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Investigating the inter-relationships between water attenuated irradiance, primary production and DMS(P)

C. J. Miles · T. G. Bell · P. Suntharalingam

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Abstract Both solar irradiance and primary production have been proposed as independent controls on seawater dimethyl sulphide (DMS) and dimethylsulphoniopropionate (DMSP) concentrations. However, irradiance also drives photosynthesis, and thus influences a complex set of inter-related processes that modulate marine DMS. We investigate the potential inter-relationships between the rate of primary production (carbon assimilation), water-attenuated irradiance and DMS/DMSP dynamics by applying correlation analysis to a high resolution, concurrently sampled in situ data set from a range of latitudes covering multiple biogeochemical provinces from 3 of the 4 Longhurst biogeochemical domains. The combination of primary production (PP) and underwater irradiance (Iz) within a multivariate regression model is able to explain 55% of the variance in DMS concentrations from all depths within the euphotic zone and 66% of the variance in surface DMS concentrations. Contrary to some previous studies we find a variable representing biological processes is necessary to better account for the variance in DMS. We find that the inclusion of Iz accounts for variance in DMS that is independent from the variance explained by PP. This suggests an important role for solar irradiance (beyond the influence of irradiance upon primary production) in mediating the relationship between the productivity of the ecosystem, DMS/DMSP production and ambient seawater DMS concentrations.

Keywords DMS · DMSP · Primary production · Solar radiation

Introduction

The CLAW hypothesis suggests that DMS could be part of a biologically mediated biogeochemical-climate feedback loop (Charlson et al. 1987) with global climatic significance. Seawater DMS concentrations are a critical link in this loop, modulating DMS flux to the atmosphere (Liss and Slater 1974) with a cloud albedo-climate control upon seawater DMS necessary for the operation of a feedback loop. DMS concentrations in the surface ocean are a product of the marine ecosystem and its environmental setting and the result of a complex interaction of sources and sinks (Stefels et al. 2007; Simó 2001). The main DMS precursor, DMSP, is closely associated with algal synthesis with phytoplankton speciation important for determining DMSP production (Keller et al. 1989;

C. J. Miles (✉) · T. G. Bell · P. Suntharalingam
Laboratory for Global Marine and Atmospheric
Chemistry (LGMAC), School of Environmental Sciences,
University of East Anglia (UEA), Norwich NR4 7TJ, UK
e-mail: c.miles@uea.ac.uk

Present Address:
T. G. Bell
University of California, Irvine, Irvine, CA, USA

Stefels et al. 2007). Once liberated within the water column, DMS can be metabolised by bacteria to dimethylsulphoxide (DMSO) and other non-volatile sulphur species (Kiene et al. 2000; Kieber et al. 1996), photo-oxidised to DMSO (Brimblecombe and Shooter 1986; Hatton 2002) or, due to its volatile nature, cross the sea/air interface (Liss and Slater 1974).

At the global scale, elevated DMS/DMSP [hereafter referred to as DMS(P)] concentrations are associated with regions of high productivity and biomass (Kettle et al. 1999; Lana et al. 2011). Water attenuated irradiance is a major control upon the productivity of marine ecosystems along with nutrients and temperature at regional to global spatial scales and at monthly to seasonal temporal scales (Behrenfeld and Falkowski 1997; Geider et al. 2001). Consequently, regional to global spatial scale and monthly to annual temporal scale DMS(P) distributions may be related to solar radiation via the modulation of productivity by water attenuated insolation.

At the local scale, underwater irradiances can be highly variable in space and time, inducing a range of physiological states from photoinhibition to light limitation as a result of mixing (depth variations), self shading, and insolation changes due to cloud cover variation or diurnal variation (Macintyre et al. 2000). A mechanism for maintaining photosynthesis at an optimum rate under the stresses of a constantly changing light environment could offer a significant selective advantage over the lifetime of a typical phytoplankton cell (hours to days). DMS(P) synthesis has been linked to the maintenance of photosynthetic efficiency in some laboratory studies (Sunda et al. 2002; Archer et al. 2010) with DMS and DMSP attributed roles as an antioxidant (Sunda et al. 2002) or as part of an overflow mechanism when growth is unbalanced (Stefels 2000). This suggests a possible inter-relationship between underwater irradiance, the rate of PP and DMS(P) synthesis.

Solar radiation also plays a role in modulating two major DMS loss processes; bacterial metabolism and photo-oxidation rates (Simó and Pedrós-Alió 1999a; Toole et al. 2003; Toole and Siegel 2004; Vallina et al. 2007). This offers the potential for an additional direct effect of solar radiation upon ambient DMS concentrations that is independent from the role of solar radiation in modulating PP. A strong positive correlation has been demonstrated between mixed layer irradiance (solar radiation dose, SRD) and monthly averaged surface DMS concentrations at regional and global scales (Vallina and Simó 2007). Miles et al. (2009) report a strong, significant correlation between DMS and SRD using a higher temporal resolution (daily) sampled dataset from the AMT programme. The mixed layer irradiance framework suggests a simultaneous increase in DMS(P) synthesis (via the antioxidant and/or overflow hypothesis), a shift in the species assemblage towards high DMS(P) producers and reduction in bacterial sulphur demand under high irradiances (Simó and Pedrós-Alió 1999a). This provides a plausible biophysical explanation as to why shallow mixed layers coincident with high summer insolation yield elevated DMS concentrations. However, the SRD methodology lacks a direct representation of biology and, although it is successful at explaining temporal DMS concentrations, a large amount of data averaging is required to observe a strong correlation across large spatial scales (Derevianko et al. 2009).

Previous analyses from in situ cruise measurements have demonstrated a correlation between PP and total DMSP (DMSPt: the sum of dissolved and particulate DMSP). Using data from the subtropical and equatorial regions of the Atlantic, Bell et al. (2010) report a strong correlation ($\rho = 0.59$, $p < 0.01$, $n = 118$) between DMSPt and PP (per hour, by cells >2 μm diameter). Using data from higher latitudes, Matrai et al. (2007) report a correlation between depth-integrated values of DMSPt and total PP (per day) over the seasonal cycle from 5 Barents Sea cruises. Bell et al. (2010) demonstrate a correlation between DMSPt and photoprotective pigments but neither of these analyses explored the direct influence of irradiance upon DMSP or DMS concentrations. In this study we apply multivariate correlation analysis to a compiled dataset of concurrently sampled DMS, DMSPt, PP and Chlorophyl *a* (Chl *a*) data from the ocean surface to the base of the euphotic zone. The dataset covers a range of seasons with data from 8 biogeochemical provinces representing 3 of the 4 biogeochemical domains as defined by Longhurst (1995) with an approximate latitudinal range of 78°N to 40°S. We use this dataset to investigate whether the water-attenuated irradiance (Iz) in the marine environment has an independent role in controlling DMSPt and DMS concentrations, beyond its role in modulating PP.

Methods

Data was collated from (1) the Atlantic Meridional Transect program (AMT), (2) the Barents Sea (BAR), (3) Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE) research campaign and (4) DImethyl Sulphide biogeochemistry within a COccolithophore bloom (DISCO) study (Fig. 1). Data was sampled from a range of ecosystems, latitudes and seasons from 8 biogeochemical provinces within 3 open ocean biogeochemical domains:

- Polar domain: Boreal Polar Province, BPLR; and Atlantic Subarctic Province, SARC.
- Westerlies domain: North Atlantic Drift Province, NADR; North Atlantic Subtropical Gyral Province West, NAST(W); and North Atlantic Subtropical Gyral Province East, NAST(E).
- Trade wind domain: North Atlantic Tropical Gyral Province, NATR; Western Tropical Atlantic Province, WTRA; and South Atlantic Gyral Province, SATL (Longhurst 1995).

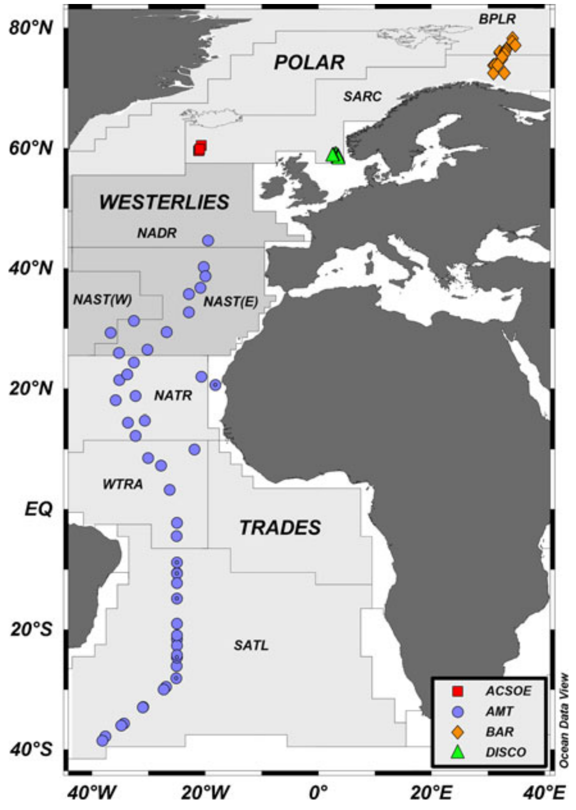

Fig. 1 Location of the four data subsets: ACSOE (*squares*); AMT (*circles*), BAR (*diamonds*), DISCO (*triangles*). Each marker represents a single depth profile, approx 6–8 samples per profile: DMSPt $n = 401$ (approx 48 profiles), DMS $n = 250$ (approx 36 profiles). *Grey lines* delineate biogeochemical provinces and shaded areas identify biogeochemical domains

The 3 cruises from AMT (AMT-12, 12th May–17th June 2003; AMT-13, 10th September–4th October 2003; and AMT-14, 26th April–2nd June 2004) were focused on the oligotrophic gyres of the North and South Atlantic, sampling from approximately 40°S to 40°N (see Bell et al. (2010) for further details). The BAR data comprises 5 cruises conducted in high latitude eutrophic waters including some sea ice zone samples during May 1993, March 1998, May 1998, June–July 1999 and July 2001 between approximately 72°N–78°N (see Matrai et al. (2007) for further details). ACSOE and DISCO were both Lagrangian bloom-tracking studies. DISCO tracked the development of a bloom of the coccolithophore, *Emiliania huxleyi* between the 16th and 26th of June 1999 in the northern North Sea at approximately 59°N [see Burkill et al. (2002) for further details]. The ACSOE North Atlantic Experiment tracked an *Emiliania huxleyi* bloom in a eddy south of Iceland between the 10th June and 4th July 1998 at approximately 60°N [see Jickells et al. (2008), Simó and Pedrós-Alió (1999b) for more details].

Data were available for analysis from 82 depth profiles of concurrently sampled DMS and DMSPt concentration (nmol l^{-1}), a measurement technique for PP, ^{14}C uptake rate (mg C m^{-3} day^{-1}), Chl *a* concentration (mg C m^{-3}), and an estimate of the fraction of surface irradiance available to the sample (Iz). For each depth profile, samples were taken from the surface to the base of the euphotic zone (1% of the surface irradiance) and at intermediate depths. Samples were considered concurrent if they were from the same profile and from the same sample depth ($z \pm 2$ m).

All DMS samples were filtered and measured using purge and trap (Turner et al. 1990) coupled with a gas chromatograph (GC) fitted with a flame photometric detector [see Archer et al. (2002), Bell et al. (2006, 2007), Burkill et al. (2002), Jickells et al. (2008), Matrai et al. (2007), Matrai (1997), Matrai and Keller (1993) for details), with the exception of DISCO samples, which were analysed using a mass spectrometer and the analytical protocol of Smith et al. (1999). DMSP samples were typically converted to DMS via cold alkali hydrolysis and, with the exception of some AMT samples that were analysed via headspace analysis (see Bell et al. 2006, 2007), were also analysed using the purge and trap GC technique. Whilst differences have been observed between different analytical techniques, what little data that has been collected on DMS inter-comparability suggests that variability between different techniques is likely to be $\leq$25% (Bell et al. 2011). Consequently we conclude that this does not present a significant problem for our study. The method of filtration used to determine dissolved DMSP (DMSPd) from particulate DMSP (DMSPp) has been reported to have a more significant influence upon results (Kiene and Slezak 2006). However, we only interpret total DMSP (DMSPp + DMSPd) data in our analysis and thus filtration artefacts were not considered to be such an issue.

Daily ^{14}C uptake rates (mg C m^{-3} day^{-1}) were determined by on-deck incubations for AMT, ACSOE, DISCO and some BAR data using filters to simulate underwater light levels. PP samples from all sources were determined as the difference between light and dark incubated samples to account for respiration. ACSOE cruises used the standard JGOFS ^{14}C methodology (see Savidge and Gilpin 1999). AMT, BAR and DI/SCO do not cite primary references for the ^{14}C methods but see Burkill et al. (2002), Poulton et al. (2006), Matrai et al. (2007), Matrai (1997) and Simó and Pedrós-Alió (1999b). In common with many other studies, some uncertainty is introduced when water samples are incubated on deck to yield daily PP rates with a potential disparity between simulated and actual abiotic and biotic environments (Marra 2002). Additionally, some BAR PP data were incubated in situ at the depths from which the water samples were made (Vernet et al. 1998) rather than on deck but this is not thought to introduce prohibitive differences in the results (Marra 2002). Studies undertaken in the North Atlantic (Joint et al. 1993) and North Sea (Joint and Pomroy 1993) did not find significant differences in the estimates of PP between on deck and in situ incubations. Chl *a* concentrations were measured using fluorometric methods: AMT and DISCO publications cite Welschmeyer (1994) as a primary reference while ACSOE and BAR publications do not cite primary references for the methods used (but see Burkill et al. (2002), Matrai et al. (2007) for further information).

Water attenuated irradiance (Iz) is the estimated 24 h averaged surface 300–3,000 nm irradiance (I_0est) at the sampling depth (z) (see Eq. 1). I_0est is a function of latitude, date and known astronomical constants (Brock 1981; Vallina and Simó 2007). I_0est is not an in situ measurement and does not take account of cloud variations as it assumes a constant 50% attenuation of top of atmosphere radiation which will dampen some variability in Iz. In common with other studies (Vallina and Simó 2007; Lana et al. 2011), we used total solar irradiance as a proxy for biologically relevant wavelengths (PAR and UV). It would be ideal to have used in situ measurements of PAR and UV from the cruises but these data were not available. Previous authors (Jerlov 1974, 1977; Jitts et al. 1976; Belviso et al. 2011) have used a fixed coefficient to estimate PAR wavelengths from total solar irradiance under clear skies. The application of this fixed coefficient approach would not change the correlation coefficients within our work. Baker and Frouin (1987) used a variable coefficient approach to adjust the clear sky coefficient and found a maximum difference of 0.06 in the ratio of I_0total:I_0PAR depending on water vapour, aerosol optical thickness and latitude. The variance introduced by cloud cover is larger than variation introduced by variable attenuation of the solar spectrum (Baker and Frouin 1987). We did try using a 10 years cloud adjusted surface PAR climatology derived from SeaWiFS data (http://www.science.oregonstate.edu/ocean.productivity/index.php) to calculate under water irradiance (Iz). This degraded the correlation relationships between DMS(P) and Iz, likely due to the poor spatial and temporal resolution of the climatological data (1/6th degree grid × only monthly resolution). This resulted in several profiles from each cruise being assigned the same irradiance value. In addition, the PAR climatology is a noon irradiance value as opposed to a 24 h average value. We calculated a daily averaged irradiance value so as to be comparable with our daily in situ PP rates. Previous authors have suggested that it is the attenuation of irradiance by the water column and its contents that offers the greater uncertainty when determining underwater irradiances (Baker and Frouin 1987; Smith and Baker 1981). We derive our underwater irradiance from a measure of the depth of the 1% surface irradiance and believe that this greater source of uncertainty has been accounted for more precisely. Light attenuation, expressed as a fraction of surface irradiance (σ) at the sample depth z (σ_z), was measured in situ concurrent with the DMS(P)/PP water samples. In some cases the σ_z value from the mid-morning cast of the previous day was used to calculate Iz because the water samples were collected at night (see Poulton et al. 2006).

$$I_z = I_0\mathrm{est} \times (\sigma_z) \tag{1}$$

From the Barents Sea data only the May 1993 cruise concurrently sampled DMS as well as DMSPt and PP. This results in a smaller dataset for DMS and PP data ($n = 250$), in comparison to concurrently measured DMSPt and PP measurements ($n = 401$). In addition there was no fractional surface irradiance data from the May 1993 cruise so there is no concurrent Iz and DMS data from the Barents Sea.

We applied direct multiple linear regression (MLR) analysis to this dataset. To account for the skewed distribution of the data, we used $\log_{10}$ transformed data in the regression analysis, and a Spearman's Rank test to evaluate bivariate correlations (Wilcox 2010). We also calculated the tolerance for the predictors to evaluate potential multicolinearity within the MLR. This is calculated as Tolerance $= 1 - R_n^2$ where R_n^2 is the coefficient of determination of the Independent Explanatory Variable (IEV) n on all other IEV's (Weisberg 2005). Tolerance is the proportion of an IEV's variance that is not accounted for by the other IEV's in the equation. A tolerance level close to 0 indicates multicolinearity (Weisberg 2005). All statistical calculations were performed using SPSS™ software. The Theil-Sen trend lines in Fig. 2 were derived by finding the median of all slopes for lines between all pairs of points with the intercept

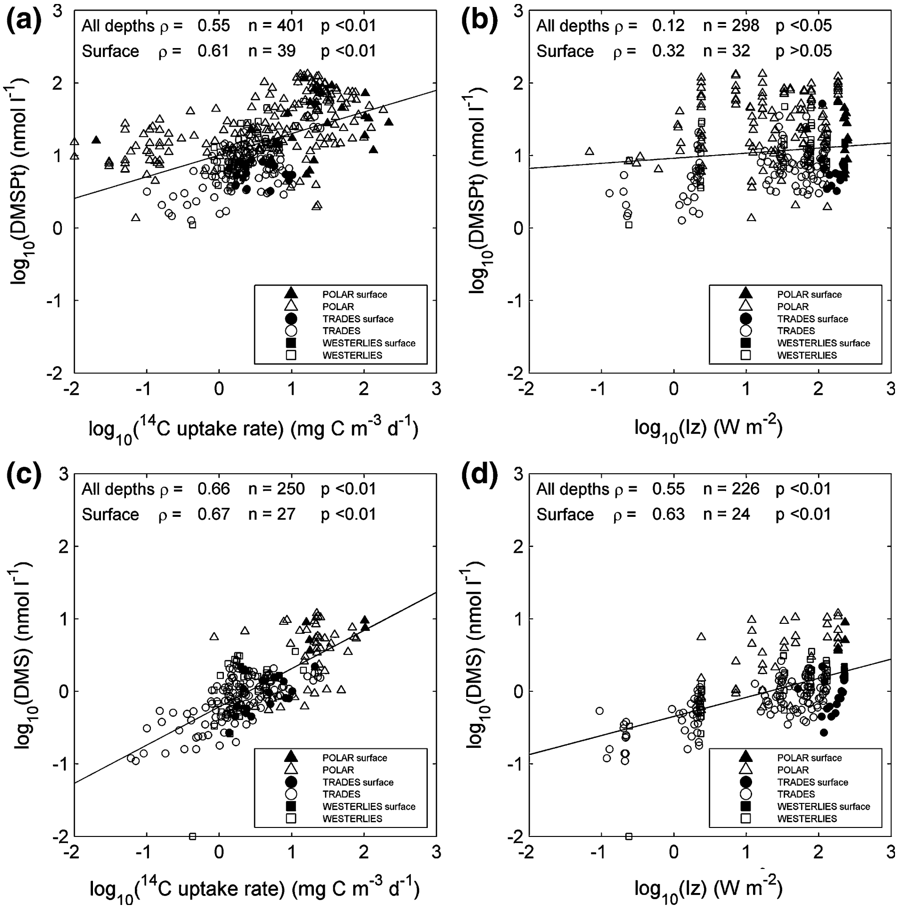

Fig. 2 Log-log (base 10) plots of DMSPt concentration (nmol l^{-1}) plotted against: **a** ^{14}C uptake rate (mg C m^{-3} day^{-1}); and **b** daily averaged underwater irradiance Iz (W m^{-2}). DMS concentration (nmol l^{-1}) plotted against: **c** ^{14}C uptake rate (mg C m^{-3} day^{-1}); and **d** daily average underwater irradiance Iz (W m^{-2}). Data shown from surface (*closed symbols*) and all other depths (*open symbols*) for the Polar biogeochemical domain (*triangles*), Trades biogeochemical domain (*circles*) and the Westerlies biogeochemical domain (*squares*) as defined by Longhurst (1995). Also shown are trendlines (*solid black line*) for data from all depths of the euphotic zone calculated using Theil-Sen (non-parametric) regression (Miller and Miller 2000)

calculated for the median slope. This non parametric technique is insensitive to outliers and thus appropriate for non-parametric data (Miller and Miller 2000).

We followed the approach of Bell et al. (2010) to define the criteria for a strong correlation, which reflects the inherent natural variability and relatively dynamic DMS(P) system. A correlation was considered strong if the absolute value of ρ was >0.5. A correlation was considered statistically significant if it met the threshold criteria of $p < 0.01$. The Hotelling-Williams test (HW test) as described by Steiger (1980) was used to evaluate the significance of any difference between correlation coefficients that share a common variable (e.g., the significance of any difference in the ρ value between DMS:PP and DMS:Chl). The HW test statistic is interpreted as one would a t-statistic with the p value reported as a measure of the error associated with rejecting the null hypothesis that the two correlation coefficients are equal (H_0: $\rho_{\mathrm{DMS:PP}} = \rho_{\mathrm{DMS:Chl}}$).

Results

All data

We analysed the data across all latitudes and found strong, significant correlations between concurrently sampled in situ PP and DMSPt ($\rho = 0.55$, $p < 0.01$, $n = 401$) and between concurrently sampled in situ PP and DMS ($\rho = 0.66$, $p < 0.01$, $n = 250$) from all depths of the euphotic zone (Fig. 2a, c; Table 1). Correlations between DMSPt and Chl *a* concentration ($\rho = 0.60$, $p < 0.01$, $n = 409$) are of comparable strength and significance to those between DMSPt and PP. The correlation between DMS and Chl *a* ($\rho = 0.40$, $p < 0.01$, $n = 250$) is weaker than that between DMS and PP. Analysis using the HW statistic (Steiger 1980) shows that the $\rho_{\mathrm{DMS:Chl}}$ coefficient value is significantly different (weaker) than the $\rho_{\mathrm{DMS:PP}}$ value ($p < 0.001$). There is little correlation between in situ DMSPt and estimated average daily water-attenuated irradiance at the sample depth (Iz) ($\rho = 0.12, p < 0.05, n = 298$). In contrast, the correlation between DMS and Iz is strong, positive and significant ($\rho = 0.55, p < 0.01, n = 226$) (Fig. 2b, d; Table 1).

A multiple linear regression (MLR) analysis of the correlation between DMS and the separate variables PP and Iz using the whole dataset yields a multiple correlation coefficient of $R = 0.74$, which is stronger than the correlation between DMS and either explanatory variable in isolation (Eq. 2).

$$\log_{10}(\mathrm{DMS}) = 0.539(\log_{10}(\mathrm{PP})) + 0.310(\log_{10}(\mathrm{Iz})) - 0.279 \qquad (2)$$

The adjusted R^2 for Eq. 2 ($R^2 = 0.55$) indicates that 55% of variability in DMS concentrations can be explained by these two variables (Table 1). The adjusted R^2 statistic corrects for the problem of additional explanatory variables increasing the correlation simply due to their inclusion (Weisberg 2005). The explanatory variables (PP and Iz) for the MLR do not exhibit a strong correlation to each other ($\rho = 0.4$, $p < 0.01$, $n = 345$) and the tolerance is significantly above zero (0.726) indicating that only ~30% of the variance in one explanatory variable is explained by the other and is not indicative of multicolinearity (Weisberg 2005). In addition, both explanatory variables in the MLR are significant ($p < 0.01$). In summary, these statistical tests indicate that the inclusion of PP explains additional variance in DMS concentrations, independent of the variance explained by Iz.

It is important to characterise concentrations of DMS as close to the surface ocean/lower atmosphere interface as possible for two reasons: (1) they are a

Table 1 Correlation coefficients are shown in bold whilst sample number (n) is shown in brackets below

	Spearman's Rank correlation coefficient (ρ)			MLR multiple correlation coefficient (R value)	Multiple linear regression (adjusted R^2 value)
	PP	Chl *a*	Iz	Input variables: PP and Iz	Input variables: PP and Iz
DMSPt	0.55 (401)	0.60 (409)	0.12* (298)	0.67	0.45
DMS	0.66 (250)	0.40 (250)	0.55 (226)	0.74	0.55

All correlations are significant with $p < 0.01$ unless marked*. R^2 is statistically adjusted to account for spurious correlation increases resulting from additional explanatory terms in MLR and/or small sample sizes (Weisberg 2005). MLR uses $\log_{10}$ transformed data to account for the non-normal distribution of data (Weisberg 2005) major control upon DMS flux to the atmosphere (Liss and Slater 1974; Johnson 2010), and (2) satellites can only typically observe the upper few metres of the surface ocean. We used the approach of Lana et al. (2011) and Kettle et al. (1999) to select surface DMS samples (i.e., <10 m) but use only the shallowest depth sample from each discrete CTD profile to capture data that is as close as possible to the sea-air interface. We find strong, significant correlations between surface PP and surface DMS ($\rho = 0.67$, $p < 0.01$, $n = 27$) and between surface DMS and Iz ($\rho = 0.63$, $p < 0.01$, $n = 24$) (Fig. 2c, d). Using the same MLR analysis as before yields a multiple correlation coefficient of $R = 0.84$, with an adjusted $R^2 = 0.66$ (see Eq. 3). As before, analysis of the tolerance level statistics does not suggest multicolinearity (tolerance = 0.822).

$$\log_{10}(\mathrm{DMS}) = 0.507(\log_{10}(\mathrm{PP})) + 0.240(\log_{10}(\mathrm{Iz})) - 0.745 \tag{3}$$

The PP and Iz data utilised here are representative of a timescale on the order of days. In contrast, DMS and DMSP typically have sub-daily turnover times (hours) and so a single sample from a discrete depth represents only a snapshot of the inherent natural variability. Individual concentrations (DMS(P) and Chl *a*) from discrete depths are also influenced by the mixing rate and mixing depth of the water body from which they are sampled and its environmental history. The same issue applies to the PP rates that are estimated from incubations either on deck at a constant replicated light level or in situ at a stationary depth. Our observed correlations in the discrete data should be interpreted within the context of this variability. To reduce the influence of discrete sampling depths on our results, we integrate data within each depth profile from the surface to the base of the euphotic zone. Applying the same statistical analyses to this data produces similar results to the discrete data; strong and significant correlations can be identified between depth integrated DMSPt and depth integrated PP ($\rho = 0.71$, $p < 0.01$, $n = 74$) and between depth integrated DMS and depth integrated PP ($\rho = 0.67$, $p < 0.01$, $n = 58$). The correlations between depth integrated DMS, DMSPt and Iz are significant but not strong (Iz and DMS, $\rho = 0.47, p < 0.01, n = 54$; Iz and DMSPt ($\rho = 0.39$, $p < 0.01$, $n = 65$). MLR analysis indicates that a combination of depth integrated PP and depth integrated Iz can explain 40% of the variance in depth integrated DMS with minimal multicolinearity ($R = 0.64$, $R^2 = 0.40$, tolerance = 0.987).

Biogeochemical domains

So far we have explored relationships across a range of ecological/biogeochemical environments but it is also interesting to examine whether these relationships persist within subdivisions of the data characterised by similar biogeochemical/ecological regimes. This dataset contains data from 8 biogeochemical provinces representing all 3 of the open ocean biogeochemical domains as defined by Longhurst (1995) (see Fig. 1). BAR, ACSOE and DISCO data come from the Polar domain with the majority located in the Boreal Polar Province (BPLR), which is characterised by eutrophic, high production environments with seasonal phytoplankton blooms. The majority of the AMT data come from the oligotrophic, gyral provinces of the North and South Atlantic (North Atlantic Subtropical Gyral Province West (NAST(W)), North Atlantic Subtropical Gyral Province East (NAST(E)), North Atlantic Tropical Gyral Province (NATR) and the South Atlantic Gyral Province (SATL)) from the Westerlies and Trades domains (see Fig. 1). These oligotrophic provinces are characterised by low production and biomass with a lack of strong seasonality (Longhurst 1995). As a result we find it appropriate to show aggregated data for the Westerlies and Trades as a single domain.

Data from within the individual biogeochemical domains displays similar trends as that from the dataset as a whole (Table 2) although all of the correlations are generally stronger in the entire dataset in comparison with the domains. Within each biogeochemical domain, the multiple correlation coefficient (R) generated using PP and Iz using MLR are strong and significant ($R = 0.66$–0.76, Table 2). These R values are stronger than the bivariate correlations between DMS and either of the explanatory variables within the MLR in isolation. MLR analysis is able to explain 41–56% of the variance in euphotic zone DMS concentrations for each biogeochemical domain using PP and Iz as explanatory variables (see Table 2). Multicolinearity analysis demonstrates that the explanatory variables explain independent variance within the MLR.

Table 2 Correlation coefficients for the data separated into Longhurst (1995) biogeochemical domains are shown in bold whilst sample number (n) is shown in brackets. All correlations are significant with $p < 0.01$ unless marked*. R^2 is statistically adjusted to account for spurious correlation increases resulting from additional explanatory terms in MLR and/or small sample sizes (Weisberg 2005). MLR uses $\log_{10}$ transformed data to account for the non-normal distribution of data (Weisberg 2005)

	Spearman's rank correlation coefficient (ρ)			MLR R	MLR adjusted R^2
	PP	Chl *a*	Iz	Input variables: PP & Iz	Input variables: PP & Iz
Polar domain					
DMSPt	0.56 (220)	0.33 (237)	0.10* (129)	–	–
DMS	0.38 (53)	0.18* (62)	0.55 (41)	0.66	0.41
Trades domain					
DMSPt	0.34 (126)	0.01*(119)	0.28 (126)	–	–
DMS	0.62 (120)	−0.10* (135)	0.53 (142)	0.72	0.50
Westerlies domain					
DMSPt	0.69 (43)	0.27 (40)	0.31 (43)	–	–
DMS	0.28* (43)	−0.42 (40)	0.62 (43)	0.76	0.56
Westerlies and Trades domains					
DMSPt	0.41 (169)	0.14* (159)	0.28 (169)	–	–
DMS	0.56 (185)	−0.10* (175)	0.58 (185)	0.70	0.49

Discussion

We find strong, significant correlations between DMS and PP and DMS and Iz in a compilation of water column measurements from a wide range of oceanic environments (Table 1). These correlations are observed in data collected from discrete depths within the euphotic zone, from near-surface waters and within depth profile integrated data. MLR analysis of the dataset as a whole suggests that to explain the maximum amount of variance in DMS concentrations a combination of PP and Iz is required. This MLR analysis is able to explain 55% of the variance in DMS concentrations from all depths of the euphotic zone, and 66% of the variance in surface DMS concentrations. These relationships are observed in a dataset that represents good latitudinal coverage and contains samples from all 3 of the open ocean biogeochemical domains defined by Longhurst (1995). The AMT cruises were focused on the oligotrophic gyres of the North and South Atlantic. ACSOE and DISCO samples were made during mid to high latitude phytoplankton (summer) blooms and the BAR cruises sampled the eutrophic high latitude Barents Sea with some samples from the sea ice zone. Despite the different trophic regimes, species assemblages, local oceanographic influences and different parts of the seasonal productivity cycle, the relationship holds across these temporal and ecological gradients.

An examination of the relative magnitude of the MLR coefficients associated with PP and Iz demonstrates that, of the parameters included, PP is the statistically dominant variable within the MLR both for the surface data and for data from all depths. This indicates that a measure of biological productivity is important for representing DMS concentrations across a gradient of ecological regimes with more productive regions yielding higher DMS concentrations. The correlation between DMS and the rate of PP ($\rho = 0.66$, $p < 0.01$, $n = 250$) is significantly stronger ($p < 0.001$; HW test) than that observed between DMS and Chl *a* ($\rho = 0.40$, $p < 0.01$, $n = 250$). A similar trend is also found within each domain or ecological/oceanographic region. Within each domain the correlation coefficient between DMS and PP is typically greater than between DMS and Chl *a*, especially in oligotrophic environments (Table 2). In addition, DMSPt is more strongly correlated to PP than to Chl *a* within the individual domains (Table 2). However, DMSPt is as closely associated with biomass (Chl *a* concentration) as it is to the rate of PP across the dataset as a whole (Table 1). The rate of PP is related to Chl *a* over larger spatial and temporal scales as high rates of PP allow the accumulation of biomass, which may hamper statistical differentiation between the two variables.

It has been suggested that the intracellular reduced sulphur cycle is involved in the optimisation of photosynthesis (Stefels 2000; Sunda et al. 2002). If so, the rate of PP may give a more instructive indication of DMS(P) production in the surface ocean rather than a measure of standing stock biomass such as Chl *a* concentration. The rate of PP may also be more comparable between different environmental conditions as it is possible for cells with different chlorophyll concentrations (due to species differences or variations in environmental conditions/photoacclimation) to photosynthesise at the same rate (Chow et al. 1990; Marra 1997). Chl *a* measurements are unable to distinguish between live, healthy cells and Chl *a* within dead, dying or photosynthetically inactive cells (Marra 1997). Attempts to correlate Chl *a* with DMS over large spatial and temporal scales have typically proved unsuccessful (e.g., Kettle et al. 1999; Kettle and Andreae 2000). Masotti et al. (2010) investigated the relationship between the Chl:DMS ratio and species dominance using remote sensing techniques, but concluded that this method could not be used to predict global fields of DMS. Smaller scale lagrangian studies, where bloom populations are dominated by a single phyla, have demonstrated such a correlation (e.g., Malin et al. 1993). This is often attributed to the difference in the ratio of carbon:DMSP produced by different species (Keller et al. 1989; Stefels et al. 2007).

Solar radiation plays a potential role in modulating the sources of DMS in the marine ecosystem and two major DMS loss processes; bacterial metabolism and photo-oxidation (Simó and Pedrós-Alió 1999a; Toole and Siegel 2004; Vallina and Simó 2007). Our results suggest an important role for solar radiation (beyond its influence on primary production) in mediating the relationship between DMS(P) synthesis activity and ambient seawater DMS concentrations. The bivariate correlations observed between DMS and Iz within the whole dataset and within each domain are strong and significant (Tables 1, 2). Although the idea that DMS may be related to Iz in oligotrophic waters is becoming more widely accepted (Toole and Siegel 2004; Toole et al. 2006; Vallina and Simó 2007; Vallina et al. 2008), it is less well established that Iz may be independently related to DMS in higher production, eutrophic waters. Iz is not statistically as important as PP within the MLR equations, but our analysis indicates that Iz explains additional variance in DMS independent of the variance explained by PP. However, we did not detect a role for the influence of irradiance upon DMSPt beyond its contribution to the rate of PP and found a weak correlation between DMSPt concentrations and Iz across all data and within each biogeochemical domain (Tables 1, 2).

The positive trend in the DMS and Iz data suggests that the suppression of the bacterial sink (Simó and Pedrós-Alió 1999a; Kieber et al. 1996), and/or the direct release of DMS under light stress (Sunda et al. 2002) is the dominant light-related process in this dataset (i.e., photo-destruction of DMS is a minor process). This is in agreement with other studies of water column DMS(P) dynamics (Kieber et al. 1996; Simó and Pedrós-Alió 1999a; Toole and Siegel 2004). Our results are also in broad agreement with the modelling study of Vallina et al. (2008), which invoked direct exudation of DMS by phytoplankton as the most important explanatory factor in resolving water column DMS concentrations at the oligotrophic Bermuda Atlantic Time-series (BATS) study station. Other global modelling studies also discuss the role of irradiance in driving modelled DMS concentrations beyond the solar forcing already driving the basic ecosystem model (Le Clainche et al. 2010; Vogt et al. 2010). Whilst the positive correlation between DMS and Iz indicates that photo-destruction of DMS is not a dominant process in this dataset, the suppression of DMS concentrations by high irradiance should not be completely discounted as a factor. For example, high surface irradiances are often experienced in the oligotrophic gyres and this process likely increases the noise observed within the overall trends identified.

If increased intracellular DMSP synthesis is related to the optimisation and maintenance of photosynthetic efficiency (Stefels 2000; Sunda et al. 2002) one might expect DMSPt concentrations to be increased under high Iz levels and/or demonstrate a stronger relationship to the rate of PP than to Chl *a*. A stronger relationship between PP and DMSPt relative to the correlation between DMSPt and Chl *a* was observed within each domain but not over the whole dataset/larger ecological gradient. A limitation of this work is that the spatial and temporal resolution of this analysis does not allow a full assessment to be made of the possible contribution of Iz and/or PP to DMSP synthesis. A PP rate compared on an equivalent timescale with a rate measurement of DMSP synthesis (rather than a DMSP concentration) would be necessary to resolve these issues.

A limitation of looking for statistical relationships between data from discrete depths is that the in situ DMS(P) concentrations and PP rates at each sampling depth reflect the environmental conditions over the range of depths that the water mass has experienced over a given time period due to vertical mixing. As such both the daily rate of PP incubated at a constant simulated light depth and an instantaneous DMS(P) or Chl *a* concentration may not be truly representative ecosystem values. To attempt to account for this issue we integrated each depth profile from the surface to the base of the euphotic zone. This depth integrated data follows similar trends to the data from discrete depths within the euphotic zone, suggesting that DMS and DMSPt concentrations are influenced by the interplay between light and PP anywhere within the euphotic zone. An advantage of collecting such a large dataset is that a general trend can be detected despite the fact that instantaneous DMS(P) concentrations from discrete depths may reflect natural variability in space and time in a dynamic and complex system with sub-daily turnover times. The strength of the observed correlations should be interpreted in this context.

The results of our analyses broadly support the proposed biophysical framework where microbial communities experiencing high average mixed layer irradiance exhibit high net surface DMS concentrations (Simó and Pedrós-Alió 1999a; Toole et al. 2003, 2006; Toole and Siegel 2004; Vallina and Simó 2007). The reported positive relationship between mixed layer irradiance (SRD) and monthly surface seawater DMS concentrations (Vallina and Simó 2007) is a necessary condition for the operation of a negative feedback as proposed by the CLAW hypothesis (Charlson et al. 1987). However, the SRD equation is constructed solely from abiotic variables and does not contain a term that directly represents the productivity or biomass of the DMS(P)-producing ecosystem. Derevianko et al. (2009) demonstrated that although the SRD has shown strong correlations to DMS at local scales, the correlation is weaker at the global level without high levels of data aggregation, and that the correlation between SRD and DMS may be largely driven by MLD variability. Derevianko et al. (2009) proposed that seasonal variation in surface DMS concentrations may be controlled by SRD (through physical changes in light and MLD altering mixing, nutrient availability, etc.) whilst spatial variation may be controlled by trophic status. Our multiple correlation analysis suggest that an indicator of biological production (PP) is important for explaining maximal variance in DMS concentrations both across a large latitudinal and ecological gradient and within different biogeochemical/trophic regimes, with an irradiance parameter explaining additional variance.

Our results suggest that when using an explanatory framework it is important to couple biological dynamics (e.g., primary production) with physical forcings such as light and MLD. It is plausible that some environmental changes impact the DMS-relevant biological system without influencing mixed layer irradiances and mixing. For example, decreased carbonate availability arising from future ocean acidification may impact calcareous, high DMSP-producing coccolithophore species such as *Emiliania huxleyi* (Beaufort et al. 2011; Caldeira and Wickett 2005; Hopkins et al. 2010; Kroeker et al. 2010). Elsewhere, increased atmospheric nutrient deposition resulting from local, regional and/or global climate change may increase algal production (Mahowald et al. 2005) while increased deposition of some toxic metals (e.g., lead) may have the opposite impact (Paytan et al. 2009). Phytoplankton species composition changes may also result from such impacts, which will either favour or inhibit DMS(P)-producing phytoplankton. Over the last century, Boyce et al. (2010) report a global decline in phytoplankton production of $\sim 1\%$ year^{-1} and future global productivity is predicted to decline further (Polovina et al. 2008). The balance of drivers affecting the present (and future) marine ecosystem and the subsequent impacts on surface ocean DMS concentrations can only be fully captured in predictive algorithms by improving existing understanding of the relationship between environmental variables and DMS(P) dynamics.

Conclusions

Within a broad ranging and large dataset, we find that a variable representing biological processes (PP) in combination with the calculated underwater irradiance level (Iz) account for maximal variance in DMS concentrations across a range of latitudes and ecosystem types. Furthermore we find that the variance explained by Iz is independent from the variance explained by PP. This confirms previous work, which suggests an important role for solar irradiance (beyond the direct influence on the rate of PP) in mediating the relationship between the productivity of the ecosystem, DMS(P) production and ambient seawater DMS concentrations. These results broadly support the proposed biophysical framework where microbial communities that experience higher mixed layer average irradiances may exhibit higher net surface DMS concentrations (Simó and Pedrós-Alió 1999a; Toole et al. 2003, 2006; Toole and Siegel 2004; Vallina and Simó 2007). In addition, whilst previous studies have been unable to identify links between DMS and biological markers such as Chl *a* or other biomarker pigments, our results suggest that a large-scale link exists between the biological community and in situ DMS concentrations, which is moderated by processes directly influenced by the in situ irradiance. It is important that these inter-relationships are well characterised within the context of global changes in physical parameters such as irradiance and mixing, and future marine ecosystem dynamics and productivity.

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