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Global oceanic DMS data inter-comparability

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Abstract The global surface seawater dimethylsulphide (DMS) database (http://saga.pmel.noaa.gov/dms/) contains >50,000 data points and is the second largest trace gas database after carbon dioxide. However, there has been relatively little quality control on the data that have been collated to date. Furthermore, the recent development of technologies capable of high frequency (>1 Hz) DMS measurements will have a disproportionate effect on the database in future years. At this juncture, the comparability of analytical techniques, sample handling methodologies and standards are pressing issues that the DMS community needs to address. In October 2010, during the Fifth International Symposium on Biological and Environmental Chemistry of DMS(P) and Related Compounds held in Goa, India, attendees participated in a discussion concerning the current DMS database and its future development. We develop some of the ideas from that session and combine them with available data. From the few inter-comparison exercises that have been conducted we show that variability between existing measurements within the DMS database is likely to be ≤25%. Tests comparing different DMSP·HCl standards demonstrate that a reference calibration standard would be beneficial for the DMS community. Confidence in future data collation would be substantially improved with a comprehensive inter-comparison experiment between new analytical techniques and sampling methodologies (e.g., mass spectrometers with equilibrators attached to a continuous flow of seawater) and more established methods (i.e., filtered samples analysed with purge and trap gas chromatography). We conclude with recommendations for the future expansion of the DMS database and its data quality control.

Keywords DMS · Dimethylsulphide · DMSP · Dimethylsulphoniopropionate · Data comparability · Quality control · Reference standard

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Introduction

Dimethylsulphide (DMS) is the dominant reduced sulphur compound in the surface ocean and is volatile under typical environmental conditions, with an estimated 17.6–34.4 Tg of sulphur transferred globally into the atmosphere each year (Lana et al. 2011). This constitutes a significant pathway in the global sulphur cycle given that the major conduit for the delivery of sulphur from the ocean to the terrestrial environment is atmospheric transport and deposition (Simó 2001). The importance of this pathway should not be underestimated as declining anthropogenic SO_2 emissions are leading to increasing incidence of sulphur-limitation in arable land and crops (Mathot et al. 2009). Furthermore, the potential roles of atmospheric DMS oxidation products as precursors for new cloud condensation nuclei and/or the contribution to growth of existing particles has been well documented (e.g., Leck and Bigg 2005; O'Dowd and De Leeuw 2007; von Glasow and Crutzen 2004). This is a fundamental component of the CLAW hypothesis (Charlson et al. 1987), which suggested a climate-feedback role for DMS production and is still subject to much debate (e.g., Ayers and Cainey 2007; Bigg 2007; O'Dowd and De Leeuw 2007; von Glasow 2007; Woodhouse et al. 2010).

The potential importance of atmospheric DMS provides ample motivation for an accurate quantification of surface ocean concentrations in order to calculate sea-to-air flux. Recently, a large stride forward was made toward achieving this goal. Working within the Surface Ocean-Lower Atmosphere Study (SOLAS) Project Integration framework (for details see http://www.bodc.ac.uk/solas_integration/), the DMS community has collated their data to increase the number of available measurements from ~15,000 to almost 50,000 data points (http://saga.pmel.noaa.gov/dms/). As part of this project, Lana et al. (2011) used extrapolative and interpolative techniques to bridge the spatial and temporal gaps in the data and generate monthly climatological fields of sea surface DMS concentration (freely available at http://tinyurl.com/yc7moge). These were then used to calculate global sea-to-air fluxes. Equivalent climatological fields were produced previously by Kettle et al. (1999) and Kettle and Andreae (2000) using the original DMS database, and these have been extensively used within the modelling community (e.g., Belviso et al. 2004; Gondwe et al. 2003; Gunson et al. 2006; Le Clainche et al. 2010; Woodhouse et al. 2010).

The current DMS database is constructed primarily from data obtained using purge and trap techniques for sample preparation and, mostly, analysis by gas chromatography. However, relatively little published work considers the comparability of data generated at different times and/or by different research groups. Purge and trap (P&T) techniques typically analyse discrete samples with an analysis time of several minutes. In contrast, more recently-developed analytical techniques, often using mass spectrometer variants (e.g., membrane inlet, atmospheric pressure chemical ionisation, proton transfer), confer the advantage of high frequency (>1 Hz) measurements. As far as we are aware, no data have been published concerning direct comparisons between these established and novel techniques. Future expansion of the database is expected to be exponential given the availability of these new higher-frequency methods, and as a result the issue of data inter-comparability will become even more pressing.

Concerns about data comparability are not unique to the DMS research community: they have already been voiced and, to varying degrees, addressed within other research fields. The CO_2 community has put a huge amount of effort into quality controlling and inter-comparing the data that is included in their global database (SOCAT, for more details see http://www.socat.info/) and the halocarbon community is actively engaging with this issue (Butler et al. 2010).

At the Fifth International Symposium on Biological and Environmental Chemistry of DMS(P) and Related Compounds (Goa, India, October 2010), a discussion session was held to debate issues relevant to the DMS database and its future development. This paper seeks to develop some of the ideas that came out of this session, drawing upon relevant published and unpublished data from the DMS measurement community as evidence. In addition, we consider the issues of greatest relevance to data inter-comparability and make recommendations for future data collation.

Comparability of standards

No reference calibration standard currently exists for the DMS research field, and the establishment of such

a standard was a specific recommendation from the discussion session in Goa. When analysing seawater for DMS, different groups have developed different approaches to calibration. Mass spectrometry techniques often ratio against an isotope-labelled internal gas standard that is then calibrated against primary gas standards from temperature-controlled permeation tubes, the mass change over time indicating the rate of delivery of sulphur (e.g., Kameyama et al. 2009; Saltzman et al. 2009). Temperature-controlled permeation tubes have also been used to calibrate GC systems (Lizotte et al. 2008; Simó et al. 1997). For P&T techniques, some laboratories have used pure liquid DMS standards dissolved in an organic solution such as ethylene glycol (Andreae and Barnard 1983) or methanol (e.g., Stefels 2009) as a stock solution. The advantage of these is that the DMS purchased off the shelf has a known purity (e.g., Sigma Aldrich Cat. # 471577, ≥99% purity). However, the difficulty in transporting and handling a volatile standard has led many research groups to calibrate their systems using dissolved dimethylsulphoniopropionate (DMSP), which can be hydrolysed to liberate DMS within a gas-tight preparation system (e.g., sealed vial or purge tube within a P&T preparation system) using a strong base such as sodium hydroxide. All of the above approaches are equally valid in principle and can be effectively applied to a single experimental or field dataset to assess relative changes. However, it is desirable that calibration standards are comparable in order to reduce complications and error when comparing results and collating data from different experiments or research groups.

In common with many other research domains, the DMS research field has evolved with relatively little top–down management and this, coupled with the inevitable financial constraints, has meant that direct methodological comparisons between groups have only been opportunistically performed and/or published. However, examples in the literature paint a favourable picture with respect to the inter-comparison of standards. Turner et al. (1990) compared a number of different standards (a permeation device, DMS in ethylene glycol and both commercial and laboratory-produced DMSP·HCl, hydrolysed by strong base) and observed a maximum difference of only ±7% between the different calibration methods for the entire concentration range tested (0.16–2.2 nmol of DMS). Hatton et al. (1994) developed a technique to measure dimethylsulphoxide (DMSO) by enzymatically converting DMSO to DMS. To cross check their conversion efficiency, they compared the DMS liberated from cold alkali hydrolysis of DMSP·HCl (assuming 100% conversion) with that produced from the DMSO-reductase method. Figure 3 in their article demonstrates extremely good agreement between the two (Hatton et al. 1994) and the DMSO stock solution used had a known purity of 99.5% (Sigma Aldrich). The inference here is that the purity of the DMSP·HCl standard is constrained to a similar level as that of the DMSO standard (i.e., >99.5%).

Notably, none of the above studies compared DMSP·HCl standards that had been generated with the same methodology but from different laboratories. In the Marine Trace Gas Biology Laboratory at the University of East Anglia, Norwich, UK, we performed a simple standard inter-comparison experiment. Three DMSP·HCl standards were compared, all of which were made up from separate batches of solid DMSP·HCl (molar mass = 170.66 g mol^{-1}) that had been synthesised in different laboratories for different DMS research groups. All were considered to be high purity. Liquid standards were generated from the solid stocks in an identical fashion, with a high concentration standard (each as close as possible to 30 mM) made up from a well-quantified mass of DMSP·HCl stock (~0.05 g on a Sartorius 1201MP2 4-place microbalance with 0.0001 g readability, serviced annually), which was dissolved and diluted in fresh MilliQ water using a calibrated, digital pipette (Gilson Scientific Ltd.) and volumetric flasks to make 7.5 mM, 750 μM and 75 μM standards. Note that, while unimportant for the comparison of standards, our own tests have demonstrated little difference between fresh and saltwater P&T and headspace calibration curves (i.e., any variation due to the effect of ionic strength on gas solubility is within analytical error); when running seawater samples we encourage groups to run their own tests. Dilution was exactly quantified by calculating the mean mass of water pipetted ($n = 5$) and the standard deviation used as part of the error propagation calculation used later. Sterility is important for the stability of dilute liquid DMSP (concentrated DMSP standard is sterile due to its high acidity), so we followed the routine method of filter-sterilising standards (Minisart 0.2 μm cellulose acetate sterile syringe filters, Sartorius Stedim UK Ltd.) and dividing into aliquots in small tubes using sterile

technique whilst working in a UK Class II Microbiological Safety Cabinet (Walkers Safety Cabinets, UK). Normally these are stored at −20°C; each aliquot is thawed quickly at room temperature when required and discarded afterwards.

Analysis involved a modified version of the headspace technique described in Steinke et al. (2000), using 5 ml glass vials (3 ml of 500 mM sodium hydroxide, NaOH) with screw caps and Teflon-coated silicone septa (Alltech UK) to make them gas-tight. Briefly, small volumes (2–10 µl) of liquid DMSP standard of varying concentrations (between 75 µM and 30 mM) were placed upon the septa and the vials rapidly sealed and inverted three times to mix standard and NaOH. Great care was taken not to spill any liquid DMSP standard and this is practical with volumes of 10 µl or less. Having made up the standards, they were then left overnight under temperature-controlled conditions (30°C) in the dark to allow the aqueous and gas headspace phases of the vials to equilibrate. Analysis the next day involved the removal and direct injection of a small volume (20 µl) of headspace gas using a heated 100 µl automated syringe injection system (MPS 2, Gerstel, Mülheim an der Ruhr, Germany). All vials were quantified in the same analysis run using the same gas chromatograph (GC 2010; Shimadzu UK Ltd., Milton Keynes, UK), equipped with a 30 m × 0.53 mm CP-Sil 5CB column (Varian Inc., Oxford, UK) and a flame photometric detector (FPD).

All three calibration regression lines (Fig. 1) have been produced with the same protocols and assumptions that would be expected during any research experiment or field campaign, although the concentration range used is greater than that typically applied and/or required. For example, the assumption was made that there would be limited or no deterioration of each standard over the time since purchase/synthesis because all standards had been stored in a dry, dark environment. For comparability, the purity levels of all standards were assumed to be 100%, which is what is typically assumed. If all standards were directly comparable, the calibration lines would be expected to overlay each other. As demonstrated in Fig. 1, this was not the case, with the regression line slope varying by as much as 30%. Some errors have not been accounted for but will have been consistent between standards (e.g., the pipette error for the volume of the drop of

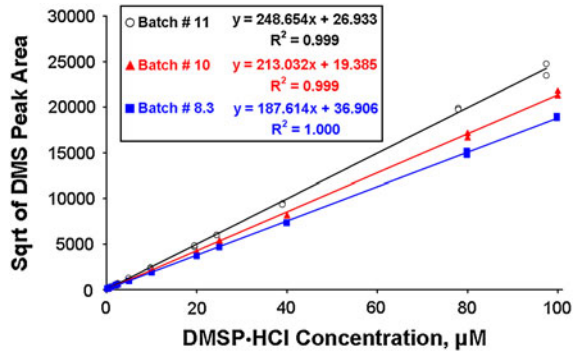

Fig. 1 Liquid phase DMSP·HCl vial concentration (µM) versus GC FPD response (DMS square root peak area) to a 20 µl gas phase direct injection of equilibrated (at 30°C) vial headspace for three batches of DMSP·HCl standard (molar mass = 170.66 g mol^{-1}), all of which had been prepared in an identical fashion. Duplicate vials were prepared per concentration (number of vials per DMSP batch = 26). DMS concentration error represents the propagated error (1σ) in preparing the liquid DMSP standard but these cannot be seen because they all lie within the plotted symbols. See text for full details

standard in the vial cap). Another potential cause of error was the mass balance, but this would require an order of magnitude higher error (5 mg) than typically expected from this balance to explain only a 10% variation in slope.

Some variation could be introduced by differences in % water content, although none of the laboratories involved routinely apply such a correction. To test if water content was a major influence on our results, a TA instruments high resolution (Hi-Res TM) Thermogravimetric Analyser TGA 2950 was used to measure the weight loss profiles of the different batches of DMSP·HCl. In brief, small quantities of DMSP·HCl (∼10 mg) were put into small aluminium boats, placed in the instrument, and continuously weighed and heated to 25°C in an oxygen-free nitrogen purge gas stream. After holding at 25°C for 2 min, the temperature was increased to 60°C at 10°C/min and held at this temperature for approximately 1 h. Triplicate runs demonstrated clear differences between the different batches of DMSP·HCl, with a mean (±SD) percent solid remaining of 90.6 (±0.3), 96.7 (0.8) and 99.4 (0.2) for batches 8.3, 10 and 11 respectively. In a study of particulate organic sulphur, Matrai and Keller (1994) found no losses of DMSP when standard was spotted onto filters and dried at 60°C for 15–30 min, but found substantial losses of DMSP in culture samples dried in the same way.

Whilst we cannot dismiss the possibility of a small percent loss of DMSP·HCl during the drying process, this would affect all samples equally if the initial mass were pure DMSP·HCl. However, the change in mass occurred during the initial temperature ramp and the first ten minutes at 60°C (data not shown), suggesting that the differences in percent solid remaining are most likely driven by variable water content. The water content pattern relates to the relative ages of the batches and may have been absorbed from the atmosphere despite the precautions for keeping the stock dry when in storage. However, we are cautious about forming any firm conclusions based on this limited dataset. Applying these percentage purities to the data in Fig. 1 brings the regression slopes closer together (207.1, 220.2 and 250.1 for Batch #s 8.3, 10 and 11 respectively) but does not fully explain the variation observed.

When considering the possible reasons for discrepancies between standards, it is also pertinent to consider how DMSP·HCl is typically synthesised and its composition/purity checked. Most methods described in the literature (Chambers et al. 1987; Howard and Russell 1995; Larher et al. 1977; Smith et al. 1999) involve mixing acrylic acid and DMS in an organic solvent (e.g., toluene, benzene, dichloromethane) for a number of days at room temperature. The solution is then bubbled with anhydrous hydrogen chloride to form the DMSP·HCl precipitate. An alternative method is described by Dickson et al. (1980), where 3-bromopropionic acid in excess DMS is refluxed at ~55–60°C for 24 h, then left to stand so that DMSP·HBr precipitates. Purification is achieved via a re-crystallisation step involving repeated dissolution in an organic solvent and drying.

Precipitate composition is typically checked using proton and/or carbon-13 nuclear magnetic resonance spectroscopy (NMR). It is unclear from the DMS(P) literature whether the techniques applied can be used to quantify the absolute purity. The standard inter-comparisons performed to date (discussed earlier: Hatton et al. 1994; Turner et al. 1990) have indicated that extensive analysis to determine a quantitative estimate of purity has not been necessary (i.e., other sources of variation in sample analysis are likely to exceed the error due to purity). Although we cannot say that the differences observed in Fig. 1 are typical, all of these standards had their composition checked immediately post-synthesis using NMR. It is not possible to rule out changes during storage although the solid standard is thought to be very stable in a cool, dark and dry environment. The broad and pertinent issue here is that a dry DMSP·HCl reference standard of quantified purity would allow simple cross-checks to be made at regular intervals and would ensure that results from different research groups could be compared with confidence.

Analytical methodologies and sample handling

Making sure that all analytical systems are calibrated with standards on the same reference scale is only the first stage in ensuring comparable results. A list of existing analytical techniques is provided in Table 1, along with example references if the reader is interested in the specific details of each methodology. In particular, we highlight Stefels (2009) for further reading, as this details the GC purge and trap (P&T) approach most commonly used to collect DMS data. The analysis of seawater for DMS using all the techniques listed in Table 1 requires certain sample-handling methodologies, some of which are common to the majority of DMS analyses. Here we address those that are particularly pertinent to the development and inter-comparability of the DMS database.

A general goal of any DMS analysis should be to incorporate standards into the sample handling process as much as possible, such that the *system* is calibrated rather than just the analytical instrument (Turner et al. 1990). This reduces the risk that the system itself is affecting the analytical result. A good example of this is the purge and trap (P&T) preparation system commonly used to pre-concentrate DMS before injection onto a GC column. A gas standard injected directly into the GC will not inform the user about the nuances of their P&T system such as the purge extraction efficiency. Also, DMS is notoriously 'sticky' and will differentially adsorb to the inner walls of tubing such that stainless steel tubes retain a greater 'memory' of the previous sample(s) than PTFE tubes. Different P&T systems constructed from different tubing types and lengths will give different results when connected to the same GC so it is essential that each P&T system is calibrated as part of the system.

Table 1 List of sample analysis and preparation systems for the quantification of DMS in seawater

Analytical system	Preparation system	Abbreviation	Example reference(s)
Gas chromatography (GC) with flame photometric detection (FPD) or pulsed FPD (PFPD)	Purge and trap using either liquid N_2 or adsorbant material with ice/salt water combination.	GC P&T	Bell et al. (2006); Turner et al. (1990); Stefels (2009)
	Headspace injection	Headspace	Steinke et al. (2000)
	Solid phase micro extraction	SPME	Yassaa et al. (2006)
Mass spectrometry (MS)	Purge and trap with gas chromatography	GC–MS P&T	Ridgeway et al. (1991)
	Membrane inlet	MIMS	Tortell (2005)
	Atmospheric pressure chemical ionisation	CIMS	Saltzman et al. (2009)
	Proton transfer reaction mass spectrometry	PTR-MS	Kameyama et al. (2009); Stefels et al. (2009)

Note that, for clarity, different standards and calibration approaches are not discussed here

Filtration

The treatment of a water sample prior to analysis is a major consideration for DMS and DMSP analysis. When phytoplankton are subjected to mechanical stress their cell walls and membranes are more prone to rupture, releasing the intracellular contents into the surrounding media. Mechanical stress during sampling can occur for a variety of reasons (Eriksen 2008), but the most common effects during sample handling are:

- Increased turbulence, which can be exacerbated by bubbling an unfiltered sample or by applying high flow rates through a relatively narrow tube;
- 'Rough' sample filtration using a high pressure difference across the filter or filtering high volume samples.

Since intracellular DMSP is a solute in the cytoplasm of algae, there is the potential for it to be released to the medium when cells are damaged. Subsequent mixing of DMSPd with cellular enzymes could convert some filtration-liberated DMSPd to DMS in situ, artificially increasing the concentration. A number of studies have observed that the sparging of unfiltered samples increases DMS concentrations (del Valle et al. 2009; Ridgeway et al. 1991; Turner et al. 1990; Wolfe et al. 2000). Due to this issue, the majority of groups that have contributed data to the DMS database have routinely filtered their seawater sample before purging for DMS. Unfortunately, filtration itself also increases the mechanical stress encountered by phytoplankton cells. The conversion of intracellular (particulate) to extracellular, dissolved, DMSP (DMSPd) is discussed at length in Kiene and Slezak (2006). The authors identified that sample volumes greater than 3.5 ml and/or high pressure filtration systems can cause substantial increases in DMSPd concentrations for various natural environments.

The potential severity of the mechanical stress effect generated by sparging a sample, and the variability due to shifts in biological community composition, means that filtration is often unavoidable during P&T analysis of DMS. Following the methodological recommendations of Kiene and Slezak (2006) will help minimise the likelihood of artificially elevating the measurement of in situ DMSPd (and thus DMS) concentrations. Stefels (2009) also discusses the pros and cons of filtration methodologies, and suggests that gravity filtration without allowing the filter to become dry (exposing cells to the air) is the optimum approach when analysing for DMS and dissolved and particulate phase DMSP. Gravity filtration would indeed be the obvious solution were it not for the inevitable partial loss of volatile DMS during filtration.

The effects of filtration have been studied during field experiments with sea-ice diatoms using stable isotope additions of DMS and analysis using a novel proton transfer reaction mass spectrometer (PTR-MS) technique with a direct 150 ml min^{-1} purge and detect method (for details, see Stefels et al. 2009). Briefly, the three-times deuterated DMS (d3-DMS) was added to

the experimental set-up and both filtered and unfiltered samples were analysed for DMS (mass 63 in the PTR-MS) and for the d3-DMS isotope (mass 66). The filtered samples had an initial volume of 40 ml and were filtered through a 4.5 cm diameter Whatman GF/F filter (nominal pore size of 0.7 μm), with the first 16 ml used for DMS analysis. The use of a relatively large filter area with open-top (gravity) filtration was likely to result in loss of DMS to the atmosphere. If so, this should have been visible in the mass 66 (d3-DMS) signal when comparing filtered and unfiltered samples. The same comparison of mass 63 signal (DMS) ought to have reflected the same process but would also include a signal if purging of the unfiltered sample was resulting in release of DMS from disrupted cells.

Results indicate that loss due to filtering was occurring but was very reproducible (Fig. 2), with filtered samples containing 86% of mass 66 compared to the unfiltered sample. The natural DMS (mass 63) content showed a slightly lower slope but was not significantly different, which indicated that no release of DMS in unfiltered samples had taken place. It must be emphasised here that the above experiments were performed with (ice) diatoms that may be less susceptible to physical stress than algae with no external skeleton (Hamm et al. 2003) and possibly possess less capability to convert DMSP to DMS than some prymnesiophyte and dinoflagellate taxa. Furthermore, the temperature of the samples was approximately 1°C, which favours extremely high DMS solubility as the dimensionless Henry's Law (Gas/Liquid) is 0.033 (Dacey et al. 1984). A different

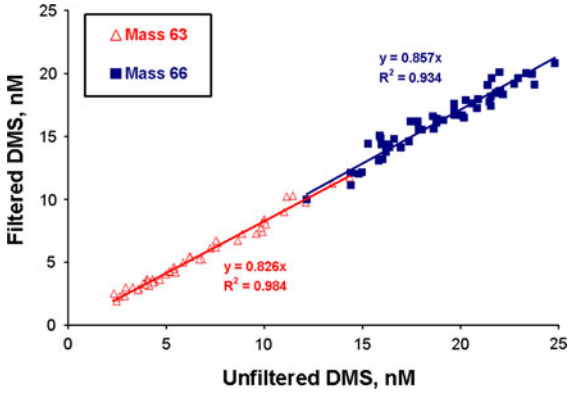

Fig. 2 Compilation of filtered versus unfiltered DMS data from ice–diatom incubations ($n = 53$). Both the DMS (mass 63, triangles) and deuterated DMS, d3-DMS (mass 66, squares), are compared

species composition could lead to increased DMS release in the unfiltered sample, and a more open-topped experimental setup and/or warmer waters would facilitate greater loss of DMS in both filtered and unfiltered samples. Within these limitations, these results suggest that, if carried out with care, sampling artefacts can be limited and quantified. In this respect, the use of d3-DMS (or an alternative isotope or internal standard) is particularly useful (see also Brugger et al. 1998; Slezak et al. 2001; Smith et al. 1999). However, even without an internal standard, frequent comparisons between filtered and unfiltered samples using established methods can be very informative.

It is important to emphasise that the magnitude of the filtration effect on DMSPd (and likely on DMS also) is variable depending on phytoplankton community composition, with certain species more or less sensitive to mechanical stress (Wolfe et al. 2002). Furthermore, it is possible that the physiological state of cells may affect their vulnerability, with propensity for lysis varying during the course of a phytoplankton bloom. In blooms of species with high enzymatic rates of DMSP-to-DMS conversion such as *Phaeocystis* sp. or *Emiliania huxleyi*, the particulate DMSP to DMS ratio is typically up to 100:1 (Stefels et al. 2007). In unfiltered samples from such blooms, agitation of only a small number of cells will result in a significant conversion of DMSP to DMS in comparison with filtered samples, leading to elevated (up to sixfold) DMS concentrations (del Valle et al. 2009; Wolfe et al. 2000).

Equilibration systems

With the advent of high frequency measurements of seawater DMS, filtration is virtually impossible and equilibration systems attached to a continuous flow of surface seawater are essential. High frequency measurements are desirable in order to best characterise surface DMS concentrations, but this leads to a number of possible issues. Equilibration systems nearly always utilise the continuous (or underway) seawater supply that flows through many oceanographic research vessels. Mechanical stresses can be generated by flow through the underway system or through the equilibrator (particularly if this uses a bubbler or shower head configuration). Secondly, biofouling may change the environment within the

underway system (e.g., Juranek et al. 2010), leading to potential interference from bacterial consumption of ambient DMS and/or DMSP-dependent DMS production.

With the above issues in mind, tests were performed in the Southern Ocean in 2008 to compare discrete samples with results from a counterflow equilibrator (Liqui-Cel Extra-Flow, 2.5 × 8) fitted to the ship's clean seawater underway (UW) system (~400 ml min^{-1}) with an intake at ~5 m depth. Nitrogen (N_2) was passed through the equilibrator at a controlled flow rate of 40 ml min^{-1} and a pressure of 50 kPa. Gaseous DMS from the N_2 gas stream was trapped on an adsorbent trap (Carbopack-X, Sigma-Aldrich) at −50°C and quantified on a Varian 3800 GC equipped with a CP-Sil 5CB capillary column (30 m × 0.53 mm) and a PFPD. A sample was analysed every 10 min and the system was calibrated and the sensitivity monitored every hour using a permeation device (Dynacal, Vici Metronics Inc.) delivering 120 ng DMS min^{-1} at 30°C. Seawater temperature was continuously monitored and liquid phase DMS concentrations calculated using the Henry's law constant for seawater according to Dacey et al. (1984). Discrete samples were taken directly from either a CTD Niskin bottle or from the UW system. These samples were gravity filtered (GF/F) and quickly transferred to a glass purge tower to minimise gas exchange, then sparged with N_2 at 60 ml min^{-1} (Archer et al. 2009). Sparged DMS was pre-concentrated on the same adsorbent trap used for the equilibrator samples. Discrete samples are compared against the mean of the previous five equilibrator samples (Fig. 3), during which time the boat was stationary. A small number of discrete samples were also taken directly from the UW system for comparison with the equilibrator.

The data in Fig. 3 do not sit on the 1:1 line, with equilibrator data consistently overestimating at higher concentrations and underestimating at lower concentrations, relative to discrete sample data. Although there are comparatively few discrete sample data points from the UW, they show a similar relationship to the equilibrator data, suggesting that the variations may not be driven by differences between water from the UW supply and from the CTD. The discrepancy between discrete and equilibrator measurements is likely to be driven by differences in either sample handling (P&T = filtered, equilibrator = unfiltered;

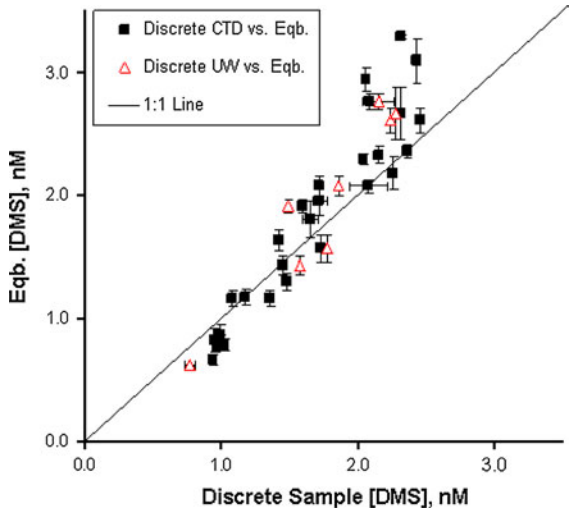

Fig. 3 Seawater DMS concentrations (nM), all measured using GC-PFPD, following pre-concentration on an adsorbent trap. Discrete sample concentrations (taken either directly from the ship's continuous flow (UW) system, *open triangles*, or from CTD Niskin bottles closed at the same depth as the UW, *filled squares*) are plotted against the mean concentration as determined from the equilibrator setup attached to the UW system during the preceding 50 min. *Error bars* represent 1σ of the mean. See text for full details

P&T = purge efficiency, equilibrator = equilibration efficiency) or differences between how the systems were calibrated (P&T = standard introduced into purge system; equilibrator = standard added post-equilibration system).

We do not suggest that these results are representative of all equilibrator setups and/or a full range of environmental conditions that can be encountered in the field. For example, some groups choose to equilibrate by sparging unfiltered seawater (e.g., Kameyama et al. 2009), and this also has the potential to impact measured DMS concentrations. The purpose of the data in Fig. 3 is merely to highlight the challenges facing future high resolution data collection efforts. Addressing such issues will be critical for the future development of the DMS database (especially in waters dominated by species sensitive to mechanical stress such as *Phaeocystis*) as it is very likely that more and more measurements will be made using equilibrators. We recommend that a method to assess the equilibration efficiency of equilibrators, which may alter over time, should be part of instrument configuration (e.g., by introducing a liquid standard into the water stream before it enters the equilibrator, rather than using a gas standard).

Previous field inter-comparison exercises

This paper would be incomplete without a discussion of the field-based DMS inter-comparison exercises that have been performed previously. The DMS community has, wherever possible, taken advantage of opportunities to compare analytical systems and to ensure that the results from different groups are comparable at least within the same fieldwork campaign. For example, the SERIES (Subarctic Ecosystem Response to Iron Enrichment Study) Lagrangian fieldwork campaign involved two research ships, the B/O *El Puma* and C.C.G.S. *John P. Tully*, both of which made in situ DMS and DMSP measurements (Levasseur et al. 2006). An indirect comparison using any data that happened to have been collected by both ships at similar points in time and space gave favourable results (Fig. 1 in Levasseur et al. 2006). In addition, a direct comparison was made using two fresh, discrete samples from each ship that were exchanged by inflatable boat. The analytical systems on both ships were P&T-based, although they did not have exactly the same setup and were calibrated with different standards (Levasseur et al. 2006). The results (sample A: 14.65 and 13.79 nM; sample B: 16.90 and 16.70 nM) demonstrated good agreement with a maximum difference of 6% of the mean concentration. Of course, a far greater number of samples would need to be compared for any kind of statistical confidence to be attributed to such a comparison.

A relatively recent technique is that of solid-phase microextraction (SPME), which has been successfully applied to DMS (Yassaa et al. 2006). The technique utilises a retractable fibre inside a septum-piercing needle that is composed of (or treated with) a sorbent substance that is tailored to the compound of interest. Briefly, the needle is injected into the headspace of a sample and left for a period of time so that equilibrium can be established between the compound adsorbed to the fibre and in the gas phase. The fibre is then injected directly into the heated port of a GC to thermally desorb DMS onto the column. Vogt et al. (2008) report results from a land-based mesocosm experiment (PeECE III) in a Norwegian fjord, close to Bergen during May/June 2005. Measurements of DMS were made using SPME and GC–MS (Max-Planck Institute for Chemistry, MPIC), and a GC P&T technique (University of East Anglia, UEA). System calibrations were performed using different standards and with separate techniques. The details of the bloom development and technique inter-comparison are discussed in Vogt et al. (2008). In brief, the data suggest good general agreement between the techniques but with a systematic offset averaging 8% higher in favour of GC P&T and poor agreement at low concentrations.

So far, we have only discussed inter-comparison experiments that are already published in the literature. We now present unpublished data from two field experiments in the North Sea and Sargasso Sea involving a number of DMS research groups. We intentionally do not detail the specifics of each methodology applied, but where appropriate highlight the differences (e.g., filtration technique, volume, calibration standard, etc.). Note that all analyses took place prior to, or at the development time of, the specific concerns raised about filtration (Kiene and Slezak 2006) and calibration standard purity (this paper) and, as a consequence, the results are to some degree not based on current 'best practise' methods. In addition, these results do not represent the full spectrum of spatial and temporal scales present in the DMS database, but they are the best retrospective approach available to provide some assessment of uncertainty in the data collected and submitted to the DMS database. We do not attempt to identify the cause(s) of variability between groups, and use the data solely to help establish a qualitative confidence (or lack thereof) in the comparability of DMS data in the database.

The first inter-comparison experiment took place aboard the RRS *Discovery* in the North Sea during the DISCO (DlmethylSulphide in COccolithophore blooms) experiment in June, 1999 (for details, see Burkill et al. 2002). Results from the Defence Evaluation Research Agency (DERA, now QinetiQ), Plymouth Marine Laboratory (PML) and the University of East Anglia (UEA) are compared. The participating laboratories utilised different techniques for DMS analysis:

- DERA: GC–MS P&T method, see Smith et al. (1999) for details.
- PML: GC–PFPD P&T method, see Archer et al. (2002a) for details.
- UEA: GC–FPD P&T methods (×2) based on Turner et al. (1990). Small differences between the methods (Table 2) justify separating these results in the data analysis.

Table 2 DISCO DMS inter-comparison experiment in the North Sea (5 seawater samples per group from the underway system)

	DERA	PML	UEA (1)	UEA (2)
Analysis type	GC–MS P&T	GC–PFPD P&T	GC–FPD P&T	GC–FPD P&T
Filtration technique	Syringe	Gravity	Syringe	Syringe
Filtration volume	50 ml	10 ml	20 ml	40 ml
Filter type	47 mm Whatman GF/F	25 mm Whatman GF/F	25 mm Millipore GF depth filter	25 mm Millipore GF depth filter
Standard used	Internal deuterated d6-DMS	Solid DMSP·HCl (CASS, University of Groningen Laboratories, The Netherlands)	Solid DMSP·HCl (Research Plus Inc., Bayonne, NJ, USA)	Solid DMSP·HCl (CASS, University of Groningen Laboratories, The Netherlands)
Mean DMS Conc. (nM)	4.63	5.34	5.46	4.90
SD (nM)	0.13	0.30	0.33	0.30
C.V. (%)	2.81	5.68	6.13	6.12

Information is provided on analysis and filtration techniques, standards, mean DMS concentration (x), standard deviation (SD) and coefficient of variance (C.V. = SD/x) for each research group

Seawater samples were collected from the surface water supply and placed into twenty 1.2 litre bottles. Five replicate bottles were distributed to each analyst and DMS concentrations determined within 2 h of sample collection (sample temperature maintained as close to in situ temperature as possible) using the methodologies summarised in Table 2. All research groups demonstrated good analytical precision, each reporting <5% coefficient of variance (C.V.) having repeatedly ($n = 5$) measured a fixed concentration DMS standard (data not shown). However, the C.V. for every method increased slightly when applied to seawater samples of unknown concentration (Table 2), which may be due to issues associated with sample handling and filtration. Another possible cause is the difficulty in preparing twenty homogeneous seawater subsamples. As Table 2 shows, the maximum difference in measured concentrations was 0.83 nM (16% of the mean value). It is also noteworthy that the GC–MS P&T system consistently underestimated DMS concentrations relative to the other systems; a 7% underestimate using a known standard concentration (data not shown) and a 15–17% underestimate for the seawater sample inter-comparison (Table 2). To a lesser degree, the UEA(2) system also underestimated seawater DMS concentrations relative to the PML and UEA(1) systems. The one similarity that this system had to the DERA system was a large sample volume, which might suggest filtration and/or purge efficiency issues.

The second inter-comparison experiment that we discuss took place aboard the R/V *Seward Johnson* in the Sargasso Sea during a Lagrangian study in a large-scale surface ocean eddy in July, 2004 (for details, see Bailey et al. 2008). Results from the Bigelow Laboratory for Ocean Sciences (BLOS), College of Charleston (CC), Institut de Ciències del Mar (ICM-CSIC), State University of New York, College of Environmental Science and Forestry (SUNY-ESF), University of South Alabama (Un.SA), and Woods Hole Oceanographic Institute (WHOI) are compared. These participating laboratories utilised different techniques for DMS analysis:

- BLOS: GC P&T method, see Matrai and Vernet (1997) and Kiene and Slezak (2006) for details.
- CC: GC P&T method, see DiTullio et al. (2001) for details.
- ICM-CSIC: GC P&T method, see Simó et al. (2000) for details.
- SUNY-ESF: GC P&T method, see Kiene and Service (1991) and Toole et al. (2003) for details.
- Un.SA: GC P&T method, filtration effects and new methodology tested during this cruise (see Kiene and Slezak 2006).
- WHOI: GC P&T method in flow through mode, see Zemmelink et al. (2006) for details.

Prior to this sample comparison, each group tested a fixed concentration, liquid DMS standard, with good analytical precision (C.V. ≤2%), with the exception of

Investigator C (C.V. = 8.45%). Cross-testing was also carried out with two temperature-controlled permeation tubes and a fixed concentration, liquid DMSP standard. A sample of surface seawater was then collected using a bucket, and subsamples were extracted from this by all investigators (n = 2–3 per investigator). DMS concentrations were determined within 2 h of sample collection (sample temperature maintained as close to in situ temperature as possible) using the methodologies summarised in Table 3. In general, all investigators demonstrated good analytical precision for their seawater analysis, with only Investigator C reporting a C.V. >4%. The maximum difference between measured concentrations was 0.68 nM (24% of the mean value).

In general, the data we have collected from various published and unpublished inter-comparison experiments suggest that, for the techniques tested at least, measured seawater DMS concentrations were broadly comparable. Within each experiment, the maximum difference between groups/techniques varied from 6 to 24% of the mean measured concentration. Since these inter-comparison exercises were conducted, improvements in sample handling (filtration) techniques based on the recommendations of Kiene and Slezak (2006) may reduce the differences between groups. A common reference standard for the community should also improve future data comparability. An important point of note, however, is that systematic differences were observed between SPME and GC P&T techniques (Vogt et al. 2008) and between GC–MS and GC–FPD/PFPD techniques (DISCO inter-comparison exercise). Many of the novel high frequency seawater DMS measurement techniques use mass spectrometer technology, substantially different standards and calibrate in very different ways. We recommend that a well-planned and inclusive inter-comparison exercise between different research groups and using many different analytical techniques be planned in the near future. Ideally this would also include the atmospheric DMS community to ensure full understanding of the comparability of DMS measurements from future research campaigns and when using substantially different techniques.

Recommendations for future data collation

Of the climatically-relevant trace gases, carbon dioxide (CO_2) is by far the best example of data collection with >4.5 million data points in the surface ocean facilitated in part by a large network of automated systems deployed on Voluntary Observing Ship (VOS) lines. In addition, well-funded European and international initiatives (notably SOCAT; http://www.socat.info/) have ensured the collation and comparability of CO_2 data from around the world. The DMS community should be striving for the same level of collection, collation and, importantly, precision and quality assurance. To achieve this, DMS researchers

Table 3 Sargasso Sea DMS inter-comparison experiment (2–3 samples per group from a bucket of surface seawater)

	Investigator A	Investigator B	Investigator C	Investigator D	Investigator E	Investigator F
Analysis type	GC P&T	GC P&T	GC P&T	GC P&T	GC P&T	GC P&T
Filtration technique	Syringe	Unfiltered	Gravity, vacuum	Syringe	Syringe	Syringe
Filtration volume	3 ml	5 ml	50 ml	3 ml	40 ml	2.5 ml
Filter type	GF/F	n/a	GF/F	GF/F	GF/F	GF/F
Standard used	DMS Liquid/ permeation tube	DMS Liquid/ permeation tube	DMS Liquid/ permeation tube	Solid DMSP·HCl (Research Plus Inc., Bayonne, NJ, USA)/DMS permeation tube	DMS liquid	DMS liquid
Mean DMS Conc. (nM)	2.62	3.19	2.67	2.60	2.77	3.00
SD (nM)	0.08	0.08	0.35	0.04	0.08	0.10
C.V. (%)	3.19	2.66	7.44	1.80	3.00	1.30

Information is provided on Analysis and filtration techniques, standards, mean DMS concentration (x), standard deviation (SD) and coefficient of variance (C.V. = SD/x) for each investigator

require substantially more community-level funding, but certain key priorities in data collection can usefully be identified at this stage. The future DMS database has the potential to develop into the equivalent of the present-day CO_2 database through the use of mass spectrometry-based techniques and the utilisation of VOS lines. This would provide the opportunity to assess interannual variability in specific biogeochemical regions of the world ocean, which is not possible with the current DMS database (Halloran et al. 2010). An assessment of the DMS variability in such areas is critical to our understanding of whether surface ocean concentrations are shifting as a result of global climate change, but any assessment of this nature is obviously reliant on the accuracy and precision of the data from which it is derived.

Nevertheless, the current DMS database has already proven to be an essential resource when developing models at various spatial and temporal scales. As part of the discussion session at the Fifth International DMS(P) Symposium (Goa, India), modellers and experimentalists alike contributed ideas as to how the DMS database might be expanded in the future. Currently the database focuses on concentration data collected from near-surface waters less than 10 m in depth because the primary consideration has been the calculation of sea-to-air flux (Kettle and Andreae 2000; Kettle et al. 1999; Lana et al. 2011). However, these concentrations are directly impacted by the biogeochemical processing of DMS and other reduced sulphur compounds such as DMSP and DMSO, and understanding of the cycling of these is relatively limited (Stefels et al. 2007). Much effort has thus been expended trying to model the reduced sulphur cycle using measurements of abiotic and biotic production and consumption pathways throughout the full euphotic depth range (e.g., Archer et al. 2002b; Gabric et al. 2008; Kloster et al. 2006; Vallina et al. 2008; Vogt et al. 2008).

Modelling efforts would benefit considerably from easy-access to as much validation data and relevant metadata as possible. To aid the development of existing models, we strongly recommend that the future DMS database be expanded to include all available data from the euphotic zone (i.e., depths >10 m), including relevant DMS precursor concentration measurements and rates of transformation between sulphur pools. Particularly relevant would be measurements of intracellular and extracellular DMSP and dimethylsulphoxide (DMSO) concentrations, rates of DMSP synthesis and DMS consumption, and the activity of DMS-producing enzymes (formerly referred to in the literature as DMSP–lyase activity). Furthermore, we recommend that datasets within the DMS database (current and future) be associated with relevant metadata about the methodology and analytical system used to collect the data.

Conclusions and recommendations

Analysis of previous *ad hoc* inter-comparison exercises suggests that variation between groups and/or analytical techniques has typically been $\leq$25%. Of course, these results may not be representative of data collected in all environments and in all seasons, but they provide some confidence in the scale of comparability (between groups) of previously-collected data. However, some systematic biases do exist and these suggest that newer techniques need to be rigorously compared across the spectrum of measurement approaches, but particularly with GC P&T.

For a period, variations of the GC P&T technique pioneered by Turner et al. (1990) were used to estimate surface seawater DMS concentrations, but this is no longer the case. Novel methods developed by different research groups are now more common, typically utilising mass spectrometers and facilitating the collection of large amounts of data per cruise. This is great news for the future expansion of the DMS database, but requires that the community be proactive in ensuring data comparability in the future. With this in mind, we recommend that all techniques give due consideration to sample handling issues. Stefels (2009) gives a detailed description of the key issues and the methodologies to combat these from a P&T perspective. In addition, we urge analysts to calibrate the whole seawater preparation and analytical system rather than just the analytical instrument, and to consider (and minimise) the effects of mechanical stress when filtering their samples or when using continuous flow seawater equilibrator systems.

Based on the discussion session held during the Fifth International Symposium on Biological and Environmental Chemistry of DMS(P) and Related Compounds (Goa, India, October 2010), we recommend that the community aim to:

(i) Expand the surface ocean DMS database to rival that of pCO_2 by developing existing technologies in conjunction with VOS sampling tracks, thus improving understanding of interannual variability against the backdrop of global change;
(ii) Expand the vertical extent of the DMS database to cover the entire euphotic zone;
(iii) Expand the database to accept related data that is often routinely collected on DMS-focussed cruises (e.g., DMSP/DMSO concentrations, rates of DMS and DMSP transformation, etc.).
(iv) Expand the database with metadata on the full sampling methodology and analytical system used.

Finally, based on the discussions in Goa, India, and the data presented within this paper, we strongly recommend the creation of a reference standard. This standard should be kept stable and stored for the DMS research community to cross check their own standards against and to help improve confidence in the comparability of data generated by different research groups. We also recommend that an extensive inter-comparison experiment be conducted, with the results informing future data collation exercises. Ultimately, the data being added to the DMS database should be quality controlled in a similar manner to the data included in the Surface Ocean CO_2 ATlas (SOCAT) database.

In spite of the issues we highlight within this paper, we are keen to stress our overall confidence in the current DMS database and the general comparability of its data. The inter-comparison exercises we discuss provide some confidence in the degree of comparability of data from different research groups. However, it is important that the community makes steps toward understanding the relative if not absolute accuracy of their measurements so that they might better compare and quality control their data. Furthermore, any inter-comparison exercises (opportunistic or, more preferably, planned and funded) that can be performed between different research groups using a range of established and novel methodologies and analytical systems can only serve to increase confidence in the rapidly-expanding DMS database. Given the pace of this expansion, the development of a reference standard would be a timely addition to the field.

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