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Optimisation of a fast DMS sensor (FDS) for real time quantification of dimethyl sulfide production by algae

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Abstract Production of dimethyl sulfide (DMS) from marine samples is often quantified using gas chromatography techniques. Typically, these are labour intensive and have a slow sample turnover rate. Here we demonstrate the use of a portable fast DMS sensor (FDS) that utilises the chemiluminescent reaction of DMS and ozone to measure DMS production in aqueous samples, with a maximum frequency of 10 Hz. We have developed a protocol for quantifying DMS production that removes potential signal interference from other biogenic trace gases such as isoprene (2-methyl-1,3-butadiene) and hydrogen sulfide. The detection limit was 0.89 pM (0.02 ppbv) when using a DMS standard gas mixture. The lowest DMS production rates quantified with the FDS and verified using conventional gas chromatography with flame photometric detection (GC-FPD) were around 0.01 nmol min^{-1}. There was a strong correlation in DMS production when comparing the FDS and GC-FPD techniques with a range of marine samples (e.g., $r^2 = 0.94$ for *Emiliania huxleyi*). However, the combined dataset showed the FDS measured 22% higher DMS production than the GC-FPD, with the differences in rates likely due to interfering gases, for example hydrogen sulfide and isoprene. This possible overestimation of DMS production is smaller than the two-fold difference in DMS production between day and night samples from a culture of *E. huxleyi*. The response time of the instrument to changes in DMS production is method dependent (e.g., geometry of incubation vessel, bubble size) and was approximately 4 min under our conditions when using a culture of *E. huxleyi* (800 ml) with aeration at 100 ml min^{-1}. We suggest the FDS can reduce sample handling, is suitable for short- and long-term measurements of DMS production in algal cultures, and will widen the range of DMS research in marine environments.

Keywords Dimethyl sulfide (DMS) · DMS production · Method · Fast DMS sensor · Chemiluminescence detector

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Introduction

Dimethylsulfide (DMS) is a volatile organic compound (VOC) produced from the secondary algal metabolite dimethylsulfoniopropionate (DMSP). Research into the production of DMS is topical due to the suggested role of DMS in climate regulation and sulfur cycling (Ayers

and Cainey 2007; Stefels et al. 2007; Schäfer et al. 2010), its proposed function as an infochemical (Steinke et al. 2006; Breckels et al. 2011; Lewis et al. 2011), and its role as an antioxidant in protecting algae against environmental stress (Sunda et al. 2002).

DMS production is typically quantified using gas chromatography combined with either a purge-and-trap method for the cryogenic enrichment of DMS or via a solid-phase microextraction technique (SPME) (Turner et al. 1990; Yassaa et al. 2006; Vogt et al. 2008). Such procedures involve the incubation of samples in gas-tight vessels over a period of time and quantifying the DMS that builds up during the incubation period. Flame photometric detection (FPD) or mass spectrometric (MS) detection are conventionally used with the gas chromatographic (GC) analysis, and can typically quantify reduced sulfur compounds at sub-nanomolar concentrations of DMS (Vogt et al. 2008). However, these GC methods are typically expensive and labour intensive, and can also have a slow sample turnover rate. Furthermore, gas chromatographs require a supply of high-quality compressed carrier gases (e.g., nitrogen and helium for the purge-and-trap system and as carrier gas, respectively) and a modern laboratory setting, restricting the ability to quantify DMS concentrations while in the field.

Recent studies have started to utilise instruments that can perform near-continuous measurements of dissolved DMS, designed predominantly for shipboard studies. These include the equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS, detection limit of 0.05 nmol l^{-1}), the atmospheric pressure chemical ionization mass spectrometry (APCI-MS, detection limit of 0.1 nmol l^{-1}), and membrane inlet mass spectrometry (MIMS, detection limit of 2 nmol l^{-1}). These can detect changes in DMS concentration with instrumental response times of 1 min or less (Tortell 2005; Kameyama et al. 2009; Saltzman et al. 2009). DMS in the atmosphere can also be measured in real-time using fluorine-induced chemiluminescence, with a detection limit of 0.4 pmol l^{-1} (10 pptv, Hills et al. 1998).

An alternative continuous-measuring technique to GC and MS analyses utilises the chemiluminescent reaction of DMS with ozone to estimate DMS concentrations (Kelly et al. 1983). The ozone chemiluminescence technique has previously been used to quantify isoprene (2-methyl-1,3-butadiene) concentrations in terrestrial and marine samples (Hills and Zimmerman 1990; Monson et al. 1991; Guenther and Hills 1998; Exton et al. 2010). The reaction of DMS with ozone is a complicated decomposition process. The attack of ozone on the carbon–sulfur bond in the DMS molecule produces radicals that, through a chain reaction, form the sulfur monoxide radical ($SO^{\bullet}$; Eqs. 1–4). This reacts further with ozone to produce an electronically excited sulfur dioxide molecule (SO_2*), which emits light at a wavelength (λ_{max}) of approximately 370 nm while returning to a relaxed state (Eq. 5) (Arora and Chatha 1984). The resultant chemiluminescence can be measured using a photomultiplier detector (PMT). The chain reaction produces several different radicals (e.g., $CH_3S^{\bullet}$) that can all produce the $SO^{\bullet}$ radical on contact with ozone (Eqs. 2, 4). The reactions can be summarised as follows:

$$(CH_3)_2S + O_3 \rightarrow CH_3O_2^{\bullet} + CH_3SO^{\bullet} \quad (1)$$

$$CH_3SO^{\bullet} + O_3 \rightarrow CH_3O^{\bullet} + SO^{\bullet} + O_2 \quad (2)$$

$$CH_3O_2^{\bullet} + SO_2 \rightarrow CH_3S^{\bullet} + 2O_2 \quad (3)$$

$$CH_3S^{\bullet} + O_3 \rightarrow SO^{\bullet} + CH_3O_2^{\bullet} \quad (4)$$

$$SO^{\bullet} + O_3 \rightarrow SO_2^{*} + O_2 \rightarrow SO_2 + h\nu \quad (\lambda_{max} = 370\,\text{nm}) \quad (5)$$

Ozone can have a chemiluminescent reaction with many different trace gases apart from DMS. Examples include other reduced sulfur gases and alkenes, which emit light at different wavelengths to DMS (Kelly et al. 1983; Guenther and Hills 1998). Utilisation of the chemiluminescent reaction of ozone with isoprene ($\lambda_{max} = 410$, 430 nm) resulted in the commercial development of an instrument to measure isoprene in the atmosphere, the fast isoprene sensor (FIS; developed by Hills Scientific, http://hills-scientific.com; Hills and Zimmerman 1990). Recently, this has been successfully used to measure isoprene production from marine samples (Exton et al. 2010).

The aim of this study was to modify and optimise a fast isoprene sensor (FIS) for real-time quantification of DMS production from marine samples. This would then enable the instrument to be utilised as a fast DMS sensor (FDS). In comparison to GC-FPD and MS analyses, the FDS is compact (the weight is ~40 kg), and can provide continuous sampling at a resolution of 0.1 s, a resolution that currently cannot be achieved with conventional GC techniques. Specifically, our objectives were to (1) examine the instrument's

detection of chemiluminescence with DMS, and identify and remove any possible interference to the DMS signal from other biogenic trace gases; (2) compare the accuracy and sensitivity of the instrument for quantifying DMS production in marine samples to the conventional GC-FPD technique; and (3) establish a standard sampling protocol for quantifying DMS production with the FDS in marine environments.

Materials and methods

Setup of the fast DMS sensor

The setup of the FDS for measuring marine samples is similar to the one described for the FIS by Exton et al. (2010). A summary of the measurement process, plus modifications and differences to the previous technique are presented here. There are two parts to the FDS: a reaction unit and an ozonizer. To operate the FDS, a cylinder of high-purity oxygen is required for ozone generation, and a DMS gas standard cylinder (6 ppmv, Scientific & Technical Gases, Newcastle-under-Lyme, UK) is required for automated instrument calibration. Teflon tubing and stainless steel fittings (Swagelok, USA) connect the gas supplies between the two parts of the FDS. The FDS reaction unit has four main inlets for the sample gas, zero air (used for providing an instrument zero to determine background levels of DMS), compressed oxygen (which is passed at 800 ml min^{-1} and 275 kPa into the ozonizer, and the resultant ozone is introduced into the reaction cell) and DMS standard (Fig. 1). The flow rates of the sample gas, compressed oxygen and DMS standard are each regulated using a mass-flow controller (Fig. 1). When sampling, a diaphragm pump actively draws in gas from the sample headspace into the reaction cell, up to a maximum flow rate of 1,200 ml min^{-1}. The sample gas passes undiluted into the reaction cell where it mixes with the ozone and, depending on the composition of sample gas, produces a compound-specific wavelength of chemiluminescence. The light emitted passes through the reaction cell window to the opposing photomultiplier tube (PMT), whilst the reaction products are passed through a catalytic converter to remove any residual ozone, and then to the exhaust outlet (Fig. 1). The user interface is a laptop computer that uses software to display and record the counts of photons s^{-1} over time

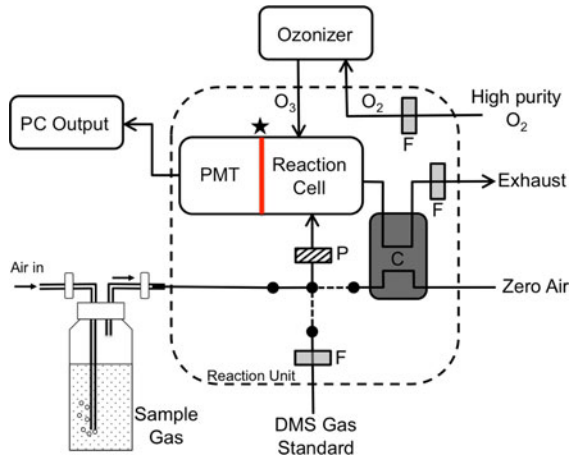

Fig. 1 Schematic of the fast DMS sensor (FDS), and sample vessel setup to measure DMS production in marine samples. The *star* marks the position of the reaction cell window that can be replaced with a 417 nm short-pass filter to remove the interference from other VOCs from the output signal when quantifying DMS (see text for details). *PMT* photomultiplier tube, *F* mass-flow controller, *P* diaphragm pump, *C* catalytic converter

(e.g., Labview version 7.1; National Instruments, USA). Further details of the instrument and settings for the detection of isoprene are described in Hills and Zimmerman (1990) and Exton et al. (2010).

Interference from other trace gases

Gas standards of four biogenic sulfur gases (carbonyl sulfide [COS], carbon disulfide [CS_2], hydrogen sulfide [H_2S], methanethiol [CH_3SH]) and four biogenic non-methane hydrocarbons (*n*-pentane [C_5H_{12}], ethene [C_2H_4], propene [C_3H_6], isoprene [C_5H_8]) were selected to identify the potential of signal interference of the FDS by the chemiluminescence of other trace gases in a sample. Tedlar bags (5 l, Sigma-Aldrich, UK) containing 1 l of oxygen-free nitrogen were injected with different volumes of gas standards (100 ppmv, Scientific and Technical Gases, Newcastle-under-Lyme, UK), resulting in final gas concentrations ranging from 0.0 to approximately 8.2 nM. Standard curves were created for each trace gas. The Tedlar bags were attached to the FDS and sampled at a flow rate of 0.5 l min^{-1}. Pseudoreplicates were performed for some of the gases. The response factor (f_i) was calculated using the slopes for each gas standard curve against the slope for DMS ($f_i = m_i\, m_{DMS}$, where m_i = the slope of a gas standard and m_{DMS} = slope of DMS standard). Hence, a response factor of

Table 1 Culture and growth conditions for the five organisms used to compare the FDS and GC-FPD measurements of DMS production

Class	Species	Strain	Biomass	Temp. (°C)	Medium	Light intensity (μmol photons m^{-2} s^{-1})
Prymnesiophyceae	*Emiliania huxleyi*	CCMP 373	4.1–9.0 × 10^8 cells l^{-1}	17	ESAW	450
Prymnesiophyceae	*Isochrysis galbana*	CCMP 1323	5.2–8.8 × 10^7 cells l^{-1}	17	ESAW	450
Dinophyceae	*Symbiodinium* sp.	A13	5.0–7.8 × 10^6 cells l^{-1}	26	ASP-8A	350
Ulvophyceae	*Ulva lactuca*	N/A	2.8–5.3 g DW l^{-1}	17	EASW	450
Anthozoa	*Aiptasia* sp.	N/A	38 individuals l^{-1}	26	EASW	350

All organisms were grown at a salinity of 34

ESAW enriched seawater, artificial water (Berges et al. 2001, 2004); *ASP-8A* Provasoli's artificial seawater medium (Provasoli et al. 1957)

1 indicates that the FDS detects the standard gas with the same sensitivity as DMS.

In order to reduce the impact of chemiluminescence of other trace gases on the DMS signal, a glass 417 nm short-pass filter (Glen Spectra, Stanmore, UK) was installed between the reaction cell and PMT, replacing the clear glass reaction cell window (Fig. 1). This blocked the chemiluminescence of any compound with $\lambda > 417$ nm, predominantly from isoprene and other non-methane hydrocarbons, from passing through to the PMT (Toda and Dasgupta 2008). A similar process performed by Exton et al. (2010), used a 450 nm long-pass filter to reduce the DMS signal by 99%, thus preventing it from interfering with isoprene detection. To assess the impact of the short-pass filter on the FDS signal, standard curves were performed for DMS and other trace gases as described above.

Method comparison between the FDS and GC-FPD

Samples of three laboratory cultures of microalgae, one temperate macroalga (collected from the Colne Estuary, Essex, UK) and a tropical sea anemone that harbours DMSP-producing symbionts (collected from a tropical aquarium at the University of Essex) were placed in 800 ml medium inside a 1 l FEP air-tight vessel (Nalgene; Table 1). The samples were aerated with filtered air (0.2 μm Millipore) at 100 ml min^{-1}. Incubation temperatures and light levels varied between species as presented in Table 1. Cultures were measured at a variety of cell densities to compare the two methods at a range of DMS production rates. All cultures and macroalgae/anemones were allowed to equilibrate under aeration for 1 h before sampling. The FDS sample inlet was attached to the waste air tube of the vessel to measure baseline DMS production for 20 min, and then removed. A 5 l Tedlar bag was attached to the waste air tube of the vessel for 10 min. The gas in the Tedlar bag was cryogenically enriched on a purge-and-trap apparatus as described in Steinke et al. (2011) before analysis using a GC-FPD (GC-2010, Shimadzu, Milton Keynes, UK). This technique was also used to quantify reduced sulfur gases that may interfere with the DMS quantification on the FDS including methanethiol, hydrogen sulfide and carbon disulfide.

All FDS measurements were performed after installation of the 417 nm short-pass filter. During FDS sampling production was measured every second, but averaged across the 20-min period to provide a single value for comparison to the GC-FPD. The relationship between GC-FPD and FDS measurements was assessed using geometric mean regression.

Optimisation of FDS sampling procedure

To assess the response time of the FDS to changes in DMS production, 800 ml cultures of *Emiliania huxleyi* CCMP 373 (growth conditions are shown in Table 1) were compared to 800 ml of DMS dissolved in sterile artificial seawater (ASW) in the same vessel as above. *E. huxleyi* and ASW samples were either (a) aerated at 500 ml min^{-1}, (b) aerated at 100 ml min^{-1} or (c) left without aeration (the headspace was still flushed at 100 ml min^{-1}). ASW headspace concentration at

$t = 0$ were as close as possible to the concentration in *E. huxleyi* (approximately 0.7 nmol min^{-1} at 500 ml min^{-1} aeration). For the aeration, air was filtered (0.2 µm Millex; Millipore UK) and passed through sintered 8 mm glass frits (100–160 µm pore size), resulting in a bubble size of ~2 mm. The response time was empirically determined as the time point when the percent of initial photon counts s^{-1} in the abiotic control fell below those of the steady state culture of *E. huxleyi*.

The ability of the FDS to measure DMS headspace production over periods of several days was also investigated. The sample inlet tube was attached to the waste air outlet of an 800 ml semi-continuous culture of *E. huxleyi* CCMP 373. The culture was maintained in a 1 l FEP vessel at 17°C and 450 µmol photons m^{-2} s^{-1} on a 14:10 light–dark cycle, and aerated using an 8 mm diameter sintered glass frit at 100 ml min^{-1}. Cell density was maintained around 500,000 cells ml^{-1}, and the culture was diluted to this density when required at 18:00 h daily. The culture was monitored for 4 days, with occasional breaks in monitoring due to maintenance of the culture or FDS.

Results

Interference from other trace gases

The FDS was most sensitive to methanethiol (Fig. 2a). When the FDS was set up without the short-pass filter, the methanethiol signal response was 3.8 times higher than the DMS signal (Table 2). All other gases tested showed a lower response factor than DMS: hydrogen sulfide and carbon disulfide had a response factor of 0.08 and 0.07, respectively (Table 2; Fig. 2b), whilst the alkenes showed factors between 0.02 and 0.05. The chemiluminescence of *n*-pentane was below the detection limit of the FDS.

Installation of the 417 nm short-pass filter reduced the DMS signal by 89.7% (Fig. 2c) and the DMS detection limit of the FDS using the standard gas mixture increased from 0.06 to 0.89 pM (0.001–0.02 ppbv). Detection limits are also dependent on background noise and the extent of by-products from the chemiluminescence reactions that can deposit on the short-pass filter, blocking light to the PMT (Fig. 1).

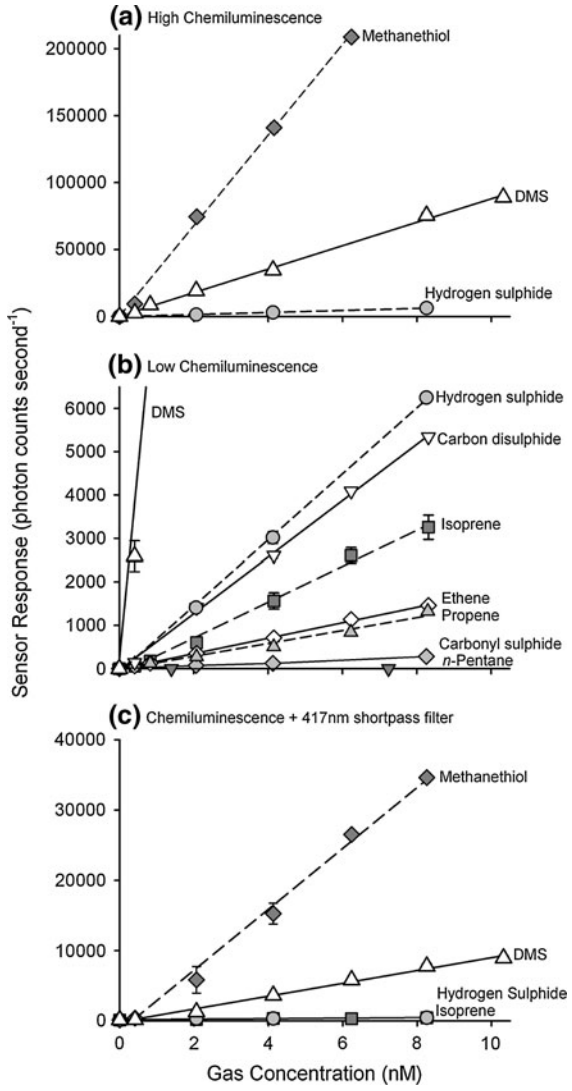

Fig. 2 Response of the fast DMS sensor (FDS) to gas standards of DMS and other volatile organic compounds (VOCs) without a 417 nm short-pass filter (**a**, **b**) and with a 417 nm short-pass filter (**c**). Installation of the filter effectively reduces interference from many gases tested in this study (note differences in scale along the *y*-axes). Intake flow rate was set to 0.5 l min^{-1}. *Symbols* indicate the mean and where *error bars* are visible the standard error is indicated for duplicate runs

With the filter, the methanethiol signal was reduced by approximately 87.2%, but the sensitivity of the FDS to methanethiol increased from 3.86 to 4.76 times the sensitivity for DMS (Table 1). Isoprene (and other alkene) chemiluminescence was not detected by the FDS. The response factor for hydrogen sulfide was reduced from 0.08 to 0.04.

Table 2 Slopes, intercepts and r^2 values of the standard curves for each trace gas measured on the FDS, with and without a 417 nm short-pass filter placed between the reaction cell and PMT

Gas	Slope (photons s^{-1} nM^{-1})	Intercept (photons s^{-1})	r^2	Response factor (f_i)
Without filter				
Methanethiol	34137.0	1730.5	0.998	3.86
DMS	8854.8	579.5	0.996	1.00
Hydrogen sulfide	708.9	278.8	0.993	0.08
Carbon disulfide	650.1	−41.18	0.998	0.07
Isoprene	415.7	138.1	0.970	0.05
Ethene	177.2	−2.89	0.982	0.02
Propene	149.6	17.84	0.961	0.02
Carbonyl sulfide	33.6	−2.9	0.993	0.00
n-Pentane	BDL	BDL	BDL	BDL
With 417 nm short-pass filter				
Methanethiol	4278.1	−889.3	0.998	4.76
DMS	898.7	−18.2	0.992	1.00
Hydrogen sulfide	38.04	13.77	0.977	0.04
Isoprene	BDL	BDL	BDL	BDL

The response factor, f_i indicates the ratio between the DMS slope and the slope of another trace gas. "BDL" indicates that the standard curve fell below the detection limits of the FDS

Comparison between FDS and GC-FPD techniques

For most samples, DMS production showed a linear relationship between the FDS and GC-FPD techniques (Fig. 3). DMS production rates (measured on the FDS) ranged from 0.079 ± 0.000 nmol min^{-1} in *E. huxleyi* to 0.154 ± 0.070 nmol min^{-1} for *I. galbana*. Geometric mean regression slopes for individual samples were centred around the 1:1 relationship with 1.148 for *E. huxleyi* ($r^2 = 0.94$), 1.021 for *I. galbana* ($r^2 = 0.57$) and 0.842 for *U. lactuca* ($r^2 = 0.97$). Only two data points are available for *Aiptasia* sp. and *Symbiodinium* sp. and one of the data points for *Symbiodinium* sp. showed a disproportionally high response on the FDS. It is evident from the combined data set that the FDS overestimated DMS production by almost 22% (slope = 1.218, $r^2 = 0.74$). Omitting the outlier data point for *Symbiodinium* sp. would bring this relationship closer to the 1:1 line (slope = 1.112, $r^2 = 0.79$).

GC-FPD analysis showed that methanethiol was not produced in any of our samples and that hydrogen sulfide was the second most abundant sulfur gas produced. Mean ratios (±SE) of the production of H_2S: DMS ranged from 0.22 ± 0.07 for *E. huxleyi*, 0.15 ± 0.06 for *U. lactuca* to 0.05 ± 0.01 for both *Aiptasia* sp. and *I. galbana*. Correcting the FDS signal for this hydrogen sulfide production using the response factor derived from the standard gas calibrations (0.04,

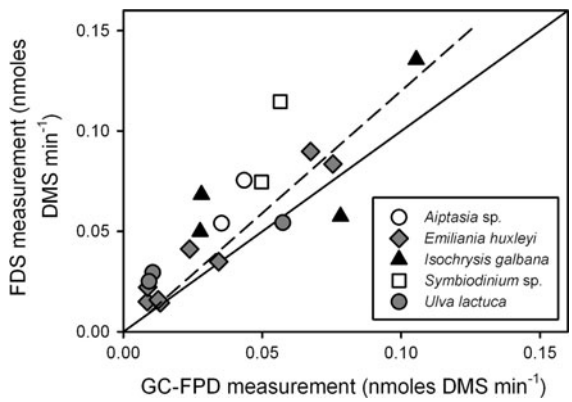

Fig. 3 Comparison of DMS production in marine organisms measured using FDS and GC-FPD techniques. *Solid line* indicates the 1:1 relationship. Geometric mean regression analysis (*dashed line*) shows the samples deviate from the 1:1 relationship as indicated by the regression equation (FDS measurement = 1.21 × GC-FPD measurement − 0.045; $r^2 = 0.74$; $n = 19$)

Table 2) had little impact on the slope of the individual organisms (e.g., *E. huxleyi* slope = 1.147, $r^2 = 0.96$) or combined data sets (slope = 1.211, $r^2 = 0.74$), with the FDS still measuring higher values for DMS production than the GC-FPD.

Optimisation of FDS sampling procedure

The time taken for the FDS to equilibrate to changes in DMS headspace concentration varied with the

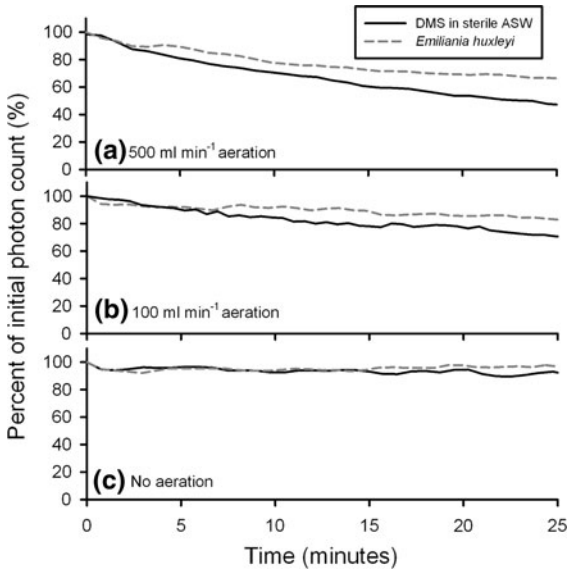

Fig. 4 Photon counts in percent of the initial FDS signal in a culture of *Emiliania huxleyi* CCMP 373 and a solution of DMS in sterile artificial seawater. Response of the FDS was measured using three methods: **a** aerating the samples at 500 ml min^{-1}, **b** aerating at 100 ml min^{-1} and **c** no aeration (but flushing the headspace at 100 ml min^{-1}). Shown are running averages (10 s of data either side). The point of divergence indicates the response time of the analytical system to changes in DMS concentrations

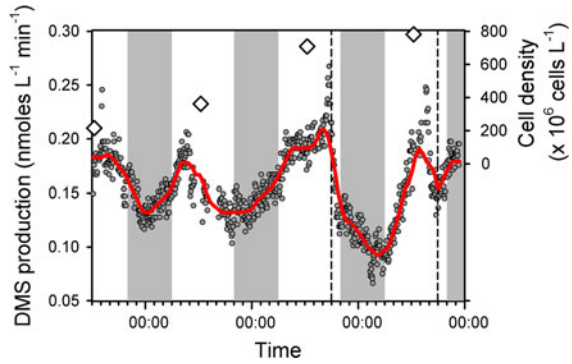

Fig. 5 DMS production in a culture of *Emiliania huxleyi* CCMP 373 over a 4-day 14:10 light/dark cycle. Shown are cell density (*large open diamonds*) and the running average (±4 h, *solid line*), with individual data points (10 min averages; *dark grey circles*) to illustrate the spread of the data. The culture was diluted with fresh ESAW medium at 18:00 h on days 3 and 4 (*dashed vertical lines*). *Shaded areas* indicate the *light–dark* transitions

sampling method (Fig. 4). When aerating 800 ml samples in 1 l vessels at 500 ml min^{-1}, equilibration occurred after 2 min of continuous measurements. Aerating samples at 100 ml min^{-1} resulted in equilibration occurring after 4.5 min of continuous measurements, and stable DMS production by algal cultures observed thereafter. Equilibration was observed after 13 min in samples that had no aeration.

Attaching the FDS sample tube to the waste air outlet of a semi-continuous 800 ml culture of *E. huxleyi* for 4 days revealed a clear pattern of diel variations in DMS production rates (Fig. 5). Mean DMS headspace production during the day was 0.168 ± 0.010 nmol DMS l^{-1} min^{-1}; mean night production was 0.136 ± 0.030 nmol DMS l^{-1} min^{-1}.

Discussion

Interference from other trace gases

This study showed that the FDS has the potential for real-time quantification of DMS production. The FDS provided data that were similar to the results using a GC-FPD technique, and can be applied to continuously measure DMS production from a wide range of organisms over periods of time ranging from minutes to days. Interference from other VOCs can pose a problem for the quantification of DMS. For example, isoprene and ethene are important NMHCs produced by algae, particularly in macroalgae such as *Ulva lactuca* (Broadgate et al. 2004; Acuña Alvarez et al. 2009), whilst hydrogen sulfide is produced by a wide variety of marine microalgae (Walsh et al. 1994). Nitric oxide, produced by algae (e.g., *Symbiodinium* sp.) and bacteria, can also chemiluminesce with ozone, emitting light at wavelengths greater than 600 nm (Bouchard and Yamasaki 2008; Toda and Dasgupta 2008).

The use of a 417 nm short-pass filter minimised the interference from biogenic gases such as isoprene (λ_{max} = 410 and 430 nm; Toda and Dasgupta 2008), and hydrogen sulfide (approximately the same λ_{max} as DMS; Kelly et al. 1983), although also reducing the sensitivity and resolution of the DMS signal. Part of the isoprene chemiluminescence would still pass through the short-pass filter but the production of isoprene by algae compared to DMS is relatively low (Exton et al. 2010). The λ_{max} of DMS is at 370 nm, but the emission spectrum ranges from 300 to 560 nm (Toda and Dasgupta 2008). As a result, using a 417 nm short-pass filter blocks approximately two-thirds of the DMS spectrum. This limits the use of the FDS to

high-biomass samples such as algal cultures, rather than natural phytoplankton communities in seawater. However, other instruments for the continuous quantification of DMS including MIMS have been used for ship-board measurements and the reported detection limit of these techniques is similar or lower than that for the FDS (Tortell 2005). The limitation in many approaches for the continuous measurement of gases in seawater is the relatively slow transfer of DMS and other gases from the water to the carrier gas that flushes the sample into the detector. As a consequence, various equilibrators are often used to enable a sufficient transfer (see the following section) and it is important that response times and detection limits are provided for an analytical system rather than the individual detector (Bell et al. 2011).

The FDS measured DMS at higher concentrations than the GC-FPD. The two techniques are different in both sampling method and analysis, and this may be responsible for some of the observed variability in the data. Variability in DMS measurement between techniques is not unusual; Vogt et al. (2008) found that measurements of dissolved DMS using the GC-FPD technique are 8% higher in comparison to a solid-phase microextraction technique (SPME-GCMS). Such differences were attributed to the efficiency of the different extraction methods. It is likely that the differences in DMS production rates between the GC-FPD and FDS technique used in this study was due to the remaining interference from the chemiluminescence spectra of other VOCs that were not completely blocked by the short-pass filter.

The choice of blocking wavelength of the short-pass filter could further reduce such interference. A short-pass filter of <417 nm may completely remove the interference from other VOCs at the trade-off of further decreasing the signal resolution and sensitivity of the FDS for DMS. Recent developments in enhanced reflective optics by Hills-Scientific resulted in a fourfold increase in the sensitivity of their FIS compared to the instrument used in this study. Such developments may enable measuring DMS from low biomass samples. As a result, future FDS models may be able to use lower-wavelength short-pass filters combined with improved optics to completely remove interference from other VOCs whilst still maintaining high DMS signal resolution and low detection limits.

Signal interference due to the overlap of the ozone chemiluminescence emission spectra of DMS and methanethiol could not be overcome through using a short-pass filter. As a microbial demethylation product of DMSP, methanethiol production is observed in marine surface waters and sediments (Kiene 1996; Schäfer et al. 2010), it is therefore important to consider its possible effect on the FDS signal with samples from marine environments. We conducted a preliminary assessment of methanethiol production in environmental samples ranging from freshly collected seawater samples, algal material and sediments. Using GC-FPD methods we could confirm methanethiol production in sediments but none of the algal cultures or environmental samples used in this study showed detectable levels of production (data not shown). Azad et al. (2006) utilised a silica gel trapping column to separate DMS and methanethiol before measuring their concentrations with ozone chemiluminescence, but such a technique cannot be applied to real-time measurements. Instead we recommend a combined approach, using a GC-based technique to conduct a preliminary assessment of biogenic sulfur gas production in the sample of interest, confirming that methanethiol and other possible interfering VOCs are not being produced, before measuring real-time DMS production on the FDS.

Method comparison and FDS setup

The FDS showed a response time to changes in DMS production of 4 min. This may be considered long in comparison to other methods and is largely affected by vessel size and the process chosen for gas equilibration. Response times are a problem with all real-time marine trace gas analysers; none of which can measure an immediate change in DMS production. Instruments with faster equilibration are often intended for ship-board use on sample seawater that is discarded after the trace gas measurement, and may utilize either increased aeration (Kameyama et al. 2009), or porous polymer membrane tubes with flow-through equilibration (Saltzman et al. 2009). When monitoring algal cultures over long periods, high aeration rates are not feasible since they can cause shear stress and interfere with DMS production (Wolfe et al. 2002). In this study, aeration at 500 ml min^{-1} decreased the DMS production over time (Fig. 4a) and we found a stable production of DMS with aeration at 100 ml min^{-1} (Fig. 4b). Such aeration is necessary in many experiments to prevent carbon limitation and remove excess

oxygen from photosynthesis. As a result, we recommend aerating cultures at a flow rate that provides adequate response times at minimal disturbance to the sample.

The relatively short response time of the FDS provides a measurement of DMS production rates more frequently than the conventionally used methods of incubating samples in gas-tight vessels followed by quantification on the GC-FPD (approximately 1–2 h per rate measurement). It would further be possible to obtain replicate samples on the FDS by switching the sampling tube between the waste air outlets of 3–4 aerated cultures at regular intervals. Future development of the FDS setup could include the integration of a 5-port electronic rotary switching valve to automate replicate sampling.

An advantage of the FDS over other more permanent GC and MS-based real-time techniques is its flexibility. The FIS had been previously used on fieldwork in remote locations (Exton et al. 2010), and the simple setup of the FDS allows that it can be dismantled and reconstructed in various situations in less than 1 h, with the only limitation being the availability of a safe position to store the compressed oxygen cylinder. Therefore the findings of this study could allow for a broad variety of fieldwork and laboratory studies on DMS production that could not easily be achieved with other instruments.

The FDS provides a relatively simple and inexpensive method to facilitate studies on DMS production at high temporal resolution. Our initial data are encouraging and indicate that DMS production was not constant over a day–night cycle. As expected, DMS production increased in the light but seems to indicate some diurnal rhythmicity that, in a natural environment, may be interpreted as a response to changes in light intensity and/or quality. However, no such changes were provided in our experiments and the sometimes twofold difference between day and night production is intriguing. This suggests that the FDS could provide new avenues of research that tackle some of the less-explored details in the global biogeochemistry of sulfur.

Conclusion

The FDS has potential for continuous measurement of DMS in algal cultures. We have emphasised the importance of considering the interference of other trace gases in the DMS signal, and there was only a relatively small difference in DMS production between the GC-FPD and FDS. It should be highlighted that the FDS is not a replacement for the gas chromatographic analysis of marine DMS samples, but provides an alternative method of approaching future questions on the physiology of DMS production. We anticipate the FDS will become a useful additional tool to elucidate DMS production both in the laboratory and in the field.

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