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Environmental control on the variability of DMS and DMSP in the Mauritanian upwelling region

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Abstract

Dimethylsulfide (DMS) and dissolved and particulate dimethylsulfoniopropionate ($DMSP_d$, $DMSP_p$) were measured in sea surface layer along the Mauritanian coast, Northwest Africa, during the upwelling season in February 2008. DMS, $DMSP_d$ and $DMSP_p$ surface concentrations of up to 10 nmol L^{-1}, 15 nmol L^{-1} and 990 nmol L^{-1}, respectively, were measured. The maximum $DMSP_p$ concentration is the highest reported from upwelling regions so far and indicates that the Mauritanian upwelling is a hot spot of DMSP and, thus, DMS production. Dinoflagellates were responsible for the DMS production. Other phytoplankton groups seemed to have only a minor or no influence on the DMS and DMSP production. Decreasing nitrogen (i.e. increasing nitrogen limitation) most likely triggered a switch from high DMSP production to high DMS production. It seems that both nitrogen limitation and the intensive solar radiation in the tropics induced stress in DMSP producing algae and activated their antioxidant system. Our results underline the importance of coastal upwelling regions as ecosystems with a pronounced temporal and spatial variability which result in high DMSP and DMS production.

1 Introduction

The oceanic distributions of dimethylsulfide (DMS) and its major precursor dimethylsulfoniopropionate (DMSP) are resulting from a complex interplay of biological and non-biological pathways such as formation by phytoplankton and microbial cleavage of DMSP to DMS, on the one hand, and microbial consumption as well as photochemical oxidation of DMS and its loss to the atmosphere, on the other hand (see e.g. Schäfer et al., 2010; Simó, 2004; Stefels et al., 2007; Vogt and Liss, 2009). Biologically productive regions of the ocean are responsible for a significant fraction of the sea surface production of DMS and DMSP and are, therefore, potentially strong sources of atmospheric DMS (Kettle and Andreae, 2000; Lana et al., 2011). Once released to the atmosphere,

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DMS is a potential precursor of sulphur aerosols which can act as cloud condensation nuclei (see e.g. Charlson et al., 1987; Faloona, 2009; Vogt and Liss, 2009).

Eastern Boundary Upwelling Systems, such as the one found along the Mauritanian coast of north western Africa, are known as highly productive oceanic areas because of the nutrient rich subsurface waters which upwell along the coast and induce pronounced phytoplankton blooms (see e.g. Chavez and Messié, 2009; Minas et al., 1986). In various coastal upwelling regions a characteristic phytoplankton composition and succession was observed which depends on the nutrient supply in close association with the temporal and spatial settings of the upwelling events: Pronounced blooms of dinoflagellates and coccolithophorids, which are well known as the most important DMSP producing algae (Keller et al., 1989; Stefels et al., 2007), occur after the decline of the diatom bloom, which is usually dominating during the first stage of an upwelling event. Therefore, coastal upwelling regions may be hot spots of DMS production. However, DMS emissions from coastal upwelling regions are of minor importance for the global atmospheric DMS budget because of the small area coverage and the transient nature of upwelling events (Kettle and Andreae, 2000; Lana et al., 2011).

Despite the fact that coastal upwelling areas have been identified as hot spots of DMS production, only a few process studies about DMS from these area have been published: DMS and DMSP have been measured in the Peruvian upwelling (Andreae, 1985; Riseman and DiTullio, 2004), off Oman (Hatton et al., 1999), off West India (Shenoy and Dileep Kumar, 2007) and in the NW African upwelling off Morocco (Belviso et al., 2003) as well as off Mauritania (Franklin et al., 2009). The parameters which influence the temporal development and spatial distribution of DMS as well as DMSP in coastal upwelling areas are not completely understood.

Here we present the DMS and DMSP distributions in surface waters during a process study along the Mauritanian coast during the upwelling period in February 2008. The influence of different parameters such as nutrient availability and phytoplankton composition and succession on the DMS and DSMP distributions within the plumes of upwelled waters was examined.

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2 Methods

DMS and DMSP surface concentrations were measured during the ATA-03 process study in the Mauritanian coastal upwelling region as well as in the open ocean between Mauritania and the Cape Verde Islands. The ATA-03 cruise was conducted on the French research vessel L'Atalante from 3rd to 20 February 2008, as part of the German SOPRAN "Surface Ocean Processes in the Anthropocene" project (www.sopran.pangaea.de). Four short onshore-offshore transects were performed between 16° W and 20° W, and a longer transect along 18° N between 16° W and 23° W (Fig. 1).

2.1 DMS and DMSP analysis

Surface seawater was sampled from 5 to 30 m depth in 250 ml aliquots from a 24-Niskin bottle rosette equipped with a CTD. The samples were collected bubble-free in brown glass bottles sealed with gas tight PTFE coated lids. Three separate samples from these bottles were taken for DMS, dissolved DMSP ($DMSP_d$) and particulate DMSP ($DMSP_p$) analysis. Samples were stored in the dark at 4 °C and measured within 4 h after sampling. In order to analyse the DMS and $DMSP_d$ concentrations, seawater was gently filtered through a glass fibre filter (GF/F; Whatman; 0.7 µm) attached to a syringe and measured using a purge and trap technique: Samples were purged with helium and the expelled DMS was preconcentrated on Tenax® TA (mesh 60/80, Alltech) at room temperature. A column filled with potassium carbonate (K_2CO_3) was used as moisture trap. DMS was desorbed by heating the Tenax® TA to 200 °C within 1 min using a heat gun and injected into a gas chromatograph (ICU 600 Carlo Erba Instruments; GC 6000 vega series 2; capillary column CP-SIL 5CB for sulphur, 30 m × 0.32 mm ID) coupled to a flame photometric detector (FPD 800 CE instruments) according to the methods of Kiene (1993) and Simó (1998). $DMSP_d$ and $DMSP_p$ were converted to DMS by hydrolysis with sodium hydroxide (NaOH). The conversion time to form DMS from $DMSP_d$ and $DMSP_p$ was at least 12 h and 24 h, respectively. $DMSP_d$ was

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measured directly out of the same sample after the analyses of DMS. For the determination of $DMSP_p$, 50 ml unfiltered alkalinized seawater was analysed for DMS. The retention time for each chromatogram was 1.5 min. The 15 ml samples and standards were purged for 15 min. DMS standards were prepared as described in Kiene (1993) using liquid DMS diluted in ethylene glycol. Standards and samples were measured in triplicates and their standard deviations were calculated according to the statistical method of David (1951). The mean analytical errors were ±0.3 nmol L^{-1} (±12 %) for DMS, ±0.8 nmol L^{-1} (±19 %) for $DMSP_d$, and ±19 nmol L^{-1} (±20 %) for particulate $DMSP_p$. Calibrations were conducted every second day during the cruise. The analytical system was tested for blanks and sparging efficiency in the laboratory before the cruise. No blanks were measured and the sparging efficiency was 100 %. Kiene and Slezak (2006) showed that syringe pressure filtration can artificially increase the $DMSP_d$ concentration in seawater samples; thus, it is possible that the $DMSP_d$ concentrations presented here are overestimated. Dissolved nutrients (nitrate, nitrite, phosphate and silicate) were measured on-board according to the methods described by Hansen and Koroleff (1999).

2.2 Pigment analysis

For the determination of pigments, 1–4 L of sea water was filtered onto 25 mm Whatman GF/F filters with a pressure of less than 120 mbar. After filtration, the filters were folded and stored in 2 ml micro centrifuge tubes (Eppendorf cups) at −80 °C until analysis. Samples were measured using a Waters HPLC-system, equipped with an auto sampler (717 plus), pump (600), PDA (996), a fluorescence detector (474) and EMPOWER software. For analytical preparation, 50 µl internal standard (canthaxanthin) and 2 ml acetone were added to each filter sample and then homogenised for 3 minutes in a cell mill. After centrifugation, the supernatant liquid was filtered through a 0.2 µm PTFE filter (Rotilabo) and placed in Eppendorf cups. An aliquot (100 µl) was transferred in the auto sampler (4 °C). Just prior to analysis the sample was premixed with 1 M ammonium acetate solution in the ratio 1:1 (v/v) in the auto sampler and injected onto the

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HPLC-system. The pigments were analysed by reverse-phase HPLC, using a VARIAN Microsorb-MV3 C_8 column (4.6 × 100 mm) and HPLC-grade solvents (Merck). Solvent A consisted of 70 % methanol and 30 % 1 M ammonium acetate and solvent B contained 100 % methanol. The gradient was modified after Barlow et al. (1997). Eluting pigments were detected by absorbance (440 nm) and fluorescence (Ex: 410 nm, Em: >600 nm). Pigments were identified by comparing their retention times with those of pure standards and algal extracts. Additional confirmation for each pigment was done with representative samples using on-line diode array absorbance spectra between 390–750 nm. Pigment concentrations were quantified based on peak areas of external standards, which were spectrophotometrically calibrated using extinction coefficients published by Bidigare (1991) and Jeffrey et al. (1997). For correction of experimental losses and volume changes, the concentrations of the pigments were normalised to the internal standard, canthaxanthin. This method separates chlorophyll-*a* and divinyl chlorophyll-*a* as well as lutein and zeaxanthin completely. Chlorophyll-*b* and divinyl chlorophyll-*b* are also distinguishable from each other, but they are not baseline separated. Chlorophyll-*a* and divinyl chlorophyll-*a* are combined to total chlorophyll-*a* (TChl-*a*) to obtain a measure for the total amount of phytoplankton biomass in the sample. The taxonomic structure of phytoplankton communities was derived from photosynthetic pigment ratios using the CHEMTAX® program (Mackey et al., 1996), applying the input matrix of Veldhuis and Kraay (2004). The phytoplankton group composition is expressed in chlorophyll-*a* concentrations.

2.3 Statistical analysis

A statistical approach was used to find correlations between the different environmental parameters (e.g. pigments, temperature, nutrients) and the dissolved sulphur compounds (MATLAB's "stepwisefit" tool): Terms were added and removed from a multi linear regression model based on their statistical significance. At each step an F-test was performed to test the regressions with and without certain terms. A term was added to the model if it contributed significantly at the 95 %-confidence level. A term

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was removed from the model if it did not contribute at the 99 %-confidence level.

3 Results and discussion

The coastal upwelling off Mauritania in February 2008 was characterized by significantly lower sea surface temperatures (SST) in the range of 18°–20°C as compared to the open ocean SST of the adjacent eastern tropical North Atlantic (>22 °C) (Fig. 2). In general, the seasonally occurring upwelling between 15° N and 21° N has its strongest intensity and expansion between January and May whereas upwelling is persistent throughout the year north of 21° N (see e.g. Mittelstaedt, 1991). In February 2008 upwelling occurred within a narrow band between 16°–18° W along the continental margin located 50–100 km from the coast. The upwelling off Mauritania is driven by the northeasterly trade winds which trigger an offshore Ekman transport and result in an ascent of nutrient rich subsurface water (Minas et al., 1986; Mittelstaedt, 1991). The trade winds are deflected towards the Intertropical Convergence Zone (ITCZ) which is usually located around 6° N in February. Thus, the southward shift of the ITCZ during winter/spring induced an expansion of the coastal upwelling region to 16° N at the time of the ATA-03 cruise. The upwelling in the northern part of the sampling region (>18° N) were at a relative older stage (as indicated by minimum SST of about 19 °C) compared to the younger (fresh) upwelled waters south of 18° N (as indicated by minimum SST of only 20 °C). The 18° N transect was sampled at last and thus the upwelling at 18° N was most advanced as indicated by a minimum SST of 18°C close to the coast. The overall distribution of nutrients such as nitrate (NO_3^-) and silicate in the surface layer off Mauritania was patchy with enhanced concentrations within and around the upwelling centres close to the coast (Fig. 2). Elevated chlorophyll-*a* (chl-*a*) concentrations coincided roughly with enhanced nutrients concentrations (Fig. 2).

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3.1 Phytoplankton distribution based on marker pigments

Since a strong gradient in temperature from the open ocean towards the coast was observed for all transects and the water temperature is a good sorting proxy to compare the various phytoplankton distributions in the following we present all data in the figures based on temperature for the various transects instead of using coordinates.

The major phytoplankton group in the upwelling were diatoms which contributed 60–90 % to the total phytoplankton chlorophyll (Fig. 3). A significant correlation of the main marker pigment of diatoms, fucoxanthin, with chl-*a* ($R^2 = 0.96$) further suggests that diatoms are mostly favoured in the upwelling close to the coast. Cyanobacteria were the major phytoplankton group (50–80 %) in the oligotrophic open ocean waters west of 18° W (Fig. 3). Dinoflagellates and hapthophytes (including coccolithophorids) occurred mainly in the transition areas between nutrient rich upwelled waters and oligotrophic waters (Fig. 3). The dinoflagellates and haptophytes proportions of the phytoplankton community were <20 % and <11 %, respectively, and thus low compared to diatoms and cyanobacteria. The pigment distribution was calculated using CHEMTAX® and is not based on direct individual pigment measurements. We observed low chl-*a* concentration and a mixed phytoplankton community in the most recently upwelled water south of 17° N (Figs. 2 and 3).

The distribution pattern of the phytoplankton community north of 17° N reflected a well characterized pattern of succession that normally occurs during spring blooms in the North Atlantic (Barlow et al., 1993): Diatoms are usually among the first phytoplankton species to occur and they dominate the nutrient (i.e. silicate) rich waters. They get replaced by haptophytes and finally by dinoflagellates. Both groups have a relatively lower nutrient demand. Cyanobacteria usually dominate oligotrophic open ocean waters due to their ability to use organic nitrogen compounds to fulfil their nutrient requirements (Zubkov et al., 2003). The general succession of the phytoplankton was also observed off Mauritania in July/August 2006 by Franklin et al. (2009) towards the end of the upwelling season.

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3.2 N:P ratio

The N:P ratio, here defined as the ratio of the sum of nitrate and nitrite (NO_2^-) to phosphate (PO_4^{3-}), is a good indicator of the nutritional status of the surface waters off Mauritania (Fig. 4): High N:P ratios indicate fresh upwelled waters. Low N:P ratios indicate N limited (i.e. aged) upwelled waters because N is consumed faster than P. High N:P ratios between 10 to 16 were detected in fresh upwelled waters close to the coast. The N:P ratios decreased to 0.1 towards the open ocean indicating a strong N depletion in the aged upwelled waters (Fig. 4). An N:P ratio of 16 (i.e. the classical Redfield ratio) was measured in 10 m depth close to the coast, whereas N:P ratios of 13 or less were determined at 5 m depth. This illustrates the fast uptake of nutrients as a consequence of the almost immediate response of phytoplankton when nutrients are brought to the surface waters by upwelling.

3.3 DMS and DMSP concentrations

The median values for DMS and dissolved DMSP ($DMSP_d$) surface (5 m) concentrations were 1.5 nmol L^{-1} and 1.6 nmol L^{-1}, respectively. The median of particulate DMSP ($DMSP_p$) was 29 nmol L^{-1}. The DMS concentrations in February 2008 are in line with previous measurements of DMS off the Mauritanian coast conducted from 1972 to 2006 which range from 0.05 to 19 nmol L^{-1} with a median value of 2.8 nmol L^{-1} (data extracted from the Global Surface Seawater DMS Database: http://saga.pmel.noaa.gov/dms). More recently, Franklin et al. (2009) measured DMS concentrations in the range from 1 to 14 nmol L^{-1} off Mauritania during the post upwelling season in July/August 2006. A comparison with data from other coastal upwelling areas reveals that the DMS concentrations off Mauritania are comparable with those found off Oman and off Morocco but they are considerably lower compared to those found off Peru and off West India (Table 1). The $DMSP_p$ concentrations off Mauritania show a clear seasonal signal, with concentrations during the upwelling season significantly higher than those from the post upwelling season (Table 1). The maximum

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$DMSP_p$ concentration observed during this study off Mauritania is the highest reported from upwelling regions so far (Table 1). However, the hidden bias introduced by seasonal and interannual variabilities as well as inadequate areal coverage of the listed data makes a direct comparison difficult.

3.4 Factors influencing DMS and DMSP off Mauritania

3.4.1 Phytoplankton composition

The DMS concentrations along the five transects were roughly associated with chl-*a*. We found statistically significant linear correlations with chl-*a* at 16° N ($R^2 = 0.56$, $p < 0.05$, $n = 10$), 17° N ($R^2 = 0.51$, $p < 0.01$, $n = 16$) and 19° N ($R^2 = 0.51$, $p < 0.01$, $n = 12$) (Fig. 5). For $DMSP_d$ only at 19° N was a significant positive correlation ($R^2 = 0.82$, $p < 0.01$, $n = 12$) with chl-*a* found, whereas $DMSP_p$ was not correlated with chl-*a* (Fig. 5). These findings most likely result from the fact that diatoms, which are not known to be important DMSP producing algae, were dominating the upwelling off Mauritania (the diatom marker pigment fucoxanthin was significantly correlated with chl-*a*, see above).

By using the statistical MATLAB tool "stepwise fit" (see Methods) a significant ($R^2 = 0.81$) correlation was found between DMS and peridinin which is a marker pigment indicator for dinoflagellates. In addition, a weak correlation was also detected between $DMSP_p$ and peridinin ($R^2 = 0.36$). We found only a weak correlation ($R^2 = 0.20$) of DMSP with 19-hexanoyloxyfucoxanthin, which serves as a marker pigment for haptophytes including the well-known DMSP producing coccolithophorids. However, it seems that haptophytes were dominated by species with low or no potential to produce DMSP. Steinke et al. (2002) found a high DMSP lyase activity (DLA) in dinoflagellates during a coccolithophorid bloom in the North Atlantic Ocean. They reported that dinoflagellates were responsible for a significant amount of the DMS production although their cell abundance was low. A significant correlation between DLA and dinoflagellate biomass as well as DLA and coccolithophorid biomass were found by Franklin et al. (2009) in the Mauritanian upwelling in 2006. Thus, it is reasonable

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to assume that dinoflagellates contributed significantly to the DMS concentrations in the Mauritanian upwelling during our study. However, in contrast to the results from Franklin et al. (2006), our results suggest that DMS production by coccolithophorids was less important in February 2008.

The $DMSP_d$ concentration showed a weak correlation with peridinin as well as with phytin a and phorbid a, which are indicators for phytoplankton senescence (Louda and Baker 1986) and phytoplankton grazers (Shuman and Lorenzen, 1975), respectively (Fig. 6). Nguyen et al. (1988) showed that DMSP producing algae were largely responsible for the production of $DMSP_d$ and DMS in seawater during their senescence stage. Wolfe et al. (1996) showed that grazing zooplankton on DMSP producing algae can cause an increase in $DMSP_d$ and DMS. In this study, only single stations showed an overlap between DMS and DMSP peaks and high grazer and aged algae abundance (Fig. 6). Factors such as aged algae and grazers most likely triggered enhanced DMS concentrations at some sampling stations (Fig. 6).

3.4.2 Mixed layer depth and solar radiation dose

We also analysed the effect of mixed layer depth (MLD) and solar radiation dose (SRD) on the DMS concentrations according to the approaches of Simó and Dachs (2002) and Vallina and Simó (2007), respectively. However, the measured DMS concentrations could not be reproduced with the DMS/MLD approach as well as with the DMS/SRD approach. The failure of the two algorithms to predict the DMS concentrations off Mauritania is most likely resulting from the fact that the algorithms are based on climatology data averaged over time and space. Our results are in line with recent findings which indicated that the SRD may only account for 14–24 % of the variance of DMS measurements (Belviso and Caniaux, 2009; Derevianko et al., 2009). It was argued that using SRD only for predicting DMS concentrations does not account for biological production of DMS and may only applicable when biological effects are small (Belviso and Caniaux, 2009; Derevianko et al., 2009) which is not the case for the upwelling off Mauritania.

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3.4.3 N limitation

In order to get an overall picture of the development of DMS and total DMSP ($DMSP_t = DMSP_d + DMSP_p$) surface concentrations during the upwelling in February 2008, we calculated median DMS and $DMSP_t$ concentrations for N:P bins from 0.5 to 16.5 (e.g. the median of DMS for N:P ratios between 6 to 7 was allocated to a N:P ratio of 6.5). Then the DMS and $DMSP_t$ data were smoothed with a 3 point moving average. A bimodal distribution of both DMS and $DMSP_t$ was found (Fig. 7). High $DMSP_t$ and low DMS concentrations were observed at N:P >7 whereas low $DMSP_t$ and high DMS were observed for N:P <7. By correlating DMS with $DMSP_t$ two distinct linear correlations were obvious for the two N:P regimes (Fig. 8). Thus, we conclude that there might have been a switch in the production and/or consumption of DMSP and DMS depending on the availability of dissolved inorganic nitrogen (i.e. NO_3^- and NO_2^-) in the surface layer.

This in line with the results of a study of DMSP production of nine strains of marine phytoplankton under N limitation (Gaul, 2004). The strains included dinoflagellates (*Amphidinium cartearae*, *Heterocapsa pygmea*, *Prorocentrum redfieldii*), haptophytes (*Emiliania huxleyi*, *Calyptrosphaera spaeroidea*, *Prymnesium parvum*), diatoms (*Thalassiosira concaviuscula*, *Nitzschia spec.*) and cryptophytes (*Rhodomonas baltica*). Gaul (2004) observed that all strains showed decreasing DMSP production rates with decreasing N concentrations. Moreover, the N specific DMSP production (i.e. the amount of DMSP produced per µmol particulate organic nitrogen per day) showed pronounced maxima at dissolved inorganic N (DIN) concentrations in the range from 0.7 to 4.8 µmol L^{-1} in six cultures (Gaul, 2004). For *E. huxleyi CCMP373*, *Rh. baltica*, and *P. redfieldii* the N specific DMSP production showed a continuous decrease with decreasing dissolved DIN (Gaul, 2004). Unfortunately, the DMS concentrations were not monitored by Gaul (2004).

The results of a recent culture study of the coccolithophorid *Emiliania huxleyi* showed a 20 times increase of DMS concentrations under nitrogen limitation at a N:P ratio of

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3.2 (here N = ammonium or nitrate). The elevated DMS concentrations were explained by increased activity of the DMSP lyase under N limitation (Sunda et al., 2007). Sunda et al. (2007) suggested that N limitation increases the oxidative stress within algae cells and, therefore, leads to increasing DMSP decomposition to DMS and acrylate, which are known for their ability to effectively scavenge harmful radicals such as hydroxyl radicals (OH). Other stressors such as UV radiation lead to enhanced DMS concentrations via increased DMSP decomposition as well (Archer et al., 2010; Sunda et al., 2002). Recently, Harada et al. (2009) suggested that exposure to UV radiation may lead to a significant decrease of DMSP in phytoplankton cells, but only when these cells are already suffering under N limitation. We conclude, therefore, that the oxidative stress induced by the increasing N limitation in combination with the high UV radiation in the tropical Atlantic off Mauritania caused DMSP algae to increase DMSP decomposition resulting in high DMS concentrations at N:P <7.

3.4.4 DMS photolysis

Various pathways of photochemical degradation of dissolved DMS have been proposed. DMS can react with various oxygen containing radicals such as hydrogen peroxide, singlet oxygen, and OH which are produced by photo excitation of chromophoric dissolved organic matter (see e.g. Vogt and Liss (2010) and references therein). Thus, upwelling events off Mauritania are ideally suited for DMS photo degradation because of the continuously high solar radiation in combination with the high concentrations of organic matter in the surface layer resulting from upwelling-driven productivity. An alternative photo degradation pathway has been suggested only recently: NO_3^- photolysis in aqueous solutions generates OH radicals which react with Br^- to from Br_2^- radicals which in turn react with DMS (Bouillon and Miller, 2005). Indeed, Toole et al. (2004) showed that DMS photochemical degradation is increasing linearly with increasing NO_3^- concentrations. Moreover, they suggested that this effect may be an important DMS loss pathway in nitrate rich surface waters as those typically found in coastal upwelling areas. Furthermore, it was shown that dissolved inorganic carbon

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(DIC) in seawater is counteracting DMS photochemical degradation by scavenging Br_2^- radicals (Bouillon and Miller, 2005). The upwelled surface waters off Mauritania in February 2008 were considerably enriched in DIC (Steinhoff, 2010). Thus, the comparably low DMS concentrations at N:P >7 (Fig 8) may, indeed, indicate that a fraction of dissolved DMS was photolysed, however, the high DIC concentrations present at the beginning of the upwelling may have reduced DMS photolysis via reaction with Br_2^-.

4 Summary

The upwelling event off Mauritania in February 2008 was dominated by diatoms at the coast, where nutrient rich subsurface water was brought to the surface fuelling the productivity. Further offshore, when the nutrients (especially NO_3^-) became depleted in the plumes of the upwelling, cyanobacteria were the most abundant phytoplankton species. Maximum concentrations of DMS, $DMSP_d$ and $DMSP_p$ of 10 nmol L^{-1}, 15 nmol L^{-1} and 990 nmol L^{-1}, respectively, were measured. The maximum $DMSP_p$ concentration is the highest reported from upwelling regions so far and indicates that the Mauritanian upwelling is indeed a hot spot of DMSP and, thus, DMS production. Analysis of the phytoplankton pigments revealed that dinoflagellates were responsible for the DMS production whereas haptophytes (including coccolithophorids) seemed to have played only a minor role for DMS production during the time of our study. Nitrogen limitation was identified to be a major factor for DMS and DMSP production. A switch from high DMSP production to high DMS production was observed when the N:P ratio was below 7. We conclude, therefore, that the oxidative stress induced by the increasing N limitation in combination with the high UV radiation in the tropical Atlantic off Mauritania caused DMSP algae to increase DMSP decomposition resulting in high DMS concentrations. Photolysis of DMS may have contributed to low DMS concentrations in the freshly upwelled waters. Microbial processes such as bacterial consumption of DMS and DMSP can make a significant contribution to the DMS and DMSP distribution. However, these processes have not been investigated in our study.

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Other factors such as MLD and SRD have not influenced the DMS surface distributions off Mauritania. The results from this study are in line with the general observations that coastal upwelling areas are important sites of DMS production. In order to understand the key processes of DMS and DMSP production and to reveal their major driving factors more studies are needed.

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References

Andreae, M. O.: Dimethylsulfide in the water column and the sediment porewaters of the Peru upwelling area, Limnol. Oceanogr., 30, 1208–1218, 1985.

Archer, S. D., Ragni, M., Webster, R., Airs, R. L., and Geider, R. J.: Dimethyl sulfoniopropionate and dimethyl sulfide production in response to photoinhibition in *Emiliania huxleyi*, Limnol. Oceanogr., 55, 1579–1589, 2010.

Barlow, R. G., Cummings, D. G., and Gibb, S. W.: Improved resolution of mono- and divinyl chlorophylls a and b and zeaxanthin and lutein in phytoplankton extracts using reverse phase C-8 HPLC, Mar. Ecol-Prog. Ser., 161, 119–123, 1997.

Barlow, R. G., Mantoura, R. F. C., Gough, M. A., and Fileman, T. W.: Pigment signatures of the phytoplankton composition in the northeastern Atlantic during the 1990 spring bloom, Deep-Sea Res. II, 40, 459–477, 1993.

Belviso, S. and Caniaux, G.: A new assessment in North Atlantic waters of the relationship between DMS concentration and upper mixed layer solar radiation dose, Global Biogeochem. Cy., 23, GB1014, doi:1010.1029/2008GB003282, 2009.

Belviso, S., Sciandra, A., and Copin-Montégut, C.: Mesoscale features of surface water DMSP and DMS concentration in the Atlantic Ocean off Morocco and in the Mediterranean Sea, Deep-Sea Res. I, 50, 543–555, 2003.

Bidigare, R. R.: Analysis of algal chlorophylls and carotenoids, in: Marine particles: Analysis

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and Characterisation, Hurd, D. C. and Spencer D. W., American Geophysical Union, 119–123, 1991.
Bouillon, R.-C. and Miller, W. L.: Photodegradation of dimethyl sulfide (DMS) in natural waters: Laboratory assessment of the nitrate-photolysis-induced DMS oxidation, Environmental Science and Technology, 39, 9471–9477, 2005.
Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655–661, 1987.
Chavez, F. P. and Messié, M.: A comparison of Eastern Boundary Upwelling Ecosystems, Prog. Oceanogr., 83, 80–96, 2009.
David, H. A.: Further applications of range to analysis of variance, Biometrika, 38, 393–409, 1951.
Derevianko, G. J., Deutsch, C., and Hall, A.: On the relationship between ocean DMS and solar radiation, Geophys Res Lett, 36, L17606, doi:17610.11029/12009GL039412, 2009.
Faloona, I.: Sulfur processing in the marine atmospheric boundary layer: A review and critical assessment of modelling uncertainties, Atmos. Environ., 43, 2841–2854, 2009.
Franklin, D. J., Poulton, A. J., Steinke, M., Young, J., Peeken, I., and Malin, G.: Dimethylsulphide, DMSP-lyase activity and microplankton community structure inside and outside of the Mauritanian upwelling, Prog. Oceanogr., 83, 134–142, 2009.
Gaul, W.: Untersuchungen zur Produktion und zum mikrobiellen Umsatz von β-Dimethylsulfoniopropionat, Kiel University, Kiel, 88 pp., 2004.
Hansen, H. P. and Koroleff, F.: Determination of nutrients, in: Methods of seawater analysis, edited by: Grasshoff, K., Kremling, K., and Ehrhardt, M., Wiley-VCH, Weinheim, 159–228, 1999.
Harada, H., Vila-Costa, M., Cebrian, J., and Kiene, R. P.: Effects of UV radiation and nitrate limitation on the production of biogenic sulfur compounds by marine phytoplankton, Aquat. Bot., 90, 37–42, 2009.
Hatton, A. D., Malin, G., and Liss, P. S.: Distribution of biogenic sulphur compounds during and just after the southwest monsoon in the Arabian Sea, Deep-Sea Res. II, 46, 617–632, 1999.
Jeffrey, S. W., Mantoura, R. F. C., and Bjørnland, T.: Data for the identification of 47 key phytoplankton pigments, in: Phytoplankton pigments in oceanography: Guideline to modern methods, Jeffrey, S. W., Mantoura, R. F. C., and Wright, S. W., UNESCO Publishing, 449–559, 1997.
Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp,

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L., Saltzman, E. S., Johnson, J. E., and Liss, P. S.: An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean, Global Biogeochem. Cy., 25, GB1004, doi:10.1029/2010GB003850, 2011.
Louda, J. W. and Baker, E. W.: The biochemistry of pigments, in: Organic marine geochemistry. ACS Symposium Series, edited by: Sohn, M. L., American Chemical Society, 107–126, 1986.
Keller, M. D., Bellows, W. K., and Guillard, R. R. L.: Dimethyl sulfide production in marine phytoplankton, in: Biogenic sulfur in the environment, edited by: Saltzman, E. D., and Copper, W. J., ACS Symposium Series No. 393, American Chemical Society, Washington DC, 167–182, 1989.
Kettle, A. J. and Andreae, M. O.: Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models, J. Geophys. Res., 105, 26793–26808, 2000.
Kiene, R. P.: Measurement of dimethylsulfid (DMS) and dimethylsulfoniopropionate (DMSP) in seawater and estimation of DMS turnover rates, in: Handbook of Methods in Aquatic microbial Ecology, Lewis Publishers, 601–610, 1993.
Kiene, R. P. and Slezak, D.: Low dissolved DMSP concentrations in seawater revealed by small-volume gravity filtration and dialysis sampling, Limnol. Oceanogr. Meth., 4, 80–95, 2006.
Mackey, M. D., Mackey, D. J., Higgings, H. W., and Wright, S. W.: CHEMTAX – a program for estimating class abundances from chemical markers: application to HPLC measurements of phytoplankton, Mar. Ecol-Prog. Ser., 144, 265–283, 1996.
Minas, J. H., Minas, M., and Packard, T. T.: Productivity in upwelling areas deduced from hydrographic and chemical fields, Limnol. Oceanogr., 31, 1182–1206, 1986.
Mittelstaedt, E.: The ocean boundary along the northwest African coast: Circulation and oceanographic properties at the sea surface, Prog. Oceanogr., 26, 307–355, 1991.
Nguyen, B. C., Belviso, S., and Mihalopoulos, N.: Dimethyl sulfide production during natural phytoplanktonic blooms, Mar. Chem., 24, 133–141, 1988.
Riseman, S. F. and DiTullio, G. R.: Particulate dimethylsulfoniopropionate and dimethylsulfoxide in relation to iron availability and algal community structure in the Peru Upwelling System, Can. J. Fish. Aquat. Sci, 61, 721–735, 2004.
Schäfer, H., Myronova, N., and Boden, R.: Microbial degradation of dimethylsulfide and related C_1-sulphur compounds: Organisms and pathways controlling fluxes of sulphur in the biosphere, J. Exp. Bot., 61, 315–334, 2010.
Shenoy, D. M. and Dileep Kumar, M.: Variability in abundance and fluxes of dimethyl sulphide

BGD
8, 8591–8618, 2011

in the Indian Ocean, Biogeochemistry, 83, 277–292, 2007.
Shuman, F. R. and Lorenze, C. J.: Quantitative degradation of chorophyll by a marine herbivore, Limnol. Oceanogr. 20, 580–586, 1975.
Simó, R.: Trace chromatophraphic analysis of dimethyl sulfoxide and related methylated sulfur compounds in natural waters, J. Chromatogr. A, 807, 151–164, 1998.
Simó, R.: From cells to globe: approaching the dynamics of DMS(P) in the ocean at multiple scales, Can. J. Fish. Aquat. Sci, 61, 673–684, 2004.
Simó, R. and Dachs, J.: Global ocean emission of dimethylsulfide predicted from biogeophysical data, Global Biogeochem. Cy., 16, 1078, doi:10.1029/2001GB001829, 2002.
Stefels, J., Steinke, M., Turner, S., Malin, G., and Belviso, S.: Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modeling, Biogeochemistry, 83, 245–275, 2007.
Steinhoff, T.: Carbon and nutrient fluxes in the North Atlantic Ocean. Kiel Unversität, Kiel, 162 pp., 2010.
Steinke, M., Malin, G., Archer, S., Burkill, P. H., and Liss, P. S.: DMS production in a coccolithophorid bloom: Evidences for the importance of dinoflagellate DMSP lyases, Aquat. Microb. Ecol., 26, 259–270, 2002.
Sunda, W. G., Hardison, R., Kiene, R. P., Bucciarelli, E., and Harada, H.: The effect of nitrogen limitation on cellular DMSP and DMS release in marine phytoplankton: climate feedback implications, Aquat. Sci., 69, 341–351, 2007.
Sunda, W., Kieber, D. J., Kiene, R. P., and Huntsman, S.: An antioxidant function for DMSP and DMS in marine algae, Nature, 418, 317–320, 2002.
Toole, D. A., Kieber, D. J., Kiene, R. P., White, E. M., Bisgrove, J., del Valle, D. A., and Slezak, D.: High dimethylsulfide photolysis rates in nitrate-rich Antarctic waters, Geophy. Res. Lett., 31, L11307, doi:10.1029/2004GL019863, 2004.
Vallina, S. M. and Simó, R.: Strong relationship between DMS and the solar radiation dose over the global surface ocean, Science, 315, 506–508, 2007.
Veldhuis, M. D. and Kraay, G. W.: Phytoplankton in the subtropical Atlantic Ocean; towards a better understanding of biomass and composition, Deep-Sea Res. I, 51, 507–530, 2004.
Vogt, M. and Liss, P. S.: Dimethylsulfide and climate, in: Surface Ocean – Lower Atmosphere Processes, edited by: Le Quéré, C., and Saltzman, E. S., American Geophysical Union, Washington, DC, 197–232, 2009.
Wolfe, G. V.: Grazing-activated production of dimethyl sulfide (DMS) by two clones of Emiliania

BGD
8, 8591–8618, 2011

huxelyi, Limnol. Oceanogr., 41, 1151–1160, 1996.
Zubkov, M. V., Fuchs, B. M., Tarran, G. A., Burkill P. H., and Aman, R.: High Rate of Uptake of Organic Nitrogen Compounds by Prochlorococcus Cyanobacteria as a Key to Their Dominance in Oligotrophic Oceanic Waters, Appl Environ Microb, 69, 1299–1304, 2003.

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Table 1. DMS and DMSP concentrations in coastal upwelling regions.

Region	DMS [nmol L^{-1}] Median (min–max)	$DMSP_d$ [nmol L^{-1}] Median (min–max)	$DMSP_p$ [nmol L^{-1}] Median (min–max)	References
Mauritania				
Upwelling (Feb 2008)	1.5 0.2–10	1.6 0.1–15	29 1.4–990	This study
Upwelling (Jan–Mar; avg. 1972–2006)	2.8 0.05–19	ng	ng	Global DMS Database[(a)]
Post upwelling (July/Aug 2006)	ng 1–14	1.9 <0.3–12	6.5 0.01–24	Franklin et al. (2008)
Morocco				
Upwelling (Sep 1999)	ng up to 16	ng	ng up to 150[(b)]	Belviso et al. (2003)
Oman				
Upwelling (Aug/Sep 1994)	1.2 <0.1–4.2	9 <1.0–25	13 1.9–22	Hatton et al. (1999)
Post upwelling (Sep/Oct 1994)	2.9 0.3–6.5	14 <1–42	19 3–36	Hatton et al. (1999)
West India				
Upwelling (Jun–Sept)	33[(c)] 0.3–526	ng	81[(b),(c)] 2.0–916	Shenoy and Dileep Kumar (2007)
Non upwelling (October)	5.8[(c)] 0.2–64	ng	26[(b),(c)] 0.5–160	Shenoy and Dileep Kumar (2007)
Peru				
Upwelling (Jun/Jul 1982)	7.0[(c)] 3–>40	nm	nm	Andreae (1985)
Upwelling (September 2000)	nm	nm	ng 1.0–46	Riseman and DiTullio (2004)

[(a)] http://saga.pmel.noaa.gov/dms;
[(b)] given as $DMSP_t = DMSP_d + DMSP_p$;
[(c)] arithmetic mean; ng and nm stand for not given and not measured, respectively.

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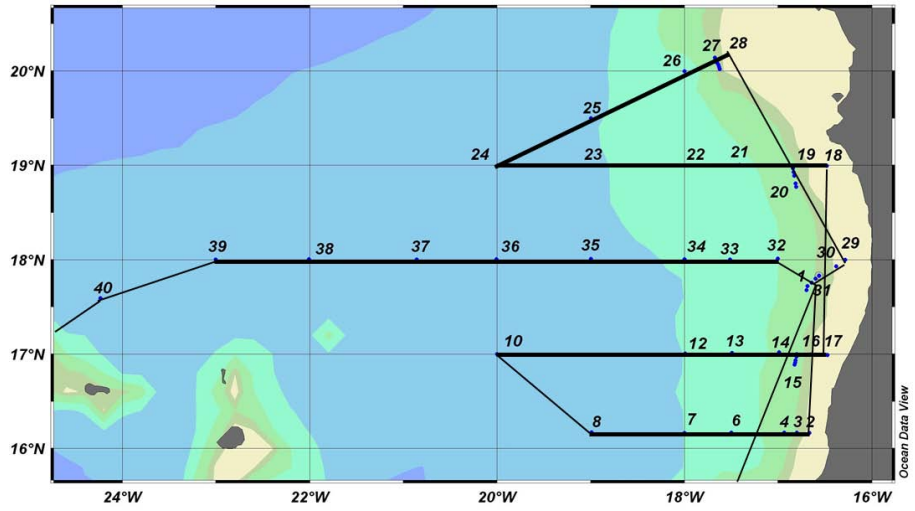

Fig. 1. Cruise track and locations of the sampling stations during the ATA-03 cruise in February 2008. Bold black lines indicate the onshore-offshore transects. The colour coding represents the bathymetry of the sampling area. Dark blue to light brown indicate deep waters (3600 m) to shallow waters (50 m).

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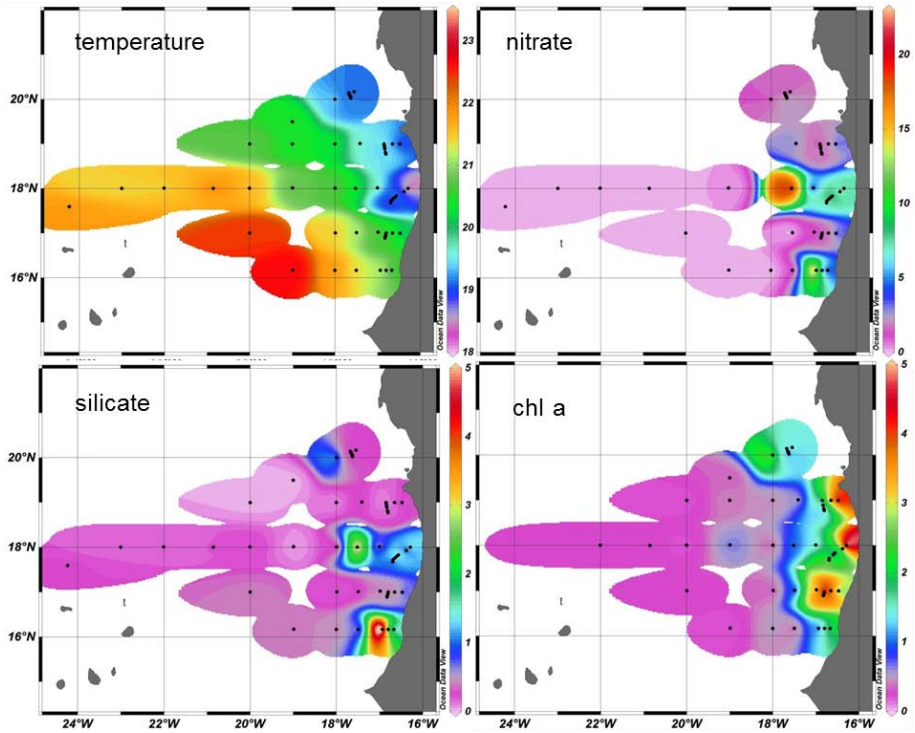

Fig. 2. Surface (5 m) distributions of temperature [°C], nitrate [µmol L^{-1}], silicate [µmol L^{-1}] and chlorophyll-*a* (chl-*a*) [mg L^{-1}] during ATA-03 in February 2008.

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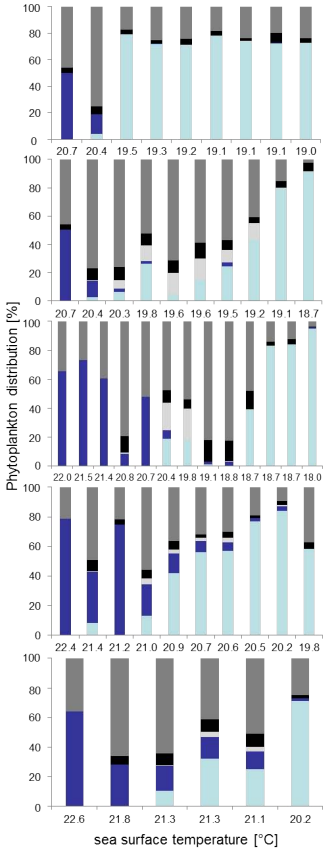

Fig. 3. Phytoplankton distribution in percentage indicated by pigments: diatoms (fucoxanthin, light blue), cyanobacteria (zeaxanthin, dark blue), dinoflagellates(peridinin, light grey), haptophytes (19-hexanoyloxyfucoxanthin, black) and other groups (e.g. cryptophytes, chlorophytes, dark grey) in 5 m depth along onshore-offshore transects of 19–20° N, 19° N, 18° N, 17° N and 16° N (from upper to lower panel, respectively). Pigment distribution was calculated by using CHEMTAX®.

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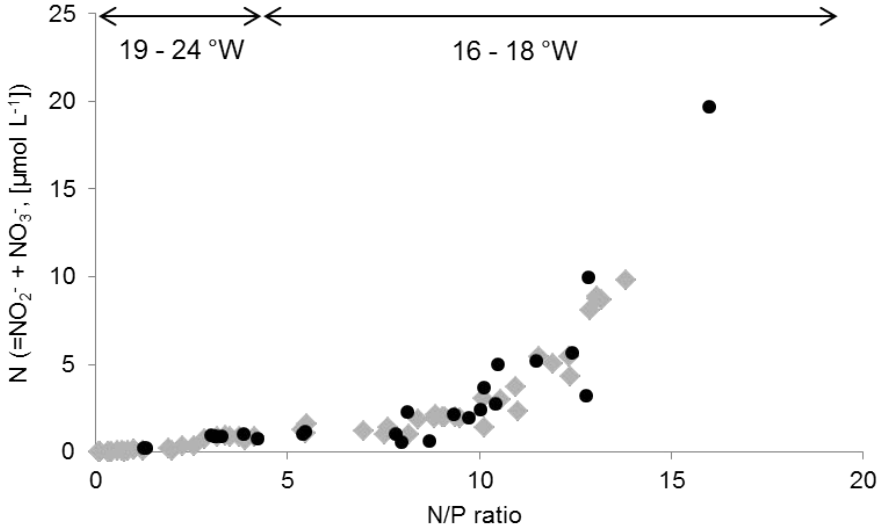

Fig. 4. Nitrogen (N = nitrate and nitrite) vs. N:P ratios in surface water (5 m (grey diamonds) and 10 to 30 m (black dots)). P stands for dissolved phosphate.

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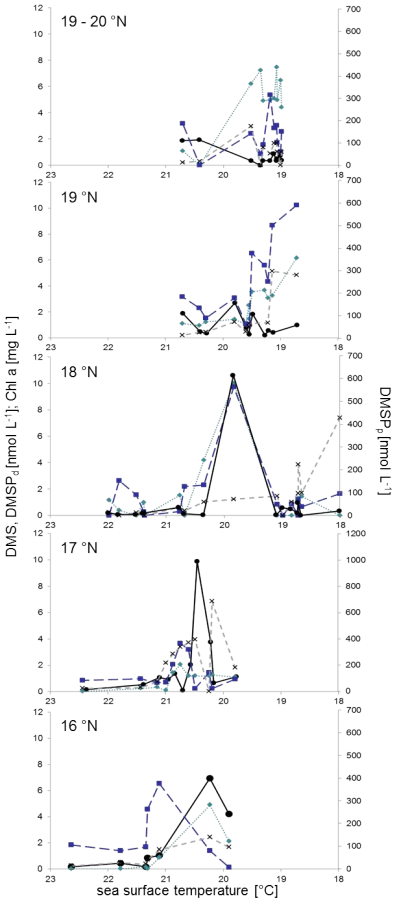

Fig. 5. DMS (diamonds, light blue dotted lines), $DMSP_d$ (squares, dark blue dashed line), $DMSP_p$ (black circles, solid lines) and Chlorophyll (chl-*a*, crosses, grey dashed lines) in 5 m depth along onshore-offshore transects between 16° and 20° N.

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Environmental control on the variability of DMS and DMSP

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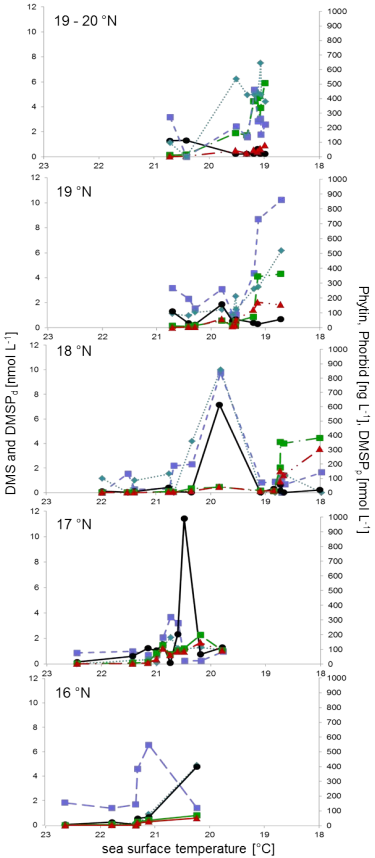

Fig. 6. DMS (diamonds, light blue dotted lines), $DMSP_d$ (squares, dark blue dashed line), $DMSP_p$ (black circles, solid lines), Phorbid (i.e. sum of Phorbid a and pPhorbid, squares, green dashed lines) and Phytin (i.e. sum of Phytin a and pPhytin, red triangles, dashed line) in 5 m depth along onshore-offshore transects between 16° and 20° N.

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Environmental control on the variability of DMS and DMSP

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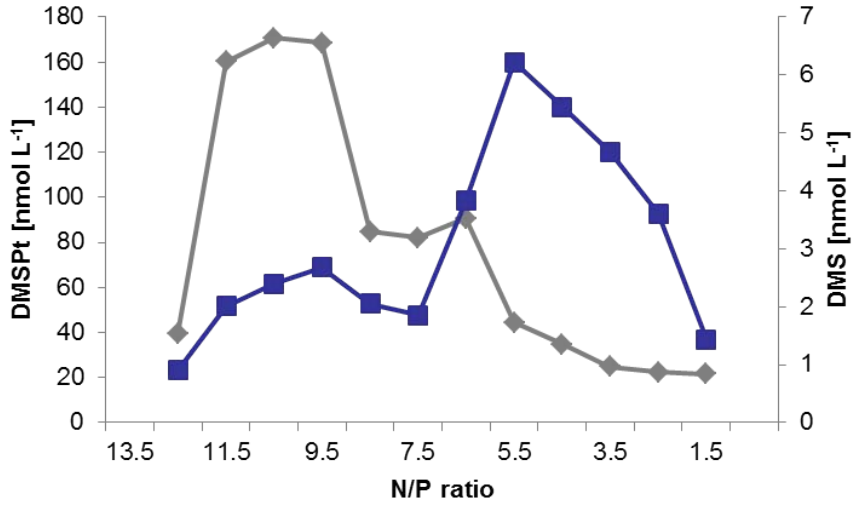

Fig. 7. N:P ratio vs. $DMSP_t$ (grey triangles) and DMS (blue squares) at 5 m depth. N stands for the sum of dissolved nitrate and nitrite, and P stands for phosphate.

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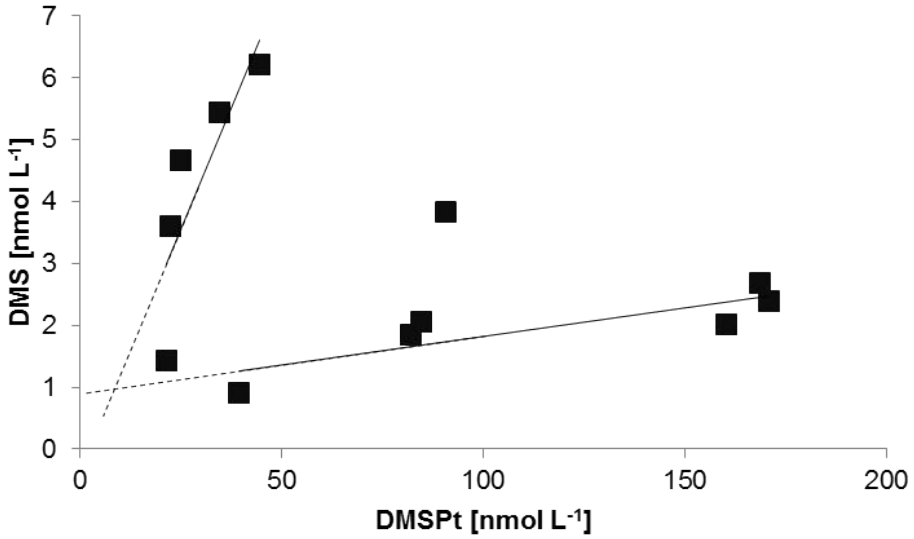

Fig. 8. Binned DMS vs. binned $DMSP_t$: (Upper regression line: $R^2 = 0.69$, $DMS = 0.158\ DMSP_t - 0.393$; lower regression line: $R^2 = 0.73$, $DMS = 0.001\ DMSP_t + 0.893$; dashed lines are elongations of the regression lines).

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