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Research Paper

Development and validation of a shipboard system for measuring high-resolution vertical profiles of aqueous dimethylsulfide concentrations using chemical ionisation mass spectrometry

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Environmental context. Dimethylsulfide, a trace gas produced by oceanic plankton, is a key chemical species in the global cycles of sulfur and aerosols, with implications that span marine ecology to climate regulation. Knowledge of what governs dimethylsulfide production in the surface ocean depends on our ability to measure concentration changes over time and depth. We describe a sampling and analytical system that provides continuous shipboard measurements of dimethylsulfide concentrations in high-resolution vertical profiles.

Abstract. A sampling and analytical system has been developed for shipboard measurements of high-resolution vertical profiles of the marine trace gas dimethylsulfide (DMS). The system consists of a tube attached to a conductivity–temperature–depth (CTD) probe with a peristaltic pump on deck that delivers seawater to a membrane equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS). This allows profiling of DMS concentrations to a depth of 50 m, with a depth resolution of 1.3–2 m and a detection limit of nearly 0.1 nmol L^{-1}. The seawater is also plumbed to allow parallel operation of additional continuous instruments, and simultaneous collection of discrete samples for complementary analyses. A valve alternates delivery of seawater from the vertical profiler and the ship's underway intake, thereby providing high-resolution measurements in both the vertical and horizontal dimensions. Tests conducted on various cruises in the Mediterranean Sea, Atlantic, Indian, and Pacific Oceans show good agreement between the Eq-APCIMS measurements and purge and trap gas chromatography with flame photometric detection (GC-FPD) and demonstrate that the delivery of seawater from the underway pump did not significantly affect endogenous DMS concentrations. Combining the continuous flow DMS analysis with high-frequency hydrographic, optical, biological and meteorological measurements will greatly improve the spatial–temporal resolution of seagoing measurements and improve our understanding of DMS cycling.

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Introduction

Dimethylsulfide (DMS) is ubiquitous in the pelagic ocean and plays a key role in the global sulfur cycle.[1–3] The knowledge gained in recent decades about this volatile sulfur compound and its precursor dimethylsulfoniopropionate (DMSP) is of such extent that they are some of the best-studied organic substances in the world's ocean. The global surface seawater DMS concentration database[4,5] is the third largest oceanic trace gas database behind those of CO_2 and N_2O. DMS plays a significant role in the formation, growth and chemistry of marine aerosols,[6] the long-term return of sulfur from the oceans to the continents via the atmosphere,[7] and the chemical ecology of many marine living beings.[8–11] It has been argued that DMS plays a central role in a plankton–climate regulatory feedback loop, but this remains controversial.[12–14]

The analytical methods most used to determine aqueous DMS concentrations over the last 40 years consist of gas chromatography (GC) with flame photometric or chemiluminescence detectors (e.g. Andreae and Barnard,[15] Turner and Liss,[16] Bates et al.,[17] Dacey et al.[18] and Simó[19]) on samples collected with Niskin bottles or shipboard pumping systems. Most of the reported oceanic DMS observations are from near-surface samples (1 to 10-m depth) or from unequally spaced and sparse samples collected from vertical profiles. The limited vertical resolution of the sampling technique (usually Niskin bottles attached to a conductivity–temperature–depth (CTD) rosette), together with the time needed for the analysis of discrete samples, result in a poor resolution of the obtained vertical concentration profiles.

Today, mass spectrometric techniques with high sensitivity and fast response allow the determination of DMS without pre-concentration. These techniques, supplied with seawater pumped continuously from the ocean and coupled to either bubbling or membrane equilibration to remove the volatiles

from their aqueous matrix, provide high-frequency measurements of seawater DMS concentrations. Recently, several systems that involve coupling of water–gas equilibrators to electron impact, chemical ionisation and proton transfer mass spectrometers have been developed.[20–22] These systems have the potential to dramatically increase the collection of surface ocean DMS data. The 30+ year global DMS database contains nearly 50 000 data points.[5] Today, a single cruise of 20 days with one of these systems working continuously provides ~10 000 measurements for 5 min averaged data. These systems are suited to resolve sub-mesoscale and short-term variability features.[23–25] However, before thousands of new data are archived into the global database, it is important to intercompare the new techniques with each other and with the traditional GC methods.[26] To our knowledge, only one study[27] has reported a comparison exercise of a high-frequency mass spectrometric technique (MIMS) with purge and trap GC. The results showed good consistency in capturing DMS variability but exhibited a variable offset.

The increasing resolution on the horizontal and temporal scales has not yet been matched in the vertical scale, because the aforementioned instruments have been coupled to shipboard underway intake systems that pump water from a single depth. To date, vertical profiles of DMS concentration are obtained from discrete samples and measured manually using non-automated instruments (e.g. GC), with a depth resolution of several meters and a time resolution of hours between casts. This lack of high-resolution concentration profiles limits description of DMS dynamics on short temporal scales and understanding of the complex biogeochemical interactions that drive oceanic DMS cycling across the water column.

Here we present the development of a technique for sampling and analysing DMS concentrations at high frequency through the upper water column along with parallel measurements of physical and biological variables. The technique consists of a profiling sampler, connected to a membrane equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS). We describe the system components and its operation, and compare the results with those from the purge and trap gas chromatograph with flame photometric detection (GC-FPD) technique. To our knowledge, this is the first time that a continuous sampling technique has enabled vertical DMS concentration profiles at high resolution over depth and time.

Experimental

The analytical system

This study used a tubular counter-flow membrane equilibrator. Details of equilibrator design, construction and operating conditions are given in Saltzman et al.[22] and Table 1. The equilibrator consists of a porous hydrophobic Teflon-membrane tube mounted inside a coiled larger internal diameter tube. Seawater flows through the annular space between the porous membrane and outer tubes and high purity (zero) air counter-flows through the porous inner tube. Dissolved gases, including DMS, diffuse across the pores in the inner tube wall into the air stream, such that the exiting air reaches equilibrium with the seawater DMS. The air exiting the equilibrator is mixed with a larger dilution flow of zero air and directed to the source of the APCIMS. The residence time of seawater and zero air in the equilibrator are respectively ~10 and 20 s.

DMS was detected using an APCIMS. The instrument used in this study is the 'mini-CIMS', developed and described in detail by Saltzman et al.[22] The mini-CIMS is a single quadrupole mass spectrometer based on the Stanford Research Systems residual gas analyser, with a heated ^{63}Ni radioactive source. DMS is ionised by proton transfer from protonated water ($H_2O{\cdot}H^+$), declustered, mass filtered and detected by an electron multiplier. Table 1 reports the lens potentials, ion source temperature and gas flow rates used to obtain optimal sensitivity for DMS. Fig. 1a shows a mass scan of the equilibrator outflow using the shipboard system on board the *R/V* Garcia del Cid in May 2012.

Table 1. Equilibrator and atmospheric pressure chemical ionisation mass spectrometer (APCIMS) operating parameters used in this study

Equilibrator	Flow rates (mL min^{-1})
Seawater flow	1800–2100
Air flow	60
Non-equilibrator gas lines	**Flow rates (mL min^{-1})**
Dilution (bypass) air	600
CH_3SCD_3 standard in air	70
APCIMS	
Region	**Lens potential (V, direct current)**
Lens	
Ion source (760 Torr)	
pinhole	65
Collision region (1 Torr)	
cone 1	34
cone 2	8
Analyser region (10^{-5} Torr)	
mesh 1	−110
aperture 2	12
aperture 3	−4
aperture 4	−90
focus plate	50
	Temperature (°C)
Ion source	350

DMS is quantified by monitoring the ratio of signals from ambient DMS ($CH_3SH_3\ H^+$, *m/z* 63) and an isotopically labelled internal standard (triple-deuterated DMS, $CH_3SCD_3\ H^+$, *m/z* 66). During regular operation in the field, data were recorded continuously by single ion monitoring (SIM) of DMS (*m/z* 63), CH_3SCD_3 (*m/z* 66), isoprene (*m/z* 69), $(H_2O)H^+$ (*m/z* 19), and $(H_2O)_2H^+$ (*m/z* 37) (Fig. 1b). The internal standard was provided by a CH_3SCD_3 permeation tube (0.78 ng min^{-1}; Dynacal, VICI Metronics, Valco Instruments, Houston, TX, USA) maintained at 30 °C in a permeation chamber diluted in a flow of 70 mL min^{-1} of zero air. The permeation rate was monitored in the laboratory before the cruises using high precision weight measurements, and validated by GC-FPD by cross calibration with a higher permeation rate DMS standard (183 ng min^{-1}) that in turn had been calibrated by high precision weighing and displayed a constant weight loss rate over a period of 4 years ($R^2 = 0.9999$). The output from the CH_3SCD_3 permeation tube was added to the air stream exiting the equilibrator. The level of DMS (*m/z* 63) impurity in the CH_3SCD_3 standard (*m/z* 66) corresponded to ~1.9 % of the signal at *m/z* 66 and was corrected from the raw *m/z* 63 data. Blank measurements in the dilution air were also run, but were typically negligible. Fig. 1b shows the raw signals typically acquired in SIM mode.

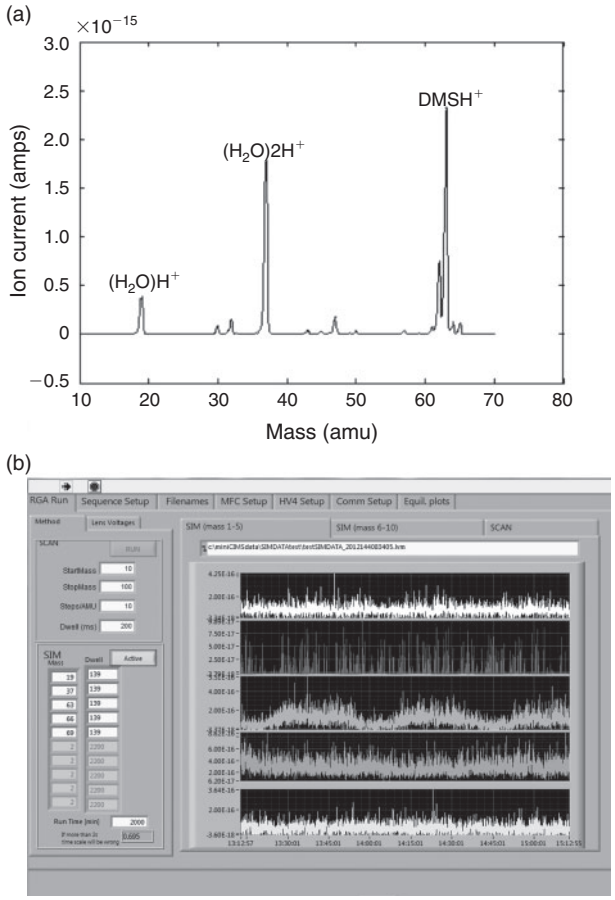

Fig. 1. (a) Ion scan from the equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS) instrument running a seawater sample with no standard on-line. Sample collected with the underway-pumping system aboard the *R*/*V* Garcia del Cid in the Mediterranean Sea, May 2012. (b) A screen capture of the signal acquisition on the Eq-APCIMS; from top to bottom, raw signal for water molecules (*m*/*z* 19, $H_2O(H^+)$), clustered water molecules (*m*/*z* 37, $(H_2O)_2(H^+)$), dimethylsulfide (DMS) (*m*/*z* 63, $(CH_3)_2S(H^+)$), trideuterated DMS standard (*m*/*z* 66, $CH_3SCD_3(H^+)$), and isoprene (*m*/*z* 69, $C_5H_8(H^+)$).

The molar mixing ratio of ambient DMS (X_{DMS}) in the gas stream exiting the equilibrator is calculated as follows:

$$X_{DMS} = (C_{63}/C_{66}) \times (p/F_{eq})$$

where C_{63} and C_{66} are the blank corrected-signals (in amps) for *m*/*z* 63 and 66, p is the permeation rate (mol s^{-1}) and F_{eq} is air flow rate in the equilibrator (mol s^{-1}) determined from the measured mass flow and ideal gas law. The gas phase DMS mixing ratio (X_{DMS}) was converted into a seawater concentration (DMS_{sw}), using the temperature- and salinity-dependent Henry's law constant for DMS (H_{DMS}, M atm^{-1}; Dacey et al.[28]):

$$DMS_{sw} = X_{DMS} \times p_{atm} \times H_{DMS}$$

where p_{atm} is the atmospheric pressure.

The instrument was operated in an automated operational cycle consisting typically of a 12-h seawater data collection period (in SIM mode), followed by equilibrator blanks (no internal standard; 5 min SIM, 10 full scans) and standard-only blanks (equilibrator bypassed; 5 min SIM, 10 full scans). The blanks were used to account for the contribution of non-isotope DMS in the internal standard and to detect DMS contamination in the system tubing and electronic noise. These were very small corrections (1.9 %), and are minor contributors to the overall uncertainty of the measurement. It is important to note that these blanks do not account for any contamination of the equilibrator itself. The regular ambient data acquisition accounted for 95 % of the operation time.

The zero air for both the equilibrator and the internal standard was supplied either from a pressurised cylinder or by an ultra-zero air generator (model GT6000, LNI Schmidlin, Neuheim, Switzerland) fed by the compressed air supply of the ship.

The overall shipboard system layout

A schematic of the whole system on board is presented in Fig. 2. The setup allowed alternation between the underway intake while steaming, and vertical profiling when the ship was on station. The Eq-APCIMS was located in one of the ship laboratories, next to the outlet of the clean underway intake system. A valve allowed switching between the underway and profiler seawater supplies. A multitap set divided the incoming water flow into three parallel flows directed to: (1) the equilibrator and Eq-APCIMS, (2) a fast repetition rate fluorometer (FRRF; FASTracka, Chelsea Technologies, Surrey, UK) recording in continuous mode and (3) a tube for filling bottles for discrete measurements.

The underway seawater intake system

The underway seawater intake system used the ship's clean water intake pump, which provides an uncontaminated (non-toxic), continuous source of near-surface seawater. The water was brought to the laboratories through epoxide-free silicone pipes. A branch of the flow was directed through continuously logged thermo-salinograph, fluorometer and temperature sensors. The data reported in the present study were collected on three cruises: one conducted aboard the *R*/*V* Hesperides across the Atlantic, Indian and Pacific oceans (Malaspina cruise, January–June 2011), and the other two aboard the *R*/*V* Garcia del Cid in the north-western Mediterranean Sea (SUMMER cruises, September 2011 and May 2012). On the *R*/*V* Hesperides, the water intake is located 5 m below sea level, and the parts of the centrifugal pump (BKMKC-10.11, Tecnium, Manresa, Spain) in contact with the fluid are made of polypropylene and glass. On the *R*/*V* Garcia del Cid, the intake is located 4 m below sea level and the interior of the pump (BKMKC-8.10, Tecnium) is also made of polypropylene.

The vertical profiling system

The system developed for measuring high-resolution vertical profiles consisted of a CTD operated manually in up and down motion, with a tied hose through which water was pumped to the ship's laboratory. The device used for drawing seawater was an in-laboratory peristaltic pump (model 620UN, Watson-Marlow, Wilmington, MA, USA), which is free of valves, seals or glands to avoid clogging or corrosion. The pumped seawater flow contacts only the bore of the tube (Marprene, inert thermoplastic elastomer, Watson-Marlow), eliminating the risk of sample contamination. The pump flow rate was 3.5 L min^{-1}. The pump intake tubing was a 50–70-m non-toxic latex hose reinforced with polyester thread mesh (model Mallalatex, Espiroflex, Barcelona, Spain), with inner and outer diameters of 15 and 21 mm. A 10-cm diameter plastic funnel was mounted at the hose inlet and covered with 5-mm nylon mesh to avoid drawing

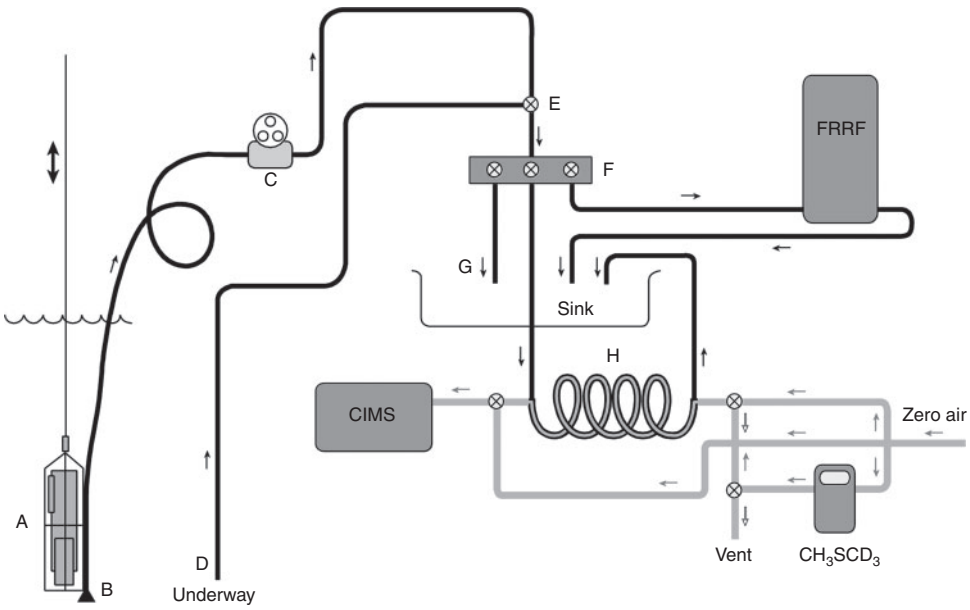

Fig. 2. Diagram of the system designed for either underway or vertically profiled high-resolution measurements of dimethylsulfide (DMS) aboard an oceanographic vessel. Black circuit represents the water flow; grey circuit corresponds to the air flow. (a) conductivity–temperature–depth (CTD) sensors in a protected cage (the double arrow indicates operation from the winch in yo-yo mode); (b) hose inlet; (c) peristaltic pump on board; (d) silicone pipe from the ship's underway pump; (e) switch tap; (f) multitap; (g) flow outlet into the sink; (h) equilibrator loop; CH_3SCD_3: standard permeation device. CIMS, atmospheric pressure chemical ionisation mass spectrometer; FRRF, fast repetition rate fluorometer. Small arrows signal the direction of the flow. In the circuit for the zero air supply to the equilibrator, filled arrows indicate the flow in normal conditions. The open arrows indicate operation through a bypass of the equilibrator and venting of the standard to check for blanks.

large jellyfish that might clog the system. The first meter of the hose was tied to the cage of the CTD probe with the aid of a segment of semi-rigid plastic tubing that prevented bending of the hose. The CTD (SBE-19, Seabird, Bellevue, WA, USA) was manually controlled to cycle from 1- to 35- or 50-m depth at a speed of ~2.5–4 m min^{-1}. A complete cycle from the surface to 35 m and back took ~20–25 min. Profiling to 50 m and back took 30 min. Vertical profiles of conductivity and temperature were measured with the CTD sensors as seawater was drawn through the hose for DMS measurements.

Parallel DMS analysis by GC-FPD

A traditional purge and trap GC-FPD was used to analyse discrete DMS samples on the cruises in parallel with the Eq-APCIMS.[29–30] Samples were collected in glass vials either from Niskin bottles (Seabird, Bellevue, WA, USA) attached to a CTD rosette or from the underway-pumped flow using the open tap. In all cases, some overflow was allowed to avoid headspace and bubbles while sampling and filling the vials. Subsamples of 3–10 mL were gently filtered through a glass fibre filter (GF/F, Whatman, GE Healthcare, Freiburg, Germany), purged for 3–5 min with ultra-high purity helium and the stripped DMS was cryogenically trapped in liquid nitrogen. The trapped volatiles were desorbed by dipping the trap in water at room temperature. Gases were separated on a Carbopack 60/80 mesh column (Supelco, Sigma–Aldrich, St Louis, MO, USA) at 170 °C. A Shimadzu GC14A gas chromatograph (Kyoto, Japan) and flame photometric detector were used. All samples were processed shortly after collection. DMS concentrations were determined by comparison with a standard curve constructed by injecting different volumes of gas standards from a DMS permeation device (183 ng min^{-1}, Dynacal, VICI Metronics) maintained at a constant temperature and diluted in zero air.[29] The detection limit was 3 pmol of DMS (0.3 nmol L^{-1} aqueous DMS in a 10-mL seawater sample). All samples were analysed in duplicate and the coefficient of variation between the duplicates was generally ≤5 %.

Results

Eq-APCIMS data averaging, measurement precision and sensitivity

The Eq-APCIMS instrument acquired data for each ion for 139 ms with a frequency of 0.5 Hz but, as depicted by Fig. 1b, time averaging (binning) of the data was required to improve the signal-to-noise ratio. In order to determine the optimal averaging time we used 6.2 h of continuous, near-surface underway measurements conducted in the Mediterranean Sea on the *R*/*V* Garcia del Cid, with the ship closely following a pair of surface Lagrangian drifters. Because we stayed in a coherent water patch, the DMS concentration underwent only a small and smooth drift during the sampling period. Raw data (*m*/*z* 63 : 66 ratios) were binned into increasing intervals between 4 and 400 s, bin averages were computed and the standard deviation of the mean of all bins over the 6.2-h period was calculated. Fig. 3 illustrates the effect of averaging (binning) time on the variance of the signal. Increasing the averaging time rapidly reduces the standard deviation essentially because it increases the signal-to-noise ratio, until a point where further lengthening the bins does not significantly reduce the variance, as shown by the flattening of the curve in the figure. Based on these results, an averaging time of 60 s was used to process underway data. With the ship steaming at 10 knots (~18.5 km h^{-1}), a 60 s averaging time yields a datum every 300 m. When profiling at an ascent–descent speed of 2.5–4 m min^{-1}, averaging every 60 s

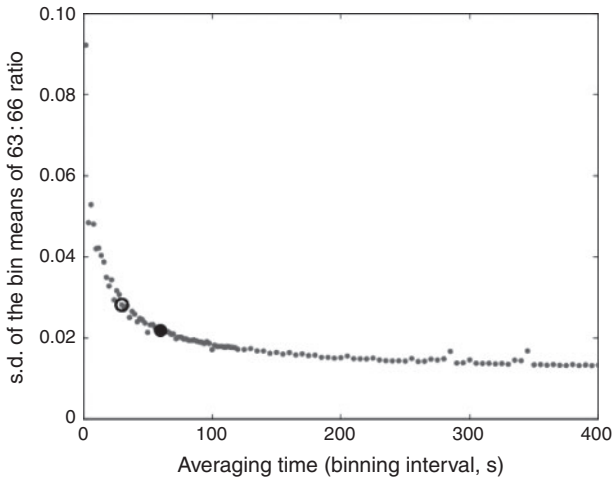

Fig. 3. Standard deviation of averaged bin means of equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS) data *v.* binning time. Data are the values of the ratio of ion 63 (dimethylsulfide (DMS)(H^+)) to ion 66 ($CH_3SCD_3(H^+)$), which is the ratio used to calculate the aqueous DMS concentration, over a period of 6.2 h. Binning times increase by 2 s until 120 s and then by 5 s up to 400 s. The filled circle shows the optimal averaging (binning) time chosen for surface underway data (60 s); the open circle shows the optimal averaging (binning) time selected for vertical profiles (30 s). See text for details.

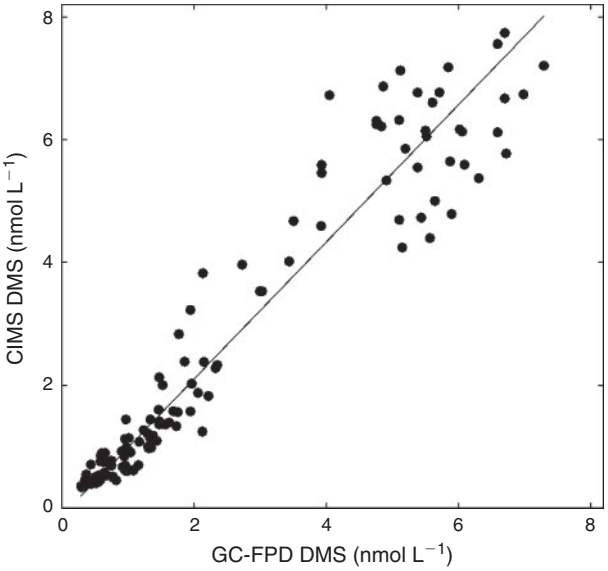

Fig. 4. Model II regression for equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS) against gas chromatography with flame photometric detection (GC-FPD) dimethylsulfide (DMS) concentrations in 125 samples; $y = 1.12\ (\pm 0.03)x - 0.13\ (\pm 0.09)$; $R^2 = 0.92$; $P < 0.0001$.

would yield a vertical resolution of 2.5–4 m, which was deemed too coarse to observe DMS gradients. Therefore, an averaging time of 30 s (equivalent to 1.3–2 m) was used for vertical profiles.

An estimate of the overall uncertainty in the DMS analysis was obtained using the same Lagrangian data series. This included the error associated with the mean of the *m*/*z* 63 : 66 ratio within each bin, and the uncertainty in solubility associated with the variance in equilibrator seawater temperatures. Assuming these uncertainties are uncorrelated, the resulting coefficient of variation of DMS concentration in 60-s bins was 8 %. This can be regarded as the experimental error or precision of the underway DMS concentration measurements. For vertical profile DMS measurements, which used a binning time of 30 s, the experimental error was 11 %.

As for the instrument's sensitivity, the detection limit of the Eq-APCIMS is estimated as 220 ppt in the equilibrated air stream.[22] Based on the solubility of DMS in seawater, this is equivalent to respective aqueous concentrations of 0.12, 0.10 and 0.08 nmol L^{-1} at temperatures of 15, 20 and 25 °C.

Eq-APCIMS v. *GC-FPD measurements*

On the *R*/*V* Hesperides 2011 cruise across oligo- and mesotrophic regions of the world's oceans, discrete DMS samples were collected from the underway pumped flow, using the open outlet of the multitap system throughout the day. These samples were analysed by purge and trap GC-FPD as described above. The exact time of discrete sampling was noted and matched to the corresponding 1-min averaged Eq-APCIMS datum. On Lagrangian cruises aboard the *R*/*V* Garcia del Cid, discrete GC samples were collected from several depths using the open outlet of the multitap system while measuring vertical profiles with the profiler. The corresponding time and depth were matched to the 30-s averaged Eq-APCIMS data. All of these GC-FPD and Eq-APCIMS data are compared in Fig. 4. Each of the two techniques was calibrated with its own permeation standard.

A Model II linear regression of the Eq-APCIMS *v.* GC data yields a significant relationship, with $R^2 = 0.92$ ($P < 0.0001$), slope of 1.12 ± 0.03 and intercept of -0.13 ± 0.09. This average discrepancy between the Eq-APCIMS and GC-FPD measurements is within the experimental error of the Eq-APCIMS (~±10 %) and within the estimated inherent variability of other DMS measurement methods.[26] The agreement is reasonably good given the independent calibrations, the differences in sample handling (e.g. the GC-FPD requires filtration, the Eq-APCIMS does not; the Eq-APCIMS method equilibrates the sample with air and measures the equilibrated fraction only, whereas the GC-FPD method sparges the sample), and the fact that GC-FPD is run on discrete 3–10-mL samples whereas the Eq-APCIMS datum is the average of 30–60 s of acquisition and therefore averages DMS concentration over 1.5–2 m of water column or 300 m of horizontal track.

Test for potential pumping artefacts

Possible concerns associated with measuring DMS using the underway intake pumping system include: (1) damage to phytoplankton cells and associated DMS release or production through enzymatic cleavage of DMSP, (2) loss of DMS as a result of bacterial metabolism associated with biofilms in the system or (3) loss of analytes through volatilisation or wall losses. To validate the use of underway pumping systems for DMS, we compared discrete samples collected from the underway intake system with samples collected simultaneously at a similar depth (3 m) using Go-Flo bottles launched overboard. Both sets of samples were analysed by GC-FPD using identical methods (Fig. 5). There is good agreement between the two series. Model II linear regression gives a strong and significant relationship ($R^2 = 0.91, P < 0.0001$), with an underway/bottle slope of 0.94 ± 0.024 and an intercept of 0.15 ± 0.036, i.e. the agreement is almost within the measurement uncertainty of the GC-FPD method (±5 %).

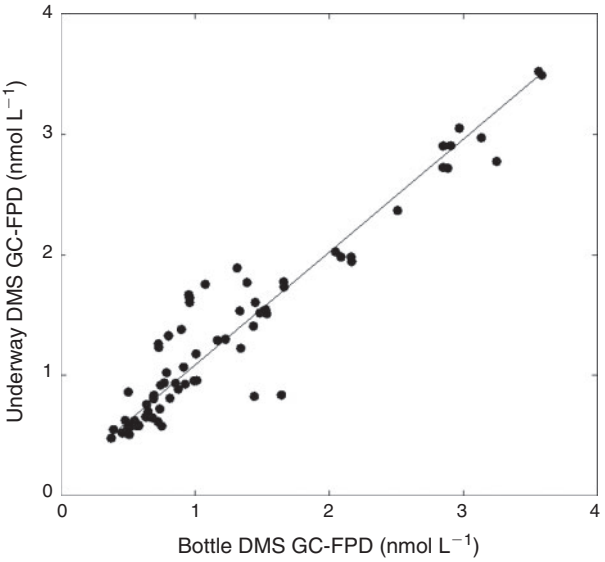

Fig. 5. Model II regression for underway dimethylsulfide (DMS) sampling against co-located overboard bottle sampling using gas chromatography with flame photometric detection (GC-FPD) for the analysis of all 75 samples; $y = 0.94\ (\pm 0.024)x + 0.15\ (\pm 0.036)$; $R^2 = 0.91$; $P < 0.0001$.

Vertical profiles at sea

The profiler–Eq-APCIMS system was field tested for high-resolution vertical profiles of DMS concentrations during the two cruises in the Mediterranean Sea on board the *R/V* Garcia del Cid in September 2011 and May 2012. As a token example, data collected during a 2.5-h run in the evening of 14 September 2011 are shown in Fig. 6 to illustrate the performance of the profiling technique. The depth *v.* time plot shown here corresponds to six complete up–down cycles from the surface water to ~35-m depth. In a later cruise, the technique was proven to work well up to a depth of 50 m.

Fig. 6 also shows profiles of seawater temperature and potential density derived from the CTD probe of the profiler, and chlorophyll *a* fluorescence measured with the FRRF installed in parallel to the Eq-APCIMS. It clearly illustrates that steep gradients with depth occur for all variables, with DMS showing maximum concentrations near the warmer surface, completely decoupled from the deeper fluorescence maximum that occurs in the colder waters at the bottom of the pycnocline. It also reveals a rapid change in stratification, with the upper mixed layer turning shallower as the sun approached sunset (~1800 hours GMT). This rapid change in water physics was not matched at the same pace by significant changes in the DMS concentration profile. The full dataset from the cruises will be presented and discussed elsewhere.

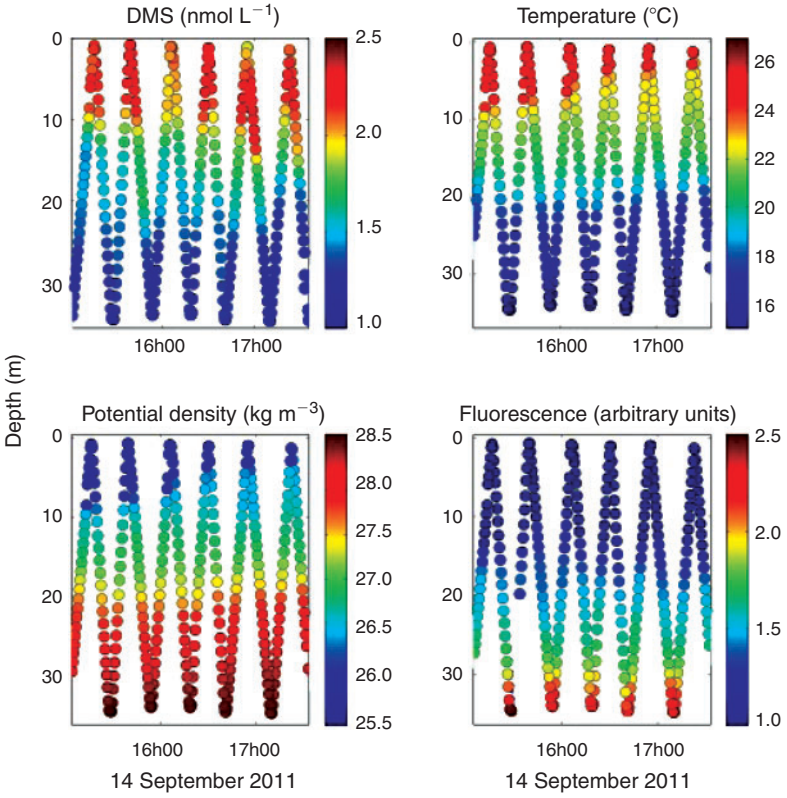

Fig. 6. Repeated depth profiles of dimethylsulfide (DMS), seawater temperature and potential density, and chlorophyll *a* fluorescence measured for 2.5 h during a Mediterranean cruise aboard the *R/V* Garcia del Cid on 14 September 2011. The profiler was cycled from the near surface to 35 m and DMS and fluorescence were measured using the equilibrator and atmospheric pressure chemical ionisation mass spectrometer (Eq-APCIMS) and the fast repetition rate fluorometer (FRRF) (see text for details). Temperature and potential density were respectively measured and calculated from the conductivity–temperature–depth (CTD) sensors of the profiler. The *x*-axis is GMT time. Half minute average data are shown.

The pressure sensor of the CTD probe provided the sampling depth at any time. However, attributing each Eq-APCIMS measurement to its corresponding depth was not trivial because the sampled water took 3.5 min to flow from the hose inlet to the Eq-APCIMS. There were some slight variations in time lag because of changes in flow rate associated with transitory bending of the hose under water. Because the Eq-APCIMS equilibrator was equipped with a temperature data-logging sensor, we matched the temperature profiles of the equilibrator and CTD sensors to determine the depth at which the equilibrator seawater was sampled.

One concern of any profiler working from a floating platform is the effect that platform motion (primarily ship roll) may have on the depth accuracy of the measured profile. In this sense, having a depth (pressure) probe continuously recording at the mobile sampling point (hose inlet) allows accounting for variations in the sampling depth attributable to ship roll. Another concern relates to the potential smearing or homogenisation of the target analyte(s) in the sampled water owing to mixing in the profiler pipe. Calculations for our hose dimensions and pumping rate following Taylor[31] give an e-folding mixing length along the hose of ~1 m or a mixing time scale of ~3 s (i.e. 13–20-cm depth resolution at speeds of 2.5–4 m min^{-1}). Laboratory experiments indicate that the response time constant for the Eq-APCIMS to a step change in seawater concentration is ~10 s due to mixing within the equilibrator and equilibration time. When these two sources of uncertainty are added together in a non-linear way, the resulting response time of the system is $SQRT(3^2 + 10^2) = 10.4$ s. Therefore, the effects of the tubing and equilibrator response times limit the best depth resolution achievable with the profiling system to ~0.4–0.7 m for profiling speeds of 2.5–4 m min^{-1}. Nonetheless, the aforementioned need for averaging the signal in 30-s bins sets the actual depth resolution of the profiler to 1.3–2 m.

Discussion

The profiling system described here achieved DMS depth profiles with a time resolution of 30 s, a depth resolution of 1.3–2 m, a measurement precision of 11 % and a detection limit of nearly 0.1 nmol L^{-1}. The resolution of the profiling system can be improved by varying the pumping and profiling rates, and improving the time response of the Eq-APCIMS and its sensitivity. The mini-CIMS used in this study is a relatively low cost, low sensitivity instrument, and a more sensitive Eq-APCIMS such as that used by Bell et al.[32] would increase signal to noise by approximately one order of magnitude. However, theoretical time resolution limits of 3 and 10 s are imposed by the mixing in the pumping pipeline and the mixing and equilibration response in the equilibrator. Even at the resolution presented here, the profiling approach represents a significant advance in data coverage from the use of Niskin bottles on CTD casts followed by purge and trap analysis.

Hale and Takahashi[33] developed a vertical profiler by which water was pumped from a SeaSoar CTD through a 750-m tube, while undulating from near the surface to depths near 200 m. Even though the Lamont Pumping SeaSoar (LPS) allows deeper profiles, it has to be operated while steaming and its launch and recovery is far from quick and easy. This prevents its use on station, either at a fixed location or in Lagrangian drift. Our profiler, conversely, is used with the ship stopped on site, and it is very easy to recover from water, which makes it particularly suited for on-station or Lagrangian studies. As for depth resolution, the LPS is less affected by ship's vertical motion and more affected by mixing in the longer pipe. The authors[33] estimated a mixing time constant of 7.5–10 s, which corresponded to a vertical resolution of 1.9–2.5 m when used at dive and climb rates of 15 m min^{-1}. These figures are similar to and even coarser than our aforementioned resolution of 1.3–2 m.

This study provides validation for the continuous flow measurement of DMS by Eq-APCIMS. The method used here involves use of an internal gas standard added after the equilibrated gas stream. This approach assumes complete equilibration in the membrane equilibrator. It does not correct for possible clogging of membrane pores in the equilibrator as a result of fouling. Extensive use of this equilibrator in prior studies suggests that the porous Teflon tube membrane does not experience biofouling in oligo- and mesotrophic conditions.[22,32,34–36] However, during the Malaspina cruise aboard the *R/V* Hesperides, abundant jellyfish in the Benguela current region caused some clogging of the equilibrator, which had to be dismounted and cleaned with 10 % hydrochloric acid. Bell et al.[32] recently modified the technique to introduce an isotopically labelled internal standard as an aqueous solution at the inlet of the equilibrator. This method corrects for any loss of signal in the event of fouling or incomplete equilibration. Neither standardisation technique accounts for possible artefact production of DMS in the equilibrator resulting from growth on the tube interior or mechanical stress to organisms in the pump and tubing. However, the observed agreement between the Eq-APCIMS and the GC-FPD methods (Fig. 5) across a broad DMS concentration range (0.3 to 8 nmol L^{-1}) suggests that under most typical oceanic conditions[5] the equilibrator provides accurate and repeatable measurements.

The agreement of GC-FPD measurements in seawater from Go-Flo bottles and underway intake indicates that the underway systems did not have a significant effect on endogenous DMS concentrations during this study. Bell et al.[32] carried out a similar comparison using the Eq-APCIMS with similar results. However, the results of these studies do not necessarily apply to all ships because of variations in shipboard underway pump types, pipe materials and maintenance procedures. The fact that some respiratory activity (oxygen consumption) has been measured in underway seawater lines of several ships[37] calls for caution regarding microbial activity that might consume DMS. Likewise, the tests in the present study were conducted with picophytoplankton-dominated waters; phytoplankton assemblages more susceptible to mechanical stress or damage by pumping and filtration (e.g. those with colonial *Phaeocystis*) may yield larger differences between underway and bottle-derived measurements.

One of the strengths of the continuous flow DMS measurement is that it can be coupled with other instruments that also provide continuous measurements. For instance, our system was coupled by a multitap split of the seawater flow to a FRRF, which provides fluorescence of organisms and data on the performance of photosystem II.[38] This is an interesting complement to DMS measurements, because DMS has been linked to algal physiological stress.[39] Like the Eq-APCIMS, the FRRF was used to either record fluorescence response in surface waters while steaming or in vertical profiles when coupled to the profiling sampler. In addition, the CTD probe of the profiler provided physical data such as salinity, temperature and the derived density profiles. Fig. 6 shows the importance of obtaining high-resolution measurements over depth and time to study

the dynamics of DMS within its biophysical context. The setup can easily be complemented by adding further sensors to the probe, thereby obtaining high-resolution vertical profiles of variables such as oxygen, underwater light, beam transmission, organic matter fluorescence, turbidity or nitrate, which will provide a more comprehensive context for the DMS profiles.

In summary, high-resolution vertical profiles and near surface underway measurements of DMS demonstrate that membrane equilibrator–APCIMS is a valuable new tool to describe short-term DMS variability and its relationship to other physical and biogeochemical parameters. This approach facilitates the study of DMS distribution, cycling and environmental forcing at unprecedented resolution, also along the vertical dimension.

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References

[1] M. O. Andreae, Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem.* **1990**, *30*, 1. doi:10.1016/0304-4203(90)90059-L

[2] T. S. Bates, B. K. Lamb, A. Guenther, J. Dignon, R. E. Stoiber, Sulfur emissions to the atmosphere from natural sources. *J. Atmos. Chem.* **1992**, *14*, 315. doi:10.1007/BF00115242

[3] R. Simó, Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links. *Trends Ecol. Evol.* **2001**, *16*, 287. doi:10.1016/S0169-5347(01)02152-8

[4] A. J. Kettle, M. O. Andreae, D. Amouroux, T. W. Andreae, T. S. Bates, H. Berresheim, H. Bingemer, R. Boniforti, M. A. J. Curran, G. R. DiTullio, G. Helas, G. B. Jones, M. D. Keller, R. P. Kiene, C. Leck, M. Levasseur, G. Malin, M. Maspero, P. Matrai, A. R. McTaggart, N. Mihalopoulos, B. C. Nguyen, A. Novo, J. P. Putaud, S. Rapsomanikis, G. Roberts, G. Schebeske, S. Sharma, R. Simó, R. Staubes, S. Turner, G. Uher, A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global Biogeochem. Cycles* **1999**, *13*, 399. doi:10.1029/1999GB900004

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

[6] A. D. Clarke, D. Davis, V. N. Kapustin, F. Eisele, G. Chen, I. Paluch, D. Lenschow, A. R. Bandy, D. Thornton, K. Moore, L. Mauldin, D. Tanner, M. Litchy, M. A. Carroll, J. Collins, G. Albercook, Particle nucleation in the tropical boundary layer and its coupling to marine sulfur sources. *Science* **1998**, *282*, 89. doi:10.1126/SCIENCE.282.5386.89

[7] J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature* **1972**, *237*, 452. doi:10.1038/237452A0

[8] R. P. Kiene, L. J. Linn, J. A. Bruton, New and important roles for DMSP in marine microbial communities. *J. Sea Res.* **2000**, *43*, 209. doi:10.1016/S1385-1101(00)00023-X

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

[10] J. R. Seymour, R. Simó, T. Ahmed, R. Stocker, Chemoattraction to dimethylsulfoniopropionate throughout the marine microbial food web. *Science* **2010**, *329*, 342. doi:10.1126/SCIENCE.1188418

[11] J.-B. Raina, D. M. Tapiolas, S. Forêt, A. Lutz, D. Abrego, J. Ceh, F. O. Seneca, P. L. Clode, D. G. Bourne, B. L. Willis, C. A. Motti, DMSP biosynthesis by an animal and its role in coral thermal stress response. *Nature* **2013**, *502*, 677. doi:10.1038/NATURE12677

[12] J. R. Charlson, J. E. Lovelock, M. O. Andreae, S. G. Warren, Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **1987**, *326*, 655. doi:10.1038/326655A0

[13] P. K. Quinn, T. S. Bates, The case against climate regulation via oceanic phytoplankton sulphur emission. *Nature* **2011**, *480*, 51. doi:10.1038/NATURE10580

[14] Y. Iizuka, R. Uemura, H. Motoyama, T. Suzuki, T. Miyake, M. Hirabayashi, T. Hondoh, Sulphate-climate coupling over the past 300 000 years in inland Antarctica. *Nature* **2012**, *490*, 81. doi:10.1038/NATURE11359

[15] M. O. Andreae, W. R. Barnard, Determination of trace quantities of dimethyl sulfide in aqueous solutions. *Anal. Chem.* **1983**, *55*, 608. doi:10.1021/AC00255A006

[16] S. M. Turner, P. S. Liss, Measurements of various sulphur gases in a coastal marine environment. *J. Atmos. Chem.* **1985**, *2*, 223. doi:10.1007/BF00051074

[17] T. S. Bates, J. D. Cline, R. H. Gammon, S. R. Kelly-Hansen, Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere. *J. Geophys. Res.* **1987**, *92*, 2930. doi:10.1029/JC092IC03P02930

[18] J. W. H. Dacey, F. A. Howse, A. F. Michaels, S. G. Wakeham, Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **1998**, *45*, 2085. doi:10.1016/S0967-0637(98)00048-X

[19] R. Simó, Trace chromatographic analysis of dimethyl sulfoxide and related methylated sulfur compounds in natural waters. *J. Chromatogr. A* **1998**, *807*, 151. doi:10.1016/S0021-9673(98)00086-7

[20] P. D. Tortell, Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr. Methods* **2005**, *3*, 24. doi:10.4319/LOM.2005.3.24

[21] S. Kameyama, H. Tanimoto, S. Inomata, U. Tsunogai, A. Ooki, Y. Yokouchi, S. Takeda, H. Obata, M. Uematsu, Equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) for sensitive, high-resolution measurement of dimethyl sulfide dissolved in seawater. *Anal. Chem.* **2009**, *81*, 9021. doi:10.1021/AC901630H

[22] E. S. Saltzman, W. J. De Bruyn, M. J. Lawler, C. Marandino, C. McCormick, A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater. *Ocean Sci.* **2009**, *6*, 1569.

[23] P. D. Tortell, M. C. Long, Spatial and temporal variability of biogenic gases during the Southern Ocean spring bloom. *Geophys. Res. Lett.* **2009**, *36*, L01603. doi:10.1029/2008GL035819

[24] E. C. Asher, A. Merzouk, P. D. Tortell, Fine-scale spatial and temporal variability of surface water dimethylsufide (DMS) concentrations and sea–air fluxes in the NE Subarctic Pacific. *Mar. Chem.* **2011**, *126*, 63. doi:10.1016/J.MARCHEM.2011.03.009

[25] S. Kameyama, H. Tanimoto, S. Inomata, H. Yoshikawa-Inoue, U. Tsunogai, A. Tsuda, M. Uematsu, M. Ishii, D. Sasano, K. Suzuki, Y. Nosaka, Strong relationship between dimethyl sulfide and net community production in the western subarctic Pacific. *Geophys. Res. Lett.* **2013**, *40*, 3986. doi:10.1002/GRL.50654

[26] T. G. Bell, G. Malin, G. A. Lee, J. Stefels, S. Archer, M. Steinke, P. Matrai, Global oceanic DMS data inter-comparability. *Biogeochem.* **2012**, *110*, 147. doi:10.1007/S10533-011-9662-3

[27] P. D. Tortell, C. Guéguen, M. C. Long, C. D. Payne, P. Lee, G. R. DiTullio, Spatial variability and temporal dynamics of surface water pCO_2, ΔO_2/Ar and dimethylsulfide in the Ross Sea, Antarctica. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2011**, *58*, 241. doi:10.1016/J.DSR.2010.12.006

[28] J. W. H. Dacey, G. Wakeham, B. L. Howes, Henry's law constants for dimethylsulfide in freshwater and seawater. *Geophys. Res. Lett.* **1984**, *11*, 991. doi:10.1029/GL011I010P00991

[29] R. Simó, J. O. Grimalt, J. Albaigés, Sequential method for the field determination of nanomolar concentrations of dimethyl sulfoxide in natural waters. *Anal. Chem.* **1996**, *68*, 1493. doi:10.1021/AC9510907

[30] M. Galí, C. Ruiz-González, T. Lefort, J. M. Gasol, C. Cardelús, C. Romera-Castillo, R. Simó, Spectral irradiance dependence of sunlight effects on plankton dimethylsulfide production. *Limnol. Oceanogr.* **2013**, *58*, 489.

[31] G. I. Taylor, Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. Roy. Soc. A.* **1953**, *219*, 186. doi:10.1098/RSPA.1953.0139

[32] T. G. Bell, W. De Bruyn, S. D. Miller, B. Ward, K. Christensen, E. S. Saltzman, Air/sea DMS gas transfer in the North Atlantic: evidence for limited interfacial gas exchange at high wind speed. *Atmos. Chem. Phys.* **2013**, *13*, 11073. doi:10.5194/ACP-13-11073-2013

[33] B. Hales, T. Takahashi, The pumping SeaSoar: a high-resolution seawater sampling platform. *J. Atmos. Ocean. Technol.* **2002**, *19*, 1096. doi:10.1175/1520-0426(2002)019<1096:TPSAHR>2.0.CO;2

[34] C. A. Marandino, W. J. De Bruyn, S. D. Miller, E. S. Saltzman, Eddy correlation measurements of the air/sea flux of dimethylsulfide over the North Pacific Ocean. *J. Geophys. Res.* **2007**, *112*, D03301. doi:10.1029/2006JD007293

[35] C. A. Marandino, W. J. De Bruyn, S. D. Miller, E. S. Saltzman, DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom. *Geophys. Res. Lett.* **2008**, *35*, L23812. doi:10.1029/2008GL036370

[36] C. A. Marandino, W. J. De Bruyn, S. D. Miller, E. S. Saltzman, Open ocean DMS air/sea fluxes over the eastern South Pacific Ocean. *Atmos. Chem. Phys.* **2009**, *9*, 345. doi:10.5194/ACP-9-345-2009

[37] L. W. Juranek, R. C. Hamme, J. Kaiser, R. Wanninkhof, P. D. Quay, Evidence of O_2 consumption in underway seawater lines: Implications for air-sea O_2 and CO_2 fluxes. *Geophys. Res. Lett.* **2010**, *37*, L01601. doi:10.1029/2009GL040423

[38] Z. Kolber, O. Prasil, P. P. G. Falkowski, Measurements of variable chlorophyll fluorescence using fast repetition rate techniques: defining methodology and experimental protocols. *Biochim. Biophys. Acta* **1998**, *1367*, 88. doi:10.1016/S0005-2728(98)00135-2

[39] W. Sunda, D. J. Kieber, R. P. Kiene, S. Huntsman, An antioxidant function for DMSP and DMS in marine algae. *Nature* **2002**, *418*, 317. doi:10.1038/NATURE00851