1 **Dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) cycling**

2 **across contrasting biological hotspots of the New Zealand Subtropical**

3 **Front**

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1 Abstract

The oceanic frontal region above the Chatham Rise east of New Zealand was investigated during the late austral summer season in February and March 2012. Despite its potential importance as a source of marine-originating and climate-relevant compounds, such as dimethylsulfide (DMS) and its algal precursor dimethylsulfoniopropionate (DMSP), little is known of the processes fuelling the reservoirs of these sulfur (S) compounds in the water masses bordering the Subtropical Front (STF). This study focused on two opposing short-term fates of DMSP-S following its uptake by microbial organisms: either its conversion into DMS, or its assimilation into bacterial biomass. Sampling took place in three phytoplankton blooms (B1, B2 and B3) with B1 and B3 occurring in relatively nitrate-rich, dinoflagellate-dominated Subantarctic waters, and B2 occurring in nitrate-poor Subtropical waters dominated by coccolithophores. Concentrations of total DMSP ($DMSP_t$) and DMS were high across the region, up to 160 nmol L^{-1} and 14.5 nmol L^{-1}, respectively. Pools of $DMSP_t$ showed a strong association with overall phytoplankton biomass proxied by chlorophyll a ($r_s = 0.83$) likely because of the persistent dominance of dinoflagellates and coccolithophores, both DMSP-rich taxa. Heterotrophic microbes displayed low S assimilation from DMSP (less than 5%) likely because their S requirements were fulfilled by high DMSP availability. Rates of bacterial protein synthesis were significantly correlated with concentrations of dissolved DMSP ($DMSP_d$, $r_s = 0.86$) as well as with the microbial conversion efficiency of $DMSP_d$ into DMS (DMS yield, $r_s = 0.84$). Estimates of the potential contribution of microbially-mediated rates of DMS production (0.1 - 27 nmol L^{-1} d^{-1}) to the near-surface concentrations of DMS suggest that bacteria alone could not have sustained DMS pools at most stations, indicating an important role for phytoplankton-mediated DMS production. The findings from this study provide crucial information on the distribution and cycling of DMS and DMSP in a critically under-sampled area of the global ocean, and they highlight the importance of oceanic fronts as hotspots of the production of marine biogenic S compounds.

2 Introduction

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69   In oceanic waters, the gas dimethylsulfide (DMS) is the predominant biogenic compound

70   contributing to the flux of sulfur (S) from the hydrosphere to the atmosphere (Bates et al.,

71   1992; Simó, 2001) with 17.6 to 34.4 Tg of S estimated to be transferred annually (Lana et

72   al., 2011). DMS has gained notoriety over several decades of research on the grounds of

73   its potential role linking ocean biology and the climate (Andreae et al., 1985; Charlson et

74   al., 1987; Lovelock et al., 1972), a role that is still under debate (Quinn et al., 2017;

75   Quinn and Bates, 2011). Produced through the enzymatic cleavage of its marine algae-

76   derived precursor, dimethylsulfoniopropionate (DMSP), DMS ventilates to the marine

77   atmospheric boundary layer (Liss et al., 1997) where it is oxidized, mainly by the

78   hydroxyl radical OH (Andreae and Crutzen, 1997). DMS oxidation products may

79   influence the atmospheric radiative budget via their role in aerosol properties and cloud

80   condensation as well as their contribution to a persistent stratospheric aerosol layer, or

81   Junge layer (Gondwe et al., 2003; Marandino et al., 2013). The significance of DMS-

82   derived particles in affecting the Earth's cloudiness and albedo is largely determined by

83   the relative importance of atmospheric DMS oxidation products compared to other

84   airborne particles originating from, for example, sea salts, dust and anthropogenic

85   pollutants (Quinn and Bates, 2011). As such, areas without significant dust or

86   anthropogenic particle inputs may offer productive grounds for new particle formation

87   emanating from DMS.

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89   Because DMS is of biogenic origin, factors controlling the distribution and productivity

90   of marine plankton play a large role in shaping DMS dynamics and standing stocks.

91   Oceanic frontal and convergence zones are regions of intense mesoscale turbulence

92   displaying enhanced levels of chlorophyll-a (Belkin et al., 2009) detectable from space

93   (Weeks and Shillington, 1996). The heightened biological activity in these regions (Llido

94   et al., 2005) is thought to lead to intensified carbon drawdown on seasonal timescales

95   (Metzl et al., 1999) as well as high concentrations of DMS (Holligan et al., 1987; Matrai

96   et al., 1996). These productive regions sometimes form unique biogeographic habitats of

97   their own such as the Subtropical Convergence province proposed by Longhurst (2007).

98   Nearly encircling the entire globe in a meridional band between 35-45°S, the Subtropical

99   Convergence, or hereafter termed the Subtropical Front (STF), spreads for the most part

100   across remote regions of the planet where anthropogenic sources of atmospheric

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103 compounds exert subordinate influence on local aerosol patterns compared to natural
104 sources. Modeling-based evidence suggests that cloud condensation nuclei seasonality is
105 driven mainly by DMS oxidation in this part of the ocean (Gondwe et al., 2003; Kloster
106 et al., 2006; Vallina et al., 2006). Episodic phytoplankton bloom events in the STF occur
107 mostly in austral spring-summer, with varying lifetimes of 8 to 60 days (Llido et al.,
108 2005). Upon reaching the Islands of New Zealand (NZ), the STF runs North along the
109 eastern continental shelf break over the Chatham Rise, a relatively shallow (250-350 m)
110 and productive seamount (Bradford‐Grieve et al., 1997; Sutton, 2001).

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112 While waters over Chatham Rise are recognized as biological hotspots (Rowden et al.,
113 2005) supporting large phytoplankton blooms visible from space (Sadeghi et al., 2012),
114 as well as accumulations of zooplankton and pelagic fish (Tracey et al., 2004), little is
115 known of their productivity in terms of climate-relevant gases such as DMS. The latest
116 DMS climatological exercise by Lana et al. (2011) shows that for the New Zealand
117 Coastal (NEWZ) province only 6 data points are available (together averaging less than
118 < 3 nmol DMS L^{-1}), with the temporal extent limited to the month of October. The
119 biological cycling of DMS in this region thus remains surprisingly under documented and
120 mainly restricted to the continental shelf of New Zealand's North Island (Walker et al.,
121 2000). The bordering ocean provinces comprised of the Subantarctic Water Ring (SANT)
122 and the South Subtropical Convergence (SSTC) have higher data coverage with greater
123 temporal resolution, displaying monthly averages of ca. 5 nmol DMS L^{-1} (December) and
124 ca. 10 nmol DMS L^{-1} (January), respectively. These results suggest that greater variation
125 in DMS concentration might be expected in the NEWZ province, a proposition confirmed
126 by a recent study showing DMS concentrations in surface waters over Chatham Rise
127 spanning an order of magnitude (from ca. 4 to 40 nmol L^{-1}, see Walker et al., 2016). It is
128 thus paramount to better constrain the factors that affect DMS concentrations in surface
129 waters above topographic plateaus and in oceanic convergence zones in view of the
130 potential for phytoplankton blooms in these biologically active systems.
131 Phytoplankton bloom dynamics, particularly their speciation and their growth phases,
132 from onset to senescence, are thought to play major roles in shaping the distribution of
133 DMS firstly through the variable biosynthesis of DMSP by different members of the
134 phytoplankton community (Keller, 1989; Matrai and Keller, 1994). DMSP production is

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135 a widespread process in phytoplankton but its magnitude varies substantially among taxa,

136 from non-detectable among certain cyanobacteria and diatoms, to considerable amounts

137 (up to 400 mmol DMSP L^{-1} of cell volume) within groups such as dinoflagellates and

138 prymnesiophytes (Keller, 1989). Furthermore, physicochemical conditions encountered

139 by algal populations in their environment, such as nutrient repletion or depletion, doses of

140 solar radiation, oxidative stresses, and modifications in salinity or temperature may also

141 impact the production of DMSP, as algal cells up- or down-regulate their production to

142 cope with these external pressures (Simó, 2001; Stefels et al., 2007; Sunda et al., 2002).

143 DMSP is released into the aqueous environment largely because of cell disruption

144 following aging, grazing or viral attack (Dacey and Wakeham, 1986; Turner et al., 1988)

145 and, to a lesser extent, by healthy algae via active exudation (Laroche et al., 1999). Some

146 non-DMSP producing algal species are thought to take up available dissolved DMSP

147 directly from the medium and assimilate sulfur from DMSP through a process yet to be

148 identified (Vila-Costa et al., 2006a).

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150 Beyond its role as the precursor of DMS, DMSP also holds global biogeochemical

151 significance as a prominent source of reduced S and carbon (C) for marine heterotrophic

152 microorganisms (Kiene et al., 2000; Simó and Dachs, 2002). Depending on bacterial

153 requirements for either S or C and the relative contribution of DMSP to the overall

154 oceanic S pool (Kiene et al. 2000; Levasseur et al 1996; Pinhassi et al. 2005), at least two

155 very different and competing outcomes are involved from the bacterial catabolism of

156 DMSP: one producing DMS, the potential climatic relevant gas, the other producing

157 methanethiol (MeSH), an important microbial substrate (Kiene and Linn, 2000b).

158 Another potential fate for DMSP is its transformation into dissolved non-volatile

159 degradation products (DNVS), including sulfate (SO_4^{2-}), however less is known of the

160 molecular pathways involved in this process (Kiene and Linn, 2000b; Reisch et al.,

161 2011). The relative importance of these competing pathways varies widely in nature and

162 the yield of DMS from $DMSP_d$ (moles of DMS produced from moles of DMSP

163 consumed) may vary from 2 to 100%. The factors controlling them, however, are still

164 poorly understood (Kiene et al., 2000; Simó and Pedrós-Alió, 1999). Bacterial production

165 of DMS is not the sole pathway bolstering reservoirs of DMS in marine waters: certain

166 species of autotrophic phytoplankton can also directly cleave DMSP into DMS. Although

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the particular enzymatic reactions that govern DMSP breakdown are not fully characterized (Todd et al., 2007), most reactions are attributed to DMSP lyases (Alcolombri et al., 2015; Schafer et al., 2010; Stefels et al., 2007). What controls the contribution of either process (autotrophic or heterotrophic DMSP to DMS conversion) in fuelling DMS stocks remains unclear but appears to vary extensively (Lizotte et al., 2012). While there are multiple sources of DMS, there are also multiple sinks, including bacterial consumption, sunlight oxidation and finally a small fraction ($< 10\%$) of the produced DMS may ventilate to the marine boundary layer (Malin, 1997) where its oxidation products, namely sulfate aerosol particles, can potentially influence the Earth's radiation budget directly through solar backscattering and indirectly by seeding brighter and longer-lived clouds (Albrecht, 1989; Ångström, 1962; Charlson et al., 1987; Twomey, 1977).

Gaining insight into how marine microorganisms influence the Earth's atmosphere and climate are topics of prime interest for the international scientific community and at the core of investigations implemented by the Surface Ocean Aerosol Production (SOAP) programme (Law et al. this issue). Under the auspices of SOAP, this study specifically explored two competing bacterial DMSP catabolic processes: (1) DMSP cleavage (Visscher et al., 1991; Yoch et al., 1997), a non S-assimilating pathway allowing bacteria to utilize the carbon contained in DMSP in the form of acrylate while the sulfur moiety is released as DMS (Kiene et al., 2000; Yoch, 2002); (2) DMSP demethylation/demethiolation (Taylor and Gilchrist, 1991; Taylor and Visscher, 1996), a S-assimilatory pathway leading to MeSH production, a portion of which is incorporated directly into methionine, and subsequently into proteins by marine bacteria (Kiene et al., 1999). The later pathway is thus linked to sulfur assimilation but also yields a methyl group that can be used as a carbon source (Kiene and Linn, 2000a; Yoch, 2002).

The present study was carried out during austral summer within three autotrophic blooms, each exhibiting varying phytoplankton assemblages and developmental stages, and sourced within the upper surface mixed layers of a section of the Subtropical Front over Chatham Rise east of New Zealand. To our knowledge, the results presented here are the first rate measurements made in the highly productive ocean region east of New Zealand,

198 and provide much needed information on the concentrations and cycling of DMS and
199 DMSP in connection to the "microbial maze" (Malin, 1997) in frontal zones.

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202 **3 Methodological approach**

203 *3.1 Oceanographic setting*

204 Large-scale remote sensing through MODIS (Aqua and Terra) and underway
205 instrumentation for Chl *a*, pCO_2, λ660 backscatter, and DMS were employed to detect
206 biologically productive areas near Mernoo Gap and the eastern end of Chatham Rise (see
207 Table 1 as well as Bell et al. (2015) and Law et al. (this issue) for further details on
208 voyage track, location map and biogeochemical characteristics of the sampling area).
209 Briefly, areas located between 43-45°S east of New Zealand were evaluated for relevant
210 bloom bio-indicators, and hotspots were marked by a drifting Spar Buoy for further
211 subsampling. Three distinct blooms were identified and each was followed during
212 relatively short (<10 days) Lagrangian-type surveys. Nomenclature used by Bell et al.,
213 (2015) and Law et al. (this issue) to describe these three sampling clusters, i.e. bloom 1,
214 bloom 2, and bloom 3 (hereafter referred to as clusters B1, B2 and B3) are also used in
215 this paper to simplify cross-referencing and data comparisons. The SOAP blooms were
216 coherent discrete areas of elevated ocean colour identified in satellite images
217 characterised by a maximum of 1 mg/m^3 chl *a* or higher. Sampling took place near the
218 center of these blooms but also at stations on the periphery and outside the blooms (Table
219 1), as defined by the distance from the bloom centre and clear demarcation in surface
220 biogeochemical variables (see Law et al., this issue)."

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222 Solar radiation dose (SRD in W m^{-2}) was calculated using Eq. (1):

$$\text{SRD} = \frac{I_0}{k \cdot \text{MLD}} \cdot \left(1 - e^{-k \cdot \text{MLD}}\right) \tag{1}$$

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224 where I_0 represents the daily-averaged irradiance of the 24 hours prior to sampling (in
225 W m^{-2}) measured using an Eppley Precision Spectral Pyronometer (285-2800 nm), k (in
226 m^{-1}) are estimates of vertical diffuse attenuation coefficients based on Photosynthetically
227 Active Radiation (PAR) offset between two depths (2 m and 10 m), MLD is the mixed

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228 layer depth defined as the point at which a 0.2°C difference from the sea surface
229 temperature occurred and was calculated according to Kara et al. (2000).

230 Ambient NO_3^- concentrations were measured using colorimetric detection by segmented
231 autoanalyser as described by (Law et al., 2011). Total chlorophyll *a* (Chl *a*: Whatman
232 glass fibre GF/F filtered) concentrations were determined using 90% acetone extraction
233 by the fluorometric technique with a Turner Design fluorometer after Strickland and
234 Parsons (1972). Bacterial samples were snap-frozen in liquid nitrogen (Lebaron et al.,
235 1998) and thawed immediately before counting by flow cytometry shortly after the cruise
236 following the methods described in Safi et al. (2007). Coccolithophore abundance in near
237 surface waters was determined using optical microscopy as described in Chang and
238 Northcote (2016). Dinoflagellate abundance was determined for surface waters (not for
239 near surface waters) and is not shown here.

240

241 *3.2 Microbial DMSP catabolism incubations*
242 Surface seawater samples were collected from a rigid-hulled inflatable boat away from
243 the ship, between 7h00 and 9h00 (NZST) in the morning, with a novel apparatus dubbed
244 "the sipper". The latter consists of a floating tubing array with peristaltic pump allowing
245 the sampling of the undisrupted first 1.6 m of the upper mixed layer waters (Walker et al.,
246 2016). Near surface water was collected in a 2-L HDPE bottle and subsampling of
247 variables (except for *in situ* DMS, see further details below) took place on the ship
248 typically within 1-2h of collection. As with most sampling procedures, potential
249 bottle/handling effects associated with the sipper-collection method cannot be completely
250 ruled out. When oceanographic conditions did not permit the deployment of the sipper
251 (higher swell and wind speeds $> 10 \text{ m s}^{-1}$), surface seawater samples were collected
252 directly from the ship with Niskin bottles mounted to a CTD rosette (water depth
253 corresponding to ca. 2 to 10 m on days of high wind speeds). Comparative studies
254 completed on surface seawater collected from both the sipper and the Niskin bottles
255 showed no significant differences in biological variables such as concentrations of DMS
256 (Walker et al., 2016). Water samples were passed gently through a 210 μm Nitex mesh
257 by gravity to remove large zooplankton.

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259   Following water collection, several types of incubation experiments were conducted

260   onboard the ship to investigate microbial DMSP uptake and metabolism. Using the [35]S-

261   DMSP$_d$ radiotracer approach we monitored and quantified several microbial pathways of

262   the degradation of DMSP$_d$ including the DMSP$_d$ loss rate constant (k$_{DMSPd}$, a measure of

263   the scavenging rate by bacteria of the substrate DMSP$_d$) following protocols described by

264   Kiene and Linn (2000b) and modifications by Slezak et al. (2007). In brief, water samples

265   were transferred into duplicate 71-mL dark HDPE Nalgene bottles and tracer amounts

266   (< 5 pmol L^{-1}) of ^{35}S-DMSP$_d$ were added to obtain a signal of ca. 1000 dpm mL^{-1}. Total

267   initial activity was first determined after gentle mixing of the bottles and subsampling of

268   1mL into a 10-mL scintillation vials containing 5 mL Ecolume[TM] liquid scintillation

269   cocktail. The bottles were then incubated for 3 h at *in situ* temperature during which time

270   1mL subsamples were taken after 0, 30, 60, and 180 min and transferred into 10-mL

271   scintillation vials containing 5 mL Ecolume[TM] in order to measure the loss of ^{35}S-DMSP$_d$

272   over time (the disappearance of ^{35}S-DMSP$_d$ representing the consumption of this pool).

273   The k$_{DMSPd}$ was then calculated as the slope of the natural log of the fraction of remaining

274   ^{35}S-DMSP$_d$ versus time. Blank abiotic controls were performed at the very beginning of

275   the incubation experiments as well as a second time at mid-cruise using 0.2 µm-filtered

276   seawater treated with ^{35}S-DMSP$_d$. Loss rates in the filtered controls were below 0.4 % of

277   those in live samples indicating that extracellular enzyme activity was not important in

278   DMSP$_d$ loss.

279

280   Determination of the DMSP$_d$-to-DMS conversion efficiency (DMS yield as measured by

281   the recovery of ^{35}S-DMSP$_d$ as ^{35}S-volatiles) was conducted via parallel 24-h incubations.

282   Tracer amounts (< 5 pmol L^{-1}) of ^{35}S-DMSP$_d$ were added to duplicate 71-mL dark HDPE

283   Nalgene bottles containing seawater samples in which unlabeled DMS was added at a

284   final concentration of 100 nmol L^{-1} to allow the determination of the gross ^{35}S-DMS

285   production. Initial total activity was monitored as described previously. The bottles were

286   incubated at *in situ* temperature for ca. 24-h, until > 90 % of the ^{35}S-DMSP$_d$ was

287   consumed (Slezak et al., 2007). Upon termination of the incubation, 5 mL of sample was

288   transferred into a 100-mL serum vial amended with; 0.1 mL sodium dodecyl sulfate

289   (SDS), and 200 nmol L^{-1} unlabeled DMSP$_d$ to prevent further uptake and degradation of

290   ^{35}S-DMSP$_d$, and 0.05 mL Ellman's reagent (to complex thiols such as methanethiol).

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298   Following the transfer of the samples into the serum vials, the bottles were quickly sealed
299   with a rubber stopper fitted with a well-cup holding a type A/E glass fiber filter soaked
300   with 0.2 mL stabilized H_2O_2 (3 %). The vials were set to trap the volatile ^{35}S on an orbital
301   shaker and stirred at 100 rpm for ca. 6 hours (Kiene and Linn, 2000b). After trapping
302   was complete, the filter wicks were removed and placed in Ecolume^{TM} scintillation fluid
303   for counting. ^{35}S activity on the filters was considered to be ^{35}S-DMS because the
304   Ellman's Reagent makes other sulfur gases (e.g. methanethiol) non-volatile. After the
305   volatiles were trapped, a new stopper with H_2O_2-soaked filter was placed in the vial.
306   Each vial was then injected with 0.2 mL NaOH (5N) through the stopper using a BD
307   precision guide needle to quantitatively cleave remaining ^{35}S-DMSP$_d$ into ^{35}S-DMS (a
308   pool known as the unconsumed ^{35}S-DMSP$_d$). The ^{35}S-DMS was trapped as described
309   above. The DMS yield was calculated from the fraction of added ^{35}S recovered as ^{35}S-
310   DMS in the live incubation divided by the fraction of ^{35}S-DMSP consumed during the
311   incubation.
312
313   To estimate the incorporation of ^{35}S-DMSP$_d$ into macromolecules (sulfur assimilation
314   efficiency), duplicate 5-mL subsamples were also taken from the previous 24-h
315   incubation bottles and gently filtered by manual pumping through a 0.2 µm Nylon filter
316   and then rinsed with trichloroacetic acid (TCA) as described in (Kiene and Linn, 2000b).
317   The filters were placed in 10-mL scintillation vials containing 5 mL Ecolume^{TM} and the
318   radioactivity remaining on TCA-rinsed filters was later quantified by liquid scintillation
319   counting. Finally, each ^{35}S pool measurement was expressed as a fraction of the initial
320   amount of added ^{35}S-DMSP$_d$ as previously described. The measurement of the above
321   variables allowed us to estimate DMSP$_d$ loss rate constants (k_{DMSPd}), rates of gross DMS
322   production from DMSP$_d$ by multiplying values of k_{DMSPd} with *in situ* DMSP$_d$
323   concentration and DMS yield. The microbial transformation rates of DMSP$_d$ measured
324   during these incubations are considered to stem mostly from bacterial processes however
325   phytoplankton-related processes cannot be totally excluded as low DMSP-producing
326   phytoplankton and picophytoplankton have been shown to assimilate DMSP$_d$-sulfur
327   (Malmstrom et al., 2005; Ruiz-González et al., 2011; Vila-Costa et al., 2006b).
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Bacterial biomass production rates were measured by the incorporation of ^{3}H-leucine into TCA-insoluble. Samples were incubated in the dark for 4 h in sterile test tubes, at ambient water temperatures and processed using standard protocols (Simon and Azam, 1989) The average CV of [^{3}H]-leucine incorporation rates for triplicate samples was ca. 10%. Rates of bacterial biomass production (μg of C L^{-1} d^{-1}) were estimated by using a ratio of cellular carbon to protein in bacterial cells of 0.86 (Simon and Azam, 1989). Analysis of all radioactive samples (^{35}S and ^{3}H) was conducted in NIWA-Hamilton (NZ) on a Packard Tricarb liquid scintillation counter immediately following the end of the cruise.

It has been suggested that light history and differential doses of solar radiation may impact the growth and activity of bacteria (Herndl et al., 1993) and potentially the fate of dissolved DMSP in seawater (Ruiz-González et al., 2012a; Slezak et al., 2001, 2007; Toole et al., 2006). To evaluate this, we exposed near surface communities to different light histories for 6 hours prior to ^{35}S-DMSP$_d$ enriched bioassays: ambient variable light (using quartz bottles in deck board incubators) or acclimation to darkness (using dark HDPE Nalgene bottles). Rates were thus obtained during post-exposure dark incubations (as explained above) conducted after 6 h pre-incubations at ambient light or in the dark. Because the communities were sourced in near-surface waters during daylight hours, the incubations conducted in quartz bottles are thought to be representative of the natural and variable light experienced by these biological communities at the surface of the ocean. On the whole, the light conditions (dark and ambient) at which the cells were pre-acclimated for 6 h had no significant effect on the ^{35}S-DMSP$_d$ metabolic rates measured. This result contrasts with findings from earlier studies (such as Galí et al., 2011; Ruiz-González et al., 2012a; Slezak et al., 2001, 2007; Toole et al., 2006) and could be related to a number of variables such as the timing and depth of sampling, the type of bacterial assemblages present and their previous light-history, as well as the different temporal and spatial scales at which exposure to solar radiation varies (Ruiz-González et al., 2013). Because of these wide-ranging and intricate light-bacteria interactions, natural solar radiation is believed to play a significant, yet challenging to predict, role in modulating bacterial dynamics and biogeochemical functions (Ruiz-González et al., 2013). In the current study, the sulfur-related metabolic activities of the marine biota sourced in the

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362 morning (between ca. 7h00 and 9h00; Table 1) from the highly irradiated near surface
363 waters may have persisted in the dark within the time period of experimental pre-
364 exposure (6 h), however the lack of information on the phylogeny of bacterial groups
365 present, for example, hampers a more detailed discussion. We therefore present rate
366 measurements made in dark-incubated samples that had been pre-exposed to ambient
367 light conditions for 6 h.

368 *3.3 Concentrations of S-compounds*
369 Duplicate samples of *in situ* dissolved DMSP ($DMSP_d$) and total DMSP
370 ($DMSP_t = DMSP_p + DMSP_d$) were collected on board the ship using the non-perturbing
371 Small-Volume gravity Drip Filtration (SVDF) procedure (Kiene and Slezak, 2006). For
372 $DMSP_d$ samples, ca. 25 mL of seawater were gravity filtered onto GF/F and the first
373 3.5 mL of samples were kept in 5-mL falcon tubes amended with 50 µL 50% H_2SO_4 and
374 maintained in the dark at 4°C. For $DMSP_t$, 3.5 mL of unfiltered water sample were
375 transferred directly into 5-mL falcon tubes and treated the same way as $DMSP_d$ samples.
376 Subsequent analysis took place at Laval University (Canada) through alkali treatment to
377 cleave DMSP into DMS, purging, cryotrapping and sulfur-specific gas chromatography
378 (GC, see Lizotte et al. (2012)). Duplicate *in situ* DMS samples were collected directly
379 from the sipper or the niskin bottles by overflowing two volumes of seawater in 150 mL
380 crimp-top glass bottles and were analysed onboard the ship within less than 5 h of
381 collection following methods described in detail by Walker et al. (2016). Briefly,
382 calibrated volumes (5 mL) of seawater samples were purged with zero-grade nitrogen
383 (99.9 % pure) and gas-phase DMS was cryogenically concentrated on 60/80 Tenax TA in
384 a stainless steel trap maintained at -20ºC via a cold finger connected to a cryo-cooling
385 unit, then thermally desorbed at 100 ºC for analysis by GC coupled with sulfur
386 chemiluminescent detection. DMS samples were also collected in 23-mL serum vials at
387 T0 and T6 during 6-h incubation experiments conducted in quartz bottles on the deck of
388 the ship (at *in-situ* light and temperature conditions) and processed as described above.

389 *3.4 Statistical analysis*
390 Statistical analyses were carried out using the Systat statistical software for Windows
391 version 12.0, and Microsoft Office Excel for Mac 2011. Normality in data distribution
392 was determined using Kolmogorov-Smirnov tests, following which Model II linear

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393   regressions and Spearman Rank Correlation coefficients were used to evaluate the
394   relationships between variables (Legendre and Legendre, 1998; Sokal and Rohlf, 1995)
395   Paired Student t-tests provided hypothesis assessments of the difference between
396   treatments.
397
398   Considering the various environmental conditions encountered during the SOAP voyage,
399   our dataset relied on the use of two different seawater collection approaches: the sipper
400   method (Walker et al., 2016) and the more standard use of Niskin bottles mounted on a
401   CTD rosette when periods of higher wind speeds and greater sea state prevented the
402   deployment of the sipper sampling equipment. Using a Wilcoxon signed-ranks test for
403   paired samples with non-parametric distributions, Walker et al. (2016) showed that no
404   significant differences ($p = 1$, $\alpha = 0.5$) were detected between samples of DMS collected
405   via the sipper method and those collected using Niskin bottles. This result, along with the
406   presence of well-mixed surface waters (MLD ranging from 14 to 40 m, Table 1) justified
407   the pooling of measurements made in the surface waters resulting from the two
408   approaches presented in the current study.
409
410   **4 Results**
411   *4.1 Environmental setting and biogeochemical background*
412   Broad scale use of ocean colour images coupled to a suite of underway sensors allowed
413   the successful location of three distinct blooms with varying signatures of phytoplankton
414   speciation and biogeochemical backgrounds (see Fig. 1, as well as (Bell et al., 2015) and
415   Law et al. (this issue) for further details on location of blooms and map of the cruise
416   track). A few general characteristics of the surface waters within sampled blooms are
417   presented in Table 1 to provide and overview of the oceanographic context for the 9
418   stations specifically sampled in this study (see Law et al. (this issue) for more detailed
419   description of the study area).
420
421   A first cluster of three stations was sampled between February 15th and 19th inside (sta. 1-
422   2) and north of (sta. 3) B1 (Fig. 1). Located in a region exhibiting Subantarctic-type
423   waters, B1 was characterized by the dominance of dinoflagellates (ca. 53% of total C
424   biomass) with *Gymnodinium* spp being responsible for an overall average of 30% of the

13

425   total dinoflagellate C biomass (Table 1). Stations 1, 2 and 3 sampled in B1 displayed an

426   average temperature of 14.2^{o}C, surface concentrations of nitrate (NO_3^-) ranging between

427   3.25 and 6.36 µmol L^{-1} (mean 5.16 µmol L^{-1}), and concentrations of chl *a* varying from

428   0.91 to 1.41 µg L^{-1} (mean 1.1 µg L^{-1}). Bacterial abundance ranged from 0.43 to 1.06 x10^9

429   cells L^{-1}.

430

431   The cruise track then extended further east near the Chatham Islands to capture a

432   coccolithophore-dominated bloom (ca. 41% of total C biomass) located in Subtropical

433   waters. In this area, a second cluster of three stations was sampled between February 22nd

434   and 26th with stations 4 and 5 inside B2 and station 6 located south of B2. Temperatures

435   in surface waters were slightly warmer (mean 15.8^{o}C) than stations in B1. Stations 4 to 6

436   exhibited low stocks of NO_3^- ranging from 0.04 to 1.32 µmol L^{-1} (mean 0.5 µmol L^{-1})

437   while near-surface concentrations of chl *a* varied between 0.53 and 1.53 µg L^{-1} (mean

438   0.91 µg L^{-1}). Bacterial abundance varied between 0.59 and 1.19 x10^9 cells L^{-1} throughout

439   the B2 sampling stations.

440

441   After sampling B2, the cruise path returned to the west near the first cluster of stations

442   sampled within Subantarctic-dominated waters. This third cluster, referred to as B3

443   (stations 7-9), was sampled during February 28th and March 5th. Stations in B3 were

444   characterized by an initial mixed phytoplankton population consisting of

445   coccolithophores, small flagellates and dinoflagellates (B3A, Table 1) that progressively

446   favoured coccolithophore biomass towards the end of the sampling period (B3B). Surface

447   temperatures were the lowest measured during the study with a cluster average of 13.6^{o}C.

448   Surface water concentrations of NO_3^- at stations 7 to 9 ranged from 2.21 to 5.28 µmol L^{-1}

449   (mean of 3.63 µmol L^{-1}) and concentrations of chl *a* varied between 0.39 to 0.97 µg L^{-1}

450   (mean 0.59 µg L^{-1}). Bacterial abundances were 0.34 and 0.51 x10^9 cells L^{-1} at stations 8

451   and 9, respectively (no data is available for sta. 7, Table 1).

452

453   A transition towards deeper mixed layer depths from cluster B1 to B2 to B3 was apparent

454   during the sampling period; with cluster average MLD's of 15 ± 1 m, 28 ± 9 m, 37 ± 5 m,

455   respectively (Table 1). Trends in daily-averaged irradiance generally exhibited a decrease

456   between clusters with averages ranging from 263 ± 14 (W m^{-2}) in B1, to 251 ± 30 (W m$^-$

457 ^{2}) in B2, and finally to 192 ± 15 (W m^{-2}) in B3 (Table 1). Patterns of Solar Radiation

458 Dose (SRD) were very similar to those of daily-averaged irradiance showing a decreasing

459 trend from the first cluster towards the last cluster sampled.

460

461 *4.2 Reservoirs of sulfur compounds across sampling clusters*

462 *In situ* sea surface reservoirs of DMSP$_t$ displayed a 5-fold span across the study region

463 (Fig. 2a). Highest DMSP$_t$ concentrations were observed in B1, with values ranging from

464 118 to 160 nmol L^{-1} (Fig. 2a). It is also within B1 that highest DMSP$_p$: chl *a* ratios

465 occurred, with a range of 89 to 141 nmol μg^{-1} (Table 1). Stations sampled within B2

466 exhibited intermediate DMSP$_t$ pools varying from 45 to 97 nmol L^{-1} and ratios of

467 DMSP$_p$: chl *a* that ranged from 51 to 90 nmol μg^{-1} (Table 1). Surface water DMSP$_t$

468 concentrations within B3 were generally lower; being below 37 nmol L^{-1} (sta. 7-8) but

469 DMSP$_t$ concentration reached 92 nmol L^{-1} in the last station (sta. 9). Despite marked

470 differences in concentrations of DMSP$_t$ between stations 7-8 and station 9, ratios of

471 DMSP$_p$: chl *a* were similar within this third cluster (range of 61 to 91 nmol μg^{-1}, Table 1)

472 owing to the high chl *a* concentration measured at station 9.

473

474 Patterns of DMSP$_d$ were broadly similar to those observed for DMSP$_t$ albeit higher

475 variability was evident from the 18-fold difference measured between highest and lowest

476 concentrations (Fig. 2b). Surface seawater within sampling cluster B1 had very high

477 concentrations of DMSP$_d$ varying between 14 and 32 nmol L^{-1}. Stations sampled in B2

478 presented DMSP$_d$ concentrations ranging between 3 and 18 nmol L^{-1}. DMSP$_d$

479 concentrations were below 3 nmol L^{-1} at stations 7-8 while DMSP$_d$ was 10 nmol L^{-1} at

480 station 9.

481

482 Concentrations of near-surface DMS also showed high variability with a 14-fold spread

483 within the stations sampled (Fig. 2c). Some of the highest values of DMS were measured

484 in sampling cluster B1 with concentrations varying between 4.9 and 14.5 nmol DMS L^{-1}.

485 Stations 4 to 6, within the most easterly of the sampling clusters (B2) had DMS

486 concentrations ranging from 1 to 6.9 nmol L^{-1}, while stations 7-9 in B3 had a range of

487 DMS concentrations from 4.8 to 10.5 nmol L^{-1}.

488

15

489 *4.3 Microbial uptake and transformation of sulfur compounds*

490 The ^{35}S-DMSP$_d$ loss rate constant (k$_{DMSPd}$; Fig. 3a) varied between 0.4 and 3.4 d^{-1}, with

491 the exception of a higher value of 19.9 d^{-1} measured in the B2 cluster at station 5. The

492 sulfur assimilatory metabolism of ^{35}S-DMSP$_d$, expressed as the percentage of ^{35}S-DMSP$_d$

493 incorporated into macromolecules (Fig. 3b), ranged from 1 to 4.2% across all stations.

494 Rates of bacterial carbon production, measured as the incorporation of ^{3}H-Leucine into

495 macromolecules, showed 5-fold variability throughout the three sampling clusters,

496 ranging from 0.27 to 1.46 nmol C L^{-1} d^{-1}.

497

498 Yields of DMS from dissolved DMSP, determined as the fraction of consumed DMSP$_d$

499 converted into DMS, ranged from 4 to 17% (Fig. 4a), with lowest and highest yields

500 found within the same cluster (B3) at stations 8 and 9, respectively. The average DMS

501 yield in clusters B1 and B2 were very similar at 12.1% and 12.7%, respectively. The

502 production of DMS from DMSP$_d$, determined as the product of DMS yields and DMSP$_d$

503 consumption rates, varied by more than two orders of magnitude across the sampling area

504 (Fig. 4b). Lowest DMS production rates from DMSP$_d$ were measured in the third

505 sampling cluster (B3) where values remained below 0.7 nmol L^{-1} d^{-1}. A wide-ranging set

506 of gross DMS production from DMSP$_d$ was estimated within B2 with 0.25 to 27 nmol L^{-1}

507 d^{-1}. Variability of DMS production from DMSP$_d$ within cluster B1 was lower, with rates

508 varying between 3.2 and 6.2 nmol L^{-1} d^{-1}.

509

510 **5 Discussion**

511 *5.1 Bloom dynamics in the Subtropical Front*

512 The Subtropical convergence region under study was characterized by overall high

513 standing stocks of both autotrophic biomass (proxied by phytoplankton C and chl *a*) and

514 biogenic sulfur compounds (Table 1; Fig. 2a-c). The frontal zone over Chatham Rise is

515 known for its high productivity (Bradford‐Grieve et al., 1997; Sutton, 2001), fostering

516 extensive phytoplankton blooms visible from space (Sadeghi et al., 2012). Plankton

517 bloom dynamics are known to play a crucial role in influencing reservoirs and driving

518 fluxes of biogenic DMSP and DMS (Simó, 2001; Stefels et al., 2007). As evidenced by

519 the patterns in nutrients and chl *a*, the cruise track crossed paths with blooms in various

520 developmental stages in contrasting water masses. Overall quasi-depletion of silicate

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524   standing stocks was evident from the < 0.6 µmol L^{-1} values detected in all stations

525   investigated in the study region (except for sta. 6 with 1.2 µmol silicate L^{-1}). Nitrate

526   concentrations found in B1 and B3 averaged 5.2 ± 1.7 µmol L^{-1} and 3.6 ± 1.5 µmol L^{-1},

527   respectively. These nutrient signatures are a common feature of Subantarctic waters to the

528   South of the STF displaying depletion of silicates relative to nitrate (Sarmiento et al.,

529   2004). Concentrations of chl a in B1 (mean 1.1 ± 0.3 µg L^{-1}) were found to be higher than

530   a threshold concentration of 0.7 µg L^{-1} used as a criterion to distinguish regions of local

531   biomass enrichment at the Subtropical Convergence (Llido et al. 2005). These results

532   coupled to the high regional phytoplankton-associated C biomass (61 µg L^{-1}) and the low

533   regional $pCO2$ minimum (260 µatm) measured in this cluster (Table1) suggests that B1

534   was productive and fuelled by ample nitrate reservoirs at the time of sampling. After

535   being away for 7 days, the cruise track returned to the Subantarctic-type waters near B1

536   on February 28th to sample the B3 cluster stations. At that time, the physicochemical and

537   biological signatures in B3 (sta. 7-9) differed slightly from those of B1 and displayed

538   higher regional $pCO2$ minimum (305 µatm), two-fold lower mean phytoplankton C

539   biomass (28 µg L^{-1}), and lower chl a concentrations at stations 7 and 8 (ca. 0.4 µg L^{-1}),

540   but comparable at station 9 (1 µg L^{-1}). Overall these results suggest that phytoplankton

541   biomass was lower in response to lower nutrient reservoirs and possibly greater grazing

542   pressure in B3, although specific information on zooplankton activity is not available.

543   The second cluster of stations (B2) was geographically distant from the two others (B1

544   and B3, Fig.1b) and had characteristics of slightly warmer Subtropical waters (Table 1).

545   Regionally, this study area displayed the highest pCO_2 but had similar mean

546   phytoplankton-associated C biomass (32 µg L^{-1}) to B3. Regional maximum chl a (max of

547   1.5 µg L^-1) and nitrate levels (cluster average of 0.5 ± 0.7 µmol L^-1) were the lowest

548   among the blooms investigated. These low nutrient features are thought to be typical of

549   Subtropical waters North of the Subtropical front which are also known to display

550   stronger vertical stratification (Llido et al., 2005). Small-celled phytoplankton (< 5µm)

551   are known to typically develop blooms that exhibit low chl a concentrations (< 2 µg L^{-1},

552   (Holligan et al., 1993)). Such is the case for the common and globally dominant bloom-

553   forming coccolithophore *Emiliania huxleyi* (Paasche, 2001) that typically has low

17

554 intracellular levels of chl *a* (< 0.4 pg chl *a* per cell, (Daniels et al., 2014)), and which
555 dominated the community (Law et al. this issue) during this study.

556

557 *5.2 Relating bloom dynamics with concentrations of reduced S-compounds*

558 Despite differences in phytoplankton dominance within blooms (Table 1), pools of
559 $DMSP_t$ measured in this study showed a strong association with overall phytoplankton
560 biomass as suggested by the positive correlation observed between $DMSP_t$ and chl *a*
561 (r_s= 0.83, p < 0.01, n = 9, Table 2). A type II linear regression model suggests that 59%
562 of the variance in pools of $DMSP_t$ can be explained by the variability in stocks of chl *a*
563 (Fig. 5a) while the strength of the relationship between $DMSP_p$ and chl *a* is also strong
564 (r^2 = 0.57, data not shown). Establishing a strong relationship between DMSP and
565 phytoplankton biomass has historically met with limited success (Bürgermeister et al.,
566 1990; Townsend and Keller, 1996; Turner et al., 1988). The main reason for this being
567 that concentrations of DMSP are generally related to the presence of specific DMSP-rich
568 phytoplankton species rather than to overall phytoplankton biomass, which is often
569 dominated by large DMSP-poor diatoms (Lizotte et al., 2012; Stefels et al., 2007). In this
570 study, concentrations of DMSP co-varied significantly with phytoplankton biomass
571 because of the persistent dominance of dinoflagellates and coccolithophores, both DMSP-
572 rich taxa, within the three blooms investigated.

573

574 Unlike the strong correlation found with $DMSP_t$, no significant relationships were
575 detected between DMS and phytoplankton biomass (chl *a*) in our study, as reported in
576 Bell et al. (2015). The lack of strong relationship between DMS and chl *a* is likely due to
577 many biological and physical processes involved in its production and overturning
578 (Dacey et al., 1998; Van Duyl et al., 1998; Kettle et al., 1999; Kwint and Kramer, 1996;
579 Leck et al., 1990; Scarratt et al., 2002; Simó and Pedrós-Alió, 1999; Stefels et al., 1995;
580 Steinke et al., 2000; Turner et al., 1988). Several studies have established links between
581 environmental forcings, such as the surface mixed layer depth and the irradiance regime,
582 and their role in driving surface DMS concentrations (Lana et al., 2012; Lizotte et al.,
583 2012; Miles et al., 2009, 2012; Vallina and Simó, 2007). The associations between DMS
584 and mixed layer depth (MLD) as well as between DMS and daily-averaged irradiance

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585 were not found to be statistically significant within the limited dataset available in this

586 study ($p = 0.86$ and $p = 0.54$, respectively). Solar radiation dose (SRD) standardized over

587 mixed MLD was not found to improve the significance of the association between DMS

588 and irradiance regime. Because the spectral attenuation of solar radiation in oceanic

589 waters varies rapidly with depth and in association with the constituents within seawater

590 (Doron et al., 2007), it cannot be excluded that differences in sampling depth (sipper

591 versus niskin) may have obscured links between DMS and light. Heterogeneity in

592 sampling times (Table 1) could also have resulted in differences in light history

593 experienced by the DMS-producing communities. Nonetheless, DMS reservoirs and

594 those of its precursor DMSP were found to be abundant in the three blooming clusters as

595 discussed in the next section.

596

597 *5.3 High concentrations of S-compounds in Subtropical Frontal surface waters*

598 In this study, concentrations of $DMSP_t$ reached 110 to 160 nmol L^{-1} in the first cluster, in

599 association with a bloom characterized by elevated concentrations of DMS (regionally up

600 to 20 nmol L^{-1}) and dominated by dinoflagellates, a diverse phytoplankton group known

601 for its prolific DMSP-producers (Belviso et al., 1990; Keller, 1989; Turner et al., 1988).

602 Few comparative DMSP datasets are available for waters near New Zealand, however the

603 current $DMSP_t$ concentrations are two to three times higher than the highest DMSP value

604 (52 nmol L^{-1}) reported for three open-water transects conducted between 49-76°S latitude

605 within the New Zealand sector of the Southern Ocean during austral spring (Kiene et al.,

606 2007). Species of *Gymnodinium* spp., the dominant dinoflagellate taxon in B1, have been

607 found to contain potentially high cytosolic DMSP (up to 244 pg DMSP/cell; (Keller,

608 1989)) that could have significantly contributed to the elevated reservoirs of $DMSP_t$

609 observed in these Subantarctic-type waters. A previous study conducted in waters of the

610 Subtropical Convergence Zone (40-45°S) South of Australia had demonstrated a link

611 between relatively high concentrations of DMSP (up to ca. 55 nmol L^{-1}) and

612 dinoflagellate biomass as well as with low microzooplankton grazing rates (Jones et al.,

613 1998). Gaps in the specific information concerning dinoflagellate abundance in our

614 sampling stations (Table 1) prevented any attempt at relating this DMSP-rich group with

615 overall *in situ* DMSP concentrations.

616

19

617 The second bloom investigated was dominated by coccolithophores and had $DMSP_t$
618 concentrations ranging from 45 to 96 nmol L^{-1} at stations 4 to 6. *Emiliania huxleyi*, a
619 species exhibiting high intracellular DMSP (Franklin et al., 2010; Liu et al., 2014) and
620 the dominant coccolithophore in this study (Law et al, this volume), has been shown to
621 represent a major component of extensive coccolithophore blooms in New Zealand's
622 coastal waters (Chang and Northcote, 2016; Rhodes et al., 1994). Maximal
623 coccolithophore cell densities (up to 21.1 x10^6 cells L^{-1}) reached in the second bloom are
624 4 to 5-fold higher than maximal cell densities reached in coccolithophore blooms in the
625 North Atlantic during summer: maximum of ca. 5.5 x10^6 cells L^{-1} (Matrai and Keller,
626 1993) and maximum of 4.0 x10^6 cells L^{-1} (Malin et al., 1993) and associated with very
627 high levels of $DMSP_t$ (> 400 nmol L^{-1}). While the $DMSP_t$ concentrations were high in
628 B2, even higher concentrations might have been expected given the high coccolithophore
629 cell abundances. Variations in cell-specific DMSP quotas, nutrient and physiological
630 statuses of the phytoplankton communities, as well as grazing pressure (Stefels et al.,
631 2007) could explain these differences. *Emiliania huxleyi* is found to dominate
632 phytoplankton community composition in both bloom and non-bloom conditions in this
633 STF region (Chang and Northcote, 2016), suggesting that these relatively high summer
634 DMSP features could extend over a larger region which encircles the entire Southern
635 Ocean during austral summer in a band dubbed the "Great Calcite Belt" (Balch et al.,
636 2011).
637
638 The third and last bloom sampled (B3) was characterized by a mixed phytoplankton
639 population with high abundances of both dinoflagellates and coccolithophores. Although
640 no data for coccolithophore abundance was available at station 9, samples collected in
641 surface waters the day before (March 4th) displayed coccolithophore abundance of
642 20.3 x 10^6 cells L^{-1} suggesting a transition towards a coccolithophore-dominated
643 assemblage at the end of the sampling period. Concentrations of $DMSP_t$ (29-37 nmol L^{-1})
644 were lower at stations 7-8 and increased to 93 nmol L^{-1} at station 9, likely reflecting this
645 phytoplankton community shift. Pools of particulate DMSP ($DMSP_p = DMSP_t - DMSP_d$)
646 ranged from 26 to 83 nmol L^{-1} in cluster B3 and were similar to measurements of $DMSP_p$
647 (ca. 28 to 40 nmol L^{-1}) made in waters surrounding an iron enrichment patch during the
648 SAGE experiment conducted in Subantarctic waters south-east of New Zealand during

20

649   the months of March and April (Archer et al., 2011). These results suggest that relatively

650   high concentrations of DMSP may persist in the STF zone well into the autumnal season,

651   which begins in mid-March in the Southern Hemisphere.

652

653   Cluster averages of DMS concentrations in this study were higher than historical data

654   represented in the latest DMS climatologies for the New Zealand (NEWZ) province (< 3

655   nmol L^{-1}, n = 6, Lana et al. (2011)). Clusters B1, B2 and B3 displayed average (n = 3 for

656   each cluster) near-surface concentrations of 9.5 ± 4.8, 3.6 ± 3.0, and 7.0 ± 3.1 nmol DMS

657   L^{-1}, respectively (Fig. 2c). These results underscore the fact that coverage in the previous

658   climatological data likely did not capture all the productive hydrographic and seasonal

659   features of this region. While many studies have reported on chl a enhancement across

660   frontal regions of the oceans, only a few studies have described regional increases in

661   DMS associated with frontal waters (Holligan et al., 1987; Matrai et al., 1996), and these

662   studies have provided only limited information on DMSP. Results from the current study

663   thus provide much needed information on the distribution of DMS but also DMSP in a

664   critically under-sampled area of the global ocean as well as highlight the importance of

665   oceanic fronts as hotspots for biogenic sulfur compounds.

666

667   Finally, an important portion of the total sea surface pools of DMSP was found as

668   dissolved material in this study, with 5 to 21% of DMSP$_t$ prevailing as DMSP$_d$ across the

669   three distinct clusters of the study region (Fig. 2b). Overall in $situ$ DMSP$_d$ concentrations

670   ranged from 2 to 32 nmol L^{-1}, with highest concentrations being one order of magnitude

671   higher than the maximum DMSP$_d$ concentration of 2.8 nmol L^{-1} found using the same

672   SVDF procedure by Kiene and Slezak (2006) over wide ranging ocean water types. By

673   examining the linear relationship between concentrations of DMSP$_p$ (DMSP$_p$ determined

674   as DMSP$_t$ - DMSP$_d$) and those of DMSP$_d$ (Fig. 5b) we are able to show that the slope

675   (0.21) of the Model II regression analysis is very similar to the slope (0.20) obtained by

676   Kiene and Slezak (2006) for SVDF DMSP$_d$ samples from the Sargasso Sea. Although it

677   is impossible to entirely circumvent bottle, filtration and/or processing effects that could

678   lead to overestimation of DMSP$_d$ concentrations, despite careful handling, it is

679   nonetheless noteworthy that, despite large contrasts in trophic status, our results show a

680   tendency for DMSP$_d$ to build up in surface waters in proportion to its particulate

21

681 counterpart, constituting up to 21% of the total DMSP pool in our study. The fuelling of

682 dissolved DMSP reservoirs in the water column has biogeochemical importance

683 considering this compound supplies heterotrophic micro-organisms with C and S as is

684 discussed in the next section.

685

686 *5.4 Cycling of S-compounds through heterotrophic bacterioplankton*

687 *5.4.1 Wide-ranging microbial DMSP$_d$ rate constants*

688 To our knowledge, this study provides the first DMSP process rate measurements across

689 a frontal zone, within three quasi co-occurring but distinct phytoplankton blooms. Except

690 for station 5, which will be discussed below, DMSP$_d$ loss rate constants (k$_{DMSPd}$) varied

691 between 0.4 and 3.4 d^{-1}, suggesting wide-ranging turnover times of DMSP$_d$ reservoirs,

692 between ca. 7 hour to 2.5 days (Fig. 3a). Assuming steady state conditions, these turnover

693 times imply that between ca. 2 to 14% of the DMSP stock was renewed hourly by

694 autolysis, exudation viral attack and grazing (Stefels et al., 2007). These results are

695 comparable with similar ranges of k$_{DMSPd}$ measurements conducted in various oceanic

696 environments (Table 3). Our highest value of k$_{DMSPd}$ (19.9 d^{-1}) was recorded at station 5,

697 within B2. High k$_{DMSPd}$ values are not commonly reported in the literature except for the

698 22.1 d^{-1} observed by Royer et al. (2010) in the NE Pacific which was similar to our

699 highest rate. These very rapid turnover times (ca. 1 hour at sta. 5) could reflect transient

700 periods of increased bacterial abundance or production. *In situ* rates of leucine

701 incorporation by bacteria were not particularly high at station 5 (0.62 compared to an

702 overall range of 0.27 to 1.46 nmol L^{-1} d^{-1}) nor was the abundance of heterotrophic

703 bacterial cells (0.85 at sta. 5, range of 0.34 to 1.19 x 10^9 cells L^{-1}) and the concentration

704 of DMSP$_d$ (9 compared to a global range of 2 to 32 nmol L^{-1}). Furthermore, in our study

705 no overall significant trends were detected between DMSP$_d$ loss rate constants (k$_{DMSPd}$)

706 and numbers of bacteria or rates of leucine incorporation. It has been suggested that loss

707 rate constants of DMSP$_d$, rather than being directly related to stocks of bacteria could be

708 more related to bacterial community composition, and particularly with certain members

709 of Alphaproteobacteria, Gammaproteobacteria, and cyanobacteria, that could all

710 potentially represent significant contributors to DMSP metabolism (Malmstrom et al.,

711 2004a, 2004b, 2005; Royer et al., 2010; Vila-Costa et al., 2007; Vila et al., 2004). On the

712 whole, microbial DMSP$_d$ rate constants were variable within the study region (50-fold

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718 range), with no specific responses related to the presence of diverging phytoplankton
719 assemblages and biological characteristics within blooms.

720

721 *5.4.2 Fulfilled bacterial sulfur requirements in a sulfur-rich environment*
722 The assimilatory metabolism of sulfur from DMSP is a key control on the amount of this
723 compound diverted away from DMS. Assimilation efficiency of sulfur from ^{35}S-DMSP$_d$
724 into bacterial macromolecules was low (< 5%) throughout the study region (Fig. 3b).
725 Values reported in this study are below a relatively narrow range of DMSP-S assimilation
726 efficiency values reported in various studies (see Table 3). Taking into account the
727 DMSP-S incorporation efficiency, the potential contribution of DMSP-S to bacterial
728 sulfur biomass production was estimated from bacterial C production and lower and
729 upper limits of bacterial C:S molar ratios (32 to 248 from (Cuhel and Taylor, 1981;
730 Fagerbakke et al., 1996). For all the reported C:S values, calculated DMSP-S
731 incorporation exceeded 100% of bacterial sulfur biomass production estimates (data not
732 shown) suggesting that DMSP availability was in excess of bacterial sulfur requirements.
733 These results agree with several studies (Kiene and Linn, 2000b; Simó et al., 2009; Vila-
734 Costa et al., 2007, 2014) suggesting that DMSP acts as a major source of S for
735 heterotrophic bacterioplankton. A possible caveat of these estimates is the fact that
736 DMSP-S assimilation includes that which might be taken up by cyanobacteria and
737 phytoplankton (Malmstrom et al., 2005; Vila-Costa et al., 2006a), which likely don't
738 contribute to leucine incorporation. This would lead to overestimation of the contribution
739 of DMSP to bacterial S production. Overall, and assuming that heterotrophic bacteria
740 dominate the uptake of DMSP, the S assimilation efficiencies (< 5%) measured in this
741 study point towards a rapid saturation of S requirements by the microbial assemblages in
742 DMSP-rich waters of the Subtropical Front.

743 *5.4.3 Microbial DMS yield and gross production of DMS from DMSP$_d$*
744 Microbial DMS yields, the conversion efficiency of DMSP$_d$ into DMS, varied from 4 to
745 17% with an overall average of 11% across the entire study region, irrespective of water
746 mass provenance and bloom association (Fig. 4a). Our results add to the mounting
747 evidence that, as a whole, the span in endogenous proportions of DMSP$_d$ consumed by
748 bacteria and cleaved into DMS is similar across various oceanic environments (see Table

23

749 3). A significant and positive relationship was found between rates of bacterial leucine
750 incorporation and DMS yields in this study ($r_s = 0.84$, $p < 0.01$, $n = 8$). This relationship
751 suggests that as carbon incorporation for protein synthesis was heightened in the
752 microbial communities, the proportional use of DMSP as a carbon source also increased,
753 leading to higher $DMSP_d$-to-DMS conversion efficiencies (Table 2). Furthermore,
754 prokaryotic protein synthesis, estimated by the bacterial incorporation of leucine
755 (Kirchman et al., 1985), appeared to be significantly associated with the supply of
756 $DMSP_d$ in this study ($r_s = 0.86$, $p < 0.01$, $n = 8$, Table 2). The fate of S in DMSP-
757 metabolizing bacterial communities is complex and most likely affected by numerous
758 factors, at least one of which is the S requirement relative to the availability of organic S.
759 Findings from this study are consistent with the hypothesis that organic S in excess of
760 bacterial requirements biases DMSP metabolism against demethylation (Kiene et al.,
761 2000; Levasseur et al., 1996; Pinhassi et al., 2005). These observations agree with results
762 from Lizotte et al. (2009) who observed an increase in DMS yields following the addition
763 of non-limiting concentrations of $DMSP_d$ and increases in microbial incorporation of
764 leucine during an Ocean Iron Fertilization experiment in the Subarctic Pacific.
765 Furthermore, at a physiological level, factors including bacterial carbon requirements and
766 concentrations of DMSP degradation products can also exert an impact on the fate of
767 DMSP (Kiene et al., 2000). Since the radioisotope technique used to examine the
768 microbial cycling of $DMSP_d$ traces only the S moiety, significant respiration of C-DMSP
769 can occur (Vila-Costa et al., 2010). As such, the combination of rather typical $DMSP_d$
770 turnover times (overall average of < 1 day) and low DMSP-S assimilation efficiencies
771 (< 5%) could be an indication of the availability of C-rich compounds, including DMSP,
772 to the bacterial assemblages in this study.

773

774 Regardless of the positive associations between bacterial carbon production and the
775 supply of $DMSP_d$, as well as $DMSP_d$ conversion efficiency into DMS, yields of DMS
776 never exceeded 17%. Altogether, our results reinforce the concept that DMSP-to-DMS
777 conversion is not the main fate of microbial $DMSP_d$ turnover in natural environments (see
778 reviews by Simó (2001) and Stefels et al. (2007)), never exceeding 31% of consumed
779 $DMSP_d$ in most ^{35}S-DMSP tracer studies (see compilation in Table 3). However, even

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modest variance in $DMSP_d$-to-DMS conversion efficiencies can result in considerable variations in the production rate of DMS in sea surface waters. In this study, gross DMS production from $DMSP_d$ ranged from near detection limits to a high of 27 nmol of DMS per liter per day (Fig. 4b). This high rate reflects the very high $DMSP_d$ scavenging by the bacteria measured on this particular day coupled to high $DMSP_d$-to-DMS conversion efficiency at station 5 (Fig. 3a, Fig. 4a). The fact that concentrations of DMS remained low (ca. 3 nmol L^{-1}) suggests that potential sinks, particularly bacterial DMS consumption, but not excluding DMS photo-oxidation and ventilation (Table 1) may have kept this pool in check. Omitting this very high rate measured on February 24th, DMS production from $DMSP_d$ contributed on average 2.3 nmol L^{-1} d^{-1} of DMS to near surface reservoirs (ranging from 0.07 to 6.2 nmol DMS L^{-1} d^{-1}) of the study region. These values are comparable to DMS production rates from $DMSP_d$ previously reported (Table 3). It is noteworthy that although production rates of DMS from $DMSP_d$ were low in B3, concentrations of DMS remained high despite slightly higher wind speeds during this period of sampling (see Bell et al. (2015)), which should have enhanced ventilation of DMS to the atmosphere. This suggests that sinks for DMS were somehow alleviated, for example through: (1) a decrease in photo-oxidation of DMS related to a reduction in irradiance fields and a deepening of the mixed layer (see Table 1); (2) a reduction in bacterial consumption of DMS, for which unfortunately no specific information is available but that could be associated with a decrease in bacterial abundance (Table 1).

Alternatively, but not excluding these potential sinks, other sources of DMS (non-bacterial) are likely to have contributed to the concentrations of DMS. Assuming steady-state conditions, the comparison between our microbially-mediated DMS production rates and the concentrations of DMS in near-surface waters suggest that bacteria alone could not have sustained the DMS pool at most stations, and particularly in B3. Average calculated DMS turnover times due to production from $DMSP_d$ were similar between B1 (2.3 days) and B2 (2.4 days) but increased to an average 36.5 days in B3. Considering that DMS sinks commonly proceed on time scales of hours to a few days (Simo et al., 2000; Stefels et al., 2007), the lengthier bacterial DMS turnover times in B3 point towards the importance of community-associated DMS production in fuelling DMS in surface waters. Community DMS production may have included indirect processes such

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818 as zooplankton grazing, viral lysis, and senescence, as well as direct algal DMSP-lyase
819 activity associated with the presence of certain species of dinoflagellates and
820 coccolithophores (Niki et al., 2000; Wolfe and Steinke, 1996), ubiquitous in Subantarctic
821 waters in early March and potential algal oxidative stress associated to light or nutrient
822 availability (Stefels et al., 2007; Sunda et al., 2002).

823 Another indication of the relative importance of phytoplankton-mediated DMS
824 production in B3 stations can be found in the comparison of standing stocks of DMS
825 relative to $DMSP_t$ which averaged 0.07 and 0.05 mol:mol in B1 and B2, respectively, and
826 increased to a mean of 0.15 mol:mol in B3. This higher average $DMS:DMSP_t$ molar ratio
827 suggests stronger $DMSP_p$ to DMS conversion efficiency in this particular sampling
828 cluster. Further, albeit limited, information on net community-associated DMS
829 production is provided by net changes in DMS concentrations (Fig. 6) calculated as the
830 difference between concentrations at the beginning and at the end of the 6-h pre-
831 acclimation incubations under *in-situ* light conditions. These net changes include all
832 sources and sinks of DMS (except for ventilation). Net changes in DMS concentrations
833 over the 6-h period showed overall accumulation of DMS in the incubation experiments
834 (maximum of 10.8 nmol L^{-1} at sta. 9 in B3). An exception to the accumulation trend was
835 seen at station 8 where a net consumption of DMS (-1.1 nmol L^{-1}) took place over the 6-h
836 incubation at station 8. Coarse calculations that assume steady-state conditions suggest
837 that transposing these net changes over a daily period amounts to a mean net community
838 production of DMS from $DMSP_t$ of 15.2 nmol L^{-1} d^{-1} (n = 6) throughout the stations
839 where data was available. This rough estimate is almost 3 times as high as the gross
840 microbial production of DMS from $DMSP_d$ (average of 5.3 nmol L^{-1} d^{-1}, n = 6) in the
841 same stations (sta. 3, 5, 6, 7, 8 and 9). The microbial DMS production rates from $DMSP_d$
842 in this study are also considerably lower than several of the community net production
843 rates required to support microlayer DMS (range of -1445 to 5529 nmol L^{-1} h^{-1}) reported
844 by Walker et al. (2016). Altogether our findings support the view that indirect and direct
845 processes of phytoplankton-mediated DMS production were important contributors to
846 standing stocks of DMS in the near-surface waters of the STF during austral summer.

847

848 **6 Conclusions**

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Our study provides information on both concentrations and cycling of dimethylated sulfur compounds within waters of the New Zealand biogeochemical province (NEWZ) and more specifically in an oceanic frontal region. The three distinct phytoplankton blooms sampled were shown to be hotspots for concentrations of DMS (max of 14.5 nmol L^{-1}) and DMSP$_t$ (max of 160 nmol L^{-1}). Regardless of physico-chemical and biological differences in bloom dynamics across the Subantarctic and Subtropical waters investigated, pools of DMSP$_t$ varied in concert with stocks of chl a, likely because of the dominance of DMSP-rich phytoplankton groups such as dinoflagellates and coccolithophores. The significant relationship between chl a and DMSP$_t$ ($r_s = 0.83$, $p < 0.01$) across blooms suggests that autotrophic biomass may be a reasonable predictor of DMSP for this region during austral summer. The high availability of reduced sulfur fully satisfied sulfur requirements of the micro-organisms leading to overall low microbial sulfur assimilation efficiencies from DMSP$_d$ (< 5 %). Microbial yields of DMS varied 4-fold over the Subtropical Front (4-17 %) and were significantly correlated with bacterial protein synthesis rates, lending support to the idea that supplies of DMSP$_d$ were non-limiting. Microbially-mediated DMS production from DMSP$_d$ generally ranged between 0.1 to 6.2 nmol DMS L^{-1} d^{-1}, but was as high as 27 nmol DMS L^{-1} d^{-1} at station 5. The comparison between standing stocks of DMS and microbially-mediated DMS production rates suggest that bacteria alone could not have sustained DMS concentrations in near-surface waters at most stations in this study. These results point towards phytoplankton-associated production of DMS as an important co-driver of DMS pools in the surface waters on either side of the STF. While the STF was already a known region of high biological activity, results from the current study reinforce the hypothesis that the STF also supports high DMSP-to-DMS conversions largely related to its abundant biogenic sulfur compounds. These findings could have important implications for global sulfur budgets and climate considering that the STF covers several hundred kilometers in a ring encircling a part of the globe with little anthropogenic influence, and where productive plankton blooms may persist over several months

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895 **8 Author contribution**
896 M. Lizotte, M. Levasseur designed the experiments and M. Lizotte, C. S. Law, C. F.
897 Walker, K. A. Safi, and A. Marriner carried out the experiments and performed the
898 measurements in the field. R. P. Kiene produced and provided ^{35}S-DMSP$_d$ for the
899 radiotracer experiments. M. Lizotte prepared the manuscript with contributions from all
900 co-authors.

902 **9 Competing interests**
903 The authors declare that they have no conflict of interest.

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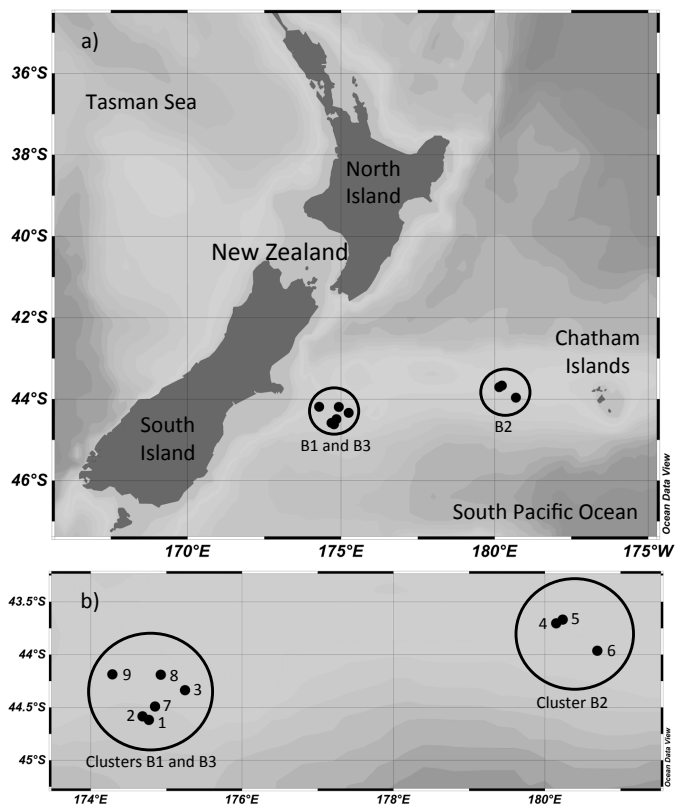
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1318   **11 Figures**

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Figure 1. (a) Map of the general sampling area over the Chatham Rise East of New
Zealand's South Island; and (b) close-up of the partitioning of the 9 stations in clusters
B1, B2 and B3 sampled during the SOAP voyage in February and March 2012.
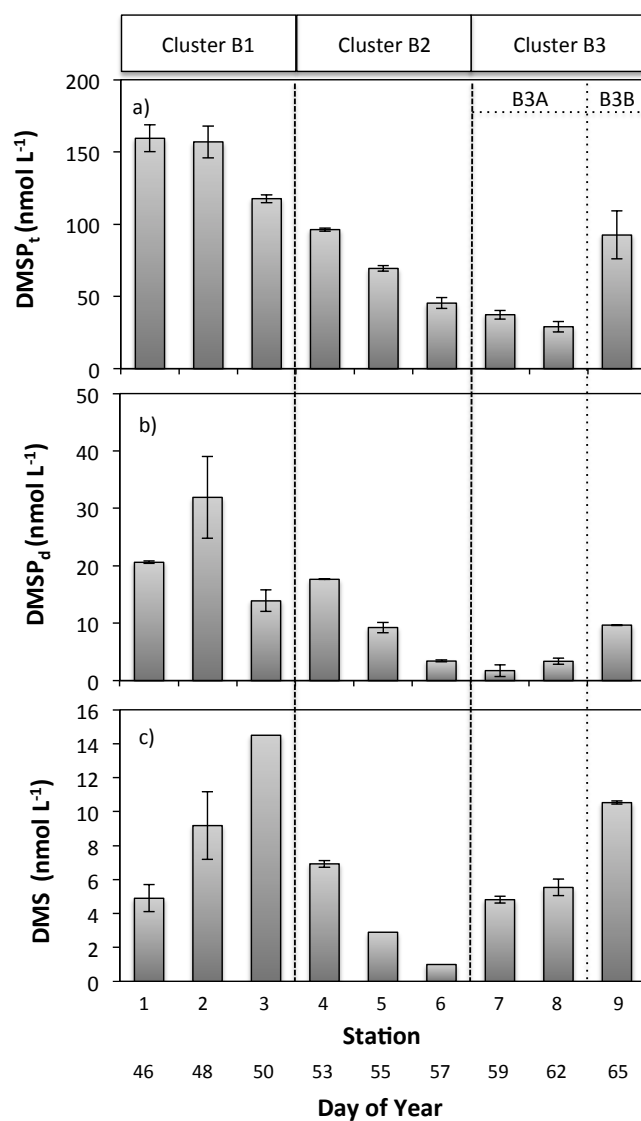
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Figure 2. Concentrations of (a) total DMSP ($DMSP_t$); (b) dissolved DMSP ($DMSP_d$); and
(c) DMS measured at nine stations during the SOAP voyage in February and March
2012. Values are means of experimental duplicates and error bars represent the absolute
deviations of data points from their mean. DMS data from stations 3,5 and 6 represent
single samples, while values from stations 7 and 8 come from matching T0 DMS values
(from incubation experiments). The three sampling clusters are noted as B1, B2, and B3.

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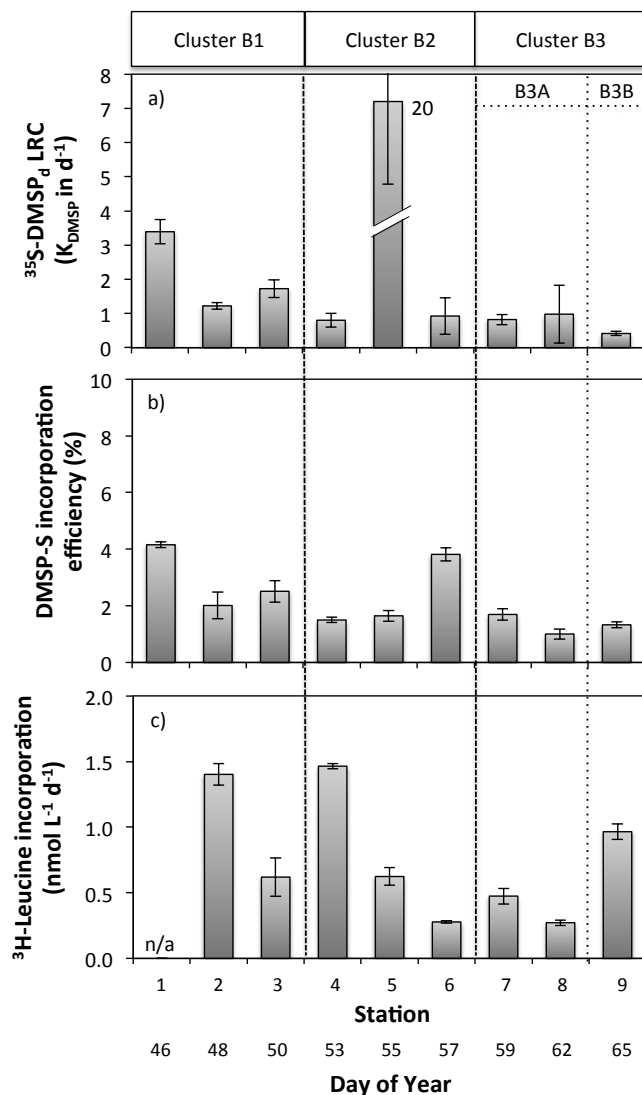
1340 Figure 3. (a) Microbial DMSP$_d$ loss rate constant (k$_{DMSPd}$ in d^{-1}); (b) Microbial
1341 assimilation efficiency of DMSP-S into macromolecules (%); (c) Microbial ^{3}H-Leucine
1342 incorporation (nmol L^{-1} d^{-1}) at nine stations during the SOAP voyage in February and
1343 March 2012. The three sampling clusters are noted as B1, B2, and B3. Stacks and error
1344 bars indicate mean and standard deviation of triplicate samples. n/a = not available.

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Figure 4. (a) Microbial DMS yields (%); (b) Gross DMS production from $DMSP_d$ (nmol L^{-1} d^{-1}) at nine stations during the SOAP voyage in February and March 2012. The three distinct sampling clusters are noted as B1, B2, and B3. Stacks and error bars indicate mean and standard deviation of triplicate samples.
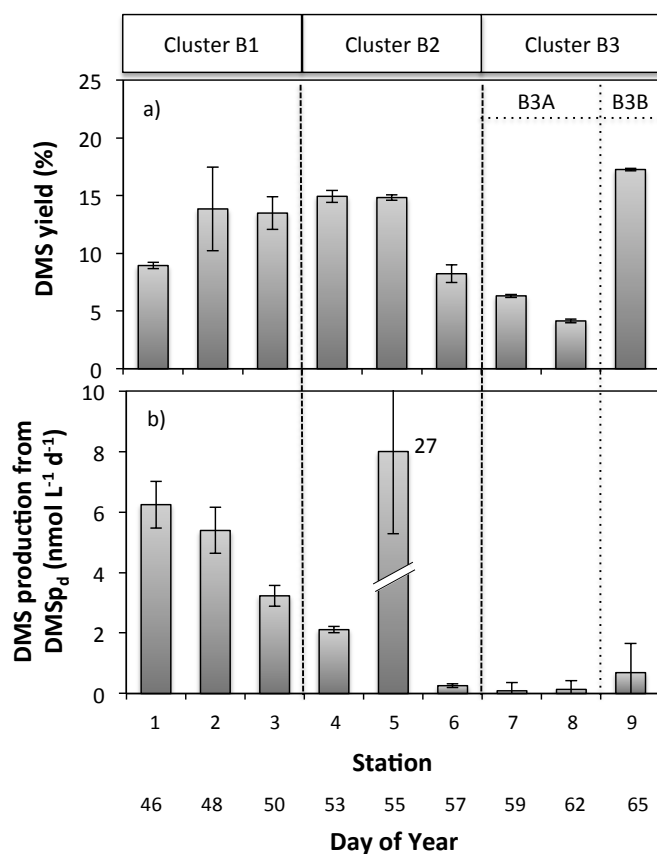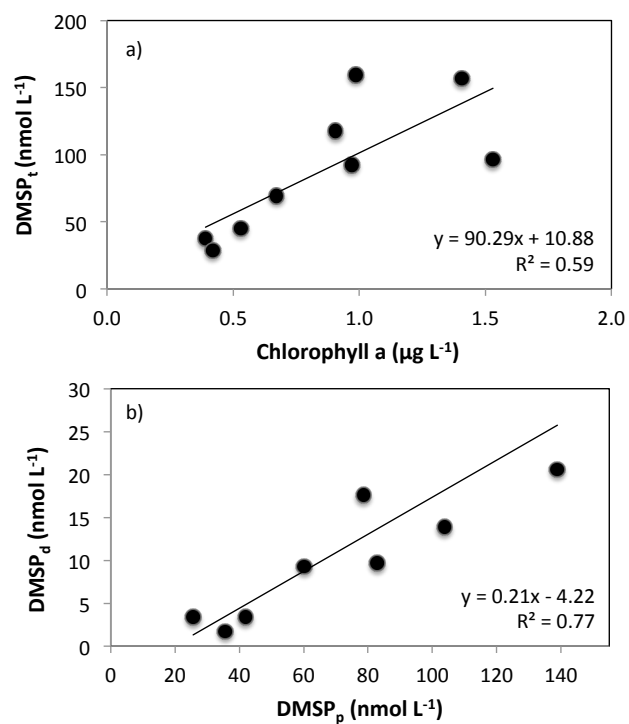
Figure 5. Model II regressions between (a) concentrations of chl *a* and $DMSP_t$; (b) concentrations of $DMSP_d$ and $DMSP_t$.

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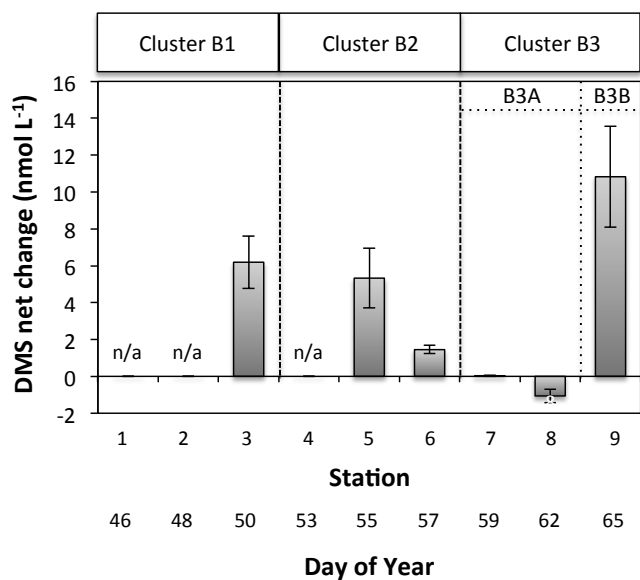
Figure 6. Net changes in DMS concentrations calculated as the difference between T0
and T6 values during 6-h incubation experiments conducted in quartz bottles (at *in situ*
light and temperature conditions) on the deck of the ship during the SOAP voyage in
February and March 2012. Stacks and error bars indicate mean and standard deviation of
triplicate samples. n/a = not available.

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1396   **12 Tables**

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Table 1. Broad biogeochemical characteristics of the stations sampled within three blooms during the SOAP voyage in February and March 2012.

	Bloom 1			Bloom 2			Bloom 3		
Regional pCO_2 min (µatm)	260			339			305		
Regional Chl$a$ max (µg L^{-1})	5			1.5			3.5		
Regional DMS max (nmol L^{-1})	20			15			10		
Regional mean phytoplankton C biomass (µg L^{-1})	61			32			28		
	Cluster B1			Cluster B2			Cluster B3A		Cluster B3B
Regional predominant phytoplankton (of C biomass)	Dinoflagellates			Coccolithophores			Mixed population		Coccolithophores
Day of Year	46	48	50	53	55	57	59	62	65
Date in 2012	15 February	17 February	19 February	22 February	24 February	26 February	28 February	02 March	05 March
Sampling time (NZST)	8h05	8h02	7h30	8h27	7h00	6h52	7h30	8h00	9h04
Sampling coordinates	44°37.3'S	44°35.2'S	44°20.7'S	43°42.9'S	43°40.4'S	43°57.44'S	44°29.27'S	44°11.23'S	44°11.10'S
	174°46.3'E	174°41.4'E	175°14.45'E	179°51.6'W	179°45.56'W	179°18.30'W	174°50.56'E	174°55.28'E	174°17.7'E
Location in relation to bloom	In Bloom 1	In Bloom 1	N of Bloom 1	In Bloom 2	In Bloom 2	S of Bloom 2	In Bloom 3	In Bloom 3	In Bloom 3
Sequential station number	1	2	3	4	5	6	7	8	9
Predominant water mass	SAW	SAW	SAW	STW	STW	STW	SAW	SAW	SAW
Sampling depth (m)	1.6	1.6	2	1.6	2	2	10*	10*	1.6
Mixed layer depth (m)	14	14	16	21	39	25	31	39	40
Daily averaged irradiance (W m^{-2})	258	279	252	222	249	282	181	185	208
Solar Radiation Dose (W m^{-2})	90	79	79	40	39	75	41	39	26
Silicate (µmol L^{-1})	0.40	0.39	0.34	0.22	0.40	1.16	0.22	0.58	0.18
Nitrate (NO$_3^-$ µmol L^{-1})	6.36	3.25	5.86	0.04	1.32	0.13	2.21	5.28	3.41
Chl$a$ (µg L^{-1})	0.99	1.41	0.91	1.53	0.67	0.53	0.39	0.42	0.97
Bacteria (*10^9 cells L^{-1})	1.06	0.69	0.43	1.19	0.85	0.59	n/a	0.34	0.51
Coccolithophores (*10^6 cells L^{-1})	1.19¶	9.46¶	5.19	12.70	5.80	21.13	4.68	3.90	n/a§
DMSP$_p$:Chl$a$ ratio (nmol µg^{-1})	141	89	115	51	90	79	91	61	85

Regional data represents maxima/minima or averages in the surface waters within blooms and encompass more stations then the 9 presented specifically in this study (See Law et al., this issue).
SAW (Subantarctic Water) STW (Subtopical Water). Data that is not available = n/a. *Prevailing high windspeeds (>10 m s^{-1}) and heavy seas prevented the sampling of near surface samples at these stations.
¶Values from matching CTD data at 2 m. §No coccolithophore data is available for this date, however samples taken on March 4th showed coccolithophore abundance of 20.3 *10^6 cells L^{-1}.

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1412 Table 2. Spearman's rank correlation coefficients (r_s) for various variables measured
1413 during SOAP.

Variables		r_s coefficient
Chl *a*	$DMSP_t$	0.83**
$DMSP_p$	$DMSP_d$	0.92***
Leucine incorporation	$DMSP_d$	0.86**
Leucine incorporation	DMS yield	0.84**

1414 ***$p < 0.001$ and **$p < 0.01$, n = 9 for all variables except for leucine incorporation where n = 8.
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Table 3. Partial compilation of microbial DMSP$_d$ and DMS cycling rates measured via the ^{35}S radioisotope technique in papers published since 2000.

Study	Area of study	Time of year	Particularities	Sampling depth (m)	Temperature (°C)	Endogenous DMSP$_d$ (nmol L^{-1})	DMSP$_d$ loss rate constant k$_{DMSPd}$ (d^{-1})	DMSP$_d$ turnover time (d)	DMSP$_d$ turnover rate* (nmol L^{-1} d^{-1})	Sulfur assimiliation efficiency** (%)	DMS yield (%)	DMS production from DMSP$_d$ (nmol L^{-1} d^{-1})
Kiene & Linn 2000a	Northern Gulf of Mexico	September 1997 (Late summer)	Coastal and oceanic waters	1 - 100	22 - 30	0.2 - 10	n/a	0.03 - 0.6 (range of means)	0.3 - 129	5 - 40	n/a	0.2 - 5.9 (range of means)
Kiene & Linn 2000b	Subtropical northern Gulf of Mexico, Northern Sargasso Sea, temperate North Atlantic.	Sept. 1997 to Jan 1999 (4 seasons)	Coastal and oceanic waters	0 - 95	3 - 28	1 - 4	n/a	n/a	n/a	n/a	2 - 21	n/a
Zubkov et al. 2002	Northern North Sea	June 1999 (Summer)	Lagrangian SF$_6$ tracer study of a E. huxleyi bloom	2 - 50	8.5 - 11.5	8.0 ± 3.6 (in patch) 10.1 ± 5.7 (out patch)	n/a	0.1 - 0.4 (in patch) 0.2 - 0.3 (out patch)	20 ± 8 (in patch) 21 ± 5 (out patch)	2.5 ± 1.3 (in patch) 2.0 ± 0.8 (out patch)	6 - 12	2 - 2.5
Pinhassi et al. 2005	Coastal Gulf of Mexico	June 2001 (Summer)	Microcosm experiment (only controls shown)	0.5	27	3 - 6	5 - 15.1	0.1 - 0.2	n/a	29	n/a	n/a
Merzouk et al. 2006	Subarctic NE Pacific	July 2002 (Summer)	HNLC waters outside an iron-enriched patch	1 - 14	n/a	2.8 - 19	1.3 - 6.2	0.2 - 0.6	4.8 - 72	n/a	n/a	n/a
Kiene et al. 2007	New Zealand sector of Southern Ocean	November 2003 & 2005 - December 2004 (Spring-summer)	Presence of ice along transects	2 - 4	-1.8 - 8.7	< 4	n/a	n/a	0 - 12.5	n/a	n/a	n/a
Merzouk et al. 2008	Northwest Atlantic	April-May 2003 (Spring)	Senescent diatom bloom	10	2.6 - 3.4	0.7 - 3.9	1.7 - 13	0.1 - 0.6	5 - 28	n/a	9 - 18	0.5 - 2.4
Vila-Costa et al. 2008	Coastal Mediterranean Sea (Blanes Bay)	January 2003 to June 2004	Seasonal survey , shallow water column (24m)	0.5	12.8 - 24.6	5 ± 2	0.8 - 6.3	0.2 - 1.3	2 - 24	n/a	3 - 37	0.1 - 7.7
Simo et al. 2009	Coastal Mediterranean Sea (Blanes Bay)	January 2003 to March 2004	Seasonal survey , shallow water column (24m)	0.5	11 - 25.2	n/a	n/a	n/a	2 - 24	1 - 46	n/a	n/a
Lizotte et al. 2009	Subarctic NW Pacific	July-August 2004 (Summer)	HNLC waters outside an iron-enriched patch	5	8.3 - 11.9	n/a	n/a	n/a	n/a	18 - 25	7 - 13	n/a
Royer et al. 2010	Subarctic NE Pacific	May-June 2007 (Early summer)	Along a natural iron gradient from coastal to open waters	10	7.1 - 11	1.3 - 3.6	2.1 - 22.1	0.1 - 0.3	8.6 (mean offshore) 42 (mean inshore)	10 - 29	3 - 13	0.7 (mean offshore) 1.6 (mean inshore)
Luce et al. 2011	Canadian Arctic Archipelago	October - November 2007 (Late fall)	20 Stations from Northern Baffin Bay to the Beaufort Sea through the Northwest Passage	2 - 3	-1.8 - 0.1	0.1 - 5	0.2 - 3.4	0.3 - 4.1	0.2 - 5.8	n/a	4 - 15	0.01 - 0.5
Lizotte et al. 2012	Northwest Atlantic	May-July-October 2003 (3 seasons)	Seasonal survey of 7 biogeochemical provinces	8 - 15	2 - 26	0.5 - 9	0.7 - 4.1	0.2 - 1.4	0.3 - 24.3	n/a	3 - 21	0.01 - 3.1
Motard-Côté et al. 2012	Canadian Arctic Archipelago	September 2008 (Fall)	Northern Baffin Bay/Lancaster Sound	5	-1.3 - 3.8	n/d - 2.1	0.7 - 2.6	0.4 - 1.4	n/a	11 - 18	12 - 31	n/a
Vila-Costa et al. 2014	Bermuda Atlantic Time-series Study (BATS) station	September 2007 (Fall)	Short-term enrichment studies (organic substrates enrichments)	10	27.5	5.9 ± 0.8	n/a	n/a	2.6 - 28.5	3 - 23	1 - 45 (control < 20)	n/a
This study	New Zealand Subtropical Front	February-March 2012 (Late summer)	Frontal zone (Subantarctic and Subtropical water masses)	1.6 - 10	13.5 - 15.7	1.7 - 31.9	0.8 - 19.9	0.1 - 1.6	1.4 - 184	1 - 4	4 - 17	0.1 - 27.3

*Also called the microbial DMSP$_d$ consumption rate. **Measured from the incorporation of ^{35}S into TCA-insoluble particles. Expressions n/a and n/d refer to data that is non-available and non-detectable, respectively. The compilation is non-exhaustive and does not include certain stressor experiments for simplicity (see additional studies including Slezak et al. 2007; Ruiz-Gonzalez et al. 2011; 2012a: 2012b).