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Strong linkages between dimethylsulphoniopropionate (DMSP) and phytoplankton community physiology in a large subtropical and tropical Atlantic Ocean data set

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[1] We present an extensive data set of dimethylsulphide (DMS, n = 651) and dimethylsulphoniopropionate (DMSP, n = 590) from the Atlantic Meridional Transect program. These data are used to derive representative depth profiles that illustrate observed natural variations and can be used for DMS and DMSP model-validation in oligotrophic waters. To further understand our data set, we interpret the data with a wide range of accompanying parameters that characterize the prevailing biogeochemical conditions and phytoplankton community physiology, activity, taxonomic composition, and capacity to cope with light stress. No correlations were observed with typical biomarker pigments for DMSP-producing species. However, strong correlations were found between DMSP and primary production by cells >2 μm in diameter and between DMSP and some photoprotective pigments. These parameters are measures of mixed phytoplankton communities, so we infer that such associations are likely to be stronger in DMSP-producing organisms. Further work is warranted to develop links between community parameters, DMS, and DMSP at the global scale.

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1. Introduction

[2] For over three decades, oceanic emissions of dimethylsulphide (DMS) and its resultant atmospheric oxidation products have been recognized as being potentially significant for the global climate [*Twomey*, 1974]. *Charlson et al.* [1987] put forward the CLAW hypothesis that the production of DMS by phytoplankton provides a mechanism by which oceanic biological processes regulate climate; this is still subject to much debate [e.g., *Ayers and Cainey*, 2007]. While phytoplankton are the primary source of DMS in oceanic waters, attempts to correlate DMS concentrations with chlorophyll *a*, the main photosynthetic pigment in most phytoplankton and hence a convenient estimate of total photosynthetic biomass, have often proven unsuccessful [e.g., *Kettle et al.*, 1999]. Scientific understanding of the pathways of reduced sulphur cycling in the upper ocean has improved substantially since the CLAW hypothesis was published, and with this an appreciation of its complexity has developed (see *Stefels et al.* [2007] for details). In particular, the central role of dimethylsulphoniopropionate (DMSP), the dominant biological precursor of DMS, is now well established.

[3] Intracellular DMSP concentrations vary between different phytoplankton groups and species [*Keller et al.*, 1989], such that good correlations between chlorophyll *a* and DMSP are usually only seen for data sets from restricted geographic areas where DMSP-producing phytoplankton dominate [e.g., *Malin et al.*, 1993]. For studies crossing a wide range of geographic zones, accessory pigment data can provide additional detail on phytoplankton community composition. Hence, instead of DMS and chlorophyll *a*, research has tended to focus on DMSP and accessory pigments. *Belviso et al.* [2001] took this approach with a surface water data set collected from the central Atlantic Ocean, the subtropical northeast Atlantic Ocean, the Ionian Sea, and the Indian sector of the Southern Ocean. A significant relationship (r^2 = 0.84, p < 0.0001, n = 189) was found between the pigments Hex+But (19'-Hexanoyloxyfucoxanthin plus 19'-Butanoyloxyfucoxanthin) and particulate DMSP in the <10 μm size fraction. The authors considered Hex+But a robust estimator of autotrophic pico- and nanoplankton biomass, and suggested that this relationship could be used to predict global nanoplanktonic particulate DMSP concentrations [*Belviso et al.*, 2001]. Their work was further developed into a global predictive algorithm for surface

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DMS concentrations [*Aumont et al.*, 2002; *Belviso et al.*, 2004b] using a community composition index derived from accessory pigment ratios [*Claustre*, 1994]. However, this predictive algorithm has had mixed success in subtropical/tropical waters relative to other predictive equations [*Bell et al.*, 2006; *Belviso et al.*, 2004a].

[4] Predictive equations and correlation analyses based on the impact of light on biological processes within the oceanic mixed layer have generally met with more success [*Larsen*, 2005; *Toole and Siegel*, 2004; *Vallina and Simó*, 2007]. Some studies have successfully focused on predicting DMS concentration from mixed layer depth, MLD [*Aranami and Tsunogai*, 2004; *Bell et al.*, 2006; *Simó and Pedros-Alio*, 1999; *Simó and Dachs*, 2002], although these have been at variable spatial and temporal scales. The scientific basis for this is that bacterial consumption of DMS will be reduced when the MLD is shallow and ultraviolet (UV) light exposure is high, while phytoplankton DMS production (or release) may increase with greater exposure to irradiance [*Simó and Pedros-Alio*, 1999]. Laboratory studies on a limited range of phytoplankton species have also shown that DMSP and DMS production is enhanced when UV levels are increased [*Sunda et al.*, 2002], although contradictory evidence does exist [*van Rijssel and Buma*, 2002]. *Sunda et al.* [2002] hypothesized that DMSP is the base of an anti-oxidant cascade mechanism to protect the cells from damaging free radicals. If this is the case, the concentration of photoprotective accessory pigments within phytoplankton cells in high light conditions would be expected to correlate with DMSP and DMS concentrations.

[5] The subtropical oligotrophic gyres are low primary production environments that account for ~60% of the global surface ocean [*McClain et al.*, 2004]. Evidence from satellite records suggests that these low production environments are tightly coupled to climate variability [*Behrenfeld et al.*, 2006]. DMS and DMSP concentrations tend to be low in these regions, but DMS emitted from the gyres vents into a relatively pristine atmosphere so the impact of any change in the flux is likely to have a greater affect upon albedo than in regions influenced by anthropogenic activity. With respect to DMS and DMSP, these areas are under-sampled and poorly understood [*Kettle et al.*, 1999], and measurements made in the central gyres would help to improve our understanding of the role these compounds play in climate and the global sulphur cycle.

[6] With this in mind, we participated in the Atlantic Meridional Transect (AMT) [*Robinson et al.*, 2006] program, and collected a substantial DMS and DMSP data set, with particular focus on the undersampled oligotrophic gyres in the North and South Atlantic. The aim of this study was to explore the statistical links between our data and a wealth of concurrently collected data that characterized the biogeochemical conditions and phytoplankton community physiology, activity, taxonomic composition, and capacity to cope with light stress. *Bell et al.* [2006] presented the near-surface DMS data, calculated DMS fluxes and used the data set to show that recently published algorithms often overestimate DMS concentrations in open ocean regions. Here we explore all of the AMT reduced sulphur data from the mixed layer (DMS, n = 651; DMSP, n = 590) in terms of the ancillary biological measurements.

2. Methods

[7] The AMT cruises relevant to this work are AMT-5, −12, −13 and −14, and the cruise tracks and sampling stations are plotted in Figure 1.

2.1. Seawater DMS and DMSP Sampling

[8] All profile samples were collected from pre-dawn (approx. 0300hrs local time) CTD casts except during AMT-5, which collected samples at approximately 1100hrs local time. Sampling depths ranged from the near-surface to just below the chlorophyll maximum (chl max), which reached depths of up to 150 m in the center of the gyres. Sampling depths were typically chosen based upon specific incident light levels (97%, 55%, 33%, 14% and 1% incident irradiance) in the water column, calculated from the previous day's mid-day cast, with extra samples taken close to the air-sea interface and just above and below the chl max. The CTD sampling system was a *Sea Bird 9/11 plus* fitted with a rosette of 20 L Niskin bottles. Samples were removed using polyvinylchloride (PVC) tubing and stored at ambient sea surface temperature in 750 ml gas-tight amber glass bottles before analysis. Every effort was made to minimize degassing and samples were processed within 1 h of collection.

2.2. DMS and DMSP Analysis

[9] DMS and DMSP analysis utilized purge and trap methodology [*Turner et al.*, 1990], and a headspace technique for some of the DMSP measurements; details of these methodologies have been discussed previously [*Bell et al.*, 2006, 2007]. Samples were analyzed using a gas chromatograph equipped with a CP-Sil 5CB capillary column (Varian Inc., Oxford, UK) and a flame photometric detector (GC2010; Shimadzu, Milton Keynes, UK). The system was calibrated using commercial DMSP (Centre for Analysis, Spectroscopy and Synthesis (CASS), University of Groningen Laboratories, The Netherlands) and the calibration checked daily. Before purging for DMS, samples were gently filtered through Whatman glass fibre filters (GF/F, nominal pore size 0.7 μm), to separate dissolved DMSP (DMSPd) from particulate DMSP [see *Bell et al.*, 2007], and converted to DMS via cold alkali hydrolysis by adding sodium hydroxide in excess. It has been suggested that concentrations of DMSPd may be artificially elevated due to cell leakage during filtration [*Kiene and Slezak*, 2006]. Using low-volume gravity filtration, maximum measured concentrations of DMSPd were 2.8 nM in the Sargasso Sea [*Kiene and Slezak*, 2006] and, based on measured DMSPd turnover rates [*Kiene et al.*, 2000], it is possible that any DMSP exuded in situ will be processed within hours and in close proximity to its producer. In view of this, we have analyzed our data set looking only at relationships with total DMSP, DMSPt (i.e., dissolved plus particulate DMSP). Tests on board (data not shown) demonstrated that the analytical uncertainty (relative standard deviation) of these measurements was ±5% for DMS and ±10% for DMSPt.

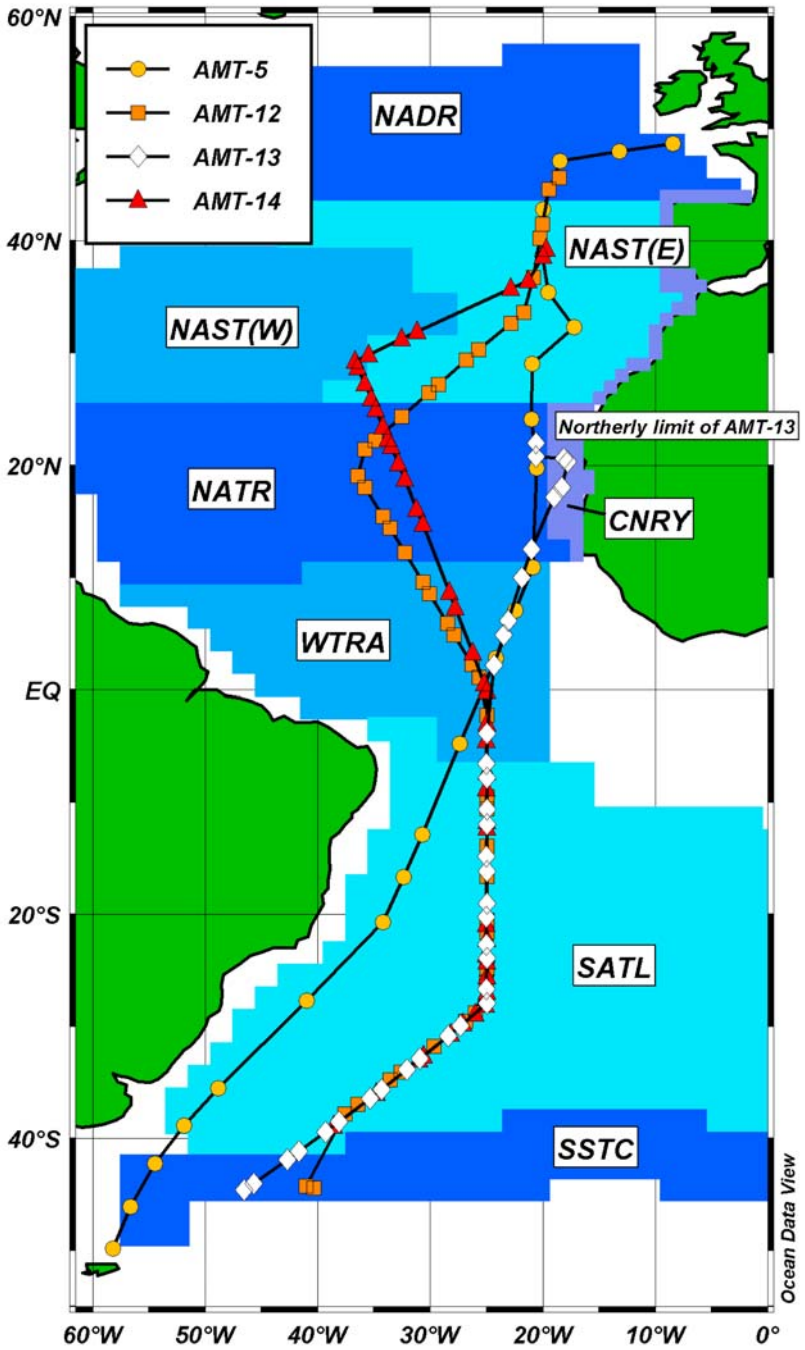

Figure 1. Cruise tracks for the four Atlantic Meridional Transect (AMT) cruises: AMT-5 (Sep. 1997); AMT-12 (May 2003); AMT-13 (Sep. 2003); and AMT-14 (May 2004). Cruises were southbound in September and northbound in May. The biogeochemical provinces defined by *Longhurst* [1995] are shown for spatial reference: North Atlantic Drift (NADR); North Atlantic Subtropical Gyre-East (NAST(E)); North Atlantic Subtropical Gyre-West (NAST(W)); Canary Current Coastal (CNRY); North Atlantic Tropical Gyre (NATR); Western Tropical Atlantic (WTRA); South Atlantic Subtropical Gyre (SATL); and South Subtropical Convergence (SSTC). Plot produced using Ocean Data View (http://odv.awi-bremerhaven.de/home.html).

Table 1. List of Pigments Focused on in This Paper, Their Abbreviation for Ease of Reference, and Chemotaxonomic Algal Class[a]

Major Pigment Role	Pigment Name	Abbreviation	Algal Class(es)
Photosynthetic Pigments	Chlorophyll *a*	Chl *a*	All major algal classes except Prochlorophytes
	Divinyl Chlorophyll *a*	DV Chl *a*	Prochlorophytes
	Total Chlorophyll *a*	TChl *a*	Sum of DV Chl *a* and Chl *a* (see above) Used as an indicator of total biomass
	19'-Hexanoyloxyfucoxanthin	Hex	Prymnesiophytes
	19'-Butanoyloxyfucoxanthin	But	Chrysophytes (Prymnesiophytes)
	Fucoxanthin	Fucox	Diatoms (Prymnesiophytes, Dinoflagellates, Chrysophytes)
	Peridinin	Perid	Dinoflagellates
Photoprotective Pigments	Diadinoxanthin	Diadinox	Diatoms, Prymnesiophytes, Dinoflagellates (Chrysophytes)
	Diatoxanthin	Diatox	(Diatoms, Prymnesiophytes, Dinoflagellates)
	Zeaxanthin	Zeax	Cyanobacteria, Prochlorophytes (Chlorophytes, Chrysophytes)
	Alloxanthin	Allox	Cryptophytes
	β-Carotene	β-Car	(Cyanobacteria, Prochlorophytes, Chlorophytes, Prasinophytes)

[a]Each pigment is grouped according to its likely major role within the cell [*Gibb et al.*, 2000]. Algal species for which the relevant pigment is considered taxonomically significant (i.e., 1–10% of total pigments) but not major are placed in brackets.

2.3. Ancillary Measurements

[10] For the vast majority of this data set, it was possible to couple ancillary data with DMS and DMSPt measurements that had been made with water from the same Niskin bottle. Where this was impossible, data obtained from different bottles at a similar depth were used. A maximum depth-difference criterion was set at 2 m, but >80% were less than 0.5 m different. Data from different CTD casts were never combined. Phytoplankton pigment samples were filtered and stored at −80°C before onshore analysis using high pressure liquid chromatography [see *Poulton et al.*, 2006a]. Note that, throughout this paper, we refer to a number of chemotaxonomic pigment markers as described in Table 1. Rates of phytoplankton carbon fixation (primary production) were determined using radio-labeled ^{14}C-uptake during on-deck incubations. A number of these samples were size-fractionated into less than and greater than 2 μm fractions using 47 mm polycarbonate filters [see *Poulton et al.*, 2006a]. Particulate organic and inorganic carbon standing stock samples were collected and analyzed using methodology detailed by *Poulton et al.* [2006b].

2.4. Correlation Analysis and Detection Limits

[11] The frequency distributions of most of the AMT data sets were not normally distributed, so non-parametric Spearman's Rank correlations were used. The definition of a 'strong' correlation is relative [*Cohen*, 1988] and varies depending upon the subject matter. For this study, we set a relatively low correlation coefficient criterion due to the inherent variability of the natural environment and relatively limited current understanding of the biological sulphur cycle in natural surface waters. Significant correlations with a Spearman's ρ value between −0.5 and +0.5, were discarded as too weak a correlation. Based on this criterion, a 'strong correlation' hereafter refers to an association between data that satisfies the following criteria: $p < 0.01$ (or ≥99% confidence level) and ρ greater than +0.5 or less than −0.5.

[12] Data were only coupled and correlated if they had been collected at the same time and from a similar depth. Inevitably this controlled the number of data pairs in many correlations. For example, fewer data pairs exist for correlations with ^{14}C-uptake compared to chlorophyll *a* because ^{14}C-uptake was not measured as frequently due to time and manpower constraints. Correlation does not necessarily mean causation, so such results should not be over-interpreted. Nevertheless, the degree of correlation or lack of correlation can help examine previous lab-based theories and generate new hypotheses for future research.

[13] Below detection limit (<DL) data values were encountered for DMS, DMSPt and accessory pigments, with respective DL values of 0.06 nM, 1.26 nM and 2 ng L^{-1}. Despite this, data < DL were incorporated into the non-parametric Spearman's Rank correlation analyses, as discarding the data would impose bias upon any results [*Helsel and Hirsch*, 2002]. Furthermore, this statistical test has been shown to interpret <DL data appropriately and without bias as long as the <DL data do not represent a large proportion of the overall data set [*Helsel*, 2005]. Where data have been presented in scatterplots, the DLs have been marked with dashed lines: all data under each line were <DL. For certain data sets, the proportion of data <DL was high, and this should be considered when interpreting the results (i.e., when interpreting certain data sets, a lack of correlation should not be given too much weight). In particular, we highlight data sets where >50% of the data was <DL (percentage of data set <DL indicated in brackets): violaxanthin (65%), divinyl chl *b* (65%), alloxanthin (70%), diatoxanthin (79%), lutein (92%) and prasinoxanthin (92%).

3. Results and Discussion

3.1. DMS and DMSPt Profiles

[14] A difficult aspect of interpreting the wealth of data from the AMT program is that presenting multiple latitudinal sections for each cruise (i.e., depth on the *y* axis, latitude on the *x* axis and concentration represented by the depth of shading) can only enable a qualitative analysis. Statistical correlation has enabled a quantitative analysis (see next section) but to help visualize the DMS and DMSP data we also present profiles representative of the data set (Figure 2). Initially, all DMS and DMSPt depth profile data were plotted on the same graphs (Figures 2a and 2b), which

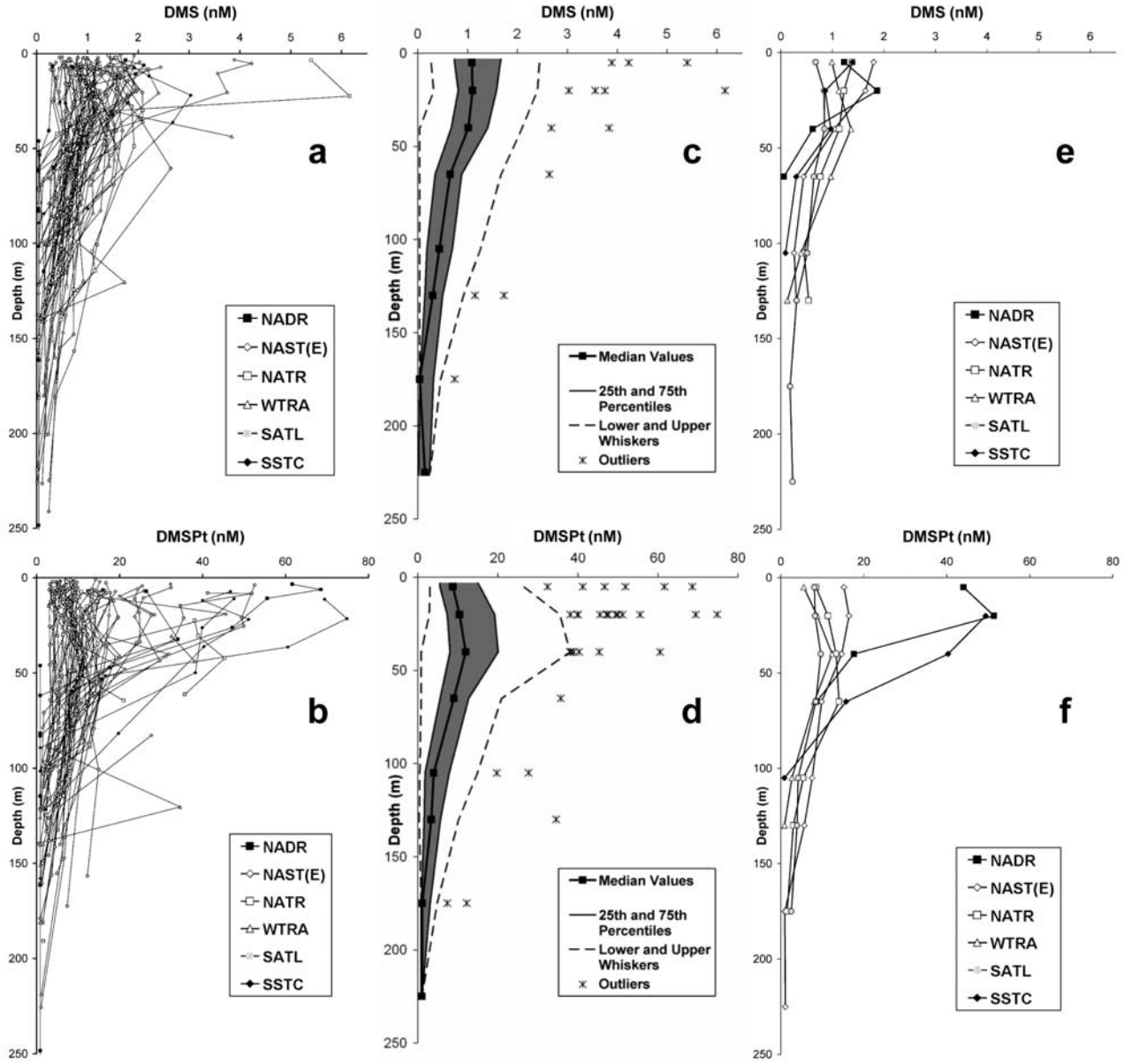

Figure 2. Depth profiles for DMS and DMSPt concentrations (nM) from all four research cruises. Plots show: (a and b) all individual profiles; (c and d) depth-binned data represented by median values (squares), inter-quartile range (shaded area delimited by 25th and 75th percentiles), range excluding outliers (dotted lines) and outliers (stars) for each depth; and (e and f) median depth-binned profiles for each major oceanographic province.

illustrates the degree of variability in the vertical distributions of these parameters. Next, the data was sorted into fixed depth bins based upon the depths typically sampled during AMT: near-surface, the 'standard' light levels of 55%, 33%, 14%, 1% and 0.1% (the 1% was coincident with the chl max), and samples from just above and below the chl max. For these 8 depth bins, the median, inter-quartile range (delimited by the 25th and 75th percentile), data range (excluding outliers) and outliers (defined as values less than the 25th percentile or greater than the 75th percentile by 150% of the inter-quartile range) were calculated. These data are shown in Figures 2c and 2d and are also tabulated (Table 2). We believe that this product is a valuable resource for oceanic DMS and DMSP model validation.

[15] Despite covering a large latitudinal range, and a number of biogeochemical provinces, the AMT profile plots (Figures 2c and 2d) are well-constrained, with relatively little variation about the median values. As expected, DMSPt demonstrates a subsurface maximum, which was generally observed in the top 50–70 m. DMSPt concentrations in the upper 50 m range from 2.9 to 38.0 nM. In comparison, the DMS profile is more uniform, with a reduction from higher

Table 2. Data Used to Generate the Representative Depth Profiles in Figures 2c and 2d[a]

Depth Bin (m)	Plotted Depth (m)	Median Values (nM)		25th Percentile Values (nM)		75th Percentile Values (nM)		Lower Whisker (nM)		Upper Whisker (nM)		Number of Data Points	
		DMS	DMSPt	DMS	DMSPt	DMS	DMSPt	DMS	DMSPt	DMS	DMSPt	DMS	DMSPt
0–10	5	1.09	8.81	0.74	5.55	1.66	15.52	0.27	3.05	2.44	26.43	86	80
10–30	20	1.10	10.45	0.82	7.37	1.58	19.22	0.32	2.90	2.40	35.47	102	92
30–50	40	1.02	12.01	0.68	8.07	1.40	20.08	0.04	0.88	2.09	38.05	66	63
50–80	65	0.65	9.04	0.35	5.58	0.89	12.75	0.04	0.88	1.67	20.97	65	58
80–110	105	0.44	4.00	0.19	1.85	0.70	7.89	0.04	0.88	1.26	14.92	48	40
110–150	130	0.30	3.39	0.15	1.59	0.50	5.67	0.04	0.43	0.92	10.22	53	46
150–200	175	0.04	1.14	0.04	0.88	0.32	3.10	0.04	0.88	0.46	4.87	21	16
200–250	225	0.15	1.07	0.02	0.88	0.24	1.11	0.01	0.88	0.25	1.11	8	3

[a]DMS and DMSPt, respectively. See Figure 2 legend and text for details.

median concentrations (~1 nM) in waters shallower than 50 m to lower median concentrations (~0.5 nM) below this depth. To provide some context for these profiles, equivalent plots for temperature and total chlorophyll *a* (TChl *a*) are shown (Figures 3a and 3b, respectively). In contrast to the DMS and DMSPt profiles, both temperature and TChl *a* exhibit greater variability and have relatively large inter-quartile ranges. The temperature data in particular has an inter-quartile range of approx. 8°C for each depth bin in the upper 80 m. Variability in TChl *a* concentrations throughout AMT skew the data distribution at each depth such that the subsurface chlorophyll maximum depth is poorly defined and a typical average profile is not clear. Considering the variability in the temperature and TChl *a* profiles, the consistency of the DMS and DMSPt profiles is very interesting.

[16] The data were further subdivided into the major biogeochemical regions encountered during the AMT cruises and the median concentrations for each depth bin calculated and plotted (Figure 2e, DMS; Figure 2f, DMSPt; Figure 3c, temperature; and Figure 3d, TChl *a*). The major regions were defined using the static biogeochemical provinces defined by Longhurst (see Figure 1). The representative temperature profiles are substantially different from each other and demonstrate that the surface water in each province was relatively well-mixed, with only a small temperature gradient between the surface and >150 m. As suggested by the small range in the representative depth profile, and in contrast to the temperature profiles, most of the DMS and DMSPt province depth profiles do not differ substantially. The exception to this was for DMSPt in provinces at higher latitudes (NADR and SSTC), where the median surface concentrations were much greater (>40 nM). This difference is replicated in the TChl *a* profiles, which also demonstrate substantially higher (>0.5 mg m^{-3}) subsurface concentrations in the NADR and SSTC provinces compared to those at lower latitudes, which have a much deeper chl max at ~100 m. This variability in concentration and depth of the chl max also explains the poorly defined median profile shape for the whole AMT data set (Figure 3b). The median DMS profiles for the high latitude NADR and SSTC provinces displayed similar concentrations to the lower-latitude median profiles despite the expectation of seasonally high concentrations. While an explanation for this difference might be a temporal decoupling of the processes driving DMSPt production, conversion to DMS and subsequent DMS turnover, this data represents only a small proportion of our data set (<10%), and thus was not investigated further.

3.2. Correlation Analyses

[17] While the representative depth profiles are useful for making generalizations about a region (e.g., when comparing data with model output), it is more informative to establish what, if any, relationships exist with the ancillary information. The AMT program provided a tremendous platform from which to make such analyses and the following section of this paper discusses the results of our efforts. The measurements that were made provide a 'snap-shot' of multiple processes taking place at that time and a correlation analysis of in situ measurements is thus a good initial step in trying to understand what influences the reduced sulphur cycle. DMSP is well-established as a dominant precursor to DMS and so it is unsurprising that our DMSPt measurements correlate to some degree with concurrent DMS measurements ($\rho = 0.44$, $p < 0.01$, $n = 577$). This correlation is not particularly strong but this is to be expected due to the short-term decoupling of the many consumption and production processes known to affect DMS and DMSP in the open ocean [*Stefels et al.*, 2007].

3.2.1. Biogeochemical Parameters

[18] A direct relationship with TChl *a* would be useful in that it is widely used in oceanography and can be detected remotely in surface waters by various types of satellite-based instruments [e.g., *McClain et al.*, 2004]. However, in common with previous studies, our AMT data confirm a lack of correlation between TChl *a* and DMS ($\rho = -0.03$, $p > 0.05$, $n = 470$) or DMSPt ($\rho = 0.34$, $p < 0.01$, $n = 415$). Aside from TChl *a*, the other major biogeochemical markers that could be investigated were particulate organic carbon (POC) and particulate inorganic carbon (PIC or calcite). POC did not correlate well with either DMS ($\rho = 0.42$, $p < 0.01$, $n = 117$;) or DMSPt ($\rho = 0.25$, $p < 0.01$, $n = 104$). These results are not unexpected as algal speciation plays a significant role in determining DMSP (and thus DMS) concentrations in the ocean [*Keller et al.*, 1989]. TChl *a* and POC are relatively static biogeochemical markers of the overall community and are unlikely to change with small shifts in algal speciation. Among the biogeochemical parameter data, it might be reasonable to consider PIC as representative of the biomass of known DMS- and DMSP-producers (i.e., coccolithophores) and therefore this should

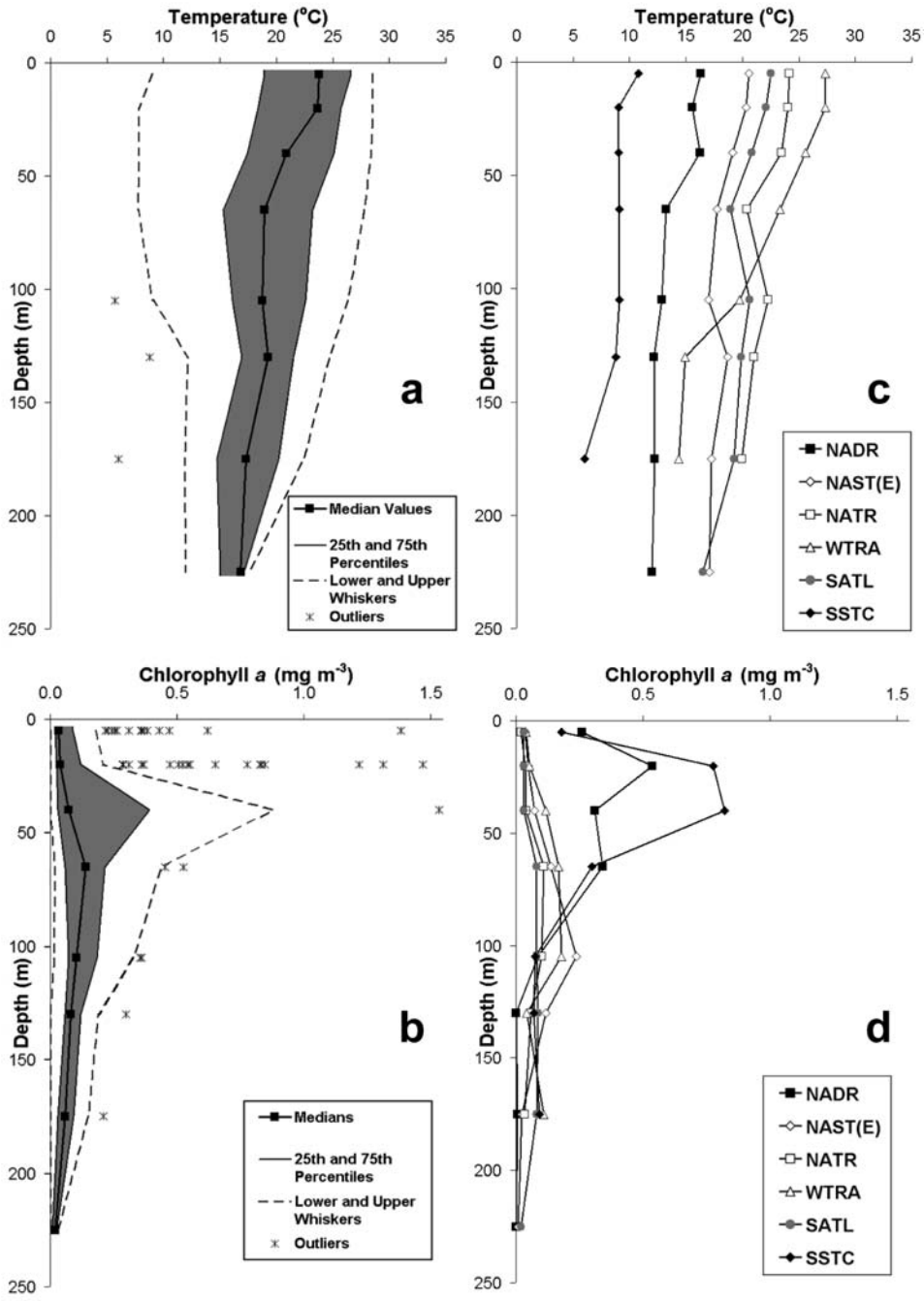

Figure 3. Depth profiles for temperature (°C) and TChl *a* (mg m^{-3}) from all four research cruises. Plots show (a and b) depth-binned data represented by median values (squares), inter-quartile range (shaded area delimited by 25th and 75th percentiles), range excluding outliers (dotted lines) and outliers (stars) for each depth; and (c and d) median depth-binned profiles for each major oceanographic province.

result in a positive correlation within our analysis. However, PIC displayed no strong correlations with DMS ($\rho = -0.01$, $p > 0.05$, $n = 86$) or DMSPt ($\rho = 0.14$, $p > 0.05$, $n = 77$). As discussed by *Poulton et al.* [2006b], the PIC signal can be attributed to both coccolithophore cells and detached coccoliths, and this may explain the weak correlations with DMS and DMSP in our data.

3.2.2. Pigments as Indicators of Phytoplankton Speciation

[19] The next logical step was to consider the degree of correlation between DMS, DMSPt and the various phytoplankton pigments. Over small spatial and temporal scales (e.g., blooms), correlations with phytoplankton 'marker pigments' have sometimes suggested that certain phyto-

Table 3. Correlation Matrix for Biomarker Pigment Groups for the Entire AMT Data Set[a]

	Spearman's Rank Correlation	
Biomarker Pigment Group	DMS (n = 299)	DMSPt (n = 268)
Cyanobacteria (Zeax:Total)	0.37	−0.09
	$p < 0.01$	$p > 0.05$
Prymnesiophytes (Hex+But:Total)	−0.07	0.35
	$p > 0.05$	$p < 0.01$
Diatoms (Fucox:Total)	−0.05	0.22
	$p > 0.05$	$p < 0.01$
Dinoflagellates (Perid:Total)	0.13	0.12
	$p < 0.05$	$p > 0.05$

[a]Cruises −5, −12, −13 and −14.

plankton groups are responsible for DMS/DMSP production [e.g., *DiTullio and Smith*, 1995; *Sunda et al.*, 2005; *Turner et al.*, 1995]. However, across the entire subtropical/tropical Atlantic this does not appear to be the case; we could not identify any strong correlations with DMS or DMSPt (Data Set S1).[1] This is in direct contrast with *Belviso et al.* [2001], who identified a strong, significant correlation between particulate DMSP and Hex+But for data collected from a range of environments.

[20] An inherent problem with any correlation analysis is that natural covariance between variables can confound the interpretation of the strength of a correlation. The degree of covariance identified within our pigment correlation matrix (Data Set S1) suggests that this is a major drawback for the interpretation of correlations between DMS/DMSP and individual pigments. As a result, a correlation observed with one biomarker pigment is likely to be confounded by covariance with another. For example, within the AMT data set there is a strong, significant correlation between Hex and Fucox ($\rho = 0.865$, $p < 0.01$, $n = 311$). Hex and Fucox are typically considered to be good indicators of the prymnesiophyte and diatom groups respectively, but it is difficult to distinguish between co-production of these individual pigments by a single species and the possibility of the covariance of different species with differing pigment levels. Hence, we decided to adopt an adjusted version of the approach used by *Vidussi et al.* [2001], who calculate ratios of specific accessory pigments to Total Pigments (TP; the sum of concentrations of But, Hex, Allox, Fucox, Perid, Zeax, Divinyl Chl *b* and Chlorophyll *b*) in order to account for the covariance and create discrete biomarker pigment groups. These groups were defined as follows:

Group 1: Cyanobacteria (Zeax: TP)
Group 2: Prymnesiophytes (Hex+But: TP)
Group 3: Diatoms (Fucox: TP)
Group 4: Dinoflagellates (Perid: TP)

[21] A similar approach has already been shown to work well with the AMT data, creating logical groups at different depths of the water column [see *Poulton et al.*, 2006a]. Current understanding of the reduced sulphur cycle suggests that ambient DMS/DMSP concentrations should correlate better with certain biomarker pigment groups. The poorest DMSPt correlation found was with cyanobacteria (Table 3), a low DMSP-producing group that is dominated by *Prochlorococcus* and *Synechococcus* along the AMT transect [*Zubkov et al.*, 2000]. However, no strong DMS or DMSPt correlations with the other biomarker pigment groups were identified (Table 3). Indeed, this approach did not yield any better correlations than when correlation analysis was performed on individual accessory pigments (Data Set S1).

[22] The absence of any strong, significant positive correlations between major biogeochemical markers and biomarker pigments is an important result. It suggests that DMS and DMSP production in oligotrophic subtropical and tropical regions cannot easily be related to phytoplankton biomass (TChl *a*) or algal groups (based on biomarker pigments). It is possible that using size fractionated biomarker pigment data and/or information about the turnover rate of DMS/DMSP would be more informative, but we were not able to test such hypotheses.

3.2.3. Phytoplankton Physiological Status and Activity

[23] DMSP is a dynamic pool subject to both production and consumption processes, so it is somewhat logical that DMSPt might correlate better with rate measurements than standing stocks. There is some precedent for this in the literature: results from the ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment) experiment, demonstrated a diel variation in both ^{14}C-uptake and the rate of DMSP-production inferred from a 24 h on-deck incubation [*Simó et al.*, 2002]. More recently, using data from 5 Barents Sea cruises conducted over an 8 year period, *Matrai et al.* [2007] presented a correlation between depth-integrated values of DMSPt and total primary production over the seasonal cycle (from multiple years). These authors suggested that these results might be used at the mesoscale for modeling purposes over seasonal and interannual scales. Our data do not demonstrate quite as strong a correlation between either DMS or DMSPt and primary production (DMS: $\rho = 0.42$, $p < 0.01$, $n = 246$; DMSPt: $\rho = 0.46$, $p < 0.01$, $n = 228$), but the correlation between DMSPt and primary production rates associated with the large (>2 μm diameter) algal size fraction was strong ($\rho = 0.59$, $p < 0.01$, $n = 118$). These data are plotted (note the log scales due to non-parametric data distribution) with data points identified by *Longhurst* [1995] biogeochemical provinces (Figure 4a) and by AMT cruise (Figure 4b).

[24] These results suggest that, despite the mixed phytoplankton assemblage that would have been present, the rate of primary production in the >2 μm size fraction is strongly associated with the in situ DMSPt concentrations. Phytoplankton have relatively short life cycles and it is possible that rates of carbon and sulphur uptake, and by extension DMSPt production, are simply coupled to growth rates [*Stefels et al.*, 2007, and references therein]. Most of the known DMSP-producers (e.g., prymnesiophytes, dinoflagellates, diatoms) exist in the >2 μm size fraction, and there is evidence that this fraction represents approximately half of the primary production along the AMT transect [*Poulton et al.*, 2006a]. Contrastingly, we know much less about the phytoplankton groups in the picoeukaryote (<2 μm) size fraction and they

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/gb/2009GB003617.

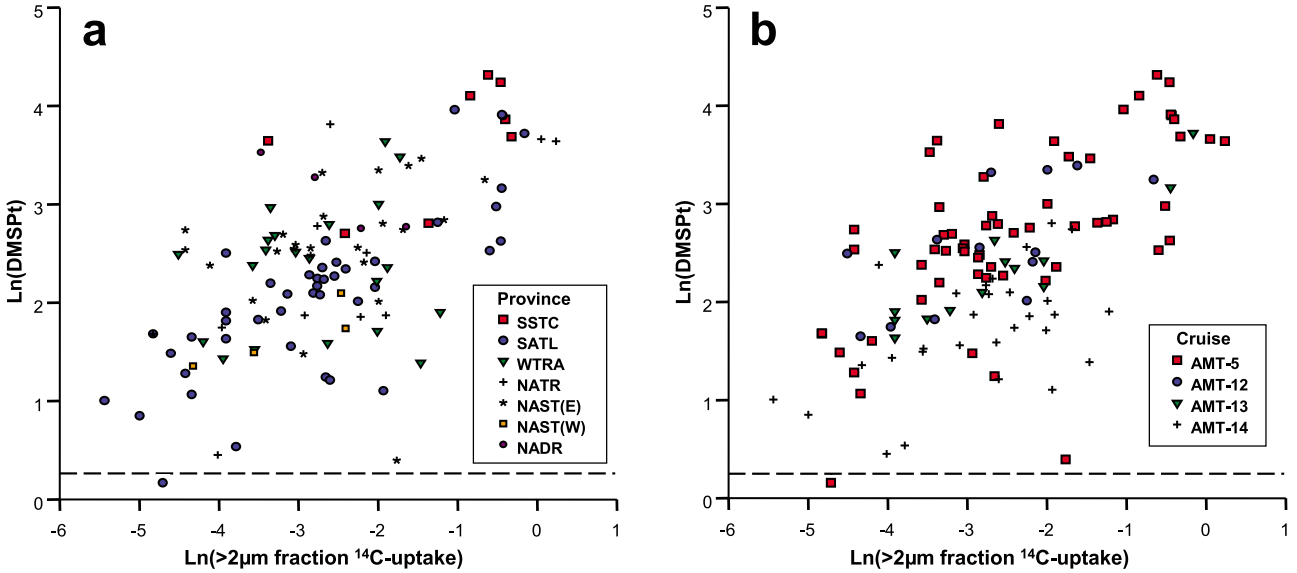

Figure 4. Log-log plot of ^{14}C-uptake (mg C m^{-3} hr^{-1}) in the >2 μm size fraction versus DMSPt (nM). (a) Each data point is identified by Longhurst biogeochemical province. (b) The same data set, identifying each data point by cruise. Detection limit for DMSPt is shown as a horizontal dashed line, and the data (n = 1) below this can only be quantified as <DL. No samples < DL for ^{14}C-uptake in the >2 μm size fraction were encountered.

may still contribute to a proportion of DMS and DMSPt production. In this regard, in a modeling study based on Sargasso Sea data, *Gabric et al.* [2008] highlight the potential importance of DMSP-producing picoeukaryotes as they may be more likely to exude DMS and DMSP.

[25] Spearman's Rank correlation identifies the strength of correlation but does not enable a trend line to be derived. Theil's Complete Regression [see *Miller and Miller*, 2000] accounts for the non-parametric distribution of all the data (unlike a Pearson's regression line) and produces the following regression equation:

$$\ln(\mathrm{DMSPt}) = 0.436.\ln\left(^{14}\mathrm{C}\right) + 3.502 \qquad (1)$$

where (DMSPt) represents the DMSPt concentration in nmol L^{-1} and (^{14}C) represents the rate of primary production in the >2 μm size fraction in mg C m^{-3} hr^{-1}. However, we urge caution in using this equation in a predictive capacity due to the variability inherent in our data.

[26] Figure 4a demonstrates that no individual ocean province is driving the relationship, but Figure 4b suggests that the results from AMT-5 are dominating the observed correlation. Although AMT-5 passed through many of the same biogeochemical provinces, the cruise track differs significantly from those of AMT-12-14 (Figure 1). These later cruises encountered more oligotrophic waters than AMT-5 and, as noted in the Methods, samples were collected pre-dawn rather than post-dawn, so we should consider the impact this might have upon the strength of the correlations identified. With AMT-5 data excluded, a correlation between DMSPt and primary production in the >2 μm fraction still exists, but just below the $\rho \geq 0.5$ correlation strength threshold defined earlier ($\rho = 0.48$, $p < 0.01$, n = 56). Interestingly, the opposite occurs for DMS, the correlation strength increasing from $\rho = 0.46$ ($p < 0.01$; n = 127) for all cruises to $\rho = 0.68$ ($p < 0.01$; n = 62) when AMT-5 data are removed. In addition, the significant ($p < 0.01$) correlations between total primary production and DMS also improve when AMT-5 data is removed, the correlation strength increasing from $\rho = 0.42$ (n = 246) to $\rho = 0.53$, (n = 181). Our data suggests that in situ DMS/DMSP concentrations cannot easily be attributed to phytoplankton groups (Section 3.2.1 and 3.2.2), yet the community primary production rate is related in some way. This has important implications for modeling such regions, suggesting that control of in situ DMSP may not be dominated by specific group(s) and that DMSP concentrations can be better represented by a net output product of the phytoplankton community. With the exception of *Matrai et al.* [2007], rather few of the DMS and DMSP data sets available are accompanied by primary production data. This work should prompt more parallel measurements of primary production and DMS/DMSP data, particularly in near-surface waters, to further investigate the potential of these correlations.

3.2.4. Photoprotective Pigments

[27] If DMSP and DMS participate in the anti-oxidative stress cascade mechanism proposed by *Sunda et al.* [2002], the rate of enzymatic conversion from DMSP to DMS via DMSP-lyase activity (DLA) would also need to increase. *Bell et al.* [2007] used AMT data to show that DLA is enhanced in surface waters relative to the chl max in the high-light environment of the subtropical oligotrophic gyres, although ancillary data were not fully able to explain the observed variability in surface DLA. These results and recent modeling studies infer an oxidative stress mechanism to explain increased summertime production of DMS and

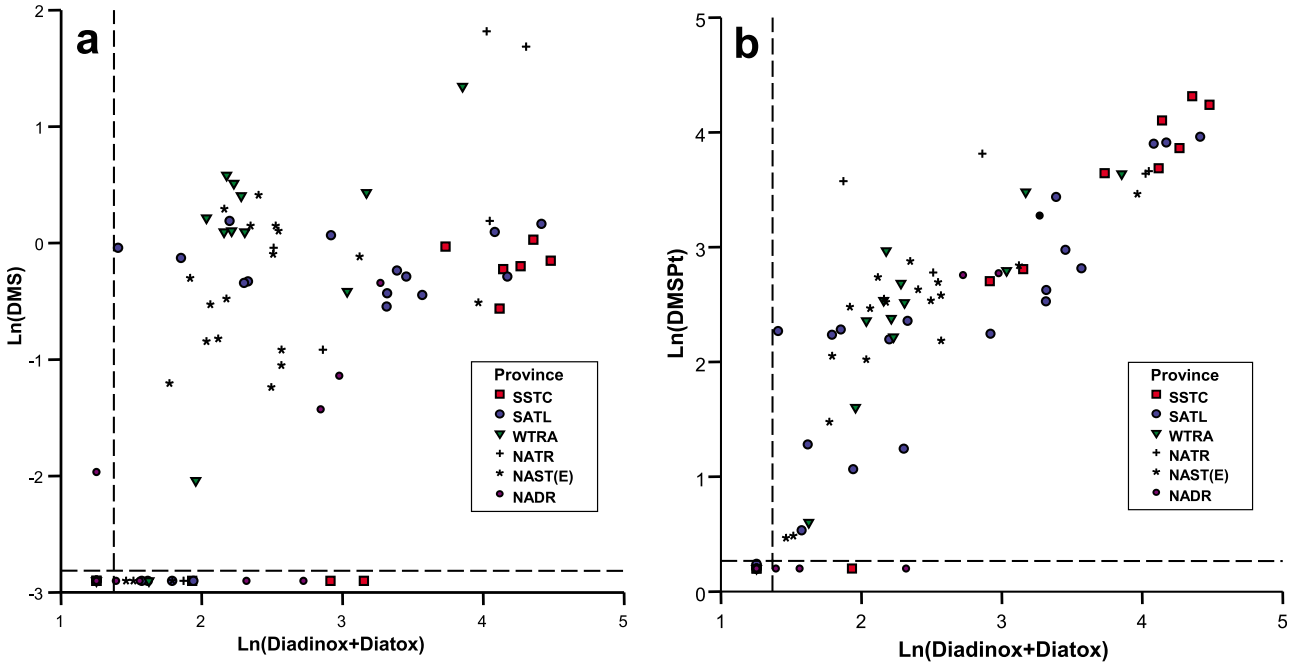

Figure 5. Log-log scatterplots of Diadinox+Diatox (ng L^{-1}) versus (a) DMS (nM) and (b) DMSPt (nM). Both plots identify each data point by Longhurst biogeochemical province. Detection limits for DMS and DMSPt are shown as horizontal dashed lines, and the data below these (DMS, n = 17 and DMSPt, n = 18) can only be quantified as <DL. In the same manner, the detection limit for Diadinox+Diatox is shown on both plots as a vertical dashed line, and the data below this (n = 14) can only be quantified as <DL.

DMSP in the Sargasso Sea [*Toole et al.*, 2008; *Vallina et al.*, 2008], and provide motivation for investigating in situ DMS/DMSP concentrations in terms of ancillary data that might indicate shifts in the physiological status of cells. In this regard, the production of accessory xanthophyll pigments involved in photoprotective cycles is of interest. The xanthophyll cycles dissipate potentially damaging energy as less harmful heat within the light-harvesting antenna through 'non-photochemical quenching' [*Porra et al.*, 1997]. Two xanthophyll cycles are known, one enzymatically removes an epoxy group from Diadinox to produce Diatox. The other cycle follows a similar process by converting Zeax to violaxanthin, with a short-lived intermediate, antheraxanthin [*Porra et al.*, 1997]. Increased concentrations of any/all of these accessory pigments could be used as an indicator of the phytoplankton community trying to cope with increased light stress.

[28] One approach used to address the role of photoprotective carotenoids (PPCs: Diadinox, Allox, Zeax and β-Car) is to consider them in the context of the photosynthetic carotenoids (PPS: But, Hex, Fucox, Perid and Prasinoxanthin). The percentage PPC (%PPC) was defined following *Gibb et al.* [2000]:

$$\%PPC = \frac{PPC}{(PPC + PPS)} \times 100 \quad (2)$$

Correlations between DMS/DMSP and %PPC were weak (DMS: ρ = 0.02, p > 0.05, n = 293; DMSPt: ρ = 0.08, p > 0.05, n = 269). This is not entirely surprising as the %PPC signal along AMT transects tends to be dominated by Zeax [*Gibb et al.*, 2000], which is a major pigment within the cyanobacteria [*Jeffrey and Vesk*, 1997] and these are poor DMSP-producers [*Keller et al.*, 1989]. Therefore we focused on the Diadinox-Diatox xanthophyll cycle, which is far less influenced by cyanobacteria.

[29] As Diadinox and Diatox are part of the same xanthophyll cycle, the total concentration of both can be used as an indicator of the prominence of this cycle within cell metabolism. Along the AMT transect, concentrations of Diatox are very low, difficult to detect and measurements of this pigment were given greater emphasis during AMT-5 than during AMT-12, −13 and −14. Data from AMT-5 displays a strong correlation between Diadinox+Diatox and both DMS (ρ = 0.63, p < 0.01, n = 87) and DMSPt (ρ = 0.90, p < 0.01, n = 83). The data are shown in Figures 5a and 5b and demonstrate that both high and low latitude (and thus variable primary production regimes) are as important in determining the strong association between these parameters. Theil's Complete Regression analysis produces the trend equations below:

$$\ln(\mathrm{DMS}) = 1.163.\ln(\mathrm{D} + \mathrm{D}) - 4.368 \quad (3)$$

$$\ln(\mathrm{DMSPt}) = 1.264.\ln(\mathrm{D} + \mathrm{D}) - 1.171 \quad (4)$$

where (DMS) and (DMSPt) represent the concentrations of DMS and DMSPt in nmol L^{-1} and (D+D) the Diadinox +Diatox concentration in ng L^{-1}. As with the primary production regression line (equation (1)), caution is urged before using these equations in a predictive capacity.

[30] Sampling for Diadinox, DMS and DMSPt occurred just before dawn (approx. 0300hrs local time) during AMT-12-14, and at this time it might be expected to find the highest Diadinox concentrations (because Diadinox is de-expoxidated during photosynthesis) and the lowest concentration of Diatox. For these samples, Diadinox alone may dominate the xanthophyll cycle signal, so it was correlated with DMS and DMSP for all cruises. A weak correlation was found between DMS and Diadinox ($\rho = 0.20$, $p < 0.01$, $n = 299$), but the correlation between DMSPt and Diadinox was strong ($\rho = 0.59$, $p < 0.01$, $n = 268$). At this juncture, the influence of the AMT-5 cruise track and data set must again be investigated. Without AMT-5 data, the correlation strength is reduced to $\rho = 0.39$ ($p < 0.01$, $n = 185$). In fact, the influence of AMT-5 is substantial and is clearly demonstrated in the DMSPt/Diadinox correlations for individual cruises: AMT-5 ($\rho = 0.91$, $p < 0.01$, $n = 83$); AMT-12 ($\rho = 0.43$, $p < 0.01$, $n = 80$); AMT-13 ($\rho = 0.40$, $p < 0.05$, $n = 38$); AMT-14 ($\rho = 0.27$, $p < 0.05$, $n = 67$). When AMT-5 is considered individually, a number of correlations between DMS/DMSPt and other phytoplankton marker pigments were stronger than in the whole data set (e.g., DMSPt versus Hex; $\rho = 0.71$, $p < 0.01$, $n = 83$). However, the DMSPt versus Diadinox and Diadinox+Diatox correlations are by far the strongest observed during AMT-5 (Data Set S1). Despite the strong influence of AMT-5, our results do suggest a linkage (either direct or indirect) between the photoprotective xanthophyll cycle and the putative antioxidant role for DMS and DMSP. Due to the differences in cruise track, time of sampling and correlations with other phytoplankton marker pigments, it is difficult to determine whether the variations in correlation strength are driven by spatial heterogeneity, variations in sampling time or differences in phytoplankton community composition.

4. Conclusions

[31] Using the substantial data set generated as part of the AMT program, we have produced representative DMS and DMSPt depth profiles and shown that these concentration profiles are remarkably consistent with depth relative to chlorophyll *a* (for example). This product should prove to be a useful model-validation tool for oligotrophic waters. The major biogeochemical markers (TChl *a*, POC and PIC) and, surprisingly, group-specific pigment biomarkers do not correlate well with DMS or DMSPt. This suggests that for the AMT data set, particular phytoplankton groups do not dominate in situ DMSP concentrations. Strong, significant associations ($\rho \geq 0.5$) were found with rates (^{14}C-uptake or primary production) or process indicators (the photoprotective xanthophyll cycle pigments). These correlations are somewhat unexpected as the primary production and Diadinox+Diatox data are from samples containing mixed phytoplankton communities. Hence, we infer that such associations are likely to be much stronger in the specific phytoplankton species producing the majority of the DMS and DMSP. Furthermore, the potential role of DMSP as the initial compound in an intracellular antioxidant defense cascade [*Sunda et al.*, 2002] would require a rapid response in cellular DMSP production. Levels of primary production and photoprotective pigment concentrations change in response to environmental conditions on relatively short timescales. In light of our results, we suggest that these parameters are worth considering as 'detectors' of physiologically induced changes in the DMSP system in plankton communities. Further work is required to establish why such correlations exist and confirm what is responsible for them, but they provide hope that a global linkage between DMS/DMSP and phytoplankton community parameters can be developed and quantified in the future.

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