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Testing the relationship between the solar radiation dose and surface DMS concentrations using high resolution in situ data

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Abstract

We tested the recently proposed, strong positive relationship between dimethylsulphide (DMS) concentrations and the solar radiation dose (SRD) received into the surface ocean. We utilised in situ daily data sampled concurrently with DMS concentrations from the Atlantic Meridional Transect (AMT) programme for the component variables of the SRD; mixed layer depth (MLD), surface insolation (I_0) and a light attenuation coefficient (k), to calculate $\mathrm{SRD}_{\text{in situ}}$. We find a significant correlation (ρ=0.53) but the slope of the relationship is approximately half that previously proposed. The correlation is improved (ρ=0.76) by replacing the in situ data with an estimated I_0 (which assumes a constant 50% removal of the top of atmosphere value; 0.5×TOA), a MLD climatology and a fixed value for k following a previously described methodology. Equally significant, but non-linear relationships are also found between DMS and both in situ MLD (ρ=0.73) and the estimated I_0 (ρ=0.76) alone. The DMS data shows an interesting relationship to an approximated UV attenuation depth profile. Using a cloud adjusted, satellite climatology of surface UVA irradiance to calculate a UV radiation dose (UVRD) provides an equivalent correlation (ρ=0.73) to DMS. With this data, MLD appears the dominant control upon DMS concentrations and remains a useful shorthand to prediction without fully resolving the biological processes involved. However, the implied relationship between incident solar/ultraviolet radiation dose and sea surface DMS concentrations (modulated by MLD) is critical for closing a climate feedback loop.

1 Introduction

Dimethylsulphide (DMS) is a climatically important biogenic sulphur compound present in surface ocean waters at sufficient concentrations to sustain a significant flux to the remote marine atmosphere (Bates et al., 1992). There, sulphate aerosols derived from the oxidation of DMS are a major source of cloud condensation nuclei (CCN), promoting cloud formation and increasing cloud albedo (Andreae and Crutzen, 1997; Ayers et al., 1991; Ayers and Gillett, 2000; Berresheim et al., 1993; Sciare et al., 2001). The resulting impact at the surface is expected to be a reduction in solar insolation and a net cooling. The CLAW hypothesis proposes a feedback loop whereby phytoplankton producing DMS alter their environment by modulating incoming solar radiation, engendering a change in surface ocean conditions whilst simultaneously increasing cloud albedo, with global climatic consequences (Charlson et al., 1987). A prerequisite for the closure of any feedback loop is that environmental variables affected by cloud cover (e.g. insolation, temperature) can in turn influence seawater DMS concentrations. However, the controls on seawater DMS concentrations (hereafter [DMS]) and its associated biological processes are complex and are yet to be resolved (Simo, 2001).

Various biogeochemical and physical parameters have been proposed as controls on seawater [DMS] and attempts have been made to incorporate some of the most rigorous into explanatory/predictive algorithms. These include an algorithm using chlorophyll concentration, light and a nutrient term based upon Michaelis-Menton kinetics (Anderson et al., 2001) and algorithms based upon plankton community composition indexes calculated from accessory pigment concentrations (Aumont et al., 2002; Belviso et al., 2004b). A proposed relationship between mixed layer depth (MLD) and [DMS] (Simo and Pedros-Alio, 1999) was adapted and extrapolated to produce global DMS fields derived from MLD and chlorophyll-*a* concentration (Simo and Dachs, 2002). Aranami and Tsunogai (2004) investigated the MLD-based relationship using regional data and suggested that much of the variance in DMS concentrations could be explained by a simpler relationship with MLD alone based on a dilution effect. Belviso et al. (2004a) compared the five aforementioned algorithms utilising a global database of surface seawater DMS concentrations (http://saga.pmel.noaa.gov/dms/) and found that different algorithms are more skilful predictors of DMS concentrations in different regions. Bell et al. (2006) analysed data collected as part of the Atlantic Meridional Transect (AMT) programme to test these predictive algorithms and found that a refined version of the Aranami and Tsunogai (2004) algorithm ([DMS] $\alpha 40/\mathrm{MLD}$) was the best

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fit for the data.

Recently, Vallina and Simo (2007) have demonstrated a strong positive relationship between sea surface [DMS] and the solar radiation dose (SRD) received into the upper mixed layer of the ocean utilising monthly averaged data. A further strong positive relationship has been reported between the SRD, atmospheric DMS oxidation and satellite derived CCN over large areas of the global ocean (Vallina et al., 2007). The SRD methodology combines a climatological mixed layer depth (MLD), the estimated solar radiation incident at the surface (I_0) derived from a top of atmosphere value (0.5×TOA) and the attenuation of total solar radiation within the water column (k) represented by a fixed value (0.06). The SRD is essentially a measure of the average light level experienced by the cells confined within the mixed layer in Wm^{-2}. This positive relationship potentially closes a negative feedback loop between incident solar radiation and marine emissions of DMS, sulphate aerosols, CCN, cloud albedo and climate postulated by the CLAW hypothesis.

Central to the relationship between SRD and seawater [DMS] is the proposed interaction between incident surface radiation and MLD. The depth of the mixed layer is expected to have a substantial influence on DMS concentrations (Simo and Pedros-Alio, 1999). Stratified waters, although sustaining a lower overall phytoplankton biomass, are characterised by a species assemblage composed of more prolific dimethylsulphoniopropionate (DMSP) producers (Simo and Pedros-Alio, 1999). DMSP is the dominant biological precursor to DMS as DMSP cleavage by lyase enzymes is a significant DMS production pathway (Steinke et al., 1998, 2002). In addition, a shallow mixed layer results in elevated exposure to UV irradiance, which inhibits heterotrophic bacterioplankton production as a result of DNA damage caused by UV-B radiation (Herndl et al., 1993; Slezak et al., 2001). This leads to a reduced sulphur demand and so reduced DMS consumption rates (Simo and Pedros-Alio, 1999). The combination of these factors increases DMS concentrations when surface waters are highly stratified.

Laboratory studies of the diatom *Thalassiosira pseudonana* and the prymnesiophyte *Emiliania huxleyi* have shown that elevated DMS production occurs in response to high UV irradiance with the largest effect under exposure to UV-A wavelengths (320–400 nm) (Sunda et al., 2002). Oxidative stressors (including UV) generate harmful free radicals in the cell, while DMSP, DMS and subsequent DMS oxidation products have been shown to readily scavenge hydroxyl radicals and other reactive oxygen species, relieving oxidative stress (Sunda et al., 2002).This suggests an antioxidant function for the DMS(P) cycle, linking it with UV-induced oxidative stress in marine phytoplankton (Sunda et al., 2002). DMS can also be removed from the water column by photo-oxidation to dimethyl sulfoxide (DMSO) following exposure to UV-B radiation (Brimblecombe and Shooter, 1986), whilst (Kniveton et al., 2003) have demonstrated that extreme changes in UV can cause a reduction in atmospheric DMS on a daily timescale. Thus the same shallow MLD and high insolation levels and durations associated with peak summer [DMS] are seemingly ideal for high photochemical loss rates. The photo-oxidation of DMS does not typically dominate as a loss term because it is dependent upon the presence of chromophoric dissolved organic matter (CDOM) which is at lowest concentrations in the summer (Siegel and Michaels, 1996). Summer is when the MLD is shallowest and UV irradiance levels are highest and these factors combined (SRD) may help explain the DMS “summer paradox” whereby peak [DMS] occur in the summer despite phytoplankton production, biomass and chlorophyll levels reaching maxima earlier in the year (Toole et al., 2003).

Considering the current state of knowledge, we decided to test the reported relationship between SRD and seawater [DMS] (Vallina and Simo, 2007). Recently, Belviso and Caniaux (2009) also tested the strength of the SRD-DMS relationship in the North-East Atlantic (using data from the Programme Ocean Multidisciplinaire Meso-Echelle (POMME) experiment). From their data, they conclude that SRD and DMS do not demonstrate a strong correlation (with SRD accounting for only 19%–24% of the variance associated with monthly surface DMS concentrations). However, their DMS data is not normally distributed and the result from their Spearman’s Rank correlation analysis may be more appropriate, suggesting a stronger correlation of ρ=0.74. The authors then conducted a sensitivity analysis using different versions of the SRD equation and suggest that the DMS-SRD relationship is heavily influenced by the choice of irradiance attenuation law (k).

In contrast to Vallina and Simo (2007) and Belviso and Caniaux (2009), our study uses in situ, daily data from the AMT project sampled concurrently with DMS concentrations for all component variables of the SRD (MLD, I_0 and k) to calculate $\mathrm{SRD}_{\mathrm{in\,situ}}$. The AMT DMS data is also compared to a SRD calculated using climatological/estimated inputs ($\mathrm{SRD}_{\mathrm{clim}}$) using the same data sources as Vallina and Simo (2007). Our results broadly support those presented in Belviso and Caniaux (2009), but also elaborate upon the importance of MLD in the SRD equation. We also attempt to directly address UVA by calculating an ultraviolet radiation dose (UVRD) adapted from the SRD equation. Finally, a comparison is made to the work of Bell et al. (2006) who previously found the best fit to the AMT DMS data to be a simple relationship with MLD alone (40/MLD) (see Methods for details).

2 Methods

The SRD combines the depth of the mixed layer (MLD), the incident solar radiation at the surface (I_0) and its attenuation within the water column (k) (Vallina and Simo, 2007):

$$\mathrm{SRD}=\frac{I_0}{k\cdot\mathrm{MLD}}\cdot\left(1-e^{-k\cdot\mathrm{MLD}}\right) \tag{1}$$

Vallina and Simo (2007) use a fixed value of k representative of the attenuation of total solar radiation by clear ocean water (0.06) and estimate I_0 on the assumption that a constant 50% of the solar radiation incident at the top of the atmosphere reaches the surface (0.5×TOA). MLD is taken from a 2°×2° resolution global climatology (Montegut et al., 2004). The mixed layer is characterised by almost vertically uniform salinity, temperature, and density profiles. The MLD is defined as the point at which a departure from this uniform state can be detected based upon an arbitrary choice of criteria such as temperature, salinity or density (Montegut et al., 2004). The climatological MLD is defined as a temperature change of 0.2°C from a near surface value (10 m) (Montegut et al., 2004).

In this study we use daily in situ data for the components of the SRD equation (I_0, MLD, k) and surface [DMS] sampled concurrently during the AMT programme. The AMT program undertakes research cruises between the UK and the Falkland Islands transecting a range of ecosystems but focusing upon the oligotrophic mid-ocean gyres of the North and South Atlantic. This study uses data collected during Northern Hemisphere autumn (cruises AMT-12 and AMT-14) and spring (AMT-13) (see Bell et al., 2006, for more detail). For incident solar radiation (I_0), daily averages of the continuous shipboard measurements of total solar radiation (300–3000 nm) in Wm^{-2} were used. The in situ MLD is defined using the same criteria as the MLD climatology, a temperature departure of 0.2°C from a reference depth of 10 m (to avoid the effect of diurnal heating) (Bell et al., 2006). The MLD measurements are sampled concurrently with [DMS] along the cruise track at pre-dawn (03:00 h local time) each day. The attenuation coefficient (k) used for the $\mathrm{SRD}_{\text{in situ}}$ was calculated using the sampled 1% light level depth (Z_e) defined as the depth (m) to which 1% of the light incident at the surface penetrated on the previous day's mid-morning (11:00 h local time) cast ($k=\ln(0.01)/Z_e$). We also calculated an ultraviolet radiation dose (UVRD) (Eq. 2) based on the SRD equation (Eq. 1) but using a satellite climatology of UV from NASA's Total Ozone Mapping Spectrometer (TOMS) in place of in situ surface total solar irradiance (I_0). This is in the form of noon irradiances at a $1^{\circ}\times 1^{\circ}$ degree grid box resolution at the surface in $\mathrm{mW\,m^{-2}\,nm^{-1}}$ at 380 nm (UVA). This product incorporates the column ozone amount and cloud conditions taking into account sun-earth distance, solar zenith angle, total ozone amount, tropospheric aerosol optical depth and cloud transmission (Herman and Celarier, 1997) and is available from the TOMS project at http://toms.gsfc.nasa.gov/ery_uv/new_uv/. A constant attenuation coefficient ($k=0.16$) appropriate for the attenuation of UV under the oligotrophic conditions sampled was applied (Diffey, 1991; Smith and Baker, 1979) as no appropriate in situ measurements were available.

$$\text{UVRD}=\frac{\text{UV 380 nm}}{k\cdot\text{MLD}}\cdot\left(1-e^{-k\cdot\text{MLD}}\right) \quad (2)$$

These results are also compared to a simpler relationship between MLD and [DMS] (Eq. 3) previously found to be the best fit to this data by Bell et al. (2006)

$$\text{DMS}\alpha\frac{40}{\text{MLD}} \quad (3)$$

3 Results

3.1 SRD

When utilising the SRD methodology in conjunction with the in situ AMT data for all of the SRD variables (k, I_0, MLD) ($\text{SRD}_{\text{in situ}}$) we find a significant correlation (ρ=0.53) between SRD and [DMS]. The slope of this relationship is approximately half that suggested by Vallina and Simo (2007) to be appropriate for the longer term climatological mean situation (Fig. 1.). Vallina and Simo (2007) demonstrate that the SRD is connected to the seasonal DMS cycle at the global level ($10^{\circ}\times20^{\circ}$ grid boxes) and at two fixed locations using monthly averaged data. In contrast the AMT data is composed of high temporal resolution data, which although exhibiting significant spatial coverage, represents less seasonal variation with only a few months of the seasonal DMS cycle represented (Northern Hemisphere autumn and spring). As such a complete comparison between the two data sets is not possible. However, it is interesting that a significant correlation still exists between the SRD and DMS concentrations over this shorter, high resolution in situ data series.

The correlation fit to the AMT [DMS] is improved (ρ=0.76) when the in situ data is replaced with climatological inputs to the SRD calculation (SRD_{clim}) following the methodology of Vallina and Simo (2007). An initial motivation of this research was to attempt to improve upon the handling by Vallina and Simo (2007) of these climatological variables, Io (0.5×TOA), MLD (climatology) and k (fixed). A comparison of the AMT in situ data with climatological data does yield statistically significant correlations. The climatological and in situ MLD compare reasonably well (ρ=0.64, n=64, p<0.01) although the climatological MLD significantly underestimates the range of MLD and exhibits a shallow bias when compared with the observed, in situ MLD data from AMT (in situ: range 11.5–221.5 m, mean 47.3 m; climatology: range 6.0 m–58.0 m, mean 19.4 m). The in situ and climatological I_0 values compare less favourably although a statistically significant correlation exists (ρ=0.45, n=64, p<0.01). The climatological I_0 also underestimates the range of solar radiation incident at the surface when compared to the in situ data (in situ: range 86.2–530.6 $\mathrm{W m^{-2}}$, mean 338.3 $\mathrm{W m^{-2}}$; climatology: range=197.8–483.8 $\mathrm{W m^{-2}}$, mean 442.0 $\mathrm{W m^{-2}}$). This relatively weak correlation and underestimated range can be explained because the estimated Io uses a 0.5×TOA value which does not account for varying cloud cover. In this shorter, high resolution dataset, variable cloud cover is expected to play an important role especially given the AMT cruise track crossing the equator and the inter-tropical convergence zone (ITCZ). The fixed value of k (0.06) utilised by Vallina and Simo (2007) falls within the range of in situ k values from the AMT dataset (0.03–0.11, mean: 0.05).

We find equally significant, but non-linear relationships between both in situ MLD and [DMS] (ρ=0.73) as previously described by Bell et al. (2006) for this data and between the 0.5×TOA I_0 and [DMS] (ρ=0.76). To investigate this further we examined the components of the SRD equation to try and determine their respective influences upon the observed correlations between the SRD and [DMS] (Table 1).

Replacing the in situ, variable light attenuation coefficient (k) within the SRD equation with a fixed value (0.06) uniformly increases the correlation with [DMS] (Table 1). This could partly explain the difference in the correlation to [DMS] between $\mathrm{SRD_{in\,situ}}$ and $\mathrm{SRD_{clim}}$. The correlation to [DMS] is also always increased when the in situ I_0 is replaced with the estimated I_0 (0.5×TOA). Furthermore, holding I_0 constant within the SRD improves upon correlations obtained using the in situ I_0 data but not upon the correlation obtained utilising estimated I_0 (Table 1). Replacing the in situ MLD with the climatological MLD generally weakens the correlation to [DMS] across the range of equations (except in combination with an estimated I_0 and a fixed k where it is unaltered) (Table 1). Fixing the MLD significantly decreases the correlation in conjunction with in situ I_0. However, a fixed MLD in combination with an estimated I_0 (0.5×TOA) returns a high correlation (Table 1). None of the SRD permutations offer a substantial improvement upon the simpler relationships between [DMS] and MLD (40/MLD) (ρ=0.73) or the I_0 that is derived from a TOA value and does not account for cloud (ρ=0.76).

3.2 UVRD

The DMS data displays interesting "partitioning" into *estimated* UVA and UVB penetration depth zones (Fig. 2). This could be interpreted as supportive of observations from the literature that link DMS and incident UV radiation (Herndl et al., 1993; Slezak et al., 2001; Sunda et al., 2002). These depth zones are based upon approximate penetration depths of UVA (60 m) and UVB (30 m) into the water column under oligotrophic conditions (Diffey, 1991; Smith and Baker, 1979). Figure 2 shows a trend line for the simple inverse relationship between DMS and MLD (DMS α40/MLD) with estimated UVA and UVB penetration depth zones and the mean DMS value for the dataset (1.42 nM). DMS concentrations are elevated to above average values when the MLD is within the combined UVB/UVA zone (<30 m). When the MLD is in the UVA zone (30–60 m), DMS levels display both above and below average values. When the MLD extends below 60m and beyond the influence of UV, most DMS values are below average.

Figure 2 led us to investigate the SRD equation from the perspective of surface UV irradiance (UVRD Eq. 3) utilising a cloud adjusted satellite climatology for surface UVA irradiance (no direct measurements of UV were available from the AMT) within the SRD methodology (see Methods for details). A fixed value for k was adopted as no direct measurements were available from the AMT with an appropriate value for these oligotrophic conditions selected from the literature (k=0.16) (Diffey, 1991; Smith and Baker, 1979). The best results were achieved when using UVA (380 nm) in this study. This is consistent with the literature. Toole and Siegel (2004) attribute observed patterns of DMS cycling in the oligotrophic Sargasso Sea to a stress forced mechanism associated with UVA (325 nm) irradiance. Sunda et al. (2002) find elevated DMS concentrations with exposure to UVA wavelengths (320–400 nm) under laboratory conditions. The best results in this study were achieved when using UVA (380 nm).

The UVRD is well correlated to DMS concentrations from AMT (ρ=0.73) (Fig. 3) and is a better fit to the DMS data than the $\mathrm{SRD_{in\,situ}}$ with either variable, in situ k values (ρ=0.53) or fixed k values (ρ=0.65). However, the UVRD does not improve upon the correlation between DMS and the $\mathrm{SRD_{clim}}$ (ρ=0.76) although it does use a more appropriate surface irradiance (i.e. cloud adjusted) component. Once again the correlation between UVRD and [DMS] is very similar to the strength of the correlations found between the simpler relationships with [DMS] and MLD alone (40/MLD) or the estimated I_0 derived from the TOA value (0.5×TOA).

4 Discussion

The SRD calculated using in situ components from the AMT ($\mathrm{SRD_{in\,situ}}$) produces a statistically significant correlation to the concurrently sampled, high resolution DMS concentrations. This application is beyond the remit originally proposed. The strength of this correlation is reduced relative to the global and fixed studies of Vallina and Simo (2007) and the slope of the relationship between SRD and DMS is approximately halved. Notably, the correlation fit is improved when in situ data is replaced with estimated/climatological values as inputs to the SRD ($\mathrm{SRD_{clim}}$), the same approach used to derive the SRD relationship of Vallina and Simo (2007). The strength of this correlation is still reduced relative to Vallina and Simo (2007) global and fixed location relationships, but this may be expected given the varying temporal and spatial nature of the cruise track sampling points and the resolution/time period of the data. Indeed the strength of any relationship found may be more significant in the context of the continually changing background conditions experienced during a cruise transect. These results are in agreement with the Spearman's Rank correlation (ρ=0.74) reported between the SRD and [DMS] from the North East Atlantic over a seasonal cycle by Belviso and Caniaux (2009).

A change from a variable, in situ light attenuation coefficient (k) to a fixed value significantly increased the correlation to [DMS] across the range of SRD equation permutations. Fixing k effectively removes it from the equation in terms of a correlation fit to the data. As Belviso and Caniaux (2009) demonstrate, the value of k can have a substantial impact on the value of SRD. Our data suggests that allowing k to vary significantly reduces the strength of correlation between SRD and [DMS] and implies that its inclusion within the SRD equation reduces its effectiveness at predicting surface [DMS]. This was the likely cause of much of the difference between $\mathrm{SRD}_{\mathrm{in\,situ}}$ and $\mathrm{SRD}_{\mathrm{clim}}$ and their strength of correlation with [DMS]. The switch from an in situ I_0 to an I_0 derived from a top of the atmosphere value (0.5×TOA) appears to account for the remainder of the difference between $\mathrm{SRD}_{\mathrm{in\,situ}}$ and $\mathrm{SRD}_{\mathrm{clim}}$ and their strength of correlation with [DMS]. Equally significant but non-linear relationships were found between [DMS] and both the estimated I_0 and in situ MLD (40/MLD) alone.

It is important to remember that MLD and I_0 are not completely independent variables and that the two are likely to be coupled over the seasonal cycle with high insolation levels in the summer coinciding with shallow mixed layers (Montegut et al., 2004). The advantage of the SRD methodology is that it combines these two interrelated variables, incorporating a physical mechanism to explain why the seasonal coherence of shallow MLD and high insolation combine to produce high DMS concentrations. The problem is that it becomes difficult to isolate the causal effect of insolation beyond a relationship with MLD driven by seasonality in I_0 (i.e. the effect of variable I_0 or SRD given a constant MLD). This is especially apparent when using a non-cloud adjusted, estimated I_0 in place of in situ I_0 data.

The main difference between the two measures of surface irradiance is that the in

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situ I_0 represents the variability introduced by cloud cover whereas the TOA derived, estimated I_0 does not (beyond the assumption that 50% of TOA irradiance is removed). The in situ, daily average I_0 values must represent more faithfully the surface irradiance that is concurrent with the daily sampled [DMS] but the TOA derived I_0 is more successful at providing a correlation fit both in combination with the SRD method and when used in isolation. The estimated, TOA-derived I_0 may be representing the longer-term mean state of the system rather than the snapshot of variability provided by the in situ AMT cruise transect data. Within this high resolution in situ dataset MLD and I_0 are less likely to be directly coupled and this could explain why the climatological/estimated data is more successful at resolving the observed DMS concentrations. The estimated I_0 could also represent seasonality in an unknown variable or combination of variables that combine with shallow summer MLD to produce high DMS concentrations. Finally, it could represent a smoothed (inverse) version of MLD itself with DMS concentrations modulated by a dilution effect independent of high resolution changes in insolation. In conjunction with smoothed monthly data the inclusion of an estimated I_0 within the SRD equation may act as a proxy for the seasonality inherent within the DMS cycle, combining latitude and date (seasonality) within one variable. The estimated I_0 could then represent the background potential for exposure to incident surface radiation whilst variations in MLD control the dose.

In contrast to the in situ I_0 and k data, the use of an in situ MLD within the SRD did not detract from the correlation to [DMS]. Indeed when applied to most variations of the SRD or UVRD equations, or when used alone (40/MLD), the in situ MLD was found to improve the strength of the correlation to [DMS]. A motivation of this work was to attempt to improve upon the handling of the climatological/estimated SRD parameters. A dominant role for MLD within the SRD could explain why using in situ values for I_0 and k did not yield any improvement in the skill of the SRD equation when applied to this daily data. The combination of a less variable, TOA-derived I_0 and fixed k would also increase the methodological importance of MLD within the SRD calculation. It should be remembered that although MLD seems to be a key variable within the SRD equation (at least in terms of the AMT data) explicit within the SRD reasoning is the implication that shallow MLD allow insolation/surface processes to influence the dynamics of the DMS(P) food web (Simo and Pedros-Alio, 1999). This is hinted at in the relationship between [DMS] and UV found in this study.

Prior to the Great Oxidation 2.4 billion years ago, life on Earth evolved without the protection of a stratospheric ozone layer and under much higher UV levels than today (Garcia-Pichel, 1998). This evolutionary history may still be reflected in efficient strategies and physiological mechanisms in modern organisms and ecosystems to prevent UV-induced damage and reduce photo-oxidative stress (Hader et al., 2003). This may be relevant in the context of DMS(P) production by marine phytoplankton (Sunda et al., 2002). The DMS data appears to show an interesting relationship to the *estimated* UV attenuation depth profile with [DMS] seemingly elevated in coincidence with sufficiently shallow MLD. Addressing UVA directly via the substitution of a cloud adjusted satellite climatology of surface UVA irradiance (UVRD) did not significantly improve or worsen the correlation to [DMS] relative to the $\mathrm{SRD_{clim}}$, estimated I_0 or 40/MLD relationship. The UVRD equation did improve upon the correlation between [DMS] and $\mathrm{SRD_{in\ situ}}$ but most importantly yields a significant correlation in conjunction with a cloud adjusted measure of surface irradiance in a wavelength previously linked to DMS dynamics. Once again the correlation to [DMS] is improved when the UVRD is calculated using in situ MLD data and was most likely influenced by fixing k. In the future, direct in situ measurements of UVA and UVB and their respective attenuation within the water column (k), ideally at a fixed location and throughout a whole seasonal cycle, may yield an improved result for this approach.

Within the AMT data, there is very little difference between the most highly correlated variation of the SRD equation ($\mathrm{SRD_{clim}}$), the UVRD and the simpler relationships based on in situ MLD (40/MLD) or estimated I_0 alone. The notion that MLD could be important in modulating DMS concentrations was introduced by (Simo and Pedros-Alio, 1999) who commented that it was useful shorthand to prediction until the mechanisms controlling DMS concentrations could be resolved. It is questionable from this AMT data whether the inclusion of the variables I_0/UV and k via the SRD methodology improves the correlation enough to illuminate causation over this resolution. Recent work by Derevianko et al. (2009) uses the recently-updated global database of surface seawater DMS concentrations (http://saga.pmel.noaa.gov/dms/) to examine the SRD relationship and comes to similar conclusions.

5 Conclusions

A challenge of Earth system science is to decouple the complex inter-relationships and feedbacks between the biosphere and climate. Vallina and Simo (2007) have demonstrated that a positive relationship may exist between the SRD and surface [DMS] over the seasonal DMS cycle using monthly averaged data. This is a necessary condition for the operation of a negative feedback (Charlson et al., 1987). The SRD methodology asserts that the interrelated seasonal cycles of MLD and surface insolation combine to produce high DMS concentrations when MLD are shallowest and summer insolation strongest. The SRD method is successful at combining these two relationships into one and provides a highly plausible bio-physical explanation for the strong correlations observed over the seasonal DMS cycle. The SRD methodology is troubled by the use of an estimated I_0 that does not realistically account for cloud cover, especially at this temporal resolution. This has implications for the CLAW hypothesis and the closure of any feedback loop which depends of the modulation of insolation by varying cloud albedo. The UVRD proposed here goes some way to addressing this issue producing a good correlation whilst utilising a cloud adjusted, surface irradiance product at a wavelength (UVA) with an implicated role in DMS(P) dynamics. Whether the SRD (or UVRD) illuminates causation beyond a simpler relationship with MLD or TOA-derived I_0 (i.e. a variable representing seasonality) at this resolution is questionable, at least within this AMT data. The MLD remains a useful shorthand to prediction without fully resolving the biological processes involved. However, it makes it harder to close the CLAW feedback loop. The suggested relationship between incident solar/ultraviolet radiation and sea surface DMS concentrations (modulated by MLD) makes it easier to close that feedback loop.

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Table 1. Spearman's rank correlation coefficients (ρ) between [DMS] and the outcome of the 3 equations on test (SRD (Eq. 1), UVRD (Eq. 2), 40/MLD (Eq. 3)) with various combinations of the available climatological/in situ data as input variables (I_0/UV$_{380\,\mathrm{nm}}$, MLD and k). **Bold** coefficients indicate that an appropriate fixed value of k is used (0.06 for $I_{0\,100\text{–}1000\,\mathrm{nm}}$, 0.16 for UV$_{380\,\mathrm{nm}}$). Plain text indicates that the in situ value for k is used. The simpler DMS α40/MLD coefficients (italics) does not utilise a k value. All coefficients significant at $p<0.01$ unless marked with * (in which case, result is significant at $p<0.05$).

	I_0 In situ	I_0 Climatology	I_0 Fixed	UV Climatology	40/MLD
MLD In situ	0.53 **0.65**	0.67 **0.76**	0.58 **0.73**	n/a **0.73**	0.73
MLD Climatology	0.38 **0.50**	0.60 **0.76**	0.45 **0.69**	n/a **0.69**	0.69
MLD Fixed	0.29* **0.29***	0.74 **0.76**	n/a **n/a**	n/a **0.30***	*n/a*

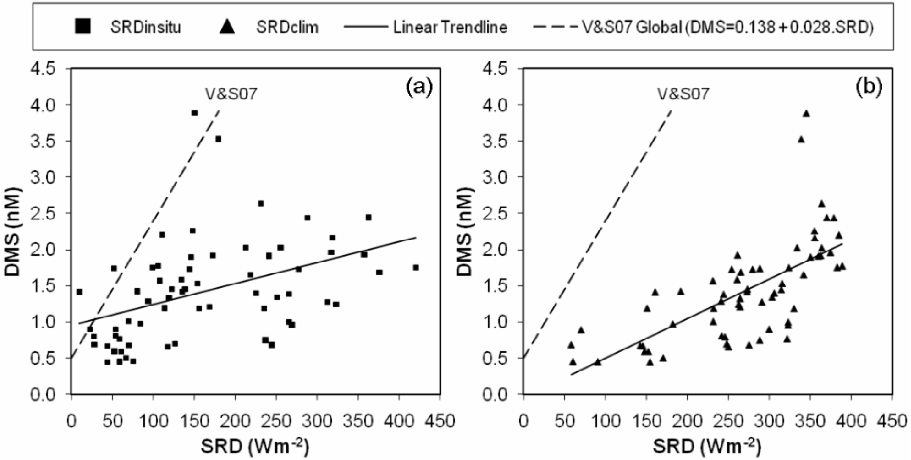

Fig. 1. [DMS] (nM) versus SRD (Wm^{-2}) calculated using: **(a)** in situ data ($SRD_{in\,situ}$, squares); and **(b)** climatological data (SRD_{clim}, triangles), for MLD, k and I_0. On both plots, solid line is linear best fit regression of the data and dashed line is the global relationship between [DMS] and SRD (DMS=0.138+0.028.SRD) proposed by Vallina and Simo (2007).

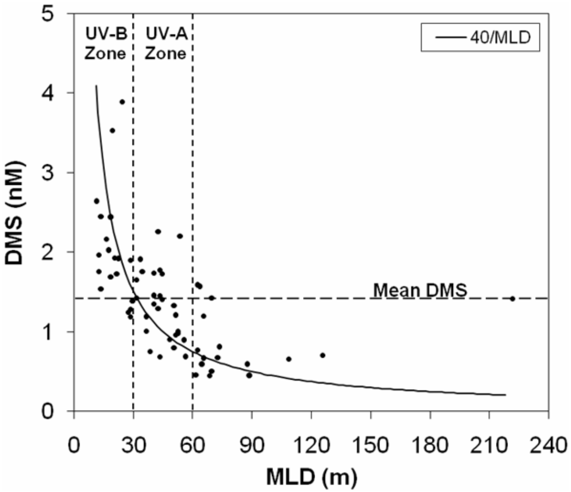

Fig. 2. [DMS] (nM) versus MLD (m) with indicated depths to which UVA (60 m) and UVB (30 m) might be expected to penetrate (vertical dashed lines). Also indicated are the mean [DMS] of the AMT dataset (1.42 nM) (horizontal dashed line) and DMS=40/MLD relationship (Bell et al., 2006, solid line).

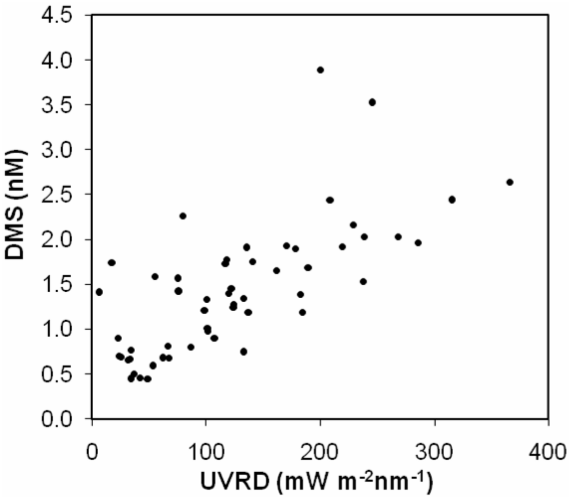

Fig. 3. [DMS] (nM) versus UV radiation dose (UVRD, mW m^{-2} nm^{-1}) calculated using in situ MLD, a constant k (0.16) and satellite derived UVA (380 nm) at the surface (ρ=0.73).