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# The use of algorithms to predict surface seawater dimethyl sulphide concentrations in the SE Pacific, a region of steep gradients in primary productivity, biomass and mixed layer depth

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## Abstract

Dimethyl sulphide (DMS) is an important precursor of cloud condensation nuclei (CCN), particularly in the remote marine atmosphere. The SE Pacific is consistently covered with a persistent stratocumulus layer that increases the albedo over this large area. It is not certain whether the source of CCN to these clouds is natural and oceanic or anthropogenic and terrestrial. This unknown currently limits our ability to reliably model either the cloud behaviour or the oceanic heat budget of the region.

In order to better constrain the marine source of CCN it is necessary to have an improved understanding of the sea-air flux of DMS. Of the factors that govern the magnitude of this flux, the greatest unknown is the surface seawater DMS concentration. In the study area there is a paucity of such data, although previous measurements suggest that the concentration can be substantially variable.

In the last decade a number of climatologies and algorithms have been devised to predict seawater DMS. Here we test some of these by comparing predictions with measurements of surface seawater made during the VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx) in October and November of 2008.

We conclude that none of the algorithms reproduce local variability in seawater DMS very well. From these findings, we recommend the best algorithm choice for the SE Pacific and suggest lines of investigation for future work.

## 1 Introduction

### 1.1 Clouds in the SE Pacific and DMS

In clean marine air the supply of cloud condensation nuclei (CCN) is often limiting, particularly in the southern hemisphere, yet in the southeast Pacific there is abundant cloud. As little rain falls here CCN may be long lived not being removed in precipitation. However, “pockets of open cells”, (POCs), periodically form, probably the result of





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a light drizzle falling, and so a break in the cloud cover is formed. The trigger for this precipitation is unknown; it may relate to the availability of CCN (Stevens et al., 2005). This hole may take several days to close up and the mechanism of refilling is uncertain (Bretherton et al., 2004). Dimethyl sulphide (DMS) is continually emitted from the ocean at all latitudes and is the principle natural source of sulphur to the atmosphere (Bates et al., 1992). Once in the air a portion is oxidised to acidic aerosols which may act as CCN. Indeed, in the marine boundary layer oxidised DMS is thought to be the principal source of CCN (Charlson et al., 1987), although the role of other substances, including gels (Bigg and Leck, 2001) and sea salt aerosol (O'Dowd et al., 1997), is not well known. The SE Pacific region suffers from scant spatial and temporal coverage of DMS concentration and flux measurements. In the limited data there are glimpses of variability; for example, against measured average DMS values of ~2 nM, there were hot spots of higher DMS concentrations (up to 5 nM) during a cruise in the region in October 2006 (B. Huebert, U. Hawaii, personal communication, 2009). The cause of these elevated values is not clear but they may result from higher light or UV levels during a POC, or were associated with a front that enhanced nutrient availability or affected the depth of the mixed layer. Much higher DMS concentrations, exceeding 40 nM, have been reported in the coastal waters of the Peruvian upwelling, with the maxima observed within 10 km of the shore, accompanied by elevated levels of phytoplankton biomass (Andreae, 1985).

### 1.2 Causes of DMS variability

The flux of DMS to the atmosphere is ultimately driven by the seawater concentration which is regulated by complex processes, with both the sources and sinks being variable. The uncertainties in seawater DMS concentrations are larger than those in the gas transfer coefficient (Nightingale et al., 2000) so, in order to improve our estimates of the flux to the atmosphere, an improved knowledge of the seawater concentrations is necessary.





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Different groups of phytoplankton produce differing amounts of DMS (Keller et al., 1989) such that simple correlations with chlorophyll or biomass do not work well over large scales (Kettle et al., 1999). At lower latitudes there is usually a succession of phytoplankton types following winter mixing, from low DMS producers (diatoms) to higher producers (haptophytes) while both chlorophyll and biomass declines (Simó and Pedros-Alio, 1999). Paradoxically, the highest DMS concentrations may occur when the chlorophyll concentration is at its lowest, for example in the Sargasso Sea (Dacey et al., 1998; Toole et al., 2003).

Dimethyl sulphoniopropionate (DMSP, occasionally called dimethylpropiothetin, DMPT) is the precursor to DMS. DMS and acrylate (and a proton) are produced from DMSP via enzymatic cleavage (Stefels and van Boekel, 1993). DMSP is known to be made by a range of micro and macroalgae as well as by a few higher plants (Stefels, 2000) yet the functions of DMSP and its metabolites may be numerous and remain controversial. It has been suggested to function as an osmolyte (Kirst, 1996), a cryoprotectant (Karsten et al., 1996), a grazing deterrent (Wolfe et al., 1997; Steinke et al., 2002), as a viral defence (Evans et al., 2006), and as an antioxidant (Sunda et al., 2002), amongst other roles. It should be noted that while phytoplankton are the main source of DMSP, recent advances in understanding the DMS cycle indicate that it is the entire marine planktonic food web that determines net DMS production along with photochemical and photobiological processes. Only a small fraction (1–2%) of the DMSP will enter the atmosphere as DMS due to the interactions of the physics, chemistry and biology in surface ocean waters (Kiene and Linn, 2000; Bates et al., 1994).

Some data show that the DMS flux to the atmosphere correlates with solar irradiation (Bates et al., 1987) yet in such conditions the photodestruction of DMS in both the atmosphere and the ocean is probably elevated. Over the Southern Ocean under high UV conditions DMS in the atmosphere is observed to decline (Kniveton et al., 2005) although the opposite can be true; in seawater the DMS concentration may increase with irradiation, despite elevated photodestruction (Toole et al., 2003).





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### 1.3 Approaches to predicting seawater DMS concentrations

We do not have a reliable global climatology for DMS despite extensive ocean exploration and sophisticated remote sensing. DMS production and loss processes are complex and the path from the cell to the atmosphere is tortuous. DMS measurements are still comparatively low in number compared to the number for other dissolved gases and there are few automated instruments enabling high resolution measurements to be made. A slew of predictive methods and algorithms have been generated in a hope to better understand DMS processes and to provide atmospheric scientists with much needed accurate flux data. Some of the more recent ones shall be considered here. For clarity we use abbreviations to identify them. Kettle et al. (1999), Kettle and Andreae (2000), Anderson et al. (2001), Aumont et al. (2002), Simó and Dachs (2002), Chu et al. (2003), Aranami and Tsunogai (2004), Belviso et al. (2004b), Vallina and Simó (2007) and Miles et al. (2009) will be referred to as K99, K00, AN01, AU02, SD02, CH03, AT04, BE04, VS07 and MI09, respectively.

A significant step in the study of DMS was the production of the global, monthly $1^{\circ} \times 1^{\circ}$ climatologies by K99 and K00. K00 was a development of K99 where new data were added and problem areas addressed. Ultimately the difference between the two sets is small excepting at the high latitudes. The global dataset encouraged modelling work and the development of algorithms and they are still a key standard to which parameterisations are shaped and tested. Algorithms AU02, SD02, and CH03 were determined using K99 whilst AN01, BE04 and AT04 used K00. The data that the Kettle climatologies were based on, along with newer measurements, can be found in the global DMS database (http://saga.pmel.noaa.gov/dms/).

In the process model AU02, chlorophyll *a* (hereafter chlorophyll) and a measure of the phytoplankton community composition, the Fp ratio, are used to estimate DMSP-particulate (DMSPp) and DMS concentrations with formulations derived from field data. In addition to being related by the climatology used the parameterisations can be grouped by their focus: those with either (a) biological (AU02, BE04, CH03) or





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(b) physical (VS07, MI09) emphasis and (c) those combining biological and physical factors (AN01, SD02, AT04).

Fp is determined from measured pigment concentrations (Claustre, 1994). However, AU02 estimates the Fp ratio using silicate-related modelling. Put simply: if silica driven production is high, diatoms are abundant so the Fp ratio will also be high and at a high Fp the DMSP:Chlorophyll ratio will be correspondingly low (Aumont et al., 2002). BE04 uses a variation of the AU02 methods to predict DMSPp and the DMS:DMSPp ratio from chlorophyll and the Fp ratio. In this case the Fp ratio is estimated using Seaviewing Wide-Field-of-view Sensor (SeaWiFS) chlorophyll concentrations and a relationship derived from Atlantic Ocean measurements. However, their empirically-derived relationship did not reproduce the substantial variability of Fp at low chlorophyll concentrations. A similar problem was found for DMSPp which displayed chlorophyll-independent variability so ultimately the predictions of DMSP at low chlorophyll were (very nearly) constant, again losing the natural variation. These factors combined resulted in poor resolution of DMS in oligotrophic regions and, for example the equatorial Pacific seasonality that is found in K00 data is not seen. More generally, BE04 underestimated seawater DMS. A further drawback of this method is, perhaps unsurprisingly, that the parameterisation leads to DMS concentration being too closely correlated with chlorophyll (Belviso et al., 2004a).

Like AU02, CH03 has a strong biological basis; a mechanistic DMS component was added to a biogeochemical ocean model. Ultimately mechanistic models are desirable as a good understanding of the involved processes is needed, and this can provide a stronger basis for prediction than observed correlation. The CH03 model results correlate fairly well with measured chlorophyll and most of the natural features are reproduced, except upwelling areas and coastal waters. Despite this, the seawater DMS concentrations have a large bias and do not reproduce seasonality well (Belviso et al., 2004a).

AN01 is a parameterisation using chlorophyll, nitrate and irradiance data; DMS concentration increases with each of these factors. For low DMS regions, including large





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portions of the subtropics and tropics, a constant DMS value is used as the model does not reproduce the variability in such zones. Belviso et al. (2004b) noted half the DMS values in K00 were below this concentration.

SD02 and AT04 also use a two-part, or "broken stick," relationship, recognising that in oligotrophic regions the DMS concentration can vary dramatically without a consistent relationship to the chlorophyll concentration. The SD02 formulation began with the K99 dataset from which the highest DMS and chlorophyll measurements were removed. In these data two relationships were found using the variables productivity, as determined from the chlorophyll concentration, and the mixed layer depth (MLD) although at low chlorophyll the estimation is made from the MLD alone.

AT04 is a refinement of SD02. The authors found that in the more productive waters the SD02 relationship was adequate; but in less productive waters DMS was effectively constant by area so the change in concentration was caused by dilution effects alone; a doubling of the MLD results in a halving of the DMS concentration.

The newest predicative approach has been the use of a linear relationship between DMS and solar radiation dose (SRD), as proposed by Vallina and Simó (2007). SRD was determined from mixed layer depth and short wave irradiance. It is attractive as the influence of solar radiation has been indicated (Bates et al., 1987; Toole and Siegel, 2004) and it requires only frequently collected data, unlike AU02. MI09 was a modification of VS07, where a strong correlation was found between an ultraviolet A radiation dose (UVRD) and DMS. MI09 used the dataset of Bell et al. (2006), collected during the Atlantic Meridional Transect (AMT) cruises, mostly in oligotrophic waters. As some studies have found phytoplankton demonstrate a particular sensitivity to UV, MI09 seems plausible. For example, under elevated UV some species produce more DMS (Sunda et al., 2002). Additionally DMSP to DMS conversion can increase (Hefu and Kirst, 1997) and bacterioplankton activity is suppressed (Herndl et al., 1993 ), reducing DMS and DMSP consumption.

Some intercomparisons of the climatologies and algorithms have already been made. Belviso et al. (2004a) assessed the Kettle databases, AN01, AU02, SD02,





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CH03 and BE04, and found substantial discrepancies between the predicted concentrations. Both AN01 and BE04 were identified as having little variability in DMS over large ocean tracts although the latter predicted a value for such regions of about half that predicted by the former. Indeed, when Belviso et al. (2004a) were comparing all the models and the Kettle climatologies with the raw data they that were constructed from, the global DMS database (http://saga.pmel.noaa.gov/dms/), a bias was found in each. Four underestimated the measured concentrations and two overestimated them. K99 and K00 underestimated by 0.36 and 0.33 nM respectively. Globally, AN01 was found to be the best overall with an overestimation of seawater DMS of only 0.16 nM while CH03 underestimated the concentration by 1.47 nM. AU02 performed only slightly better, the mean underestimation of the measured values was 1.38 nM. Summarising, SD02 and CH03 were deemed to be best in the equatorial Pacific as they reproduced the observed seasonal changes. AN01 predictions were a good fit to the annual mean concentrations but did not resolve either the spatial or seasonal variation at lower latitudes. They found that no model performed well in the North Pacific. A comparison approach like this cannot be used to test the performance of the models and climatologies in the SE Pacific as there are so few measurements in the DMS database for that region.

Bell et al. (2006) also reviewed the performance of K99, K00 and algorithms AN01, AU02, BE04, SD02 and AT04 and compared the estimate from each with their dataset Their list, ranked from worst to best was: AT04 (when using a constant optimised to their dataset), AU02 , SD02, BE04 and AN01. In the cases of SD02, AT04, AN01 and BE04, most or all of the Bell et al. (2006) sampling stations fitted into the low productivity part of the two part relationships. For the Bell et al. (2006) dataset, AN01 predicts a constant DMS concentration for all stations over five cruises, and the authors note that in 92% of cases this was an overestimation.

More recently, Miles et al. (2009) compared the Bell et al. (2006) data with the predictions made by VS07 and by their development of the relationship, MI09. They found that the VS07 estimates were very good for the Bell et al. (2006) optimised





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AT04 relationship. This was the strongest relationship found, and in this case they determined the SRD using a MLD climatology and calculated irradiance (which does account for variability caused by clouds). Interestingly, the relationship was found to be weaker if calculated using in situ measurements of either MLD or irradiance. The MI09 UVRD approach was found to be nearly as useful as a predictor of DMS as either VS07 or the optimised AT04 ($\rho = 0.67$ with SRD calculated using the MLD climatology). However, UV value used was for solar noon only as it is the only data available. Thus, the effects of both day length and cloud induced daily variation were not considered.

More recently, Belviso and Caniaux (2009) reviewed the VS07 method using data from the NE Atlantic and did not find as strong a relationship between SRD and DMS as was found in the NW Atlantic (the Sargasso Sea). Additionally, Derevianko et al. (2009) criticized the VS07 binning procedure as it artificially strengthened the SRD and DMS relationship. Miles et al. (2009) disputed the conclusions of the Belviso and Caniaux (2009) study and cited an incorrect use of statistics, leading to an underestimation of the strength of the relationship; the same criticism would stand against the Derevianko et al. (2009) paper. However, this issue alone does not explain the poor performance in these studies.

### 1.4 Aims

The SE Pacific is poorly sampled and published seawater DMS data are limited to just a handful of measurements. An improved knowledge of the flux of DMS from the ocean to the atmosphere is needed to better describe the cloud processes that regulate the most persistent stratocumulus deck in the world (Bretherton et al., 2004; Serpetzoglou et al., 2008). These clouds have a high albedo that exert a significant cooling that influences the heat budget over a substantial region of the Pacific Ocean (Cronin et al., 2006). Occasionally, small breaks, or POCs, open rapidly, these allow more incoming radiation to reach the surface ocean. These holes take several days to close and the closure is probably the result of CCN of marine origin, particularly at locations far from the coast. DMS is very likely an important sulphur source to





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the atmosphere in the region, some if which will become CCN. Herein, we use high resolution DMS and mixed layer depth measurements to test the suitability of the DMS predictive algorithms for use in the SE Pacific and judge the reliability of the published DMS climatologies within the region. This provides a unique opportunity to test all of these predictive algorithms with a single dataset, encompassing a wide range of contrasting hydrographic conditions from open ocean oligotrophic gyre to the eutrophic upwelling near the coast.

## 2 Methods

### 2.1 Collection of in situ data

Measurements were made on the VOCALS (VAMOS Ocean-Cloud-Atmosphere-Land Study; VAMOS – Variability of the American MOnsoon Systems, information at http://www.clivar.org/science/vamos.htm) Stratus 9 cruise as part of the VOCALS Regional Experiment (REx, information at http://www.eol.ucar.edu/projects/vocals/) on the NOAA research vessel Ronald H. Brown. The first leg was from Charleston, SC, USA to Arica, Chile (29th September–3rd November 2008) and the second from Arica to ~20° S, 85° W and returning to Arica (9th November–2nd December 2008).

DMS in seawater was either discretely or semi-continuously sampled and determined according to the methods of Matrai and Keller (1993) and Bates et al. (2000), respectively. The discrete samples were either taken from Niskin bottles on the CTD rosette closed at depths less than 10 m or from the ship's non-toxic supply fed from an inlet at approximately 5 m below the sea surface. The semi-continuous instrument sampled water from the ship's non-toxic supply approximately every 30 min. Both systems are based on a "purge and trap" GC-FPD design. They differed only in that the discrete instrument was calibrated using liquid DMS standards whilst the semi-continuous instrument employed gravimetrically calibrated DMS and MES permeation tubes.





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Chlorophyll fluorescence was measured continuously in water taken from the ship's non-toxic supply using a 10AU fluorometer fitted with a flow through cell (Turner Designs, Sunnyvale, CA). Discrete samples were taken in triplicate at least twice daily and used to calibrate the continuous instrument. The samples were filtered onto 25 mm filters (GF/F, Whatman Ltd., Kent, UK) and immediately frozen at −20 °C for subsequent analysis according to Holm-Hansen et al. (1965). These were measured with a second 10AU fluorometer fitted with a discrete sample cell and calibrated using pure chlorophyll *a* (Sigma Biochemicals).

Measurements of temperature and salinity were made on station using a SeaBird 911 plus CTD/rosette augmented with data from 425 deployments of a towed Oceanscience underway CTD system (Oceanscience, Oceanside, California) which contained a Sea-Bird CTD probe 10-400. These data were used to determine the in situ MLD. This is defined as the depth at which there is a 0.1 °C departure from the temperature at 10m below the surface. This removes the influence of shallow, short lived, surface stratification. The resultant data were high resolution but in order to provide MLD data to correspond with the positions where seawater DMS was measured a weighted average method was used to interpolate between points (R. Schlitzer, Ocean Data View, http://odv.awi.de, 2009).

Samples collected for nitrate concentration determination were taken from either the CTD rosette or from the ship's non-toxic supply and frozen at −20 °C for analysis using standard techniques (Parsons et al., 1984) by the MSI Nutrient Lab at the Marine Science Institute, UC Santa Barbara. To correspond with DMS sample points between nitrate samples the weighted average method was used.

Incoming short wave (SW) radiation (300–3000 nM) was obtained from two Eppley PSP units. For each sampling time the mean incoming radiation over the preceding 24 h was determined. These were mounted on platforms that corrected for the motion of the ship. The UV wavelength range of 355–399 nM was measured using a SAtlantic Hyper-OCR hyperspectral radiometer (SAtlantic Inc, Nova Scotia, Canada). Data were binned into 5 nm wide bands and averaged hourly.





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## 2.2 Testing of climatologies and algorithms

If the algorithm required a MLD, it was tested using the in situ MLD (defined in 2.1) and also with data from two MLD climatologies. The first climatology used was Monterey and Levitus (1997), hereafter ML97, using a definition of a potential temperature change of 0.5 °C from the surface (at shallow depths considered here the change in temperature caused by density change is negligible, potential temperature change ≡ in situ temperature change). The second was from the de Boyer Montegut et al. (2004) climatology, hereafter BM04, using the definition of a temperature change of 0.1 °C from a depth of 5 m as used in VS07 and MI09.

For algorithms requiring irradiance both in situ measured data and estimated values are used. The estimated values are calculated using the same method as used by Vallina and Simó (2007) and Miles et al. (2009). The top of atmosphere (TOA) solar irradiation was estimated using the equations of Brock (1981) with an atmospheric loss factor of 50% applied. These data are refereed to as TOA/2.

Unfortunately, NASA's Total Ozone Mapping Spectrometer (TOMS), used by MI09 to obtain a midday 380 nM UV surface irradiation, ceased operation in 2005 and data from the replacement instrument were not yet available in a gridded form. In place of this, we used the NCAR Tropospheric Ultraviolet and Visible (TUV) Radiation Model (http://cprm.acd.ucar.edu/Models/TUV/; Lee-Taylor and Madronich, 2007) which is based on the TOMS dataset so is comparable. As an in situ equivalent, we used the hourly value over solar noon from the 380–384 nM data band produced by the SAtlantic radiometer, although the whist measurements similar but not interchangeable.

The performance of each predictive method was assessed in three ways: the size of the mean residual, the strength of the correlation coefficient ($r^2$) and the Spearman's rank correlation coefficient ($\rho$). None is an ideal statistic. As the data were not normally distributed $r^2$ is not entirely appropriate; however, it is used elsewhere (including Belviso and Caniaux, 2009; Vallina and Simó, 2007; Belviso et al., 2004a) thus is useful to include for comparison. Spearman's considers only the similarity between the





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order or rank of the $x$ and $y$ data not the absolute magnitude of them (used by Miles et al., 2009; Vallina and Simó, 2007). In this paper all quoted $\rho$ values are significant to $< 0.01$ unless otherwise stated. Finally, the mean residual may not show how well the relationship accounts for variability. A similar statistic to this, the median modulus, was used by Bell et al. (2006). By using all three assessments an overall performance rank could be generated. The comparison gives a clearer picture and hence, a better understanding of overall performance.

The algorithms examined in this work are AN01, SD02, AT04, VS07 and MI09. AU02 was not tested as the supporting measurements to determine Fp were not made. BE04 also was not used as it is described as performing poorly in the VOCALS region.

### 2.3 Results and discussion

#### 2.3.1 Cruise description

After leaving Panama the *Ronald H. Brown* sailed southwest to ~8° S there beginning a southerly transect along ~85° W until ~20° S; thereon the ship followed longitudinal transects to survey mesoscale features and to service moorings. The cruise track is shown in Fig. 1. Data reported here begin on the 85° W transect at ~11.5° S on 23rd October 2008. Unless otherwise stated the data described or plotted are in situ values or are derived from them. Figure 2 contains three frequency plots showing the distribution of the concentrations of DMS (Panel A) and chlorophyll (Panel B) and the depth of mixed layer (Panel C). The chlorophyll concentrations were mostly low and typical of oligotrophic gyre conditions; 75% of DMS sampling locations having a concentration $< 0.5\,\mu g\,l^{-1}$ and 93% $< 1.0\,\mu g\,l^{-1}$. The DMS concentrations ranged from 1.0 to 14.1 nM, but the data was strongly skewed to the lower end of the range; the median was 2.5 nM and the mean was 2.9 nM. 92% of the DMS measurements were between 1.0 and 4.5 nM; 43% being less than 2.3 nM. The median MLD was 61 m but varied between 16 and 145 m. A summary of these data is given in the first section of Table 1.





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In terms of Longhurst's biogeochemical provinces, the initial section of the cruise was located within the Pacific Equatorial Divergence (PEQD), and the parts within ~230 km of the coast were within the Humboldt Current Coastal Province (HUMB). The remainder, the majority of the sampling points (89%), were within the South Pacific Subtropical Gyre (SPSG) (Longhurst, 1995).

### 2.3.2 The Pacific Equatorial Divergence (PEQD)

The first section, from 11.5–15.5° S, is within the PEQD province (Fig. 1). MLD was ~50 m in the northern part, 11.5–13.5° S, from where it steadily deepened to ~120 m by 15.5° S. Chlorophyll was quite variable until 13.5° S, between 0.07–0.35 $\mu g\,l^{-1}$ whereafter it increased steadily the as the MLD increased; by 15.5° S it was ~0.5 $\mu g\,l^{-1}$, The mean chlorophyll concentration in this province was 0.22 $\mu g\,l^{-1}$, the same as the SeaWiFS mean for the province for October/November 1997–2001 (Longhurst, 2007). DMS was variable, with concentrations between 1.3 and 4.4 nM, and a mean of 2.3 nM. It did not co-vary clearly with either MLD or chlorophyll although there was a net decline over the section of ~0.3 nM/degree latitude south.

### 2.3.3 The South Pacific Subtropical Gyre (SPSG)

Most of the cruise was within the SPSG province, located south of PEQD (Fig. 1). The MLD range was large, varying between 19–145 m with a median depth of 61 m. The chlorophyll concentration range was broad, from 0.01–2.2 $\mu g\,l^{-1}$, with median of 0.25 $\mu g\,l^{-1}$. This is much higher than the SeaWiFS mean for the province of 0.10 $\mu g\,l^{-1}$ for October/November 1997–2001 (Longhurst, 2007). Even for points in the SPSG west of 85 ° W, more than 1500 km offshore, the average chlorophyll concentration was still 0.16 $\mu g\,l^{-1}$ (range 0.04–0.49 $\mu g\,l^{-1}$). This discrepancy is probably the product of several factors. SPSG is a very large province, of almost $40\times10^6$ $km^2$ (the fourth largest of fifty-two globally) so, assuming these irregularities do not extend much further into the province, they will be lost in averaging. Secondly, the stratocumulus cloud impairs





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the SeaWiFS "view" in this area thereby missing observations. Marín and Delgado (2004) note that as only partial SeaWiFS images are usually available mesoscale features are not generally identified, particularly when large scale analyses are performed. The potential errors arising from reduced satellite observations are likely compounded by the limited in situ sampling. Indeed, in the description of the province, Longhurst (2007) describes the eastern side of SPSG as "bounded by the offshore eddy field of the Humboldt Current," which more properly places this region in a transition zone between the SPSG "proper" and coastal HUMB province. The range of DMS concentrations in this province was large, 1.0–14.1 nM, with a median of 2.5 nM. Over the whole province there was a trend of W-E shoaling of the MLD. The regression line estimates a mean change of ~6.3 m/degree longitude ($r^2 = 0.74$, $\rho = 0.90$, $n = 1456$) but with considerable variation related to westward propagating eddies. This strong longitudinal trend is not found in either the chlorophyll or DMS data. Over the province there is a positive correlation between chlorophyll (C) and DMS (DMS = (3.10×C) + 1.78; $r^2 = 0.35$, $\rho = 0.61$, $n = 1324$).

The highest DMS concentrations in this dataset, which peaked at 14.1 nM, were near 19° S, 80° W on the 17–18th November. As the ship travelling westwards from 81.2° W the MLD shoaled from ~50 m to ~27 m (the shallowest MLD in this province) over a distance of about 7 km. The DMS concentration rose, from a background level of 2.5–3.0 nM, very sharply over the 7 km; the DMS peak of 14.1 nM occurred at the shallowest mixed layer depth. Chlorophyll also rose over the same distance from ~0.4 to ~0.7 $\mu g\,l^{-1}$ although the chlorophyll peak of ~1.4 $\mu g\,l^{-1}$ was further west than the DMS maxima, where the MLD had begun to deepen and to ~35 m. The changes in MLD, chlorophyll and DMS are plotted against longitude in Fig. 3. The elevated chlorophyll so far offshore probably relates to some local upwelling that enhanced the supply of nutrients. However, these high DMS concentrations are not explained entirely by the elevated chlorophyll as similar concentrations are found at the coast but there the DMS is not so elevated. Further to this, the combination of chlorophyll and MLD do not explain the high DMS. For example, at the DMS hotspot at 19° S, 80° W the chlorophyll





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concentrations were 0.6 µg l$^{-1}$ and higher. Very similar chlorophyll and MLDs were also found on the 29/30th November; DMS was 1.6–5.3 nM; elevated in parts but not so strongly. The influence of this feature is also seen in Fig. 4 even though the influence of this spike in DMS and chlorophyll is moderated by more typical measurements which were taken during an earlier (28–29 October) transect at 19.7° S, about 110 km north of this section.

### 2.3.4 The Humboldt Current Coastal Province (HUMB)

In the narrow HUMB province, the MLD was shallow with a median depth of 19 m and the range of ~16–25 m. Chlorophyll and DMS concentrations were highly variable; chlorophyll was between 0.03 and 8.22 µg l$^{-1}$ with a median of 1.32 µg l$^{-1}$ and DMS was from 1.3–13.4 nM, with a median of 2.6 nM. The chlorophyll mean (1.32 µg l$^{-1}$) is again much greater than the SeaWiFS mean for the province of 0.70 µg l$^{-1}$ for October/November 1997–2001 (Longhurst, 2007). There remains a correlation between MLD and longitude, the depth reduces by ~2.7 m/degree longitude east ($r^2 = 0.46$, $\rho = 0.71$, $n = 89$). The MLD definition used (of a temperature deviation of 0.1 °C from 10 m) makes it unlikely for MLD values to be much smaller than this. In the HUMB province the correlation between chlorophyll and DMS was stronger than in the other provinces (DMS = (5.31×C) + 0.16; $r^2 = 0.41$, $\rho = 0.69$, $n = 89$).

In order to describe the trends in MLD, DMS and SRD over the whole cruise especially as most was conducted with a narrow latitudinal band, the MLD, chlorophyll, DMS and SRD data were averaged over 0.5° longitudinal bins, and this is plotted in Fig. 4. The strong trend was the eastward shoaling of MLD of ~5.8 m/degree longitude is ($r^2 = 0.72$, $\rho = 0.90$, $n = 1632$). There was a positive correlation between chlorophyll and DMS (DMS = (3.10×C) + 1.78; $r^2 = 0.35$, $\rho = 0.57$, $n = 1531$). As the SRD is strongly influenced by the MLD it strongly negatively correlates with it.





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## 2.4 Algorithm application

### 2.4.1 MLD comparison

The two featured MLD climatologies, ML97 and BM04, reported a shallower MLD than was determined from the in situ measurements, BM04 was the shallowest of all three (See Table 1). The correlations between the MLD values are strong, the greatest is between in situ and BM04, ($r^2 = 0.83$, $\rho = 0.92$, $n = 1538$), followed by that between ML97 and BM04 ($r^2 = 0.72$, $\rho = 0.89$, $n = 1538$), the least well correlated was in situ and Ml97 ($r^2 = 0.64$, $\rho = 0.81$, $n = 1538$).

During the cruise it was necessary to use a reference depth of 10 m when defining the mixed layer to avoid the influence of the temporary, shallow stratification caused by solar heating (Fiamma Straneo, WHOI, personal communication, 2009). Solar heating is intense in the tropics and when wind speed is low a temporary mixed later occurs frequently, but typically only lasting a few hours. As DMS data were collected throughout the day and night it was particularly important to use a definition which removed this diurnal variability and reflected the depth of the mixed layer the majority of the time. Whilst the ML97 reference is from the surface, the potential temperature change of 0.5 °C is quite large, although the temperature change at the sea surface due to solar heating over the course of a day in light winds may be 1–2 °C (Price et al., 1986). Furthermore, when there is not a shallow mixed layer caused by diurnal heating this definition can overestimate the depth of the mixed layer.

### 2.4.2 Short wave irradiance and UV

For each sampling point the mean in situ SW irradiance over the preceding 24 h was calculated. The summarised data is given in Table 1. The mean and the median values were similar but the in situ measurements were much more variable than the estimates from TOA/2. The average percentage of the top of atmosphere SW irradiance that reached the surface was 53% and the median was 52%. Thus, the use of the Vallina





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and Simó's (2007) assumption that 50% of the incident radiation was lost in the atmosphere was a good approximation (for a fixed value) .

The in situ data showed a weak, yet significant trend with latitude (S–N) of ~4 W m$^{-2}$/degree° ($r^2 = 0.02$, $\rho = 0.31$, $n = 1538$) and a net decrease with longitude (W–E) of ~2.3 W m$^{-2}$/degree ($r^2 = 0.01$, $\rho = 0.10$, $n = 1538$) although in both cases there was significant variability so the correlations were weak yet significant. The longitudinal change in SW irradiance of ~2.3 W m$^{-2}$/degree is in agreement with longer term measurements. During 2007 the mean SW irradiance at the WHOI/Stratus buoy (19.7° S, 85.6° W) was 206 W m$^{-2}$ whilst over the same period at the SHOA/DART buoy (19.6° S, 74.8° W) the average was 178 W m$^{-2}$ (Robert Weller, WHOI, personal communication, 2009); this is a change of ~2.6 W m$^{-2}$/degree longitude.

The TOA/2 values increased with latitude by ~2 W m$^{-2}$/degree, so the net effect of the change in cloud cover southwards is ~6 W m$^{-2}$/degree. There was a small longitudinal trend in the TOA/2 data of ~0.3 W m$^{-2}$/degree. This was resulting from the increase in day length over the duration of the cruise. The net effect of the cloud is a decrease of ~2.6 W m$^{-2}$/degree. The in situ and TOA/2 datasets do not correlate strongly ($r^2 = 0.10$, $\rho = 0.336$, $n = 1538$) although the relationship is again significant.

For each sample the UV irradiance at noon on that day was determined from both TUV and in situ measurements. There are minor trends in the TUV data. The UV level from TUV increased slightly with distance southwards (~1.1%/degree) but the strength of the relationship was weak ($r^2 = 0.0731$, $\rho = 0.077$, $n = 1538$). The W–E trend was a little larger (~1.3%/degree) and the relationship was much stronger ($r^2 = 0.95$, $\rho = 0.95$, $n = 1538$). The measured data show a small decline in UV southward and no significant variation with longitude. There is a weak correlation between TUV and the measured data ($r^2 = 0.05$, $\rho = 0.09$, $n = 1408$). The correlation between measured UV and measured irradiance is stronger ($r^2 = 0.10$, $\rho = 0.56$, $n = 1338$). The means, medians, maxima and minima of the TOA/2, TUV and the measured equivalents are given in Table 1.





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### 2.4.3 Kettle databases

To retrieve DMS values from K99 and K00 for each sampling point a weighted mean method was used to interpolate between the grid points of the climatologies and the DMS concentrations for October, November and December. A weighted average was then applied temporally to interpolate to the sampling date.

As expected, the K99 and K00 data are similar although those from K00 are a little lower; the difference between the means is ~0.1 nM. Both K99 and K00 are similar to measured values although the mean residuals are both ~1.0 nM although the differences between the mean and median values over the study region are very small (Table 4). The difference between the measured and the predicted DMS are plotted by longitude in Fig. 5. Both give values above and below the measured concentrations (52% of K99 values are larger than measured. Slightly fewer, 47% of K00 are larger than measured). K99 and K00 substantially underestimate DMS around 79–80° W where the measured DMS values were high along the ~19° S transect (see Sect. 3.1.3 and Figs. 3, 4 and 5).

### 2.4.4 Predicted DMS concentrations from algorithms

AN01

The AN01 model was produced to predict surface seawater DMS concentrations from chlorophyll ($C\,\mu g\,l^{-1}$), irradiance (J, $W\,m^{-2}$) and a nitrate limitation term, the Michaelis-Menten nutrient limitation factor (Q, dimensionless).

$$DMS = \alpha, \log_{10}(CJQ) \leq s \quad (1)$$

$$DMS = b\left[\log_{10}(CJQ - s)\right] + \alpha, \log_{10}(CJQ > s) \quad (2)$$

Where Q=N/($K_N$+N) and $K_N$ is the half saturation constant for nitrate uptake by phytoplankton, given as 0.5 mmol $m^{-3}$. Anderson et al. (2001) determined the values for *a* (2.29), *b* (8.24) and *s* (1.72) by fitting data from K99 to SeaWiFS chlorophyll data and to





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light fields which applied seasonality to a global annual nitrate climatology. log10(CJQ) increases with increases in chlorophyll, irradiance or nitrate. Large regions of the surface ocean of the tropics and subtropics have low nutrients and chlorophyll. These places, where the log10(CJQ) term is less than the AN01 *s* value of 1.72, are deemed likely have low seawater DMS concentrations, so are assigned a prescribed value of 2.29 nM.

In this analysis the AN01 algorithm reproduced the observed pattern of DMS fairly well although many of the sampling sites were in waters where $\log_{10}$(CJQ) was <1.72 so were assigned the DMS value 2.29 nM. This occurred in at 75% of the sampling sites when using the calculated irradiance. As the measured SW irradiance data had more low values than TOA/2, at more of the sampling sites $\log_{10}$(CJQ) > 1.72 when calculated using these irradiance values so 73% of these were assigned 2.29 nM. Overall, the DMS concentrations were similar when predicted using either the in situ or TOA/2 SW irradiance data . When the TOA/2 SW irradiance data was used, it was the best performing parameterisation of all tested and, when using the in situ SW irradiance data, the second best. Belviso et al. (2004a) also found that AN01 performed well, globally it reproduced DMS concentrations best of those they tested.

The predicted data from AN01 using TOA/2 had a mean value of 2.9 nM and median value of 2.3 nM (Table 2). Of the predicted datasets this had the smallest mean residual ($\bar{e}$) of 0.85 nM, the largest $r^2$ of 0.32 and the third largest $\rho$ of 0.53. The predicted data from AN01 using the in situ SW irradiance values had a slightly lower mean of 2.8 nM and a median also of 2.3 nM. The performance statistics were similar and are given in Table 2.

SD02, like AN01, uses a two part relationship. The authors drew on a previous observation that in regions where chlorophyll is always quite low, less than 0.5 µg $l^{-1}$, there is a negative correlation between both MLD and chlorophyll and DMS (Simó and Pedros-Alio, 1999). Contrastingly, in more eutrophic regions, there is a positive relationship between chlorophyll and DMS. The proposed relationship is:

$$\mathrm{DMS} = Ln\,(\mathrm{MLD}) + 5.7 \qquad \mathrm{C/MLD} < 0.02\ \mathrm{mg\ m^{-2}} \tag{3}$$





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$$DMS = 55.8\,(C/MLD) + 0.6 \qquad C/MLD \geq 0.02\ mg\ m^{-2} \tag{4}$$

MLD was mixed layer depth defined as the depth the density was 0.125 kg m$^{-3}$ higher than at the surface. A modification of this was made for AT04 whose parameterisation retains the C/MLD division and the DMS relationship for above this. They proposed that below this value, DMS was constant per area and that the variation in concentration was driven by the relative dilution caused by changes in the MLD, thus:

$$DMS \times MLD = \text{constant} \tag{5}$$

The authors gave a value for the constant of 60 ± 30 µmol DMS m$^{-2}$, so, for comparison, the values of 30 and 90 µmol m$^{-2}$ are used in addition to 60 µmol m$^{-2}$, as performed by Bell et al. (2006). Bell et al. (2006) determined the most appropriate constant for their dataset as the value corresponding to the lowest median modulus between the predicted values and those measured.

When the situ MLD data were used, 91% of the sampling points had C/MLD < 0.02 mg m$^{-2}$, while fewer sampling points were in this category when using either the ML97 (85%) or the BM04 (65%) MLD climatologies.

The SD02 DMS concentration was determined using each of the three MLD sets; the data are given in Table 2. The SD02 algorithm did not perform very well. With this algorithm the best performance was obtained using in situ MLD data, followed by the BM04, and then the ML97 climatologies. The values of the predicted DMS concentrations were sensitive to the choice of MLD. Using the in situ data produced the lowest DMS values with a mean of 1.8 nM and a median of 1.7 nM. Using the ML97 values gave a DMS mean of 2.4 nM and a similar median of 1.8 nM. When the BM04 MLD values were used, the predicted DMS values were much higher than for either the in situ or the ML97 MLD datasets.

The DMS concentrations predicted using the AT04 algorithm were sensitive to the choice of MLD. This was because, like the SD02 algorithm using the same criteria, at the majority of the data points C/MLD < 0.02 mg m$^{-2}$. As the in situ MLD were the deepest of the three MLD datasets, it gave the lowest DMS concentration estimations and





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of the three MLD datasets overall in situ performed the best. However, the strongest individual performance was using the BM04 MLD and a constant of 30 µmol $m^{-2}$. This was the 3rd best of all algorithms/variable combinations tested (Table 2). In this best case scenario, the AT04 relationship was a significant improvement over SD02 for the VOCALS REx, region. However, it did not perform as well as in the original paper or when tested by Miles et al. (2009).

In the case of AT04 with the BM04 MLD and a constant of 30 µmol $m^{-2}$ its success was both from the combined estimates high (C/MLD $> 0.02$, $n = 1394$) and the low (C/MLD $< 0.02$, $n = 409$) parts of the relationship. The $r^2$ and $\rho$ value for the high part alone was 0.02 and 0.56 respectively while for the low part these were 0.09 and 0.55.

As, when using the AT04 relationship, the in situ MLD dataset was the best overall for estimating the DMS concentrations, we used these MLD values to determined the constant which estimated a DMS dataset with the smallest median modulus value, using the method of Bell et al. (2006). The constant, 141 µmol $m^{-2}$, produced a dataset with a median modulus value of 0.99 nM and the mean residual was 1.27 nM. However, whilst this fitted constant gave the lowest residual, the other metrics indicated a worse fit than when using the AT04 constants of 30, 60 or 90 µmol $m^{-2}$ (Table 2).

We attempted to merge the overall most successful algorithm, AN01, with AT04 which had previously been found to perform well in low DMS regions (Bell et al., 2006). We used the "low DMS" part of the AT04 relationship where AN01 would assign the low DMS value of 2.29 nM (s):

$$\mathrm{DMS} \times \mathrm{MLD} = \mathrm{constant}, \log_{10}(\mathrm{CJQ}) \leq 8 \quad (6)$$

$$\mathrm{DMS} = b\left[\log_{10}(\mathrm{CJQ} - s)\right] + \alpha, \log_{10}(\mathrm{CJQ}) > s \quad (7)$$

For the first (low DMS) part we tried both the best performing combination of the BM04 MLD and a constant of 30 µmol $m^{-2}$ and also the in situ MLD and the constant of 60 µmol $m^{-2}$. For the constants a, b and s we used the original AN01 values. However, this modification did not perform more strongly than AN01 (data not shown).





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Vallina and Simó's (2007) algorithm dispensed with the need for chlorophyll or nutrient measurements. They found linear relations between "solar radiation dose" (SRD) and the monthly mean DMS concentrations at two time series stations and over the global ocean. At the time series stations, the extinction rate for light, k, was measured in situ but for the global work they used a constant from the literature of $0.06\,m^{-1}$. An analysis of the strength of the algorithm in Atlantic, mostly oligotrophic, waters found that it was greater when the $0.06\,m^{-1}$ constant was used rather than in situ measurements of $k$ (Miles et al., 2009). The equation to determine SRD is:

$$\mathrm{SRD} = \frac{I_O}{k \cdot \mathrm{MLD}} \cdot (1 - e^{(-k \cdot z)}) \quad (8)$$

The VS07 regression lines for the slopes of the relationships for each set of data were reported as follows: (a) Blanes Bay DMS=0.138+0.028.SRD, (b) Sargasso Sea DMS=0.51+0.017.SRD, and (c) Global Ocean DMS=0.492+0.019.SRD.

Using data collected on Atlantic Meridional Transect (AMT) cruises, Miles et al. (2009) found a stronger correlation between an UVA exposure term and surface seawater DMS concentrations. They replaced irradiance in the VS07 SRD equation with the estimated 380 nM irradiance at solar noon, derived from the NASA Total Ozone Mapping Spectrometer (TOMS). The light extinction coefficient, $k$, was changed to $0.10\,m^{-1}$, a value more appropriate to the shorter wavelength.

The SRD was calculated for each of the possible combinations of the three MLD dataset choices and each of the four SW irradiance/UV datasets. For those determined using SW irradiance (rather than UV), each of the three VS07 regression lines (optimised for Blanes Bay, Sargasso Sea or the Global Ocean) was applied. Additionally, the line of best fit to the measured data, that with the largest $r^2$ value, was used. As MI09 did not give a regression line for the UVRD relationship, only the best fit line was tested. Table 3 shows the mean residuals ($\bar{e}$) for the possible MLD/irradiance combinations. Overall, based on the size of the mean residual for each dataset, the Global Ocean ($b$) relationship was the strongest, followed by the local Sargasso Sea





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(*c*) and Blanes Bay (*a*) relationships. The best individual performing example was for the Sargasso Sea (*c*) with a mean residual of 0.89 nM when using the BM04 MLD and TOA/2. This is perhaps unsurprising as the MLD and irradiance choices were the same used to derive the original relationship.

In assessing the performance of the variables used in VS07 and MI09, it was clear that the best MLD choice was the in situ dataset (Table 4). There was little difference observed in the predictions based on ML97 and BM04. This is in contrast to MI09 who found that climatological MLD was better than in situ data to predict the DMS concentration. The irradiance choice was less critical as the MLD definition dominated the performance ranking. The light parameter datasets, ranked in descending order of performance was TOA/2, TUV, SW in situ and UV in situ. Whereas the performance varied by metric, the calculated irradiance/UV values performed better overall than the in situ ones, in agreement with Miles et al. (2009). Like Miles et al. (2009) found, the slope of the regression line of SRD plotted against measured DMS was much shallower than in the original paper (see Tables 2 and 4).

## 3 Discussion

The application of published algorithms to this dynamic tropical oligotrophic-eutrophic zone is a useful companion to the oligotrophic tropical and subtropical comparison studies of Bell et al. (2006) and Miles et al. (2009) as well as to the temperate ones of Belviso and co-workers (Belviso et al., 2004a; Belviso and Caniaux, 2009). Furthermore, the latitudinal range is small and the sampling occurred over a fairly short period, so seasonal effects are likely small yet the MLD and productivity vary greatly.

Interest in the SE Pacific region stems from the need to realistically model its radiative budget and this requires a quantitative description of its stratocumulus clouds and their complex aerosol microphysics. The source of aerosols could be either homogeneous nucleation from local gas-phase precursors or entrainment of land-derived pollution particles from above the marine boundary layer inversion. In either case,





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the particles probably grow to become effective cloud condensation nuclei by adding sulphate derived from DMS (and probably also biogenic organic material). Quantifying a natural source requires the understanding of the oxidation of DMS to sulphate aerosol, its flux to the atmosphere and, ultimately, its biological production; predicting the required DMS concentrations is addressed here. Unfortunately in this study we were unable to study the influence of POCs as we passed under only one during the fieldwork and any variability in measurements during this period was more likely in response to physical ocean variability.

Predictive algorithms have been devised to estimate oceanic DMS concentrations in a hope to better understand DMS processes and to provide atmospheric scientists with accurate flux data. The unavailability of a reliable global climatology for DMS is mostly due to the limited number of measurements. We have applied a number of published algorithms to the SE Pacific and compared the results from these to the high resolution surface DMS measurements made during the VOCALS expedition. In Fig. 5, a summarising plot, the difference between the measured and estimated DMS concentrations is plotted against latitude for each algorithm or climatology.

The surface seawater DMS measurements observed in the SE Pacific were not reproduced very well by any of the algorithms. At best, the mean residual was of the order of 30% of the measured values and, at worst, ~90%. The highest Spearman's correlation ($\rho$) between measured and predicted values was 0.56, which was lower than that found by either Miles et al. (2009) or Vallina and Simó (2007). Overall, the data were best reproduced by Anderson et al. (2001). In this case, the uncertainty in the seawater DMS concentrations was smaller than the uncertainty in the gas transfer velocity which is around a factor of 1.5 for the moderate windspeeds of the region (Kettle and Andreae, 2000; Calleja et al., 2009 and references therein).

AN01 performed better than the other algorithms notably in offshore eddy and productive coastal conditions (see Fig. 5). At the offshore hotspot, all estimates were too low although AN01 was too low by the least. In the coastal waters (east of ~73° W) all, excepting AN01, overestimated DMS concentrations. The chlorophyll concentration,





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whilst not explaining all variability, did correlate with DMS concentration. The best performing algorithms, AN01 and AT04, do use chlorophyll as a variable, while VS07 and MI09 do not.

AN01 also underestimated DMS by the least at the offshore DMS hotspot. Despite this good performance, it did not reproduce the variability in the lower-level DMS regions – this was recognised in the original paper as well as in subsequent studies (Anderson et al., 2001; Bell et al., 2006; Belviso et al., 2004a). Attempts to merge AN01 with the next most successful algorithm, AT04, did not improve the DMS predictions in this study, although this approach might be useful when considering more oligotrophic regions.

The SRD and UVRD relationships reproduced DMS concentrations reasonably well, with MI09 performing slightly better than VS07. This is interesting as this algorithm used climatological UVR noon data which might not be expected to be a very good predictor of the total UV irradiance, as it does not account for day length, variability in cloud or day length change (although this last factor would be small during the course of the cruise). Indeed, the algorithms always estimated DMS concentrations more accurately when either the TOA/2 irradiance or the TUV UVR were used in place of in situ measurements. This suggested that if the irradiance (SW or UV) was important in modulating seawater DMS concentrations, it was over longer timescales than one day as these climatology data are probably closer to average conditions over a number of days than the in situ data – it may be that the biological processes governing DMS concentration are sensitive to the light history. Contrastingly, the best performing MLD choice in most cases (excepting the case of AT04 with the BM04 MLD) was the in situ dataset. In contrast to previous findings where climatological values were found to be superior (Miles et al., 2009; Bell et al., 2006). Perhaps this was because the MLD in the VOCALS study was quite variable over small distances, detail that would be lost in a climatology, whereas in the AMT studies MLD trends were more gradual and less influenced by mesoscale features. As the TOA/2 and TUV data did not change very much, the only significant source of variation in the input to these algorithms was the





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MLD. When DMS concentrations were high, the MLD was usually shallow, although a shallow MLD did not always co-occur with high DMS. This was especially true especially further east (e.g. 30th November, 21.5° S, 71° W; DMS was only 2–3 nM while the MLD was only 16–22 m). The expectation that a shallow MLD will cause high DMS concentrations was the source of the overestimations of DMS by all of the algorithms that used MLD, and why AN01, which does not, did not. The Kettle databases also have high DMS concentrations at these most easterly locations, due to the very high inshore concentrations measured by Andreae (1985).

As the uncertainty in DMS predictive algorithms is still substantial and as studies in different locations, times or scales often do not agree, caution must be used if they are used to predict changes in flux of DMS to the atmosphere in future climate scenarios.

In summary, to predict surface seawater concentrations in this region of the SE Pacific, the Anderson et al. (2001) algorithm (AN01) using in situ chlorophyll and nitrate data with the estimated surface SW irradiance values from TOA/2 was found to be most effective. It must be reiterated that this algorithm does not reproduce the changes in DMS in the more oligotrophic regions but it does capture the variability produced by offshore eddy features and near the coast better than any other. In more oligotrophic waters, AT04, VS07 and MI09 have been found to be better choices (e.g. Bell et al., 2006; Miles et al., 2009). Combining AN01 with one of these may offer the best solution for resolving DMS variability in disparate regions although a process model that replicates the biology, chemistry and physics of DMS production and loss processes is ultimately desirable.

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**Table 1.** A summary of cruise data, firstly the mean, median and range of measured DMS, chlorophyll, irradiance, MLD and UV and secondly, from calculations or climatologies, the mean, median and range of estimated irradiance (TOA/2), UV (TUV) and the mixed layer depths from the climatologies (ML97, BM04).

| Parameter | Units | Mean | Median | Max. | Min. |
|---|---|---|---|---|---|
| DMS | nM | 2.9 | 2.6 | 14.1 | 1.0 |
| Chlorophyll | $\mu$ g l$^{-1}$ | 0.43 | 0.26 | 8.23 | 0.01 |
| Irradiance in situ | W m$^{-2}$ | 235 | 229 | 334 | 153 |
| MLD in situ | m | 70 | 61 | 145 | 16 |
| UV in situ | W m$^{-2}$ nm$^{-1}$ | 0.50 | 0.49 | 0.74 | 0.31 |
| TOA/2 | W m$^{-2}$ | 220 | 222 | 230 | 208 |
| TUV | W m$^{-2}$ nm$^{-1}$ | 0.89 | 0.91 | 0.99 | 0.81 |
| ML97 | m | 52 | 50 | 98 | 7 |
| BM04 | m | 20 | 19 | 26 | 13 |





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**Table 2.** A summary of predicted DMS values and the relation of these to the measured values. The table contains the predictor type (algorithm or climatology code), MLD and irradiance used, the mean and median DMS (nM). Also $n$, the slope and the intercept of the regression, the mean residual (, nM), the correlation coefficient ($r^2$), and Spearman's rank correlation coefficient ($\rho$) are given. All $\rho$ are significant at $p < 0.01$. The columns to the right of , $r^2$ and $\rho$ are the rank of that metric in relation to the other predictors, numbered 1–19, 1 being the best performing. The final column is the overall position, the order (smallest to largest) of the sum of the ranks for the metrics. For reference the mean and median of measured DMS data were 2.5 and 2.9 nM. For VS07 and MI09 the best performing couplets are given (see Table 4).

| Type | MLD | Irradiance | Mean | Median | $n$ | slope | intercept | $\bar{e}$ | $\bar{e}$ rank | $r^2$ | $r^2$ rank | $\rho$ | $\rho$ rank | Overall rank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K99 | – | – | 2.6 | 2.9 | 1538 | 0.56 | 1.39 | 1.01 | 7 | 0.06 | 13 | 0.27 | 15 | 11 |
| K00 | – | – | 2.5 | 2.7 | 1538 | 0.53 | 1.52 | 1.00 | 6 | 0.06 | 14 | 0.26 | 16 | 14 |
| AN01 | – | in situ | 2.8 | 2.3 | 1374 | 0.66 | 0.95 | 0.88 | 2 | 0.31 | 2 | 0.55 | 2 | 2 |
| AN01 | – | TOA/2 | 2.9 | 2.3 | 1374 | 0.71 | 0.83 | 0.85 | 1 | 0.32 | 1 | 0.53 | 3 | 1 |
| SD02 | in situ | – | 1.6 | 1.7 | 1394 | 0.78 | 1.60 | 1.33 | 13 | 0.09 | 8 | 0.43 | 10 | 7 |
| SD02 | ML97 | – | 1.8 | 1.7 | 1394 | 0.59 | 1.79 | 1.18 | 10 | 0.04 | 17 | 0.37 | 14 | 17 |
| SD02 | BM04 | – | 2.8 | 2.6 | 1394 | 0.52 | 1.42 | 0.93 | 5 | 0.05 | 16 | 0.25 | 17 | 15 |
| AT04 30 | in situ | – | 0.7 | 0.5 | 1394 | 0.69 | 2.39 | 2.23 | 19 | 0.10 | 7 | 0.47 | 6 | 8 |
| AT04 60 | in situ | – | 1.1 | 1.1 | 1394 | 0.71 | 2.04 | 1.78 | 16 | 0.10 | 6 | 0.46 | 7 | 6 |
| AT04 90 | in situ | – | 1.6 | 1.6 | 1394 | 0.56 | 1.96 | 1.39 | 14 | 0.08 | 9 | 0.42 | 11 | 10 |
| AT04 30 | ML97 | – | 0.8 | 0.6 | 1394 | 0.61 | 2.36 | 2.08 | 18 | 0.07 | 10 | 0.48 | 5 | 9 |
| AT04 60 | ML97 | – | 1.3 | 1.2 | 1394 | 0.61 | 2.36 | 1.58 | 15 | 0.07 | 11 | 0.43 | 9 | 12 |
| AT04 90 | ML97 | – | 1.9 | 1.7 | 1394 | 0.57 | 2.09 | 1.25 | 11 | 0.06 | 12 | 0.38 | 12 | 13 |
| AT04 30 | BM04 | – | 2.0 | 1.8 | 1394 | 0.68 | 1.49 | 1.06 | 8 | 0.20 | 3 | 0.56 | 1 | 3 |
| AT04 60 | BM04 | – | 3.0 | 2.6 | 1394 | 0.26 | 2.08 | 1.08 | 9 | 0.02 | 18 | 0.17 | 18 | 18 |
| AT04 90 | BM04 | – | 4.0 | 3.8 | 1394 | −0.15 | 3.44 | 1.93 | 17 | 0.02 | 19 | 0.15 | 19 | 19 |
| HI 141 | in situ | – | 2.6 | 2.1 | 1491 | 0.19 | 2.33 | 1.27 | 12 | 0.06 | 15 | 0.37 | 13 | 16 |
| VS07 | in situ | TOA/2 | 2.9 | 2.8 | 1538 | 0.02 | 1.46 | 0.89 | 3 | 0.14 | 4 | 0.46 | 8 | 5 |
| MI09 | in situ | TUV | 2.9 | 2.8 | 1538 | 6.53 | 1.82 | 0.89 | 4 | 0.12 | 5 | 0.49 | 4 | 4 |





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**Table 3.** Mean residuals ($\bar{e}$ nM) between measured DMS concentrations and those predicted by VS07 using all MLD and irradiance combinations and the three linear relationships reported in Vallina and Simó (2007). The relationships were determined for: *a*=Blanes Bay, DMS=0.138+0.028.SRD; *b*=the global ocean, DMS=0.492+0.019.SRD and *c*=the Sargasso Sea, DMS=0.51+0.017.SRD.

| Datasets used to calculated SRD | | $\bar{e}$ (nM) | | |
|---|---|---|---|---|
| MLD | Irradiance | *a* | *b* | *c* |
| in situ | in situ | 1.13 | 1.22 | 1.31 |
| in situ | TOA/2 | 1.17 | 1.26 | 1.34 |
| ML97 | in situ | 1.03 | 1.08 | 1.15 |
| ML97 | TOA/2 | 1.01 | 1.10 | 1.19 |
| BM04 | in situ | 1.70 | 1.13 | 1.03 |
| BM04 | TOA/2 | 1.40 | 0.96 | 0.89 |





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**Table 4.** Performance summary for VS07 and MI09 relationships. These values were determined from the regression equations. Data given are the number of points ($n$), the slope and intercept of the relationship, the mean residuals ($\bar{e}$ nM), the correlation ($r^2$) and the Spearman coefficients ($\rho$). In the column to the right of each of the assessment criteria the rank (ascending) is given. The final column is the overall performance rank based on the sum of the three other scores.

| MLD | IR | $n$ | Slope | Intercept | $\bar{e}$ | $\bar{e}$ rank | $r^2$ | $r^2$ rank | $\rho$ | $\rho$ rank | Overall |
|---|---|---|---|---|---|---|---|---|---|---|---|
| is | SW is | 1538 | 0.02 | 1.63 | 0.91 | 5 | 0.12 | 4 | 0.45 | 3 | 3 |
| is | TOA/2 | 1538 | 0.02 | 1.46 | 0.89 | 2 | 0.14 | 2 | 0.46 | 2 | 1 |
| is | TUV | 1538 | 6.53 | 1.82 | 0.89 | 4 | 0.12 | 3 | 0.49 | 1 | 2 |
| is | UV is | 1338 | 0.12 | 1.77 | 0.96 | 7 | 0.14 | 1 | 0.43 | 8 | 6 |
| ML97 | SW is | 1538 | 0.01 | 2.11 | 0.94 | 6 | 0.03 | 11 | 0.39 | 9 | 9 |
| ML97 | TOA/2 | 1632 | 0.01 | 1.85 | 0.98 | 9 | 0.08 | 7 | 0.44 | 7 | 7 |
| ML97 | UV is | 1408 | 0.06 | 2.24 | 1.06 | 12 | 0.09 | 6 | 0.39 | 10 | 10 |
| ML97 | TUV | 1632 | 3.26 | 2.21 | 0.98 | 10 | 0.07 | 9 | 0.44 | 6 | 8 |
| BM04 | SW is | 1538 | 0.00 | 2.59 | 0.97 | 8 | 0.00 | 12 | 0.10 | 12 | 12 |
| BM04 | TOA/2 | 1538 | 0.03 | −1.45 | 0.89 | 3 | 0.09 | 5 | 0.44 | 5 | 5 |
| BM04 | UV is | 1338 | 0.05 | 1.80 | 1.01 | 11 | 0.05 | 10 | 0.34 | 11 | 11 |
| BM04 | TUV | 1538 | 5.32 | 0.73 | 0.89 | 1 | 0.08 | 8 | 0.45 | 4 | 4 |





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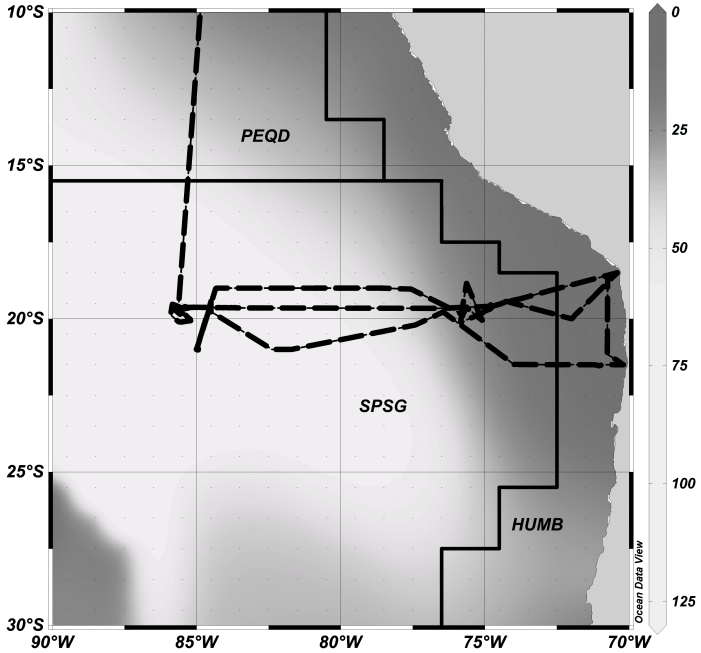


**Fig. 1.** The cruise track for VOCALS, southbound from Panama to northern Chile (October–December 2008). The most northerly data reported in this paper is from ~11.5° S. The shading on the plot represents the MLD (m) from the Monterey and Levitus (1997) climatology for the month of November, defined as the depth at which there is a potential temperature change of 0.5 °C. The Longhurst (1995) biogeochemical provinces Pacific Equatorial Divergence (PEQD), South Pacific Subtropical Gyre (SPSG) and Humboldt Current Coastal Province (HUMB) are shown to provide a spatial reference. The plot was produced using Ocean Data View (http://odv.awibremerhaven.de/home.html).





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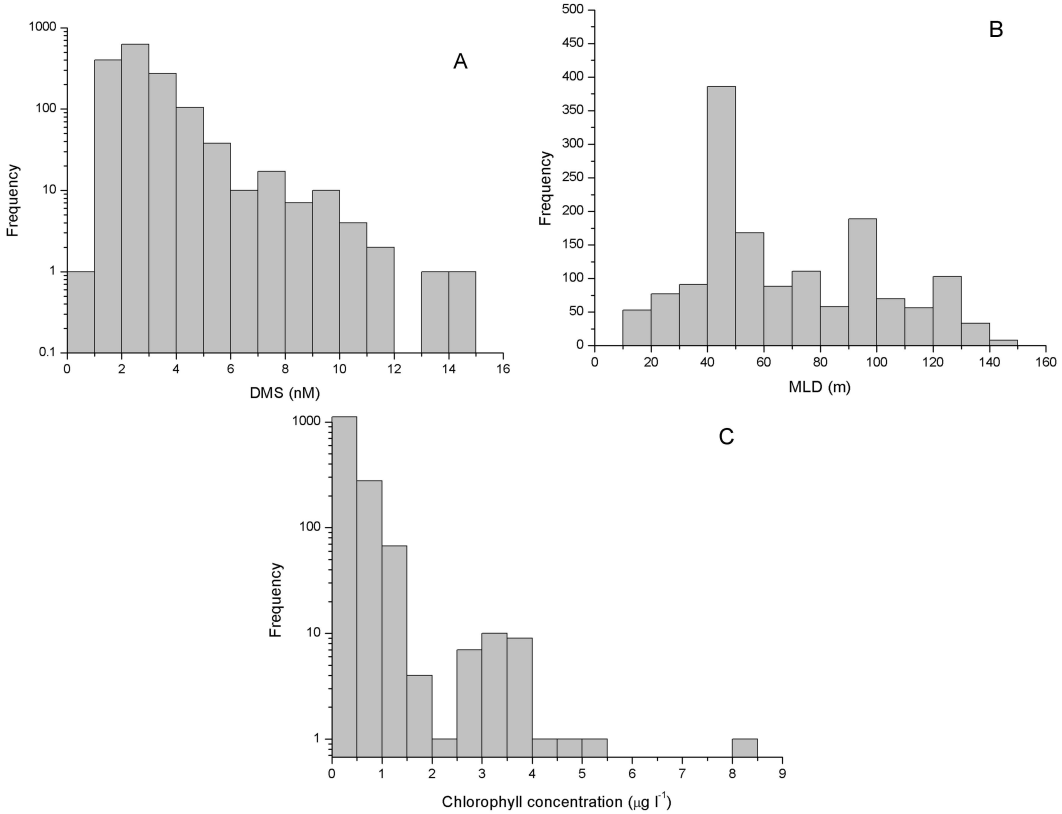


**Fig. 2.** Frequency plots of measured DMS (Panel **A**), MLD (Panel **B**) and Chlorophyll (Panel **C**).





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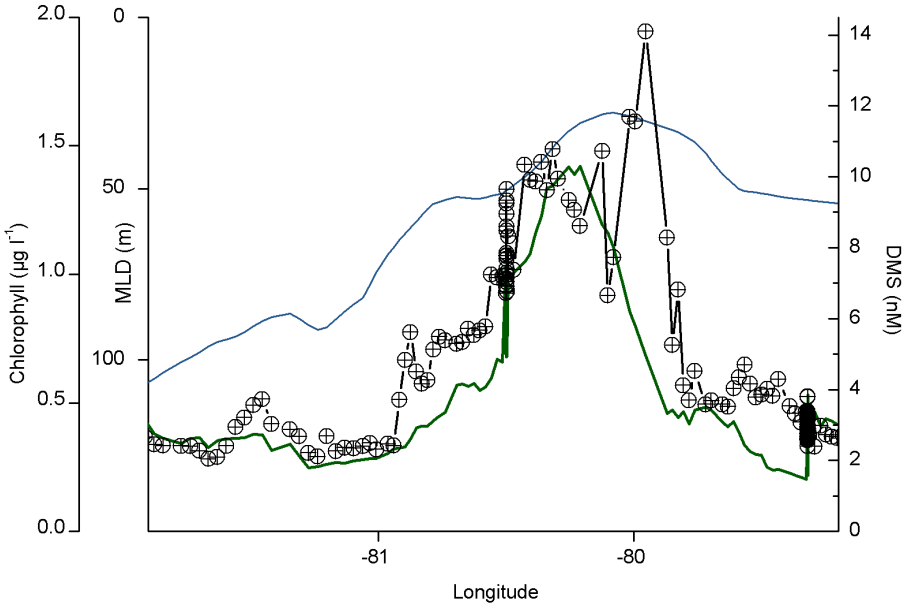


**Fig. 3.** The highest DMS concentrations were associated with a rapid shoaling of the MLD. Chlorophyll (green line) and DMS (black line, with crosshair symbols) concentrations increased as the MLD (blue line) shoaled. The data are plotted against longitude (° E). The latitude was ~19° S. For reference, this is ~1000 km from the coast.





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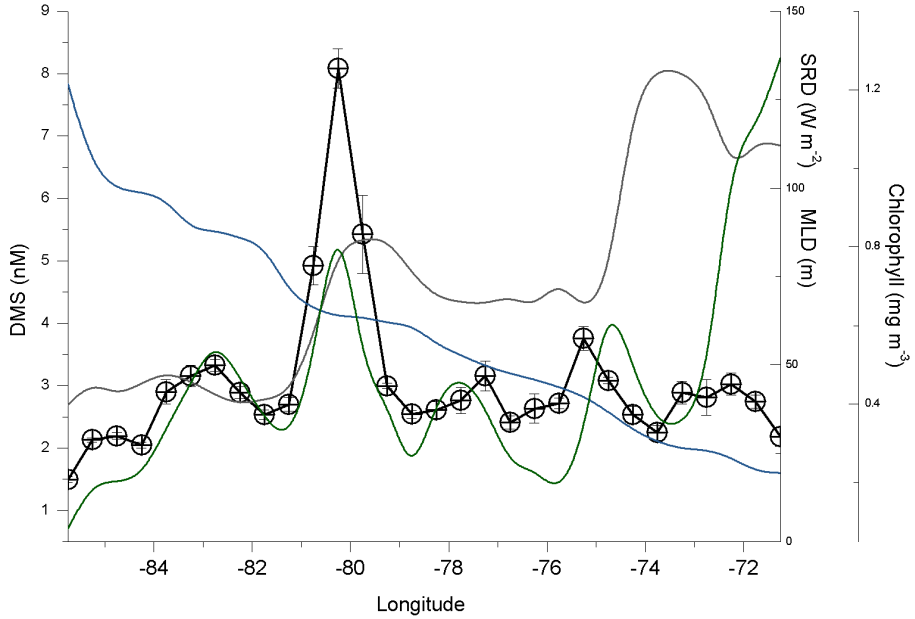


**Fig. 4.** A west-east section summarising the changes in seawater DMS (black), MLD (blue), SRD (pink) and chlorophyll (green) during the VOCALS cruise. Data are averaged over 0.5° latitudinal bins. The error bars on the DMS points represent ± 1 standard error. All data was in situ or derived from in situ data. MLD is defined as a change of 0.1 °C from 10 m depth. SRD and MLD share the same axis to aid readability.





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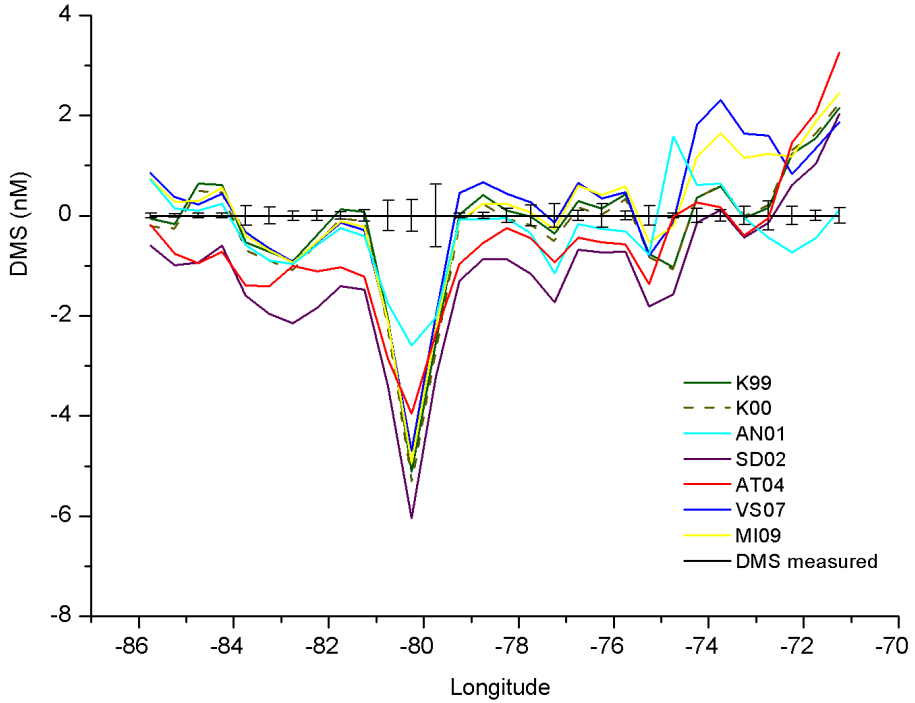


**Fig. 5.** The difference between predicted DMS and measured DMS concentrations plotted against longitude for the VOCALS REx cruise in the SE Pacific. The measured DMS is plotted as 0 and the error bars represent 1 standard error. For each predicted DMS dataset the optimum parameters are chosen as determined using the overall ranking system shown in Table 5.3. The algorithm acronyms are explained in the text.





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