



PERGAMON

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Deep-Sea Research I 50 (2003) 543–555

DEEP-SEA RESEARCH  
PART I

[www.elsevier.com/locate/dsr](http://www.elsevier.com/locate/dsr)

# Mesoscale features of surface water DMSP and DMS concentrations in the Atlantic Ocean off Morocco and in the Mediterranean Sea

Sauveur Belviso<sup>a,\*</sup>, Antoine Sciandra<sup>b</sup>, Claire Copin-Montégut<sup>b</sup>

<sup>a</sup>Laboratoire des Sciences du Climat et de l'Environnement (LSCE), UMR CEA-CNRS 1572, CEN-Saclay, Bât 709, Orme des Merisiers, 91191 Gif-sur-Yvette, France

<sup>b</sup>Laboratoire d'Océanographie de Villefranche-sur-Mer, UMR7093 OSU/UPMC/CNRS, BP 28, 06234 Villefranche-sur-Mer, France

Received 22 January 2002; received in revised form 12 November 2002; accepted 23 January 2003

## Abstract

Surface water small-scale variability of dimethylsulfide (DMS), total dimethylsulfoniopropionate (tDMSP) concentrations and supporting parameters were investigated in upwelling cells north of Cap Ghir (Morocco) and during a transect from this area to the eastern Mediterranean Sea in late summer 1999. Off the Moroccan coast, tDMSP concentration was in the range 20–300 nM and was linearly correlated ( $r^2 = 0.93$ ,  $n = 61$ ) with measurements from a particle counter of the total volume of suspended particles in the range 1.5–100  $\mu\text{m}$ . This suggests that DMSP off the Moroccan coast was homogeneously distributed amongst planktonic communities not resolved at the organismic level. Conversely, the spatial distribution of the DMS-to-tDMSP ratio calculated either from measured or reconstructed tDMSP levels from particle counts was much more heterogeneous. DMS-to-tDMSP ratios were in the range 2–30%. Four plumes of upwelled waters were clearly identified from maxima in density excess and plankton biomass, and from minima in the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) at the constant temperature of 13°C which result mainly from the cumulative biological uptake of  $\text{CO}_2$ . The higher the  $p\text{CO}_2$  at 13°C, the lower the DMS-to-tDMSP ratio. Thus, DMS was relatively less abundant in recently upwelled waters. The main patterns of DMS variability in the southern Mediterranean Sea in summer were: (1) an eastward unsteady increase of the DMS-to-tDMSP ratio from roughly 10% in the Alboran Sea up to 40% in the Ionian Sea and (2) sharp and broad DMS enhancements associated with either cold or warm water masses illustrating the complex origin of DMS in the Mediterranean Sea. There is evidence that shifts in the regime of DMS production-removal occur at the entrances to the western and eastern basins of the Mediterranean Sea.

© 2003 Elsevier Science Ltd. All rights reserved.

**Keywords:** Dimethylsulfide; DMS; DMSP; Atlantic Ocean; Upwelling; Mediterranean Sea

## 1. Introduction

Ocean dynamics and biological activity at the mesoscale can be responsible for large variations in dimethylsulfide (DMS) distribution in surface waters (Matrai et al., 1996; Sciare et al., 1999;

\*Corresponding author. Tel.: +33-1-6908-8151; fax: +33-1-6908-8546.

E-mail address: [belviso@lscce.saclay.cea.fr](mailto:belviso@lscce.saclay.cea.fr) (S. Belviso).

Belviso et al., 2000). The usual way to elucidate the details of the DMS distribution in frontal areas is to determine the concentrations of supporting parameters. Chlorophyll *a*, a descriptor of phytoplankton biomass, yields conflicting results. For example, the mesoscale variations in sea surface DMS and satellite chlorophyll concentrations in frontal systems of the Indian Ocean (Sciare et al., 1999; Belviso et al., submitted) were in phase. In the South Atlantic Ocean, they were clearly out of phase (Belviso et al., 2000). Moreover, although satellite chlorophyll levels in both frontal systems were quite similar, average DMS levels in the Indian Ocean were about an order of magnitude higher than in the Atlantic Ocean. Upwelling areas also exhibit steep gradients of chlorophyll *a* on scales of kilometers to tens of kilometers. The latitudinal distribution of DMS in surface waters of the Peru upwelling area (Andreae, 1985) was very patchy and clearly not correlated with the biomass of phytoplankton. Along surface transects across the shelf break and tidal fronts to the southwest of the British Isles, much of the DMS variability was ascribed to the species composition of phytoplankton rather than chlorophyll, with localized populations of *Phaeocystis* and coccolithophores being important sources of DMS (Holligan et al., 1987). Unfortunately, taxonomic determinations are largely unavailable with high spatio-temporal resolution. Although it is well known that DMS results from the enzymatic lysis of the precursor compound dimethylsulfoniopropionate (DMSP, in the particulate (pDMSP), and dissolved (dDMSP) phases), high-resolution transects of surface DMSP are almost nonexistent. DMSP is a very labile compound which is transferred and transformed through the food web with DMS as one of the by-products (Simo et al., 2002). Aumont et al. (2002) have shown that the large-scale changes in the DMS-to-pDMSP ratio can be deduced from a trophic status ratio ( $F_p$ ), which characterizes the proportion of microphytoplankton (diatoms and dinoflagellates) within the whole phytoplankton community (Claustre, 1994). The latter has shown that the variation of the  $F_p$ -ratio with Chl *a* concentration and modelled primary production (PP) suggests strong similarities between  $F_p$ - and the  $f$ -ratio

(new production:total production). Although the  $F_p$ - and  $f$ -ratios do not derive from the same concepts, Claustre (1994) found that both indices compared well for oligotrophic provinces, mainly regulated by their regenerative capacity (low  $F_p$ - and  $f$ -ratios), and upwelling regimes which are regularly enriched by nutrients (high  $F_p$ - and  $f$ -ratios). The DMS-to-pDMSP ratio was shown to be roughly inversely proportional to the  $F_p$ -ratio (for  $F_p < 0.6$ , Aumont et al., 2002). No clear relationship between  $F_p$ -ratios higher than 0.6 and DMS-to-pDMSP ratios seemed to exist. Here we report for the first time on the spatial variations of the DMS-to-DMSP ratio from high-resolution horizontal profiles of DMS and total DMSP (tDMSP) concentrations made in a coastal upwelling area north of Cape Ghir (Morocco) and across the Mediterranean Sea, in combination with a series of supporting parameters to help understand the controlling factors of the DMS-to-tDMSP ratio at mesoscale and along a gradient of PP. This research was carried out as part of the project Productivité des Systèmes Océaniques Pélagiques (PROSOPE).

## 2. Methods

### 2.1. Sampling

Samples were collected for DMS along the cruise track for the R.V. *Thalassa* in the Atlantic and the Mediterranean Sea (Fig. 1). DMS sampling started in the upwelling region north of Cape Ghir (Morocco), where a series of six longshore traverses was carried out. The cruise then consisted of a transect from the southwestern edge of this area to the Central Ionian Sea.

During the PROSOPE cruise, underway seawater samples were collected 3 m below the ocean surface with the ship's clean seawater pump and circuit. Temperature, salinity, fluorescence of chlorophyll, particle granulometry and the partial pressure of  $\text{CO}_2$  were measured on-line. During the 2D survey in the upwelling area north of Cape Ghir, samples were taken for tDMSP occasionally according to the changes in DMS. Samples were collected for tDMSP at least every hour during the

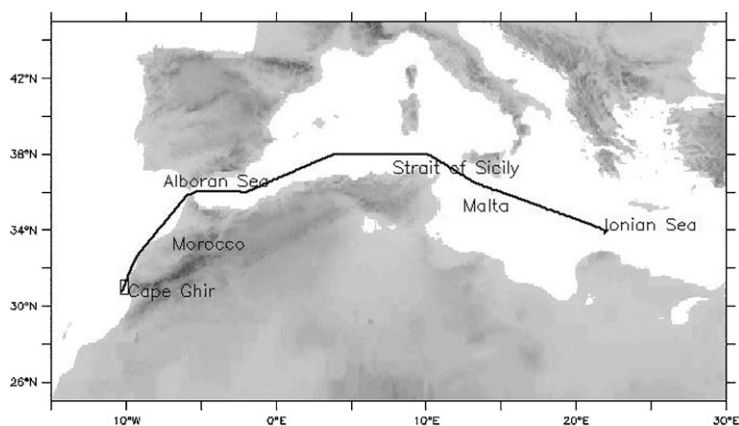


Fig. 1. R.V. *Thalassa* cruise track which started from Cape Ghir (Morocco, 11 September 1999) and ended in the Central Ionian Sea (20 September 1999), passing through the Strait of Gibraltar, the Alboran Sea, the southwestern basin of the Mediterranean Sea and the Strait of Sicily (the entrance to the eastern basin of the Mediterranean Sea).

transect from the upwelling north of Cape Ghir to the Central Ionian Sea. Samples were collected for DMS continuously over 24 h, roughly every 20 min from 11 September to 20 September 1999, except 14 September 1999 when the ship moored in front of Gibraltar. We were able to check for pump effects only in oligotrophic waters of the Ionian Sea. DMS was not biased by the pump system since DMS collected from the seawater circuit and from bottle samples collected at about 5 m depth exhibited similar hourly variations during a 4-d time series at a fixed location (data not shown). Average DMS from the seawater circuit was  $3.9 \pm 0.6$  nM (1 SD,  $n = 50$ ) and  $4.0 \pm 0.4$  nM ( $n = 24$ ) from the bottle samples.

## 2.2. Analysis of DMSP and DMS

Unfiltered whole water was used for the analysis of tDMSP. An 8 ml aliquot of unfiltered whole water was transferred to nonsilanated glass tubes, treated with cold alkali (200  $\mu$ l of 20 M NaOH), sealed with a Teflon-faced septa and allowed to sit at room temperature for at least 12 h. The content of a sample tube was drawn into a plastic syringe and immediately injected into the sparging device through a Teflon-faced septum. Samples sparged with helium for 10 min at 70 ml/min were cryotrapped in liquid nitrogen in a 0.16 mm diameter FEP-Teflon loop filled with a small amount of

Tenax GC. The trap was heated to 95°C, and its content was immediately injected onto the Poraplot Q capillary column (Chrompack). Water vapor had been previously removed with a Permapure mini-dryer (model MD050-72F). For DMS analysis we used 25 mm diameter Whatmann GF/F glass-fiber filters mounted on Teflon cylinders that were allowed to sink slowly through seawater contained in a clean 0.3 l Teflon beaker, thus producing GF/F filtrates by reverse filtration (Belviso et al., 2001). Then a 1–10 ml aliquot of the filtrate was immediately sparged with helium. DMSP and DMS samples were analyzed onboard R.V. *Thalassa* with a Varian 3800 gas chromatograph equipped with a pulsed flame photometric detector (PFPD). DMS was calibrated from DMSP standards (Research Plus) prepared in the laboratory, in 8 ml glass tubes sealed with Teflon-faced septa, a few days before the cruise. Total DMSP was obtained by subtracting the DMS content of the GF/F filtrate from the tDMSP + DMS content of unfractionated whole water.

## 2.3. Supporting parameters

The surface water temperature was deduced from the signal of a quartz temperature probe located at the ship's bow, and the salinity was measured with a SeaBird SBE 21 thermosalinometer.

### 2.3.1. Total suspended particle biovolume

Suspended particles in the range 1.5–100  $\mu\text{m}$  were routinely counted and sized by the optical HIAC counter (Pacific Scientific) every 2 min in discrete aliquots, directly sampled in the pumped subsurface seawater. The principle of the size measurement lies in the blockage of a collimated laser beam illuminating a photodiode. Practically, the loss of energy due to a single particle entering the laser beam is converted into an electrical signal proportional to the cross section of the particle. Suspended particle volume concentration  $B$ , a proxy of the particle biomass in a sample of volume  $V$ , was derived from size measurements under the assumption of particle sphericity as follows:

$$B = \frac{1}{V} \frac{\sum_{i=1}^{i=100} n_i v_i}{\sum_{i=1}^{i=100} n_i}, \quad (1)$$

with  $n_i$  being the number of particles of volume  $v_i$  counted in the  $i$ th bin.

The lower size limit of 1.5  $\mu\text{m}$  was defined by the manufacturer. The higher limit of size distribution was fixed at 100  $\mu\text{m}$  because it provided a satisfactory spectral definition taking into account the volume sampled. Because of the general power function of size distribution of particles in seawater, the large particles are better characterized by counting large volumes of seawater, but this increases the counting time and limits the spatio-temporal resolution. During the surface monitoring, the volume of seawater sampled by the HIAC was fixed at 40 ml. The HIAC counter identifies all particles whose refractive index differs significantly from that of seawater. Consequently biovolume is potentially related to live auto- and heterotrophic organisms, detritus (including amorphous organic aggregates of size lower than 100  $\mu\text{m}$ ) and mineral particles (of size lower than 100  $\mu\text{m}$ ), without distinction. At the Moroccan upwelling site, the submicron Saharan dust was very likely present; nevertheless, in situ optical measurements provided evidence that dust in suspension within the upper layer did not affect its optical properties, typical of open-ocean Case-1 waters (Claustre et al., 2002).

### 2.3.2. Fluorescence data

A Westar fluorometer was used to monitor continuously over 24 h the chlorophyll  $a$  fluorescence variations. Despite the multiple sources of fluorescence variations (Marra, 1997), the data used to calibrate the fluorometer, obtained from a series of casts carried out in upwelled waters off Cape Ghir and HPLC measurements, were surprisingly not very noisy ( $r^2 = 0.88$ ,  $n = 60$ , H. Claustre, pers. commun.), suggesting that the fluorescence signal acquired over the Prosope survey was driven mainly by the chlorophyll biomass.

### 2.3.3. Partial pressure of carbon dioxide

The measurements of the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) were performed according to Copin-Montégut (1985). A LI-COR\*LI6252  $\text{CO}_2$  gas analyzer with a pressure transducer was used for the determination of  $\text{CO}_2$  concentration in gas equilibrated with sampled water. The analyzer was calibrated twice a day with two  $\text{CO}_2$ -air mixtures (Air Liquide). The partial pressure of  $\text{CO}_2$  (in  $\mu\text{atm}$ ) in the equilibration cell was determined as  $p\text{CO}_2 = x\text{CO}_2(P_{\text{atm}} - f)/1013.25$ ,

where  $P_{\text{atm}}$  is the measured atmospheric pressure (in hPa),  $x\text{CO}_2$  the measured  $\text{CO}_2$  mole fraction in dry air (in ppm) and  $f$  the water vapor pressure at 100% humidity computed at the observed seawater temperature and salinity (in hPa). The  $p\text{CO}_2$  values at in situ temperature and at 13°C were calculated from the empirical equation proposed by Takahashi et al. (1993).

## 3. Results

### 3.1. Mesoscale variations off northwest Africa

Upwelling off northwest Africa as depicted by infrared/visible satellite observations and by large-scale patterns in seasonal wind variations has been investigated extensively by Van Camp et al. (1991). Their analyses of daily winds have shown them to be related to the near-shore temperature and pigment patterns. Pigment concentrations from satellite are also used in the present work as a first indicator for upwelling. The PROSOPE cruise

benefited from SeaWiFS scheduling in local area coverage (LAC) mode (1-km resolution) for real-time chlorophyll image support (Fig. 2). The image of chlorophyll suggests upwelling occurs north of Cape Ghir. A filament stretching approximately 150 km northwestwards off Cape Ghir (F1) is clearly visible in the image. Other filaments are noticeable on the image along the coast northwards (F2–F4).

The density excess deduced from the temperature and salinity data (UNESCO, 1985) and  $p\text{CO}_2$  (at  $13^\circ\text{C}$ ) are also used to indicate where upwelling occurred in September 1999 off the Moroccan

coast (Figs. 3a and b). Run-off is negligible in the area in summer. Maxima in density excess between  $30.7^\circ\text{N}$  and  $33.4^\circ\text{N}$  were due to temperature decreases since salinity was about 0.15 lower in cooler than in warmer waters. The most intense upwelling zone (F1) was off Cape Ghir where density excess and  $p\text{CO}_2$  (at  $13^\circ\text{C}$ ) along the cruise track were at most  $26\text{ kg m}^{-3}$  and  $280\text{ }\mu\text{atm}$  (Figs. 3a and b). Closer to the coastline off Cape Ghir, F1 exhibited higher values in density excess and  $p\text{CO}_2$  (at  $13^\circ\text{C}$ ) as will be shown later. Salinities were in the range 36.10–36.15 from the surface to the seafloor (data not shown). Since the

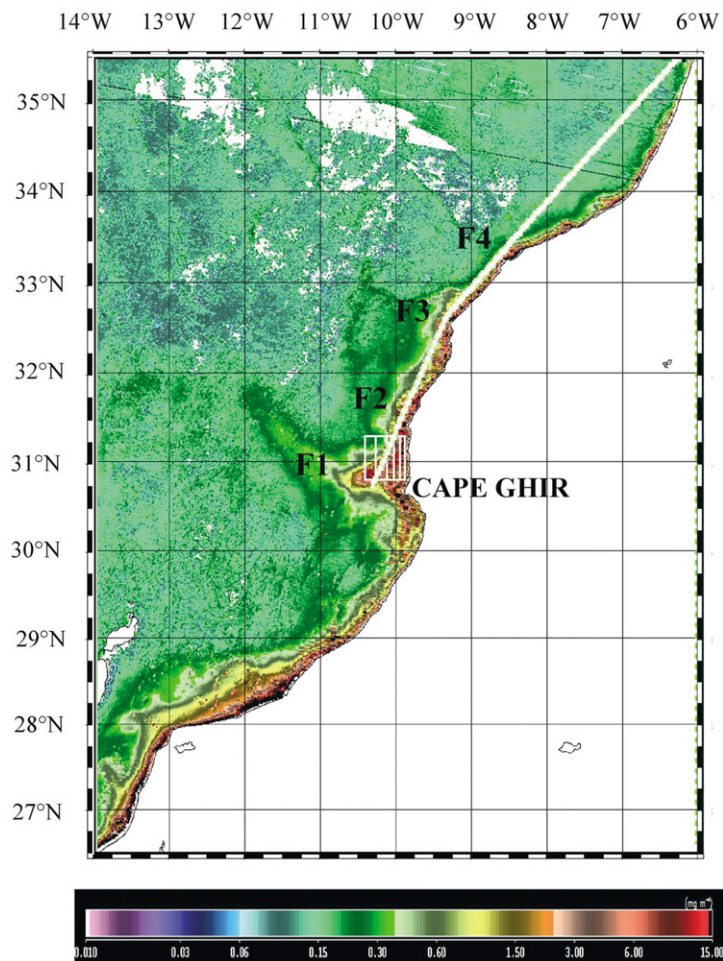


Fig. 2. SeaWiFS chlorophyll composite image in LAC mode for 6–9 September 1999. Superimposed is the R.V. *Thalassa* cruise track. Chlorophyll filaments are numbered F1–F4.

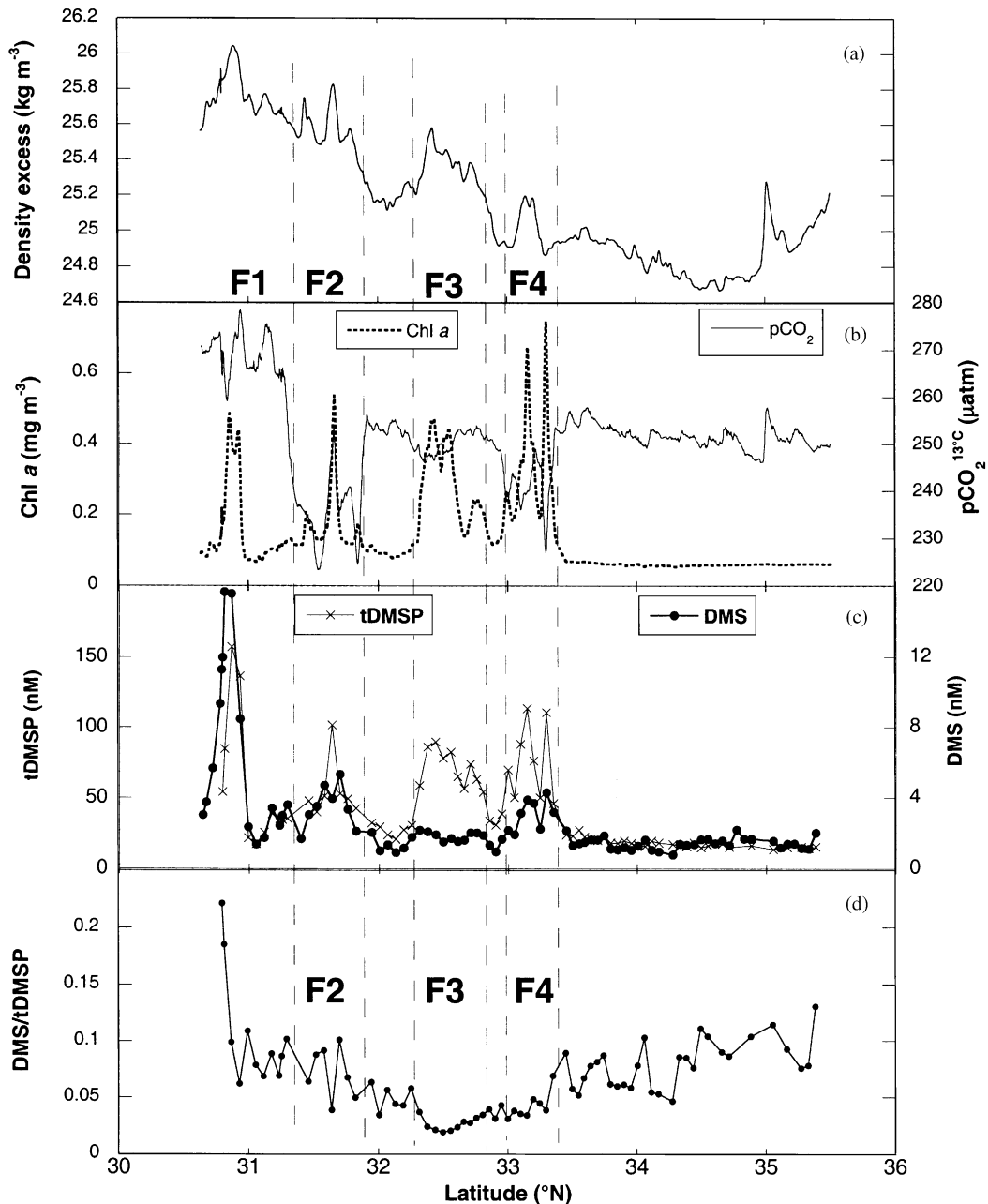


Fig. 3. Distribution of (a) density excess, (b) Chl *a* concentration and partial pressure of CO<sub>2</sub> at 13°C, (c) DMS and tDMSP concentrations, and (d) DMS-to-tDMSP ratio along the R.V. *Thalassa* transect in September 1999 between the southwestern edge of the upwelling off Cape Ghir (see the thick white line in Fig. 2) and the entrance to the Mediterranean Sea. The dashed lines mark the boundaries of areas with maxima in density excess corresponding to filaments of upwelled waters.

salinities corresponding to the temperature minima in F2–F4 were also in the range 36.10–36.15, maxima in density excess most probably also result

from upwelling of the same water mass. Total DMSP and DMS concentrations in F1 were up to 150 and 16 nM, respectively (Fig. 3c). Then the

ship crossed three other upwelled water masses (F2–F4) also exhibiting maxima in tDMSP, DMS and Chl *a*. The average DMS-to-tDMSP ratio in F3 was  $0.027 \pm 0.006$  (1 SD) (Fig. 3d). Ratios on average were  $0.071 \pm 0.023$  in F2 and  $0.043 \pm 0.012$  in F4. In areas F2–F4, the higher the  $p\text{CO}_2$  at  $13^\circ\text{C}$ , the lower the DMS-to-tDMSP ratio. There was an inverse correlation observed between these two parameters ( $n = 25$ ,  $r^2 = 0.44$ ,  $p < 0.001$ ). Along the Moroccan coast north of  $33.4^\circ\text{N}$  upwelling was virtually absent and the average DMS-to-tDMSP ratio was  $0.08 \pm 0.02$  (1 SD). The DMS-to-tDMSP ratio, which ranged in F1 between 0.05 and 0.2 (Fig. 3d), exhibited even larger variations closer to the coastline off Cape Ghir as will be shown later.

The high variability of the DMS-to-tDMSP ratio in surface waters off Morocco contrasts with the uniformity of the ratio between tDMSP and the volume of suspended particles. Indeed, Fig. 4 shows that the linear correlation between tDMSP concentration and the total volume of suspended particles, calculated with log-transformed data, is stronger than that between concentrations of tDMSP and Chl *a*. The utility of the total volume of suspended particles as a surrogate of tDMSP is clearly better than that of Chl *a* in the upwelling system investigated. The estimation of tDMSP (in nM) from the total volume of suspended particles ( $B$  in  $\text{mm}^3 \text{l}^{-1}$ ) is as follows:

$$\begin{aligned} \text{tDMSP}' &= 151.4B + 16.7 \\ (n = 61, r^2 &= 0.93, p < 0.001). \end{aligned} \quad (2)$$

From this equation, tDMSP was diagnosed from the volume of suspended particles routinely measured by the optical HIAC counter every 2 min during the series of six longshore traverses carried out in F1 (Fig. 5c).

The survey off Cape Ghir was carried out in the offshore direction. The track of R.V. *Thalassa* cut across the plume of upwelled waters F1 six times as shown in Fig. 5a from the six similar maxima in density excess ( $26\text{--}26.2 \text{ kg m}^{-3}$ ) numbered F1-1 to F1-6. The maxima in density excess were associated with maxima in Chl *a* (Fig. 5b) and tDMSP' concentrations (Fig. 5c). The tDMSP' concentration decreased steadily with increasing distance from the coast, whereas the Chl *a* concentration was higher in F1-2 and F1-3 than in F1-1. Thus, the ratio of Chl *a* to the total volume of suspended particles was lower in F1-1 than elsewhere in the plume of upwelled waters.  $p\text{CO}_2$  at  $13^\circ\text{C}$  also decreased steadily with increasing distance from the coast. No similar maximum in DMS (Fig. 5c) was observed in the main plume of upwelled waters because of the existence of a less dense water mass ( $25.4\text{--}25.7 \text{ kg m}^{-3}$ ) in the southern sector of the investigated area (south of the main plume of upwelled waters) which exhibited similar or higher DMS levels than in the main plume of upwelled waters. In both water masses the DMS-to-tDMSP' ratio increased with increasing distance from the coast (Fig. 5d). However, in the main plume of upwelled waters, the higher the  $p\text{CO}_2$  at  $13^\circ\text{C}$ , the lower the DMS-to-tDMSP' ratio, as noticed for F2–F4, while in the adjacent

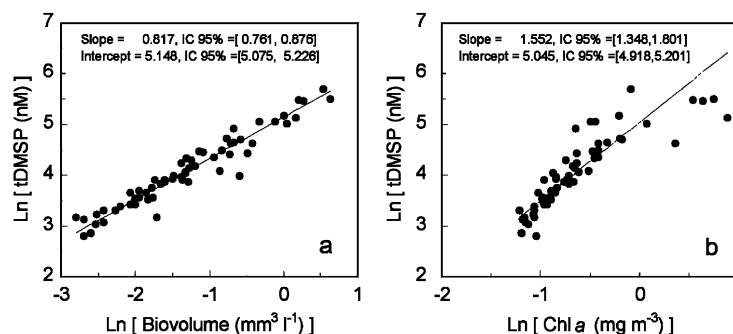


Fig. 4. Scatter diagram of tDMSP sea surface concentration plotted against (a) total volume of suspended particles from the HIAC profiler and (b) sea surface Chl *a* concentration, in log-transformed data. This plot is for coastal northeastern Atlantic waters only and includes data obtained during the 2D survey of F1 and during the transect from F1 to F4.

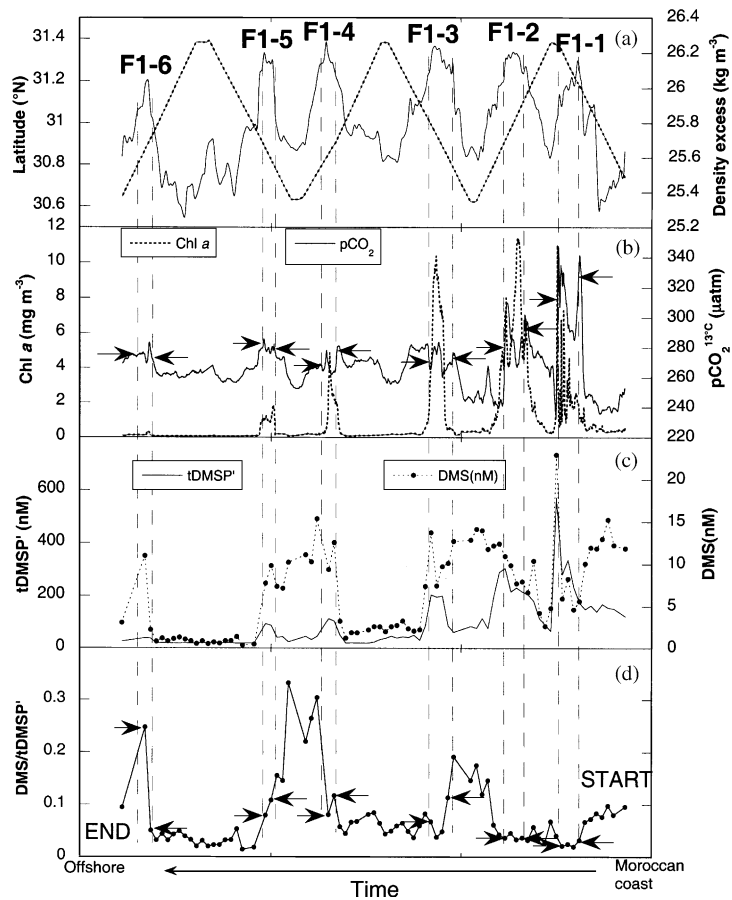


Fig. 5. Spatio-temporal variations of (a) density excess, (b) Chl *a* concentration and partial pressure of CO<sub>2</sub> at 13°C, (c) DMS and tDMSP' concentrations (tDMSP' is diagnosed from Eq. (2) and from the volume of suspended particles routinely measured by the optical HIAC counter every 2 min), and (d) DMS-to-tDMSP' ratio during the six longshore traverses carried out by R.V. *Thalassa* in plume F1 off Cape Ghir in 11–12 September 1999. The longshore navigation is illustrated in panel 5a as temporal changes in latitude coordinates. The start of the survey is on the right side of the panels. The dashed lines mark the boundaries of areas numbered F1-1 to F1-6 which exhibit maxima in density excess characterizing the same plume of upwelled waters. Horizontal arrows in panel b point at the levels of *p*CO<sub>2</sub> at 13°C at the boundaries of areas F1-1 to F1-6. Horizontal arrows in panel d point at the values of the DMS-to-tDMSP' ratio at the boundaries of areas F1-1 to F1-6.

water mass south of F1, the higher the *p*CO<sub>2</sub> at 13°C, the higher the DMS-to-tDMSP' ratio.

### 3.2. Mesoscale variations in Mediterranean waters

The large-scale trend of SST in the Mediterranean Sea was positive eastwards except between 6°E and 14°E (Fig. 6a). Moreover, a series of mesoscale abrupt decreases in SST were observed in the Alboran Sea and in the Algerian Basin (southwestern Mediterranean Sea).

Satellite-derived surface temperatures (AVHRR data not shown) show that the declines in SST in the Alboran Sea and in the Algerian Basin was related to cooler water masses of Atlantic origin entering the Mediterranean Sea and to the circulation of Modified Atlantic Water in the western Mediterranean Sea (Millot, 1999). Quasi-permanent eddies in the Algerian Basin increase the mixing between the resident and surface waters which recently entered the Mediterranean (Millot, 1999). Highest wind speeds were recorded in the

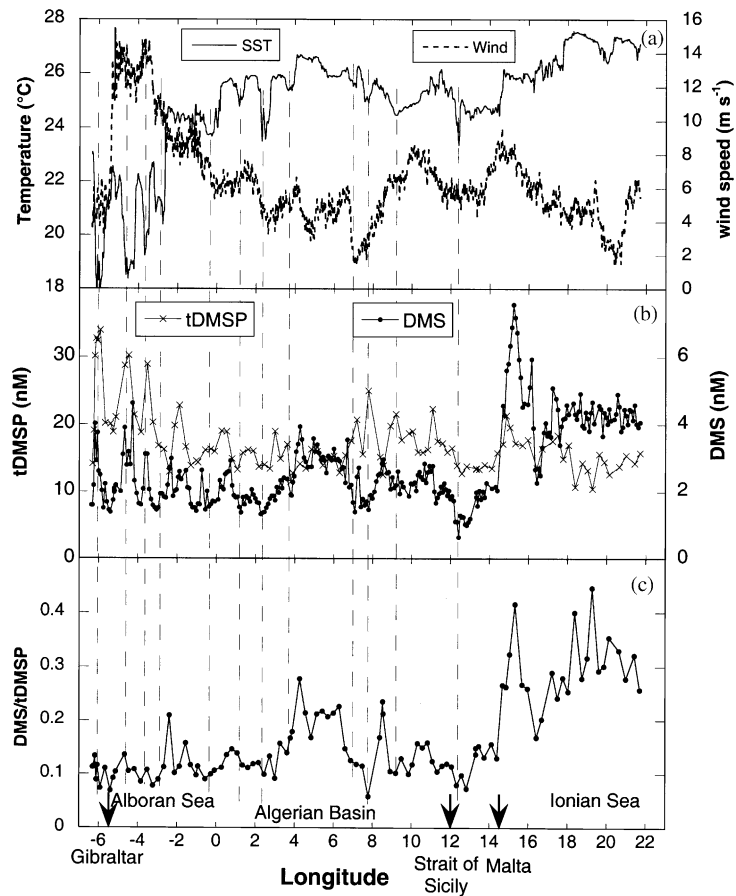


Fig. 6. Distribution of (a) sea surface temperature (SST) and wind speed, (b) DMS and tDMSP concentrations, and (c) DMS-to-tDMSP ratio along the R.V. *Thalassa* transect in September 1999 between the Strait of Gibraltar and the Central Ionian Sea. The dashed lines mark the major abrupt decreases in SST. Vertical arrows in panel c mark the entrances to the Mediterranean Sea basins.

Alboran Sea (Fig. 6a). The large-scale trend of wind speed was decreasing eastwards except between 7°E and 14°E. On the sole basis of the ship's data-logging system, it is difficult to address the effect of wind speed and wind direction on SSTs.

In the whole study area, the amplitude of the variations in tDMSP concentrations was lower than that of DMS (Fig. 6b). In the Strait of Gibraltar and in the Alboran Sea until longitude 3.5°W, sharp DMS and tDMSP enhancements up to twice the background levels were associated with the declines in SST. The declines in SST found in the Alboran Sea from 3°W eastwards and in the Algerian Basin, conversely, were

systematically associated with declines in DMS concentration. Patterns of tDMSP were less clear because the horizontal resolution of tDMSP was about one-third of that of DMS. Nevertheless, in these areas, the declines in SST were associated with either lows (between 0°E and 4°E) or highs (between 6°E and 11°E) in tDMSP concentrations. In the western basin of the Mediterranean Sea the background value of the DMS-to-tDMSP ratio was about 0.1 (Fig. 6c). Clear deviations from this background to reach values twice as high were observed in the Algerian Basin between 4°E and 7°E and between 8°E and 9°E. The former anomaly was found in the warmest waters of the area. The second one was also associated with a

rise of SST somewhat lower than the former. In the eastern basin from the Strait of Sicily to the Ionian Sea, the higher the temperature, the higher the DMS-to-tDMSP ratio. The correlation between this ratio and SST in the range 23–28°C, however, explains only about 60% of the variability (data not shown).

#### 4. Discussion

The PROSOPE cruise has offered a first opportunity to investigate with high spatial resolution the sea surface distribution of DMS, tDMSP, and the ratio of both compounds in coastal upwellings along the Moroccan coasts and in the Mediterranean Sea as far as possible from coasts. A series of supporting parameters were used to help understand the controlling factors of the DMS-to-tDMSP ratio at the mesoscale. The ratio also occurs along a gradient of primary production (PP) since, according to PP measurements made aboard by the  $^{14}\text{C}$  technique, PP of the Ionian Sea was at most half that of the Alboran Sea (Moutin et al., 2002). This gradient in PP compares well with the respective estimates derived from coastal zone color scanner (CZCS) observations (Antoine et al., 1995).

The survey carried out in the southern sector of the upwelling zone off Cape Ghir demonstrates that the spatial extension of a DMS plume can be larger than expected from a mapping of the distribution of planktonic biomass (Fig. 5c) as suggested by the earlier data of Andreae (1985) and Mihalopoulos et al. (1992) from different upwelling zones.

Since the linear correlation between tDMSP concentration and the total volume of suspended particles explained about 93% of the variability, it is suggested that DMS was homogeneously distributed amongst planktonic communities from the four plumes of upwelled waters and surrounding waters north of Cape Ghir. The stronger relationship obtained between tDMSP and the total volume of suspended particles than between tDMSP and Chl *a* is consistent with algal DMS being transferred through the food web to biogenic particles which are routinely counted and sized by

the optical HIAC counter. The DMS-to-tDMSP ratio calculated either from measured or HIAC-reconstructed tDMSP levels was much more variable than the DMS per unit biovolume ratio. In filament F1 the DMS-to-tDMSP' increased markedly with increasing distance from the coast (Fig. 5d). Since the water mass in the filament was obviously coastal in origin (Fig. 5a), the increase of the DMS-to-tDMSP' ratio with increasing distance from the coast may be interpreted qualitatively as resulting from the turnover of DMSP advected from the coast. Moreover, in F1 the higher the  $p\text{CO}_2$  at 13°C, the lower the DMS-to-tDMSP' ratio (Fig. 5d). Because  $p\text{CO}_2$  at in situ temperatures was within a range of 50  $\mu\text{atm}$  of atmospheric  $p\text{CO}_2$  (data not shown), air-sea exchanges of  $\text{CO}_2$  were of minor importance compared to the biological uptake. Consequently, spatial changes in seawater  $p\text{CO}_2$  at the constant temperature of 13°C resulted mainly from the cumulative biological uptake of  $\text{CO}_2$  since the water reached the surface. Marine  $\text{CO}_2$  levels thus indicate that algal growth in F1-3 to F1-6 started earlier than in F1-2 and F1-1 (Fig. 5b). Thus, it is possible that different stages of a bloom were sampled within the limited area of investigation, and that the variations of the DMS-to-tDMSP ratio between F1-1 and F1-6 were related to the aging of the DMSP-containing planktonic community. Moreover, the fact that DMS concentrations remained high despite the decrease of tDMSP may be an indication of a late stage in the decay of the algal development in filaments of upwelled waters. In this respect, lags between chlorophyll and DMS peak concentrations observed in mesocosms (Nguyen et al., 1988) and in in situ seawater (Leck et al., 1990; Simo et al., 1997) indicated that maximal DMS production takes place during the declining phase of algal blooms. Nevertheless, it is also possible that the plankton community composition changed or that ecological changes due to grazing and bacterial consumption took place as Ekman transport moved the upwelled water mass. Unfortunately, there is not sufficient data to determine this possibility since (1) process studies were not carried out during the PROSOPE cruise, and (2) phytoplankton community composition was

studied underway from HPLC-determined pigments solely between 31.4°N and 30.7°N along 9.93°W when the ship crossed F1-2 (Fig. 5a). The biomass proportion associated with the microphytoplankton (dinoflagellates and diatoms) defined as the sum of concentrations of peridinin and fucoxanthin divided by the sum of seven diagnostic pigments (Claustre, 1994; Vidussi et al., 2001) was in the range 40–50% ( $n = 5$ ) north of F1-2 and in F1-2 (H. Claustre, pers. commun.). The microphytoplankton (fucoxanthin + peridinin) was composed of  $60 \pm 10\%$  of fucoxanthin. In adjacent waters south of F1-2 the biomass proportion associated with the microphytoplankton was in the range 75–100% ( $n = 4$ ) and microphytoplankton was composed of  $75 \pm 18\%$  of fucoxanthin (diatoms). Thus, the increase in the DMS-to-DMSP' ratio south of F1-2 (Fig. 5d) and in a different water mass is coincident with a phytoplankton community composition change.

F2–F4 correspond to plumes of the same upwelled water mass which were crossed roughly at the same distance from the coastline (Fig. 2). Their spatial extension is smaller than that of F1. They exhibit the same DMSP-to-biovolume ratio. According to  $p\text{CO}_2$  at the constant temperature of 13°C, algal growth in F2 started earlier than in F4 and F3 (Fig. 3d). So it is unlikely that changes in the DMS-to-DMSP' ratio result from phytoplankton community composition changes.

Shifts in the regime of DMS production-removal appear to take place at the entrances to the western and eastern basins of the Mediterranean Sea in summer. Indeed, in the Alboran Sea near 3°W, peak concentrations in DMS shifted from cold Atlantic waters to warm Mediterranean surface waters (Fig. 6c). Throughout the Algerian Basin, the DMS-to-tDMSP ratio alternated between highs and lows, warmer water being associated with higher DMS-to-tDMSP ratio. Between the entrance to the Ionian Sea at the Strait of Sicily and the central Ionian Sea, the ratio increased about three-fold up to 40%. No production and removal rates of DMS were measured during the transect. Only a small series of discrete samples collected daily between Gibraltar and the central Ionian Sea was made available to us to help understand some of the

spatial variations of the DMS-to-tDMSP ratio. Kiene et al. (2000) suggested that the assimilatory metabolism of DMSP by bacteria is the proximate control on DMS formation in the sea and that it is controlled by dDMSP availability relative to the sulfur demand of the bacterial populations. The mean dDMSP concentration in the central Ionian Sea obtained from GF/F filtered samples was  $5.8 \pm 1.4$  nM ( $n = 24$ ), slightly higher than that of DMS ( $3.9 \pm 0.6$ ,  $n = 50$ ) and roughly one-third of tDMSP. A mean dDMSP concentration of about 6 nM might thus be sufficient to shift the branching ratio toward DMS in the oligotrophic waters of the Ionian Sea. The phosphorous demand of bacteria was investigated by Van Wambeke et al. (2002) in the eastern basin of the Mediterranean Sea during the cruise. The data showed that (1) orthophosphate concentrations were well below 1 nM in surface waters (Moutin et al., 2002), (2) orthophosphate was found to stimulate bacterial production, and (3) the ratio of alkaline phosphatase activity to bacterial production was severely reduced in orthophosphate enrichment experiments carried out in the eastern basin of the Mediterranean Sea (Van Wambeke et al., 2002). Thus, the data suggest that heterotrophic bacterial production in surface waters of the eastern Mediterranean in September 1999 was strongly limited by phosphorous availability. Organic carbon (C, glucose) stimulation of heterotrophic bacterial production was observed only at two stations, one in the Alboran Sea and one in the Strait of Sicily (Van Wambeke et al., 2002), where the DMS-to-tDMSP ratio was only about 10%. Consistent with the hypothesis of Kiene et al. (2000), we found a shift toward more DMS in waters where the availability of inorganic nutrients (orthophosphate in this case) limits bacterial growth.

## 5. Conclusion

The PROSOPE cruise has offered a first opportunity to investigate with high spatial resolution the sea surface distributions of DMS, tDMSP and the ratio of both compounds. The DMS-to-tDMSP ratio was far from being constant

in the areas investigated. Data show that this ratio increases with increasing distance from the coast in the coastal upwelling off Morocco. Samples collected roughly at the same distance from the coast show that the ratio increases when  $p\text{CO}_2$  at constant temperature decreases. So data suggest that the age of the upwelled waters is the proximate control on the variability of the DMS-to-DMSP ratio. There is evidence that shifts in the regime of DMS production-removal occur at the entrances to the western and eastern basins of the Mediterranean Sea. Consistent with the hypothesis of Kiene et al. (2000) we found a shift toward more DMS in waters where orthophosphate availability limits bacterial growth.

### Acknowledgements

We gratefully acknowledge scientists, officers and crew aboard R.V. *Thalassa* for their help during the cruise PROSOPE. In particular, we extend our thanks to the chief scientist, H. Claustre, and to J. Ras, M. Begovic and F. Bruyant who contributed to DMSP/DMS analysis. J. Ras also kindly provided some pigment data. This work was supported by the national program Processus Biogéochimiques dans l'Océan et Flux (PROOF) of INSUE/CNRS. We wish to thank Dr. Marra and the three anonymous referees for their helpful comments on the manuscript. Information and data relative to the PROSOPE cruise can be found at <http://www.obs-vlfr.fr/jgofs/html/prosope/home.htm>. This is LSCE contribution number 833.

### References

- Andreae, M.O., 1985. Dimethylsulfide in the water column and the sediment pore waters of the Peru upwelling area. *Limnology and Oceanography* 30, 1208–1218.
- Antoine, D., Morel, A., André, J.-M., 1995. Algal pigment distribution and primary production in the Eastern Mediterranean Sea as derived from coastal zone color scanner observations. *Journal of Geophysical Research* 100, 16193–16209.
- Aumont, O., Belviso, S., Monfray, P., 2002. Dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) sea surface distributions simulated from a global three-dimensional ocean carbon cycle model. *Journal of Geophysical Research* 107, C4, 10.1029/1999JC000111.
- Belviso, S., Morrow, R., Mihalopoulos, N., 2000. An Atlantic meridional transect of surface water dimethylsulfide concentrations with 10–15 km horizontal resolution and close examination of ocean circulation. *Journal of Geophysical Research* 105, 14423–14431.
- Belviso, S., Claustre, H., Marty, J.-C., 2001. Evaluation of the utility of chemotaxonomic pigments as a surrogate for particulate DMSP. *Limnology and Oceanography* 46, 989–995.
- Belviso, S., Moulin, C., Bopp, L., Stefels, J., submitted. Assessment of a global climatology of oceanic dimethylsulfide (DMS) concentrations based on SeaWiFS imagery (1998–2001). *Canadian Journal of Fisheries and Aquatic Sciences*.
- Claustre, H., 1994. The trophic status of various oceanic provinces as revealed by phytoplankton, pigment signatures. *Limnology and Oceanography* 39 (5), 1206–1210.
- Claustre, H., Morel, A., Hooker, S.B., Babin, M., Antoine, D., Oubelkheir, K., Bricaud, A., Leblanc, K., Quéguiner, B., Maritorea, S., 2002. Is desert dust making oligotrophic waters greener? *Geophysical Research Letters* 29 (10), 10.1029/2001GL014056.
- Copin-Montégut, C., 1985. A method for the continuous determination of the partial pressure of carbon dioxide in the upper ocean. *Marine Chemistry* 16, 277–300.
- Kiene, R.P., Linn, L.J., Bruton, J.A., 2000. New and important roles for DMSP in marine microbial communities. *Journal of Sea Research* 43, 209–224.
- Holligan, P.M., Turner, S.M., Liss, P.S., 1987. Measurements of dimethyl sulphide in frontal regions. *Continental Shelf Research* 7, 213–224.
- Leck, C., Larrson, U., Bagander, L.E., Johansson, S., Hajdu, S., 1990. Dimethyl sulfide in the Baltic Sea: annual variability in relation to biological activity. *Journal of Geophysical Research* 95, 3353–3363.
- Marra, J., 1997. Analysis of diel variability in chlorophyll fluorescence. *Journal of Marine Research* 55, 767–784.
- Matrai, P.A., Cooper, D.J., Saltzman, E.S., 1996. Frontal enhancement of dimethylsulfide concentrations across a Gulf Stream meander. *Journal of Marine Systems* 7, 1–8.
- Mihalopoulos, N., Nguyen, B.C., Putaud, J.P., Belviso, S., 1992. The oceanic source of carbonyl sulfide (COS). *Atmospheric Environment* 26, 1383–1394.
- Millot, C., 1999. Circulation in the western Mediterranean Sea. *Journal of Marine Systems* 20, 423–442.
- Moutin, T., Thingstad, T.F., van Wambeke, F., Marie, D., Slawyk, G., Raimbault, P., Claustre, H., 2002. Does competition for nanomolar phosphate supply explain the predominance of the cyanobacterium *Synechococcus*? *Limnology and Oceanography* 47, 1562–1567.
- Nguyen, B.C., Belviso, S., Mihalopoulos, N., Gostan, J., Nival, P., 1988. Dimethyl sulfide production during natural phytoplanktonic blooms. *Marine Chemistry* 24, 133–141.

- Sciare, J., Mihalopoulos, N., Nguyen, B.C., 1999. Summertime seawater concentrations of dimethylsulfide in the Western Indian Ocean: reconciliation of fluxes and spatial variability with long-term atmospheric observations. *Journal of Atmospheric Chemistry* 32, 357–373.
- Simo, R., Grimalt, J.O., Albaiges, J., 1997. Dissolved dimethylsulphide, dimethylsulfoniopropionate and dimethylsulphoxide in western Mediterranean waters. *Deep-Sea Research II* 44, 929–950.
- Simo, R., Archer, S.D., Pedros-Alio, C., Gilpin, L., Stelfox-Widdicombe, C.E., 2002. Coupled dynamics of dimethylsulfoniopropionate and dimethylsulfide cycling and the microbial food web in surface waters of the North Atlantic. *Limnology and Oceanography* 47, 53–61.
- Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W., Sutherland, S.C., 1993. Seasonal variation of CO<sub>2</sub> and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochemical Cycles* 7, 843–878.
- UNESCO, 1985. The international system of units (SI) in Oceanography. UNESCO technical papers in marine science, No. 45.
- Van Camp, L., Nykjaer, L., Mittelstaedt, E., Schlittenhard, P., 1991. Upwelling and boundary circulation off Northwest Africa as depicted by infrared and visible satellite observations. *Progress in Oceanography* 26, 357–402.
- Van Wambeke, F., Christaki, U., Giannakourou, A., Moutin, T., Souvemerzoglou, K., 2002. Longitudinal and vertical trends of bacterial limitation by phosphorous and carbon in the Mediterranean Sea. *Microbial Ecology* 43, 119–133.
- Vidussi, F., Claustre, H., Manca, B.B., Luchetta, A., Marty, J.-C., 2001. Phytoplankton pigment distribution in relation to upper thermocline circulation in the eastern Mediterranean Sea during winter. *Journal of Geophysical Research* 106 (C9), 19939–19956.