https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 reactive gases. Enrichment of dimethyl sulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP) have 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 calculated air-sea DMS loss, confirming that the DMS cycling within the SML is unlikely to influence regional DMS emissions.

1 Introduction

The climate reactive trace gas dimethyl sulfide (DMS) is the primary natural aerosol precursor (Yu and Luo, 2010; Leaitch et al., 2013; Park et al., 2017; Sanchez et al., 2018) that contributes 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 are the net result of production and consumption by a variety of 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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 influenced by phytoplankton, 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 climate regulation as a significant source of atmospheric particles and organic aerosol (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 of dissolved organic substances (Gibbs adsorption surface, (Adamson and Gast, 1967)) and high surface tension which energetically favours DMSP adsorption (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 also consumption are 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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 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 influence DMSP and DMS both directly and indirectly (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 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 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., in revision), and will be referred as S-M1 thereafter), in contrast to a previous 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.

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

2 Method

2.1 Regional setting

The Sea2Cloud voyage took place on 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, and mixed water (Mixed) at station 6 (see Figure 1, Table 1). The mixed water had elevated nutrient content relative to the subtropical water (STW) reflecting a mixture of coastal and shelf water with STW (Sellegri et al., in revision). 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).

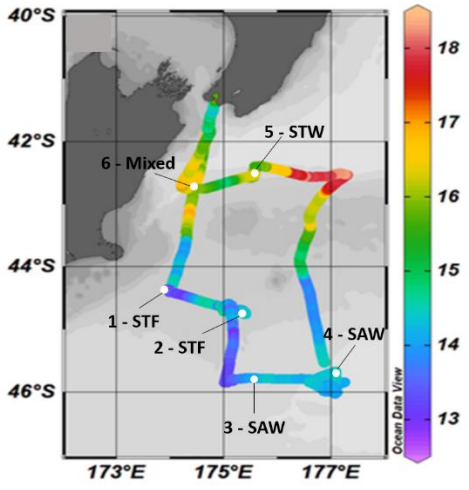

Figure 1: Sea2Cloud voyage track with workboat station positions overlain on sea surface water temperature (ºC). Figure plotted using Ocean Data View, Schlitzer and Reiner (2020). The grey shading shows the undersea topography, with the darker grey band along 43.5˚S indicating the Chatham Rise. Station 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, and windspeed was measured by an Automatic Weather Station, 25.2 m above the sea level.

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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 where no incubation was carried out as sampling occurred in the afternoon in contrast to the other stations. 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 were placed next to the deck incubation to record incoming irradiance in the wavelength range 400 – 700 nm.

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 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 preconcentration at −110 °C on a Tenax® trap. The trap was then heated to 120 °C to release the DMS onto an Agilent Technology 6850 Gas Chromatography coupled to an Agilent 355 Sulfur Chemiluminescent Detector (GC-SCD). The daily sensitivity and detection limit of the detector 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 before gas-tight sealing the vials. DMSP samples were stored in the dark at ambient temperature with analysis 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®, with 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.

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 net DMSP dark bacterial consumption rate, $k_{DMSP\ cn}$, was calculated using the change in DMSP concentration in set B over the 6-hour incubation. Net 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 net 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 and turnovers.

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

2.5 Statistical analysis

The Shapiro test was used to verify the normality of variable distribution. 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.

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 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, $k_{DMSP\ ir}$ 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 $k_{DMSP\ ir}$, 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 ($\tau_{DMSP\ cn}$) was faster than $\tau_{DMSP\ ir}$ with average values of 1.1 d (range: 0.7 – 1.4 d) and 7.3 d (1.7 – 16 d), respectively (Figure 2b). $\tau_{DMSP\ cn}$ was fastest in STF water but relatively uniform across the other stations, whereas $\tau_{DMSP\ ir}$ did not show any pattern in relation to water mass. Overall, only $k_{DMSP\ cn}$ showed 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).

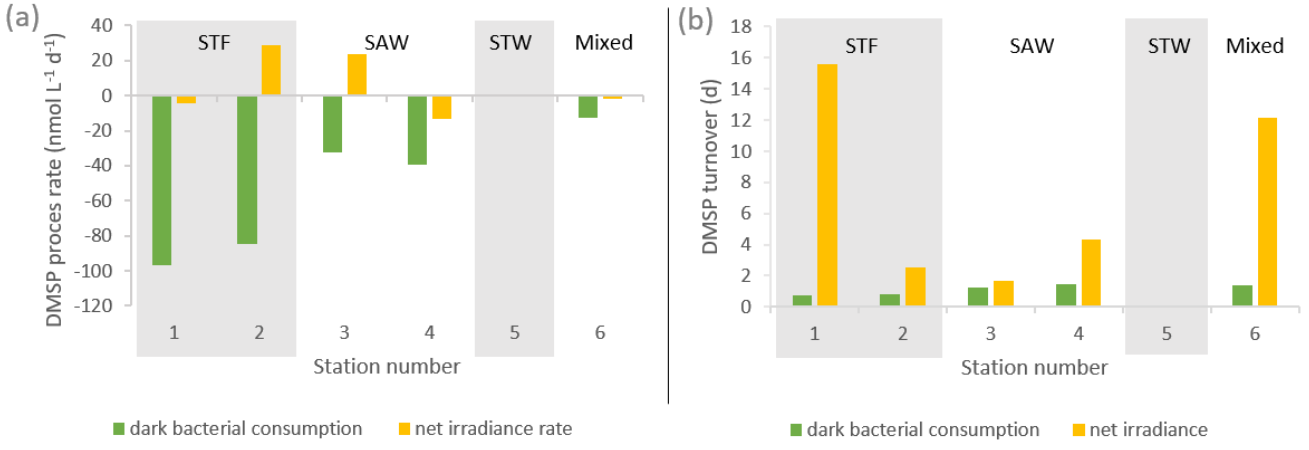

Figure 2: (a) DMSP process rates (nmol L^{-1} d^{-1}), and (b) DMSP consumption and net irradiance turnover (days) determined in deck incubation of SML water at each station. Water mass type is indicated by the label at the top of the figure and also the shading. Station 5-STW was sampled for SML characterisation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

3.2 DMS process rates

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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 $k_{DMSP\ cn}$ 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).

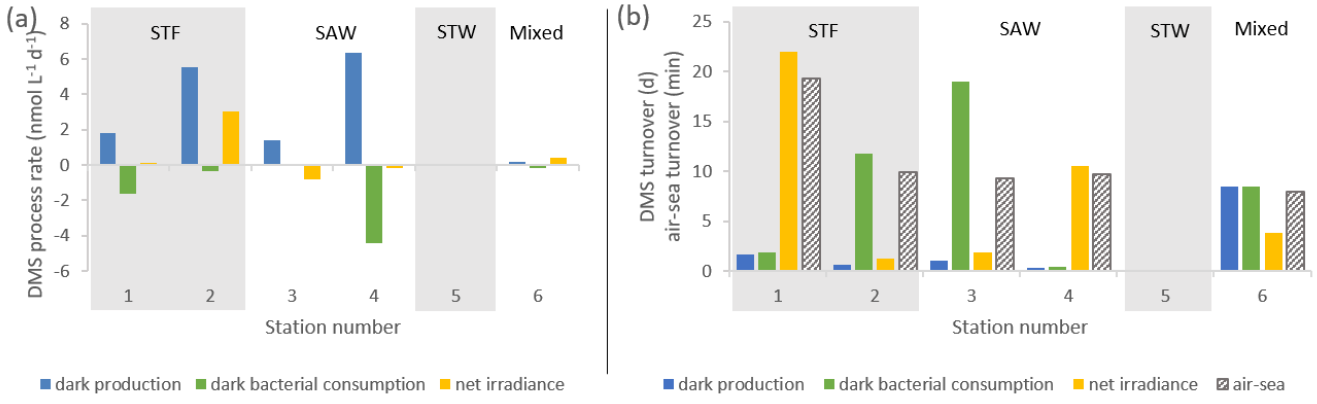

Figure 3: (a) DMS process rates (nmol L^{-1} d^{-1}) at each sampling station. (b) DMS turnover time in days for dark production, dark bacterial consumption and net irradiance response, and in minutes for air-sea turnover, with water mass type indicated by the label at the top of the figure and also the shading. 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.

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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

Table 4: Summary of DMS process rates (nmol L^{-1} d^{-1}), turnover (d) and air-sea turnover (min) 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.

Date	Station #	$[DMS]_{SML}$	$k_{DMS\ pr}$	$k_{DMS\ cn}$	$k_{DMS\ ir}$	Net accumulation rate	DMS dark yield	$\tau_{DMS\ cn}$	$\tau_{DMS\ pr}$	$\tau_{DMS\ ir}$	$\tau_{a/s}$
Mar-18	1-STF	3.08	1.8	−1.6	0.1	0.3	1.9	1.9	1.7	22	19
Mar-19	2-STF	3.76	5.6	−0.3	3.1	8.3	6.6	12	0.7	1.2	10
Mar-21	3-SAW	1.52	1.4	−0.1	−0.8	0.7	4.3	19	1.1	1.9	9.3
Mar-23	4-SAW	1.69	6.4	−4.4	−0.2	1.8	16.1	0.4	0.3	10.6	9.7
Mar-26	6-Mixed	1.52	0.2	−0.2	0.4	0.4	1.4	8.4	8.4	3.8	8.0
Average	-	*2.31*	*3.1*	*−1.3*	*0.5*	*2.3*	*6.1*	*8.3*	*3.1*	*7.9*	*11*

3.3 DMS:DMSP ratio

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 set A and B at each station, except for 3-SAW where it was higher in set B (dark).

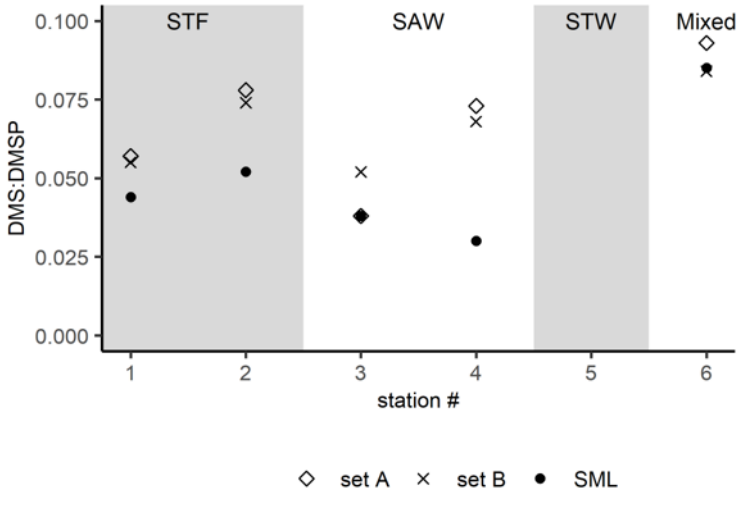

Figure 4: DMS:DMSP ratio in the SML at T_0, and at the end of the 6 hour deck incubations in set A and B at each station. At 3-SAW, the ratio in set A is equal to, and so obscured, by the initial ratio in the SML. Station 5-STW was sampled for SML characterisation (S-M1) but had no deck-board incubation.

4 Discussion

The characteristics of the SML during the current study contrasted with a previous 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;

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 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 EF DMS in different water masses. In the EF columns, depletion is indicated by "–", enrichment by "+", and "n/s" is not significant. Station 3-SAW where DMS enrichment occurred is highlighted in the shaded row. 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} 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 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, confirming 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 is higher than regional rates determined in SSW with the ^{35}S-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).

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 4.1). 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 SOAP (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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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).

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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), 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 the associated influence of the SML on air-sea DMS emissions (Walker et al., 2016), but has found no evidence to support this. The previous study noted the large inconsistency between measured DMS production rates in the SML and inferred production rates required to support air-sea flux estimates. This inconsistency is further confirmed by net DMS accumulation rates of 0.3 – 8 nmol L d^{-1} in the current study, that are consistent with previous regional estimates (mean 15 nmol L d^{-1}, (Lizotte et al., 2017)). The significant correlation between $k_{DMSP\ cn}$ with DMS and DMSP concentration, dinoflagellates and *Gymnodinium* biomass (Suppl. Info. Table S1, S-M1), confirms that this phytoplankton group and species play are important determinants of DMSP and DMS cycling in the SML. This further emphasises the requirement for an optimal combination of biogeochemical, physical and meteorological factors - low winds, near-surface stratification and a bloom of high-DMSP dinoflagellates - for significant DMS enrichment to occur in the SML (S-M1), as during the SOAP voyage (Walker et al., 2016). The combined observations from S-M1 and the current study confirm that SML DMS enrichment is rare in the South-west Pacific, reflecting that DMSP and DMS cycling in the SML are insufficient to maintain DMS enrichment concurrent with elevated air-sea loss.

Acknowledgment. We would like to thank Theresa Barthelmeß for her contribution to the SML sampling, and Antonia Cristi and Wayne Dillon for their help during the Sea2Cloud campaign. This research was supported by NIWA SSIF funding to the Ocean-Climate Interactions Programme. We would also like to thank the support and expertise of the Officers and Crew of the R/V Tangaroa.

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

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

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 conflict of interests.

5 References

Adamson, A. W. and Gast, A. P.: Physical chemistry of surfaces, Interscience publishers New York1967.

Agogué, H., Casamayor, E. O., Bourrain, M., Obernosterer, I., Joux, F., Herndl, G. J., and Lebaron, P.: A survey on bacteria inhabiting the sea surface microlayer of coastal ecosystems, FEMS microbiology ecology, 54, 269-280, 2005.

Archer, S. D., Ragni, M., Webster, R., Airs, R. L., and Geider, R. J.: Dimethyl sulfoniopropionate and dimethyl sulfide production in response to photoinhibition in Emiliania huxleyi, Limnology and oceanography, 55, 1579-1589, 2010.

Archer, S. D., Stefels, J., Airs, R. L., Lawson, T., Smyth, T. J., Rees, A. P., and Geider, R. J.: Limitation of dimethylsulfoniopropionate synthesis at high irradiance in natural phytoplankton communities of the Tropical Atlantic, Limnology and Oceanography, 63, 227-242, 10.1002/lno.10625, 2018.

Bailey, C. A., Neihof, R. A., and Tabor, P. S.: Inhibitory effect of solar radiation on amino acid uptake in Chesapeake Bay bacteria, Appl Environ Microbiol, July, 44-49, 1983.

Belviso, S., Christaki, U., Vidussi, F., Marty, J.-C., Vila, M., and Delgado, M.: Diel variations of the DMSP-to-chlorophyll a ratio in Northwestern Mediterranean surface waters, Journal of marine systems, 25, 119-128, 2000.

Bouillon, R.-C., Lee, P. A., de Mora, S. J., Levasseur, M., and Lovejoy, C.: Vernal distribution of dimethylsulphide, dimethylsulphoniopropionate, and dimethylsulphoxide in the North Water in 1998, Deep Sea Research Part II: Topical Studies in Oceanography, 49, 5171-5189, 2002.

Brimblecombe, P. and Shooter, D.: Photo-oxidation of dimethysulphide in aqueous solution, Marine Chemistry, 19, 343-353, 1986.

Brugger, A., Slezak, D., Obernosterer, I., and Herndl, G. J.: Photolysis of dimethylsulfide in the northern Adriatic Sea: Dependence on substrate concentration, irradiance and DOC concentration, Marine Chemistry, 59, 321-331, 1998.

Carlucci, A., Craven, D., and Henrichs, S.: Surface-film microheterotrophs: amino acid metabolism and solar radiation effects on their activities, Marine Biology, 85, 13-22, 1985.

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

Conrad, R. and Seiler, W.: Influence of the Surface Microlayer on the Flux of Nonconservative Trace Gases (CO, H2, CH4, N20) Across the Ocean-Atmosphere Interface, Journal of Atmospheric Chemistry, 6, 83-94, 1988.

Cunliffe, M., Upstill-Goddard, R. C., and Murrell, J. C.: Microbiology of aquatic surface microlayers, FEMS Microbiol Rev, 35, 233-246, 10.1111/j.1574-6976.2010.00246.x, 2011.

Cunliffe, M., Engel, A., Frka, S., Gašparović, B., Guitart, C., Murrell, J. C., Salter, M., Stolle, C., Upstill-Goddard, R., and Wurl, O.: Sea surface microlayers: A unified physicochemical and biological perspective of the air–ocean interface, Progress in Oceanography, 109, 104-116, 10.1016/j.pocean.2012.08.004, 2013.

Curson, A. R., Liu, J., Martínez, A. B., Green, R. T., Chan, Y., Carrión, O., Williams, B. T., Zhang, S.-H., Yang, G.-P., and Page, P. C. B.: Dimethylsulfoniopropionate biosynthesis in marine bacteria and identification of the key gene in this process, Nature microbiology, 2, 1-9, 2017.

Dacey, J. W., Howse, F. A., Michaels, A. F., and Wakeham, S. G.: Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea, Deep Sea Research Part I: Oceanographic Research Papers, 45, 2085-2104, 1998.

Frew, N. M., Nelson, R. K., Mcgillis, W. R., Edson, J. B., Bock, E. J., and Hara, T.: Spatial variations in surface microlayer surfactants and their role in modulating air-sea exchange, Washington DC American Geophysical Union Geophysical Monograph Series, 127, 153-159, 2002.

Frew, N. M., Bock, E. J., Schimpf, U., Hara, T., Haußecker, H., Edson, J. B., McGillis, W. R., Nelson, R. K., McKenna, S. P., and Uz, B. M.: Air-sea gas transfer: Its dependence on wind stress, small-scale roughness, and surface films, Journal of Geophysical Research: Oceans, 109, 2004.

Gali, M., Ruiz-Gonzàlez, C., Lefort, T., Gasol, J. M., Cardelús, C., Romera-Castillo, C., and Simó, R.: Spectral irradiance dependence of sunlight effects on plankton dimethylsulfide production, Limnology and Oceanography, 58, 489-504, 10.4319/lo.2013.58.2.0489, 2013.

Galí, M. and Simó, R.: A meta-analysis of oceanic DMS and DMSP cycling processes: Disentangling the summer paradox, Global Biogeochemical Cycles, 29, 496-515, 2015.

Galí, M., Simó, R., Pérez, G. L., Ruiz-González, C., Sarmento, H., Royer, S. J., Fuentes-Lema, A., and Gasol, J. M.: Differential response of planktonic primary, bacterial, and dimethylsulfide production rates to static vs. dynamic light exposure in upper mixed-layer summer sea waters, Biogeosciences, 10, 7983-7998, 10.5194/bg-10-7983-2013, 2013.

Hardy, J. T.: The sea-surface microlayer - biology, chemistry and anthropogenic enrichment, Progress in Oceanography, 11, 307-328, 10.101016/0079-6611(82)901-5, 1982.

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

Hefu, Y. and Kirst, G. O.: Effect of UV-radiation on DMSP content and DMS formation of Phaeocystis antarctica, Polar Biology, 18, 402-409, 1997.
Herndl, G. J., Muller-Niklas, G., and Frick, J.: Major role of ultraviolet-B in controlling bacterioplankton growth in the surface layer of the ocean, Nature, 361, 1993.
Hunter, K. A.: Processes affecting particulate trace metals in the sea surface microlayer, Marine Chemistry, 9, 49-70, 1980.
Keller, M. D. and Korjeff-Bellows, W.: Physiological aspects of the production of dimeyhtlsulfoniopropionate (DMSP) by marine phytoplankton, in: Biological and environmental chemistry of DMSP and related sulfonium compounds, Springer, 131-142, 1996.
Keller, M. D., Bellows, W. K., and Guillard, R. L.: Dimethyl Sulfide Production in Marine Phytoplankton, Biogenic Sulfur in the Environment, 393, 167-182, 10.1021/bk-1989-0393.ch011, 1989.
Kieber, D. J., Jiao, J., Kiene, R. P., and Bates, T. S.: Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean, Journal of Geophysical Research: Oceans, 101, 3715-3722, 10.1029/95jc03624, 1996.
Kiene, R. P.: Production of methanethiol from dimethylsulfoniopropionate in marine surface waters, Marine Chemistry, 54, 69-83, 1996.
Kiene, R. P. and Linn, L. J.: The fate of dissolved dimethylsulfiniopropionate (DMSP) in seawater: Tracer studies using 35S-DMSP, Geochimica et Cosmochimica Acta, 64, 2797-2810, 2000.
Lana, A., Bell, T., Simó, R., Vallina, S., Ballabrera-Poy, J., Kettle, A., Dachs, J., Bopp, L., Saltzman, E., and Stefels, J.: An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean, Global Biogeochemical Cycles, 25, 2011.
Leaitch, W. R., Sharma, S., Huang, L., Toom-Sauntry, D., Chivulescu, A., Macdonald, A. M., von Salzen, K., Pierce, J. R., Bertram, A. K., Schroder, J. C., Shantz, N. C., Chang, R. Y.-W., and Norman, A.-L.: Dimethyl sulfide control of the clean summertime Arctic aerosol and cloud, Elementa: Science of the Anthropocene, 1, 10.12952/journal.elementa.000017, 2013.
Leck, C. and Bigg, E. K.: Source and evolution of the marine aerosol—A new perspective, Geophysical Research Letters, 32, 2005.
Lizotte, M., Levasseur, M., Law, C. S., Walker, C. F., Safi, K. A., Marriner, A., and Kiene, R. P.: Dimethylsulfoniopropionate (DMSP) and dimethyl sulfide (DMS) cycling across contrasting biological hotspots of the New Zealand subtropical front, Ocean Science, 13, 961-982, 10.5194/os-13-961-2017, 2017.
Matrai, P. A., Tranvik, L., Leck, C., and Knulst, J. C.: Are high Arctic surface microlayers a potential source of aerosol organic precursors?, Marine Chemistry, 108, 109-122, 10.1016/j.marchem.2007.11.001, 2008.
Miles, C. J., Bell, T. G., and Lenton, T. M.: Testing the relationship between the solar radiation dose and surface DMS concentrations using in situ data, Biogeosciences, 6, 1927-1934, 2009.
Muller-Niklas, G., Heissenberger, A., Stasa, P., and Herndl, G. J.: Ultraviolet-B radiation and bacterial metabolism in coastal waters, Aquatic Microbial Ecology, 9, 111-116, 1995.
Nguyen, B. C., Gaudry, A., Bonsang, B., and Lambert, G.: Reevaluation of the role of dimethyl sulphide in the sulphur budget, Nature, 275, 637-639, 10.1038/275637a0, 1978.
Ortega-Retuerta, E., Passow, U., Duarte, C. M., and Reche, I.: Effects of ultraviolet B radiation on (not so) transparent exopolymer particles, Biogeosciences, 6, 3071-3080, 2009.
Park, K. T., Jang, S., Lee, K., Yoon, Y. J., Kim, M. S., Park, K., Cho, H. J., Kang, J. H., Udisti, R., Lee, B. Y., and Shin, K. H.: Observational evidence for the formation of DMS-derived aerosols during Arctic phytoplankton blooms, Atmos. Chem. Phys., 17, 9665-9675, 10.5194/acp-17-9665-2017, 2017.
Quinn, P. K. and Bates, T. S.: The case against climate regulation via oceanic phytoplankton sulphur emissions, Nature, 480, 51-56, 10.1038/nature10580, 2011.
Reinthaler, T., Sintes, E., and Herndl, G. J.: Dissolved organic matter and bacterial production and respiration in the sea-surface microlayer of the open Atlantinc and western Mediterranean Sea, Limnology and Oceanography, 53, 122-136, 2008.
Rellinger, A. N., Kiene, R. P., del Valle, D. A., Kieber, D. J., Slezak, D., Harada, H., Bisgrove, J., and Brinkley, J.: Occurrence and turnover of DMSP and DMS in deep waters of the Ross Sea, Antarctica, Deep Sea Research Part I: Oceanographic Research Papers, 56, 686-702, 2009.
Roslan, R. N., Hanif, N. M., Othman, M. R., Azmi, W. N., Yan, X. X., Ali, M. M., Mohamed, C. A., and Latif, M. T.: Surfactants in the sea-surface microlayer and their contribution to atmospheric aerosols around coastal areas of the Malaysian peninsula, Mar Pollut Bull, 60, 1584-1590, 10.1016/j.marpolbul.2010.04.004, 2010.
Saint-Macary, A. D., Barthelmess, T., Marriner, A., Deppeler, S., Safi, K., Costa Santana, R., Harvey, M., and Law, C. S.: DMS cycling in the Sea Surface Microlayer in the South West Pacific: 1. Enrichment portential determined using a novel sampler, Ocean Science, in revision.
Sanchez, K. J., Chen, C.-L., Russell, L. M., Betha, R., Liu, J., Price, D. J., Massoli, P., Ziemba, L. D., Crosbie, E. C., Moore, R. H., Müller, M., Schiller, S. A., Wisthaler, A., Lee, A. K. Y., Quinn, P. K., Bates, T. S., Porter, J., Bell, T. G., Saltzman, E. S., Vaillancourt, R. D., and Behrenfeld, M. J.: Substantial Seasonal Contribution of Observed Biogenic Sulfate Particles to Cloud Condensation Nuclei, Scientific Reports, 8, 3235, 10.1038/s41598-018-21590-9, 2018.
Ocean Data View: https://odv.awi.de, last
Sellegri, K., Law, C. S., Peltola, M., Trueblood, J., Saint-Macary, A., Barthelmess, T., Rocco, M., Moore, K. A., Cristi, A., Peyrin, F., Barr, N., Lanbonnote, L., Marriner, A., McGregor, J., Safi, K., Deppeler, S., Archer, S., Picard, D., Dunne, E., Harnwell, J., Delanoe, J., Colomb,

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

A., Freney, E., Saiz Lopez, A., Quintanilla-Lopez, J., Lebron-Aguilar, R., and Harvey, M.: Sea2Cloud R/V Tangaroa voyage: from biogenic emission fluxes to Cloud properties in the South Western Pacific, Bulletin of the American Meteorological Society, in revision.

Sieburth, J.: Microbiological and organic-chemical processes in the surface and mixed layers, Air-sea exchange of gases and particles, 121-172, 1983.

Simó, R. and Dachs, J.: Global ocean emission of dimethylsulfide predicted from biogeophysical data, Global Biogeochemical Cycles, 16, 26-21-26-10, 10.1029/2001gb001829, 2002.

Simó, R. and Pedrós-Alió, C.: Short-term variability in the open ocean cycle of dimethylsulfide, Global Biogeochemical Cycles, 13, 1173-1181, 10.1029/1999gb900081, 1999.

Simó, R., Pedrós-Alió, C., Malin, G., and Grimalt, J. O.: Biological turnover of DMS, DMSP and DMSO in contrasting open-sea waters, Marine Ecology Progress Series, 203, 1-11, 2000.

Slezak, D., Brugger, A., and Herndl, G. J.: Impact of solar radiation on the biological removal of dimethylsulfoniopropionate and dimethylsulfide in marine surface waters, Aquatic Microbial Ecology, 25, 87-97, 2001.

Slezak, D., Kiene, R. P., Toole, D. A., Simó, R., and Kieber, D. J.: Effects of solar radiation on the fate of dissolved DMSP and conversion to DMS in seawater, Aquatic Sciences, 69, 377-393, 10.1007/s00027-007-0896-z, 2007.

Stefels, J.: Physiological aspects of the production and conversion of DMSP in marine algae and higher plants, Journal of Sea Research, 43, 183-197, 2000.

Stefels, J., Steinke, M., Turner, S., Malin, G., and Belviso, S.: Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling, Biogeochemistry, 83, 245-275, 10.1007/s10533-007-9091-5, 2007.

Stolle, C., Ribas-Ribas, M., Badewien, T. H., Barnes, J., Carpenter, L. J., Chance, R., Damgaard, L. R., Durán Quesada, A. M., Engel, A., Frka, S., Galgani, L., Gašparović, B., Gerriets, M., Hamizah Mustaffa, N. I., Herrmann, H., Kallajoki, L., Pereira, R., Radach, F., Revsbech, N. P., Rickard, P., Saint, A., Salter, M., Striebel, M., Triesch, N., Uher, G., Upstill-Goddard, R. C., van Pinxteren, M., Zäncker, B., Zieger, P., and Wurl, O.: The MILAN Campaign: Studying Diel Light Effects on the Air–Sea Interface, Bulletin of the American Meteorological Society, 101, E146-E166, 10.1175/bams-d-17-0329.1, 2020.

Sunda, W. G., Kieber, D. J., Kiene, R. P., and Huntsman, S.: An antioxidant function for DMSP and DMS in marine algae, Letters to Nature, 418, 2002.

Toole, D., Slezak, D., Kiene, R., Kieber, D., and Siegel, D.: Effects of solar radiation on dimethylsulfide cycling in the western Atlantic Ocean, Deep Sea Research Part I: Oceanographic Research Papers, 53, 136-153, 2006a.

Toole, D. A., Slezak, D., Kiene, R. P., Kieber, D. J., and Siegel, D. A.: Effects of solar radiation on dimethylsulfide cycling in the western Atlantic Ocean, Deep Sea Research Part I: Oceanographic Research Papers, 53, 136-153, 10.1016/j.dsr.2005.09.003, 2006b.

Upstill-Goddard, R. C., Frost, T., Henry, G. R., Franklin, M., Murrell, J. C., and Owens, N. J.: Bacterioneuston control of air-water methane exchange determined with a laboratory gas exchange tank, Global biogeochemical cycles, 17, 2003.

Vallina, S. M. and Simó, R.: Strong relationship between DMS and the solar radiation dose over the global surface ocean, Science, 315, 506-508, 2007.

van Rijssel, M. and Buma, A. G.: UV radiation induced stress does not affect DMSP synthesis in the marine prymnesiophyte Emiliania huxleyi, Aquatic microbial ecology, 28, 167-174, 2002.

Vila-Costa, M., Kiene, R. P., and Simí, R.: Seasonal variability of the dynamics of dimethylated sulfur compounds in a coastal northwest Mediterranean site, Limnology and Oceanography, 53, 198-211, https://doi.org/10.4319/lo.2008.53.1.0198, 2008.

Vogt, M. and Liss, P.: Dimethylsulfide and climate, Surface Ocean-Lower Atmosphere Processes, edited by: Le Quéré, C., and Saltzman, ES, American Geophysical Union, Washington, DC, 197-232, 2009.

Walker, C. F., Harvey, M. J., Smith, M. J., Bell, T. G., Saltzman, E. S., Marriner, A. S., McGregor, J. A., and Law, C. S.: Assessing the potential for dimethylsulfide enrichment at the sea surface and its influence on air-sea flux, Ocean Science, 12, 1033-1048, 10.5194/os-12-1033-2016, 2016.

Wang, W.-L., Song, G., Primeau, F., Saltzman, E. S., Bell, T. G., and Moore, J. K.: Global ocean dimethyl sulfide climatology estimated from observations and an artificial neural network, Biogeosciences, 17, 5335-5354, 2020.

Wolfe, G. V. and Kiene, R. P.: Effects of methylated, organic, and inorganic substrates on microbial consumption of dimethyl sulfide in estuarine waters, Applied and Environmental Microbiology, 59, 2723-2726, 10.1128/aem.59.8.2723-2726.1993, 1993.

Yang, G.-P.: Dimethylsulfide enrichment in the surface microlayer of the South China Sea, Marine Chemistry, 66, 215-224, 1999.

Yang, G.-P. and Tsunogai, S.: Biogeochemistry of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the surface microlayer of the western North Pacific, Deep Sea Research Part I: Oceanographic Research Papers, 52, 553-567, 10.1016/j.dsr.2004.11.013, 2005.

Yang, G.-P., Tsunogai, S., and Watanabe, S.: Biogenic sulfur distribution and cycling in the surface microlayer and subsurface water of Funka Bay and its adjacent area, Continental Shelf Research, 25, 557-570, 10.1016/j.csr.2004.11.001, 2005a.

Yang, G.-P., Watanabe, S., and Tsunogai, S.: Distribution and cycling of dimethylsulfide in surface microlayer and subsurface seawater, Marine Chemistry, 76, 137-153, 2001.

https://doi.org/10.5194/egusphere-2022-504
Preprint. Discussion started: 22 June 2022

Yang, G.-P., Levasseur, M., Michaud, S., and Scarratt, M.: Biogeochemistry of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the surface microlayer and subsurface water of the western North Atlantic during spring, Marine Chemistry, 96, 315-329, 10.1016/j.marchem.2005.03.003, 2005b.

Yang, G.-P., Levasseur, M., Michaud, S., Merzouk, A., Lizotte, M., and Scarratt, M.: Distribution of dimethylsulfide and dimethylsulfoniopropionate and its relation with phytoneuston in the surface microlayer of the western North Atlantic during summer, Biogeochemistry, 94, 243-254, 10.1007/s10533-009-9323-y, 2009.

Yoch, D. C.: Dimethylsulfoniopropionate: Its sources, role in the marine food web, and biological degradation to dimethylsulfide, Applied and Environmental Microbiology, 68, 5804-5815, 10.1128/AEM.68.12.5804-5815.2002, 2002.

Yu, F. and Luo, G.: Oceanic Dimethyl Sulfide Emission and New Particle Formation around the Coast of Antarctica: A Modeling Study of Seasonal Variations and Comparison with Measurements, Atmosphere, 1, 34-50, 2010.

Zemmelink, H. J., Houghton, L., Frew, N. M., and Dacey, J. W. H.: Dimethylsulfide and major sulfur compounds in a stratified coastal salt pond, Limnology and Oceanography, 51, 271-279, 2006.

Zemmelink, H. J., Houghton, L., Sievert, S. M., Frew, N. M., and Dacey, J. W.: Gradients in dimethylsulfide, dimethylsulfoniopropionate, dimethylsulfoxide, and bacteria near the sea surface, Marine Ecology Progress Series, 295, 33-42, 2005.

Zhang, H.-H., Yang, G.-P., and Zhu, T.: Distribution and cycling of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the sea-surface microlayer of the Yellow Sea, China, in spring, Continental Shelf Research, 28, 2417-2427, 10.1016/j.csr.2008.06.003, 2008.

Zhang, H.-H., Yang, G.-P., Liu, C.-Y., and Li, C.: Seasonal variations od dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the sea-surface microlayer and subsurface water of Jiaozhou Bay and its adjacent area, Acta Oceanologica Sinica, 28, 73-86, 2009.