Below we reproduce the comments from both reviewers and reply to these:

Reviewer 1

We thank the reviewer for their informed response and recognition of the value of our data.

1. *For the methodology, what is the precision for the continuous DMS measurements using an atmospheric pressure chemical ionization mass spectrometer equipped with a porous membrane equilibrator?*

   The mean relative standard error on the 5 min averaged SOAP data was +/-5%. We have now included this in the methods section 2.3.1. A detailed description of the miniCIMS can be found in Bell et al. 2013, as referenced in the manuscript.

2. *Gas phase DMS was cryogenically concentrated on 60/80 Tenax TA in a 1/8" Restek Sulfinert-treated stainless steel trap at -20ºC. Usually, the dry ice-ethanol liquid at -78ºC or liquid nitrogen liquid at -190ºC were used to trap DMS more efficiently. According to my previous studies, the temperature of -20ºC is not high enough to trap all the DMS.*

   As the reviewer points out, there are a number of methods for trapping DMS; we have previously used both liquid nitrogen cold trap as well as the stated method with Tenax. Our laboratory first adopted the Tenax preconcentration method 18 years ago, following the well established procedures used by DMS measurement experts at NOAA and UEA UK. The trapping capacity of a Tenax trap is design dependent, primarily determined by the air flow rate through the trap and the mass of Tenax, which control the trap breakthrough volume which is strongly temperature dependent. Our findings for trap capacity are consistent with Kroupa et al (2004) who only tested to -10^{o}C. For our trap set-up at -20^{o}C we have a breakthrough volume of 40 Litres per gram (DMS) and for the flow rate used, our trapping phase was 10 minutes which is well within the 50% retention time of 40 minutes. Recent interlaboratory comparisons (Swan et al, 2014) and previous studies have confirmed the accuracy of our trapping method.

3. *In section 3.5 DMS production rates in the SSM, the authors assumed that other DMS loss terms (photolysis, bacterial oxidation and vertical diffusion to subsurface water) were negligible. However, it should be pointed out, that this hypothesis might produce some bias because the photochemical oxidation rates and bacterial oxidation rates of DMS are also main sinks in actual oceans. The authors need to point out how this affects the results.*

   The reviewer is correct that these processes are potential DMS sinks, but as we did not measure either in the sea surface microlayer, we have no confirmation of their contribution. However, as the SSM photoproduction rate calculation does not include these processes, it is perhaps misleading to say that these are negligible, and so we have clarified this in the following revised text:

   "This approach assumes that DMS production in the SSM was the source of the 'excess' air–sea flux in B1. Other potential DMS loss processes such as photolysis and bacterial oxidation, may have also been significant DMS sinks (Kieber et al., 1996; Gali et al., 2013); however as these rates were not quantified they are not considered, and so the estimate of PR$_{SSM}$ may represent an underestimate."

As this raises further questions regarding DMS production in the SSM, so we have also added in the Discussion:

"To maintain the observed and calculated enrichment in the SSM, DMS production must dominate over loss terms such as photolysis and bacterial oxidation, and occur at a significantly greater rate than previously reported for the open ocean (Simo, 2004)."

4. *In section 4 Discussion. In this study, DMS did not show any gradient in near-surface waters (see Fig. 4). This result is a little strange. Please explain this point using chlorophyll-a and phytoplankton species data. Did chlorophyll-a distribute uniformly as well in the near-surface waters?*

   The absence of a near-surface DMS gradient would be expected, unless near-surface production or consumption rates were significant. As mentioned in the Discussion, previous observations (Zemmelink et al, 2005) have identified a near-surface DMS gradient which they attributed to degassing. However our observations of no significant DMS gradient between 1 and 1.6m are indicative of a balance between production and loss processes, in agreement with the other reported studies, as stated in the Discussion. We did not obtain measurements of chlorophyll or phytoplankton species data in the microlayer, only in the 1cm depth RHIB sample and the 2m CTD sample which would not provide robust data on near-surface gradients. This paper focuses on DMS concentration and flux data, whereas the biogeochemical data from near-surface waters will be presented in another paper.

5. *"Furthermore, the presence of surfactants may have suppressed ventilation across the air–sea interface (Salter et al., 2011) under these conditions, leading to accumulation of DMS in the SSM". Please add data or references to support the presence of surfactants in the microlayer.*

   Surfactant measurements were not obtained; however, other related parameters were measured at 1cm depth and 1.6m. These include chlorophyll-*a*, which showed a mean enrichment of 1.4 at 1cm, CDOM which showed a mean enrichment of 1.3 at 1cm, and DOC which showed no significant enrichment. However, the enrichments in B1 for CDOM and chlorophyll-*a* were not significantly greater than mean values for the entire dataset. As mentioned above, the biogeochemical data from near-surface waters will be presented in another paper.

   We have rephrased the sentence in question to read:

   "Furthermore, if surfactants were present, they may have suppressed ventilation across the air-sea interface (Salter et al., 2011) under these conditions, leading to an accumulation of DMS in the SSM."

6. In addition, we have added the following information to the Discussion on Pg 12, L 31:

   "The coincidence of elevated phytoplankton DMS production, inhibition of bacterial DMSP consumption, and tolerance of bacterial DMSP degradation under elevated UV-A reported for BATS (Levine et al., 2012), provides further support for potential DMS accumulation in the SSM."

Reviewer 2

We thank the reviewer for their support and constructive critique of our manuscript.

1. *Bacterioplankton are also an important source of DMS, which they produce from phytoplankton-derived DMSP. This needs to be considered within your proposed paradigm. Did you count bacterioplankton and/or bacterioneuston?*

   Bacterial abundance was measured at 1 cm and at 1.6m; however, this paper focuses on DMS concentration and flux data, and bacterial utilisation of DMSP in near-surface waters in SOAP is addressed by Lizotte et al. (manuscript to be submitted).

2. *DMS as a source of CCN - has this ever been proven? A more contemporary view of marine CCN sources needs to be acknowledged. What about carbohydrate-based microgels?*

   As the basis of the CLAW hypothesis, DMS has long been regarded as a potential source of CCN. There is, however, evidence both for and against this (as summarised in Quinn and Bates (2011), including the potential role of organics and microgels. Consequently we have revised this sentence to read:

   "It has been hypothesised that DMS-derived aerosols may have a significant impact on the radiation budget (Charlson et al., 1987; Andreae and Crutzen, 1997; Ayers and Gillett, 2000) via direct scattering of sunlight and changes to cloud properties. However, more recent experiments highlight additional biogenic sources and pathways for the production of CCN even in the absence of sulfate aerosol (Quinn & Bates 2011; Bianchi et al., 2016; Kirkby et al., 2016)."

3. *Did you quantify phytoneuston? Please explain how dinoflagellates, coccolithophores and other phytoplankton were counted and identified? Given 'biological conditions' (Page 10 L24) are a key factor in your conclusions, then I think that some biological data should be included.*

   Biological data was not included in this manuscript as it focuses on DMS concentrations and flux, and the full biogeochemical description for SOAP will be provided in the overview paper (Law et al., draft to be published) and other papers. We feel there is sufficient biogeochemical distinction of the three blooms to warrant attribution of differences in [DMS] and DMS flux to biological conditions without presentation of this data. Phytoplankton community composition and abundance measurements were made at 1cm depth and also at 1.6m. We have now included the following sentence in the Methods:

   "Phytoplankton identification, biomass and abundance data were obtained by optical microscopy of Lugols-preserved samples. These data are presented elsewhere."

4. *Page 1 L25 This statements needs a reference.*

   The reference McCoy et al. (2015) has now been added to the statement "In remote, relatively pristine marine environments such as the Southern Ocean, the production of aerosols and clouds is predominantly governed by natural sources."

5. *Page 2 L 20 Natural degassing or methodological degassing?*

We believe the sentence in question is on L28. This has been modified to read:

"To date, studies characterising near-surface [DMS] have shown a decreasing gradient towards the interface, indicative of degassing to the atmosphere (Zemmelink et al., 2005)."

6. *Page 3 L1 What is the 'challenge'? Please explain.*

   This sentence now reads:

   "Despite the challenge of maintaining a DMS source in a relatively thin (10-100 µm) layer at the air-water interface that is subject to extreme physicochemical conditions (Zuev et al., 2001), a number of studies have examined and identified enrichment of DMS in the sea-surface microlayer as summarised in Fig. 1 and references therein."

7. *Page 12 L27 Dinoflagellates are DMSP producers. OK, but what about DMS?*

   Enzymatic cleavage of DMSP is currently viewed as the primary process for DMS production. As dinoflagellates are a major source of both DMSP and DMSP lyase, the enzyme which coverts it to DMS (Steinke et al, 2002), it is assumed that dinoflagellates are responsible for DMS production. Steinke et al (2002 & references within) identify that dinoflagellates can convert DMSP to DMS, and there are a number of empirical studies that have identified elevated DMS associated with dinoflagellates (e.g. Zhang et al., 2014; Zindler et al., 2012). We have included some of this information in the Discussion.

Assessing the potential for DMS enrichment at the sea-surface and its influence on air–sea flux

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Abstract. The flux of dimethylsulfide (DMS) to the atmosphere is generally inferred using water sampled at or below 2 m depth, thereby excluding any concentration anomalies at the air–sea interface. Two independent techniques were used to assess the potential for near-surface DMS enrichment to influence DMS emissions and also identify the factors influencing enrichment. DMS measurements in productive frontal waters over the Chatham Rise, east of New Zealand, did not identify any significant ~~DMS~~ gradients between 0.01 and 6 m in sub-surface seawater, whereas DMS enrichment in the sea-surface microlayer was variable, with a mean enrichment factor (EF; the concentration ratio between DMS in the SSM and in sub-surface water) of 1.7. Physical and biological factors influenced sea-surface microlayer DMS concentration, with high enrichment (EF > 1.3) only recorded in a dinoflagellate-dominated bloom, and associated with low to medium wind speeds and near-surface temperature gradients. On occasion, high DMS enrichment preceded periods when the air–sea DMS flux, measured by eddy covariance, exceeded the flux calculated using COARE parameterised gas transfer velocities and measured sub-surface seawater DMS concentrations. The results of these two independent approaches suggest that air–sea emissions may be influenced by near-surface DMS production under certain conditions, and highlights the need for further study to constrain the magnitude and mechanisms of DMS production in the sea surface microlayer.

1 Introduction

In remote, relatively pristine marine environments such as the Southern Ocean, the production of aerosols and clouds is predominantly governed by natural sources (McCoy et al., 2015). In order to represent these sources in Earth system models and project their response to climate change, the exchange of volatiles between the atmosphere and ocean requires rigorous constraint. Dimethylsulfide (DMS) is derived from phytoplankton, and constitutes the largest natural source of non-sea-salt sulfate aerosol to the global troposphere of 10–20 nmol L^{-1} h^{-1} (Simó, 2001; Andreae and Crutzen, 1997), with an estimated annual input of 28.1 Tg S (Lana et al., 2011). Once in the atmosphere, DMS reacts to form sulfate aerosol which acts as a source of cloud condensation nuclei (CCN). It has been hypothesised that DMS-derived aerosols may thus have a significant impact on the radiation budget (Charlson et al., 1987; Andreae and Crutzen, 1997; Ayers and Gillett, 2000), via direct scattering of sunlight and changes to cloud properties. However, more recent experiments highlight additional biogenic sources and pathways for the production of CCN, even in the absence of sulfate aerosol (Quinn and Bates 2011; Bianchi et al., 2016; Kirkby et al., 2016). Current global flux estimates of DMS are poorly constrained, with estimates varying by as much as a factor of two (Lana et al., 2011).

Direct measurements of the air–sea exchange or flux (F) of a gas are challenging and so F is often computed using an empirically determined gas transfer coefficient (k) and the air–sea concentration disequilibria (ΔC), according to the equation $F = k\Delta C$ (Liss, 1983). The variability in flux estimates is widely considered to be driven by uncertainties in k (Zemmelink et al., 2004), which have been determined by a variety of methods including field observations using deliberately released tracers (Nightingale et al., 2000; Wanninkhof et al., 2004; Ho et al., 2011), wind and wave tank experiments (McGillis et al., 2000), global oceanic ^{14}C uptake (Sweeney et al., 2007), and simultaneous measurements of waterside gas concentrations and air–sea flux (Huebert et al., 2004; Marandino et al., 2009; Bell et al., 2013). As gas exchange is primarily driven by shear-generated turbulence, k is often parameterised as a function of wind speed (Liss and Merlivat, 1986; Wanninkhof, 1992; Ho et al., 2006). However, gas fluxes are inadequately modelled by wind speed alone (Blomquist et al., 2006; Zemmelink et al., 2004), as other factors such as wave-breaking, sea-state (e.g. Woolf, 2005; Asher et al., 1996), rain (e.g. Ho et al., 2000), and surface films (e.g. Schmidt and Schneider, 2011) also influence gas exchange at the sea-surface. To enable prediction of gas fluxes for a range of compounds including DMS, the National Oceanographic and Atmospheric Administration (NOAA) COARE model has been developed to incorporate many of the above factors. The model has been tuned to (Fairall et al., 2011) and validated against DMS eddy covariance field data (Blomquist et al., 2006; Yang et al., 2011).

The air–sea concentration disequilibria of DMS, and consequently air–sea exchange, are essentially controlled by the concentration in seawater ([DMS]) as atmospheric concentrations are typically at least two orders of magnitude lower. However, [DMS] is invariably measured at or below 2 m depth in both discrete and underway modes, and not at the sea-surface microlayer (SSM), the interface where gas exchange occurs. This assumes that there are no significant sources or sinks of DMS between the sample depth and the sea-surface.

[DMS] in the surface mixed layer is generally determined by the biomass, activity, and species composition of phytoplankton that produce dimethylsulfoniopropionate (DMSP), the precursor to DMS (Turner et al., 1988). Intracellular DMSP is regulated by factors such as nutrient availability and ultraviolet radiation dose (Archer et al., 2010; Toole and Siegel, 2004), whereas extracellular DMSP is influenced by grazing and bacterial processing (Yoch, 2002). To date, studies characterising near-surface [DMS] have shown a decreasing gradient towards the interface, indicative of degassing to the atmosphere (Zemmelink et al., 2005). However, direct measurements of the air–sea flux of DMS by eddy covariance (EC) over coccolithophore-rich North Atlantic waters significantly exceeded those calculated from bulk seawater concentrations (Marandino et al., 2008). This discrepancy between predicted and observed fluxes was attributed to near-surface [DMS] gradients (above latitudes of 55 ºN; Marandino et al., 2008).

Despite the ~~biophysical~~ challenge of maintaining a DMS source in a relatively thin (10–100 µm) layer at the air–water interface that is often subject to extreme physicochemical conditions (Zuev et al., 2001), a number of studies have examined and identified enrichment of DMS in the sea-surface microlayer, as summarised in Fig. 1 and references therein. Microlayer thickness, as defined by near-surface biogeochemical gradients, is of the order of 100 µm (Zhang et al., 2003). Given the challenges of sampling this thin surface layer, the thickness has been operationally defined as 1 mm by Liss and Duce (1997). In the current paper we evaluate properties for both 100 µm and 1 mm microlayer thickness. The physicochemical and biological properties of the SSM are often distinct from underlying waters, and may support enhanced biogeochemical activity (Liss and Duce, 1997). For example, the SSM is often enriched with surface-active organic material and bacteria, and is subject to elevated ultraviolet radiation and temperature (Cunliffe et al., 2013). DMS measurements in the SSM have identified both enrichment and depletion relative to sub-surface seawater (SSS) concentrations; however, enrichment has tended to dominate (Fig. 1). The source and controls of this excess DMS have not been identified, and the assumption that the SSM may influence DMS emissions to the atmosphere remains untested.

A variety of devices have been successfully deployed for sampling biological assemblages and dissolved compounds in the SSM (Cunliffe and Wurl, 2014). Trace gas SSM analyses are more challenging given the difficulties of sampling a volatile gas in a thin film that is subject to airside and waterside turbulence. Indeed, laboratory experiments have shown that a proportion of DMS is inevitably lost during SSM sampling, regardless of the device used (Yang et al., 2001). The aim of ~~this~~ the current work was to test the potential for near-surface processes to influence air–sea DMS exchange using a novel combination of direct sampling of the SSM and SSS, and EC measurement of air–sea DMS flux. Measurements were made during the Surface Ocean Aerosol Production (SOAP) voyage (Bell et al., 2015; Law C. S. et al., submitted). The influence of biogeochemical variability on spatial and temporal variation in near-surface DMS enrichment and flux was assessed by measurements in three phytoplankton blooms of differing community composition in productive frontal waters east of New Zealand. This location is currently under-represented in the global DMS database and climatology (Kettle and Andreae, 2000; Lana et al., 2011). In addition, the meteorological and physical factors influencing near-surface [DMS] were also examined in this assessment of DMS enrichment in the SSM, and its potential contribution to air–sea flux.

2 Methodology

2.1 Study location

Sampling was conducted aboard the R/V *Tangaroa* between February and March 2012 along the Chatham Rise, an underwater plateau separating suba~~A~~ntarctic and subtropical waters in the South-West Pacific, east of New Zealand. This is a region of high productivity in which frontal activity enhances mixing in the water column, fostering large phytoplankton blooms in the spring and summer seasons (Murphy et al., 2001). Satellite imagery in combination with continuous measurement of surface (6 m depth) chlorophyll-*a* fluorescence and seawater [DMS], measured by atmospheric pressure chemical ionization mass spectrometry (API-CIMS; Bell et al., 2015), were used to locate phytoplankton blooms for focussed studies on a range of air–sea parameters during the SOAP voyage (Law C. S. et al., submitted). SSM and SSS sampling were undertaken in three distinct blooms: B1 (DOY 45.8 to 48.8), B2 (DOY 52.8 to 55.0), and B3 (DOY 58.1 to 65.1), located as shown in Fig. 2. Day of year (DOY) is defined as 1 on January 1st at 00:00 h.

2.2 Seawater collection

Near-surface seawater samples were collected from a rigid-hulled inflatable boat (RHIB) during periods of low swell, and wind speeds <10 m s^{-1}. The light wind conditions reduced both DMS loss during collection (Zemmelink et al., 2005) and physical disruption of the in situ SSM (Carlson, 1983). The RHIB was positioned at least 500 m upwind of the R/V *Tangaroa* to avoid ship-borne contamination and artefacts associated with downstream turbulence. A total of 11 SSM stations were sampled, with station coordinates and sampling dates and times indicated in Table 1.

2.2.1 Sea-surface microlayer

A number of devices have been used to sample the SSM, but there have been few comparisons of techniques (Cunliffe and Wurl, 2014, and references therein). In this study the Harvey glass plate (Harvey, 1966; Harvey and Burzell, 1972) and Garrett metal screen (Garett, 1965) were deployed as these are two of the most frequently used techniques (see Fig. 1). The glass plate works on the principle that the ~~microlayer~~ SSM adheres to its surface as it is withdrawn, while the screen relies on surface tension to trap SSM water and matter in the interstitial spaces within a wire grid. The surface areas of the rectangular plate and round screen (with 0.6 mm wires) were 600 and 804 cm^2, respectively. The glass plate was silanised to avoid DMS loss through surface adsorption. Samplers were inserted vertically into the sea–surface on the downwind side of the boat where the SSM was less disturbed. The plate was slowly removed in the vertical position, whereas the screen was rotated 90º while submerged and then removed at a near-horizontal angle. Seawater adhering to the collection device was immediately drained through a funnel into prewashed 30 ml glass serum bottles for 30 seconds. Although a wiper is often used with the plate for sampling particulates and surfactants (Cunliffe and Wurl, 2014), this was not used in the current study to avoid DMS loss and potential disruption of algal cells. DMS concentrations in the SSM are referred to herein as $[DMS_{SSM}]$.

2.2.2 Sub-surface water

In addition to the SSM, seawater for the determination of [DMS] was collected in duplicate from four sub-surface depths (< 1, 7, 30, and 162 cm) in 150 ml crimp top, glass bottles that were pre-washed in a solution of phosphate-free detergent and rinsed with ultrapure water. Seawater from just below the SSM was collected using a “sipper”, with seawater pumped from a network of floating silicone tubes (each ~300 mm long and 3.2 mm outer diameter) using a peristaltic pump into a collection bottle. The tube intake ends were slightly weighted, to minimise disturbance of the SSM and air bubble introduction, for sampling at a depth of 1–2 cm that precluded the SSM. Seawater from depths of 7, 30, and 162 cm was collected using three fixed-depth stainless steel tubes attached to a floating buoy and connected to a peristaltic pump. Samples from 162 cm (referred to herein as $[DMS_{1.6\ m}]$) were assessed for pump-associated artefacts by comparison with samples collected at 2 m depth using standard Niskin bottles on a CTD rosette. The latter was collected within one hour of the RHIB sampling. A Wilcoxon signed-ranks test for paired samples with non-parametric distributions indicated no significant ($p = 1$, $\alpha = 0.5$) difference between the two approaches.

Phytoplankton identification, biomass and abundance data were obtained by optical microscopy of Lugols-preserved samples. These data are presented elsewhere.

2.3 Analytical methods

2.3.1 Seawater DMS (continuous)

[DMS] was continuously measured in the ships seawater intake (6.0 m depth; [$DMS_{6.0m}$]) using an atmospheric pressure chemical ionization mass spectrometer equipped with a porous membrane equilibrator, UCI miniCIMS (Bell et al. (2013). The miniCIMS data was averaged over 5 minutes and has a mean relative standard error of ± 5%. A one hour moving average algorithm was used to further smooth [$DMS_{6.0m}$].

2.3.2 Seawater DMS (discrete)

Discrete seawater samples were analysed for DMS while at sea using a semi-automated purge and trap system with a HP 6850 gas chromatograph interfaced with an Agilent flame photometric detector (Walker et al., 2000) up until DOY 47.0. An Agilent (Sievers) 355 sulphur chemiluminescent detector (SCD) was used after DOY 47.0. Seawater samples were gently filtered through an inline 25 mm GF/F filter to remove particulates, and a calibrated volume (5 ml) of the filtrate transferred to a 10 ml silanised glass chamber fitted with a quartz frit and purged with zero-grade nitrogen (99.9% pure). The chamber and frit were cleaned daily with 5% HCl and ultrapure water to prevent organic matter build-up. The GF/F filter was changed between each sample and the filter holder rinsed with ultrapure water. Gas phase DMS was cryogenically concentrated on 60/80 Tenax® TA in a 1/8" Restek Sulfinert®-treated stainless steel trap at -20°C and thermally desorbed at 100 °C for GC analysis.

Calibration was carried out using two temperature controlled VICI® Metronics wafer permeation tubes, one filled with methylethylsulphide (MES) and the other DMS. MES was used as an internal standard, with samples doped during analysis to allow for correction of short-term changes in detector sensitivity. The DMS permeation tube, housed in a Dynacalibrator®, provided the external standard. A five-point calibration was performed twice per day, and a running standard every 12 samples. A subsequent international intercalibration (Swan et al., 2014) indicated that the analytical method was 93.5 ± 3.8% accurate with 2.6% variation. Blank samples were tested regularly, using both ultrapure water and DMS-free seawater from a depth of 500 m, with a mean blank of < 0.1 nmol L^{-1} DMS.

Water samples were analysed within 5 hours of collection. Throughout the voyage, the SCD and miniCIMS techniques were compared using seawater from the ship's intake system. The SCD technique gave slightly higher concentrations, with the mean of the residuals indicating an average difference of 1.2 nmol L^{-1} DMS (Fig. 3). This difference is possibly attributable to DMS production during sample storage prior to SCD analysis, as deck incubation of SSS and SSM water from B2 and B3 indicated mean in-bottle production rates in the dark of 0.23 nmol L^{-1} h^{-1} (Cliff Law, pers. comm.); a total production of 1.2 nmol L^{-1} over 5 hours. In addition, the ~~deviation~~ pattern of deviation from the 1:1 line of [DMS] in samples with both low and high storage times, suggests storage time is not a significant driver of the difference between the two analytical techniques (Fig. 3). Further investigation also showed a lack of relationship between analysis time and EF, particularly for B1 samples ($r^2 = 0.002$), suggesting that there was no significant DMS production between collection and analysis.

2.3.3 SSM enrichment factors

The anomaly between the SSM and underlying SSS is indicated by the enrichment factor (EF), the concentration ratio between DMS in the SSM and at 1.6 m depth:

$$\mathrm{EF} = \frac{[\mathrm{DMS_{SSM}}]}{[\mathrm{DMS_{1.6m}}]} \qquad (1)$$

EFs were calculated using [$DMS_{1.6m}$] from the RHIB~~,~~ rather than [$DMS_{6.0m}$] from the ship's seawater intake, to minimise error arising from spatio-temporal variability. An EF > 1 indicates DMS enrichment and < 1 indicates DMS depletion, in the SSM.

2.3.4 Eddy covariance-derived DMS air–sea flux

Although the basic principles of turbulent flux exchange are well established (Swinbank, 1951), refinements have been made to adapt the micrometeorological technique of EC for use on a moving platform (e.g. Edson et al., 1998). In addition, the development of atmospheric pressure chemical ionization mass spectrometry (API-CIMS) for high frequency DMS measurement (Bandy et al., 2002; Huebert et al., 2004; Marandino et al., 2007) has enabled direct measurements of air–sea DMS flux on time-scales on the order of tens of minutes. By combining airside and waterside gas concentrations, these high-resolution measurements allow the response of *k* in relation to spatial variation in biological and environmental conditions to be determined. In the current study, continuous measurement of air–sea DMS flux at 10 minute intervals on the ship's bow was achieved using EC and API-CIMS, as described in Bell et al. (2013). EC flux data (F_{EC}) were smoothed using a moving average algorithm with a span of 1 hour, and used to calculate the inferred DMS concentration in surface waters (see Sect. 2.4.2).

2.3.5 Near-surface temperature gradients

A spar buoy was deployed in each bloom for autonomous sampling of near-surface temperature gradients. Temperature loggers (RBR TR-1060) recorded temperature at 0.5 m intervals between 0.25 and 4.25 m depth, with deployments typically lasting 4 days.

2.4 Computations

2.4.1 Air–sea DMS fluxes

DMS flux (F_{DMS}) was calculated using the gas transfer coefficient *k* and the concentration difference at the air–sea interface according to:

$$\mathrm{F_{DMS}} = k\left(\mathrm{C_w} - \frac{\mathrm{C_a}}{\mathrm{H}}\right) \qquad (2)$$

where H is the dimensionless Henry's law solubility coefficient for DMS (Dacey et al., 1984), $\mathrm{C_w}$ is [$DMS_{6.0m}$], and $\mathrm{C_a}$ is the DMS concentration measured in air. Most conceptual models assume that *k* is dependent on molecular diffusion across the surface layer, the thickness of which is modulated by near-surface turbulent processes (Liss and Slater, 1974). For DMS in temperate waters, the waterside diffusive layer provides the dominant control on air–sea flux. This assumes there is no significant internal loss or production in the thin diffusive layer at the surface (Nightingale, 2013), and also that there is more rapid mixing below. The transfer velocity *k* was calculated using the NOAA COARE model (version 3.1g; Fairall et al., 2011), and parameterised in terms of local wind speed scaled to 10 m height, as in Bell et al., (2015). *k* was then adapted for DMS using the Schmidt number for local seawater temperature and salinity at 6.0 m depth (Saltzman et al., 1993).

2.4.2 Flux-inferred seawater [DMS]

[DMS_{inf}], the inferred DMS concentration in surface waters required to support the observed air–sea flux, was derived from Eq. (2), using the measured EC flux, F_{EC}, and a *k* predicted by the NOAA COARE model, which incorporates bulk meteorological variables including wind speed, temperature, and stability (Bell et al., 2015). To generate [DMS_{inf}] at the same sampling frequency as the smoothed [$DMS_{6.0m}$], *k* was calculated at ten minute intervals and smoothed using a moving average algorithm with a span of 1 hour. To facilitate comparison with [DMS_{SSM}], a mean [DMS_{inf}] was generated for each RHIB station for the period three hours before SSM sampling until five hours afterwards.

2.4.3 DMS production in the SSM

The excess or residual [DMS] in the SSM, relative to underlying waters, was calculated using two independent approaches. Subtracting [$DMS_{1.6m}$] from [DMS_{SSM}] provided an estimate of *SSM-derived residual [DMS]*, the excess [DMS] in the SSM determined by direct measurement. A second approach was to subtract the observed [$DMS_{6.0m}$] from the estimated [DMS_{inf}] to derive an estimate of *EC-derived residual [DMS],* the excess [DMS] in the SSM calculated indirectly from flux measurements. The latter was used to estimate the net DMS production rate in the SSM (PR_{SSM}) required to support the observed air–sea flux:

$$\mathrm{PR_{SSM}} = \frac{\mathrm{F_{EC}} - \mathrm{F_{6.0m}}}{z} \qquad (3)$$

where F_{EC} is the flux measured by EC, $F_{6.0m}$ is the flux estimated using [$DMS_{6.0m}$] and Eq. (2), and *z* is the SSM thickness (100 µm and 1 mm). As PR_{SSM} was calculated using the measured and expected DMS flux, it is independent of the measured [DMS_{SSM}].

3 Results

3.1 Comparison of SSM sampling techniques

Comparison of [DMS_{SSM}] measured by the Garret metal screen and Harvey glass plate, using Wilcoxon signed-ranks test for paired samples, indicated a significant difference in results ($p = 0.0078$, $\alpha = 0.05$), with mean [DMS_{SSM}] from plate sampling 42% lower than the Garret screen. This difference was substantially greater than the sampling blanks, which were determined using both ultrapure water and seawater from 500 m depth (consistently < 0.3 nmol L^{-1} DMS for both devices; 1.6% of the average sample concentration). One potential factor is that the Garret screen collects thicker SSM samples than the plate (Cunliffe and Wurl, 2014); however, there are also other differences in collection efficiency between the two methods. The screen is considered to recover more of the phytoplankton assemblage than the plate (Momzikoff et al., 2004; Agogué et al., 2004). In the current study, the screen appeared to trap aggregates, particularly in B1, and this may have led to overestimates of [$\mathrm{DMS_{SSM}}$]. Consequently, we will only discuss SSM data collected using the plate method, as these provide more conservative estimates of DMS enrichment in the SSM.

3.2 Direct measurements of [DMS] in the SSM and SSS

[$\mathrm{DMS_{SSM}}$] and [$\mathrm{DMS_{1.6m}}$] ranged from 3.8 to 41.5 nmol L^{-1}, and 4.9 to 13.8 nmol L^{-1}, respectively (Table 1, Fig. 4), and showed similar spatial variability to [$\mathrm{DMS_{6.0m}}$] (Fig. 5b, Bell et al., 2015). Maximum concentrations were observed in B1 (DOY 45.8 to DOY 48.8), with mean [$\mathrm{DMS_{SSM}}$] and [$\mathrm{DMS_{1.6m}}$] of 23.5 ± 13.5 nmol L^{-1} and 9.5 ± 4.2 nmol L^{-1}, respectively, coincident with a mean [$\mathrm{DMS_{6.0m}}$] of 10.6 ± 5.2 nmol L^{-1} (range 2.9 - 24.7 nmol L^{-1}). B1 was dominated by dinoflagellates (Law C. S. et al., submitted), with a mean chlorophyll-*a* of 1.6 mg m^{-3} at 1–2 cm depth. A striking feature of B1 was the high [$\mathrm{DMS_{SSM}}$], which exceeded [$\mathrm{DMS_{6.0m}}$] (Fig. 5b), resulting in high average EFs (2.8 ± 2.0, Table 1). Furthermore, two B1 stations exhibited EFs > 4.0, which exceed the majority of [$\mathrm{DMS_{SSM}}$] maxima reported in the literature (Fig. 1). Conversely, B2 and B3 were characterised by lower [$\mathrm{DMS_{SSM}}$], which was typically indistinct from [$\mathrm{DMS_{6.0m}}$] (see Fig. 5b). The mean [$\mathrm{DMS_{SSM}}$] and [$\mathrm{DMS_{1.6\,m}}$] in B2 were 7.9 ± 1.2 and 7.0 ± 0.1 nmol L^{-1} respectively, with near-surface seawater at 1–2 cm depth of 1.0 mg m^{-3} chlorophyll-*a*, ~40% lower than B1, and dominated by coccolithophores. Although B3 was in a similar location to B1, it was temporally distinct and with lower phytoplankton biomass (Law C. S. et al., submitted). Near-surface seawater was dominated by dinoflagellates and coccolithophores, with mean chlorophyll-*a*, [$\mathrm{DMS_{SSM}}$], and [$\mathrm{DMS_{1.6m}}$], of 0.8 mg m^{-3}, 6.5 ± 2.8 nmol L^{-1}, and 8.0 ± 2.0 nmol L^{-1}, respectively, and EFs near or below 1.0. Throughout the study there was no evidence of near-surface [DMS] gradients between 1 cm and 1.6 m depth, including at the B1 stations exhibiting high levels of SSM enrichment (Fig. 4). The absence of near-surface DMS gradients was further confirmed by the agreement between [$\mathrm{DMS_{1.6m}}$] and [$\mathrm{DMS_{6.0m}}$] (Fig. 5b).

3.3 Flux-inferred estimates of [DMS]

F_{EC} was elevated during B1, with fluxes up to ~100 µmol m^{-2} d^{-1} (Bell et al., 2015). Highest DMS fluxes were recorded between DOY 48.0 and 50.0 during B1, reflecting the elevated [$\mathrm{DMS_{6.0m}}$] (Fig. 5b, Bell et al., 2015). [$\mathrm{DMS_{inf}}$], the inferred DMS concentration in SSS required to support the F_{EC}, was calculated using NOAA COARE gas transfer coefficients and compared to [$\mathrm{DMS_{6.0m}}$] (Fig. 5b). [$\mathrm{DMS_{6.0m}}$] was used to represent SSS, since continuous measurement at this depth provided greater temporal resolution (Bell et al., 2015). Overall, comparison of [$\mathrm{DMS_{inf}}$] and [$\mathrm{DMS_{6.0m}}$] in Fig. 5b shows good agreement. Where [$\mathrm{DMS_{inf}}$] and [$\mathrm{DMS_{6.0m}}$] agree in magnitude (e.g. DOY 55.0 to 58.0) the application of [$\mathrm{DMS_{6.0m}}$] and *k* provides a robust estimate of air–sea DMS flux. However, between DOY 44.8 and 52.0, and to a lesser extent between DOY 58.0 and 61.0, a disparity was apparent with anomalously high [$\mathrm{DMS_{inf}}$] observed that were not reflected in [$\mathrm{DMS_{6.0m}}$]. During these periods, the use of [$\mathrm{DMS_{6.0m}}$] with *k* would underestimate the DMS flux. This disparity is evident during B1 in the comparison of EC- and SSM-derived residual [DMS], with the maxima of these independent approaches appearing close to each other (Fig. 5c). EC- and SSM-derived residual [DMS] were significant during B1 occupation, with maximum values of 20 and 33 nmol L^{-1}, respectively, during

Station 4 (DOY 47.7 to 48.1), whereas EC- and SSM-derived residual [DMS] were generally not significant in B2 and B3.

These trends are confirmed by comparison of [DMS$_{6.0m}$] and [DMS$_{inf}$] for each bloom period in Fig. 6a–c. B1 shows a positive anomaly in [DMS$_{inf}$] relative to [DMS$_{6.0m}$], particularly at elevated [DMS$_{6.0m}$], indicative of an additional source of DMS contributing to the flux. At two of the four stations during B1, the mean [DMS$_{inf}$] was significantly greater than the mean [DMS$_{6.0m}$], with this positive bias in [DMS$_{inf}$] in B1 generally highest at intermediate wind speeds (Fig. 6a). Conversely, B2 and B3 generally showed good agreement between [DMS$_{inf}$] and [DMS$_{6.0m}$], although there was evidence of a negative anomaly at low to intermediate wind speeds (Fig. 6b–c), and a positive anomaly at high wind speeds in B3 (Fig. 6c). Comparison of the mean EC- and SSM-derived residual [DMS] for each station confirmed that the B2 and B3 stations generally cluster around the zero intercept (Fig. 6d), as expected if near-surface DMS sources were negligible. Conversely, B1 stations exhibited significant deviation from the zero intercept, with two stations characterised by high EC- and SSM-derived residual [DMS] coincident with high EF. At both of these stations the SSM-derived residual [DMS] exceeded the EC-residual [DMS], which may reflect the spatial variability of DMS in the SSM, non-representativeness of the single-point SSM measurements, or methodological artefacts.

3.4. Meteorological influences on near-surface structure

B1 was sampled during a high pressure system with low wind speeds (mean 6.0 ± 2.7 m s^{-1}; Fig. 5a and 7) and calm sea-state (waves < 0.2 m), conditions conducive to SSM formation and preservation. A brief atmospheric front traversed the region during B2 with winds reaching 18 m s^{-1}, and multiple weather fronts occurred during B3 including a period of sustained high wind speeds up to 30 m s^{-1} (Fig. 5a). At wind speeds >10 m s^{-1} the SSM is disrupted, with its constituents dispersed and diluted by sub-surface water (Wurl et al., 2011), and ventilation increases. The influence of physical processes on a potential SSM source of DMS was examined between DOY 45.5 and 49.5 in B1 by comparison of EC- and SSM-derived residual [DMS] with U_{10} (wind speed at a reference height of 10 m above the ocean) and near-surface temperature gradient (Fig. 7). Low wind speeds reduce air–sea exchange and enhance near-surface stratification, providing optimal conditions for maintenance of the SSM and retention of DMS. If this is the case then the contribution of the SSM to DMS flux would be most significant when the SSM is subsequently ventilated upon an increase in wind speed. This scenario is apparent on DOY 47.0 to 48.0 when a period of low wind speeds (< 3 m s^{-1}), significant near-surface temperature gradients (~1°C m^{-1}), and elevated SSM-derived residual [DMS] was followed by a period of higher wind speed (~5–8 m s^{-1}), during which the EC-derived residual [DMS] increased (Fig. 7). However, the high SSM-derived residual [DMS] was also recorded at wind speeds of 6–9 m/s during DOY 45.8, indicating that DMS enrichment in the SSM may be maintained at moderate wind speeds.

3.5 DMS production rates in the SSM

The SSM production rate, PR$_{SSM}$, was estimated by subtracting the expected flux, calculated using [DMS$_{6.0\ m}$] and the COARE algorithm, from the observed air–sea flux, and dividing by the thickness of the SSM (Eq. 3). This approach assumes that DMS production in the SSM was the source of the 'excess' air–sea flux in B1. Other potential DMS loss processes, such as photolysis and bacterial oxidation, may have also been significant DMS sinks (Kieber et al., 1996; Gali et al., 2013); however, as these rates were not quantified they are not considered and so the estimate of PR_{SSM} may represent an underestimate.

~~-~~Mean PR_{SSM} was estimated using SSM thicknesses of 100 and 1000 µm. Assuming a thickness of 1000 µm, PR_{SSM} was 217 ± 162, -80 ± -33 and 74 ± 22 for stations B1, B2 and B3 respectively (Table 1). An alternative microlayer thickness of 100 µm resulted in PR_{SSM} one order of magnitude higher. The large uncertainty for each estimate is partially attributable to variation in the measured F_{EC} and [$DMS_{6.0m}$] (see Fig. 5b). This approach of estimating PR_{SSM} from flux measurements has several advantages in that it is independent of the measured [DMS_{SSM}], integrates horizontal variability, eliminates inherent uncertainty in the wind speed-gas transfer relationship, and does not rely on a single-point SSM measurement.

4 Discussion

The results of two independent techniques to assess the potential contribution of the sea surface microlayer to the air–sea exchange of DMS provide intriguing evidence that this may be significant under certain physical and biological conditions. This study adds to a number of other reports of DMS enrichment in the SSM (Fig. 1), but raises challenging questions regarding the source and maintenance of elevated DMS in the SSM. Consequently it is instructive to consider the validity of these results, and the physical and biological factors that may influence DMS in the SSM.

Near-surface gradients in dissolved gases have been reported previously for DMS and carbon dioxide (Zemmelink et al., 2005; Calleja et al., 2005), with potential implications for air–sea flux estimates. The vertical DMS profile in near-surface waters in B2 and B3 was uniform (see Fig. 4) indicating that DMS production and loss terms, such as ventilation, bacterial oxidation and photolysis, were in balance (Galí et al., 2013). Furthermore the profiles do not show significant near-surface depletion in [DMS], which has been previously reported and attributed to ventilation and photolysis (Kieber et al., 1996).

The presence of significant DMS enrichment in the SSM at the B1 stations (Table 1) is surprising, as vertical diffusion from the SSM would be expected to elevate [DMS] immediately below the SSM. As elevated [DMS] was not apparent at 1–2 cm (Fig. 4), this suggests that density stratification and/or preferential retention of DMS in the SSM suppressed vertical diffusive losses from the SSM. Elevated [DMS_{SSM}] has been previously reported relative to concentrations at 25 cm depth, associated with near-surface density gradients arising from ice melt in the Weddell Sea (Zemmelink et al., 2005). The near-surface temperature data in the current study indicated episodic formation of a gradient in the upper 4 m at the B1 stations (see Fig. 7) and, assuming this gradient extended to the sea-surface, the resulting stratification may have created optimal conditions for SSM enrichment, with concentration and retention of phytoplankton whilst suppressing diffusive loss to sub-surface water. Furthermore, ~~the presence of~~ if surfactants were present they may have suppressed ventilation across the air–sea interface (Salter et al., 2011) under these conditions, leading to an accumulation of DMS in the SSM.

The surface microlayer sampling, storage, and analysis may have introduced potential artefacts, particularly for trace gases. The mesh screen sampling produced higher [DMS_{SSM}] than the plate, potentially due to preferential retention of algal and suspended material on the mesh as previously reported (Turner and Liss, 1985). These authors also reported significant DMS enrichment coincident with elevated sub-surface productivity, and partially attributed the enrichment to "stressing of microlayer organisms as a result of the sampling procedure". This may have occurred in the current study in B1, as dinoflagellates are sensitive to shear stress (Wolfe et al., 2002), but this was not tested. However, in contrast to other applications (Cunliffe and Wurl, 2014), we avoided scraping the SSM off the glass plate to reduce transfer of particulate material and ventilation of DMS, and this may also have reduced shear stress and exposure time of the phytoplankton. Exposure to air during SSM sampling enhances DMS evasion, with ~ 50% loss at zero wind speed (Zemmelink et al., 2005), which suggests that the majority of previous DMS measurements in the SSM (see Fig. 1) are underestimates (Zemmelink et al., 2006).

This raises the question as to how DMS enrichment is maintained in the SSM whilst ventilation is occurring across the air–sea interface. Zemmelink et al. (2006) calculated a DMS residence time in the SSM on the order of 40–60 seconds, and consequently a very high production rate would be required to maintain enrichment. To maintain the observed and calculated enrichment in the SSM, DMS production must dominate over loss terms such as photolysis and bacterial oxidation, and occur at a significantly greater rate than previously reported for the open ocean. Indeed, the PR_{SSM} estimates in Table 1, which are determined indirectly from F_{EC} and are independent of the SSM concentration measurements, significantly exceed reported DMS production rates for sub-surface waters (Simó, 2004). For example, in a compilation of 65 studies the maximum gross DMS production rates of 10–20nmol L^{-1} hr^{-1} (Simó, 2004) were up to two orders of magnitude lower than the calculated PR_{SSM} based upon a 1000 um SSM thickness. Microorganisms in the SSM are exposed to extreme physicochemical conditions, including high irradiance (Zuev et al., 2001), whereas the DMS production rate estimates reported in Simó (2004) were from dark incubations that exclude the influence of light on DMS production. The conversion of intracellular DMSP to DMS is considered to be sensitive to both the quantity and spectra of light (Sunda et al., 2002; Archer et al., 2010), and so exposure to high irradiance in the SSM will have a significant influence on DMS production. This is supported by the "DMS summer paradox" where higher DMSP and DMS levels have been observed in shallow mixed layers that are exposed to high light levels (Simó and Pedrós-Alió, 1999). Laboratory and field experiments have also demonstrated that DMS has a positive, dose-dependent response to solar radiation (Galí et al., 2013; Sunda et al., 2002; Vallina et al., 2007). In particular, gross DMS production is stimulated by Ultra-Violet Radiation (UVR), which causes a reduction in algal cell integrity and enhanced release of DMSP, DMS, and cleavage enzymes, and also up-regulation of intracellular DMSP cleavage (Galí et al., 2013). No relationship was observed between either $[DMS_{SSM}]$ or $[DMS_{6.0m}]$ with incident solar radiation in the current study, although this was confounded by differences in other factors such as phytoplankton biomass and community composition. The SSM was often sampled in the morning (0800–0930 h) which may suggest that the high DMS EFs in B1 may be a response to a night-day change in irradiance. Rapid changes in light can stimulate intracellular and dissolved DMSP production in coccolithophores (Darroch et al., 2015), with low-light cultures exposed to irradiance (including UVR) exhibiting an increase of 24–62 nmol L^{-1} h^{-1} DMS (Archer et al., 2010). These production rates are still 1–2 orders of magnitude lower than many of the calculated PR_{SSM} for B1 (Table 1), but nevertheless confirm the potential for rapid DMS accumulation in response to increased light stress. Deck board incubations of SSM and SSS seawater from B2 and B3 stations showed that DMS production in the light was approximately double that in the dark (Cliff Law, pers. comm.), consistent with other reports (Galí et al., 2013). The highest net production rate of 3.7 nmol L^{-1} h^{-1} in the light (Cliff Law, pers. comm.) was again substantially lower than the calculated PR_{SSM} in Table 1. Bacterial inhibition by high summertime UVR in the SSM (Zemmelink et al., 2006; Slezak et al., 2007) can decouple DMS production and consumption, with increased DMS observed in sub-surface waters (Vila-Costa et al., 2008). The coincidence of elevated phytoplankton DMS production, inhibition of bacterial DMSP consumption, and tolerance of bacterial DMSP degradation under elevated UV-A reported for BATS (Levine et al., 2012), provides further support for potential DMS accumulation in the SSM. However, the absence of a significant difference in DMSP cycling between light and dark incubations of SSS during SOAP (Lizotte M. et al., submitted) suggests bacterial oxidation was not inhibited by light; although this was not measured in the SSM.

The different phytoplankton community composition of the three blooms may have influenced DMS enrichment in the SSM, particularly as all the blooms contained phytoplankton that are significant DMSP producers. B2 and B3 contained a higher proportion of coccolithophores but, despite evidence of their increased production of DMS and DMSP under high light stress (Archer et al., 2010), DMS levels were low in these two blooms. Conversely, B1 was dominated by dinoflagellates (>50 % of the phytoplankton biomass) and [DMS_{SSS}] levels and SSM enrichment were significantly higher. Dinoflagellates are significant DMSP producers, with intracellular DMSP content and DMSP lyase activity that generally exceeds that reported for coccolithophores (Caruana and Malin, 2014). Enzymatic cleavage of DMSP is currently viewed as the primary process for DMS production, and dinoflagellates have been identified as capable of converting DMSP to DMS (Steinke et al., 2002, and references within). An association between elevated DMS and dinoflagellate biomass has been observed by a number of empirical studies (e.g. Zhang et al., 2014; Zindler et al., 2012).

Of the four dominant dinoflagellate species observed in B1, *Gyrodinium,* has been reported in association with high DMSP concentrations in the field (see Table 1, Caruana and Malin, 2014). Some dinoflagellate species migrate to the surface during the day, which influences the vertical distribution of associated DMSP and DMS. For example, a 10-fold increase in [DMS] was recorded due to diel vertical migration of a dinoflagellate bloom in the St Lawrence River (Merzouk et al., 2004). Analysis of phytoplankton community composition at the B1 stations showed only one dinoflagellate genus, *Ceratium,* which was more abundant at 1-2 cm relative to 2 m (data not shown), although this family does not generally exhibit high intracellular DMSP.

The EC data provide further evidence of a contribution of near-surface DMS production to air–sea flux, notably the close coincidence of significant EC- and SSM-derived residual [DMS] during B1 (Fig. 5c). The validity of this evidence is in part dependent upon generation of robust *k* values from the COARE model. Comparison with observational DMS datasets has confirmed that the COARE gas transfer model is a good predictor of *k* for DMS in most conditions, (Blomquist et al., 2006; Yang et al., 2011), including the SOAP voyage (Fig. 5b). A discrepancy with COARE has been reported under high winds (> 11 m s^{-1}) in the North Atlantic, with lower measured *k* values attributed to the suppression of turbulence due to wind–wave interaction, by Bell et al. (2013). In the current data analysis this suppression would result in a lower [DMS_{inf}], in contrast to the elevated values observed. In addition, the largest deviations between [DMS_{inf}] and [$DMS_{6.0m}$] during B1 occurred at mid-range wind speeds (6–8 m s^{-1}, Fig. 6a), where Bell et al. (2013) found good agreement with

COARE. Consequently previous analysis does not indicate any significant bias in the COARE parameterization that could account for the high [DMS_{inf}] during B1.

Spatial decoupling of airside and waterside measurements inevitably introduces error into the estimate of residual [DMS]. For example, Bell et al. (2015) identify a spatial offset between measurements of DMS flux and seawater DMS of up to 2 km during SOAP. However this is unlikely to have generated the significant differences between [DMS_{inf}] and [$DMS_{6.0m}$] observed in B1, as these anomalies were observed when the ship was stationary or travelling slowly (< 2 knots), when wind speeds were < 10 m s^{-1} (see Fig. 5a). During these conditions, the flux footprint (Bell et al., 2015) would be much smaller. In addition, [DMS_{inf}] exceeded 20 nmol L^{-1} on a number of occasions during B1, whereas [$DMS_{6.0m}$] rarely exceeded 20 nmol L^{-1} throughout the entire voyage, suggesting that horizontal transport of DMS in the marine boundary layer from another bloom was not the source of the anomalously high [DMS_{inf}] during B1.

5 Summary

DMS fluxes are traditionally computed using [DMS] at depths below the air–sea interface; consequently significant near-surface DMS has important implications for flux estimates. Sub-surface [DMS] between 1 and 160 cm depth was relatively uniform at all stations on the Chatham Rise, in contrast to suggestions that DMS concentration should decrease near the air–sea interface as a result of surface sinks (Kieber et al., 1996). Although near-surface DMS gradients were generally absent, a significant exception was recorded in a dinoflagellate bloom during light to mid-range wind speeds (i.e. <10 m s^{-1}) and near-surface temperature stratification. On several occasions in this bloom, significant enrichment of DMS in the SSM coincided with measured DMS fluxes that exceeded predicted fluxes calculated using sub-surface [DMS] and the COARE algorithm. Although SSM enrichment of DMS (see Table 1) and anomalously high air–sea DMS fluxes have previously been reported (e.g. Marandino et al., 2008, 2007), this study's results are the first to link these two phenomena.

There are some aspects of this dataset that are surprising, and require further investigation to establish the significance of the sea surface microlayer to air–sea DMS flux. For example, the study raises questions as to how significant DMS enrichment is maintained in the SSM without influencing the [DMS] in the underlying water. In addition, the elevated SSM [DMS], both measured and inferred from flux measurements in the dinoflagellate bloom B1, necessitates a substantial in situ DMS production in the SSM. To maintain this enrichment, DMS production is required at a rate that significantly exceeds previous estimates for the open ocean (Simó, 2004). Nevertheless, the two independent approaches used in this study indicate that the SSM may influence DMS air–sea flux under certain biogeochemical and meteorological conditions, and so production at the air–sea interface may contribute to anomalously high DMS fluxes recorded in other regions of high productivity (Marandino et al., 2009, 2008).

6 Author contribution

C. Walker designed and conducted the experiments, developed and optimized the analytical methods and instrument, analysed the SSM and 1.6 m depth seawater samples for DMS, and interpreted the data. C. Walker also prepared the manuscript with contributions from C. Law, M. Harvey, M. Smith and T. Bell. C. Law helped with the experimental design, instrument optimisation, sample collection, data interpretation and drafting of the manuscript. C. Law also assisted with sampling logistics, and coordinated the overall measurement programme through his role as voyage leader. M. Harvey and J. McGregor assisted in the development of the analytical instrument, as did A. Marriner who also helped with the collection and analysis of seawater DMS samples. C. Law, M. Harvey and M. Smith provided invaluable mentoring and assisted with data interpretation and analysis. T. Bell and E. Saltzman supplied the air–sea DMS flux and miniCIMS seawater DMS data, and contributed to data interpretation.

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9 Tables

DOY UTC	NZDT dd/mm/yy HH:MM	Lat (º)	Lon (º)	$[DMS_{1.6m}]$ (nM)	$[DMS_{SSM}]$ (nM)	EF	$PR_{SSM\_100\mu m}$ (nmol L^{-1} h^{-1})	$PR_{SSM\_1000\mu m}$ (nmol L^{-1} h^{-1})
B1								
45.8	15/02/12 08:05	44.62S	174.77E	4.9±0.8	26.1±0.0	5.3	1153±522	115±52
46.8	16/02/12 08:06	44.59S	174.68E	13.6±0.6	25.9±8.2	1.9	-486±270	-49±27
47.1	16/02/12 15:51	44.59S	174.69E	13.8±n/a	19.9±n/a	1.4	n/a	n/a
47.8	17/02/12 08:02	44.59S	174.69E	9.2±2.0	41.5±9.7	4.5	5529±655	553±66
48.8	18/02/12 08:04	44.59S	174.69E	5.9±0.4	4.1±0.2	0.7	2468±454	247±45
Mean				*9.5±4.2*	*23.5±13.5*	*2.8*	*2166±2546*	*217±255*
B2								
52.8	22/02/12 08:27	43.72S	179.86W	6.9±0.2	8.7±1.1	1.3	-1445±348	-145±35
55.0	23/02/12 13:03	43.59S	179.75W	7.1±1.8	7.0±0.0	1.0	-153±52	-15.3±5
Mean				*7.0±0.1*	*7.9±1.2*	*1.2*	*-799±914*	*-80±91*
B3								
58.1	27/02/12 14:39	44.11S	175.14E	8.7±0.0	5.0±0.2	0.6	614±162	61±16
59.8	29/02/12 08:03	44.60S	174.87E	6.6±0.9	3.8±0.4	0.6	867±129	87±13
64.8	05/03/12 09:04	44.18S	174.33E	10.5±0.1	10.2±1.1	1.0	n/a	n/a

65.1	05/03/12 14:12	44.18S	174.33E	6.3±0.0	7.1±0.8	1.1	n/a	n/a
Mean				*8.0±2.0*	*6.5±2.8*	*0.8*	*740±179*	*74±18*

Table 1: SSM station variables: DMS concentration in the SSM ([DMS_{SSM}]), collected using the plate method, and in seawater at 1.6 m depth ([$DMS_{1.6m}$]); DMS enrichment factor (EF); and DMS production rate (PR_{SSM}) for a 100 µm and 1000 µm thick microlayer. Day of year (DOY) is where 1 is January 1st at 00:00 h. [DMS] errors are 1 standard deviation from the mean of duplicate samples. EF is the ratio of microlayer and 1.6 m concentrations, with an EF > 1 indicating enrichment and <1 depletion. Production rates are averages for the period three hours before and five hours after microlayer sampling.

10 Figures

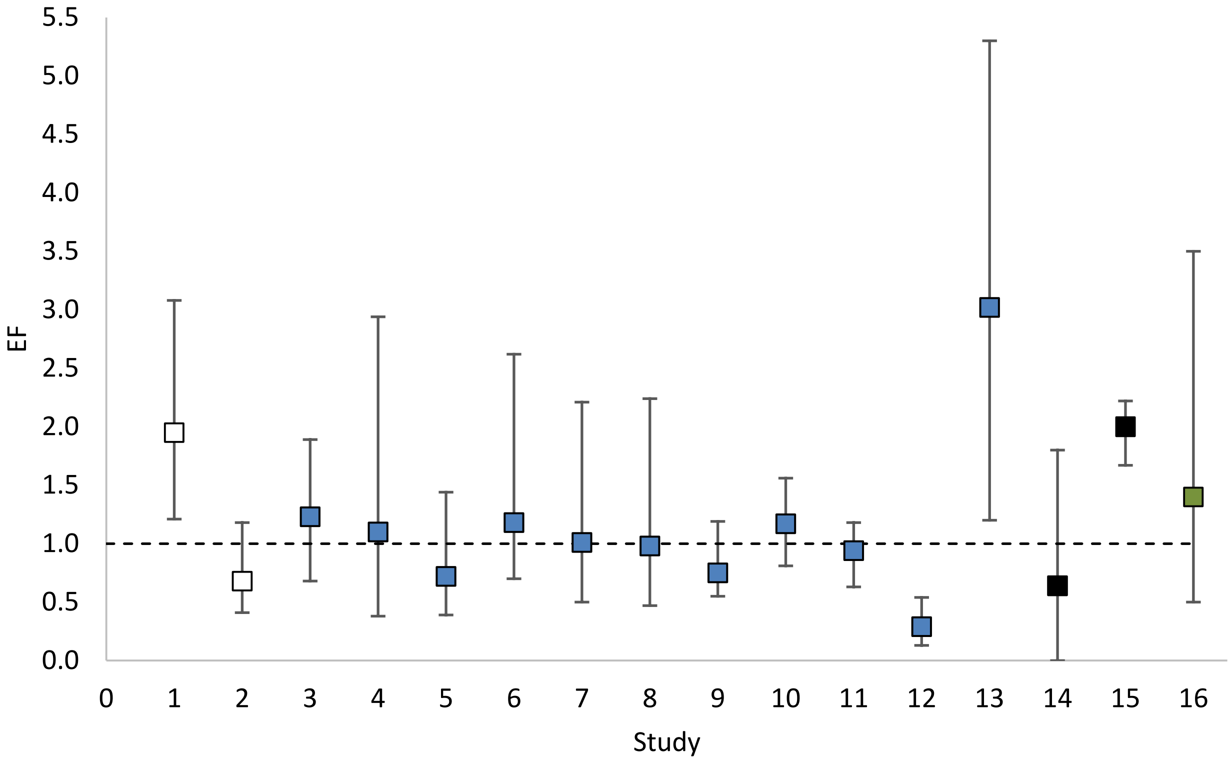

Figure 1: Mean enrichment factors (EF) for DMS in the SSM reported in previous studies. Upper and lower bars indicate the highest and lowest value reported in each study. An EF of 1.0, shown by the horizontal dashed line, indicates no difference between [DMS_{SSM}] and [DMS_{SSS}], with EF > 1 denoting enrichment in the SSM relative to SSS, and values < 1 a deficit relative to SSS. The sampling method is indicated by the symbol colour: plate (white), mesh (blue), drum (black) and cryogenic (grey). References: 1 (Yang, 1999); 2 & 3 (Yang et al., 2001); 4 (Yang and Tsunogai, 2005); 5 (Yang et al., 2005a); 6 (Yang et al., 2005b); 7 (Yang et al., 2006); 8 (Zhang et al., 2008); 9 (Yang et al., 2008); 10 & 11 (Zhang et al., 2009); 12(Yang et al., 2009); 13 (Matrai et al., 2008); 14 (Zemmelink et al., 2006); 15 (Turner and Liss, 1985); 16 (Nguyen et al., 1978).

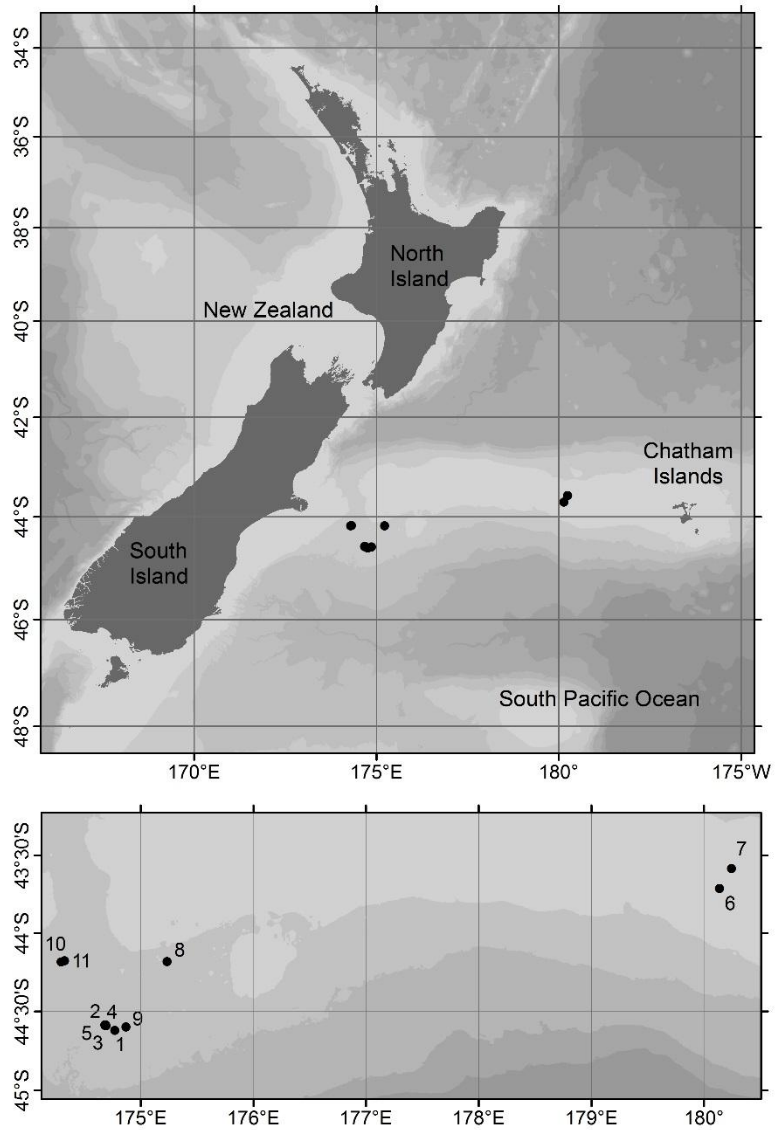

Figure 2: A map of New Zealand waters showing the location of the eleven SSM sampling stations (solid dots). Station numbers are shown in the expanded Chatham Rise region in the lower panel. Blooms B1, B2, and B3 encompass stations 1 – 5, 6 – 7, and 8 – 11, respectively.

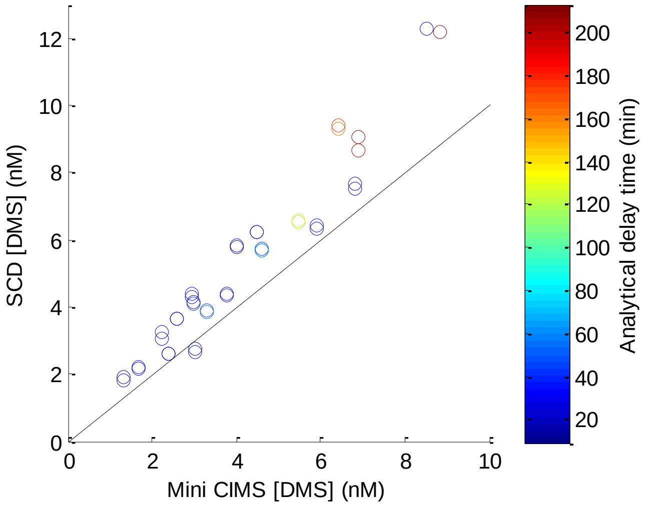

Figure 3: Comparison between [DMS] measured using the miniCIMS and SCD methods. Colour bar indicates the time elapsed between sample collection and analysis on the SCD. miniCIMS analysis was near real-time so data are averaged over a 1 hour period surrounding the SCD sample collection. The black solid line is 1:1.

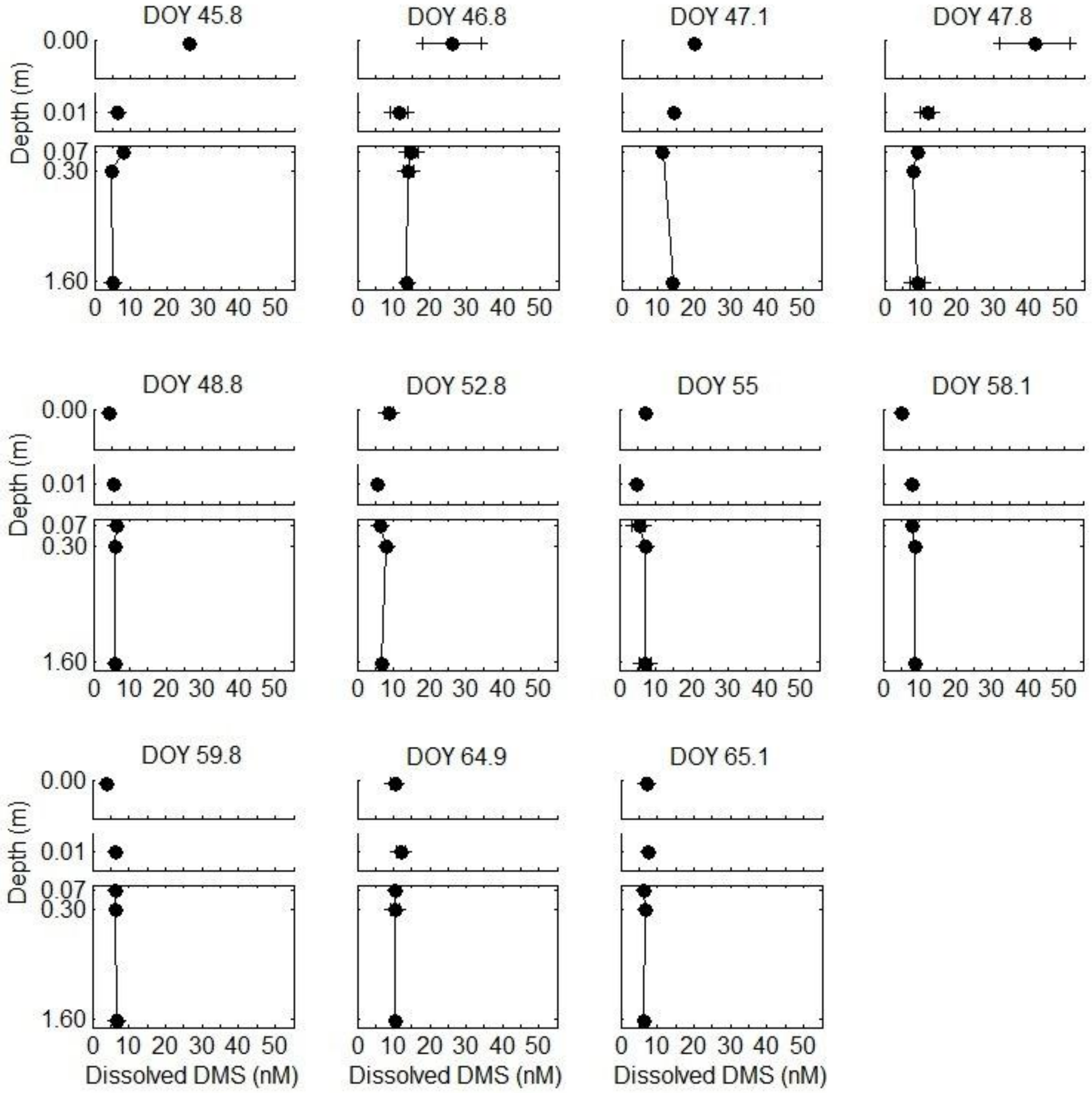

Figure 4: Near-surface concentration gradients of [DMS] in the SSM and in the upper 1.6 m. Measurements presented are the mean replicate samples, and error bars represent one standard deviation.

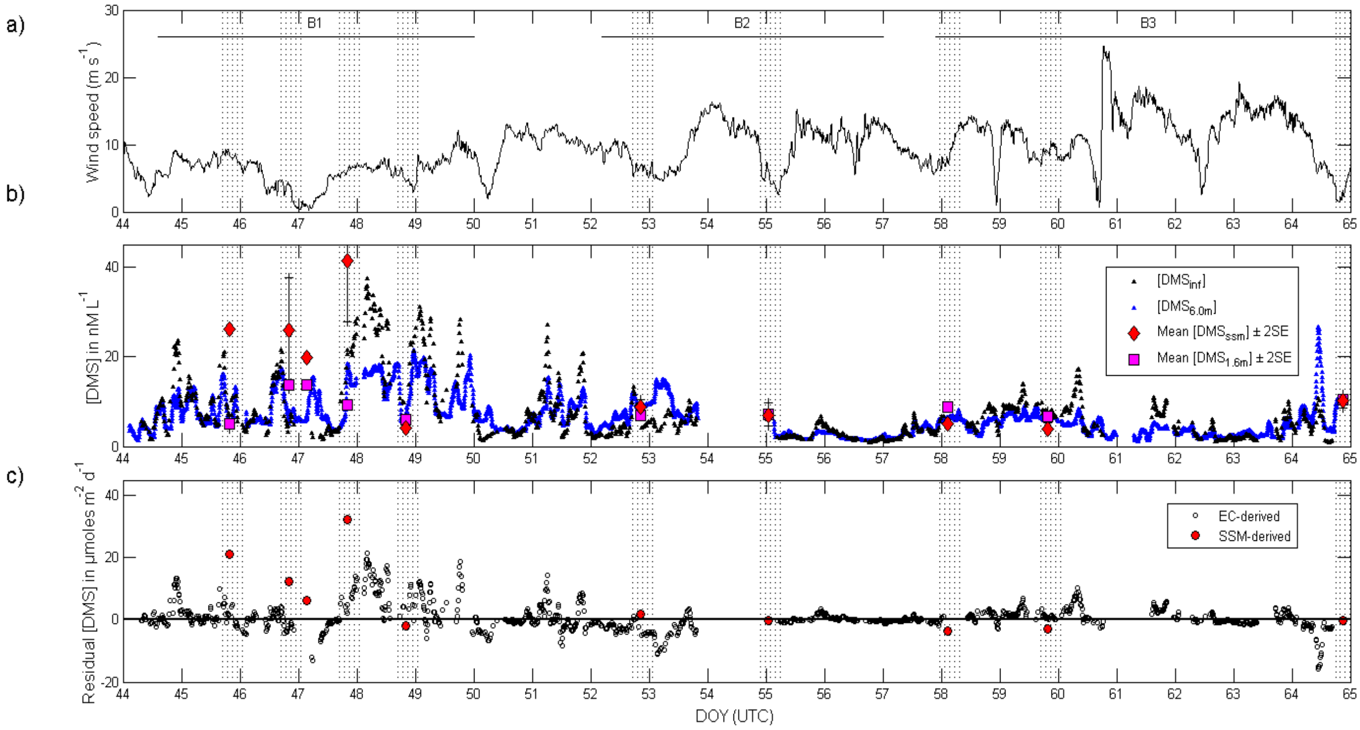

Figure 5: a) Wind speed normalized to 10 m. b) Flux-inferred concentrations of seawater DMS ([DMS_{inf}] black triangles), overlain with the mean for [DMS_{ssm}] (red diamonds), [$DMS_{1.6m}$] (pink squares), and [$DMS_{6.0m}$] (blue triangles). [DMS_{inf}] was calculated from continuous EC flux measurements and COARE k values based on local conditions. [DMS_{inf}] and [$DMS_{6.0m}$] datasets were smoothed using a moving average algorithm with a span of 1 hour. Error bars indicate 2 x standard error of the mean of replicate samples. Shaded areas indicate the period from 3 hours prior, to and 5 hours after SSM sampling. Periods encompassing intense sampling within algal blooms (B1, B2 and B3) are indicated by the horizontal lines at the top of the graph. SSM measurements for DOY 47.1 and 65.1 coincide with a gap in EC air–sea flux data. On DOY 48.8, changes in [$DMS_{6.0m}$] during station occupation indicate the SSM sample is unlikely to be representative of the SSM for the entire station. c) SSM-derived residual [DMS] (red circles) compared with EC-derived residual [DMS] (black circles).

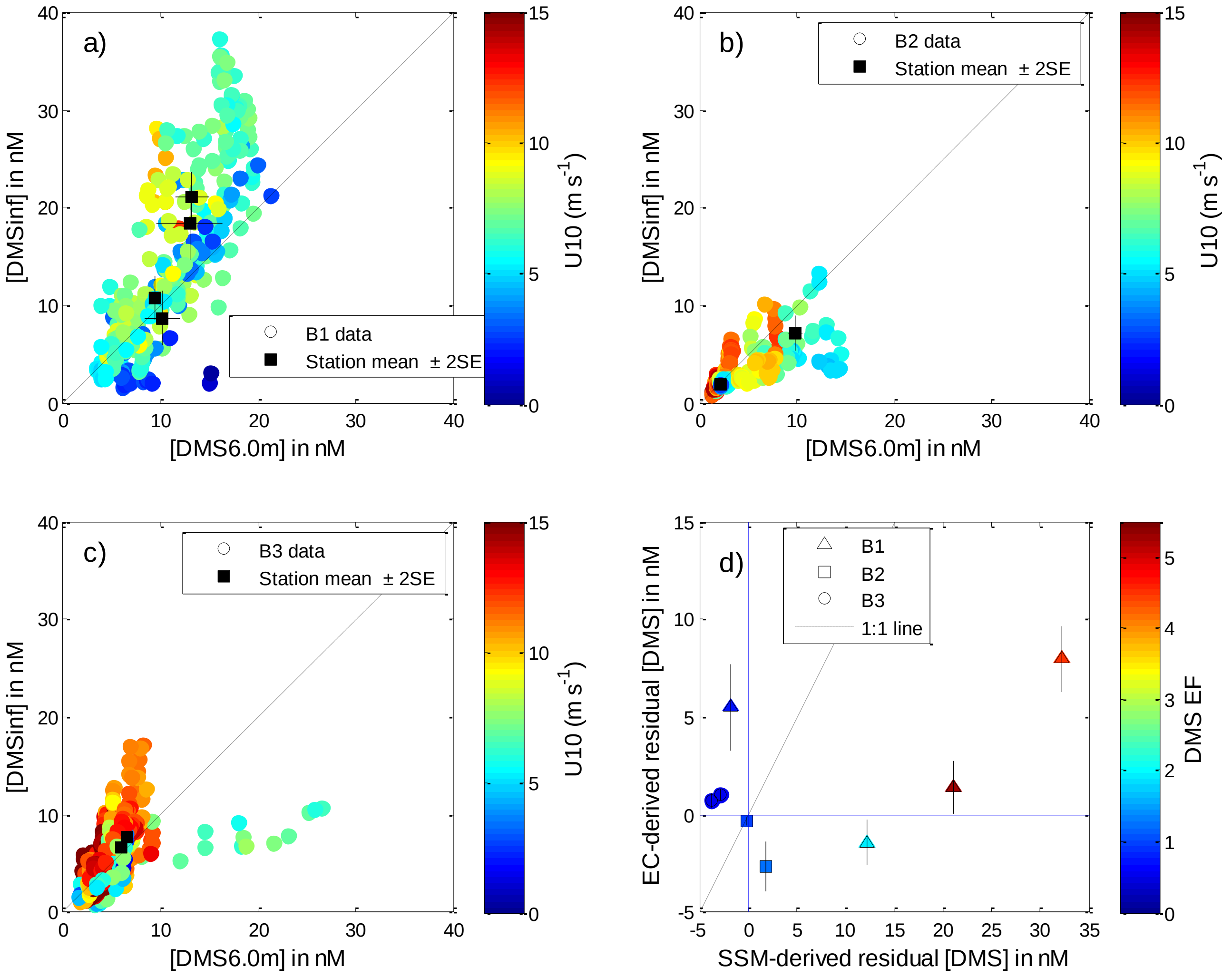

Figure 6 (a – c): Comparison between smoothed [DMS_{inf}] and [$DMS_{6.0m}$] (10 min intervals) during each bloom period. The dashed line indicates the 1:1 relationship. The black squares indicate the mean during the period from 3 hours prior to 5 hours post-sampling the SSM, with error bars indicating 2 x the Standard Error. The symbol colour indicates wind speed (U_{10}), as shown in the colour bar. **d)** Relationship between SSM-derived residual [DMS] and EC-derived residual [DMS] for each SSM station. Data is not available for stations sampled on DOY 47.1, 64.8 and 65.1. Solid vertical and horizontal lines indicate zero residual [DMS], and the dashed line the 1:1 relationship. Symbol colour indicates enrichment factor (EF). The periods used to calculate station means are denoted by shading in Fig. 5.

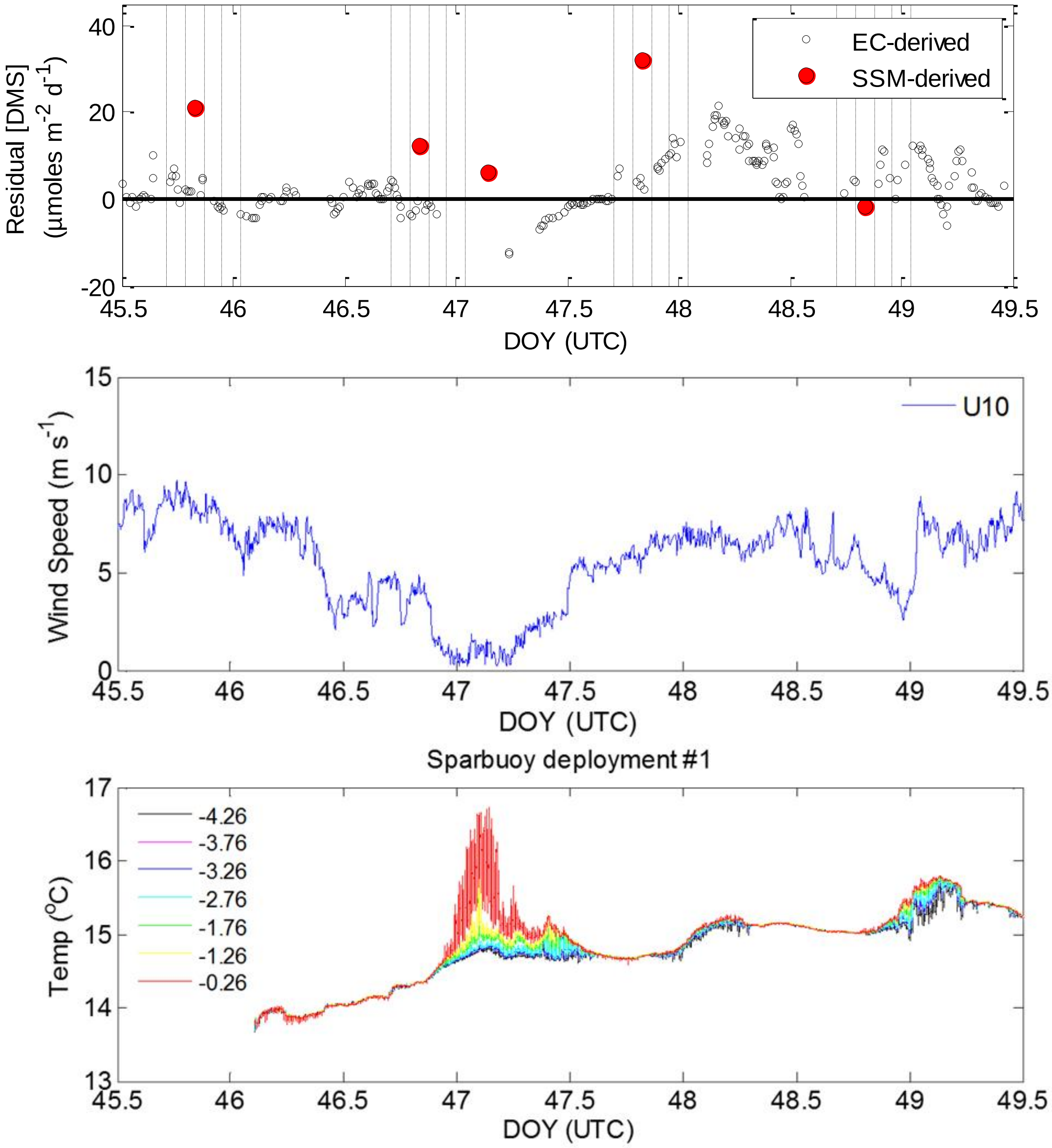

Figure 7: The period between DOY 45.5 and 49.5 in Bloom 1 showing: SSM-derived residual [DMS] (red circles) and EC-derived [DMS] (black circles) in the top plot. SSM measurements for DOY 47.1 coincided with a gap in EC air–sea flux data. Vertical dashed lines indicate the period from 3 hours before to 5 hours after sampling. Wind speed normalized to 10 m (middle plot). Near surface temperatures (bottom plot; legend shows depth in metres).