples) and a mean value was calculated.

2.2 Phytoplankton biomass and enumeration, bacterial count

For Chlorophyll *a* (Chl *a*) quantification, 1000 ml to 1500 ml replicates of in situ pond water were filtered onto Whatman GF/F 25mm filters. Pigments were extracted in 90% acetone for 18h to 24h in the dark at 4°C (Parsons et al., 1984). Fluorescence of the extracted pigments was measured with a 10-005R Turner Designs fluorometer before and after acidification with 5% HCl. The fluorometer was calibrated with a commercially available Chl *a* standard (*Anacystis nidulans*, Sigma). Chl *a* concentrations were calculated using the equation provided by Holm-Hansen et al. (1965).

Microscopic identification and enumeration of eukaryotic cells >2µm was conducted in each melt ponds. Samples of 250 ml were collected and preserved with acidic Lugol solution (0.4% final concentration; Parsons et al. 1984), then stored in the dark at 4°C until analysis was conducted by inverted microscopy (Lund et al., 1958, Parsons et al., 1984). For each sample, a minimum of 400 cells (accuracy ± 10%) and three transects of 20mm were counted at a magnification of 400x. The main taxonomic references used to identify the eukaryotic cells were Tomas and Haste, (1997) and Throndsen et al. (2003).

The abundance of bacteria was determined by flow cytometry (Marie et al. 2005). Duplicate 4 ml subsamples were fixed with 20 µl of 25% glutaraldehyde Grade I (0.1% final concentration; Sigma-Aldrich G5882), stored in liquid nitrogen, and kept frozen at -80°C until analysis. Samples were analysed using a FACS Calibur FCB3 flow cytometer (Becton Dickinson).

2.3 DMS(P) sampling, conservation and analysis

Duplicate samples for total DMSP ($DMSP_t$), dissolved DMSP ($DMSP_d$) and DMS measurements were collected from the melt ponds using a submersible pump (Cyclone – Aquameric™) connected to a sealed Lead-Acid battery and fitted with LDPE tubing to fill the glass serum bottles. The serum bottles were temporarily sealed with a butyl cap and an aluminum lid, and kept in the dark in a cooler until analysis upon return to the ship. Analyses were performed using a purge and trap (PnT)

system coupled to a Varian™ 3800 gas chromatograph (GC), equipped with a Pulsed Flame Photometric Detector (PFPD). The analytical detection limit (d.l.) was 0.01 nmol l^{-1} for all sulfur compounds. The protocol is a modified version of the method of Leck and Bågander (1988) as described in Scarratt et al. (2000) and further revised in Lizotte et al. (2012). Briefly, DMS was stripped from liquid samples using helium gas (Praxair™ He, purity 99.999%) flowing at 50 ± 5 ml min^{-1} in the PnT system. One to 5 ml of sample was injected in the PnT. Five ml of MilliQ™ water were subsequently pushed into the system to completely flush the sample into the glass bubbling chamber. The outer walls of the bubbling chamber were heated at 70°C with a circulating bath. Humidity in the gas sample downstream of the bubbling step was minimized using a 4°C circulating bath to trigger condensation. A Nafion™ membrane separated the gas sample and He-carrier gas from a drying He counter-flow set at 100 ml min^{-1} to further desiccate the gas sample. Fluxes in the PnT system were monitored using a flowmeter (Varian™).

For $DMSP_t$ samples, 3.5 ml of melt pond water was collected in duplicate into a 5 ml Falcon™ tube, while $DMSP_d$ was quantified using the less disruptive Small-Volume gravity Drip Filtration (SVDF) method (Kiene and Slezak, 2006). Particulate DMSP ($DMSP_p$) concentrations were calculated by subtracting $DMSP_d$ from $DMSP_t$. DMSP samples were preserved with 50 µl of 50% sulfuric acid (H_2SO_4) to prevent DMSP transformation and remove pre-existing DMS (Kiene and Slezak, 2000). Samples were analysed using the same methods as described above for DMS samples, following mole-to-mole conversion of DMSP into DMS via NaOH (5 M) hydrolysis as described in Levasseur et al. (2006).

2.4 Process studies

In order to examine the pathways of in situ DMS production in melt ponds, three 24h incubation experiments were conducted with water from the first melt pond sampled (i.e. MP1s) at stations Ice1, Ice3, and Ice4. Water from the melt ponds was collected using the pump described in sect. 2.3, pooled in clean 5 gallon Coleman™ cooler jugs on site, and then transferred into gas-tight 3 l polyvinyl fluoride Tedlar™ bags. Light transmittance through the incubation bag material diminished with decreasing light wavelength. Between 99 to 92% of the photosynthetically active radiations (PAR, 700-400 nm) were transmitted through the bag material. Transmittances of Ultraviolet A radiations (UVA, 400-315 nm), and Ultraviolet B radiations (UVB, 315-290 nm) ranged between 92 to 82%, and 82 to 38%, respectively. The incubation bags were rinsed once with ~10% HCl, three times with fresh water, and twice with melt pond water to avoid contamination. The bags were custom-built and pre-closed on three sides (Dalian Delin Gas Packaging Co., Ltd.). After the addition of the melt pond water, the bags were sealed with Clip-n-seal™ Teflon closure devices. A valve was fitted to each bag to allow the removal of any remaining bubbles.

The samples were subjected to three duplicated treatments (total of 6 bags): 1) two bags of unaltered melt pond water incubated under natural light (control), 2) two bags amended with D6-DMSP and ^{13}C-DMSO (100 nmol l^{-1}, final concentration each) incubated under natural light (Light-DMSP/O or L-DMSP/O), and 3) two bags amended with D6-DMSP

and ^{13}C-DMSO (100 nmol l^{-1}, final concentration each) incubated in the dark (Dark-DMSP/O or D-DMSP/O). L- and D-DMSP/O bags were amended with ca. 100 µl of freshly thawed aliquots of two D6-DMSP and ^{13}C-DMSO stock solutions (high purity >99%, Sigma-Aldrich®). The high concentrations of isotopes added aimed to trigger a rapid biological response (i.e. potential DMS production rates) measurable during our 24h incubations. DMSP and DMSO uptake are not expected to be mutually exclusive and have been observed concomitantly both in live cultures (Spiese et al., 2009) and in situ (Asher et al., 2011).

Bags were incubated on the foredeck of the ship. The temperature was kept as near to in situ water temperature as possible by continuously flowing surface seawater in the incubator. The temperatures of the incubation water for Ice1-MP1, Ice3-MP1 and Ice4-MP1 were 1.29 ± 1.75°C, -0.28 ± 0.26°C, and -0.73 ± 0.09°C, respectively. These mean values were within 1°C of the in situ melt pond water temperatures (Table 2). $DMSP_t$, $DMSP_d$ and DMS concentrations were measured in duplicate every 6h during the incubation period as described above.

DMS production from DMSP cleavage and DMSO reduction were determined through GC/mass spectrometry (MS) analysis as an increase of D6-DMS and ^{13}C-DMS, respectively, in the L-DMSP/O and D-DMSP/O treatments. Discrimination by the microorganisms toward lighter (natural) isotopes of DMSP and DMSO is expected to be minimal (< 10%) according to Asher et al. (unpublished data). The observed rates of change in the concentration of DMS stable isotopes are thus assumed to be representative of the potential for DMS cycling in these melt ponds.

This experimental setup allows the measurement of the following rates over 6h and 24h : 1) net changes of in situ $DMSP_d$ and $DMSP_p$ in natural light derived from the difference of $DMSP_d$ and $DMSP_p$ concentrations versus time in the controls, respectively, 2) net in situ microbial DMS production in natural light derived from the regression slope of DMS versus time in the controls, 3) net potential $DMSP_d$ changes in natural light and in the dark derived from the regression slope of $DMSP_d$ versus time in L-DMSP/O and D-DMSP/O, 4) net potential DMS production rate in natural light and in the dark derived from the regression slope of DMS versus time in L-DMSP/O and D-DMSP/O. The daily rates were obtained from the slopes between final and initial concentrations over 24h. Our experimental setup also allows the estimation of the relative contribution of DMSP and DMSO to the production of DMS, using the discrimination of the different isotopes of DMS (see sect. 2.5).

2.5 DMS isotopic signatures

The discrimination of the different isotopic forms of DMS, including D6-DMS and ^{13}C-DMS stemming from D6-DMSP cleavage and ^{13}C-DMSO reduction, respectively, was performed using GC-MS analysis following purging as described hereafter. Two sets of DMS sample duplicates were taken for the incubation experiments. The first set of duplicates was measured directly on-board using the Varian™ 3800 GC described in sect. 2.2. The second set of DMS duplicates was preserved through cryo-trapping. Cryo-trapping of DMS was conducted using glass GC liners filled with Tenax-TA polymer

(high sulfur affinity) (Pio et al., 1996; Zemmelink et al., 2002; Pandey and Kim, 2009) kept at -80°C prior to their use, and maintained below -10°C during the 5 minute purging and trapping process. The Tenax-filled deactivated liners were mounted downstream of the PnT system described earlier. After gas extraction from the liquid samples, Tenax liners and their DMS content were wrapped individually in aluminum foil, placed in a Pyrex™ glass tube sealed with a Teflon lid, and returned to the -80°C freezer for several weeks until analysis on a land-based GC-MS.

Quantification of D6-DMS and ^{13}C-DMS was conducted via GC-MS analysis (6978 GC coupled to a 7000B Triple-Quad MS from Agilent). Mass spectra were collected both in full scan (m/z 45–100) and in selected ion monitoring (m/z 62, 63 and 68) modes. Final concentrations were calculated from standard curves using known concentrations of both unlabelled DMS and labelled DMS carrying the D6-DMS and ^{13}C-DMS signatures. The comparison between fresh DMS samples measured directly on-board during the NETCARE/ArcticNet campaign and cryo-preserved DMS samples shows excellent agreement between the two methods ($r^2 = 0.96$, Fig. 2).

2.6 Satellite data

Distances between stations Ice1 to Ice4 and the open ocean were assessed using scaled NASA's Earth Observing System Data and Information System (EOSDIS) imagery. Maps of the ice cover were accessed for the sampling dates in July 2014 through the MODIS (Terra/Aqua) Corrected Reflectance (True Color) layer combined with MODIS (Terra) Corrected Reflectance (Bands 3,6,7). These data are accessible in open source through the Global Imagery Browse Services (GIBS) (https://worldview.earthdata.nasa.gov). The imagery had a resolution of 250m on a daily scale.

2.7 Statistical analyses

Normality of the data was assessed using the Shapiro-Wilk test with a 0.05 significance level (R statistical software, R Core Team, 2016), which revealed that most variables were non-normally distributed. Non-parametric Spearman's rank correlation test (r_s) with a 0.05 significance level was used to assess correlation between key variables since normality could not be achieved uniformly through standard normalization methods. Model I linear regressions (r^2) were used to determine biological rates during the incubation experiments (Sokal and Rohlf, 1995). Student *t*-tests were performed to seek significant differences between the responses of the various treatments during the incubation with a 0.05 significance level.

3 Results

3.1 Ponded sea ice and snow properties

The physical characteristics of the sea ice surrounding the melt ponds are presented in Table 1. All the sampling sites were characterized by FYI, which was the predominant ice type of the region under study. Sea-ice thickness around the melt ponds of stations Ice1, Ice3 and Ice4 varied between 113 and 127cm at the different sites while freeboard varied between -1 and 10cm. In order to estimate the permeability of the ponded sea ice, ice temperature and salinity of the top 10cm of sea ice were measured within 5m distance of the melt ponds. Temperatures in the top 10cm of all the ice stations were stable at -0.2°C and the bulk salinity of the top 10 cm of the sea ice varied from 0 to 0.8 psu. Based on the "rule of five's", these temperature and salinity values suggest that the top sea ice was permeable around the melt ponds (Golden et al., 1998). Visual estimates of maximum pond fraction ranged from 30 to 60% (see Fig. 1c). The fraction of surface sea ice not covered with melt ponds was either bare or covered with refrozen snow.

3.2 Physical, chemical and biological characteristics of the melt pond water

The physical, chemical and biological characteristics of the water in the melt ponds are presented in Table 2. The mean depth of the individual melt ponds ranged from 7 to 29cm, with length and width varying between 1 and 25m. Melt pond water temperatures and salinities varied between 0.21 and 1.86°C and between 0.2 and 8.5 psu. Chl *a* concentrations were variable, ranging from 0.03 to 0.48 µg l^{-1} with a mean of 0.20 µg l^{-1}. The composition of the algal assemblages present in the melt ponds will be described in details in a companion paper but is summarized in Table 3. Briefly, the algal assemblages were dominated by unidentified flagellates, Baccillariophyceae (mostly sympagic pennate diatoms), and Chrysophyceae. Empty Baccillariophyceae frustules were abundant in all melt ponds. Abundance of heterotrophic bacteria with high nucleic acid content (HNA) varied between 0.02 and 0.24 × 10^9 cells l^{-1}.

In situ $DMSP_p$ and $DMSP_d$ concentrations ranged from 1.8 to 4.0 nmol l^{-1}, and from below d.l. to 1.4 nmol l^{-1}, respectively. Melt pond DMS concentrations ranged from below detection limit (d.l. < 0.01 nmol l^{-1}) to 6.1 nmol l^{-1} (Table 3). The relationships between DMS, salinity, temperature and Chl *a* in melt ponds are presented in Table 4. DMS concentrations significantly co-varied with salinity ($r_s = 0.84$, $p < 0.05$) and Chl *a* ($r_s = 0.84$, $p < 0.05$). None of the other variables measured displayed significant relationships between each other.

3.3 Dynamics/cycling of reduced sulfur compounds in Arctic melt ponds

Results from the Ice1-MP1 and Ice4-MP1 incubation experiments are presented in Fig. 3 (3a-b left and 3c-d right, respectively). Note that the results from the Ice3-MP1 experiments are not shown since $DMSP_d$ and DMS concentrations showed no variation during the 24h incubation period in the controls and in the amended treatments (see Discussion).

During the Ice1-MP1 incubation, initial $DMSP_d$ concentration was 1.30 nmol l^{-1} in the control and slightly increased to reach 5.3 nmol l^{-1} during the 24h incubation period (Fig. 3a). In the light (L-DMSP/O) and dark (D-DMSP/O) amended

treatments, $DMSP_d$ concentrations started at 102 nmol l^{-1}, decreased to ca. 35 nmol l^{-1} at T_6, and remained stable (dark treatments) or decreased to 10 nmol l^{-1} (light treatments) until T_{24} (Fig. 3a). Concentrations of DMS in the control of Ice1-MP1 started at 3.0 nmol l^{-1}, increased to 8.8 nmol l^{-1} between T_0 and T_6, and then decreased regularly to 4.2 nmol l^{-1} at T_{24} (Fig. 3b). The addition of labelled -DMSP and -DMSO stimulated DMS production. In the L-DMSP/O treatment, DMS concentrations increased to 12.6 nmol l^{-1} at T_6, remained at this level between T_6 and T_{12}, increased again between T_{12} and T_{18} and remained stable at ca. 19 nmol l^{-1} between T_{18} and T_{24} (Fig. 3b). DMS concentrations were consistently higher in the D-DMSP/O treatment than in L-DMSP/O (Fig. 3b). They first reached 15.6 nmol l^{-1} at T_6, increased gradually to reach a peak value of 24.2 nmol l^{-1} at T_{18}, and decreased slightly to 21.6 nmol l^{-1} at T_{24}. Note that dissolved DMSO was not measured during this study due to methodological issues.

In the Ice4-MP1 incubation, $DMSP_d$ concentrations started at 3.0 nmol l^{-1} in the control and remained close to this value during the whole experiment (Fig. 3c). In the L-DMSP/O and D-DMSP/O amended treatments, $DMSP_d$ concentrations started at 87 and 96 nmol l^{-1}, respectively. As observed in the previous melt pond, the concentrations decreased to ca. 45 nmol l^{-1} at T_6, and then slowly decreased to a value of ca. 30 nmol l^{-1} at T_{24} (Fig. 3c). DMS concentrations in the control of Ice1-MP1 started at 2.6 nmol l^{-1} and remained at this level during the 24h experiment (Fig. 3d). In the L-DMSP/O treatment, DMS concentrations increased more or less linearly from 2.6 nmol l^{-1} at T_0 to 6.7 nmol l^{-1} at T_{24}. In the D-DMSP/O treatment, the increase in DMS concentrations was steeper than in the light treatment, and a maximal value of 11.5 nmol l^{-1} was reached at T_{24}.

In situ and potential change rates of the sulfur compounds during the incubation experiments are presented in Tables 5 and 6, respectively. Changes in $DMSP_d$ and to a lesser extent DMS concentrations were generally not linear over the 24h incubation period, with more pronounced variations during the first 6h. To take into account this non-linearity, both hourly rates measured between T_0 - T_6 and T_6 - T_{24}, as well as daily rates (T_0 - T_{24}) are presented in these tables.

In Ice1-MP1, the concentrations of $DMSP_p$ in the control decreased at a rate of 2.2 nmol $l^{-1}d^{-1}$ (Table 5). We measured no change in $DMSP_d$ during the first 6h, but a positive net increase of 4.0 nmol l^{-1} over the full 24h incubation period was observed. In situ DMS changes show an increase rate of 1.0 nmol l^{-1} h^{-1} during the first 6h and of 1.2 nmol $l^{-1}d^{-1}$ over 24h. Potential net $DMSP_d$ change rates of - 11.6 and - 10.2 nmol l^{-1} h^{-1} were measured during the first 6h of incubation in L- and D-DMSP/O treatments, respectively (Table 6). These rates became - 1.2 and - 0.6 nmol l^{-1} h^{-1} between T_6 and T_{24} in L- and D-DMSP/O, respectively. Over 24h, negative potential net $DMSP_d$ change rates of ca. -91 nmol l^{-1} and -71 nmol l^{-1} for the L-DMSP/O and D-DMSP/O treatments were calculated. Positive potential net DMS change rates of 1.6 and 2.1 nmol l^{-1} h^{-1} were measured during the first 6h of incubation in L-DMSP/O and D-DMSP/O, respectively. For the complete 24h incubation, potential net DMS change rates reached 15.4 nmol l^{-1} d^{-1} in the light and 18.6 nmol l^{-1} d^{-1} in the dark.

In Ice4-MP1, in situ $DMSP_p$ decreased at a rate of 1.9 nmol $l^{-1} d^{-1}$ over the course of the incubation (Table 5). Meanwhile, in situ $DMSP_d$ changes rates were below the d.l. during the first 6h and almost null over 24h (Table 5). In situ DMS change rates were ca. zero after 6h, and below d.l. after 24h. Potential net $DMSP_d$ change rates of - 8.1 nmol l^{-1} h^{-1} were measured during the first 6h of incubation in both L- and D-DMSP/O (Table 6). These rates slowed down to -0.5 and - 0.9 nmol l^{-1} h^{-1} between T_6 and T_{24}, respectively. Over one day, average potential net $DMSP_d$ change rates of ca. - 59 nmol l^{-1} and -62 nmol l^{-1} were calculated for the L-DMSP/O and D-DMSP/O treatments. Potential net DMS change rates remained low in both L-DMSP/O and D-DMSP/O treatments during the first 6h of incubation with values at 0.1 and 0.3 nmol l^{-1} h^{-1}, respectively. For the complete 24h incubation, potential net DMS change rates in light and dark reached 4.2 and 8.9 nmol l^{-1} d^{-1}, respectively.

During these incubation experiments, the light treatment had no effect on the net changes in $DMSP_d$ but significantly impacted the net accumulation of DMS (Table 6). The accumulation of DMS over 24h in the L-DMSP/O treatments were consistently and significantly lower than in the corresponding D-DMSP/O treatments ($p < 0.05$) (Fig. 3b, d). Based on the difference between the L- and D-DMSP/O treatments after 24h, we estimated the light-associated DMS sinks at 3.2 nmol l^{-1} d^{-1} in Ice1-MP1 and at 4.7 nmol l^{-1} d^{-1} in Ice4-MP1 (Table 6).

3.4 Isotopic discrimination of DMS sources

Table 7 shows the concentrations of DMS isotopes (m/z 62) and (m/z 68) after 24h incubation in the three incubation treatments and their relative contribution (%) to the total DMS measured at T_{24}. As expected, 100% of the total DMS in the controls of these two experiments (3.0 nmol l^{-1} and 2.3 nmol l^{-1}) showed the isotopic signature of natural DMS (m/z 62). In the L-DMSP/O treatment of the Ice1-MP1 incubation, 78% (14.4 nmol l^{-1}) of the DMS measured at T_{24} derived from D6-DMSP additions (m/z 68), with the remaining 22% (4.1 nmol l^{-1}) being natural DMS (m/z 62) (Table 5). Similarly, 73% (18.2 nmol l^{-1}) of the DMS measured at T_{24} derived from D6-DMSP additions (m/z 68) in the D-DMSP/O treatment, with the remaining 27% (6.6 nmol l^{-1}) carrying the signature of natural DMS (m/z 62).

In Ice4-MP1, 80% (5.1 nmol l^{-1}) of the DMS measured at T_{24} in the L-DMSP/O treatment derived from the added D6-DMSP (m/z 68), with the remaining 20% (1.3 nmol l^{-1}) carrying the signature of natural DMS (m/z 62). For the D-DMSP/O treatment, 65% (7.9 nmol l^{-1}) of the DMS at T_{24} derived from the D6-DMSP addition (m/z 68) with 35% (4.2 nmol l^{-1}) originating from natural DMS. The absence of (m/z 63) DMS, regardless of the treatment, indicates that ^{13}C-DMSO reduction was not contributing to the production of DMS during these two experiments (m/z 63 not shown in Table 7). The match between the sum of DMS isotopes (m/z 62 and m/z 68) and the total fresh DMS concentration measured on board (Fig. 2) also confirms the absence of DMSO reduction during our experiments.

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4 Discussion

The study of DMS dynamics in melt ponds is in its infancy. Before this study, only two studies reported DMS concentrations in melt ponds, one in the Antarctic and the other one in the Arctic (Sharma et al., 1999, Asher et al., 2011). Maximum DMS concentrations reported by these two studies were vastly different, 2 nmol l^{-1} in the Arctic and 250 nmol l^{-1} in the Antarctic. Our current limited understanding of the mechanisms responsible for the cycling of DMS in melt ponds prevents the identification of the underlying causes of these differences. Results from this study show that DMS concentrations in Arctic melt ponds may be at least three times higher than the first Arctic measurements (up to 6 nmol l^{-1}) and that both physical and biological processes can contribute to the accumulation of this climate-active gas in these transient environments.

4.1 Physical controls of DMS concentrations in melt ponds

The strong relationship observed between DMS concentrations and salinity in the melt ponds sampled ($r_s = 0.84$, $p < 0.05$, Table 4) suggests that salinization processes may play a crucial role in the initial seeding of DMS (and probably DMS-producing microbial assemblages) and the resulting cycling of DMS within melt ponds. Three main mechanisms could be involved in the salinization of closed melt ponds: 1) deposition of sea spray from the ice margin/leads, 2) ice brine intrusion, and 3) seawater intrusion through porous/low freeboard sea ice. For the reasons explained below, seawater intrusion appears to be the most likely mechanism responsible for the salinization of the melt ponds during our study.

Sea spay probably did not contribute significantly to the salinization of the melt ponds during our study. The salinization of melt ponds could occur through sea spray deposition or seawater overflow during stormy events. Sea spray can transport salts over distances ranging from a few meters for the largest particles to a maximum distance of ca. 30 km for finer aerosols, depending on wind speed (McArdle and Liss, 1995). This requires favourable wind direction, a relative proximity of the melt ponds with open water areas, and as demonstrated hereafter regarding the melt ponds studied here, unrealistic volumes of sea spray. During our study, the average volume of the melt ponds was 8m³. We conservatively estimated that 19 to 367 litres of sea spay (assuming an average sea surface salinity of 33 psu) was required to increase melt pond salinity from zero to 0.2 psu or 8.5 psu, as measured during our study. Considering both the relatively large volume of sea spray required and the far-reaching distances (>15km, estimated from MODIS data) of the sampled melt ponds from open water at the time of sampling, sea spray was unlikely the main source of salt in the melt ponds studied.

Intrusion of sea-ice brine probably did not contribute significantly either to the salinization of the melt ponds. FYI undergoes desalinization through gravity drainage well before summer (Jardon et al., 2013). This major brine flushing process affecting the full depth of the ice occurs as soon as a temperature threshold dependent on bulk salinity and thickness is reached. This often predates the time when the threshold point defined by the “rule of fives” is reached (Golden et al., 1998). Considering that averaged bulk salinity of the upper part of the ice surrounding the melt ponds never exceeded

0.8 psu, we argue that full depth ice desalinization had already occurred at the station sampled and sea-ice brine enrichment of melt ponds is thus excluded as a significant salinization mechanism.

This leaves seawater intrusion through highly porous, low-freeboard sea ice as the main process responsible for bringing salts, microorganisms, and DMS in melt ponds. Melt ponds form and persist despite the high porosity of FYI due to the infiltration and subsequent freezing of freshwater into the pore structure of sea ice that prevents percolation drainage of pond meltwater (Polashenski et al., 2017). Later in the melt season, the decrease in sea-ice thickness directly translates into a loss of freeboard. Our data show that sea-ice freeboard was either low or negative near the melt ponds sampled (Table 1). The somewhat higher freeboard of 10cm at station Ice3 was highly influenced by the presence of refrozen snow on top of the sea ice. When the freeboard height approaches the melt pond depth, diffusive exchanges can occur between closed melt ponds and seawater. Additionally, full depth desalinization of the ice, as observed during our campaign, is associated with upward flushing of seawater (Hudier et al., 1995; Widell et al., 2006). This explanation is supported by the presence of both pelagic and sympagic algae in the microbial assemblages of the melt ponds, along with the similarity observed between algal species composition in the waters of the melt ponds and those beneath the ice (Charette et al., *personnal comm.*). The seeding of these seawater microorganisms into melt ponds may also affect the cycling of DMS as discussed in sect. 4.2.

4.2 Biological control of DMS production in melt ponds

4.2.1 Simulated in situ conditions

In addition to the physical mechanisms mentioned above, results from our incubation experiments show that biological production of DMS may take place in Arctic melt ponds under simulated in situ conditions, and to a higher extent following DMSP enrichment. A significant daily net DMS production of 1.2 nmol l^{-1} d^{-1} was measured without substrate addition in one of the three melt ponds tested, Ice1-MP1 (Table 5). The absence of net daily increase in DMS in the two other melt ponds tested does not necessarily preclude potential gross production since, as discussed below, this production could be balanced by microbial DMS uptake and photolysis. Such balance between DMS sources and sinks over a 24h period has been previously observed during incubation experiments conducted with Labrador Sea water (Wolfe et al., 1999). However, this explanation probably does not explain the absence of accumulation of DMS in the freshwater melt pond Ice3-MP1 since the addition of substrate failed to stimulate DMS production.

4.2.2 Source of DMS under substrate amended conditions

Bacterial $DMSP_d$ metabolism was the main mechanism underlying DMS production in the melt ponds tested. None of the DMS measured carried the (m/z 63) isotopic signature that would have indicated its ^{13}C-DMSO origin. The absence of DMSO reduction during our incubation contrasts with the results of Asher et al. (2011) who concluded that this process was the main pathway driving extremely high gross DMS production rates within sea-ice brines (up to 105 ± 24 nmol l^{-1} d^{-1}), as

well as high concentrations of DMS (250 nmol l^{-1}) in melt ponds in Antarctica. The absence of DMS production from ^{13}C-DMSO in the melt ponds in our study may reflect potential differences in microbial assemblages, as the metabolic ability to convert DMSO into DMS is not ubiquitous among bacterial communities (Hatton et al., 2012; Hughes et al., 2014). Discrepancies could also be linked to differences in the genesis of these melt ponds and how this affects inherent biological characteristics. In the Antarctic melt ponds studied by Asher et al. (2011), the high DMS concentrations may be linked to the over-flooding of sea ice. This process whereby the weight from large amounts of snow precipitations induces a temporary sinking down of sea ice is typical of the Southern Ocean (Drinkwater and Lytle, 1997; Morris and Jeffries, 2001), but seldom occurs in the Arctic. These over-flooding events may bring bacteria and phytoplankton at the snow-ice interface and eventually to the melt ponds when they form. Highly productive surface sea-ice assemblages or "freeboard layers" develop following these flooding events (Haas et al. 2001, Massom et al. 2001), with concentrations such that they cause sea-ice discoloration (Kattner et al., 2004). The extent of measurements precludes us to firmly conclude on the specific reasons of the absence of DMS production from ^{13}C-DMSO, which compels additional exploration.

4.2.3 Substrate limitation of microbial DMSP uptake and DMS production

The addition of DMSP had a strong stimulating effect on the bacterial uptake of DMSP and the resulting production of DMS in the two brackish melt ponds tested. In both Ice1-MP1 and Ice4-MP1, the response of the microbial assemblage to the addition of DMSP was rapid and strong (Fig. 3) as ca. half of the $DMSP_d$ added was consumed over the first 6h and potential net DMS production increased substantially.

In the amended treatments, changes in the $DMSP_d$ concentrations over time proceeded into two distinct phases during the incubation period (Figs. 3a-c). Irrespective of the light regime, the first phase (T_0 to T_6) was characterized by a rapid net decrease of $DMSP_d$ concentrations. Potential net $DMSP_d$ change rates of ca. -11 nmol l^{-1} h^{-1} in Ice1-MP1 and of -8.1 nmol l^{-1} h^{-1} in Ice4-MP1 (Table 6) were calculated. These estimates represent minimum rates since our calculation assumes a linear uptake during the first 6h. Even so, these rates already translate an extremely steep decrease of $DMSP_d$ in comparison with those of -0.01 to -0.2 nmol l^{-1} h^{-1} previously measured in the same region in the water column and under the ice cover in spring (Luce et al., 2011; Galindo et al., 2015). This difference most probably reflects the large amount of DMSP added in our experiments. The second phase of the incubation (from T_6 to T_{24}) shows an abrupt slowing down of the potential net $DMSP_d$ change rates, still slightly superior but closer to the range of in situ rates reported by the previous studies (Table 6). These results clearly show that an active microbial assemblage, predisposed to $DMSP_d$ consumption, inhabited the brackish melt ponds under study and that our DMSP amendments fulfilled their need in substrate.

The bi-phasic DMSP uptake dynamics observed in our experiment suggests that DMSP additions at least temporarily fulfilled the microbial requirement for this substrate. Phytoplankton biomass, and probably dissolved organic carbon, was low in the melt ponds. In this context of substrate limitation, rapid uptake of $DMSP_d$ was expected. Fast and transient intracellular accumulation of compatible solutes, such as DMSP, may serve as an adaptive strategy by microbial

cells to help cope with fluctuations of the surrounding environment, increasing their tolerance to osmotic and thermal stresses for example (Welsh et al. 2000). Such accumulations which could occur under replete conditions allow a so-called "luxury uptake" of compounds by microorganisms above their immediate requirements. Finally, the low HNA bacterial abundances measured in the melt ponds (Table 3) might explain the curtailing of $DMSP_d$ uptake measured after the initial rapid consumption.

Following $DMSP_d$ addition, the potential daily net DMS production rates varied between 4.2 and 18.6 nmol l^{-1} in the two brackish melt ponds tested (Table 6). As previously mentioned, it was only within the freshwater Ice3-MP1 melt pond that potential to process DMSP and produce DMS was not detected, even when substrate limitation was alleviated by $DMSP_d$ addition. These different in situ and potential DMSP metabolisms and DMS production rates suggest that de novo DMS production in melt ponds is triggered only once a threshold in microbial biomass is reached. In support of this hypothesis, Chl *a* concentration (0.05 µg l^{-1}) and bacterial abundance (0.02x x 10^9 cells l^{-1}) were extremely low in the unproductive freshwater Ice3-MP1: one order of magnitude lower than in the two productive brackish Ice1-MP1 and Ice4-MP1 (Table 3).

In contrast with the simulated in situ conditions, net potential DMS production in the amended treatments constantly exceeded DMS loss through photolysis and bacterial consumption, resulting in a net accumulation of DMS throughout the 24h of incubation (Fig. 3b, d). In spite of the atypically high DMSP level added, our $DMSP_d$ amendments could be considered as analogues of the $DMSP_d$ pulses that take place in the natural environment during the senescence phase of algal blooms, or under high viral attack and grazing pressure. These pulses are known to contribute to transient DMS build-up at lower latitudes (e.g. Malin et al., 1993; Locarnini et al., 1998; Scarratt et al., 2000). At high latitudes, the inhibitory effect of low temperature on microbial DMS consumption may even exacerbate these build-ups. For instance, temperatures below 2 °C were found to potentially inhibit DMS consumption rates in the Labrador Sea (Wolfe et al., 1999). The sensitivity of DMS microbial uptake to low temperature was proposed by Wolfe et al. (1999) as a potential driving mechanism responsible for the large pulses of DMS often measured in the Arctic environment. Cold and biologically active melt ponds may thus be prone to such DMS accumulation when the limitation in substrate is alleviated. However, our observations suggest that such events, that would require high biomass, may be rare in Arctic melt ponds.

4.4.4 Influence of light on DMSP bacterial metabolism

Light affected the accumulation of DMS in the DMSP/O amended melt ponds. The continuous light conditions prevailing during our incubation experiments reduced DMS accumulation in the L-DMSP/O treatments compared to the D-DMSP/O treatments by ca. 15% and up to 40% in Ice1-MP1 and Ice4-MP1, respectively (Figs. 3b, d). This negative effect of light was expected since photolysis is know as an important sink for DMS in the open ocean, sometimes as important as bacterial consumption in the near surface waters (Royer et al., 2016). However, removing light did not increase $DMSP_d$ removal rates (Fig. 3a, c). It should be pointed out that our incubation setup did not aim to reproduce the exact light field of the melt ponds

where light backscattering could considerably increase DMS loss by photolysis. The importance of light as a sink for DMS in melt ponds should be thoroughly investigated in future studies. Light-induced DMS losses may be particularly relevant in melt ponds since DMS ventilation, another important sink for DMS (absent from our incubation setup), is probably limited at least in small melt ponds where fetch is minimal.

5 Conclusion

Results from this study confirm the presence of DMS in Arctic melt ponds, with concentrations up to three times higher than those reported by the sole previous Arctic study. Salinization of melt ponds appears to be a prerequisite to the presence of DMS and its de novo biological production. Intrusion of seawater through porous sea ice and freeboard flooding seems to be a fundamental mechanism for bringing salt and DMS in the melt ponds as well as allowing the establishment of potential DMS-producing communities. Results from our incubation experiments reveal a modest but significant in situ net production of DMS in one of the melt ponds tested and show that melt ponds can host an active bacterial assemblage associated with rapid DMSP uptake when available and significant daily production of DMS. Freshwater ponds lacked the potential to produce DMS, further confirming the importance of the seawater intrusion mechanism in the biological cycling of DMS in melt ponds. In contrast with observations from Antarctic melt ponds, no DMSO to DMS reduction was detected in our study. We tentatively attribute this discrepancy to the presence of different bacterial clades and to the prevalence of 'over-flooding' in Antarctica, a process that seldom occurs in the Arctic and which can explain the high algal biomass seen in Antarctic melt ponds.

To this day, most climatologies assume the absence of DMS fluxes above ice-covered waters (e.g. Lana et al., 2011) even though DMS venting from snow-covered Antarctic MYI has already been observed in spring (Zemmelink et al., 2008). Arctic studies have also reported DMS exchanges above the ice-covered ocean, specifically highlighting the importance of particular zones such as open leads (Levasseur et al., 1994), cracks in sea ice, and melt ponds (Sharma et al., 1999; Mungall et al., 2016). Although estimation of the actual DMS flux from the melt ponds sampled here is beyond the scope of our study, based on our results, we argue that FYI melt ponds could represent a reservoir of DMS ranging from ca. 6 to 11 tons of sulfur in the Arctic during July-August available for potential flux. This estimate is based on the average melt pond DMS concentration of 2.1 nmol l^{-1} measured during this study, an average depth of 0.15 m, and the MODIS observations showing that the mean Arctic melt pond area reached ca. 1.5 x 10^6 km² between 2000 and 2011 (Rösel et al., 2012) with 40% to 70% of those melt ponds being on FYI. The estimation of the importance of melt ponds as net sources of DMS for the atmosphere will require an accurate evaluation of their spatial and temporal coverage, wind velocity, as well as a comprehensive measurement of DMS within melt ponds at large, both FYI and MYI, and particularly at higher latitudes.

How the strength of these DMS emissions from melt ponds will respond to changes in Arctic climate is still unknown. Both the spatial extent of melt ponds and their temporal span have increased over the last three decades in connection with regional climate alterations (Stroeve et al., 2014; Agarwal et al., 2011). Increased heat accumulation in

surface waters in summer cause delays in the September freeze-up (Rösel et al., 2012), while a trend in the earlier onset of melt significantly contributes to the lengthening of the melt period (Stroeve et al., 2014).

Data availability

Metadata are available on the Polar Data Catalog website at www.polardata.ca. Data are available on request by contacting the first author.

Authors contribution

Margaux Gourdal was responsible for the elaboration of the experimental design, the sampling process, the data analysis and processing, and the redaction of this paper. Several co-authors provided specific data included in the paper and all co-authors contributed to the final edition of the paper.

Competing interests

The authors declare that they have no conflict of interest.

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References

Agarwal, S., Moon, W., and Wettlaufer, J. S.: Decadal to seasonal variability of Arctic sea ice albedo, Geophys. Res. Lett., 38, L20504, doi:10.1029/2011GL049109, 2011.

Albrecht, B. A.: Aerosols, cloud microphysics, and fractional cloudiness, Science, 245(4923), 1227-1231,1989.

Asher, E. C., Dacey, J. W., Mills, M. M., Arrigo, K. R., and Tortell, P. D.: High concentrations and turnover rates of DMS, DMSP and DMSO in Antarctic sea ice, Geophys. Res. Lett., 38, L23609, doi: 10.1029/2011GL049712, 2011.

Bates, T. S., Kiene, R. P., Wolfe, G. V., Matrai, P. A., Chavez, F. P., Buck, K. R., Blomquist, B., W., and Cuhel, R. L., The cycling of sulfur in surface seawater of the northeast Pacific, J. of Geophys. Res.-Oceans, 99(C4), 7835-7843, 1994.

Browse, J., Carslaw, K. S., Arnold, S. R., Pringle, K., and Boucher, O.: The scavenging processes controlling the seasonal cycle in Arctic sulphate and black carbon aerosol, Atmos. Chem. Phys., 12, 6775–6798, doi:10.5194/acp-12-6775-2012, 2012.

Bursa, A.: Phytoplankton in coastal waters of the Arctic Ocean at Point Barrow, Alaska. Arctic, 16(4), 239-262, 1963.

Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G.W., Spracklen, D.V, Woodhouse, M.T., Regayre, L.A. and Pierce, J. R.: Large contribution of natural aerosols to uncertainty in indirect forcing. Nature, 503(7474), 67-71, 2013.

Chang, R. Y. W., Sjostedt, S. J., Pierce, J. R., Papakyriakou, T. N., Scarratt, M. G., Michaud, S., Levasseur, M., Leaitch, W. R. and Abbatt, J. P. D.: Relating atmospheric and oceanic DMS levels to particle nucleation events in the Canadian Arctic, J. Geophys. Res.-Atmos. 116(D00S03), doi, 10.1029/2011JD015926, 2011.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326(6114), 655-661, 1987.

Collins, D. B., Burkart, J., Chang, R. Y. W., Lizotte, M., Boivin-Rioux, A., Blais, M., Mungall, E., L., Boyer, M., Irish, V., E., Massé, G., Kunkel, D., Tremblay, J-É, Papakyriakou, T., Bertram, A., K., Bozem, H., Gosselin, M., Levasseur, M., Abbatt, J., P., D.: Frequent Ultrafine Particle Formation and Growth in the Canadian Arctic Marine Environment, Atmos. Chem. Phys. Discuss., doi.org/10.5194/acp-2017-411, 2017.

Croft, B., Martin, R. V., Leaitch, W. R., Tunved, P., Breider, T. J., D'Andrea, S. D. and Pierce, J. R.: Processes controlling the annual cycle of Arctic aerosol number and size distributions, Atmos. Chem. Phys., 16(6), 3665–3682, doi:10.5194/acp-16-3665-2016, 2016.

del Valle, D. A., Kieber, D. J., and Kiene, R. P.: Depth-dependent fate of biologically-consumed dimethylsulfide in the Sargasso Sea, Mar. Chem., 103(1), 197-208, 2007.

del Valle, D. A. D., Kieber, D. J., Toole, D. A., Brinkley, J., and Kiene, R. P.: Biological consumption of dimethylsulfide (DMS) and its importance in DMS dynamics in the Ross Sea, Antarctica, Limnol.and Oceanogr., 54(3), 785-798, 2009.

Dickson, D.M.J., Wyn Jones, R.G., and Davenport, J.: Steady state osmotic adaptation in Ulva lactuca. Planta, 150, 158-165, doi: 10.1007/BF00582360, 1980.

Drinkwater, M. R., and Lytle, V. I.: ERS 1 radar and field-observed characteristics of autumn freeze-up in the Weddell Sea, J. Geophys. Res.-Oceans., 102(C6), 12593-12608, doi:10.1029/97JC00437, 1997.

Ehn, J. K., Mundy, C. J., Barber, D. G., Hop, H., Rossnagel, A. and Stewart, J.: Impact of horizontal spreading on light propagation in melt pond covered seasonal sea ice in the Canadian Arctic, J. Geophys. Res., 116, C00G02, doi:10.1029/2010JC006908, 2011.

Eicken, H., Grenfell, T. C., Perovich, D. K., Richter-Menge, J. A., and Frey, K.: Hydraulic controls of summer Arctic pack ice albedo, J. Geophys. Res.-Oceans., 109, C08007, doi:10.1029/2003JC001989, 2004.

Elliott, A., Mundy, C. J., Gosselin, M., Poulin, M., Campbell, K., and Wang, F.: Spring production of mycosporine-like amino acids and other UV-absorbing compounds in sea ice-associated algae communities in the Canadian Arctic, Mar. Ecol. Prog. Ser., 541, 91-104, doi:10.3354/meps11540, 2015.

Fetterer, F. and Untersteiner, N.: Observations of melt ponds on Arctic sea ice, J. Geophys. Res.-Oceans., 103(C11), 24821-24835, doi: 10.1029/98JC02034, 1998.

Galindo, V., Levasseur, M., Scarratt, M., Mundy, C. J., Gosselin, M., Kiene, R. P., Gourdal, M. and Lizotte, M.: Under-ice microbial dimethylsulfoniopropionate metabolism during the melt period in the Canadian Arctic Archipelago, Mar. Ecol. Prog. Ser., 524, 39-53, doi:10.3354/meps11144, 2015.

Garrison, D. L., and Buck, K. R.: The biota of Antarctic pack ice in the Weddell Sea and Antarctic Peninsula regions, Polar Biol., 10(3), 211-219, 1989.

Golden, K. M., Ackley, S. F., and Lytle, V. I.: The percolation phase transition in sea ice, Science, 282(5397), 2238-2241. doi:10.1126/science.282.5397.2238, 1998.

Gradinger, R. R., Meiners, K., Plumley, G., Zhang, Q., and Bluhm, B. A.: Abundance and composition of the sea-ice meiofauna in off-shore pack ice of the Beaufort Gyre in summer 2002 and 2003, Polar Biol., 28(3), 171-181, doi: 10.1007/s00300-004-0674-5, 2005.

Giamarelou, M., Eleftheriadis, K., Nyeki, S., Tunved, P., Torseth, K., and Biskos, G.: Indirect evidence of the composition of nucleation mode atmospheric particles in the high Arctic, J. of Geophys. Res -Atmos., 121(2), 965-975, 2016.

Haas, C., Thomas, D. N., and Bareiss, J.: Surface properties and processes of perennial Antarctic sea ice in summer, J. Glaciol., 47(159), 613-625, 2001.

Hatton, A. D., Shenoy, D. M., Hart, M. C., Mogg, A., and Green, D. H.: Metabolism of DMSP, DMS and DMSO by the cultivable bacterial community associated with the DMSP-producing dinoflagellate Scrippsiella trochoidea, Biogeochemistry, 110(1-3), 131-146, doi: 10.1007/s10533-012-9702-7, 2012.

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., and Strickland, J. D.: Fluorometric determination of chlorophyll ICES, J. Mar. Sci., 30(1), 3-15, 1965.

Hudier E.J.-J., Ingram, R.G., and Shirasawa, K.: Upward flushing of sea water through first year ice, Atmos.-Ocean, 33(3), 569-580, doi: 10.1080/07055900.1995.9649545, 1965.

Hughes, R. N., Hughes, D. J., and Smith, I. P.: The CLAW hypothesis: a new perspective on the role of biogenic sulphur in the regulation of global climate, Oceanography and Marine Biology, An Annual Review, 52, 315-336, 2014.

Jardon, F. P., Vivier, F., Vancoppenolle, M., Lourenço, A., Bouruet-Aubertot, P., and Cuypers, Y. Full-depth desalination of warm sea ice, J. Geophys. Res.-Oceans., 118(1), 435-447, doi:10.1029/2012JC007962, 2013.

Karsten, U., Kück, K., Vogt, C., and Kirst, G. O. (Eds.): Dimethylsulfoniopropionate production in phototrophic organisms and its physiological functions as a cryoprotectant. In Biological and environmental chemistry of DMSP and related sulfonium compounds, Springer, New York, USA, 1996.

Kattner, G., Thomas, D. N., Haas, C., Kennedy, H., and Dieckmann, G. S.: Surface ice and gap layers in Antarctic sea ice: highly productive habitats, Mar. Eco. Prog. Series, 277, 1-12, 2004.

Kieber, D. J., J. Jiao, R. P. Kiene, and T. S. Bates: Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean, J. Geophys. Res., 101(C2), 3715–3722, doi:10.1029/95JC03624, 1996.

Kiene, R. P., Linn, L. J., and Bruton, J. A., New and important roles for DMSP in marine microbial communities, J. Sea Res., 43(3), 209-224, 2000.

Kiene, R. P., and Slezak, D.: Low dissolved DMSP concentrations in seawater revealed by small-volume gravity filtration and dialysis sampling, Limnol. and Oceanogr.: Methods, 4(4), 80-95, 2006.

Kirst, G. O., Thiel, C., Wolff, H., Nothnagel, J., Wanzek, M., and Ulmke, R.: Dimethylsulfoniopropionate (DMSP) in icealgae and its possible biological role, Mar. Chem., 35(1-4), 381-388, doi: 10.1016/S0304-4203(09)90030-5, 1991.

Kirst, G. O. (Eds): Osmotic adjustment in phytoplankton and macroalgae. In Biological and environmental chemistry of DMSP and related sulfonium compounds , Springer, New York, USA, 1996.

Lana, A., T. G. Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp, L., Saltzman, E. S., Stefels, J., Johnson, J. E. And Liss, P. S.: An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean, Global Biogeochem. Cy., 25, GB1004, doi:10.1029/2010GB003850, 2011.

Leck, C., and Bågander, L. E.: Determination of reduced sulfur compounds in aqueous solutions using gas chromatography-flame photometric detection, Anal. Chem., 60(17), 1680-1683, doi: 10.1021/ac00168a011, 1988.

Levasseur, M., Gosselin, M., and Michaud, S.: A new source of dimethylsulfide (DMS) for the arctic atmosphere: ice diatoms, Mar. Biol., 121(2), 381-387, 1994.

Levasseur, M., Scarratt, M. G., Michaud, S., Merzouk, A., Wong, C. S., Arychuk, M., Richrdson, W., Rivkin, R. B., Hale., M. Wong, E. Marchetti, A. and Kiyosawa, H.: DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast Pacific—Part I: Temporal and vertical distributions, Deep-Sea Res. Pt. II, 53(20), 2353-2369, 2006.

Lizotte, M., Levasseur, M., Michaud, S., Scarratt, M. G., Merzouk, A., Gosselin, M., and Kiene, R. P.: Macroscale patterns of the biological cycling of dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) in the Northwest Atlantic, Biogeochemistry, 110(1-3), 183-200, doi:10.1007/s10533-011-9698-4, 2012.

Locarnini, S. J. P., Turner, S. M., and Liss, P. S.: The distribution of dimethylsulfide, DMS, and dimethylsulfoniopropionate, DMSP, in waters off the Western Coast of Ireland. Cont, Shelf Res., 18(12), 1455-1473, 1998.

Luce, M., Levasseur, M., Scarratt, M. G., Michaud, S., Royer, S. J., Kiene, R., Lovejoy, C., Gosselin, M., Poulin, M. Gratton, Y. and Lizotte, M.: Distribution and microbial metabolism of dimethylsulfoniopropionate and dimethylsulfide during the 2007 Arctic ice minimum, J. Geophys. Res.-Oceans., 116(C00G06), doi:10.1029/2010JC006914, 2011.

Lund, J. W. G., Kipling, C., and Le Cren, E. D.: The inverted microscope method of estimating algal numbers and the statistical basis of estimations by counting, Hydrobiologia, 11(2), 143-170, 1958.

Lüthje, M., Feltham, D. L., Taylor, P. D., and Worster, M. G.: Modeling the summertime evolution of sea-ice melt ponds, J. Geophys. Res.-Oceans., 111(C02001), doi:10.1029/2004JC002818, 2006.

Malin, G., Turner, S., Liss, P., Holligan, P., and Harbour, D.: Dimethylsulphide and dimethylsulphoniopropionate in the Northeast Atlantic during the summer coccolithophore bloom, Deep-Sea Res. Pt. I, 40(7), 1487-1508, doi: 10.1016/0967-0637(93)90125-M , 1993.

Marie D, Simon N, Vaulot D (Eds.), Phytoplankton cell counting by flow cytometry. Andersen R., Algal culturing techniques, Academic Press, London, U.K., 2005.

Massom, R. A., Eicken, H., Hass, C., Jeffries, M. O., Drinkwater, M. R., Sturm, M., Worby, A. P., Wu, X, Lytle, I., Ushio, S., Morris, K., Reid, P.A., Warren, S. G., and Allison. I.: Snow on Antarctic sea ice, Rev. Geophys., 39(3), 413-445, 2001.

McArdle, N. C., and Liss, P. S.: Isotopes and atmospheric sulphur, Atmos. Environ., 29(18), 2553-2556, doi:10.1016/1352-2310(95)00188-5, 1995.

Morris, K., and Jeffries, M. O.: Seasonal contrasts in snow-cover characteristics on Ross Sea ice floes, Ann. Glaciol., 33(1), 61-68, 2001.

Mundy, C. J., Gosselin, M., Ehn, J. K., Belzile, C., Poulin, M., Alou, E., Roy, S., Hop, H., Lessard, S., Papakyriakou, T. N., Barber, D. G., Stewart, J., Characteristics of two distinct high-light acclimated algal communities during advanced stages of sea ice melt, Polar Biol., 34(12), 1869-1886, doi:10.1007/s00300-011-0998-x, 2011.

Mungall, E. L., Croft, B., Lizotte, M., Thomas, J. L., Murphy, J. G., Levasseur, M., Randall V. Martin R.V., Wentzell, J.J.B. , Liggio, J. and Abbatt, J. P.: Dimethyl sulfide in the summertime Arctic atmosphere: measurements and source sensitivity simulations, Atmos. Chem. Phys., 16(11), 6665-6680, 2016.

Niki, T., Kunugi, M., and Otsuki, A.: DMSP-lyase activity in five marine phytoplankton species: its potential importance in DMS production, Mar. Biol., 136(5), 759-764, 2000.

Pandey, S. K., and Kim, K. H.: A review of methods for the determination of reduced sulfur compounds (RSCs) in air. Environ. Sci. Technol.43(9), 3020-3029, doi:10.1021/es803272f, 2009.

Parsons, T. R., Maita, Y., and Lalli, C. M. (1984). A manual of biological and chemical methods for seawater analysis. Publ. Pergamon Press, Oxford.

Perovich, D. K., Richter-Menge, J. A., Jones, K. F., Light, B., Elder, B. C., Polashenski, C., Laroche, D., Markus, T. and Lindsay, R.: Arctic sea-ice melt in 2008 and the role of solar heating, Ann. Glaciol., 52(57), 355–359, doi:10.3189/172756411795931714, 2011.

Pio, C. A., Castro, L. M., Cerqueira, M. A., Santos, I. M., Belchior, F., and Salgueiro, M. L.: Source assessment of particulate air pollutants measured at the southwest European coast., Atmos. Environ., 30(19), 3309-3320. doi: 10.1016/1352-2310(96)00058-1, 1996.

Polashenski, C., Golden, K. M., Perovich, D. K., Skyllingstad, E., Arnsten, A., Stwertka, C., and Wright, N.: Percolation blockage: A process that enables melt pond formation on first year Arctic sea ice, J. of Geophys Res.-Oceans, 122(1), 413-440, 2017.

Rösel, A., and Kaleschke, L.: Exceptional melt pond occurrence in the years 2007 and 2011 on the Arctic sea ice revealed from MODIS satellite data., J. Geophys. Res.-Oceans., 117(C05018), doi: 10.1029/2011JC007869, 2012.

Royer, S. J., Galí, M., Mahajan, A. S., Ross, O. N., Pérez, G. L., Saltzman, E. S., and Simó, R.: A high-resolution time-depth view of dimethylsulphide cycling in the surface sea, Sci. Rep.-UK., 6, 32325, 2016.

Rysgaard, S., Glud, R. N., Sejr, M. K., Bendtsen, J., and Christensen, P. B.: Inorganic carbon transport during sea ice growth and decay: A carbon pump in polar seas, J. Geophys. Res.-Oceans., 112(C03016), doi: 10.1029/2006JC003572, 2007.

Scarratt, M. G., Levasseur, M., Schultes, S., Michaud, S., Cantin, G., Vezina, A., 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.

Sharma, S., Barrie, L.A., Plummer, D., McConnell, J.C., Brickell, P.C., Levasseur, M., Gosselin, M. and Bates, T.S.: Flux estimation of oceanic dimethyl sulfide around North America, J. Geophys. Res., 104, 21327-21342, 1999.

Simó, R.: Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links, Trends Ecol. Evol., 16(6), 287-294, 2001.

Simó, R., and Pedrós-Alió, C.: Role of vertical mixing in controlling the oceanic production of dimethyl sulphide, Nature 402:396–399, 1999a.

Simó, R., and Pedrós-Alió, C.: Short-term variability in the open ocean cycle of dimethylsulfide, Global Biogeochem. Cy., 13, 1173–1181, 1999b.

Sokal, R. R., and Rohlf, F. J. (Eds): Biometry: the principles and practice of statistics in biological research, WH Freeman and Co., New York, USA, 1995.

Spiese, C. E., Kieber, D. J., Nomura, C. T., and Kiene, R. P.: Reduction of dimethylsulfoxide to dimethylsulfide by marine phytoplankton, Limnol. and Oceanogr., 54(2), 560-570, 2009.

Stefels, J.: Physiological aspects of the production and conversion of DMSP in marine algae and higher plants, J. Sea Res., 43(3), 183-197, doi:10.1016/S1385-1101(00)00030-7, 2000.

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(1-3), 245-275, doi: 10.1007/s10533-007-9091-5, 2007.

Stroeve, J. C., Markus, T., Boisvert, L., Miller, J., and Barrett, A.: Changes in Arctic melt season and implications for sea ice loss, Geophys. Res. Lett., 41(4), 1216-1225, doi: 10.1002/2013GL058951, 2014.

Sunda, W. K. D. J., Kieber, D. J., Kiene, R. P., and Huntsman, S.: An antioxidant function for DMSP and DMS in marine algae, Nature, 418(6895), 317-320, 2002.

Throndsen, J., Hasle, G. R., and Tangen, K. (Eds.): Phytoplankton of Norwegian coastal waters, Almater Forlag AS, Oslo, Norway, 2003.

Tomas, C. R., and Haste, G. R. (Eds): Identifying marine phytoplankton, Academic Press, New York, USA, 1997.

Toole, D. A., and Siegel, D. A.: Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: Closing the loop, Geophys. Res. Lett., 31(9), doi:10.1029/2004GL01958, 2004.

Twomey, S.: Pollution and the planetary albedo, Atmos. Environ, 8(12), 1251-1256, doi:10.1016/0004-6981(74)90004-3, 1974.

Van Bergeijk, S. A., 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, Eur. J. Phycol., 38(4), 341-349, doi:10.1080/09670260310001612600, 2003.

Van Rijssel, M., and Gieskes, W. W. : Temperature, light, and the dimethylsulfoniopropionate (DMSP) content of Emiliania huxleyi (Prymnesiophyceae), J. Sea Res., 48(1), 17-27, 2002.

Vila-Costa, M., Simó, R., Harada, H., Gasol, J. M., Slezak, D., and Kiene, R. P., Dimethylsulfoniopropionate uptake by marine phytoplankton, Science, 314(5799), 652-654, doi: 10.1126/science.1131043, 2006.

Welsh, D. T.: Ecological significance of compatible solute accumulation by micro-organisms: from single cells to global climate, FEMS Microbiol. Rev., 24(3), 263-290, 2000.

Widell, K., Fer, I. and Haugan, P. M.: Salt release from warming sea ice, Geophys. Res. Lett., 33(L12501), doi:10.1029/2006GL026262, 2006.

Willis, M. D., Burkart, J., Thomas, J. L., Köllner, F., Schneider, J., Bozem, H., Hoor, P. M., Aliabadi, A. A., Schulz, H., Herber, A. B., Leaitch, W. R. and Abbatt, J. P. D.: Growth of nucleation mode particles in the summertime Arctic: a case study, Atmos. Chem. Phys., 16(12), 7663–7679, doi:10.5194/acp-16-7663-2016, 2016.

Wolfe, G. V., Levasseur, M., Cantin, G., and Michaud, S.: Microbial consumption and production of dimethyl sulfide (DMS) in the Labrador Sea, Aquat. Microb. Ecol., 18(2), 197-205, doi:10.3354/ame018197, 1999.

Zemmelink, H. J., Gieskes, W. W. C., Klaassen, W., De Groot, H. W., De Baar, H. J. W., Dacey, J. W. H., Hintsa E.J., and McGillis, W. R.: Simultaneous use of relaxed eddy accumulation and gradient flux techniques for the measurement of sea-to-air exchange of dimethyl sulphide, Atmos. Environ., 36(36), 5709-5717, doi:10.1016/S1352-2310(02)00577-0, 2002.

Zemmelink, H. J., Dacey, J. W., Houghton, L., Hintsa, E. J., and Liss, P. S.: Dimethylsulfide emissions over the multi-year ice of the western Weddell Sea, Geophys. Res. Lett., 35(6), 2008.

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Figure captions

Figure 1: (a) Regional map showing the location of the four sampling stations (Ice1 to Ice4) (red circles) during the NETCARE/ArcticNet 2014 campaign. (b) MODIS imagery above the four sampling station (red circles) showing the ice conditions on 18 July 2014 in the sampling area. (c) Left to right, pictures of stations Ice1, Ice2, Ice3, and Ice4.

Figure 2: Relationship between the concentrations of fresh DMS samples measured on board the ship via gas chromatography during the campaign and the concentrations of the corresponding preserved duplicate samples measured via coupled gas chromatography and mass spectrometry in a laboratory setting. The concentrations of the preserved DMS samples plotted are the sum of the three isotopes of DMS investigated in this study (m/z of 62, 63, and 68; see Materials and Methods).

Figure 3: Temporal variations in $DMSP_d$ (a, c), and DMS (b, d) concentrations during the Ice1-MP1 and Ice4-MP1 incubation experiments. Both light (○) and dark (●) treatments were initially amended with 100 nmol l^{-1} of both D6-DMSP and ^{13}C-DMSO. Control treatments (△) mimic natural concentration changes over time. In (a) and (c), vertical bars represent standard errors of mean values between duplicate samples.

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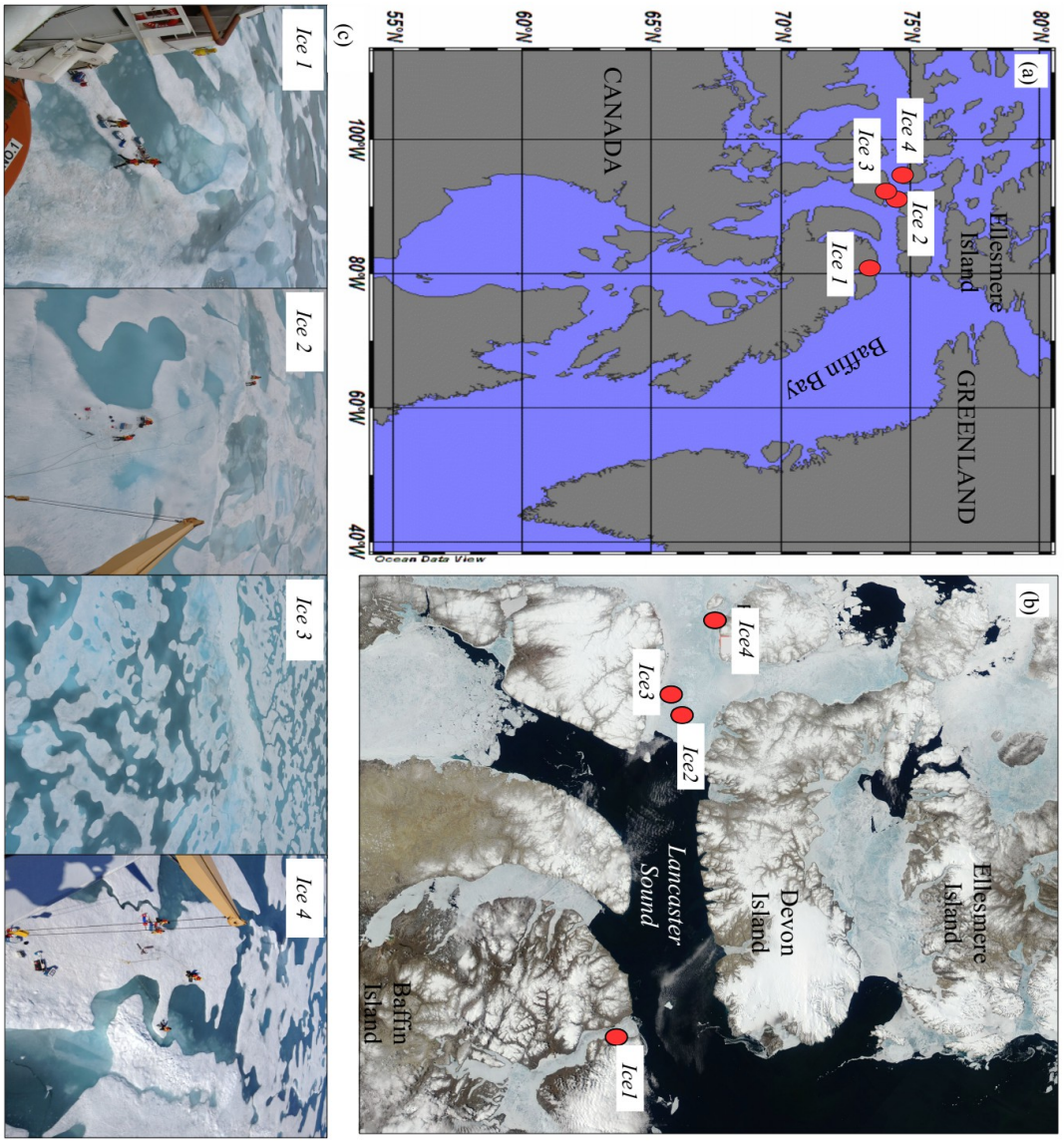

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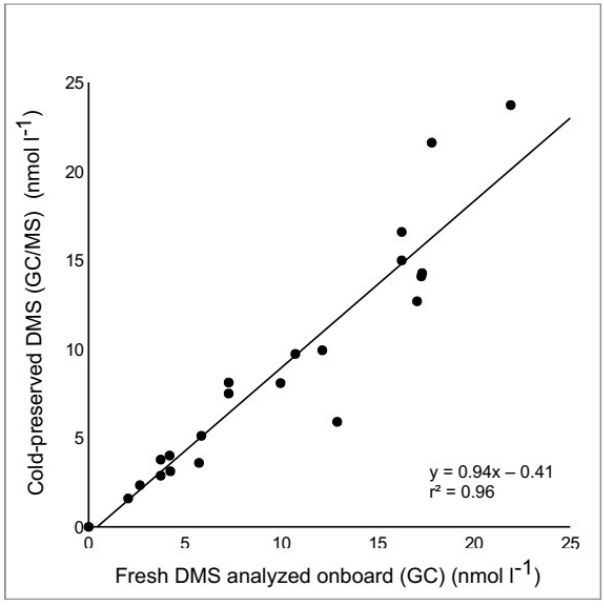

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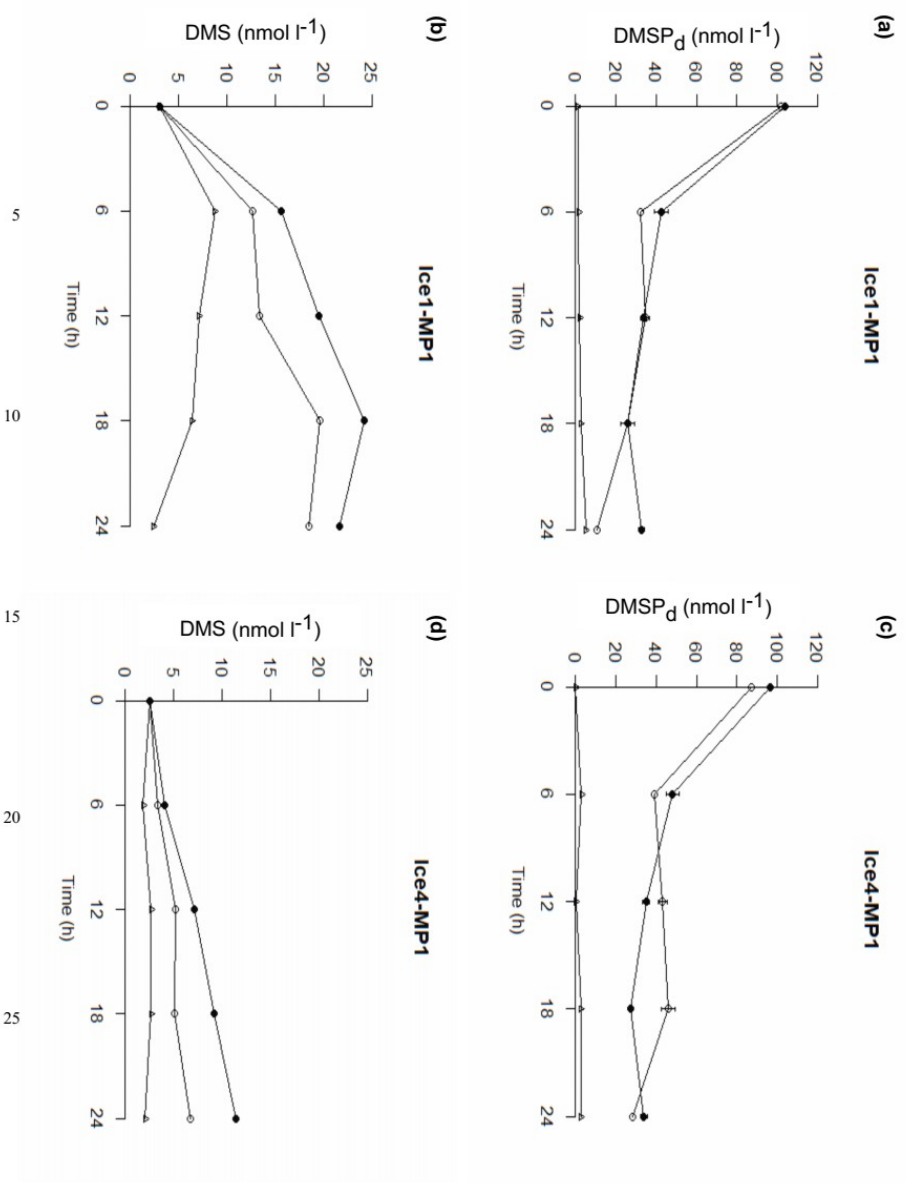

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Table 1: Physical characteristics of the sea ice surrounding the melt ponds. Note that only melt pond sampling (i.e. no ice sampling) was conducted at station Ice2 due to ship-related logistical constraints. A negative freeboard height indicates that the ice surface was locally below the mean sea level. n/a stands for non-available data.

Station	Sampling date	Snow and frozen snow* depth (cm)	Ice Thickness (cm)	Freeboard (cm)	Top 10 cm ice Temperature (°C)	Top 10 cm ice salinity (psu)	Melt pond coverage estimate (%)
Ice1	18 Jul 2014	0	121 ± 2	-1 ± 1	-0.2	0.4	60
Ice2	20 Jul 2014	0	n/a	n/a	n/a	n/a	40
Ice3	21 Jul 2014	0 + 7*	113 ± 7	10 ± 2	-0.2	0.0	50
Ice4	23 Jul 2014	0	127 ± 1	7 ± 4	-0.2	0.8	30

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Table 2: Physical, chemical and biological characteristics of the melt pond water. For melt pond depth, mean ± standard deviation values are presented.

Station	Melt pond #	Melt pond depth (cm)	Melt pond salinity (psu)	Melt pond Temperature (°C)
Ice1	MP1	18 ± 1	5.2	1.86
Ice1	MP2	18 ± 4	4.1	1.82
Ice2	MP1	29 ± 5	0.7	0.42
Ice2	MP2	19 ± 3	0.4	0.31
Ice2	MP3	12 ± 1	0.2	0.23
Ice3	MP1	7 ± 1	1.1	0.22
Ice3	MP2	10 ± 0	0.9	0.21
Ice4	MP1	12 ± 1	8.1	0.24
Ice4	MP2	11 ± 2	8.5	0.28

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Table 3: Reduced sulfur compound concentrations measured in situ in the melt ponds and the associated biological characteristics (abundance of high nucleic acid (HNA) bacteria, Chl *a* concentrations, and relative abundances of major taxonomic groups) of the melt pond water.

Station	Melt pond	*In situ* DMSPp (nmol l^{-1})	*In situ* DMSPd (nmol l^{-1})	*In situ* DMS (nmol l^{-1})	Abundance of bacteria (HNA) (x 10^9 cells l^{-1})	Chl *a* (µg l^{-1})	Total abundance of algae (x 10^6 cells l^{-1})	Dominant algal group
Ice1	MP1	2.2	1.3	3.0	0.24	0.48	2.00	Unidentified flagellates (50 %) Prasinophytes (ca. 25%)
	MP2	2.0	1.4	3.1		0.40		Unidentified flagellates (55 %) Prasinophytes (ca. 25 %)
Ice2	MP1	1.8	d.l.	d.l.	0.04	0.03	0.50	Unidentified flagellates (90 %) Pennate diatoms (ca. 28 %)
	MP2	2.4	d.l.	d.l.		0.09		Unidentified flagellates (50 %) Pennate diatoms (ca. 28 %)
	MP3	2.3	d.l.	d.l.		0.06		Unidentified flagellates (70 %) Pennate diatoms (ca. 28 %)
Ice3	MP1	2.0	d.l.	d.l.	0.02	0.05	0.30	Unidentified flagellates (45 %) Chrysophytes (29 %)
	MP2	2.3	d.l.	d.l.		0.04		Unidentified flagellates (55 %) Chrysophytes (23 %)
Ice4	MP1	4.0	d.l.	2.6	0.15	0.18	1.00	Unidentified flagellates (50 %) Pennate diatoms (20 %)
	MP2	3.7	1.1	6.1		0.20		Unidentified flagellates (60%) Pennate diatoms (25 %)

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Table 4: Spearman's rank correlation coefficients between key in situ variables measured in the melt ponds. * indicates a 0.05 significance level.

	DMS	Salinity	Temperature	Chl *a*
DMS		0.84*	0.51	0.84*
Salinity			0.40	0.56
Temperature				0.60

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Table 5: In situ $DMSP_p$, $DMSP_d$ and DMS change rates measured during the incubation experiments conducted in melt ponds Ice1-MP1 and Ice4-MP1. Hourly rates for $DMSP_d$ and DMS net changes measured between T_0 and T_6 as well as T_6 and T_{24} are derived from the slope of $DMSP_d$ and DMS concentrations vs. time, respectively. Daily $DMSP_d$ change rates are calculated as the difference between the $DMSP_d$ concentrations measured at T_{24} and T_0. Daily DMS change rates are calculated as the difference between the DMS concentrations measured at T_{24} and T_0. Rates measured over the first 6h and between T_6 and T_{24} are expressed in nmol l^{-1} h^{-1}. Other rates are expressed in nmol l^{-1} d^{-1}.

	In situ $DMSP_p$ change rates	In situ $DMSP_d$ change rates		In situ DMS change rates	
Station	(nmol l^{-1} d^{-1})	(nmol l^{-1} h^{-1}) (6h)	(nmol l^{-1} d^{-1})	(nmol l^{-1} h^{-1}) (6h)	(nmol l^{-1} d^{-1})
Ice1-MP1	-2.2	0.0	4.0	1.0	1.2
Ice 4-MP1	-1.9	0.0	-0.1	-0.1	0.0

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Table 6: Potential net $DMSP_d$ change rates, potential net DMS change rates and light-associated DMS sinks measured during the incubation experiments conducted in melt ponds Ice1-MP1 and Ice4-MP1. Clear and shaded horizontal lines regroup the rates measured under natural light (L-DMSP/O) and in the dark (D-DMSP/O), respectively. Hourly rates for potential $DMSP_d$ and DMS net changes between T_0 and T_6 as well as T_6 and T_{24} are derived from the slope of $DMSP_d$ and DMS concentrations vs. time, respectively. Daily potential net $DMSP_d$ change rates are calculated as the difference between the $DMSP_d$ concentrations measured at T_{24} and T_0. Daily potential net DMS change rates are calculated as the difference between the DMS concentrations measured at T_{24} and T_0. Rates of light-associated DMS sink were measured as the difference of DMS accumulation between L-DMSP/O and D-DMSP/O after the 24h incubation. Rates measured over the first 6h and between T_6 and T_{24} are expressed in nmol l^{-1} h^{-1}. Other rates are expressed in nmol l^{-1} d^{-1}.

	Potential net $DMSP_d$ change rates			Potential net DMS change rates		Light-associated DMS sinks
Station	(nmol l^{-1} h^{-1}) (T_0-T_6)	(nmol l^{-1} h^{-1}) (T_6-T_{24})	(nmol l^{-1} d^{-1})	(nmol l^{-1} h^{-1}) (T_0-T_6)	(nmol l^{-1} d^{-1})	(nmol l^{-1} d^{-1})
Ice1-MP1	-11.6	-1.2	-91.5	1.6	15.4	3.2
	-10.2	-0.6	-71.3	2.1	18.6	---
Ice 4-MP1	-8.1	-0.5	-59.2	0.1	4.2	4.7
	-8.1	-0.9	-62.6	0.3	8.9	---

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Table 7: (m/z 62) and (m/z 68) DMS concentrations after 24h incubation in the control, L-DMSP/O and D-DMSP/O treatments. Relative contribution (%) of natural DMS and D6-DMSP to the total DMS measured at T_{24} in the Control, L-DMSP/O and D-DMSP/O treatments during the incubation experiments with water from Ice1-MP1 and Ice4-MP1. Natural DMS signature = (m/z 62); signature of DMS derived from D6-DMSP = (m/z 68). No (m/z 63), which represents the signature of DMS derived from ^{13}C-DMSO, was retrieved either after 12 h (not shown) or 24h.

Incubation	Treatment	(m/z 62) DMS (nmol l^{-1})	(m/z 68) DMS (nmol l^{-1})	(m/z 62) % of total DMS	(m/z 68) % of total DMS
Ice1-MP1	Control	3.0	0.0	100	0
	L-DMSP/O	4.1	14.4	22	78
	D-DMSP/O	6.6	18.2	27	73
Ice4-MP1	Control	2.3	0.0	100	0
	L-DMSP/O	1.3	5.1	20	80
	D-DMSP/O	4.2	7.9	35	65