DMS cycling in the Sea Surface Microlayer in the South West Pacific: 2. Processes and Rates

Alexia D. Saint-Macary[1,2], Andrew Marriner[1], Stacy Deppeler[1], Karl Safi[3], Cliff S. Law[1,2]

[1]National Institute of Water and Atmospheric research, Wellington, 6021, New Zealand
[2]Department of Marine Science, University of Otago, Dunedin, 9016, New Zealand
[3]National Institute of Water and Atmospheric Research, Hamilton, 3216, New Zealand

Correspondence to: Alexia D. Saint-Macary (alexia.stmac@gmail.com) and Cliff S. Law (cliff.law@niwa.co.nz)

Abstract. As the sea surface microlayer (SML) is the uppermost oceanic layer and differs in biogeochemical composition to the underlying subsurface water (SSW), it is important to determine whether processes in the SML modulate gas exchange, particularly for climate active gases. Enrichment of dimethyl sulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP) has been reported in the SML, but it remains unclear how this is maintained whilst DMS is lost to the atmosphere. To examine this, a comprehensive study of DMS source and sink processes, including production, consumption and net response to irradiance, were carried out in deck-board incubations of SML water at five locations in different water masses in the South West Pacific east of New Zealand. Net consumption of DMSP and production of DMS in the light and dark occurred at all sites. The net response of DMS and DMSP to irradiance varied between stations but was always lower than conversion of DMSP to DMS in the dark. In addition, DMS photolytic turnover was slower than reported elsewhere, which was unexpected given high light exposure in the SML incubations. Although no relationships were apparent between DMS process rates and biogeochemical variables, including chlorophyll-*a*, bacteria and phytoplankton group, net bacterial DMSP consumption was correlated with DMSP and DMS concentrations, and also dinoflagellate and *Gymnodinium* spp. biomass, supporting the findings of a companion study that dinoflagellates play an important role in DMS cycling in the SML. However, net DMS production rates and accumulation were low relative to regional air-sea DMS loss reported elsewhere, confirming that the DMS cycling within the SML is unlikely to influence regional DMS emissions.

1   Introduction

The climate active trace gas dimethyl sulfide (DMS) is the primary natural sulfate aerosol precursor (Yu and Luo, 2010; Leaitch et al., 2013; Park et al., 2017; Sanchez et al., 2018) that has been hypothesized to contribute to the regulation of climate via formation of cloud condensation nuclei (Charlson et al., 1987; Quinn and Bates, 2011). DMS concentration in the surface mixed layer and emission to the atmosphere is the net result of production and consumption by a various biological, photochemical and physical processes (Stefels et al., 2007). DMS is mainly produced by enzymatic cleavage of its precursor dimethylsulfoniopropionate (DMSP), with acrylate as the other product (Keller et al., 1989; Stefels et al., 2007). DMSP

concentration in seawater is determined by phytoplankton biomass and speciation (Keller et al., 1989) and also bacterial composition and production (Curson et al., 2017), and occurs in dissolved and particulate forms with the latter accounting for ~80% of total DMSP (Keller and Korjeff-Bellows, 1996; Belviso et al., 2000; Yang et al., 2005a; Zhang et al., 2009). It is the dissolved DMSP that constitutes the source for bacterial conversion to DMS, but phytoplankton also release DMS directly during senescence-related cell-lysis (Yoch, 2002; Stefels, 2000). There are at least four independent pathways by which DMSP can be degraded enzymatically by bacteria, three of which lead to the production of DMS; yet, DMS production represents only 5 to 10% of the available DMSP, as the primary DMSP removal pathway of bacterial demethylation results in production of methanethiol (MeSH) (Kiene and Linn, 2000). As DMS production is largely influenced by phytoplankton type and density, its concentration in the euphotic zone generally reflects the vertical distribution of primary production and biomass, with a DMS maximum in near-surface waters and concentration decreasing with depth (Dacey et al., 1998; Bouillon et al., 2002; Rellinger et al., 2009). The main DMS sink in the surface mixed layer is biological consumption, which accounts for 50 to 88% (Galí et al., 2013), with photochemical oxidation and emission to the atmosphere accounting for $8 – 34\%$ and $4 – 6\%$ of DMS loss, respectively (Galí and Simó, 2015). Both production and loss processes are in turn influenced by environmental drivers, such as irradiance, nutrient concentration, temperature and pH, resulting in regional and temporal variation in DMS concentration (Stefels et al., 2007).

The sea surface microlayer (SML) plays a key role in air-sea gas exchange as the interface between the ocean and the atmosphere. It is a very thin layer ($1 – 1000$ µm) with differing physicochemical and biological properties to the underlaying water (Hunter, 1980), including elevated concentrations of carbohydrates, proteins and lipids (Sieburth, 1983; Cunliffe et al., 2013). The SML is more biologically active than the underlying subsurface water (SSW), due to high bacterial activity and abundance (Cunliffe et al., 2011). Elevated respiration by bacterioneuston in the SML is reflected in O_2 and CO_2 emissions (Reinthaler et al., 2008), and altered cycling of trace gases such as CH_4, H_2, N_2O and CO (Sieburth, 1983; Conrad and Seiler, 1988; Upstill-Goddard et al., 2003). The SML also contributes to possible climate regulation when air-sea exchanged trace gases are oxidised leading to secondary organic aerosol, which may influence atmospheric radiative properties (Leck and Bigg, 2005; Roslan et al., 2010). Dissolved DMSP is often enriched in the SML (Yang et al., 2005b; Yang and Tsunogai, 2005; Yang et al., 2005a; Zhang et al., 2008; Matrai et al., 2008; Zhang et al., 2009; Yang et al., 2009), potentially due to stabilization by dissolved organic substances (Gibbs adsorption surface, (Adamson and Gast, 1967)) and high surface tension which energetically favours dissolved DMSP adsorption to dissolved organic substances (Zhang et al., 2008; Zhang et al., 2009). As a result of elevated dissolved DMSP and enrichment of bacterioneuston in the SML (Sieburth, 1983), DMS production from enzymatic cleavage and consumption is also elevated in the SML relative to SSW (Yang et al., 2001; Yang et al., 2005b; Yang et al., 2005a; Yang and Tsunogai, 2005; Zhang et al., 2008). DMS enrichment in the SML is often associated with underlaying phytoplankton blooms dominated by DMSP-producers (Walker et al., 2016) and with high phytoplankton biomass in general (> 2 mg m^{-3} (Yang et al., 2005a; Zhang et al., 2009)). Indeed, DMS enrichment in the SML may require specific biological, biogeochemical and meteorological conditions, which may result in anomalously high air-sea DMS flux in regions of high

productivity (Walker et al., 2016). However, understanding of the factors that maintain DMS enrichment in the SML is limited, particularly as few studies have examined the biogeochemical composition of the SML.

Drivers of DMSP and DMS cycling are more intense in the SML than the SSW. Wind increases ventilation of DMS from the SML (Yang et al., 2001; Yang and Tsunogai, 2005; Yang et al., 2005a; Zhang et al., 2008) and may also concentrate particulate organic material in surface patches that act as hotspots for DMS cycling. In addition, incident light and ultra-violet (UV) exposure are greater, in the absence of water column attenuation (Hardy, 1982; Stolle et al., 2020), which may, directly and indirectly, influence DMSP and DMS (Zemmelink et al., 2005; Zemmelink et al., 2006). DMS photo-oxidation to dimethyl sulfoxide (DMSO) under a full light spectrum (Kieber et al., 1996) is enhanced in the presence of photosensitizers, such as chromophoric dissolved organic matter (CDOM) (Brimblecombe and Shooter, 1986; Brugger et al., 1998; Vogt and Liss, 2009), which is generally enriched in the SML (Frew et al., 2002; Frew et al., 2004). Conversely, this may also limit light exposure in the SML as organic matter enrichment and gel particles may attenuate UV and photosynthetically active radiation (PAR) in the SML (Bailey et al., 1983; Carlucci et al., 1985; Agogué et al., 2005). Irradiance represents a SML sink for DMS via photo-oxidation, but also stimulates intracellular production of DMSP in phytoplankton under light stress and inhibits the bacterial consumption of DMS (Sunda et al., 2002). Consequently, light may enhance both DMS production and consumption, and so the net effect of these processes may be particularly significant in the SML. Although solar radiation dose is an important factor in determining temporal and spatial variability of DMS in surface water (Simó and Pedrós-Alió, 1999; Simó and Dachs, 2002; Vallina and Simó, 2007; Miles et al., 2009), only two previous studies have considered the impact of light on DMSP and DMS in the SML (Zemmelink et al., 2005; Zemmelink et al., 2006).

In situ measurements in the SML and SSW in South West Pacific waters during the *Sea2Cloud* voyage (Sellegri et al., in revision) identified only minor DMSP and DMS enrichment (see companion paper (Saint-Macary et al., egupshere-2022-499), and will be referred as S-M1 thereafter), in contrast to a previous South West Pacific regional study (Walker et al., 2016), and also measurements in other regions, as synthesised in Walker et al. (2016). The apparent absence of DMS enrichment in the same region, as determined by a new technique for sampling DMS in the SML (S-M1), and the requirement for high DMS production to maintain SML enrichment relative to ventilation losses (Walker et al., 2016) highlights the need for processes studies of DMS in the SML. In this paper, SML process rates were measured in deck-board incubations of SML water from five stations across different water masses in the South West Pacific east of New Zealand, to determine the controls of DMSP and DMS, and ultimately the significance of DMS cycling in the SML.

2   Method

2.1   Regional setting

The Sea2Cloud voyage took place from the 16 to 28 March 2020 (austral autumn) around the Chatham Rise, east of New Zealand, onboard R/V *Tangaroa* (Figure 1). The characteristics of the water masses sampled during this voyage and meteorological conditions are summarized in Table 1, and detailed in the Sea2Cloud introduction paper (Sellegri et al., in revision). Six workboat deployments were carried out to sample the SML and SSW in different water mass types: the subtropical front (STF) at stations 1 and 2, subantarctic water (SAW) at stations 3 and 4, the subtropical water (STW) at station 5, and mixed water (Mixed) at station 6 (see Figure 1, Table 1). The mixed water had elevated nutrient content relative to the STW reflecting a mixture of coastal and shelf water with STW (Sellegri et al., in revision). Station 5-STW was sampled for SML characterisation (S-M1) but had no deck-board incubation as sampling occurred in the afternoon in contrast to the other stations. A sipper consisting of a silicon tube with multiple inlets (internal diameter 2.2 mm) that floated on the surface with water enabled sampling of 2.4 L of water from the SML, which was drawn up using a peristaltic pump or manually by syringe (S-M1).

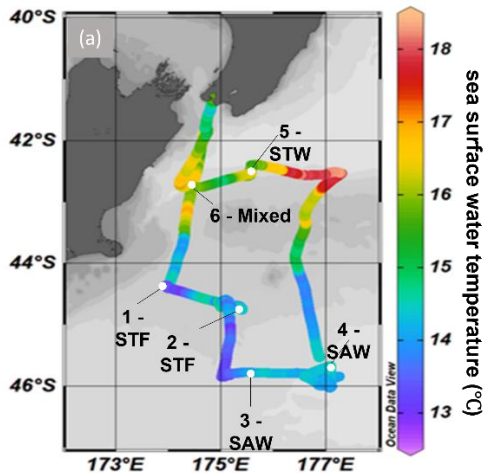



Figure 1: Sea2Cloud voyage track with workboat station positions overlain on sea surface water temperature (ºC). Figure plotted using Ocean Data View, Schlitzer and Reiner (2020). The grey shading shows the undersea topography, with the darker grey band along 43.5°S indicating the Chatham Rise. Station 5-STW was sampled for SML characterisation (S-M1) but had no deck-board incubation.

Table 1: Summary of environmental conditions during the workboat deployments. The water side variables were determined using data from the vessel underway system which sampled at 5 m depth (n = 1), and an Automatic Weather Station measured windspeed, 25.2 m above the sea level. N.D. stands for no data.

Date	Workboat station and water masses	Workboat sampling time t_0-t_{end} (NZDT)	Average wind speed ($\pm$sd) previous 12 h (m s^{-1})	PAR (μM m^{-2} s^{-1})	Temperature (°C)	Salinity (psu)	Chl-a at 5 m (μg L^{-1})	Dominant phytoplankton group (carbon biomass) at 5 m
18 March	1-STF	0900-1050	3.79 ($\pm$2.20)	481 $\pm$ 576	13.03	34.55	1.54	Diatom
19 March	2-STF	0830-1034	7.50 ($\pm$0.87)	101 $\pm$ 32	14.15	34.44	3.64	Diatom
21 March	3-SAW	1020-1159	7.88 ($\pm$2.54)	315 $\pm$ 263	13.37	34.33	0.37	Dinoflagellate
23 March	4-SAW	0845-1022	7.36 ($\pm$2.56)	185 $\pm$ 154	13.94	34.36	0.43	Dinoflagellate
25 March	5-STW	1533-1714	5.4 ($\pm$ 2.80)	N.D.	16.18	34.88	1.02	Diatoms
26 March	6-Mixed	0950-1138	8.19 ($\pm$3.55)	582 $\pm$ 478	16.24	34.78	0.89	Diatom

2.2 Deck incubation set up

Each deck incubation was carried out after workboat SML sampling, as described in S-M1, except at 5-STW. The SML water was transferred by gravity into pre-rinsed and flushed 6 x 250-mL UV transparent borosilicate glass bulbs that transmit 90% of UV-A and UV-B, with the bulbs filled completely to eliminate any headspace. The bulbs were incubated in a shallow 37-L seawater bath (17-cm depth), half-immersed in continually flowing surface water to maintain temperature whilst maximizing irradiance to mimic the SML. PAR light Odyssey® photosynthetic irradiance recording system was placed next to the deck incubation to record incoming irradiance in the wavelength range 400 – 700 nm. However, the variation in PAR between experiments was not considered in the interpretation.

Each of the five deck incubations was of 6-hour duration (from midday or 1400 to 1800 or 2000) and used DMS process rate measurement techniques (Simó et al., 2000; Yang et al., 2005b; Yang and Tsunogai, 2005; Yang et al., 2001), modified to small water volumes. Three treatments were each carried out in duplicate. The first pair of bulbs (A) were exposed to ambient deck irradiance to simulate *in situ* conditions in the SML but excluded air-sea loss. The second treatment (B) was maintained in the dark with the bulbs covered by black tape. Exclusion of light eliminated DMS photo-oxidation and light stress and provided an estimate of the net biological effect on DMSP and DMS in the dark. Light was also excluded in set (C) which included addition of DMS free dimethyl disulfide (DMDS), an inhibitor of DMS bacterial consumption, at a final concentration of 200 nmol L^{-1} (Wolfe and Kiene, 1993), so providing a dark DMS production rate.

2.3 DMSP and DMS analytical system

Time zero (T$_0$) DMSP and DMS concentrations were determined from the original water sample. After 6 hours incubation, water was sub-sampled from the borosilicate bulbs into 118 mL amber bottles for DMSP and DMS analysis. For DMS measurements, water from the amber bottles was withdrawn in plastic Terumo® syringes and injected through a 25-mm glass

microfiber filter (GF/F) into a 1-mL loop, before transfer to a silanized sparging tower where the sample was sparged for 5 minutes with nitrogen (N_2) at a flow rate of 50 mL min^{-1}. Nafion® dryers removed water vapor from the gas samples before DMS pre-concentration at −110 °C on a 60/80 Tenax® TA trap. The trap was then heated to 120 °C to release the DMS onto an Agilent Technology 6850 Gas Chromatograph (DB-megabore sulfur SCD column, 70 m length, 0.530 megabore diameter, and film thickness 4.30 μm) coupled to an Agilent 355 Sulfur Chemiluminescent Detector (GC-SCD). The detector's daily sensitivity and detection limit were confirmed using VICI® methyl ethyl sulfide and DMS permeation tubes, with an average detection limit of 0.14 (± 0.03) pgS sec^{-1}. For DMSP measurements, 20-mL glass vials were filled and 2 pellets of NaOH added, to hydrolyse DMSP to DMS, before gas-tight sealing the vials. DMSP samples were stored in the dark at ambient temperature with analysis of the liberated DMS within 24 hours of sampling, using the semi-automated purge and trap system and GC-SCD as described above. A wet standard calibration curve was made daily from a stock solution of DMSP diluted in Milli-Q® water, with DMS calibration concentrations ranging from 0.1 to 95 nmol L^{-1}. These were decanted into 20-mL gas tight glass vials, hydrolysed with 2 pellets of NaOH, and then injected into the sparging unit and processed as samples.

2.4   Rate calculation

The rate of change in DMSP and DMS concentration, k, was calculated from the linear slope between T_0 and T_6 hours and converted to per day rates (nmol L^{-1} d^{-1}), with turnover time (d) subsequently calculated by dividing the initial DMS/P concentration by the rate, as described in Table 2. The incubation design had some limitations, with only 2 data points and a short incubation time; however, the 6-hour period was compatible with natural light availability and minimised bottle effects. The net irradiance response of DMSP, $k_{DMSP\ ir}$, and DMS, $k_{DMS\ ir}$, were calculated as the differences between the set exposed to light (A) and dark (B). The DMSP dark bacterial consumption rate, $k_{DMSP\ cn}$, was calculated using the change in DMSP concentration in set B over the 6-hour incubation. DMSP dark bacterial consumption rate has been previously calculated using a first order loss rate constant as the slope of the natural log of DMSP concentration versus time (Kiene, 1996); however, as there were only 2 time points (T_0 and T_6) the slope of the linear decrease in DMSP concentration was used in the current study. The DMS dark bacterial consumption rate, $k_{DMS\ cn}$, was calculated as the difference between the dark sets (C) and (B), with and without DMDS addition, respectively (Yang et al., 2005b; Yang et al., 2001). The DMS dark production rate, $k_{DMS\ pr}$, was estimated as the change in DMS concentration in the DMDS treated samples in set (C) (Yang et al., 2005b; Yang et al., 2001; Simó et al., 2000). DMS dark yield was calculated as the ratio between the DMS dark production rate and the DMSP dark bacterial consumption rate. Process rates were compared with the calculated DMS air-sea flux (S-M1) and a DMS air-sea turnover, $\tau_{a/s}$, was also generated by relation to the initial DMS concentration in the SML.

Table 2: Definition and calculation of DMSP and DMS process rates in nmol L^{-1} d^{-1} and turnovers in d and min for air-sea turnover.

Process	Abbreviation	Process calculation (nmol L^{-1} d^{-1})	Turnover (d)
DMSP dark bacterial consumption rate	$k_{\text{DMSP cn}}$	(DMSP slope set B)	$\tau_{\text{DMSP cn}}$
Net irradiance response rate of DMSP	$k_{\text{DMSP ir}}$	(DMSP slope set A – DMSP slope set B)	$\tau_{\text{DMSP ir}}$
Net irradiance response rate of DMS	$k_{\text{DMS ir}}$	(DMS slope set A – DMS slope set B)	$\tau_{\text{DMS ir}}$
DMS dark production rate	$k_{\text{DMS pr}}$	(DMS slope set C)	$\tau_{\text{DMS pr}}$
DMS dark yield	DMS dark yield	($k_{\text{DMS pr}}$ / $k_{\text{DMSP cn}}$)	
DMS dark bacterial consumption rate	$k_{\text{DMS cn}}$	(DMS slope set C – DMS slope set B)	$\tau_{\text{DMS cn}}$
DMS air-sea flux	F_{SML}	See S-M1	$\tau_{\text{a/s}}$ (in min)

2.5 Statistical analysis

The Shapiro test was used to verify the normality of variable distribution (see results in Suppl. Info. Table SI 1). For the non-normally distributed variables Spearman's rank correlation was carried out, and for the normally distributed data a Pearson test was applied. Linear correlation was considered significant where the coefficient of correlation (rho for Spearman's rank and r for Pearson test) was higher than 0.5 and p-value was lower than 0.05.

3 Results

3.1 DMSP process rates

DMSP concentrations decreased over the 6 hour incubation in all treatments, with highest losses at the frontal stations 1 and 2 and lowest at 3-SAW and 6-Mixed (Suppl. Info. Figure S1). The DMSP loss was generally similar for all treatments within each station, except for 3-SAW which showed higher DMSP loss in set B. Although variable between stations, $k_{\text{DMSP ir}}$ was negative at 3 stations (range: −13 to +29 nmol L^{-1} d^{-1} average: +7 nmol L^{-1} d^{-1}), with the lowest rate at 4-SAW and highest at 2-STF (Figure 2a). The DMSP dark bacterial consumption rate was generally greater than $k_{\text{DMSP ir}}$, with an average loss of 53 nmol L^{-1} d^{-1} (range: 13 – 97 nmol L^{-1} d^{-1}), with the lowest at 6-Mixed and highest rates in STF waters. As a result, there was a net loss of DMSP at all stations (average 47 nmol L^{-1} d^{-1}; range: 9 – 101 nmol L^{-1} d^{-1}). The DMSP data from the deck incubation are summarized in Table 3, with the rates also considered in terms of turnover of DMSP concentration in the SML (T$_0$ concentration), as described in the Methods. DMSP dark bacterial consumption turnover ($\tau_{\text{DMSP cn}}$) was faster than $\tau_{\text{DMSP ir}}$ with average values of 1.1 d (range: 0.7 – 1.4 d) and 7.3 d (1.7 – 16 d), respectively (Figure 2b). $\tau_{\text{DMSP cn}}$ was fastest in STF water but relatively uniform across the other stations, whereas $\tau_{\text{DMSP ir}}$ did not show any pattern in relation to water mass. Overall, only $k_{\text{DMSP cn}}$ was indicated to be correlated to biogeochemical variables in the SML, such as dinoflagellate and

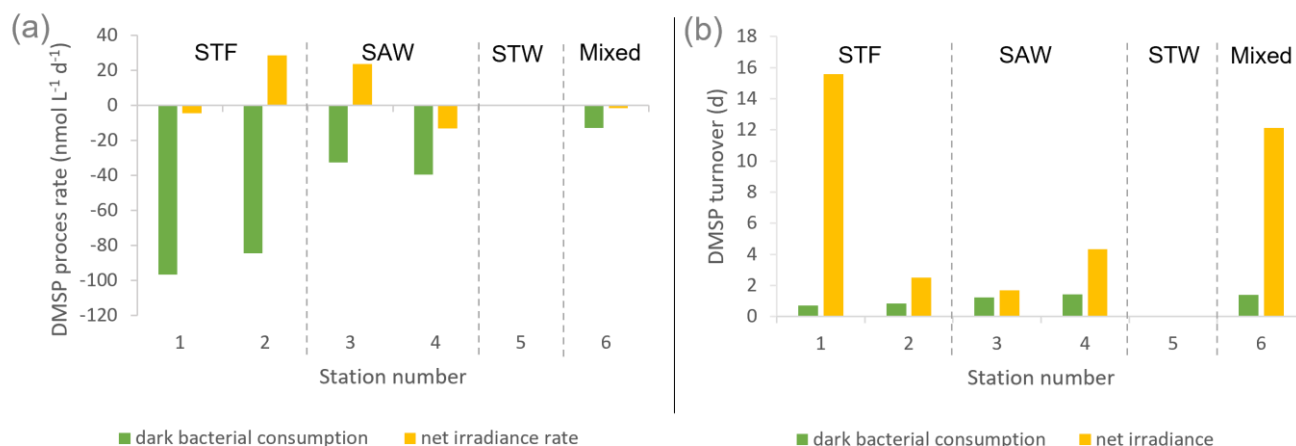
Gymnodinium biomasses, DMSP and DMS concentrations, and the >50 µm phytoplankton size fraction (Suppl. Info. Table S1).

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Figure 2: (a) DMSP process rates (nmol L^{-1} d^{-1}), and (b) DMSP consumption and net irradiance turnover (days) determined in deck incubation of SML water at each station. Water mass type is indicated by the label at the top of the figure and also is separated by vertical dashed lines. Station 5-STW was sampled for SML characterisation (S-M1) but had no deck-board incubation.

3.2 DMS process rates

195 In contrast to DMSP, DMS concentration increased in all incubations with significant differences between stations (Suppl. Info. Figure S2). Station 2-STF showed the largest increase in DMS in set A relative to T_0 (8 nmol L^{-1} d^{-1}), whereas there were only minor increases at 1-STF and 6-Mixed (< 1 nmol L^{-1} d^{-1}). There were also variations within stations, with DMS increases in the dark treatment (set B) at 2-STF, 3-SAW and 4-SAW (Suppl. Info. Figure S2). Dark production was the dominant DMS process at an average of 3 nmol L^{-1} d^{-1}, exceeding $k_{DMS\,cn}$ and $k_{DMS\,ir}$ at all stations except 6-Mixed (Figure 3a). The $k_{DMSP\,cn}$

200 varied from 0 to 4.44 nmol L^{-1} d^{-1} and was higher at 1-STF and 4-SAW. $k_{DMS\,ir}$ was positive and also highest at 2-STF, whereas it was negative at 3-SAW and 4-SAW. DMS dark yield was on average 6%, with maximum yield at 4-SAW (16%) and minimum at 6-Mixed (1.4%, Table 4).

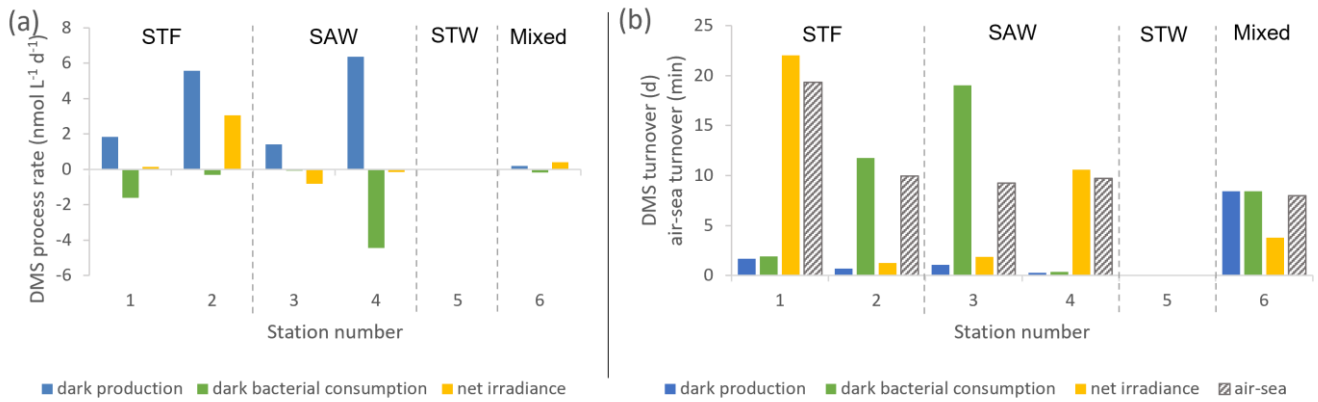



Figure 3: (a) DMS process rates (nmol L^{-1} d^{-1}) at each sampling station. (b) DMS turnover time in days for dark production, dark bacterial consumption and net irradiance response, and in minutes for air-sea turnover, with water mass type indicated by the label at the top of the figure and also is separated by vertical dashed lines. Station 5-STW was sampled for SML characterisation (S-M1) but had no deck-board incubation.

The DMS rates were assessed in relation to DMS concentration to generate a turnover, as described in the Methods section and summarized in Table 4. $\tau_{DMS\,cn}$ varied between 0.4 and 19 d with an average of 8.3 d (Figure 3b) and was generally similar to $\tau_{DMS\,ir}$ (average 7.9 d; range 1.2 – 22 d). DMS dark production turnover was faster than $\tau_{DMS\,ir}$ and $\tau_{DMS\,cn}$ at all stations, except 6-Mixed, at an average of 3 d (range: 0.3 – 8.4 d). However, the air-sea turnover $\tau_{air\text{-}sea}$, calculated from the air-sea flux (S-M1), was considerably shorter at an average 11 min (8 – 19 min), and so ~ 1,100 fold faster than $\tau_{DMS\,pr}$. In addition, DMS process rates and turnover did not show any significant correlations with ancillary variables (chl-*a*, phytoplankton community composition, bacterial abundance (S-M1, correlation coefficients in Suppl. Info. Table S1).

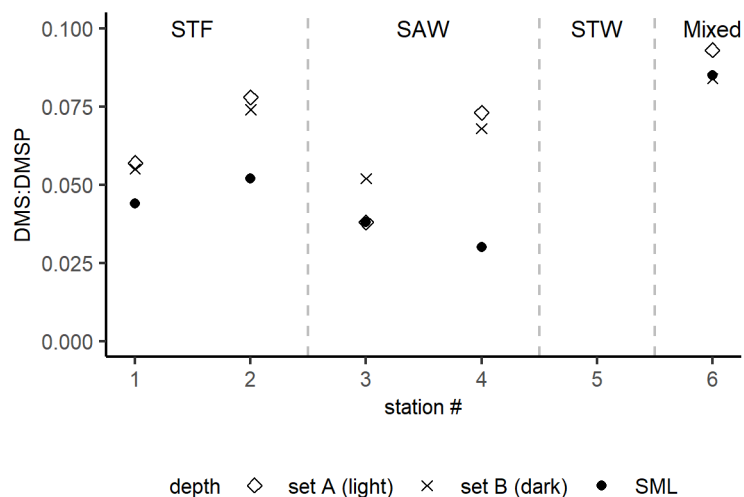
Table 3: Summary of DMSP process rates (nmol L^{-1} d^{-1}) and turnover (d) in SML water for each station. The DMSP concentration is in nmol L^{-1}. The calculation details for the rates and turnovers are given in Table 2. Results are the mean value of duplicate incubations.

Date	Station #	[DMSP]$_{SML}$	$k_{DMSP\,cn}$	$k_{DMSP\,ir}$	$\tau_{DMSP\,ir}$	$\tau_{DMSP\,cn}$
18 March	1-STF	69.75	−97	−4.5	16	0.7
19 March	2-STF	72.13	−84	29	2.5	0.9
21 March	3-SAW	40.06	−33	24	1.7	1.2
23 March	4-SAW	56.38	−40	−13	4.3	1.4
26 March	6-Mixed	17.95	−13	−1.5	12	1.4
Average	-	*51.25*	*−53*	*6.7*	*7.3*	*1.1*

Table 4: Summary of DMS process rates (nmol L^{-1} d^{-1}) and turnovers (d) in SML water for each station. The DMS concentration is in nmol L^{-1}. The calculation details for the rates and turnovers are given in Table 2. Results are the mean value of duplicate incubations.

Date	Station #	[DMS]$_{SML}$	k DMS pr	k DMS cn	k DMS ir	Net accumulation rate	DMS dark yield	τ DMS cn	τ DMS pr	τ DMS ir	τ a/s
18 March	1-STF	3.08	1.8	−1.6	0.1	0.3	1.9	1.9	1.7	22	0.013
19 March	2-STF	3.76	5.6	−0.3	3.1	8.3	6.6	12	0.7	1.2	0.007
21 March	3-SAW	1.52	1.4	−0.1	−0.8	0.7	4.3	19	1.1	1.9	0.006
23 March	4-SAW	1.69	6.4	−4.4	−0.2	1.8	16.1	0.4	0.3	10.6	0.007
26 March	6-Mixed	1.52	0.2	−0.2	0.4	0.4	1.4	8.4	8.4	3.8	0.006
Average	*-*	*2.31*	*3.1*	*−1.3*	*0.5*	*2.3*	*6.1*	*8.3*	*3.1*	*7.9*	*0.008*

3.3 DMS:DMSP ratio

225 The DMS:DMSP ratio in sets A (light) and B (dark) were compared to the initial *in situ* DMS:DMSP in the SML (incubation T$_0$, Figure 4). DMS:DMSP was on average 0.05 in the SML (range: 0.03 – 0.08), and increased to 0.07 in the absence of air-sea loss in the incubations in both set A and B (ranges 0.04 – 0.09 and 0.05 – 0.08, respectively). DMS:DMSP was similar in sets A and B at each station, except for 3-SAW where it was higher in set B (dark).

230 **Figure 4: DMS:DMSP ratio in the SML at T$_0$, and at the end of the 6 hour deck incubations in set A (light) and B (dark) at each station. At 3-SAW, the ratio in set A is equal to, and so obscured, by the initial ratio in the SML. Set C results are not included as**

4   Discussion

235   The characteristics of the SML during the current study contrasted with a previous South West Pacific regional study (Walker et al., 2016), and results from other regions (Nguyen et al., 1978; Yang, 1999; Yang and Tsunogai, 2005; Yang et al., 2005a; Zhang et al., 2009; Zemmelink et al., 2006), with only limited enrichment of DMSP, DMS and chl-*a* at one of six stations (S-M1). Consequently, the DMS air-sea flux was not significantly affected by DMS in the SML (S-M1), and was generally consistent with the climatological estimates of Lana et al. (2011) and Wang et al. (2020). Although DMS dark production was

240   the dominant process in the deck-board incubations, net DMS accumulation was low (Table 4) which, combined with the reported variation in enrichment, raises questions as to how excess DMS is maintained in the SML when air-sea loss is significant (Figure 3b). The following discussion considers the processes and factors influencing DMSP and DMS cycling in the SML, and whether these are sufficient to generate DMS enrichment (S-M1).

Table 5: Summary of DMS and DMSP processes in the SML and potential factors influencing enrichment factor (EF) DMS in
245   **different water masses. In the EF columns, depletion is indicated by "−", enrichment by "+", and "n/s" is not significant. DMSP enrichment was measured at station 5-STW, and so is not presented in this Table. For the dominant phytoplankton group in the SML, "D" and "F" stands for diatom and dinoflagellate, respectively. For the processes, a "−" indicates DMS loss and a "+" indicates DMS production, with triplicate symbols indicating the dominant DMS/P transformation process at the respective station (air-sea flux was always a loss process for DMS, and always exceeded other process rates). The maximum air-sea flux (>5 µmol m⁻²**
250   **d⁻¹) is indicated by 2 "−" signs. Results from SM-1 are indicated by * and n/d stands for "not determined".**

Station number	EF DMSP*	EF DMS*	Dominant phyto-plankton*	DMS:DMSP	DMS dark yield (%)	DMS air-sea flux*	k DMS pr	k DMS cn	k DMS ir	k DMSP cn	k DMSP ir
1-STF	−	−	F	0.04	1.9	−	+++	− −	+	− −	−
2-STF	−	−	n/d	0.05	6.6	− −	+++	−	++	− −	+
3-SAW	−	+	F	0.04	4.4	−	+++	−	− −	− −	+
4-SAW	−	−	F	0.03	16	−	+++	− −	−	− −	−
6-Mixed	−	n/s	F	0.08	1.4	−	+	−	++	− −	−

4.1   DMSP processes

The current study is, to our knowledge, the first to determine DMSP process rates in the SML. DMSP loss occurred in all treatments at all stations, with the highest k DMSP cn in the diatom bloom at 2-STF. As chl-*a* and bacterial abundance were elevated at this station (S-M1), DMSP loss was enhanced in association with elevated biological activity; however, bacterial

255   community composition is considered a more significant determinant of k DMSP cn than bacterial abundance (Vila-Costa et al., 2008). In the current study, k DMSP cn was correlated to the dinoflagellate and *Gymnodinium* biomass in the SML, and to DMS/P concentrations in the SML, suggesting the importance of dinoflagellate on DMS/P dynamics in the SML (Suppl. Info. Table S1, S-M1). The k DMSP cn, range of 13 – 97 nmol L⁻¹ d⁻¹ measured in the SML (Table 3) is higher than regional rates determined in SSW with the ³⁵S-DMSP method (3 – 60 nmol L⁻¹ d⁻¹; Lizotte et al. (2017)), consistent with the SML being more biologically

active than the SSW (Cunliffe et al., 2011). However, this difference in regional consumption rates may reflect methodological differences, as the net concentration change method used in the current study generally delivers higher consumption rates than the dissolved ^{35}S-DMSP method (Vila-Costa et al., 2008). That dark bacterial consumption was the dominant DMSP process is consistent with bacterial demethylation being the primary DMSP removal process in the surface ocean (Kiene and Linn, 2000).

The net response of DMSP to irradiance was variable (Figure 2a and Table 5), as reported in other studies (Slezak et al., 2001; Slezak et al., 2007). Exposure to light can affect intracellular synthesis of DMSP (Stefels, 2000; Hefu and Kirst, 1997), and phytoplankton DMSP production is enhanced during antioxidant response to light stress (Sunda et al., 2002). Exposure to UV and UV + PAR may have differential effects on intracellular accumulation of DMSP in the coccolithophore *Emiliania huxleyi* (Sunda et al., 2002; Van Rijssel and Buma, 2002; Archer et al., 2010), with DMSP synthesis inhibited under high UV radiation (Archer et al., 2018; Herndl et al., 1993; Muller-Niklas et al., 1995; Slezak et al., 2001; Sunda et al., 2002; Van Rijssel and Buma, 2002). However, UV radiation may also inhibit bacterial DMSP removal (Slezak et al., 2001), and result in DMSP accumulation. As the response of phytoplankton DMSP synthesis and bacterial cycling varies with light intensity, and light exposure also varied between deck incubations, this limits interpretation of the irradiance-related processes and factors influencing DMSP cycling in the SML. Regardless, the net effect of irradiance on DMSP was minor relative to dark bacterial consumption, indicating potential for DMS production in the SML.

4.2 DMS production and bacterial consumption

DMS dark production was the dominant DMS process in the SML, whereas the net response to irradiance and dark bacterial consumption of DMS varied between stations, with no single factor responsible for this variation (Figure 3, Table 4). DMS is produced by enzymatic cleavage of DMSP and also direct phytoplankton release (Yoch, 2002), as supported by the correlations between DMSP and DMS concentration in both the SSW and SML (S-M1). The mean $\tau_{DMS\ pr}$ and $\tau_{DMS\ cn}$ in the SML were 3 d and 8.3 d, within the range reported elsewhere for the SML (0.1 to 4.2 d; (Yang et al., 2005b; Yang and Tsunogai, 2005; Yang et al., 2005a; Zhang et al., 2008)). In terms of DMS consumption, $\tau_{DMS\ cn}$ in the SML was more rapid than $\tau_{DMS\ cn}$ reported for subsurface water during the Surface Ocean Aerosol Production voyage (SOAP) conducted in the same region of the South West Pacific (2.3 to 36.5 d; (Lizotte et al., 2017), again reflecting faster biological turnover in the SML (Yang and Tsunogai, 2005; Yang et al., 2005a; Zhang et al., 2008).

4.3 Effect of irradiance on DMS

As with DMSP, the response to irradiance was variable, with a net decrease in DMS at 3-SAW and 4-SAW in set A (Figure 3, Table 5), suggesting photo-oxidation of DMS (Brimblecombe and Shooter, 1986), and a positive effect at the other stations indicating stimulation of DMS production. This is consistent with the higher DMS:DMSP ratio in the light incubation (set A) at most stations, indicating elevated DMS production or inhibition of DMS bacterial consumption by light (Figure 4). That the

net response of DMS to irradiance was negative only at the SAW stations suggests differing sensitivity to light between water masses, although no significant relationships were identified between PAR and DMS concentration, process rates or enrichment in the SML (S-M1, Suppl. Info. Table S1). Under light stress, phytoplankton may elevate DMS production via three pathways - overflow, antioxidant system and cell damage (Gali et al., 2013). Under stress, such as nitrogen-limited conditions with the overflow hypothesis (Stefels, 2000), and iron limitation with the antioxidant pathway (Sunda et al., 2002), excess intracellular DMSP is produced and released, so increasing substrate for conversion to DMS. In surface water exposed to high solar radiation with low UV attenuation the cell damage pathway may result in increased cell permeability, further increasing DMSP availability for conversion to DMS (Gali et al., 2013). An additional impact of irradiance is the inhibition of bacterial DMS consumption (Slezak et al., 2007; Toole et al., 2006a), which may enhance DMS accumulation (Gali et al., 2013). As the net response of DMS to irradiance was more often positive (Figure 3, Table 5) this indicates that biological responses, such as stress production of DMS and inhibition of DMS consumption had greater losses to photo-oxidation.

With the exclusion of air-sea exchange in the deck-board incubation, DMS:DMSP in set A and B would be expected to exceed the *in situ* ratio in the SML, as observed at most stations (Figure 4). Only 3-SAW showed a different trend, with a similar DMS:DMSP in set A to the *in situ* ratio but higher ratio in set B, potentially indicating suppression of DMS production by irradiance at this station. Determination of the DMS photolysis constant, which is the inverse of $\tau_{DMS\ ir}$, generated rates of $0.004 – 0.035\ h^{-1}$, which are significantly lower than rates reported for subsurface water (0.026 to $0.14\ h^{-1}$ (Toole et al., 2006b; Brimblecombe and Shooter, 1986; Brugger et al., 1998; Kieber et al., 1996). This slower photolytic DMS turnover was unexpected due to the elevated solar and UV radiation exposure in the SML, although this may reflect variability of irradiance both during and between the deck incubation, in contrast to laboratory studies that use constant radiation often with wavelength cut-offs (Brimblecombe and Shooter, 1986; Brugger et al., 1998; Kieber et al., 1996; Toole et al., 2006a). In addition, previous photolysis studies have used filtered seawater (Kieber et al., 1996; Toole et al., 2006a; Brimblecombe and Shooter, 1986; Brugger et al., 1998), in contrast to the unfiltered samples in this study in which particle scattering and absorption may have buffered photolytic DMS losses. The slower photolytic DMS turnover from the current study can also be due to the SML biogeochemical properties; often the SML is enriched in gel-like particles which can protect the SML compounds from high solar irradiance (Ortega-Retuerta et al., 2009).

4.4 DMS dark yield

Notwithstanding differences between the ^{35}S-DMSP and dark net loss methodologies (Vila-Costa et al., 2008) DMS dark yields in the SML were in agreement with previous regional estimates (Lizotte et al., 2017; Vila-Costa et al., 2008). DMS dark yield was highest at 4-SAW due to high $k_{DMS\ pr}$ (Table 5), potentially due to the elevated dinoflagellate and small flagellate biomass at this station (S-M1), although no relationships were identified between DMS dark yield and other variables (see Suppl. Info. Table S1). The DMS:DMSP ratio indicated that 5 to 10% of DMSP was converted to DMS, consistent with previously reported estimates, and supporting the hypothesis that the proportion of DMSP cleaved to DMS is relatively constant across the ocean

and independent of regional influences and phytoplankton composition (Lizotte et al. (2017) and references therein). Although this is surprising considering the reported enrichment of bacteria and dissolved DMSP in the SML (Yang et al., 2009; Yang et al., 2005b; Zhang et al., 2008; Matrai et al., 2008), it is consistent with the general absence of enrichment in the current study (S-M1, see Table 5).

4.5 Relating SML processes to DMS enrichment

Air-sea emission was the dominant process controlling DMS concentration in the SML, with the air-sea turnover rate in the SML, calculated from the air-sea flux in S-M1, ranging from 8 to 19 min which is within the range reported in other studies (0.1 – 24.4 min (Yang et al., 2005a; Yang and Tsunogai, 2005; Yang et al., 2001)). Consequently, despite net DMS accumulation in the SML (Table 4), the significantly greater air-sea loss should deplete DMS in the SML and so prevent enrichment (Table 5). As the SML DMS production rates in the current study are consistent with others reported (Yang et al., 2005b; Yang and Tsunogai, 2005; Yang et al., 2001; Zhang et al., 2008) DMS production in the SML is unlikely to match air-sea loss, and consequently, regional DMS air-sea flux should not be influenced by DMS cycling in the SML (Yang and Tsunogai, 2005). Furthermore, at the single station where DMS enrichment was significant (3-SAW, S-M1), DMS production did not dominate and the DMS dark yield was low (Table 5). SML DMS might interact with the organic material in the SML which can then lower DMS volatility leading to an enrichment. However, no correlations between DMS and organic materials in the SML were found, and so the enrichment cannot be explained. It should be borne in mind that the apparent disconnect between SML process rates and enrichment may reflect comparison of *in situ* conditions with artificial conditions in the deck-board incubation. It is challenging to simulate the SML *in vitro*, particularly in recreating the SML thickness and interaction with the overlaying atmosphere and subsurface water, and the incubation design may have introduced artefacts (particle concentration, wall effects) and altered light exposure and attenuation relative to *in situ* conditions.

The current study was motivated by previous regional observations of high DMS enrichment and inferred influence of the SML on air-sea DMS emissions during the SOAP voyage (Walker et al., 2016), but has found no evidence to support this. The previous study noted the large inconsistency between estimated SML DMS production rates and the inferred production rates required to support air-sea flux estimates. This inconsistency is further confirmed by the similarity in net DMS accumulation rate of $0.3 – 8$ nmol L d^{-1} ($n = 5$) between the current study and during SOAP (range: -1 to 11 nmol L d^{-1}; Lizotte et al. (2017). The significant correlations observed in the current study between $k_{DMSP\,cn}$ with DMS ($r = -0.87$; $p = 0.05$; Spearman's rank correlation; Suppl. Info. Table S1), and also between $k_{DMSP\,cn}$ with DMSP concentration, dinoflagellates and *Gymnodinium* biomass ($r = -0.92$; $p = 0.03$, $r = -0.99$; $p = 0.01$, and $r = -0.95$; $p = 0.05$, respectively, Pearson tests, Suppl. Info. Table S1, S-M1), indicates that phytoplankton community composition is an important determinant of DMSP and DMS cycling in the SML. This then supports the contention that an optimal combination of biogeochemical, physical and meteorological factors - low winds, near-surface stratification and a bloom of high-DMSP dinoflagellates – resulted in the significant DMS enrichment

in the SML during the SOAP voyage (Walker et al., 2016), whereas these conditions were not experienced during the current study (SM-1).

5 Summary and conclusion

360 The current study presents the results of a comprehensive investigation into DMSP and DMS processes in the SML that is, to our knowledge, the first to assess DMSP cycling and the net effect of irradiance on both DMSP and DMS in the SML. Bacterial consumption of DMSP and dark production of DMS were the dominant processes in the SML, with irradiance having relatively minor impact on both species. Although these results are only representative of one region of the South West Pacific during the austral autumn, the combination of in situ SML observations in S-M1 and process rates in the current study indicate that

365 DMS enrichment in the SML is rare and that net accumulation of DMS in the SML is insufficient to balance DMS air-sea loss.

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Author contribution. Alexia D Saint-Macary developed the experiment set up. Alexia Saint-Macary wrote the manuscript, analysed DMSP and DMS. Andrew Marriner contributed to DMSP and DMS analysis. Stacy Deppeler analysed samples on the Flowcam and processed results, and Karl Safi identified the species by optical microscopy. Alexia D Saint-Macary, interpreted the results, with guidance from Cliff Law. There are no conflicts of interest.

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