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# Spatial and temporal variability of the dimethylsulfide to chlorophyll ratio in the surface ocean: an assessment in the light of phytoplankton composition determined from space

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## Abstract

Dimethylsulfide (DMS) is biologically produced in the surface ocean and is the dominant natural source of sulfur to the atmosphere. Although DMS is an algal by-product, the ratio of DMS to chlorophyll (DMS:Chl) varies widely in the surface ocean. This is presumably because dimethylsulfoniopropionate (DMSP), the major precursor of DMS, DMSP-lyases, which catalyze the conversion of DMSP to DMS, and Chl vary as well with taxonomic composition than with the physiological state of the algal assemblage. Here we use remote sensing of Chl and phytoplankton dominance from PHYSAT with in-situ measured DMS concentrations to assess on an unprecedented spatial scale the affect of species composition on the DMS:Chl ratio in the surface ocean. Meridional distributions at 22° W in the Atlantic, and 95° W and 110° W in the Pacific, showed the same marked drop in DMS:Chl ratios near the equator, down to few  $\text{mmol g}^{-1}$ , yet the basins exhibited different species dominance signatures. Hence, our results suggest that species composition was of secondary importance in controlling DMS and DMS:Chl variations in equatorial upwellings as well as physiological shifts in algal DMS production since mixed layer growth conditions (i.e., nutrient stress, temperature and light) were relatively homogeneous over the eastern equatorial Pacific. In the Indian sector of the Southern Ocean, warm core eddies with contrasting PHYSAT signatures displayed similar DMS levels. However, DMS:Chl ratios in eddies dominated by *Synechococcus* (SYN) were about 50% lower than that found in eddies showing nanoeucayotes or *Phaeocystis*-like signatures. DMS:Chl ratios varied with latitude in SYN dominated regions with ratios at low latitudes (away from equatorial upwellings) about twice that found at high northern and southern latitudes. This is the sole piece of coherent observations which indicates that species composition and growth conditions affect the large-scale dynamics of the DMS:Chl ratio. Overall, it appears that the DMS:Chl ratio is not consistent within specific phytoplankton groups determined from space. So DMS concentrations can not be derived from water-leaving radiance spectra obtained simultaneously from ocean color sensor measurements of Chl concentrations

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and dominant phytoplankton functional types. To proceed with the global investigation and better discriminate between factors affecting DMS:Chl ratios in the surface ocean, we recommend the use of PHYSAT records with higher spatial resolution in conjunction with other satellite products (e.g. particulate backscattering coefficients and indices of phytoplankton physiology and bloom status).

## 1 Introduction

The flux of dimethylsulfide (DMS) from the ocean to the atmosphere is an important term in climate models. The flux is generally calculated from a wind speed derived gas transfer coefficient (e.g. Liss and Merlivat 1986) and a regional and seasonal average sea surface DMS concentration. These average concentrations are derived from a large database of surface seawater DMS measurements collected over the past 25 years (<http://saga.pmel.noaa.gov/dms/>). The high temporal and spatial variability of DMS concentrations, however, leads to large uncertainties in the calculated fluxes. Surface seawater DMS concentrations can not be measured from space and attempts to correlate DMS concentrations to remotely sensed chlorophyll (Chl) have not proven robust (Kettle et al., 1999). However, if the ratio of DMS to chlorophyll (DMS:Chl) was consistent within specific phytoplankton groups, DMS concentrations could be derived from water-leaving radiance spectra obtained solely from ocean color sensor measurements.

Seawater concentrations of DMS are driven by numerous biological production and consumption processes (recently reviewed by Stefels et al., 2007, and Vogt and Liss, 2009). One of the most important controls on DMS production is the combination of phytoplankton species composition and zooplankton grazing (Stefels et al., 2007). Microzooplankton grazing of prokaryotic picoplankton (cyanophytes and prochlorophytes) is expected to yield no DMS since this algal group produces almost no dimethylsulfoniopropionate (DMSP, the major precursor of DMS) and displays no DMSP-lyase activity to catalyze the conversion of DMSP to DMS. In contrast, the zooplankton grazing

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of phytoflagellates, including the bloom-forming *Phaeocystis* and high-lyase *Emiliania huxleyi* strains, strongly stimulates DMS production. In addition to these taxonomic effects, the physiological condition of algal cells also influences the DMS and DMSP production of phytoplankton (Sunda et al., 2007 and references therein). Diatoms, for example, which typically are low DMS(P)-containing algae, respond to nitrogen limitation by markedly increasing their DMSP cell content. Although the production of DMS by phytoplankton has been the object of extensive research in the laboratory (Stefels et al., 2007), the role that species composition plays in controlling DMS concentrations and the DMS:Chl ratio in the ocean remains elusive because of the difficulty in accessing phytoplankton speciation with a spatio-temporal resolution comparable to that of DMS measurements.

The detection from space of the main dominant phytoplankton groups in marine surface waters is now possible using the PHYSAT algorithm (Alvain et al., 2005). The PHYSAT approach is based on empirical relationship between dominant phytoplankton groups and specific anomalies in the remote sensed signal. The PHYSAT methodology allows to detect the following groups of phytoplankton: diatoms, cyanophytes, prochlorophytes and nanoeucaryotes. This latter group includes the non bloom-forming phytoflagellates. Two new categories were introduced recently (coccolithophores and *Phaeocystis*-like prymnesiophytes; Alvain et al., 2008). Here we use the PHYSAT algorithm, in association with ship-based DMS and satellite-based Chl data to assess the affect of phytoplankton speciation on the variability of the DMS:Chl ratio. We use the Pacific Marine Environmental Laboratory (PMEL) global DMS database (<http://saga.pmel.noaa.gov/dms/>), some published and unpublished DMS transect data not yet available in the PMEL database, and the PHYSAT records over the 1997–2007 period. We compare DMS:Chl ratios to groups dominance derived from PHYSAT, both spatially and temporally, to assess the role of phytoplankton speciation in controlling the regional and large scale variations of surface ocean DMS:Chl ratios. This rather linear approach differs from that of Belviso et al. (2004) who used nonlinear parameterizations to compute DMS concentrations from Chl (SeaWiFS) and an index of the

community structure of marine phytoplankton, the Fp-ratio, which represents the proportion of microphytoplankton within the phytoplankton community, itself nonlinearly related to Chl.

## 2 Methods

### 2.1 DMS datasets

DMS datasets used in this work are for the 1997–2007 period and cover contrasted areas of the Atlantic, Pacific and Indian basins (Fig. 1 and Table 1). Six of the eight cruises were carried out in late spring and during the summer period, including all Southern Ocean cruises.

The methods for the PMEL group are described in Bates et al. (1987). Extensive tests comparing DMS measurements from Niskin bottles, a bucket, and ship's pumping systems showed no significant differences in the DMS data collected from these different samplers. Details regarding the UCI and UBC experimental setups are given by Marandino et al. (2007) and Tortell and Long (2009), respectively.

In the Indian sector of the Southern Ocean, DMS data were obtained during a transit from Kerguelen Island to La Réunion (see Fig. 1). Water samples were collected underway by means of the Marion Dufresne II's clean seawater supply line used currently for CO<sub>2</sub> fugacity measurements. During the KEOPS cruise (19 January–13 February 2005) in the Indian sector of the Southern Ocean, a comparison was conducted between the clean seawater system and the CTD (conductivity, temperature, depth) rosette sampler (Belviso et al., 2008). Figure S1 (<http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>) shows that there is indeed a pump effect on the dissolved and particulate material. Particulate DMSP is lower in pump samples (Fig. S1b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>), while dissolved DMSP is higher (Fig. S1c: <http://www.biogeosciences-discuss.net/>)

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7/3605/2010/bgd-7-3605-2010-supplement.pdf). This suggests that cell lysis in the seawater pumping system transfers DMSP from the particulate to the dissolved phase. Total DMSP (DMSPt), however, appears to be conserved (Fig. S1a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>)

and DMS concentrations from the CTD and pump samples are linearly correlated (Fig. S1d: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). The slope of the relationship ( $DMS_{CTD}:DMS_{pump}$ ) is equal to 0.65 when it is forced to pass through zero ( $r^2=0.89$ ,  $n=29$ ,  $P<0.01$ ). Thus, this correction factor was applied to this specific set of underway DMS measurements.

During cruise UM0506 of the RT/V Umitaka-Maru (Tokyo University of Marine Science and Technology) carried out in January 2006, seawater was analyzed for DMS and Chl concentrations. Water samples were collected with a rosette sampler equipped with 20-L Niskin bottles and a CTD probe (Falmouth Scientific, Inc.). Surface seawater was also collected with the means of the ship's pumping system from a depth of approximately 5 m. For Chl concentrations, seawater samples were filtered onto 25 mm Whatman GF/F filters. Chl was extracted with N, N-dimethylformamid, and Chl concentrations were determined using a Turner Designs Model 10-AU Fluorometer (Hori-moto et al., 2007). DMS concentrations were measured as described by Kasamatsu et al. (2004). No significant differences in the DMS data collected from these different samplers were found.

## 2.2 Phytoplankton composition from space

The PHYSAT method was used in order to obtain maps of dominant phytoplankton composition along the transects described in Table 1. It is based on classical ocean color measurements in the visible spectrum and allows the classification of specific spectral anomalies (for  $Chl < 4 \text{ mg m}^{-3}$  and clear sky conditions) defined as:

$$nLw^*(\lambda) = nLw(\lambda)/nLw_{ref}(\lambda, Chl)$$

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where  $nLw_{ref}(\lambda, Chl)$  is a simple model of  $nLw$  that accounts only for the Chl concentration. Using this relationship, the first order signal variation (a function of Chl) is removed and the second order variation from the total  $nLw$  spectra variability is isolated and defined by  $nLw^*(\lambda)$ . Specific shapes and amplitudes of  $nLw^*$  have been associated with specific dominant phytoplankton groups using in situ measurements of biomarkers pigments.

The PHYSAT algorithm was applied to the SeaWiFS data archive from 1997 to 2007 (Alvain et al., 2005, 2008) to identify the following Phytoplankton Functional Types (PFTs) in surface waters: Prochlorococcus (PRO), Synechococcus (SYN), nanoeucaryotes (NANO), Phaeocystis-like (PHAEO), coccolithophores (COC), and diatoms (DIAT).

The dominant PFT monthly maps used in this study were computed with PHYSAT applied to SeaWiFS daily L3-binned GAC data between 1997 and 2007 (processing version 5.2n – <http://oceancolor.gsfc.nasa.gov/>). Daily maps of phytoplankton groups at a resolution of  $1/12^\circ$  were used to generate monthly maps of dominant phytoplankton group at  $1/4^\circ$  by selecting the most frequently detected group for at least half of the valid (including unidentified) pixels. Note that no phytoplankton group is assigned to a grid box for which no phytoplankton group dominates or for which unidentified pixels prevail. As for all ocean color observational methods, it is not possible to validate PHYSAT everywhere. The main difficulty of the PHYSAT validation is that in situ observations should match up good quality daily pixels in terms of atmospheric conditions (very clear sky conditions are necessary because second order signal variations are used) and in terms of phytoplankton bloom conditions. Indeed, the PHYSAT method detects phytoplankton groups only when they are dominant, i.e. in situations where a given phytoplankton group (evaluated from pigment biomarkers) is a major contributor (at least 60%) to the total pool of pigments (Alvain et al., 2005). However, a large validation exercise of PHYSAT has been carried out at the global scale from in situ measurements available mainly from the NOMAD (Werdell and Bailey, 2005) and Gep&CO projects (Dandonneau et al., 2004). This PHYSAT validation work has been published

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in Alvain et al. (2008). According to this validation, the signatures of DIAT, NANO, SYN and PRO are validated. The main result of this validation is that PHYSAT leads to only a few wrong identifications, mostly between PRO and SYN in the equatorial Pacific. This result is not surprising considering the close characteristics (geographical distribution, size and specific radiances) of the two groups. The geographical distributions and seasonal successions of major phytoplankton groups were also investigated. The comparisons are in good agreement with non-satellite studies (Marty and Chiavérini, 2002; Longhurst, 2007). Phaeocystis-like phytoplankton and coccolithophores are the more uncertain groups. They have not been directly validated from coincident in situ measurements, but have been detected in areas where blooms of both organisms have been reported and during periods of favorable growth (Alvain et al., 2008; Goffart et al., 2000; Smith et al., 2003). Phaeocystis is known for its peculiar optical properties related to the white mucus exuded by cells during blooms. Hence, validation of PHAEO is still in progress.

PHYSAT PFT information which matches the DMS measurements according to month and year was extracted from the PHYSAT database. However, there could be times when the succession of phytoplankton groups is too fast and would not be detected by this method. We have also used the monthly climatology (1998–2006) of the most dominant phytoplankton groups detected by PHYSAT to detect local anomalies in PFT composition and fill the spatial gaps if necessary (for example when clouds or aerosol loading of the atmosphere are unfavorable for running the PHYSAT algorithm). Moreover, monthly Chl concentration was extracted from the 9 km SeaWiFS archives to produce DMS:Chl ratios at the location of the DMS measurements.

### 3 Results

The PFT records from PHYSAT (monthly data and monthly climatological data) were extracted along the cruise tracks displayed in Fig. 1 and compared to sea surface DMS concentrations. These datasets were selected based on 3 criteria: (1) the overlap in

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time with the PHYSAT data (1997–2007), (2) the high horizontal resolution and (3) the spatial extension of the data set (long cruise tracks across the major oceanic basins). In the region of the eastern equatorial Pacific Ocean where the November 2003 cruise (CN-148, Fig. 1) was carried out, the mixed layer growth conditions of phytoplankton (i.e., nutrient stress, temperature and light) were relatively homogeneous (Behrenfeld and Boss, 2006). Under such conditions, physiological shifts in intracellular chlorophyll concentration are better constrained than in highly variable environments such as along the Atlantic transect (CN-139). The reasonable homogeneity of the eastern equatorial Pacific with respect to phytoplankton physiology (Behrenfeld and Boss, 2006) makes this area more suitable to investigating the affect of species composition on DMS:Chl ratios. That is why the eastern equatorial Pacific Ocean is of central importance in our study.

First, an overview of the main patterns of monthly sea surface Chl concentrations and PFT composition is made at the regional scale for all cruise tracks. The PHYSAT monthly climatology is investigated in this case because the monthly maps corresponding in time with the cruise tracks would have displayed too many unfavorable situations because of cloud coverage and aerosol loading of the atmosphere. Then, we extracted data from the satellite records along the track of each survey for subsequent comparison with field observations according to the date (month-year) of the DMS measurements.

### 3.1 Overview of the main patterns of chlorophyll and PFT composition

Chl monthly fields (left panels) and dominant PFT from the PHYSAT climatology (right panels) are presented in Figs. 2, 3 and 4.

#### 3.1.1 North and Equatorial Pacific

In the western Pacific, the track of the research vessel cut across the western warm pool (WWP) in spring. Ultra-oligotrophic ( $\text{Chl} < 0.1 \text{ mg m}^{-3}$ , Fig. 2a) and oligotrophic

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waters ( $\text{Chl} \sim 0.1 \text{ mg m}^{-3}$ ) occupy the center of the zone. Mesotrophic and eutrophic waters ( $0.15 < \text{Chl} < 1 \text{ mg m}^{-3}$ , Fig. 2a) are found north of  $30^\circ \text{ N}$ , around Papua New Guinea and at the equator at  $175^\circ \text{ E}$ . Climatological PFT dominance in this region displays also latitudinal variations (Fig. 2b). NANO dominates north of  $30^\circ \text{ N}$  and around Papua New Guinea. The center of the zone is occupied by SYN where most of the DMS survey was carried out. In between the two zones, there is either a  $5^\circ$ -wide zone where PRO dominates (around  $25^\circ \text{ N}$ , Fig. 2b) or a much wider zone roughly south of  $5^\circ \text{ N}$  where PRO and SYN alternate over short distances. The cruise ended in such mixed PRO-SYN areas.

In the central Pacific during early summer (June 2004), oligotrophic waters are found roughly between  $10^\circ \text{ N}$  and  $35^\circ \text{ N}$  (North Pacific Gyre – NPG, Fig. 2c). The transition from oligotrophy to mesotrophy is not the same northward (towards subtropical waters and the North American coasts) or southward (towards the equatorial divergence zone) in terms of PFT composition (Fig. 2d). Northward, there is a band dominated by PRO and NANO. Some DIAT hot spots are also observed there. Southward, there are no marked changes in PHYSAT signatures. Indeed, oligotrophic waters of the NPG and the more productive ones near the equator display the same mixed (SYN-PRO) signatures. In fact, “pure” SYN signatures are only detected in a zone west of  $170^\circ \text{ W}$  between  $10^\circ \text{ N}$  and  $25^\circ \text{ N}$ .

In November 2003, mesotrophic waters were found off the Central and South American coasts and along the equator (Fig. 2e). The main PFT features in this region for November are: (1) NANO dominates off Central America, (2) DIAT dominates off Peru, and (3) PRO is well represented along the equator (Fig. 2f). A highly dominant SYN signature is found south of  $4^\circ \text{ S}$  and west of  $100^\circ \text{ W}$ . The PHYSAT signatures in the eastern equatorial Pacific will be described afterwards.

### 3.1.2 Atlantic Ocean

The January 1999 Chl map (Fig. 3a) shows three zones of high productivity (Guinea dome, Benguela upwelling and the equatorial divergence) and two zones poor in Chl (north and south subtropical gyres). Unfortunately, the ship did not cut across the ultra-oligotrophic waters of the western South Atlantic gyre ( $\text{Chl} < 0.1 \text{ mg m}^{-3}$ ). In January, the oligotrophic waters of the north Atlantic gyre ( $20^\circ \text{ N}$ ) exhibit a PRO signature (Fig. 3b) while the northern edge of the south Atlantic gyre exhibits PRO and NANO signatures. Elsewhere, the NANO signature prevails especially in the productive tropical and equatorial waters. In summer, the northwestern Atlantic is a rather productive region with Chl concentrations north of  $44^\circ \text{ N}$  rising up to  $2 \text{ mg m}^{-3}$  (Fig. 3c). The PHYSAT climatology of the area shows a general prevalence of the NANO signature (Fig. 3d). Diatoms are confined in the northeast quarter of the sector. According to the climatology, coccolithophores are dominant only over the Icelandic shelf. However, the SeaWiFS data used by the PHYSAT method, i.e. level 3 daily GAC products, are screened to remove coccolithophorid blooms using a threshold on nLw during the data processing, so that the PHYSAT results likely underestimate the actual size of coccolithophorid blooms (Alvain et al., 2008).

### 3.1.3 Indian and Pacific sectors of the Southern Ocean

In the Indian and Pacific sectors of the Southern Ocean, the PFT composition is considerably more patchy than at lower latitudes in the Atlantic and Pacific oceans (Fig. 4, right panels). Nevertheless, a yellow band (SYN dominated waters) coincides with the strong frontal systems north of  $48^\circ \text{ S}$  which separate subtropical waters (NANO + PRO signatures) from subantarctic and Antarctic waters (NANO + PHAEO + DIAT signatures, Fig. 4b). A clear NANO signature is observed near the ice edge south of  $64^\circ \text{ S}$  between  $20^\circ \text{ E}$  and  $70^\circ \text{ E}$  (Fig. 4d). The DIAT signature predominates in December in the Pacific sector of the southern Ocean (Fig. 4h). The distribution of Chl is also patchy but, nevertheless, some general features can be drawn (Fig. 4, left panels).

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The subtropical and subantarctic fronts of the Indian Ocean where SYN dominates are rich in Chl (Fig. 4a). There are island effects over the Kerguelen Plateau (Fig. 4a and c). In the Pacific sector of the Southern Ocean, a huge increase in Chl concentration is observed at the end of springtime (Fig. 4e and g) when diatoms bloom (Fig. 4h).

### 3.2 DMS:Chl ratios and PHYSAT monthly data extracted along cruise tracks

The spatio-temporal variations of the following parameters were investigated: Sea Surface Temperature (SST), Chl from the SeaWiFS sensor, species composition (NANO, PRO, SYN, DIAT, PHAEO and COC) from PHYSAT, DMS concentration and DMS concentration normalized to Chl concentration (DMS:Chl).

#### 3.2.1 Pacific basin

Figure 5 shows the spatio-temporal variations of these parameters in tropical and equatorial areas of the Pacific basin. In the Pacific western warm pool (WWP), SST was over 29 °C (Fig. 5a) and surface waters displayed low phytoplankton biomass ( $\text{Chl} < 0.1 \text{ mg m}^{-3}$ , Fig. 5b). The DMS:Chl ratio ranged between 13 and 55  $\text{mmol g}^{-1}$  and was on average  $25 \pm 7.5 \text{ mmol g}^{-1}$  (Fig. 5c,  $n=65$ ). The PFT signatures alternated between SYN and PRO (Fig. 5c). Climatological (May) and monthly (May 2004) PHYSAT data extracted from maps are in agreement.

In the central Pacific, there was an equatorward positive gradient of SST, Chl and DMS concentrations (Fig. 5a and b). PFT signatures in this region and in the previous one were similar except near the equator where some NANO were present (Fig. 5c). Although the DMS:Chl ratio was about twice as high a few degrees north of the equatorial divergence (EU) than in the area where the north equatorial counter current (NECC) and the north equatorial current (NEC) flow (4–15° N), overall the ratio was 2–3 fold lower in the central than in the western Pacific.

In the eastern equatorial Pacific, water column density profiles indicated a shallow (10–25 m) surface mixed layer throughout the study region, and daily mixed layer

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growth irradiances were relatively high and invariant (Behrenfeld and Boss, 2006). Under such conditions, light-dependent physiological changes within the mixed layer are expected to be minimal. The gradients of SST were considerably higher than elsewhere in the equatorial Pacific (Fig. 5d). Density contours between 12° N and 8° S along the 95° W longitudinal line and 8° S and 8° N along the 110° W longitudinal line (see Fig. 2a and b in Behrenfeld and Boss, 2006) indicated that the EU was located between 0° and 2° S at 95° W and between 1° N and 2° S at 110° W. The convergent equatorial front (CEF), which separates the warm and light waters of the NECC from the cooler and denser waters of the EU, is an area where DMS accumulates. The CEF was crossed 3 times during the cruise and DMS concentrations were systematically higher there than in the surrounding areas (Fig. 5e). Water masses south of the equator (south equatorial current (SEC) and north of the NECC (eastern warm pool – EWP – and the transition zone – T – between EWP and NECC), also displayed relatively high DMS levels. DMS concentrations were lowest in the EU. Since Chl concentrations were highest here, the DMS:Chl ratio (Fig. 5f) was very low. The PFT signatures in EU vary with longitude. At 95° W, in the vicinity of the Galapagos Island (GP, date: 3 and 4 November), SYN dominated whereas far to the west (110° W) PRO dominated (date: 11 and 12 November). Based on the PFT climatology, PRO is more typical in the EU than SYN. SYN clearly dominated in the SEC both in November 2003 and in the PFT climatology. NANO was a rather rare PFT signature in the eastern Pacific in November. Hence, the area was reasonably homogeneous with respect to phytoplankton physiology and species composition.

In the northern Pacific, the DMS:Chl ratio increased from 5–12 mmol g<sup>-1</sup> at 20–25° N to 58–67 mmol g<sup>-1</sup> at about 40° N, but not steadily (Fig. S2c: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). The ratio paralleled the steady latitudinal decrease of SST (Fig. S2a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>) and was controlled by the DMS concentration (Fig. S2b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). An increase of the DMS:Chl

ratio, also paralleling the SST but of smaller amplitude, was observed off the north American coasts towards the center of the north Pacific at 45° N. Between 40° N and 45° N, the ratio dropped to low values when the vessel cut across a phytoplankton bloom. Unfortunately, no satellite data was available to produce PHYSAT signatures in this bloom area. Away from this bloom the signatures alternate between NANO, PRO and SYN.

### 3.2.2 Atlantic basin

The January 1999 cruise cut across a series of currents from 38° N to 30° S (Gulf Stream – GS – NECC, SEC and the Benguela current, Fig. 6a). It also crossed the Sargasso Sea, central waters of the north Atlantic subtropical gyre (SG), a westward extension of the Guinea Dome (GD-ext), the equatorial divergence (EU) and the northern edge of the south Atlantic subtropical gyre before entering the more biologically productive areas off the African coasts. The SG waters were poorer in Chl but about twice richer in DMS than the Gulf Stream and the Sargasso Sea (Fig. 6b) yielding DMS:Chl ratios up to 35 mmol g<sup>-1</sup> (Fig. 6c). The PFT signature in the SG was mainly PRO. In the northern and southern edges of the north Atlantic SG, the signatures alternated between PRO and NANO. The January PFT climatology depicts a slightly different picture since PRO is not detected north of 25° N while PRO occurred up to 30° N in January 1999. NANO was the dominant PFT signal in the equatorial region from 10° N to 10° S. This signature was associated with low DMS:Chl ratios and the EU was characterized by the lowest values (3 mmol g<sup>-1</sup>). The northern edge of the south Atlantic subtropical gyre was dominated by PRO with DMS:Chl ranging between 30 and 50 mmol g<sup>-1</sup> (Fig. 6c). However, to the east the influence of the Benguela current was noticed. DMS and Chl highs and lows alternated over short distances. While DMS concentrations were over 2 nM everywhere, a clear positive gradient of Chl was observed towards the African coasts. The DMS:Chl ratio follows a similar trend since it is mainly controlled by Chl. The lowest ratios were observed in the core of the coastal

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upwelling (off Namibia) were SSTs drop below 16 °C (Fig. 6a). The PFT signature was NANO there. Offshore it alternated between NANO and PRO. The SYN signature was extremely rare in January along the track of the research vessel.

The July 2007 cruise cut across cold (Fig. 7a) and poorly productive (Fig. 7b) waters between 49° W and 53° W where the Labrador current flows. This is a transition area separating continental shelf waters (low salinities in the range 30.5–31.5) from the Atlantic subarctic waters (higher salinities in the range 34–35, Fig. 7a). The lowest DMS levels encountered on this cruise (0.9–1.0 nM) were observed there. A major change in PFT composition took place at about 45° W (Fig. 7c). The southwestern sector was dominated by NANO and the DMS:Chl ratio was in the range 2–10 mmol g<sup>-1</sup>. The northeastern sector displayed a larger range (2–20 mmol g<sup>-1</sup>) and a much less homogeneous PFT composition. The six PHYSAT categories were represented in this sector. However, the COC and PHAEO signals were recorded outside the area surveyed for DMS (Fig. 7c). The highest DMS levels were associated with DIAT and SYN signatures. This is apparently in contradiction with the observations of Marandino et al. (2008) who found that the DMS variability in this sector was related to the satellite-derived distributions of suspended calcite in the form of coccoliths and coccolithophores. However, it should be reminded that the SeaWiFS data used by the PHYSAT method are screened to remove coccolithophorid blooms, so that the PHYSAT results likely underestimate the actual size of coccolithophorid blooms (Alvain et al., 2008). This result can also be explained by the fact that monthly syntheses have been used so that episodic blooms could be missed.

### 3.2.3 Indian and Pacific sectors of the Southern Ocean

Data were collected from four surveys carried out in the Indian and Pacific sectors of the Southern Ocean.

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5 About 200 seawater samples were analyzed for DMS along the cruise track of RV Mar-  
ion Dufresne II in late February 2005 between the islands of Kerguelen and Crozet,  
and across the frontal system north of Crozet Island on the way to La Réunion (Fig. 8a  
and b). The ship followed the same route as in December 1997, along which DMS  
measurements were performed for the first time by Sciare et al. (1999). DMS concen-  
trations range between 0.25 and 6.1 nM (Fig. 8c and d). The amplitude of the DMS  
10 concentrations measured in 2005 was large (factor of 25) but not as large as observed  
in 1997 (Sciare et al., 1999; factor of 40). The lowest DMS concentrations were ob-  
served in shallow waters (<200 m) over the Kerguelen Plateau, north of the polar front  
during a phytoplankton bloom (Fig. 8d; see also Park et al., 2008). As a consequence,  
DMS:Chl ratios were as low as  $0.5 \text{ mmol g}^{-1}$  (Fig. 8f). Unfortunately, few PHYSAT sig-  
natures are available in this area to evaluate the species composition of the bloom  
15 (Fig. 8f). However, the few PHYSAT data suggest NANO or SYN but not DIAT or  
PHAEO. In the warm core eddy over the slope (200 m–2000 m depth) between  $65^\circ \text{ E}$   
and  $68^\circ \text{ E}$  (Fig. 8b), Chl levels were 2–6-fold lower than over the plateau. The DMS  
trend was the exact opposite (Fig. 8d). The DMS:Chl ratio peaked over the slope with  
values up to  $22 \text{ mmol g}^{-1}$ , increasing by a factor of 40 over one degree longitude. The  
20 dominant PFT signature was PHAEO both climatologically and in the February 2005  
data (Fig. 6f). The ship cut across a second warm core eddy between  $56^\circ \text{ E}$  and  $60^\circ \text{ E}$   
(Fig. 8b). Satellite altimetry suggests that this anticyclonic eddy detached from the  
Antarctic circumpolar current several weeks before (data not shown). It was as rich  
in DMS as the eddy located over the slope but its pigment content was roughly twice  
25 higher. Consequently the DMS:Chl ratios were not as high as they were eastward and  
the associated PFT signature was mainly SYN. A third hydrologic structure was sur-  
veyed between  $56^\circ \text{ E}$  and the coasts of Crozet. It was as rich in DMS as the other  
structures but displayed intermediate Chl levels (Fig. 8d). The highest ratios (up to

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18 mmol g<sup>-1</sup>) were measured in a salinity front (Fig. 8b) and they were associated with NANO signatures (Fig. 8f).

Unfortunately the horizontal transects of DMS, Chl (Fig. 8c) and PHYSAT (Fig. 8e) across the three fronts located north of Crozet (Fig. 8a) are not at the same spatial resolution. Some coherence between the February 2005 data and the PHYSAT monthly climatology was found for NANO but not for PRO. A NANO signature was detected between the Agulhas front and the subtropical front in association with two peaks of DMS and Chl which coincided spatially (Fig. 8e). However, the DMS:Chl ratio was not homogeneous there but decreased by a factor of three over half a degree of latitude. The transition zone between the Agulhas front and the warm subtropical water was also the place of large spatial variations in this ratio but PFT signatures from PHYSAT are missing.

RT/V Umitaka Maru explored also the Indian Sector of the Southern Ocean during summer but mainly south of the polar front and along the pack-ice where SSTs were below zero (Fig. S3a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). Only one DMS “hot spot” (8–9 nM) was found during the transect at the limit of the pack-ice in mid-January ( Fig. S3b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). Since samples were also analyzed for pigments, the opportunity is taken to compare DMS:Chl<sub>in situ</sub> to DMS:Chl<sub>sat.</sub> ratios. This is important because satellite and in situ Chl concentrations can differ markedly at high latitudes (Preunkert et al., 2007). The DMS:Chl “hot spot” (30 mmol g<sup>-1</sup> vs. 50 mmol g<sup>-1</sup>, respectively) is seen in both records (Fig. S3c: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>) and it coincides with the sole PHAEO signature of the area. In late January, the ship cut across a diatom bloom which was associated with considerably lower ratios (i.e. about a 10-fold decrease was observed between the PHAEO and DIAT areas). The mean DMS:Chl ratio associated with DIAT was highly variable 8.2±7.4 mmol g<sup>-1</sup> (n=8).

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Tortell and Long (2009) surveyed the latitudinal distribution of DMS in the Southern Ocean roughly along the dateline from 53° S down into the Ross Sea.

Two transects were carried out, southbound in November and northbound in December. In the present study, the investigation area was restricted to surface waters free of ice so roughly between 53° S and 64° S. SSTs decreased more steadily in December (Fig. S4b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>) than in November (Fig. S4a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>).

The subantarctic and polar fronts (SAF and PF, respectively) were crossed between 56° S and 60° S. In November, the DMS concentrations were close to the detection limit of the instrument (1 nM) while Chl concentrations were generally equal or over 0.15 mg m<sup>-3</sup> (Fig. S4c: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). DMS:Chl ratios were generally lower than 10 mmol g<sup>-1</sup>. NANO was the predominant PFT signature north of 60° S (Fig. S4c: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>).

However, the broad Chl maximum located south of the SAF displayed mainly PRO and SYN signatures. In December, SSTs were roughly one degree warmer than in November (Fig. S4b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>). Chl concentrations rose markedly everywhere except at the location of the November broad maximum south of the SAF (Fig. S4d: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>).

The largest phytoplankton bloom was observed north of 55° S, but since the ship did not investigated exactly the same areas (east of the line of changing date in November (Fig. S4a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>), west of the line of changing date in December (Fig. S4b: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>), the amplitude of the growth cannot be assessed

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from these figures but only from the SeaWiFs images (see Fig. 4). The comparison is not allowed for DMS for the same reason. This bloom was associated with the lowest values of the DMS:Chl ratio of the area (Fig. S4f: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>).

Unfortunately, PHYSAT records were very few in this area. Nevertheless, when combined, the monthly climatology and the December 2006 map suggest that the species composition of the bloom differs from north to south (i.e. SYN dominates in the north and NANO in the south). Whatever the composition is, the ratios are similarly low. A huge rise of the ratio is seen when travelling south of this bloom area. The DMS:Chl ratio culminated up to  $35 \text{ mmol g}^{-1}$  in the center of the SAF where the PFT signature was PRO. A similar high-DMS and low-Chl zone was found between  $57^\circ \text{ S}$  and  $58^\circ \text{ S}$  but in this case the PFT signature was NANO. In between, where Chl concentrations remained unchanged, the PFT signature was free of PRO. So the PRO signature was lost between the two surveys but SYN remained. South of  $58^\circ \text{ S}$ , that is in the area of the polar front, the permanent open ocean zone (POOZ) and the seasonal ice zone (SIZ), PHYSAT detected several blooms of diatoms and *Synechococcus* but nanoeucaryotes were rare. The mean DMS:Chl ratios associated with DIAT and SYN were  $11.3 \pm 4.8 \text{ mmol g}^{-1}$  and  $7.6 \pm 2.9 \text{ mmol g}^{-1}$ , respectively.

## 4 Discussion

Laboratory cultures have shown that phytoplankton taxonomy strongly affects DMS(P) production (Stefels et al., 1997 and references therein). The question of whether phytoplankton abundance and species composition are major drivers of DMS variations in coastal and open marine waters is much more difficult to address. For example, to evaluate how important the taxonomic composition of the phytoplankton was in the spatio-temporal distribution of DMS around mainland Britain, Turner et al. (1988) first identified, enumerated and converted to carbon biomass each particular group or species of phytoplankton. Then they investigated the relationship between DMS

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and Chl concentrations for samples containing an identifiable dominant group. This way, they found that the main sources of DMS were coccolithophores and various dinoflagellates. The PHYSAT tool provides a way to trace at an unprecedented scale the dominant phytoplankton populations from space. However, the PHYSAT tool is not quantitative which is why it is used here in conjunction with relative changes in DMS (i.e. DMS normalized to Chl) but not with absolute concentrations of this gas. For example, we are searching here for high DMS:Chl ratios in NANO- or COC-dominated areas and low ratios in SYN-, PRO- or DIAT-dominated ones because, according to culture work, NANO and COC are higher DMS producers than SYN, PRO and DIAT. There are limitations to this approach since DMS production can derive from a sub-fraction of marine organisms classified as non-dominant by PHYSAT. The survey in the North Atlantic between the US coasts and Iceland (CN-233) illustrates such a limitation to our approach. Indeed, Marandino et al. (2008) showed that the variability in seawater DMS levels was related to the satellite-derived distributions of coccoliths and, to a lesser extent, chlorophyll. However, PHYSAT did not detect COC signatures along the cruise track except in the vicinity of Iceland where, unfortunately, DMS was not measured. Instead, according to PHYSAT phytoplankton was dominated by diatoms and cyanobacteria (Fig. 7c). The distribution of calcifying and silicifying phytoplankton in relation to environmental and biogeochemical parameters during the late stages of the 2005 north Atlantic spring bloom was investigated by Leblanc et al. (2009). The spatial distributions of fucoxanthin, biogenic silica, 19'-hexanoyloxyfucoxanthin, particulate inorganic carbon (calcite) and peridinin concentrations, showed that diatoms dominated the phytoplankton community over prymnesiophytes, coccolithophores and autotrophic dinoflagellates in the Icelandic basin and shelf in early July. So both PHYSAT and ship observations show that diatom blooms in the northwest Atlantic in summer are not free of coccolithophores. Thus, the rather low mean DMS:Chl ratio in DIAT dominated areas ( $4.8 \pm 1.5 \text{ mmol g}^{-1}$ ,  $n=23$ ) could result from the production of DMS by coccolithophores (DMS vs. calcite relationship of Marandino et al., 2008, which supports earlier findings of Matrai and Keller, 1993) and diatoms responsible for the high chlorophyll levels. In

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the study of Vogt et al. (2008) carried out in a Norwegian fjord, DMS:Chl ratios were even lower (in the range  $1\text{--}2\text{ mmol g}^{-1}$ ). When most of the DMS was accumulated, the phytoplankton bloom was dominated by diatoms and prymnesiophytes, including lithed *Emiliana huxleyi* cells. However, a dominant population (DIAT for example) may be in such an unfavorable physiological state (nitrogen-limitation of growth for example) that its DMS production would be unusually higher than expected (Sunda et al., 2007). Also, by comparing DMS:Chl ratio with PHYSAT signatures we implicitly underestimate the role played by the chemical and biological removal processes of DMS, and the well known physiological adaptation of the Chl content of phytoplankton cells. With this caveats in mind, we have explored the potential of PHYSAT in the field of the marine sulfur cycle in a more systematic way than Colomb et al. (2009) in their study carried out in the Indian sector of the Southern Ocean.

#### 4.1 Phytoplankton speciation and DMS:Chl ratios in equatorial upwellings

Based on PHYSAT data presented here, phytoplankton speciation is of second order of importance in controlling the spatial distribution of DMS:Chl ratio in equatorial surface waters. The meridional distributions of DMS:Chl in a  $10^\circ$ -wide band around the equator, at  $15\text{--}35^\circ\text{ W}$  in the Atlantic,  $95^\circ\text{ W}$  and  $110^\circ\text{ W}$  in the Pacific are shown in more detail in Fig. 9a and b. The DMS:Chl ratios were very similar in the two basins, yet the groups composition signatures were different (SYN and PRO in the Pacific, NANO in the Atlantic). Abrupt decreases in DMS:Chl ratios were observed when entering the equatorial divergence zone (EU,  $5\text{ mmol g}^{-1}$  in the Pacific and  $3\text{ mmol g}^{-1}$  in the Atlantic) from the north (NECC) or from the south (SEC). Dynamic models computing the meridional variations in phytoplankton C:Chl ratio as a function of temperature, light, nitrate and iron concentrations produce a reduced sea surface C:Chl ratio in the eastern equatorial Pacific divergence zone (Wang et al., 2009). However, the meridional reduction in C:Chl ratio in November 2003 is moderate (about 50%, X. W. Wang, personal communication, 2010) and results from

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the higher increase in Chl than in phytoplankton carbon in the equatorial divergence zone. The meridional reduction in DMS:Chl is considerably higher and results from DMS lows associated with Chl highs in the equatorial divergence zone. Moreover, observational evidences indicated that chlorophyll was functioning as a reliable measure of phytoplankton biomass in the eastern equatorial Pacific in November 2003 (Behrenfeld and Boss, 2006). Indeed, the particulate beam attenuation coefficient ( $c_p$ ), a measure of suspended material mostly of phytoplanktonic origin, was extremely well correlated with fluorescence-based chlorophyll estimates (Fig. S5a: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>,  $r^2=0.93$ ,  $n=8,880$ ) over the 6600 km transect. As Fig. S5: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf> shows,  $c_p$  was much better linearly correlated with Chl than with DMS ( $r^2=0.19$ ,  $n=424$ ). However, when EU data is removed, the coefficient of determination of DMS vs.  $c_p$  markedly increases ( $r^2=0.40$ ,  $n=375$ , Fig. S5d: <http://www.biogeosciences-discuss.net/7/3605/2010/bgd-7-3605-2010-supplement.pdf>), but the intercept remains positive (1.2 nM). So only part of the lack of homogeneity of the DMS:Chl ratio in the surveyed area found its origin in the EU. It appears that the eastern equatorial Pacific in November 2003 was a region where DMS and phytoplankton dynamics were decoupled since the regression analysis of DMS versus  $c_p$  indicated a positive intercept and explained only about 20% of the variability in an area where the algal assemblage, dominated everywhere by picophytoplakton, was in a rather stable physiological state (Behrenfeld and Boss, 2006). The highly significant linear relationship observed between total particulate organic carbon and  $c_p$  (see Fig. 4b in Behrenfeld and Boss, 2006) suggests that community responses were rapid enough to cause phytoplankton biomass changes to be well matched to changes in the other components comprising POC (bacteria, detritus and small grazers). Hence little evidence of coupling between DMS and ecological dynamics is found in the eastern equatorial Pacific in November 2003.

The Pacific convergent equatorial front (CEF) is a transition zone between the eastward-flowing NECC and the westward-flowing SEC. It is located north of the

equator and, as our results show, is a place where gradients in DMS:Chl are especially steep. Moreover, in the central Pacific (at 140° W) where SST gradients were considerably weaker than at 95° W and 110° W (Fig. 5a), the ratio also rose markedly between 0° and 2° N (Fig. 5c). It is known that the CEF accumulates buoyant organic material that can be seen from space and attracts foraging seabirds and other trophic level species (Pennington et al., 2006 and references therein). Clearly, DMS accumulates there too. This is consistent with the fact that DMS serves as a foraging cue for seabirds (Nevitt et al., 1995). The eastern equatorial Pacific zone is also characterized by a major plume of nutrient rich water located mostly south of the Equator. There, mean surface nitrate concentrations are over 5  $\mu\text{M}$  in the longitudinal band 95° W–110° W (Fiedler and Talley, 2006). Since nitrate photolysis is related to DMS photochemistry (Bouillon and Miller, 2004), it is probable that an enhancement in nitrate concentration increases the photochemical removal efficiency of DMS resulting in less DMS accumulating in the surface ocean.

Thus, the DMS dynamics in the eastern equatorial Pacific would be impacted by physical and chemical forcings more directly than by physiological and ecological processes. Because the latitudinal variations in DMS:Chl are roughly the same in the equatorial Atlantic and Pacific, it is suggested that the decoupling between DMS and phytoplankton biomass observed in the equatorial Pacific also operates in the equatorial Atlantic though we lack the supporting material (e.g.  $c_p$  measurements, indices of changes in algal physiology) in the later case.

When zooplankton prey upon phytoplankton rich in DMSP and in DMSP-lyases, part of the particulate material is released to solution and converted to DMS. Nanoeucaryotes are richer in DMSP and lyases than cyanophytes and prochlorophytes. This is true on a per cell basis, or when DMSP is normalized to cell carbon or chlorophyll (Stefels et al., 2007). Because the NANO signature dominates in the equatorial Atlantic and because chlorophyll levels are slightly higher in the Atlantic than in the Pacific, higher phytoplankton production of DMS is expected in the Atlantic than in the Pacific. Assuming that the DMS concentration is mainly driven by phytoplankton production, the

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Atlantic should display higher DMS levels than the Pacific. Definitely, this is not the case in equatorial waters as the comparison of Fig. 5e and Fig. 6b shows. Consequently, phytoplankton speciation does not control the concentration of DMS in equatorial waters neither in absolute nor in relative. It appears that the upper ocean dynamics near the equator is important in two aspects: upwelling areas are not favorable for DMS accumulation whereas convergent fronts are important.

Since the equatorial Pacific Ocean is subject to large interannual variations in upper ocean dynamics during El Niño–Southern Oscillation (ENSO) cycles, it is expected that the spatio-temporal DMS distribution will change accordingly. Indeed, there appears to be large changes in DMS in the vicinity of the equatorial divergence during El Niño and La Niña events as shown from historical data gathered in Fig. 10. During non El-Niño events (La Niña or transition phase), data collected between the equator and 5° N, hence at the position of the convergent front, show an accumulation of DMS of varying intensity (4–11 nM) in the central (140° W, Fig. 10a) and eastern (110° W, Fig. 10b) equatorial Pacific. This local accumulation apparently disappears during El-Niño events (1.2–2.3 nM) suggesting a relationship between ENSO cycles and the DMS distribution. However, the DMS loss at the location of the convergent equatorial front during El-Niño events can be partly compensated by an increase in DMS in the area of the equatorial divergence at 110° W (Fig. 10b, April 1983). No such compensation is observed at 140° W in March 1992 (Fig. 10a). Hence, the changes in physical features associated with ENSO events appear to have a stronger effect on the concentration of DMS at the local scale than over large distances across the Equatorial Pacific (Bates and Quinn, 1997). SeaWiFS and PHYSAT surveys show a marked drop in phytoplankton biomass and a shift from cyanophytes (SYN) to nanoeucaryotes (NANO) in the equatorial Pacific during El Niño events (Masotti et al., 2010). Since DMS concentrations and the phytoplankton biomass drop simultaneously, the ratio of both is expected to remain roughly constant. So a shift from SYN to NANO during El Niño events would not affect the DMS:Chl ratio. This is consistent with our observations which show no significant difference in the DMS:Chl ratio of surface waters exhibiting

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PHYSAT signatures typical of cyanophytes ( $14.8 \pm 5.0 \text{ mmol g}^{-1}$ ,  $n=396$ , Fig. 11b) and nanoeucaryotes ( $13.7 \pm 2.7 \text{ mmol g}^{-1}$ ,  $n=25$ , Fig. 11a).

## 4.2 Phytoplankton speciation and DMS:Chl ratios in subtropical upwellings

When approaching the coastal upwelling of southern Benguela, the DMS:Chl ratio dropped to values even lower than those measured in the equatorial upwelling (Figs. 5c and 11). In this zone where the gradient in DMS:Chl was negative in the onshore direction, PHYSAT signatures were NANO or PRO (Fig. 6c). However, according to the PHYSAT climatology for February, NANO is more typical than PRO in southern Benguela (Fig. 6c). Although no DIAT signal was found along cruise track, it is likely that diatoms accounted for a significant fraction of phytoplankton biomass, at least at inshore localities (Barlow et al., 2005). On the basis of our PHYSAT observations, it appears that the species composition is not of first order importance in controlling DMS:Chl ratios in the southern Benguela in summer. This situation very much resembles that observed in the upwelling off the Moroccan coast, where a transect through different plumes of upwelled waters and six longshore traverses of the same plume were carried out in September 1999 (Belviso et al., 2003). Because the sea surface concentration of total DMSP (tDMSP) was highly correlated with the total volume of suspended particles measured by an optical HIAC counter, it was concluded that DMSP was homogeneously distributed amongst planktonic communities. The uniformity of the ratio between tDMSP and the volume of suspended particles in surface waters off Morocco contrasted with the high variability of the DMS:Chl and DMS:tDMSP ratios. The ratios decreased in the onshore direction both in the plume and in an adjacent water mass. Marine  $\text{CO}_2$  levels suggested that the age of the upwelled waters was the proximate control on the variability of the ratios there, but not the phytoplankton community composition. A similar conclusion can be drawn for southern Benguela since the DMS:Chl ratio decreases in the onshore direction regardless of the PHYSAT signature (NANO or PRO, Fig. 6c). Decreases in DMS:Chl ratio were also found in the

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onshore direction along a transect off Mauritania at about 18° N (Franklin et al., 2009). However, the decrease in the ratio was in this case alongside diatom domination of the microplankton biomass. PHYSAT records with higher horizontal resolution (<9 km) are necessary to proceed with the investigation in other diatom-dominated areas such as the coastal and open waters of the North Atlantic and North Pacific oceans. We recommend the use of PHYSAT in conjunction with satellite-derived calcite concentrations to investigate diatom blooms free of coccolithophores.

### 4.3 Growth conditions and the meridional distribution of DMS:Chl ratios

In the Indian sector of the Southern Ocean, warm core eddies with contrasting PHYSAT signatures displayed almost similar DMS levels (Fig. 8d), but DMS:Chl ratios were at least twice lower when associated with SYN than with PHAEO or NANO signatures (Fig. 8f). This is consistent with our current understanding of DMS(P) production in cyanophytes. However, culture studies have shown considerably higher differences than a factor of two between cyanophytes and haptophytes (e.g. a difference of 3 orders of magnitude is reported by Stefels et al., 2007, in terms of DMSP normalized to Chl). Moreover, we have observed that surface waters with a SYN signature exhibit ratios about two times higher at low latitudes than high northern or southern latitudes (Fig. 11b). This is the sole piece of coherent information we have obtained which indicates the existence of an impact of growth conditions (SST, nutrients, light or the three forcings combined) on the meridional dynamics of the DMS:Chl ratio. There are no coherent meridional trends in NANO- and PRO-dominated areas because high DMS:Chl ratios were measured in the Indian and Pacific sectors of the Southern Ocean ( $12.7 \pm 6.3 \text{ mmol g}^{-1}$  (Fig. 11a) and  $23.1 \pm 5.3 \text{ mmol g}^{-1}$  (Fig. 11c), respectively). Nevertheless, DMS:Chl ratios up to  $35 \text{ mmol g}^{-1}$  were observed in the North Atlantic subtropical gyre in winter (Fig. 6c). In the Sargasso Sea, where the dominant PHYSAT signature was NANO, the ratio ranged between 2 and  $8 \text{ mmol g}^{-1}$  (Fig. 6c). Similar values were reported by Le Clainche et al. (2010) at the Bermuda Atlantic Time Series (BATS, 32° N–64° W) site during wintertime. Thus there appears to be a huge

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5 difference in DMS:Chl ratios between NANO and PRO dominated areas in winter in the North Atlantic subtropical gyre, a difference likely driven by the growth conditions and the physiological state of the non-dominant algae because prochlorophytes are poor DMS producers. The highest ratios in January 1999 coincided with the transition zone  
10 between the NANO and PRO dominated areas (Fig. 6c). The PHYSAT climatology suggests that the highest ratios coincide with the northern limit of the PRO dominated areas (Fig. 6c). Thus, we propose that the seasonal expansion towards the north of the PRO signature, as observed by Alvain et al. (2008) in the North Atlantic basin, would trace that of oligotrophy and the associated relative accumulation of DMS that  
15 characterizes oligotrophic systems. The expansion of the PRO signature reaches the BATS station in summer where the relative accumulation of DMS over DMSP and Chl peaks (Dacey et al., 1998).

## 5 Conclusion and perspectives

15 The PHYSAT tool allows the characterization from space of several phytoplankton functional types at different spatial scales. It was applied for the first time to the marine sulfur cycle in an effort to assess whether the DMS:Chl ratio is consistent within specific phytoplankton groups determined from space. Whatever the phytoplankton composition is, the equatorial divergence zone of the Atlantic and Pacific oceans exhibits among the lowest ratios. The only region where the spatial variations in the  
20 DMS:Chl ratio appear to be consistent with the generally accepted classification between high and low DMS-producing phytoplankton is the Indian sector of the Southern Ocean. There, the ratios in SYN-dominated areas are roughly one half of that found in NANO- and PHAEO-dominated areas. However, the DMS:Chl ratio is not consistent within the Synechococcus group since it exhibits clear latitudinal variations in SYN-  
25 dominated areas. Because the large-scale variations in DMS:Chl are not consistent within phytoplankton groups, it seems impossible to derive an empirical relationship solely from different water-leaving radiance spectra obtained from ocean color sensor

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measurements. Our results suggest that the species composition is not a first order controller of the global DMS dynamics.

The spatial resolution of the PHYSAT records will improve markedly in the near future. The new PHYSAT products will display 4 to 9 km horizontal resolution. The temporal resolution should be also improved (daily observation matchup) to investigate times when the succession of phytoplankton groups is too fast. This will offer a unique opportunity to investigate the affect of phytoplankton abundance and composition on the small-scale distribution of DMS especially in coastal waters. However, in order to better discriminate between factors affecting DMS:Chl ratios in the surface ocean, the use of other satellite products is recommended. Particulate backscattering coefficients would help quantifying the total phytoplankton biomass. The calcite product will be useful to identify and quantify an important DMS producer and to evidence the minor component of the algal assemblage when SYN, PRO and DIAT dominate. Phytoplankton fluorescence and colored dissolved and detrital organic materials observed from space would be also useful since they could allow the characterization at the global scale of the physiological status of phytoplankton and the development stages of phytoplanktonic blooms.

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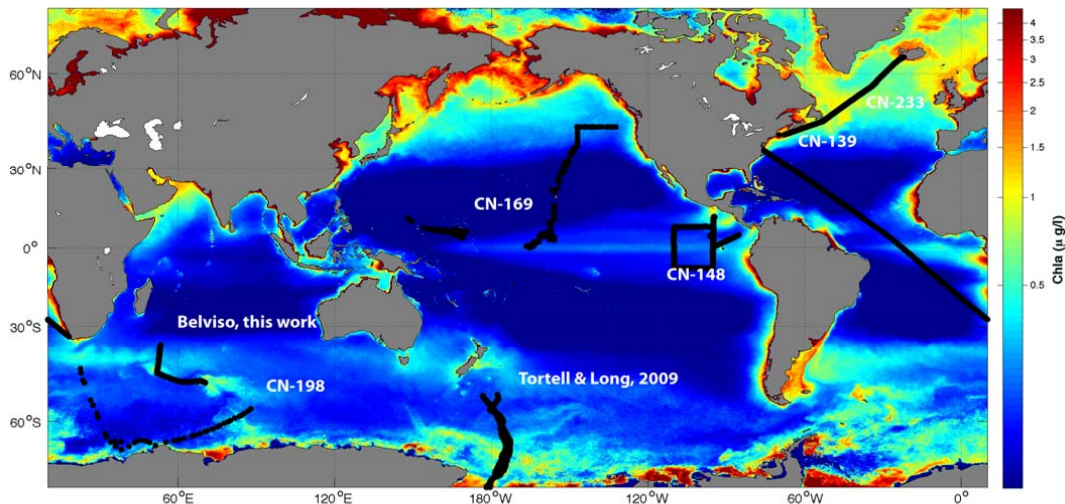
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**Table 1.** Sea surface DMS datasets used in this study.

Oceanic regions		DATE: year/start/end (Comments)	Number samples	Contribution <i>n</i> <sup>o</sup> and/or references
Pacific	Eastern Central	2003/27 October/20 November (no ENSO)	1057	CN-148, this work
		1983/25 April/1 May (El Niño)	71	CN-13 Bates and Quinn, 1997
	1989/17 February/26 February (La Niña)	55	CN-56 Bates and Quinn, 1997	
	2004/8 June/1 July	142	CN-169 Marandino et al., 2007	
Western	2004/23 May/29 May	70	CN-169 Marandino et al., 2007	
Atlantic	North-South	1999/15 January/8 February	666	CN-139 Bates et al., 2001
	North	2007/17 July/24 July	215	CN-233 Marandino et al., 2009
Southern Ocean	Indian sector	2005/14 February/19 February	178	this work
	Indian sector	2006/6 January/23 January	55	CN-128, this work
	Pacific sector	2006/3 November/14 November	11 520	Tortell and Long, 2009
		2006/7 December/11 December	10 161	

CN: Contribution number to the PMEL global DMS database (<http://saga.pmel.noaa.gov/dms/>).



**Fig. 1.** DMS transects in the Pacific and Atlantic Oceans, and in the Indian and Pacific sectors of the Southern Ocean. Details of the data sets are shown in Table 1. The color background is a sea surface Chl climatology (2002–2007) from the MODIS AQUA sensor.

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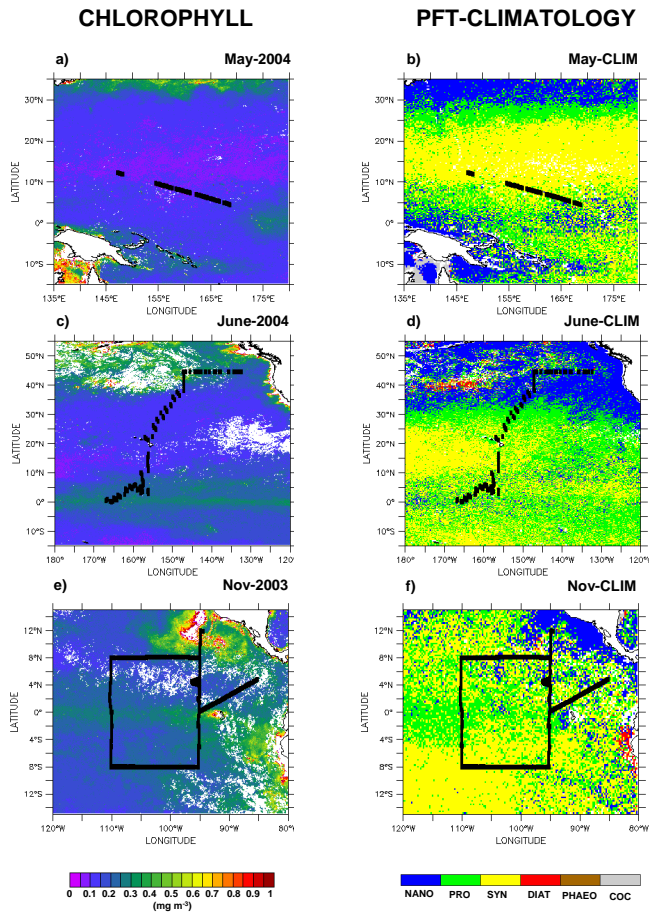
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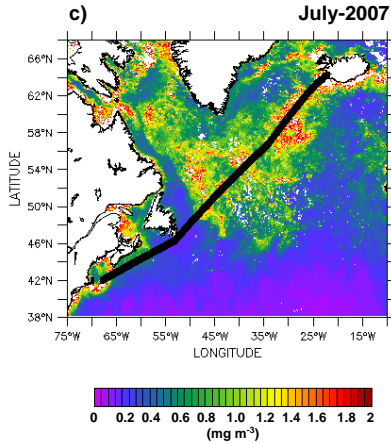
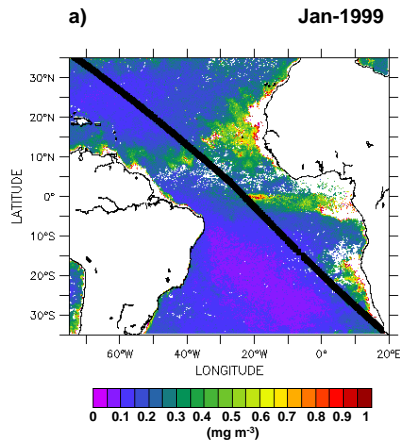
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**Fig. 2.** Monthly composites of Chl concentration (left panels, unit  $\text{mg m}^{-3}$ ) and monthly climatologies (1998–2006) of the dominant Phytoplankton Functional Types (PFT) (right panels) around the DMS transects investigated in the Pacific basin. PFT signatures detected by PHYSAT are nanoecaryotes (NANO), Prochlorococcus (PRO), Synechococcus (SYN), diatoms (DIAT), Phaeocystis-like (PHAEO) and coccolithophores (COC).

# CHLOROPHYLL



# PFT-CLIMATOLOGY

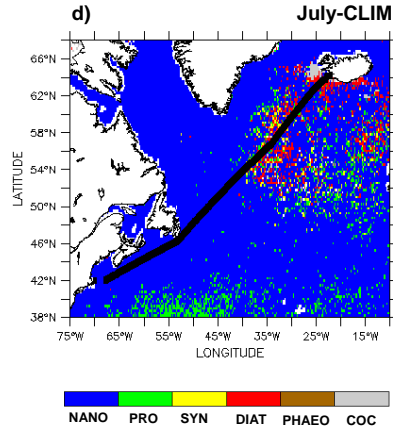
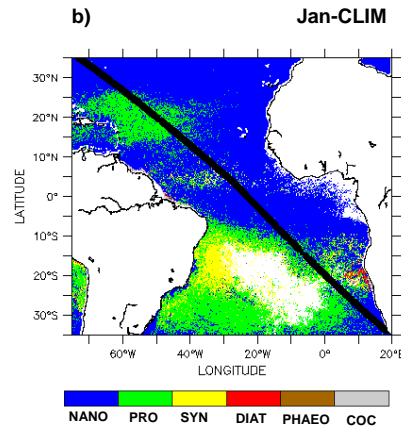
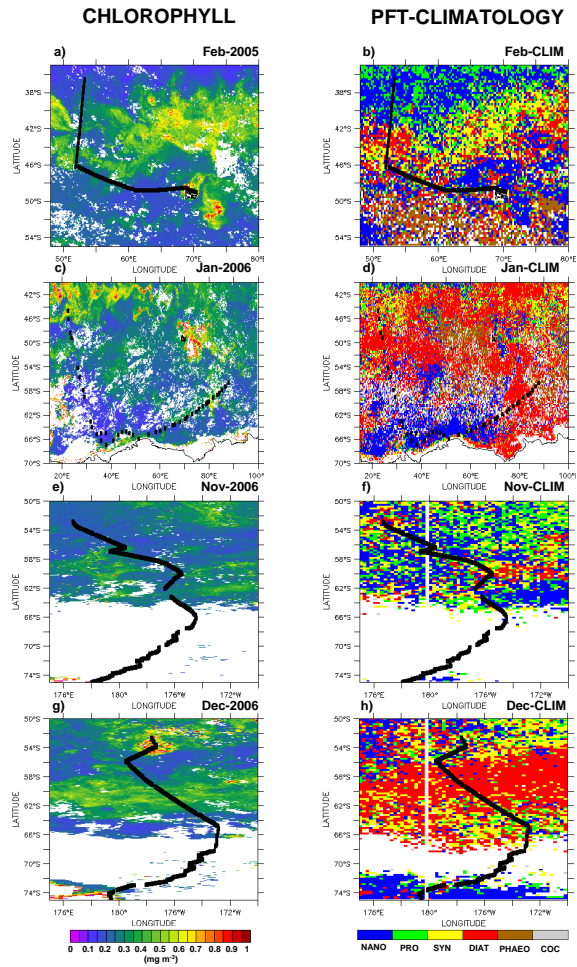


Fig. 3. Same as Fig. 2 but for the Atlantic Ocean.



**Fig. 4.** Same as Fig. 3 but for the Indian and Pacific sectors of the Southern Ocean. The large white line along the dateline (lower panels) is intrinsic to the PHYSAT data treatment.

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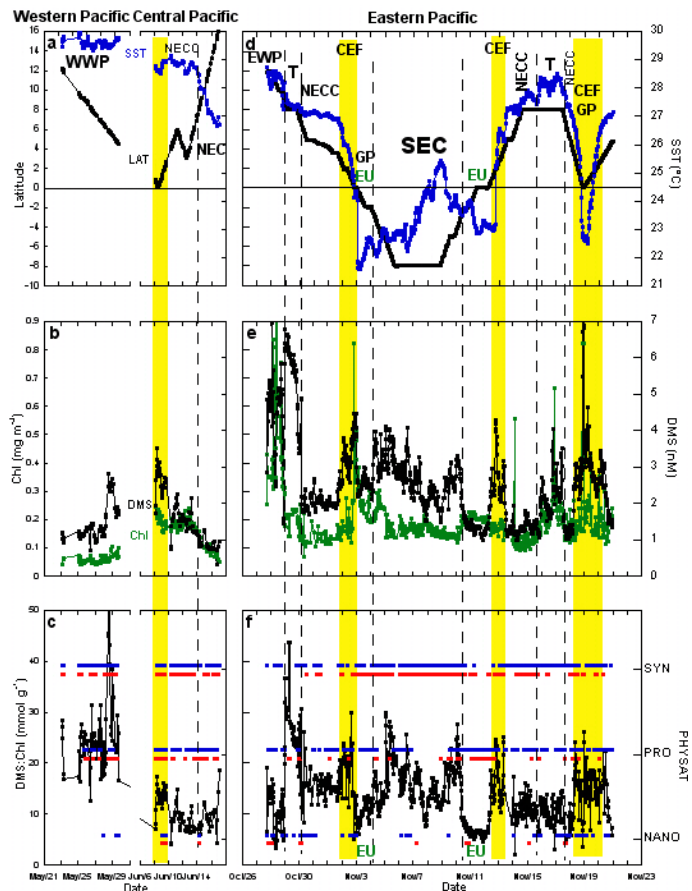
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**Fig. 5.** Spatio-temporal variations of sea surface temperature (SST: °C), phytoplankton biomass (Chl:  $\text{mg m}^{-3}$ ), dimethylsulfide concentration (DMS: nM), DMS normalized to Chl (DMS:Chl,  $\text{mmol g}^{-1}$ ) and observed (red dots) and climatological (blue dots) monthly PFT composition along the DMS transects carried out in the Pacific basin. Water mass acronyms are defined in the text. The yellow vertical bands correspond to main frontal zones associated with DMS accumulations.

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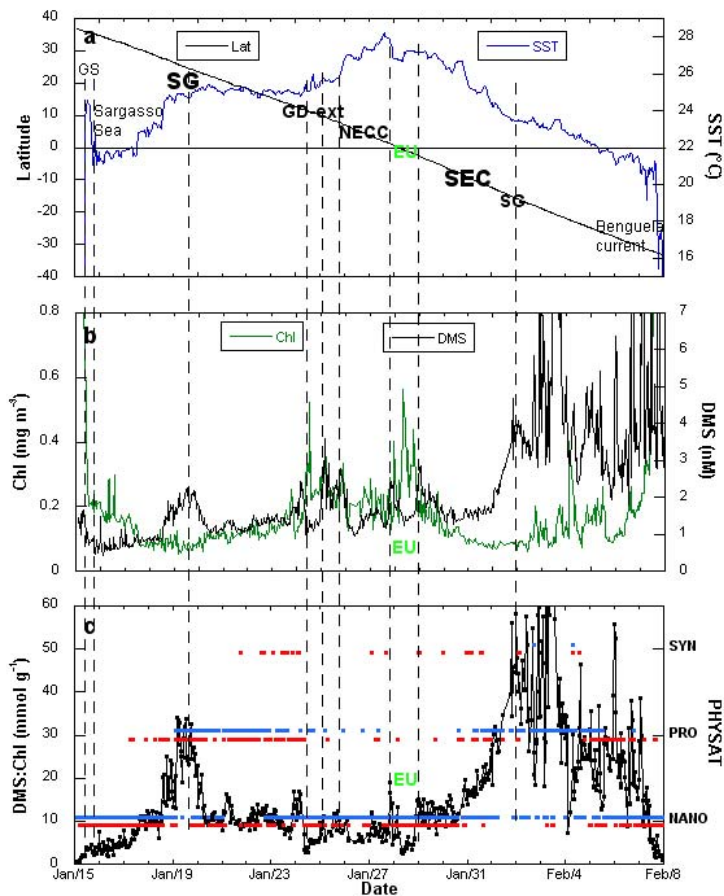
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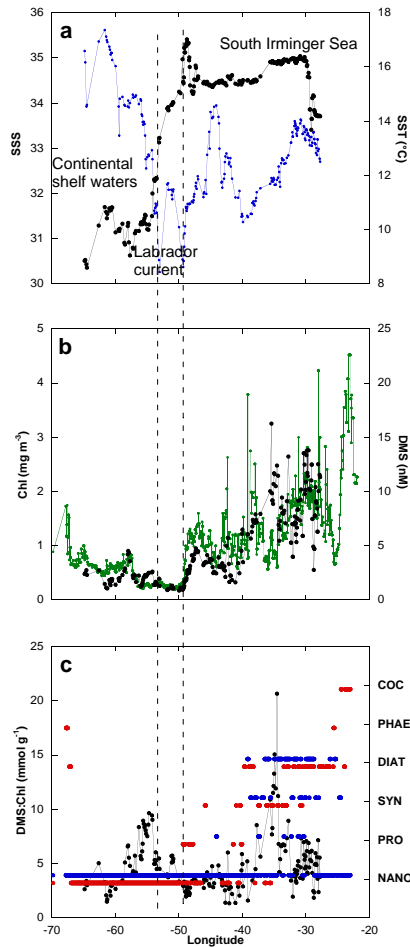
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**Fig. 6.** Same as Fig. 5 but for the Atlantic basin. Chl levels over  $0.8 \text{ mg m}^{-3}$  were up to  $2.7 \text{ mg m}^{-3}$  and  $9.1 \text{ mg m}^{-3}$  off the North American and South African coasts, respectively. DMS levels over  $7 \text{ nM}$  were up to  $10.1 \text{ nM}$  and  $11 \text{ nM}$  on 3 and 7 February, respectively.



**Fig. 7.** Same as Fig. 6 but at higher latitudes of the Northwestern Atlantic. Sea surface salinities are also reported in the upper panel plotted in black.

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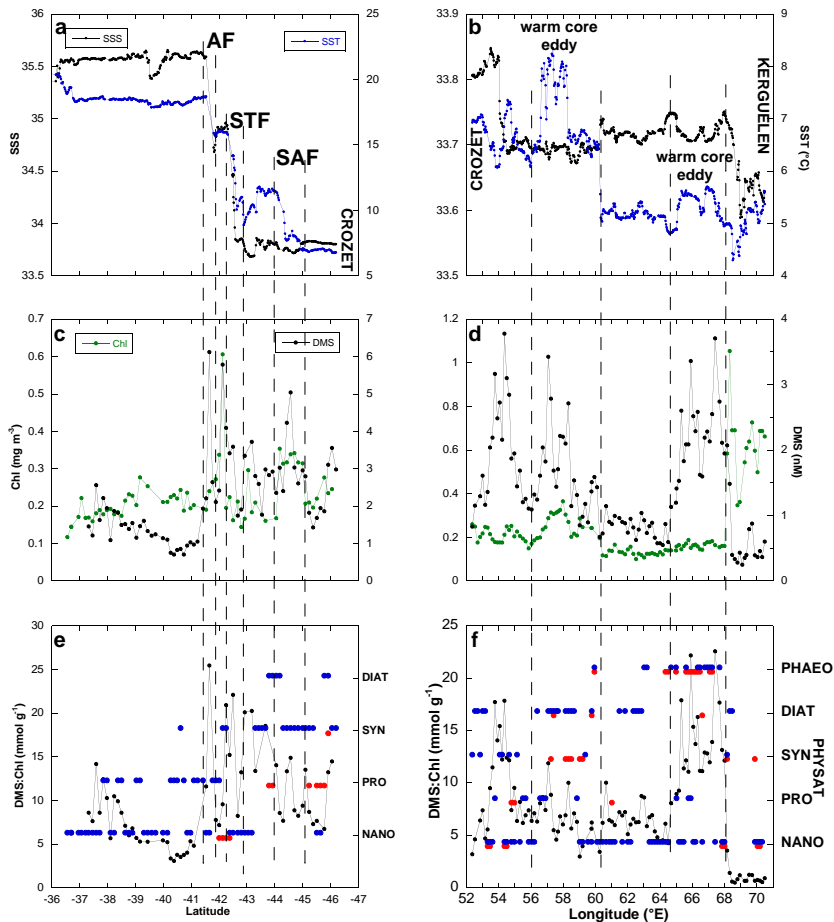
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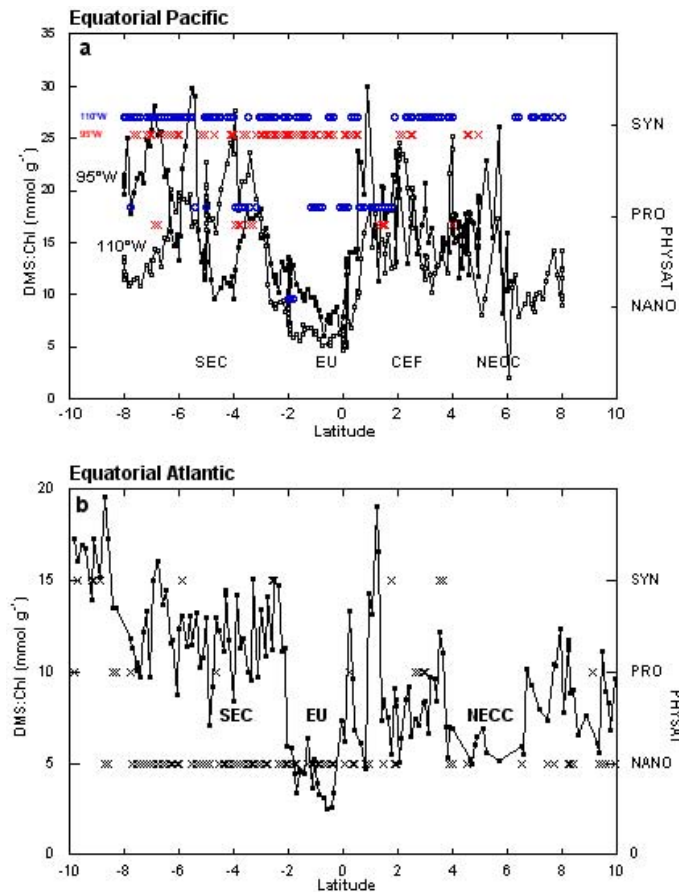




**Fig. 8.** Same as Fig. 7 but for the Indian Sector of the Southern Ocean.

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**Fig. 9.** Comparison between DMS:Chl ratios at 110°W and at 95°W (empty and full circles, respectively) and observed monthly PFT signatures (blue circles and red crosses, respectively) obtained in the equatorial Pacific (a). Similar comparison in the Atlantic basin at 15°–35°W is shown in (b). For details of acronyms see text.

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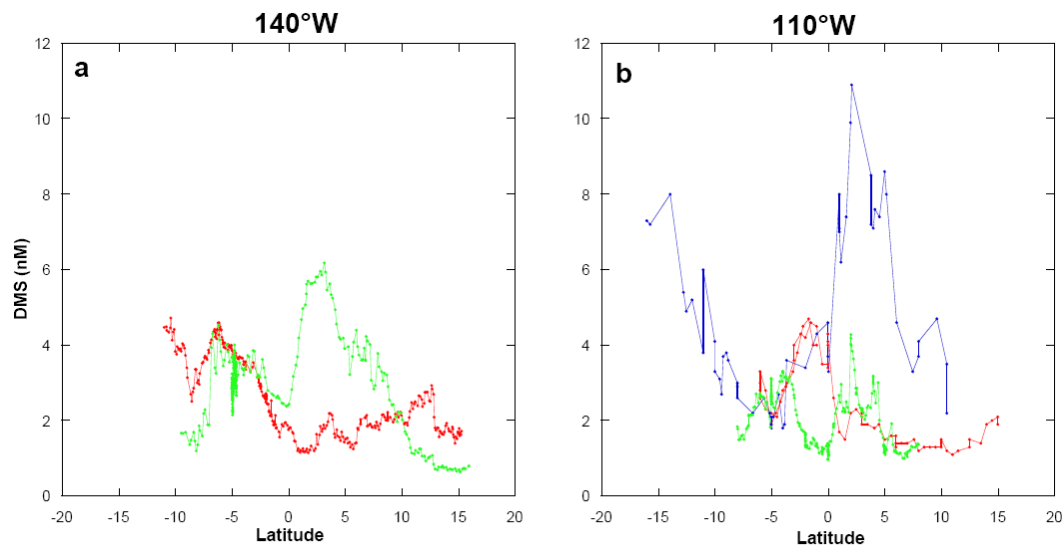
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**Fig. 10.** Spatio-temporal variations of DMS concentrations (nM) during ENSO events (El Niño (red), La Niña (blue) and apart of those events (green), in the equatorial Pacific at 140° W (left panel) and 110° W (right panel).

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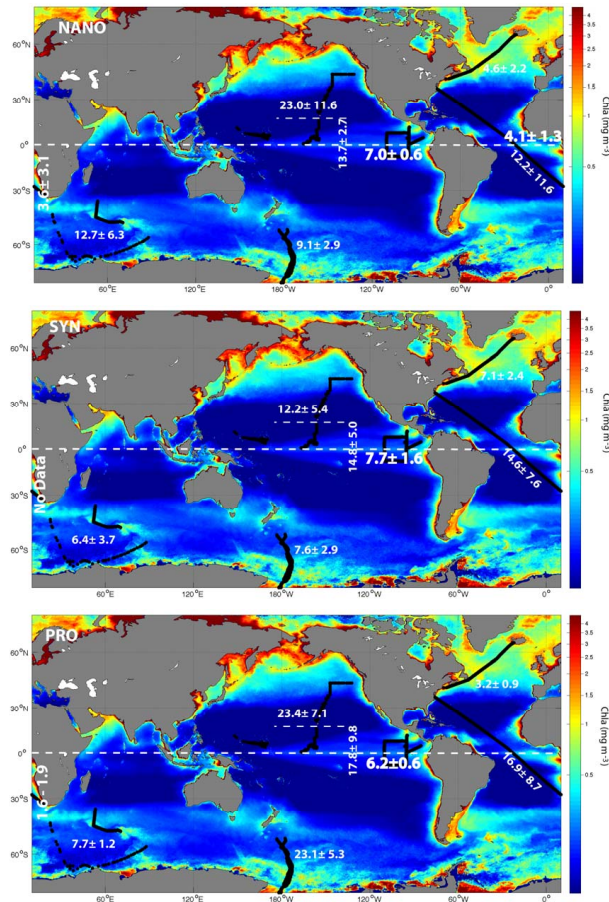
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**Fig. 11.** Mean values  $\pm 1$  SD of DMS:Chl ratios ( $\text{mmol g}^{-1}$ ) in surface waters of the Pacific, Atlantic and Indian basins, sorted by dominant PFT (NANO, SYN and PRO PHYSTAT signatures in upper, central and lower panels, respectively). In the southern Benguela only two samples displayed a PRO signature. The color background is a sea surface Chl climatology (2002–2007) from the MODIS AQUA sensor. Numbers printed in large white characters close to the equator line and the South African coasts are for equatorial and subtropical upwelling systems only.