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Influence of phytoplankton taxonomic profile on the distribution of total and dissolved dimethylated sulphur (DMSx) species in the North Aegean Sea (Eastern Mediterranean)

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Abstract

The distribution of total and dissolved forms of DMSP and total DMSO was surveyed during two sampling cruises conducted in September 2003 and July 2004 in the North Aegean Sea. During the first cruise surface concentrations of DMSPt, DMSPd and DMSOt in the coastal group of stations ranged from 20.92 to 23.71 nM, 15.46 to 15.53 nM and 14.90 to 18.73 nM, respectively, while the offshore group mean concentrations were 27.41 nM (DMSPt) and 14.66 nM (DMSOt). At that time, phytoplankton assemblage was dominated by dinoflagellates. During the second cruise, the surface DMSPt, DMSPd and DMSOt concentrations in the coastal group were not significantly changed compared to the first cruise, while the offshore group presented more elevated values (DMSPt: 33.52 nM; DMSPd: 18.78 nM; DMSOt: 36.49 nM). Interestingly, the vertical distribution and phytoplankton abundance in this cruise were found to have changed, with diatoms being the dominant group in the study area. On both cruises statistically significant correlations between small-sized dinoflagellates (≤ 20 μm) as well as coccolithophores and the concentrations of DMSx compounds were obtained, suggesting the importance of the above phytoplankton groups in the production and distribution of these sulphonic forms. At the same time, no significant correlations were observed between DMSx and diatom species. The strong correlation of DMSx species with the group of dinoflagellates coupled with their decorrelation with Chl-*a* may serve as indirect evidence of heterotrophic forms dominating dinoflagellate taxa thriving in the area during the stratified period.

Keywords: Dimethylsulphoniopropionate, dimethylsulphoxide, phytoplankton assemblage, size distribution, North Aegean.

Introduction

Dimethylsulphoniopropionate (DMSP) is a ubiquitous sulphur compound present in the euphotic layers of marine ecosystems. It is considered to be a major pool for reduced sulphur derivatives while it presents a wide variance in concentrations ranging from nanomolar, in the open ocean, up to the order of several micromolar during phytoplankton blooms. Being produced by different algal species, DMSP may serve as an important osmolyte (Vairavamurthy *et al.,* 1985; Kirst, 1990), cryoprotectant (Karsten *et al.,* 1996), antioxidant (Sunda *et al.,* 2002) and as a surface inhibitor of antifouling defense (Saha *et al.,* 2012). The role of DMSP as an organic osmoregulator is highlighted due to its ability to function in both significantly low and high concentrations (reviewed in Reisch *et al.,* 2011) and thus, through its osmotic potential, regulate cell volume (Kirst, 1990). According to the literature, the biosynthesis of DMSP is reported to begin with methionine as the initial component and it is completed through three different biochemical pathways (Gage *et al.,* 1997; Rhodes *et al.,* 1997; Kocsis & Hanson, 2000). Although the genes implicated in the biosynthesis of the compound are not yet identified (Reisch *et al.,* 2011), DMSP production has been found to be species-specific with certain taxonomic groups being especially rich in DMSP (DMSP-producers). In fact, the ability of phytoplankton species to produce DMSP increases in the following order (Shenoy & Patil, 2003):

Diatoms < Dinoflagellates < Phaeocystis < Coccolithophores

DMSP release from phytoplankton mainly occurs during lysis of the cells, a process that takes place upon senescence (Stefels & van Boeckel, 1993), grazing by zooplankton (micro- and macro-zooplankton predators) (Wolfe *et al.,* 1997; Simo, 2001) and viral infections (Hill *et al.,* 1998). Upon its release, DMSP is transformed into a reduced organic source that can flow and recycle through the microbial food web affecting sulphur and carbon fluxes on various trophic levels (Archer *et al.,* 2002; Vila-Costa *et al.,* 2007). Subsequent DMSP cleavage results in the production of dimethylsulphide (DMS), an active gas that emanates from the oceans and affects the climate (Andreae, 1980). While bacteria are considered the primary mediators of DMSP catabolism, there is evidence that some marine phytoplankton species have also the capacity to produce DMS. Studies in the North Atlantic have shown that photosynthetic dinoflagellates can contribute to the release of DMS during phytoplankton blooms (Steinke *et al.,* 2002), while enzymes such as DMSP-lyases were purified from marine algae (Storey

et al., 1993; de Souza & Yoch, 1996). The possible role of DMS in climate regulation is described in the CLAW hypothesis, according to which the oxidation of DMS in the marine boundary layer results in sulphate aerosols that could increase cloud's albedo leading to a negative feedback loop towards a global temperature increase (Charlson *et al.,* 1987). Even though it is accepted that DMS contributes in the complex dynamics of climate and active aerosols in the lower atmosphere (Amrani *et al.,* 2013), the limited direct evidence for local climate regulation via DMS emissions raised a case against this hypothesis (Scarratt *et al.,* 2002; Quinn & Bates, 2011).

The cleavage of DMSP and the production of volatile sulphur species such as DMS is only one of the possible fates of this compound. DMSP can also be transformed through demethylation/demethiolation pathways into sulphur sources required for protein synthesis, or can be converted into non-volatile products such as dimethylsulphoxide (DMSO) and sulphate. DMSO may also be derived from seawater as a degradation product of DMS. Specifically, in the marine environment the dissolved form of DMSO can be produced through photochemical oxidation or biological consumption of DMS (del Valle *et al.,* 2009).

Although the intracellular production of DMSO is not well investigated, observations have indicated that phytoplankton can biosynthesize and release DMSO in the environment due to their membrane permeability (Liu *et al.,* 1997). According to Sunda *et al.* (2002) the biosynthesis of DMSO might be a defence mechanism and in particular part of a radical scavenging system that protects phytoplankton cells under oxidative stress induced by UV radiation. This suggests that light penetration, UV radiation as well as phytoplankton biomass can be potential factors determining the fate of DMSO released into the water (del Valle *et al.,* 2009).

The Eastern Mediterranean Sea (EMS) is an ultra-oligotrophic environment characterised by extremely low dissolved nutrient concentrations in the surface waters, chlorophyll-*a* values and phytoplankton biomass (Krom *et al.,* 2004). Some studies in the region have determined concentrations and spatial distribution of DMSx species (Vassilakos *et al.,* 1996; Belviso *et al.,* 2003; Besiktepe *et al.,* 2004; Amrani *et al.*, 2013), yet very little is known on the possible role of the local phytoplankton assemblage in the production and distribution of these compounds in the water column. The North Aegean Sea is a region of particular interest in the northern part of the EMS, because it is influenced by the input of the less saline waters from the Black Sea (BSW) which are modified by the Levantine waters and create cyclonic gyres around the island of Lemnos (Zodiatis, 1994) and from fresh water discharges mainly from rivers located in mainland Greece (Velaoras & Lascaratos, 2005). These features create an interesting structure in the water column, which seems to have a significant role in a rather elevated productivity status of the area compared to the rest of the EMS (Ignatiades *et al.,* 2002).

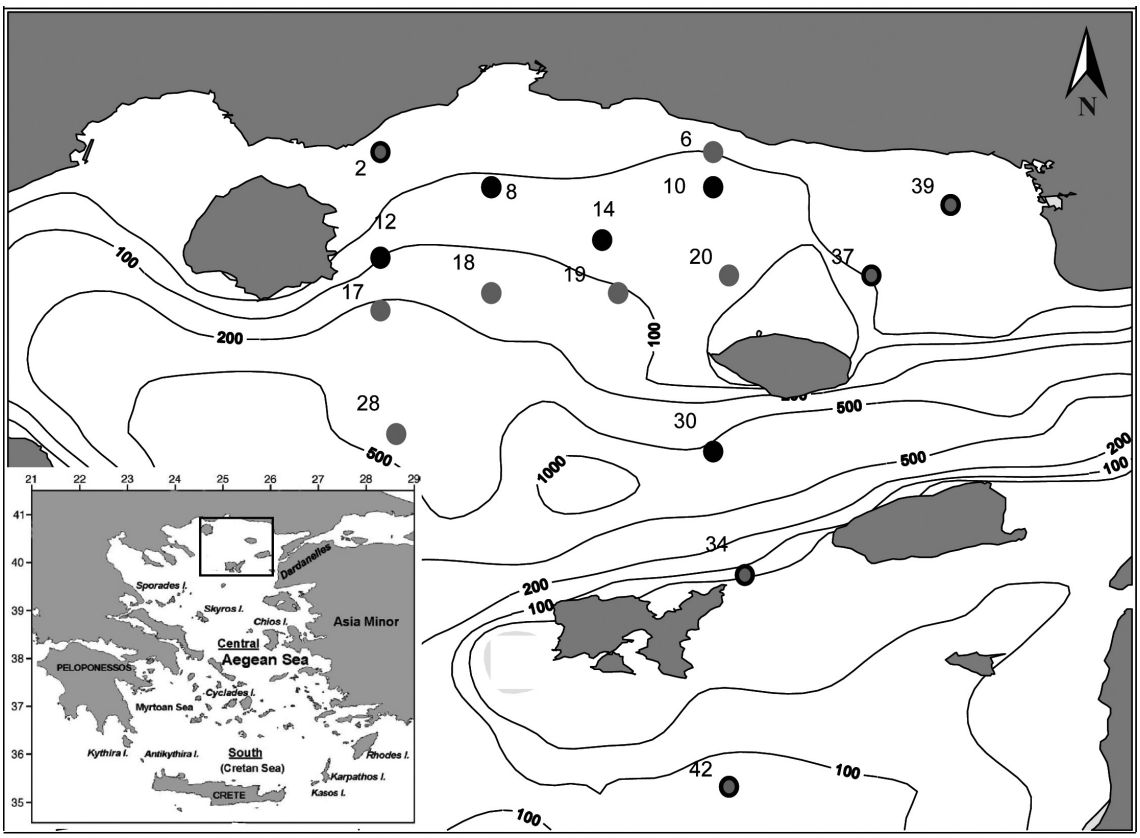
In this study, we describe the temporal and vertical variability of DMSP and DMSO in the North Aegean Sea and we make a first attempt to assess the relative importance of the local phytoplankton assemblage and their distribution in the water column. Our main aim was to study the behaviour of the above mentioned organic sulphur compounds in the area and to examine potential relations with phytoplankton communities and in particular with certain size groups. This has been reported in the literature following laboratory experiments (e.g. Keller *et al.,* 1989; Jean *et al.,* 2005), but was never checked, verified and reported for the area under study.

Experimental section

Samples were collected on board the R/V AEGAEO during two 10-day sampling campaigns, undertaken in September 2003 (1st sampling cruise) and July 2004 (2nd sampling cruise). Both cruises covered a wide grid of stations located in the coastal and the pelagic zone of the N. Aegean Sea (Fig.1). Temperature, salinity and fluorescence data were collected using a CTD system (Sea Bird Electronics, USA). Water samples for total and dissolved DMSP (DMSPt, DMSPd), total DMSO (DMSOt) and phytoplankton cells counts were collected from discrete depths in the 0 - 20 m layer, and thereafter at intervals up to 100 m, with a rosette sampler equipped with 12 Go-Flo Niskin bottles of 10 L. Chl-*a* samples were also collected from all the stations investigated and were analyzed in the laboratory using the fluorometric method (Yentch & Menzel, 1963; Holm-Hansen & Riemann, 1978).

Phytoplankton samples for counting and taxonomic identifications (cells ≥5 μm) were collected from each sampling depth in all the twenty-one stations investigated during the two campaigns. Samples were fixed with alkaline Lugol's solution (final concentration 2%) and identified under an inverted light microscope (Utermöhl, 1958).

Seawater samples for DMSP and DMSO analysis were collected from the Niskin bottles immediately after the rosette was lifted on board and transferred into 250 ml Nalgene bottles using a short length silicone tube. The dissolved form of DMSP (DMSPd) was obtained by gravity filtration through GF/F filters (Whatman 47 mm dia, 0.7 μm porosity). The filtrates for the DMSP analysis were placed in a 50 ml glass bottle to which 1 ml of 5 M NaOH (pH ~13) was added. The sampling of the total form of DMSP followed the same procedure, without pre-filtration. The DMSO samples had 1 ml of 12 M HCl (pH~1) added to the 50 ml bottle. After the alkali treatment and the addition of the HCl, the samples were tightly sealed with no headspace and left in the dark at 4° C.



Stations	Depth (m)	Latitude	Longitude	Description
St.2	25	40º49´N	24º51´E	shallow coastal station
St.6	29	40º51´N	25º27´E	shallow coastal station
St.37	29	40º37´N	25º43´E	shallow coastal station
St.39	28	40º46´N	25º52´E	shallow coastal station
St.8	63	40º46´N	24º03´E	deeper coastal station
St.10	60	40º51´N	24º40´E	deeper coastal station
St.12	78	40º39´N	24º51´E	deeper coastal station
St.14	78	40º40´N	25º15´E	deeper coastal station
St.17	131	40º34´N	24º51´E	deeper coastal station
St.18	141	40º36´N	25º03´E	deeper coastal station
St.19	117	40º36´N	25º15´E	deeper coastal station
St.20	83	40º36´N	25º26´E	deeper coastal station
St.34	71	40º04´N	25º29´E	deeper coastal station
St.28	539	40º17´N	24º51´E	offshore station
St.30	500	40º17´N	25º26´E	offshore station
St.42	134	39º41´N	25º30´E	offshore station

Fig. 1. The stations investigated in the two sampling campaigns in the N. Aegean. Grey circles: stations during the 1st sampling cruise (September 2003). Black circles: stations during the 2nd sampling cruise (July 2004). Black/Grey circles: the common stations between the 2 cruises.

DMSP and DMSO measurements

DMSP and DMSO samples were analyzed following the cryo-trapping gas chromatographic technique that analyses the produced DMS from the hydrolysis and the reduction of DMSP and DMSO, respectively (Simo, 1998).

The hydrolysis of DMSP in acrylate and DMS was induced by alkali treatment while DMSO reduction was performed with the use of appropriate reduction agents as described below. The gas chromatograph (Hewlett Packard 5890 Series II) was equipped with a flame photometric detector (FPD) and a 1/8 in. PTFE column filled with Chromosil 310 (Supelco). Sub-samples of 5 - 10 ml for total and dissolved DMSP were taken from the alkaline solution with a polyethylene needle. DMS was stripped

by purging the solution with helium (99.9996% quality) at a flow rate of 120-150 ml min^{-1} for 10 min. By means of this procedure, DMS was trapped into the Tenax trap system, which was submerged in liquid ethanol at -80° C using magnesium perchlorate as a drier. After a 10-min purging period, the trap system was lifted from the liquid ethanol and heated with boiling water. During this procedure DMS was injected into the PTFE column.

Aqueous DMSO samples were determined by reduction to DMS using borohydride pellets (NaBH4), as described in Simo *et al.* (1997). During the NaBH4 addition, a gentle helium flow (~50-60 ml min^{-1}) was applied to the sample in order to facilitate slow dissolution of borohydride and its effective reaction with DMSO (Simo *et al.,* 1997). On completion of the reaction, the flow of the stripping gas was at a constant rate of 120~150 ml min^{-1} for 12 minutes. DMSO concentrations were calculated after subtraction of the DMSP, which is also decomposed to DMS by borohydride (Simo *et al.,* 1997).

Direct measurements of seawater DMS in both cruises were not feasible due to technical reasons and constraints of ship time. For accuracy reasons, we need to mention that the seawater DMSP values in the text reflect seawater DMSP+DMS while in our graphs and tables this clarification is further illustrated.

Data analysis

A separation between coastal and offshore areas was performed according to bathymetry, natural geography and hydrological conditions influencing the stations. The robustness of the separation was also verified by statistical means such as the Bray-Curtis similarity index performed for the phytoplankton assemblage of both cruises (data not shown). Based on the Bray-Curtis similarity index the spatial distribution of phytoplankton species seems to be influenced by the hydrographic features occurring in the investigated region: the offshore group of stations is under the influence of the BSW while the coastal cluster is under the influence of fresh water discharges including river plumes.

DMSx concentrations, phytoplankton abundance and Chl-*a* mean values were calculated for the 0 - 20 m depth layer. This surface layer was selected as it comprises a zone of intense biological activity with a possible role in the sea-atmosphere interactions and in the same time it corresponds to both the mixed and BSW layers influencing the area. The mean values for all the investigated depths and stations are summarized in Tables 1 and 2.

Concerning the presentation of the vertical distributions (Fig. 5 and Fig. 6) of the DMSx compounds and of the phytoplankton groups, two representative stations from the offshore group located in the bathymetric zone of the 500 m were selected: Station 28 (September 2003) and Station 30 (July 2004) which were considered typical deep pelagic stations. Accordingly, from the coastal cluster the selected stations were the shallow Stations 6 (September 2004) and 39 (common to both cruises) and Stations 18 (September 2003) and 14 (July 2004) which were representative deeper coastal stations.

Finally, in order to highlight the influence of the taxonomic profile in the distribution of the DMSx compounds among the stations, statistical tools were employed: a 2-tailed Spearman nonparametric rank correlation at each station in both sampling cruises and a factor analysis for the whole data-set.

Results

Hydrological Conditions

Strong thermohaline stratification was observed in the surveyed area during both sampling cruises. The temperature in the shallow coastal stations ranged between 15.8 and 25.2 (September 2003) and 14.6 to 23.8 °C (July 2004), while in the deeper coastal and offshore investigated stations the respective ranges were 20.6 to 24.7 °C (September 2003) and 20.8 to 24.5 °C (July 2004) (Fig. 2A and Fig. 3A). The salinity in the shallow coastal stations ranged between 34.7 to 38.5 (September 2003) and 33.8 to 38.8 psu (July 2004) while in the rest of the stations values ranged from 34.4 to 39 and 32 to 39.2 psu, for the first and the second cruises, respectively (Fig.2B and Fig.3B). The depth of the surface mixed layer ranged between 0 - 15 m and 0 - 20 m in all stations for the two cruises. On both cruises a sharp decrease in temperature (of ca. 6 - 10°C) and an increase in salinity (of ca. 4-5 psu) values was observed along the thermocline that extended down to 50 m. The sharp gradient in the salinity values was attributed to the influence of the low salinity BSW that occupy the surface layers in the sampling area. Below the thermocline, temperature and salinity values were quite homogenous ranging from 14.8 to 16.5 °C and from 38.5 to 39.1 psu, respectively, characterizing the Levantine Intermediate Waters (LIW) occupying the deeper layers in the area.

Phytoplankton composition and size distribution of the cells

During the first campaign (September 2003) the average total abundance of phytoplankton cells in the upper 20 m ranged from 28×10^2 to 52×10^2 cells / L. The highest mean abundance was observed in the shallow coastal Station 39, while the lowest values were observed in Station 37 (Fig.4A). The phytoplankton composition, expressed as an average percentage of each group identified in the upper 20 m, was dominated by dinoflagellates (81%), followed by diatoms and coccolithophores (10% and 9% respectively). Diatoms were relatively more abundant in the coastal stations 2, 6 and 39, where in the case of the latter they comprised almost 40% of the assemblage. Dinoflagellates were dominated by cells < 20 μm more than

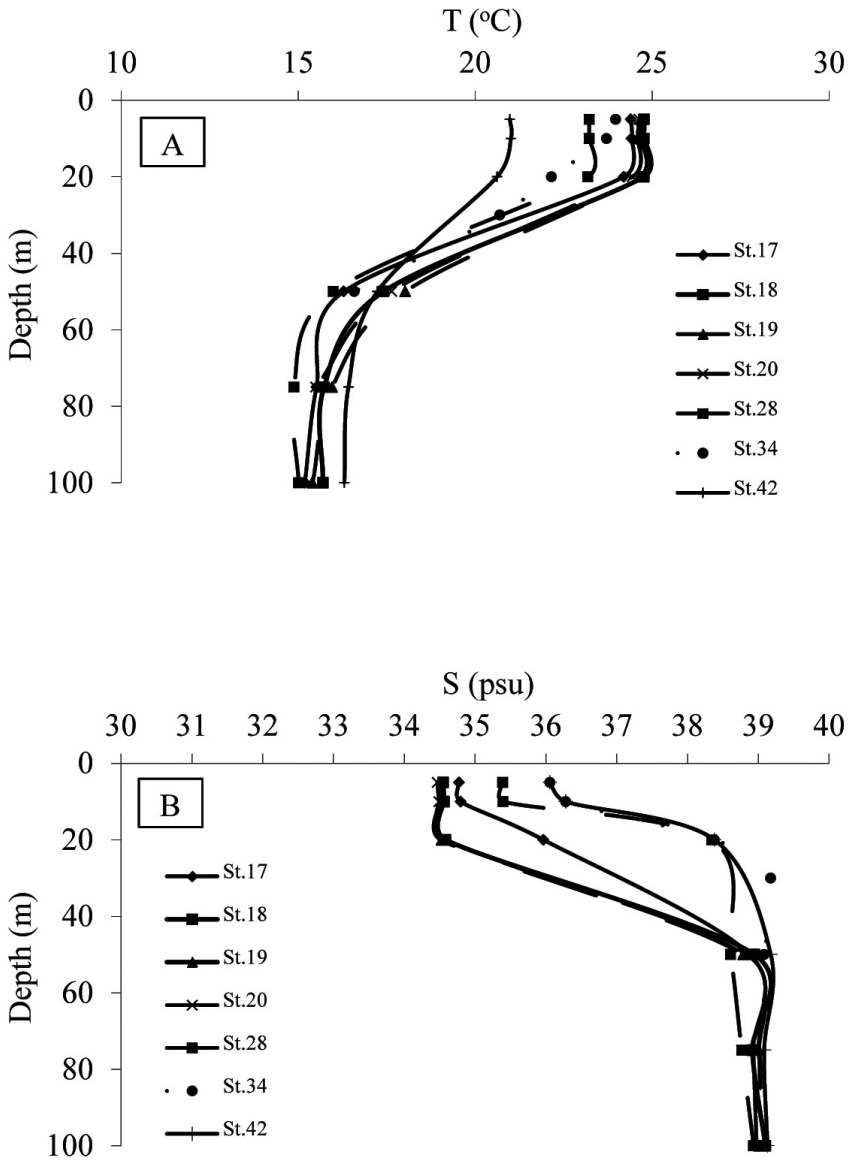


Fig. 2. Vertical profiles of temperature (A) and salinity (B) in the deeper coastal and offshore stations (September 2003).

80% of which belonged to *Gymnodinium* species (10 - 15 μm), while other abundant taxa were *Nitzschia* spp. (diatoms) and *Syracosphaera pulchra* (coccolithophores). Chl-*a* ranged from 0.03-0.39 μg / L (0.09±0.07) with the highest values observed mainly in Stations 2 and 39 that were close to the river plumes of Nestos and Evros in the North West (NW) and North East (NE) respectively, with the lowest values were recorded at Stations 20 and 42.

During July 2004, the average total phytoplankton abundance in the upper 20 m layer ranged from 87×10^2 to 177×10^2 cells/ L. This 3 to 3.5-fold increment in cell abundance compared to the first cruise was attributed primarily to the elevated presence of diatoms (Fig.4B). Indeed, during the second cruise diatom species occupied almost 60% of the total abundance recorded throughout the water column in all the investigated stations, with the exception of the offshore Stations 30 and 42. This observation was also reflected in the upper 20 m layer, since the highest average phytoplankton abundance was observed in Station 2 which displayed a 5-fold increase in diatoms, while the lowest was presented in Station 30. Similarly to what was observed in the first cruise, the total cell abundance presented higher values within the investigated surface layer, followed by a considerable decrease below 20 m in all stations. The average percentage contribution of the different phytoplankton species in the total abundance was diatoms with 60%, dinoflagellates as the second most abundant group (33%) while coccolithophores formed the minority in the phytoplankton assemblage (7%). In the second cruise the dominant species within diatoms were *Proboscia alata* (35%), *Dactyliosolen fragilissimus* (24%), *Cylindrotheca closterium* (16%) while other diatoms such as *Chaetoceros* spp. were present in lower abundances. Regarding dino-

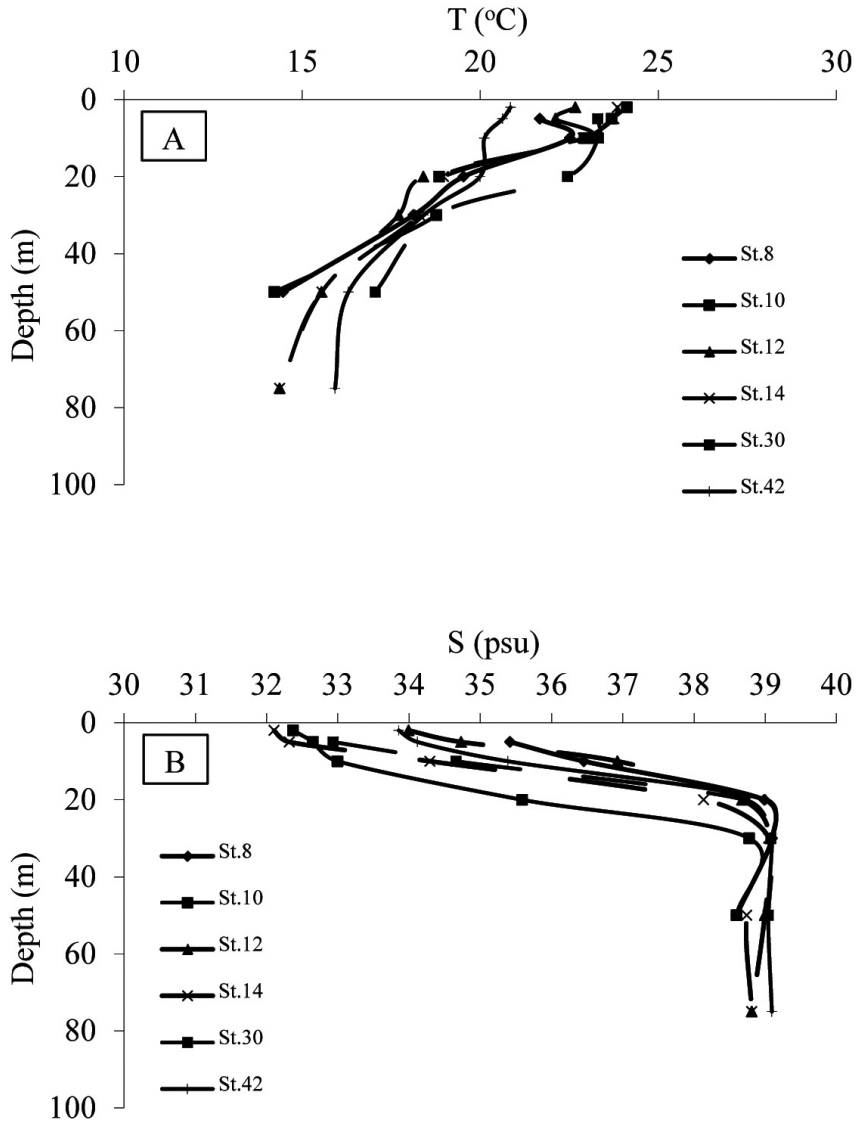


Fig. 3. Vertical profiles of temperature (A) and salinity (B) in the deeper coastal and offshore stations (July 2004).

flagellates, the assemblage was again dominated by small sized dinoflagellates (< 20 μm) among which species of the genera *Gymnodinium* and *Ceratium* spp. were most important. Coccolithophore abundance was attributed mainly to the species *Syracosphaera pulchra* and *Dactylethra pirus*. In the second campaign Chl-*a* values ranged from 0.04 to 0.47 μg/ L (0.14±0.07) presenting again the highest values in Stations 2 and 39. Below the 20 m layer Chl-*a* values (0.26±0.18) were 2-fold higher compared to those observed in the first campaign, reflecting the higher diatom and total phytoplankton abundance.

Dissolved and total sulphur distributions

Surface concentrations of DMSPt and DMSPd

The mean upper 20 m layer concentrations of the total DMSP did not show significant variability between the stations investigated during September 2003. As presented in Table 1, the mean DMSPt concentration in the coastal group ranged from 20.92 to 23.71 nM, while in the offshore group the mean value was slightly elevated (27.41 nM). The highest DMSPt concentrations were observed in Stations 39 and 42 while the lowest in Stations 18 and 37. Concerning the dissolved form of DMSP, results can be only obtained for the coastal group of stations; the mean DMSPd value was similar in both the shallow and deeper coastal stations (Table 1) with Station 18 presenting, as in the case of DMSPt, the lowest value and Station 17 the highest.

During July 2004, the mean concentration of DMSPt in the ten investigated stations presented a similar spatial pattern and similar concentration levels compared to that observed during the first cruise, with values in the coastal group of stations ranging from 21.15 to 23.92 nM (Table 2) while in the offshore stations they were elevated (33.52 nM). This is interesting since the phytoplankton abundance in the second cruise presented a significant increase compared to that recorded during the first cruise. In the investigated upper 20 m layer the highest concen-

Table 1. Average DMSx concentrations and phytoplankton group abundances in the surface layer (0-20 m) and below 20 m (>20 m) in coastal (shallow and deeper) and offshore stations during September 2003.
n.d.: not determined, sd: standard deviation, n: number of samples, C: coccolithophores, D: diatoms, DF: dinoflagellates.

Stations		DMSPt+DMS (nM)	DMSPd+DMS (nM)	DMSOt (nM)	C (x10² cells/ L)	D (x10² cells/ L)	DF (x10² cells/ L)
Costal shallow stations *(0-20m)*	**average**	23.71	15.46	14.90	2.7	7.81	29.93
	sd	6.30	5.16	12.86	1.4	12.6	6.12
	n	16	4	13	14	15	15
	range	14.16-38.37	8.7-21.23	3.63-50.22	0.8-6.1	0.9-52.3	19.8-41.2
Coastal deeper stations *(0-20m)*	**average**	20.92	15.53	18.73	4.55	1.79	36.3
	sd	7.40	3.81	8.27	2.03	10.8	10.6
	n	15	9	8	15	15	15
	range	15.11-41.06	10.38-21.99	9.10-34.63	1.1-5.8	0.6-3.1	18.3-61.3
Coastal deeper stations *(> 20m)*	**average**	13.85	n.d.	5.88	1.53	1.97	29.48
	sd	6.98		3.76	1.35	0.94	15.92
	n	13		11	13	13	13
	range	2.84-25.35		1.40-14.72	0.2-5.3	1-3.9	7.8-56.8
Offshore stations *(0-20m)*	**average**	27.41	n.d.	14.66	5.18	1.85	36.88
	sd	4.51		10.82	2.87	0.56	10.46
	n	6		6	6	6	6
	range	21-33.27		4.59-35.02	2.9-10.2	1-2.6	26.7-55.1
Offshore stations *(>20m)*	**average**	13.87	n.d.	3.53	1.68	1.35	17.18
	sd	8.50		2.63	0.96	0.94	10.57
	n	6		5	6	6	6
	range	3.62-23.25		1.23-6.47	0.3-2.8	0.2-2.8	5.9-33

trations were observed again in Stations 39 and 42 while the lowest in Stations 2 and 34.

A similar spatial distribution pattern seemed to occur also in the DMSPd concentrations. Specifically, the offshore group of stations presented elevated mean DMSPd values compared to those recorded for the coastal cluster (Table 2). The highest concentrations were in Stations 39 and 42 and the lowest in Stations 2, 30 and 34. Furthermore the DMSPd concentrations seemed to be statistically correlated ($r^2 = 0.71$, $p \leq 0.05$) with the DMSPt values demonstrating the dependence of DMSPd on the DMSPt level.

Vertical distributions of DMSPt and DMSPd

Figures 5 and 6, present the vertical distributions of DMSPt, DMSPd and DMSOt in parallel with the main phytoplankton groups in the representative stations of the two sampling cruises. During the first cruise both forms of DMSP were well stratified in the water column, showing maxima in the upper layers (0-20 m) followed by a 2-fold decrease in the deeper layers. The vertical profiles of DMSP were in accordance with the general trend of the temperature profile and especially with the profile of total phytoplankton abundance that was dominated by dinoflagellates (mostly by *Gymnodinium* spp.) (Fig. 5).

In the second cruise the vertical distribution profile of the DMSx compounds in the three representative stations (Fig. 6) showed again strong stratification with the concentrations of the compounds restricted to the upper 20 m layer. As in the first cruise, below the 20 m, a sharp decrease was observed. Contrary to the pattern observed in the first cruise, the second cruise's vertical profile of DMSP did not follow the vertical profile distribution of the total phytoplankton abundance, which on this occasion was dominated by diatoms. Instead, it mostly followed the vertical distribution of the dinoflagellates which were the second most important group in the assemblage. In particular, as was the case in September, the distribution profile of DMSP followed the depth distribution profile of *Gymnodinium* spp.

Surface and vertical DMSOt distribution in the water column

The mean upper 20 m layer concentrations of the total DMSO in the coastal group of stations during September 2003 ranged from 14.90 to 18.73 nM (Table 1) while in the offshore group it was 14.66 nM. Contrary to the observations for DMSPt, DMSOt followed a different spatial pattern: the offshore group of stations presented slightly decreased values compared to the coastal group. Furthermore, in this cruise the highest DMSOt concentrations were observed in Stations 39 and 18, with the lowest in Stations 37 and 17.

During July 2004, the concentrations of total DMSO in the upper surface layer ranged from 14.18 to 21.18 nM in the coast group of stations (Table 2). The highest concentration was observed in Stations 37 and 8 with the lowest in Stations 39 and 14. Concerning the offshore stations, due to the small number of DMSOt samples (n=3), it is not feasible to compare their spatial distribution with the rest of the stations. Nevertheless, from these three measurements it seems that the spatial pattern is different compared to the first cruise. Specifically, the offshore group of stations presented increased DMSOt values compared to September 2003, but still this can be considered as a rough estimation.

The vertical distribution profile of DMSOt was, as in the case of DMSPt, well stratified in both cruises reaching a peak in the upper layers of the water column. In the deeper layers the concentrations decreased sharply in all stations. On both cruises the vertical profile of the compound seemed to follow the profile of *Gymnodinium* spp. abundance. On the second cruise, the vertical profile of DMSO had a similar trend with the vertical abundance profiles of dinoflagellates and coccolithophores, despite the dominance of diatoms. The concentration profiles of DMSO versus depth also seemed to follow the same general trend with the vertical profile of temperature.

Statistical analysis

A statistical analysis was carried out to investigate the potential relations between total and dissolved DMSx forms, salinity, temperature, Chl-*a* and phytoplankton abundance. A 2-tailed Spearman nonparametric rank correlation (Rs) between the above parameters was applied for each station and on each sampling cruise. Firstly, a highly significant correlation ($0.83 \leq Rs \leq 0.94$, $0.001 < p \leq 0.01$) was observed in both cruises between DMSPt/d and DMSOt concentrations with the abundance of dinoflagellates cells < 20 μm. Significant correlations ($Rs = 0.94$, $0.001 < p \leq 0.01$) were also present between total DMSP and DMSO with coccolithophores, namely *Rhabdosphaera* spp. and *Syracosphaera pulchra*. In all the DMSx forms, significant correlations were obtained with the small-sized *Gymnodinium* spp. (10-15 μm), which were the most abundant genera during both cruises as well as with *Ceratium* spp. During both campaigns, no significant correlation was observed between any of the

Table 2. Average DMSx concentrations and phytoplankton group abundances in the surface layer (0-20 m) and below 20 m (>20 m) in coastal (shallow and deeper) and offshore stations during July 2004.
n.d.: not determined, sd: standard deviation, n: number of samples, C: coccolithophores, D: diatoms, DF: dinoflagellates.

Stations		DMSPt+DMS (nM)	DMSPd+DMS (nM)	DMSOt (nM)	C (x10^2 cells/ L)	D (x10^2 cells/ L)	DF (x10^3 cells/ L)
Costal shallow stations *(0-20 m)*	**average**	23.92	17.11	14.18	12.03	102	41.44
	sd	10.11	4.15	8.93	14.05	60.2	13.42
	n	12	9	7	12	12	12
	range	13.81-50.62	11.55-23.41	3.15-26.56	1.8-51	43.3-228	19.7-75
Coastal deeper stations *(0-20m)*	**average**	21.15	11.04	21.18	8.28	77.01	42.6
	sd	6.05	5.11	9.67	6.09	47.67	9.29
	n	18	14	13	19	18	18
	range	6.79-34.35	2.63-20.59	8.82-45.09	1.2-23.4	12.25-219	32.8-62.9
Coastal deeper stations *(>20 m)*	**average**	22.79	15.38	18.05	13.3	23.39	40.39
	sd	5.87	8.42	8.44	20.34	30.48	12.64
	n	10	10	7	10	10	10
	range	16-34.48	3.09-25.46	9.42-32.93	5.1-71.1	2.1-92.45	21-60
Offshore stations *(0-20 m)*	**average**	33.52	18.78	36.49	6.21	35.89	50.14
	sd	11.21	5.95	28.24	3.11	37.87	11.95
	n	7	7	3	7	7	7
	range	22.15-55.66	8.16-25.01	8.79-65.23	2.2-10.8	1.7-87.3	31.3-67
Offshore stations *(>20 m)*	**average**	18.78	12.84	21.37	5.07	3.38	43.67
	sd	15.88	10.11	12.42	2.94	1.61	21.72
	n	7	3	6	6	6	6
	range	3.31-45.61	3.37-23.49	8.33-44.11	0.3-7.8	1.95-6.45	15.2-74.1

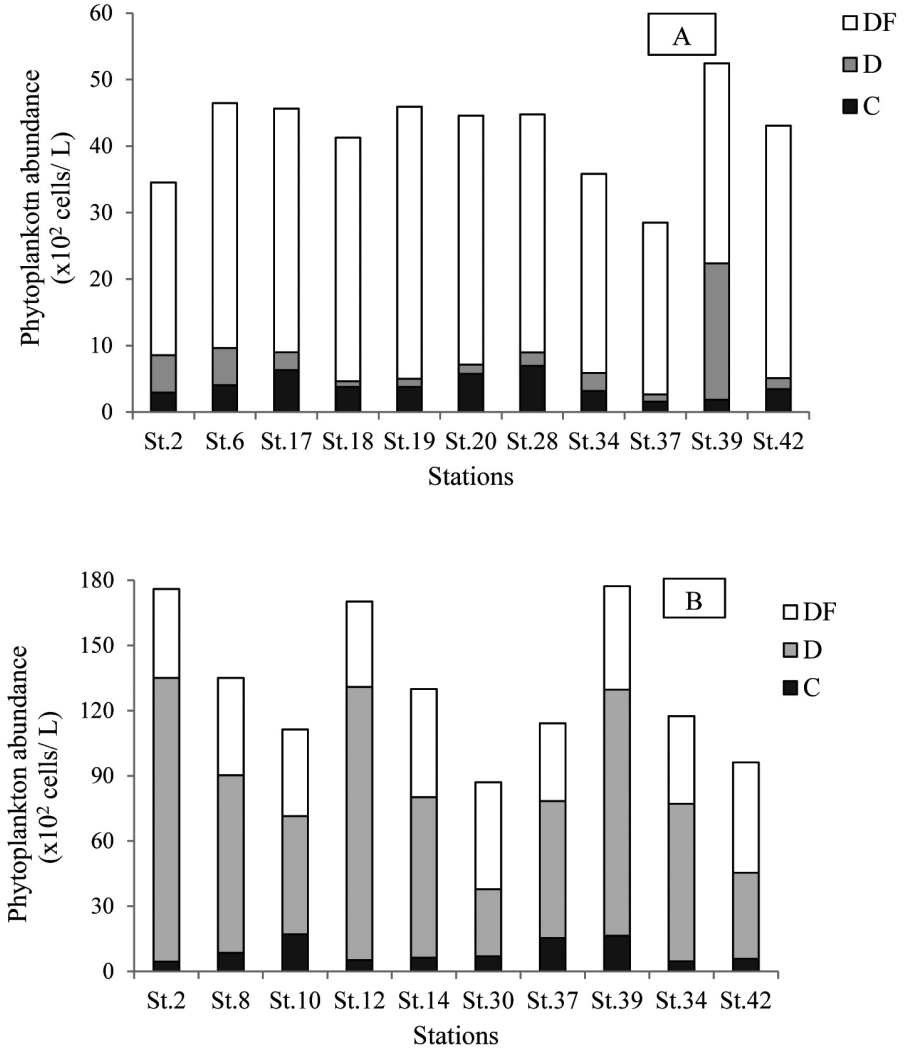


Fig. 4. The average surface abundances (0-20 m) of the major taxonomic groups in the investigated stations during September 2003 (A) and July 2004 (B). C: Coccolithophores, D: Diatoms, DF: Dinoflagellates.

organic sulphur pools and diatoms, the latter having been the dominant species during July 2004.

The other variables tested in Spearman rank correlation followed a different correlation pattern with the sulphur compounds. A possible influence of fresh water discharges from rivers was depicted in the three coastal stations during both cruises; this was shown by the significant correlations (Rs=0.84-0.90, $0.01<p\leq0.04$) of DMSPt, DMSPd and DMSO with Chl-*a* at Stations 2, 6 and 12. Furthermore, despite the plethora of diatoms, total Chl-*a* did not show significant correlations with the most abundant species. Apparently, this is due to the fact that a good part of the dinoflagellate species is known to be heterotrophic. The only exceptions were Station 39, which presented significant correlation (Rs= 0.8, $p\leq0.05$) with *Proboscia setigera,* and Station 10 where significant correlations were observed with *Cylindrotheca closterium* (Rs= 0.99, $p \leq 0.05$) and *Chaetoceros* spp. (Rs= 0.98, $p\leq0.05$). Temperature was significantly correlated with DMSO in the majority of the stations ($0.88\leq$ Rs ≤0.90, $0.01<p\leq0.05$), while salinity did not seem to be highly correlated with the DMSx compounds in both cruises.

Varimax rotated factor analysis has been also applied to all stations during each cruise for the levels of DMSx species, salinity, temperature, Chl-*a* and phytoplankton abundance. Only the factor loadings > 0.7 were taken into consideration as statistically significant. Commonalities have been identified between DMSP (total and dissolved) and dinoflagellates on both cruises in agreement with the Spearman rank correlation indicating the significant role of dinoflagellates in controlling the DMSP levels. The same existed for DMSO where additionally the Varimax rotated factor analysis verified the correlation with temperature in both cruises as well as the significant role that coccolithophores may play in the fate of the specific sulphur compound.

Discussion

Ever since the CLAW hypothesis was expressed, many oceanographic missions have been dedicated to

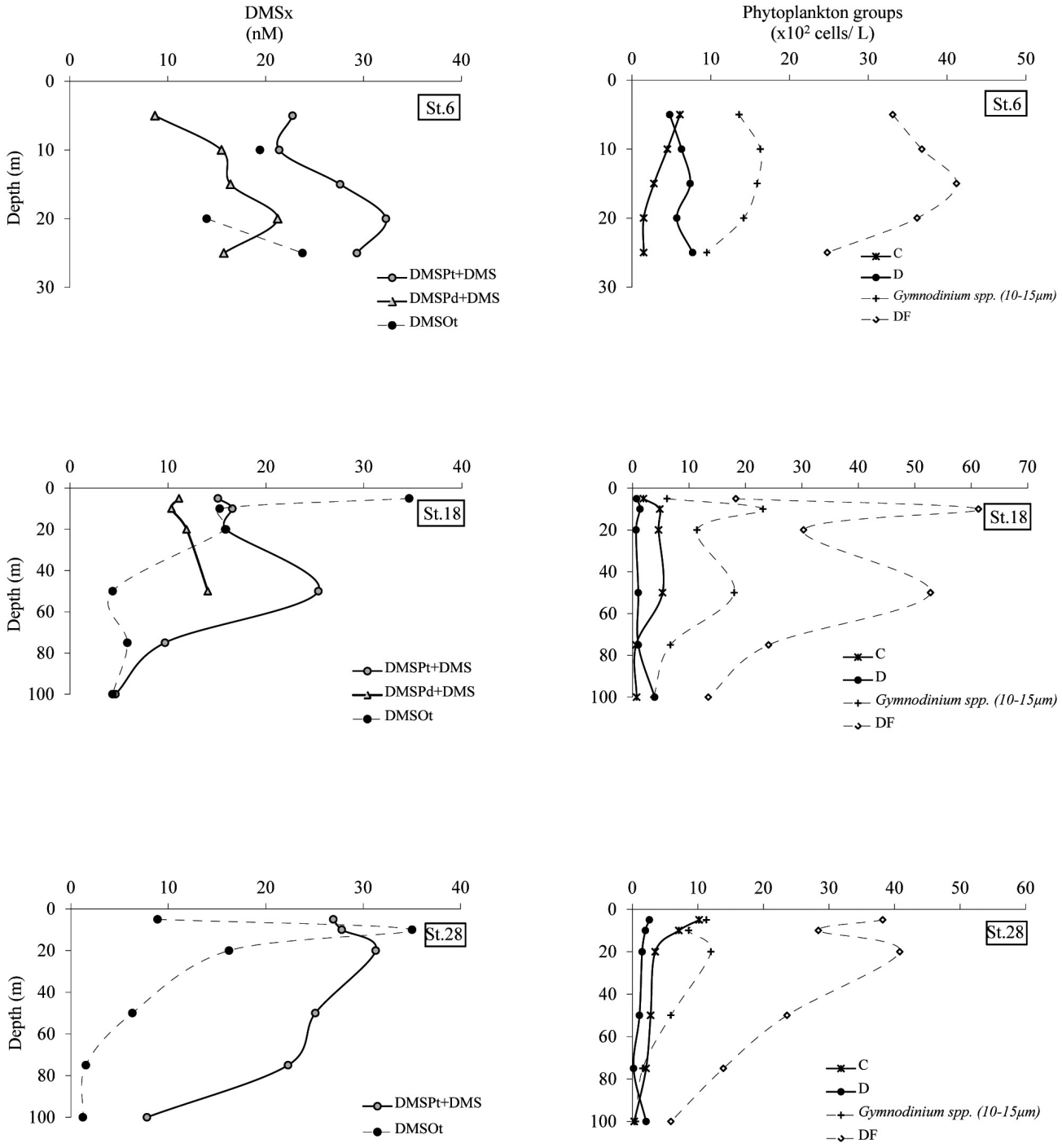


Fig. 5. The vertical distribution of DMSx compounds and phytoplankton abundances in three representative stations during September 2003.

study the sulphur cycle in the global ocean and marine ecosystems. At the same time, some studies have evoked the role of "larger" phytoplankton cells in the sulphur cycle and in particular their involvement in the production of DMSP and DMS compounds (Keller *et al.*, 1989; Keller & Korjeff-Bellows, 1996). However, only a few studies have been carried out in the Eastern Mediterranean so far, while the influence of the phytoplankton composition in the production and distribution of the DMSx species has not extensively been studied in this area. The phytoplankton community presented a strong differentiation between the two sampling cruises since the dominance among the species shifted from dinoflagellates (September 2003) to diatoms (July 2004). The genera that dominated on both cruises were mainly *Gymnodinium*, *Proboscia*, *Cylindrotheca* and *Chaetoceros*,

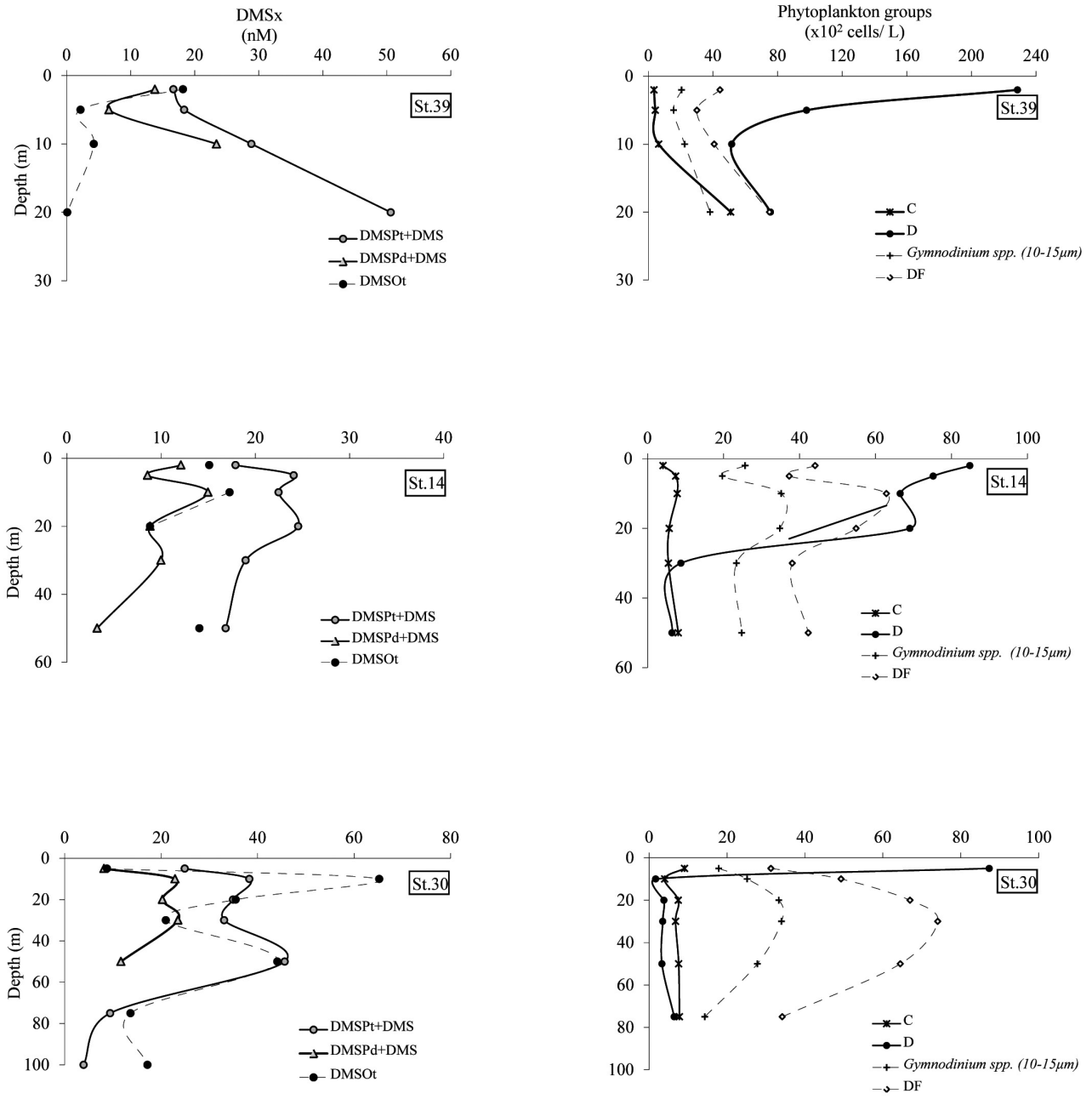


Fig. 6. The vertical distribution of DMSx compounds and phytoplankton abundances in three representative stations during July 2004.

while the presence of phytoplankton cells in the size class of 5-20 μm was elevated. Coccolithophores were found on both cruises at low abundances. However, they seemed to influence in large extent the production and distribution the DMSx compounds.

Diatoms, which dominated phytoplankton community during July 2004, did not show any significant correlations with DMSx forms in either the coastal or offshore stations, during both cruises. Furthermore, the average surface layer concentration of the DMSx compounds did not change significantly from September 2003 to July 2004, despite the fact that the phytoplankton community structure as well as the total abundance of the cells changed drastically. Based on the above, it seems that the dominance of diatoms did not influence the concentration levels of the DMSx compounds. Furthermore, as shown in Fig. 4A and 4B, the dinoflagellates' abundance was in the range of 25.8-40.9 x10^2 cells/ L and 35.9-50.85 x 10^2 cells/ L in September 2003 and July 2004, respectively. This may explain why there was not any significant difference in DMSx concentrations between the two periods. This aspect brings under discussion the possible role of diatoms in the distribution and production of DMSx in the N. Aegean, an issue that it is known

but, yet, poorly studied in other ecosystems too (Shenoy & Patil, 2003).

Based on the vertical distribution patterns the concentrations of the measured DMSx forms were higher in the upper layers of the column, which seem to correspond to the layers of the fresher water due to the discharges mostly of the Black Sea and Nestos and Evros rivers, namely at the northernmost coastal stations. Even though the DMSP concentrations in this study correspond to DMSP+DMS, the recorded values of the surface layers (0-20 m) in the North Aegean Sea during September 2003 and July 2004 fall in the range of those reported by Belviso *et al*. (2003) in "offshore" Mediterranean waters, characteristically populated by pico- and nanoplankton, with almost no larger phytoplankton (Table 3). During the second cruise (July 2004) the entire planktonic food web was considered (Isari *et al.,* 2007). However, no correlation was found between any of the DMSx species and pico- or nanoplankton, confirming the significant role of "larger" phytoplankton cells and especially dinoflagellates in controlling DMSx levels in the North Aegean Sea.

During both cruises, the vertical distribution of DMSP had a pattern similar to the vertical distribution profile of the total phytoplankton abundance, and especially of *Gymnodinium* spp. (10-15 μm). Based on the Spearman correlation test, significant correlations were obtained with specific phytoplankton taxa (dinoflagellates and coccolithophores), which are characterized of high levels of intracellular DMSP concentrations. As reviewed in Yoch (2002), the cytosolic concentrations in dinoflagellates can account from 40 up to 640 nM, compared to diatoms where the intercellular concentrations can reach up to 50 nM. Generally, significant correlations were found with dinoflagellate cells < 20 μm, implying that the distribution of DMSx compounds can be influenced by dinoflagellate cells within a range 5-20 μm. Significant correlations were found in all the stations investigated on the cruises with dinoflagellates and particularly with *Gymnodinium* spp., and *Ceratium* spp. (dinoflagellates), *Rhabdosphaera* spp. and *Syracosphaera pulchra* (coccolithophores).

With respect to DMSO, to our knowledge, this was the first time that its vertical distribution was studied in relation to phytoplankton abundance in the Mediterranean Sea (Fig.5, Fig.6). The concentrations recorded in the surface layer during July 2004 (Table 3) were slightly elevated compared to the concentrations recorded during the same season in regions of the West Mediterranean basin (Simo *et al.,* 1997), while they were higher in comparison to values found in open Eastern Mediterranean waters during the late autumn period (Besiktepe *et al.*, 2004). This decreasing trend from summer (July), to early (September; present study) and late autumn (October; Besiktepe *et al.,* 2004) may be attributed to increased light intensity over the summer period in comparison to the autumn, which

Table 3. Comparison of DMSPt, DMSPd and DMSO concentrations with previous studies performed in the Mediterranean Sea *DMSP+DMS

LOCATION	DMSPt (nM)	DMSPd (nM)	DMSO (nM)
West Mediterranean Basin July 1994 (Simo *et al.,* 1997)			16.6 ± 13.7 n= 29
Central Ionian Sea September 1999 (Belviso *et al.,* 2003)	13-28 (n=22) (*range estimated from the graph*)		
Aegean Sea October 2000 (Besiktepe *et al.,* 2004)	7.1 ± 0.8 n=4	9.2 ± 0.4 n = 2	
South Eastern Mediterranean Sea October 2000 (Besiktepe *et al.,* 2004)	7.7 ± 1.6 n=7	5.7 ± 2.2 n=3	1.6 ± 1.1 n=2
Eastern Mediterranean (Haifa) April 2013 (Amrani *et al.,* 2013)	15.0 n=1 *(value obtained from S8)*		
North Aegean September 2003 (present study*)	23.2 ± 6.8 n=37	15.5 ± 3.9 n=13	21.1 ± 13.9 n=23
North Aegean July 2004 (present study*)	23.4 ± 8.0 n=37	14.3 ± 5.9 n=30	16.0 ± 10.7 n=28

activates the photochemical processes responsible for the formation of DMSO (Sunda *et al.,* 2002).

Incubation experiments with ^{35}S conducted during summer in the oligotrophic Sargasso Sea revealed that up to 72% of the DMSO present in the upper and mixed layer is produced by the biological consumption of DMS (del Valle *et al.*, 2007). A similar situation might have occurred also here, yet taking under consideration the highly significant correlations of DMSO with *Gymnodinium* spp., and *Ceratium* spp. (dinoflagellates), *Rhabdosphaera* spp. and *Syracosphaera pulchra* (coccolithophores) and temperature, we consider the intracellular production of DMSO also possible, in agreement with previous works of Besiktepe *et al.* (2004) and Simo & Vila-Costa (2006).

With respect to the other parameters examined, especially Chl-*a*, the results indicated that dimethylated sulphur compounds are not proportional to Chl-*a* concentrations, neither spatially nor with depth. Even though DMSP and in turn DMS are of biogenic origin they do not always correlate well with Chl-*a* (Shenoy & Patil, 2003; Simo & Vila-Costa, 2006). Despite the efforts to relate certain known pigments with phytoplankton DMSP-producers and thus obtain DMSP distribution information *in situ* (Yoch, 2002), it was evident that DMSP might be present in phytoplankton DMSP-producers that do not contain common pigments (Dacey *et al.,* 1998). Finally, the taxonomic composition of phytoplankton and the structure of the food web may be critical factors that shift sulphur compounds from matching Chl-*a* distribution.

Conclusion

This study was a first attempt to describe and interpret the vertical and surface distribution of DMSx compounds in relation to measurements of physical (temperature and salinity) and biological (Chl-*a* and phytoplankton abundance) parameters in the North Aegean Sea. Based on our findings we can support that dinoflagellates and coccolithophores contributed significantly to the DMSP and DMSO pool, in all twenty-one stations investigated. The dominance of diatoms (mainly *Proboscia spp.* and *Cylindrotheca* spp.) during the second cruise did not influence the production of the DMSx compounds. A preliminary approach to estimate the possible role of the different phytoplankton species in the production of DMSx in the region of the North Aegean Sea would present the following order:

Diatoms < Dinoflagellates (> 20 μm) <
Coccolithophores < Dinoflagellates (< 15 μm)

The general distribution trend of the DMSx compounds followed the temperature profile on both cruises. In addition, the vertical distribution pattern of DMSP was similar to the vertical distribution profile of the total phytoplankton abundance and especially of *Gymnodinium* spp. (10-15 μm). The similarity of the data on DMSx species reported during this study to that found elsewhere in "offshore" Mediterranean waters could imply that larger areas of the oligotrophic Mediterranean populated by pico- and nano- plankton are also significant sources of these important S compounds. This is in agreement with the findings of Kouvarakis *et al.* (2002) and Kubilay *et al.* (2002) suggesting an important, marine biogenic contribution to atmospheric sulphur in the area.

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