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Dimethylated sulfur compounds in seawater, seston and mesozooplankton in the seas around Turkey

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Abstract

The spatial distribution of dimethylated sulfur compounds among particulate, dissolved matter and mesozooplankton in the Black, Marmara, Aegean and NE Mediterranean Seas were studied during October 2000. The surface concentration of particulate dimethylsulfoniopropionate ($\mathrm{DMSP_p}$) ranged from 5.4 (NE Mediterranean Sea) to 51.3 nM (Marmara Sea), and dimethylsulfoxide ($\mathrm{DMSO_p}$) from 0.8 (NE Mediterranean Sea) to 6.2 nM (Marmara Sea). Total particulate DMSP and DMSO concentrations from the depth of fluorescence maximum were comparable to or lower than those at the surface. Most of the particulate DMSP and DMSO were associated with particles $<18\,\mu\mathrm{m}$. The dissolved dimethylsulfide (DMS) + $\mathrm{DMSP_d}$ pool in surface waters varied from a minimum of 5 nM in the NE Mediterranean Sea to a maximum of 17 nM in the Marmara Sea. Values of DMS:chlorophyll *a* (Chl-*a*), $\mathrm{DMSP_p}$:Chl-*a* and $\mathrm{DMSO_p}$:Chl-*a* ratios were lower in productive surface waters of the Black Sea and the Marmara Sea than in the oligotrophic waters of the Aegean and NE Mediterranean. None of the dimethylated sulfur compounds correlated significantly with Chl-*a* in the Black Sea. On the other hand, significantly negative correlation between Chl-*a* and $\mathrm{DMSP_p}$ was found in surface waters of Aegean and NE Mediterranean Seas (data from the two seas were combined). We also found no significant correlations between the distribution of any particulate or dissolved dimethylated sulfur compounds and the abundance of mesozooplankton. Mesozooplankton constituted only $\leqslant 5\%$ of the total particulate DMSP in the water column. A preliminary estimate for average flux of dimethyl sulfide from the NE Mediterranean basin (including the Black Sea) to the atmosphere is $17.6\,\mu\mathrm{mol\,m^{-2}\,d^{-1}}$, indicating the potential importance of NE Mediterranean basin as a source of biogenic sulfur to the atmosphere, even in the less productive period.

Keywords: Dimethylsulfoniopropionate; Dimethylsulfide; Mesozooplankton; Black Sea; Mediterranean Sea; Emission flux

1. Introduction

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound in the surface ocean. It makes the largest contribution to biogenic sulfur emissions from the ocean, and forms

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methanesulfonate and sulfate aerosols in the atmosphere, leading to the formation of cloud condensation nuclei and thereby influencing cloud albedo.

The Eastern Mediterranean and adjacent seas are under the influence of negative radiation balance by backscattering because of sulfate aerosols (Charlson et al., 1991 *cf.* Kouvarakis et al., 2002). Studies on the seasonal variation of atmospheric DMS and its oxidation products (non-sea salt sulfate (nss-$SO_4^=$) and methanesulfonic acid (MSA)) over the Eastern Mediterranean Sea suggest that there is an important, yet unidentified, marine biogenic contribution to atmospheric sulfur during summer time (Ganor et al., 2000; Kouvarakis and Mihalopoulos, 2002; Kouvarakis et al., 2002; Kubilay et al., 2002). Furthermore, Kubilay et al. (2002), based on air mass back trajectory and SeaWiFS data, suggested that the majority of MSA over Erdemli (Turkish coast of the Eastern Mediterranean) is related to summer blooms of coccolithophores, a prominent dimethylsulfoniopropionate (DMSP) producing group of phytoplankton, in the Black Sea (Cokacar et al., 2001). To fully understand the regional sulfur biogeochemistry and climate processes, these atmospheric measurements need to be analyzed in relation to the regional sea surface distribution of related sulfur compounds and their production processes. Unfortunately, basic information such as the distribution of methylated sulfur compounds in the Turkish seas is very limited.

DMS is a breakdown product of DMSP, an abundant cellular component in some marine phytoplankton taxa, particularly haptophytes and dinoflagellates (Keller et al., 1989). DMSP is found ubiquitous in oceanic seston (Malin and Kirst, 1997; Kiene et al., 2000) together with the oxidized form of DMS, dimethylsulfoxide (DMSO, Simó et al., 1998a; Simó and Vila, in preparation). There is accumulating evidence that unicellular algae synthesize DMSP from methionine, as a compatible solute, for its important physiological roles in osmoregulation, chemical signaling and excess sulfur regulation (Malin and Kirst, 1997; Wolfe et al., 1997; Stefels, 2000). Although the intracellular production of DMSO is not so well constrained, recent observations indicate that DMSO, DMSP and DMS may all be part of a radical scavenging system that protects the cell from reactive oxygen species under oxidative stress (Sunda et al., 2002).

The conversion of algal DMSP into volatile DMS is not direct but tightly coupled with a number of biochemical and trophic processes in the water column (Simó et al., 2002), such as enzymatic activities (Stefel et al., 1995; Steinke et al., 1998), bacterial activities (Kiene, 1992; Ledyard and Dacey, 1996), herbivorous and carnivorous grazing (Dacey and Wakeham, 1986; Belviso et al., 1990; Kwint et al., 1996; Archer et al., 2001). Heterotrophic bacteria have the capability of transforming DMSP to both DMS and non-DMS products, and therefore they play a key role in controlling the fate of DMSP once this compound is released from algal cells (Kiene et al., 2000; Simó, 2001). But in order to understand why and how a small fraction only of the large amounts of DMSP produced in phytoplankton cells ends up as extracellular volatile DMS, the role of micro- and mesozooplankton has to be taken into account. If grazers do not accumulate or transform ingested DMSP, they promote the release of undegraded DMSP into solution, thus making it more available to bacteria (Archer et al., 2001, 2002; Simó et al., 2002; Tang and Simó, 2003). When grazing on certain microalgae, however, herbivorous zooplankton facilitate the mixture of DMSP with algal DMSP-lyases that cleave it into DMS and acrylate (Wolfe et al., 1997). That is, in some cases grazers increase the efficiency at which DMSP is converted into DMS. On the other hand, grazers that do accumulate DMSP either in tissues or guts or vacuoles, transfer this DMSP to higher trophic levels, thus uncoupling DMSP and DMS production (Tang et al., 1999, 2000a; Tang and Simó, 2003).

There have been few studies of the contribution of mesozooplankton to the pool of DMSP (DMSP in organisms) (Tang et al., 1999, 2000a) or its transformation rates (Kwint and Kramer, 1995; Daly and DiTullio, 1996; Kwint et al., 1996; Levasseur et al., 1996; Tang et al., 1999, 2000a, b). In a coastal site, Tang et al. (2000a) observed that mesozooplankton make up a significant pool of particulate DMSP at certain times and insignificant over the rest of the year.

We present data on the fall concentrations of dissolved DMS and DMSP, particulate DMSP and DMSO in the Black, Marmara, Aegean and NE Mediterranean Seas, based on which we estimate the sea-to-air emission of DMS in the region. In addition, we report DMSP concentrations in size-fractionated mesozooplankton and assess their contribution to the total dimethylated sulfur in the water column.

2. Material and methods

Sampling concentrations of DMS, dissolved DMSP ($DMSP_d$), particulate DMSP ($DMSP_p$), particulate DMSO ($DMSO_p$) and DMSP in mesozooplankton ($DMSP_z$) were measured in the eastern Black Sea, Marmara Sea, Aegean Sea and the Eastern Mediterranean in October 2000 (Fig. 1). Water samples were taken from the surface and the depth of the fluorescence maximum with a rosette of 5-l Niskin bottles attached to a CTD system. For chlorophyll *a* (Chl-*a*) measurements, seawater samples were filtered through GF/F filters and stored at −20°C until analysis. Filters were ground in 90% acetone with a grinder and kept overnight in the dark at 4°C for a complete extraction. Chl-*a* concentrations were determined with a Hitachi F-3000 Model Spectrofluorometer (IOC, 1994). Fluorescence readings were recorded before and after acidification with two drops of 10% HCl. Nitrate + nitrite concentrations in sea-

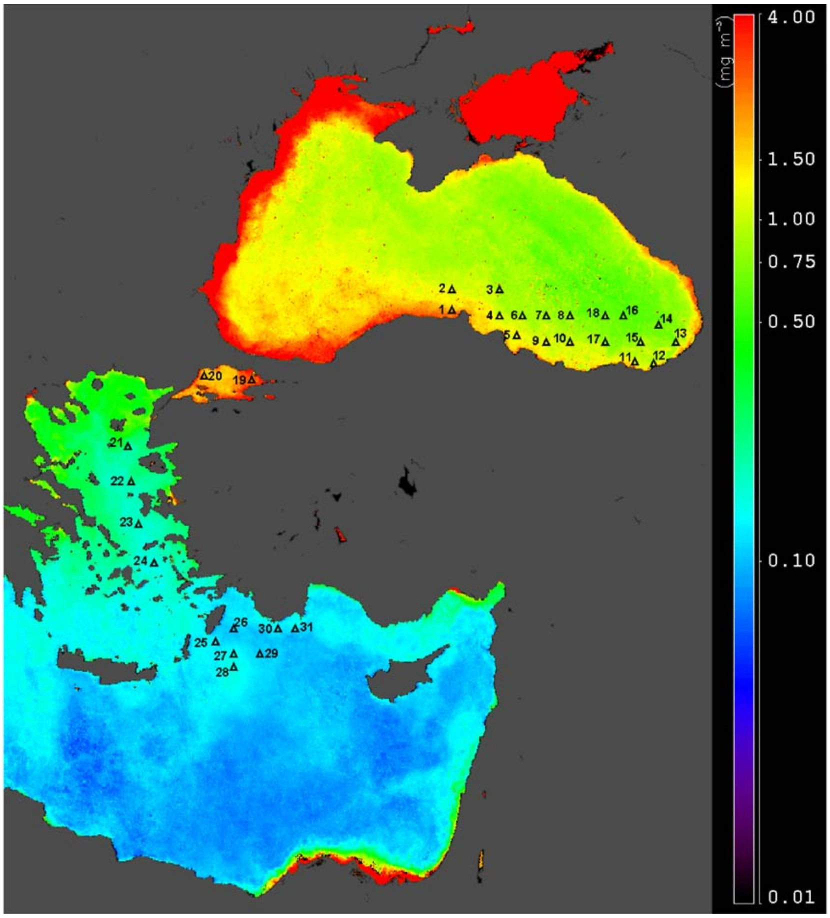

Fig. 1. SeaWiFS image of the average chlorophyll concentrations for October 2000. Triangles represent sampling stations.

water were determined with a Technicon Model two-channel Autoanalyzer using the modified method of Strickland and Persons (1972).

2.1. Dissolved DMS, DMSP and DMSO

Seawater samples were transferred to 500-ml pre-washed glass vials. In all, 100 ml of seawater was filtered by gentle pressure through 25 mm Whatman GF/F filter. Filtrates for $DMSP_d + DMS$ measurements were immediately treated with 2 ml of 10 M NaOH in air-tight serum bottles. In parallel, 100-ml seawater filtrates were sparged on board for 15 min with high purity nitrogen to remove the ambient DMS, then treated with NaOH in air-tight serum bottles to hydrolyze $DMSP_d$. All alkalinized samples were kept at −20°C for 6 months until they were analyzed by a purge-and-trap gas chromatographic method (Simó et al., 1996). Aliquots of 40 ml were run in duplicate. The DMS concentrations in the samples were calculated by subtracting the $DMSP_d$ from $DMSP_d + DMS$. The average difference between the two amounts subtracted was $26 \pm 3\%$, $n = 24$, i.e. well above the average coefficient of variation between replicate analyses ($4 \pm 1\%$, $n = 48$). The detection limit was 12 pmol DMS, equivalent to a concentration of 0.3 nM in a 40-ml aliquot. Because of time constraints, dissolved DMSO was not measured.

2.2. Particulate DMSP and DMSO

A volume of 50 ml of seawater was filtered gently through a GF/F filter with a syringe to collect total $DMSP_p$. Another 50-ml aliquot was first passed through a 18-μm nylon sieve, and then filtered through a GF/F filter to collect $DMSP_p$ of the size fraction $< 18\,\mu m$. $DMSP_p$ filter samples were immediately transferred to cryogenic vials and preserved in liquid nitrogen. The samples were transported in abundant dry ice and stored at −75°C for 12 months until analysis. Total $DMSO_p$ was determined in the same GF/F-retained particles after removal of $DMSP_p$ and reduction with borohydride (Simó et al., 1998b).

2.3. DMSP in zooplankton

Zooplankton samples were collected by towing a Nansen net (70 cm mouth diameter with 200 μm mesh) from the depth of the fluorescence maximum to the surface. Zooplankton from the first tow were fractionated into different size classes (200–1000 and 1000–2000 μm) by filtering through mesh filters; each size fraction was then collected on GF/F filters and preserved in liquid nitrogen. The samples were transported in abundant dry ice and stored at −75°C for 12 months until DMSP analysis. Zooplankton from the second tow were fractionated into the same size classes and each size class was subsampled into two: one subsample was preserved with 4% borax-buffered formaldehyde for species identification, enumeration and biovolume estimation under a stereomicroscope and the second was collected on a pre-weighed GF/C filter and kept at −20°C. In the laboratory, zooplankton on GF/C filters were dried at 65°C for 24 h and weighed for dry weight. Spatial concentration of DMSP associated with zooplankton ($DMSP_z$) is the amount of DMSP attributed to zooplankton per unit volume of water. Weight specific ($DMSP_{z\text{–}B}$) zooplankton DMSP is the amount of DMSP attributed to zooplankton per unit dry weight. Assuming a cylindrical shape for the zooplankton, we estimated their body volume based on their linear dimensions, and the body concentration of DMSP in zooplankton ($DMSP_{z\text{–}v}$) is then estimated as DMSP per unit biovolume of zooplankton.

3. Results

3.1. General characteristics of the waters of the studied regions

The SeaWiFS derived surface Chl-*a* image (Fig. 1) of the studied regions for monthly average of October 2000 clearly shows the difference between the productive waters of the Black Sea and oligotrophic waters of the Mediterranean Sea. The cruise track did not include stations in the very high Chl-*a* areas, except in the Sea of Marmara (Table 1). Fig. 2 shows temperature, salinity, Chl-*a* and $NO_3 + NO_2$ concentration from the surface and the depth of fluorescence maximum (DFM) of the four interconnected seas. Sea surface temperature and salinity of the Black Sea were almost constant at all stations, at around 21°C and 18, respectively. Temperature at the DFM varied between 10°C and 21°C. Note that the temperature at the subsurface maximum of chlorophyll was almost equal to that at the surface at the few stations where the DFM occurred within the mixed layer. The Sea of Marmara and Aegean Sea exhibited lower temperature and higher salinity than the Black Sea. The salinity of the Marmara Sea clearly shows its transitional position between the low salinity waters of the Black Sea and the highly saline waters of the Aegean Sea. The temperature of NE Mediterranean varied between 14°C and 23°C, with a salinity of nearly 39. Chl-*a* concentrations were generally low during the cruise, varying between 0.03 (NE Mediterranean) and 1.31 $\mu g\,l^{-1}$ (Marmara) at the surface, and between 0.18 (NE Mediterranean) and 2.25 $\mu g\,l^{-1}$ (Marmara) at the DFM. The station with the highest Chl-*a* concentration, station 45-C in the Sea of Marmara, is under the influence of domestic and industrial wastes, as well as productive waters from the Black Sea via the Bosphorus Strait. Estimated average primary production was low in the regions: 209, 179 and 127 mg $C\,m^{-2}\,d^{-1}$ for the Black Sea, Aegean Sea and NE Mediterranean stations, respectively (Yilmaz, unpublished data).

Table 1
Locations, sampling dates and surface temperature of the stations visited during study period

Station no.	Station name	Latitude (E)	Longitude (N)	Sampling date	Surface temp. (°C)	Wind speed ($m\,s^{-1}$)
1	M06.50R40	34.4	42.065	06.10.2000	20.17	
2	M30R40	34.4	42.3	06.10.2000	20.75	5
3	M30T00	36	42.3	07.10.2000	20.72	
4	M00T00	36	42	08.10.2000	20.47	
5	L37.5T30	36.3	41.375	09.10.2000	20.52	9
6	M00T40	36.4	42	09.10.2000	20.72	
7	M00V20	37.2	42	10.10.2000	20.8	12
8	M00W00	38	42	10.10.2000	20.95	
9	L30V20	37.2	41.3	11.10.2000	20.65	
10	L30W00	38	41.3	11.10.2000	21.33	
11	L07.5 × 50	39.50	41.075	13.10.2000	21.35	
12	L05Y22	40.22	41.05	13.10.2000	21.5	6
13	L30Z00	41	41.3	14.10.2000	2.32	
14	L50Y30	40.3	41.5	14.10.2000	21.41	
15	L30Y00	40	41.3	14.10.2000	21.4	
16	M00 × 30	39.3	42	15.10.2000	21.19	
17	L30 × 00	39	41.3	16.10.2000	21.04	8
18	M00 × 00	39	42	16.10.2000	20.77	2
19	45-C	29	40.46	20.10.2000	17.82	20
20	K51J40	27.4	40.51	21.10.2000	18.19	18
21	J30G30	25.3	39.3	25.10.2000	18	13
22	H49G36	25.36	38.49	25.10.2000	18.23	15
23	H00G48	25.48	38	26.10.2000	18.98	
24	G15H15	26.15	37.15	26.10.2000	19.25	
25	F45K00	28	35.45	27.10.2000	22.36	1
26	G00K30	28.3	36	27.10.2000	23.21	
27	F30K30	28.3	35.3	27.10.2000	19.78	1
28	F15K30	28.3	35.15	28.10.2000	18.42	8
29	F30L15	29.15	35.3	29.10.2000	21.09	
30	G00L45	29.45	36	29.10.2000	23.52	
31	G00M15	30.15	36	29.10.2000	23.07	

Note: Wind speeds are also presented at the stations at which DMS concentrations were measured.

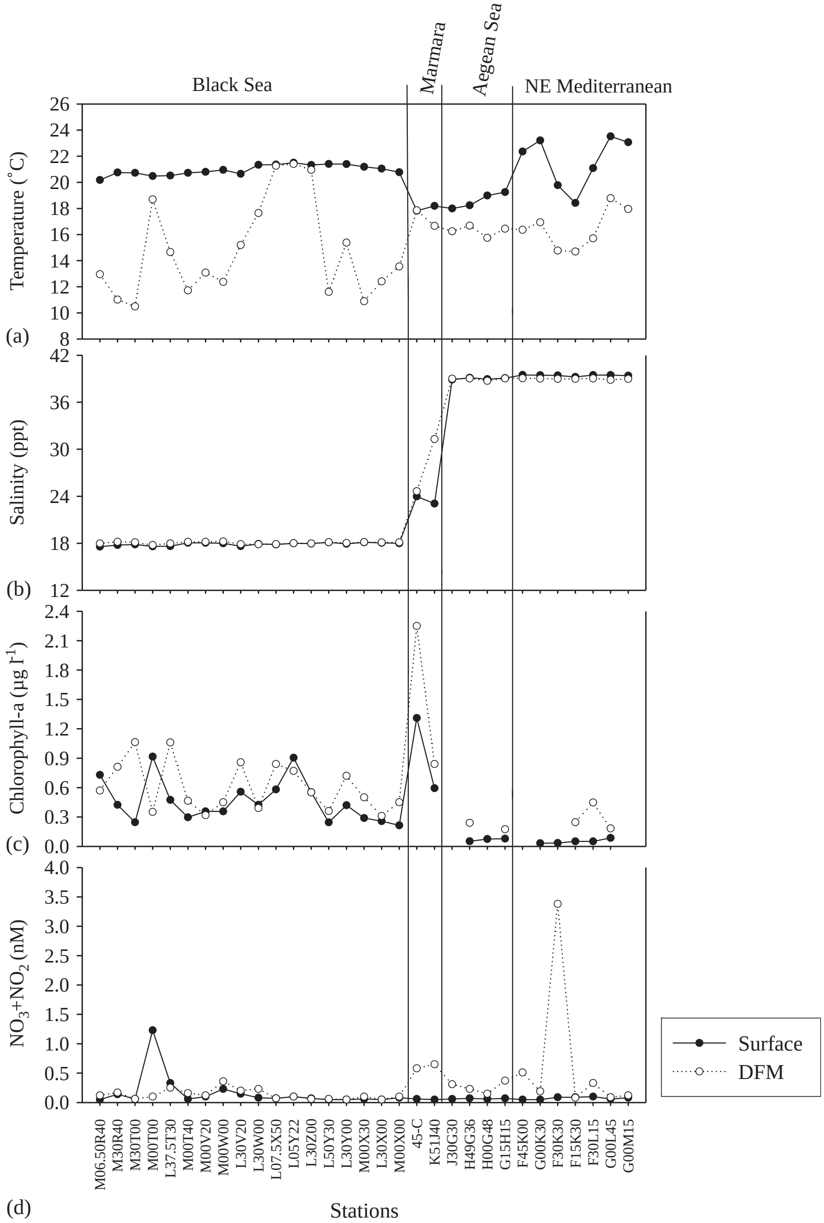

Fig. 2. Surface (black circles) and DFM (empty circles) values of (a) temperature, (b) salinity, (c) Chl-*a* and (d) NO_3+NO_2 concentrations.

For the Sea of Marmara, Yayla (1999) reported a primary production as high as 1192 mg C m^{-2} d^{-1} in September 1997, when the surface Chl-*a* concentration was 1.45 μg l^{-1}. Nitrate and nitrite concentrations were low throughout the study area, with the exception of one station (F30K30) where the NO_3+NO_2 concentration was 3.38 nM at the DFM. At this station, the DFM coincided with the nitracline (Tugrul, unpublished data).

3.2. Dissolved and particulate dimethylated sulfur distributions

Fig. 3 shows the concentrations of $DMSP_p$ and $DMSO_p$ in total and $<18\,\mu m$ particles from the surface and the DFM. $DMSP_p$ concentrations were generally invariant between the regions, with the exception of the Marmara Sea, station 45-C, where the concentrations were 51 nM at the surface and 56 nM at the DFM (Fig. 3a). The average surface concentrations were 9.7 nM in the Black Sea, 7.1 nM in the Aegean Sea and 7.7 nM in

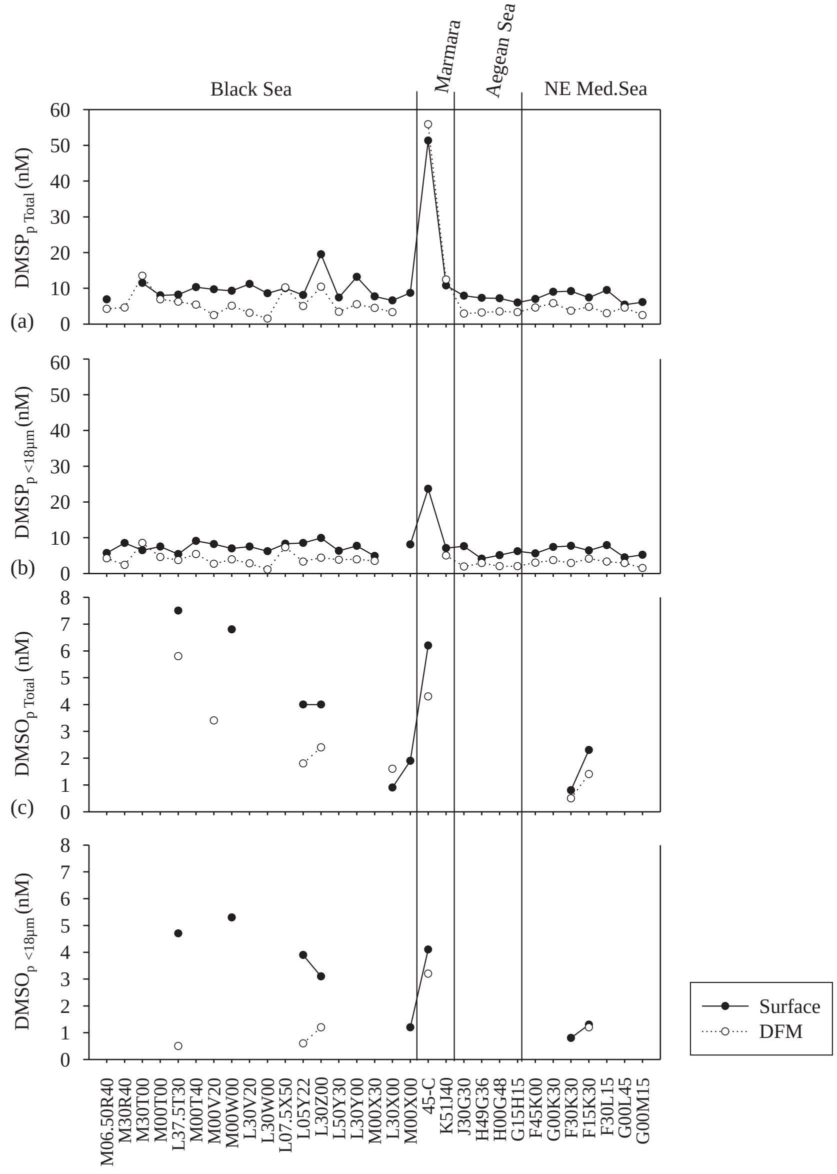

Fig. 3. Surface (black circles) and DFM (empty circles) concentrations of (a) total particulate DMSP, (b) DMSP associated with $<18\,\mu m$ particles, (c) total particulate DMSO and (d) DMSO associated with $<18\,\mu m$ particles.

Table 2
DMS, dissolved DMSP (DMSP$_d$) and particulate DMSP (DMSP$_p$) and DMSO (DMSO$_p$) (nM) and total Chl-*a* ($\mu g\,l^{-1}$) concentrations (mean ± standard deviation) from the surface and depth of fluorescence maximum (DFM) in the Black Sea, Marmara Sea, Aegean Sea and Mediterranean Sea

	Black Sea		Marmara Sea		Aegean Sea		Mediterranean Sea	
	Surface	DFM	Surface	DFM	Surface	DFM	Surface	DFM
DMSP$_p$								
Total	9.7 ± 3.1 (6.6–19.5) $n = 17$	5.6 ± 3.1 (1.5–13.5) $n = 17$	31.1 ± 28.6 (10.8–51.3) $n = 2$	34.15 ± 30.8 (12.4–55.9) $n = 2$	7.1 ± 0.8 (6.0–7.9) $n = 4$	3.2 ± 0.25 (2.9–3.5) $n = 4$	7.7 ± 1.6 (5.4–9.5) $n = 7$	4.1 ± 1.1 (2.5–5.8) $n = 7$
$<18\,\mu m$	7.4 ± 1.4 (4.9–9.9) $n = 16$	4.1 ± 1.8 (1.1–8.5) $n = 16$	15.4 ± 11.7 (7.1–23.7) $n = 2$	5.0 $n = 1$	5.8 ± 1.5 (4.1–7.6) $n = 4$	2.2 ± 0.5 (1.9–2.9) $n = 4$	6.4 ± 1.3 (4.5–7.9) $n = 7$	3.1 ± 0.8 (1.5–4.1) $n = 7$
DMSO$_p$								
Total	4.2 ± 2.4 (0.9–7.5) $n = 6$	3.4 ± 1.6 (1.6–5.8) $n = 6$	6.2 $n = 1$	4.3 $n = 1$	—	—	1.6 ± 1.1 (0.8–2.3) $n = 2$	1.0 ± 0.6 (0.5–1.4) $n = 2$
$<18\,\mu m$	3.2 ± 1.3 (1.2–5.3) $n = 4$	0.8 ± 0.3 (0.5–1.2) $n = 3$	4.1 $n = 1$	3.2 $n = 1$	—	—	1.1 ± 0.4 (0.8–1.3) $n = 2$	1.2 $n = 1$
DMS	1.4 ± 0.8 (0.6–2.6) $n = 6$	0.8 ± 0.4 (0.3–1.5) $n = 6$	4.2 ± 3.8 (1.5–7.0) $n = 2$	5.4 ± 6.3 (0.8–9.8) $n = 2$	2.4 ± 0.45 (2.1–2.7) $n = 2$	1.4 ± 0.4 (1.1–1.7) $n = 2$	2.4 ± 0.9 (1.5–3.3) $n = 3$	1.6 ± 0.3 (1.4–1.9) $n = 2$
DMSP$_d$	7.2 ± 2.56 (5.1–12.2) $n = 6$	3.6 ± 2.5 (0.9–7.7) $n = 6$	7.7 ± 2.8 (5.7–9.6) $n = 2$	9.6 ± 8.0 (4.1–15.3) $n = 2$	9.2 ± 4.1 (6.3–12.1) $n = 2$	3.7 ± 0.86 (3.1–4.3) $n = 2$	5.7 ± 2.2 (3.2–7.4) $n = 3$	2.6 ± 1.03 (1.4–3.3) $n = 3$
DMSP$_d$ + DMS	8.8 ± 2.3 (6.4–13.2) $n = 7$	4.0 ± 2.4 (1.7–8.0) $n = 7$	11.9 ± 6.6 (7.3–16.6) $n = 2$	14.9 ± 14.3 (4.8–25.1) $n = 2$	8.7 ± 3.9 (5.6–14.2) $n = 4$	4.7 ± 0.9 (4.0–6.0) $n = 4$	7.2 ± 1.7 (5.0–8.9) $n = 5$	3.5 ± 0.8 (2.9–4.7) $n = 4$
Chl-*a*	0.46 ± 0.22 (0.21–0.91) $n = 18$	0.6 ± 0.25 (0.31–1.1) $n = 18$	0.95 ± 0.51 (0.59–1.31) $n = 2$	1.55 ± 1.0 (0.84–2.25) $n = 2$	0.07 ± 0.015 (0.05–0.08) $n = 3$	0.21 ± 0.05 (0.17–0.24) $n = 2$	0.051 ± 0.02 (0.03–0.09) $n = 5$	0.29 ± 0.14 (0.18–0.45) $n = 3$

Note: Values in parenthesis are data range, *n* is the number of samples.

the NE Mediterranean Sea (Table 2). In the Marmara Sea, only two stations were sampled, one (45-C) is under the domestic and industrial wastes and with high measurements of dimethylated sulfur compounds, and other is K51J40, its dimethylated sulfur concentrations are within the range of the studied area. So, averaging these two stations may not represent well enough the concentrations of dimethylated sulfur compounds in the Marmara Sea. At the DFM, the DMSP$_p$ concentrations were comparable to or lower (down to half) than those at the surface, whereas Chl-*a* levels were generally 1.2–8.8 times higher. In the Black and the Marmara Seas, the contribution of DMSP$_{p<18\,\mu m}$ to the total DMSP$_p$ was around 75% and 50% at the surface and the DFM, respectively (Fig. 3b). In the Aegean and the Eastern Mediterranean Seas, around 80% of the DMSP$_p$ in surface waters was associated with particles $<18\,\mu m$, whereas at the DFM the contribution of the smaller particles was nearly 70%.

Surface particulate DMSO ($DMSO_p$) concentrations ranged from 0.8 nM in the NE Mediterranean to 7.5 nM in the Black Sea (Fig. 3c and Table 2). In most of the samples, more than 70% was associated with small particles (Fig. 3d), as occurred with DMSP. On average, $DMSO_p$ at the DFM was 1.5 times lower than that at the surface.

Fig. 4 shows DMS, $DMSP_d$ and total dissolved ($DMS + DMSP_d$) concentrations from the surface and the DFM. DMS concentrations were low (0.3–3.3 nM) in most of the sites and exhibited little variation between stations (Fig. 4a). The only exception was station 45-C in the Marmara Sea, where a DMS maximum (7.0–9.8 nM) was coincident with a maximum of chlorophyll (Fig. 2c). At some stations in the Black Sea, higher chlorophyll values were not correlated with higher DMS levels. Surface DMS concentrations averaged 1.4 nM in the Black Sea and 2.4 nM in the Aegean and NE Mediterranean Seas (Table 2). Dissolved DMSP concentrations were generally higher than DMS concentrations, and showed greater variation between regions (Fig. 4b). The peaks of $DMSP_d$ were not coincident with those of DMS. Surface $DMSP_d$ concentrations varied from 3.2 nM in the NE Mediterranean Sea and 12.2 nM in the Black Sea (Table 2). Both $DMSP_d$ and DMS

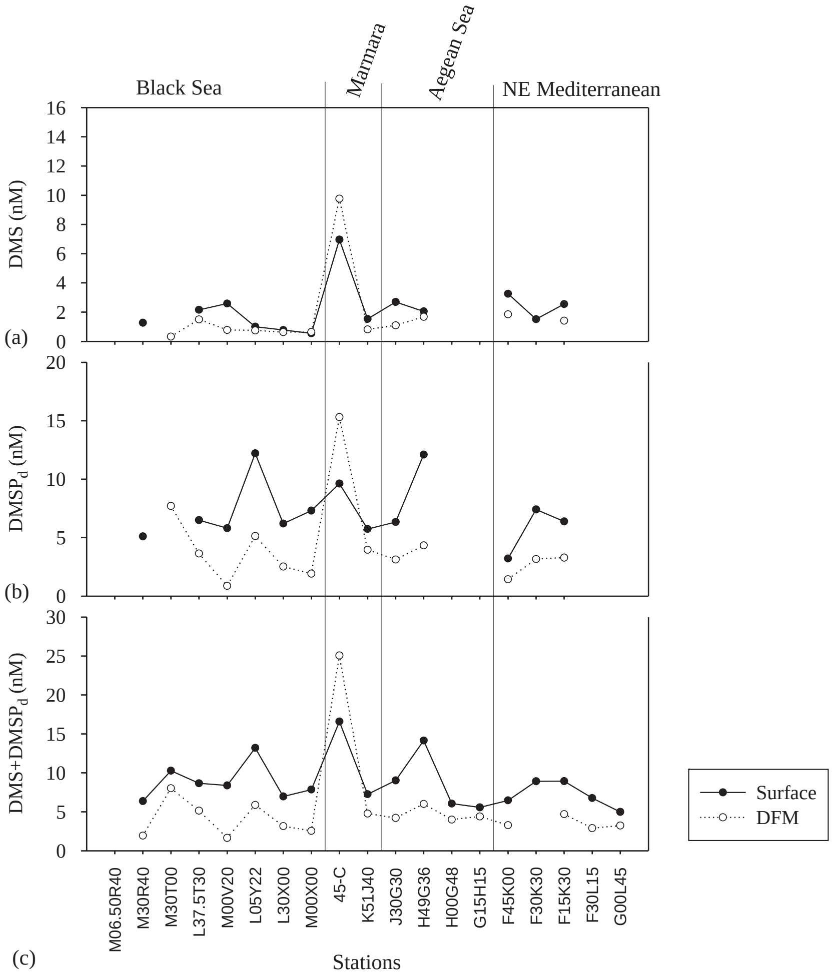

Fig. 4. Surface (black circles) and DFM (empty circles) concentrations of (a) DMS, (b) dissolved DMSP and (c) dissolved DMS + DMSP.

concentrations from the DFM were lower than those at the surface, except in the Marmara Sea. Total dissolved ($DMS+DMSP_d$) concentrations in surface waters varied from a minimum of 5 nM in the NE Mediterranean Sea (average 7.2 nM) to a maximum of 17 nM in the Marmara Sea (Fig. 4c and Table 2). Dissolved concentrations at the DFM ranged between 1.7 nM (Black Sea) and 25.1 nM (Marmara), and were always lower than those at the surface with the exception of station 45-C (Fig. 4c).

Spearman rank correlation analysis was applied to evaluate the statistical relationship between variables (Table 3). Because of sample numbers in the Aegean and NE Mediterranean Seas, we combined the data from the two regions that have similar oligotrophic characteristics. No significant correlation was found between Chl-*a* and particulate and dissolved fractions of dimethylated sulfur at either the surface or the DFM of the Black Sea, at the DFM in the Aegean or NE Mediterranean Seas (Table 3). Significantly negative correlation between Chl-*a* and $DMSP_p$ was found for surface waters of the Aegean and NE Mediterranean Seas. No significant correlation was found between Chl-*a* and any other dimethylated sulfur compounds (Table 3).

The ratios DMS:Chl-*a* and $DMSP_p$:Chl-*a* can be used to compare the distribution of these compounds in different trophic regimes (e.g. Iverson et al., 1989; Simó et al., 1997). Values of DMS:Chl-*a* were clearly lower in productive surface waters of the Black Sea ($3.6\,\mathrm{nmol\,\mu g^{-1}}$) and the Marmara Sea ($3.95\,\mathrm{nmol\,\mu g^{-1}}$) than in the oligotrophic waters of the Aegean ($39.4\,\mathrm{nmol\,\mu g^{-1}}$) and NE Mediterranean ($46.6\,\mathrm{nmol\,\mu g^{-1}}$) (Table 4). Values of DMS:Chl-*a* at the DFM from both mesotrophic and oligotrophic regimes were much lower than those at the surface, with a minimum value of $1.4\,\mathrm{nmol\,\mu g^{-1}}$ in the Black Sea and a maximum of $7\,\mathrm{nmol\,\mu g^{-1}}$ in the Aegean Sea. $DMSP_p$:Chl-*a* showed a similar pattern but with values 2–10-fold higher, and a minimum of $25\,\mathrm{nmol\,\mu g^{-1}}$ in the Black Sea and a maximum of $190\,\mathrm{nmol\,\mu g^{-1}}$ in Mediterranean surface waters. The same pattern was observed for the $DMSO_p$:Chl-*a* ratio, which increased from $10\,\mathrm{nmol\,\mu g^{-1}}$ in the Black to $34\,\mathrm{nmol\,\mu g^{-1}}$ in the NE Mediterranean (Table 4).

3.3. *Mesozooplankton abundance and their DMSP contents*

Mesozooplankton abundance and their DMSP content were determined for two size fractions: 200–1000 and 1000–2000 μm. Small mesozooplankton were more abundant than large mesozooplankton (Fig. 5 and Table 5). The size fraction 200–1000 μm was dominated by copepods (Fig. 5), as was the size fraction 1000–2000 μm in the Black Sea. In the 1000–2000 μm size fraction, Thaliacea (mostly salps and doliolids) and chaetognaths

Table 3
Spearman rank correlation coefficient between chlorophyll, DMS, $DMSP_d$, total $DMSP_p$, $DMSP_{p<8\,\mu m}$ and $DMSO_p$ in the surface and depth of fluorescence maximum (DFM) in the Black Sea and combined data from Aegean and NE Mediterranean Seas

	Black Sea		Aegean + Mediterranean Sea	
	Surface	DFM	Surface	DFM
Chl-*a* vs $DMSP_p$	0.02	0.47	−0.87***	−0.3
Chl-*a* vs $DMSP_{p<18\,\mu m}$	0.2	0.16	−0.71*	0.87
Chl-*a* vs $DMSO_p$	0.46	0.60	—	—
Chl-*a* vs $DMSP_d$	0.2	0.77	—	—
Chl-*a* vs DMS	0.5	−0.03	−0.72	—
Chl-*a* vs $DMS+DMSP_d$	0.3	0.57	−0.2	−0.2
$DMSP_p$ vs $DMS+DMSP_d$	0.3	0.89*	0.67*	0.04
$DMSP_{p<18\,\mu m}$ vs $DMS+DMSP_d$	−0.2	0.8	0.2	−0.15
$DMSP_p$ vs $DMSO_p$	0.38	0.20	—	—
$DMSO_p$ vs DMS	0.80	−0.30	—	—

*** $P<0.01$, *$P<0.05$, not enough number of data for the statistical analysis.

Table 4
Chlorophyll normalized concentrations (nmol μg^{-1}) (mean ± standard deviation) of dissolved and particulate dimethylated sulfur compounds from the surface and depth of fluorescence maximum (DFM) in the Black Sea, Marmara Sea, Aegean Sea and Mediterranean Sea

	Black Sea		Marmara Sea		Aegean Sea		Mediterranean Sea	
	Surface	DFM	Surface	DFM	Surface	DFM	Surface	DFM
DMS:Chl-*a*	3.6±2.1 (1.1–7.3) $n=6$	1.43±0.76 (0.3–2.5) $n=6$	3.95±1.9 (2.6–5.3) $n=2$	2.65±2.38 (0.97–4.3) $n=2$	39.4 $n=1$	7.0 $n=1$	46.6±4.75 (43.3–50) $n=2$	5.73 $n=1$
DMSP$_{d}$:Chl-*a*	18.97±8.6 (12.0–34.14) $n=6$	5.4±2.2 (2.7–8.1) $n=6$	8.5±1.6 (7.3–9.7) $n=2$	5.75±1.5 (4.7–6.8) $n=2$	232.69 $n=1$	18.06 $n=1$	168.4±61.2 (125.1–211.7) $n=2$	13.35 $n=1$
DMSP$_{d}$ + DMS:Chl-*a*	25.3±10.7 (14.6–41.9) $n=7$	6.2±2.5 (2.4–10.2) $n=7$	12.45±0.3 (12.25–12.7) $n=2$	8.4±3.86 (5.7–11.14) $n=2$	141.1±113.6 (70.5–272.1) $n=3$	25.17±0.16 (25.06–25.3) $n=2$	155.2±82.3 (58.0–255) $n=4$	14.46±6.9 (6.5–19.1) $n=3$
DMSP$_{p\,total}$:Chl-*a*	25.14±11 (8.95–46.9) $n=17$	9.6±4.5 (3.6–19.6) $n=17$	28.7±14.8 (18.2–39.2) $n=2$	19.8±7.1 (14.8–24.8) $n=2$	104.1±32.97 (75.9–140.4) $n=3$	16.2±3.98 (13.3–18.96) $n=2$	189.5±91.6 (62.8–290.3) $n=5$	17.17±9.5 (6.7–25.3) $n=3$
DMSP$_{p<18\,\mu m}$:Chl-*a*	18.6±8.2 (7.8–37.9) $n=17$	7.1±3.2 (2.96–13.1) $n=16$	15.03±4.3 (11.97–18.1) $n=2$	5.95 $n=1$	75.1±6.2 (68–78.8) $n=3$	11.8±0.4 (11.5–12.1) $n=2$	158.2±75.2 (52.3–238.7) $n=5$	13.3±5.2 (7.4–15.9) $n=3$
DMSO$_{p\,total}$:Chl-*a*	9.82±6.29 (3.5–19.05) $n=6$	4.33±1.41 (2.34–10.72) $n=5$	4.73 $n=1$	1.91 $n=1$	—	—	33.98±15.7 (22.86–45.1) $n=2$	5.69 $n=1$
DMSO$_{p<18\,\mu m}$:Chl-*a*	8.06±4.34 (4.3–14.8) $n=5$	1.14±0.91 (0.47–2.18) $n=3$	3.13 $n=1$	1.42 $n=1$	—	—	24.17±1.86 (22.86–25.49) $n=2$	4.88 $n=1$

Note: Values in parenthesis are data range, n is the number of samples.

accounted for more than half of the abundance in the Marmara, Aegean and the NE Mediterranean Seas (Table 5).

DMSP concentrations in zooplankton (Fig. 6) are presented here in three respects: spatial zooplankton DMSP (DMSP$_{z}$), dry-weight specific DMSP (DMSP$_{z\text{–}B}$) and body DMSP concentrations (DMSP$_{z\text{–}v}$) (see Section 2). Zooplankton in the Black Sea contributed significantly less DMSP$_{z}$ than those from the other regions (Mann–Whitney Rank Sum Test, $P<0.01$) (Fig. 6a). In the Black Sea, DMSP$_{z\text{–}B}$ in the small size fraction was identical to that in the large size fraction, whereas in the Marmara and Aegean Seas the small size fraction contained more DMSP$_{z\text{–}B}$ than did the larger zooplankton. In the NE Mediterranean, DMSP$_{z\text{–}B}$ was higher in the large size fractions at the two stations dominated by salps and doliolids (around 62% of the abundance) (Fig. 6 and Table 5). Mesozooplankton body DMSP (DMSP$_{z\text{–}v}$) concentrations showed similar trends as DMSP$_{z}$ and DMSP$_{z\text{–}B}$ did, low in the Black Sea and high in the other seas (Fig. 6c).

Differences in DMSP$_{z\text{–}B}$ between small and big size mesozooplankton assemblages were not significant. Correlations between abundance of mesozooplankton, DMSP$_{z}$ and DMSP$_{z\text{–}B}$, and particulate and dissolved fractions of dimethylated sulfur in the water column were searched taking the average values of the surface and the DFM. The distributions of particulate and dissolved fractions of dimethylated sulfur were not

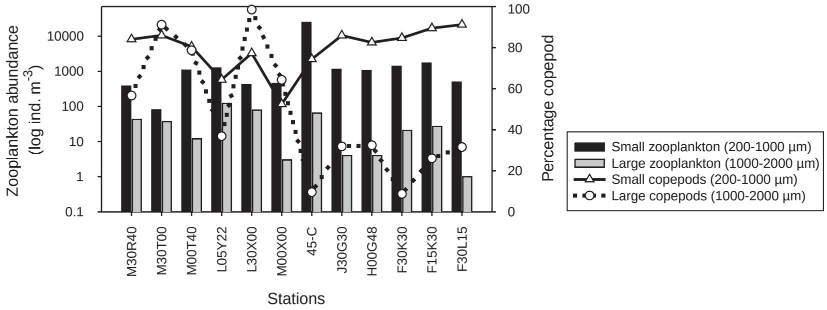

Fig. 5. Small (black bar) and large (gray bar) size zooplankton abundance (log ind m^{-3}), and percentage contribution of copepods to small (triangles) and large (circles) size zooplankton asssemblages.

statistically related to abundance of mesozooplankton. We also found no significant correlations between DMSP$_{z\text{–}B}$ and particulate and dissolved fractions of dimethylated sulfur. Significantly positive correlation was observed only between DMSP$_z$ and DMSP associated with $<18\,\mu m$ particles in the Black Sea (Spearman rank correlation, $P<0.01$).

4. Discussion

The data presented here represent the first results of the spatial distribution of DMS(P;O) on the Turkish sides of the Black, Aegean, NE Mediterranean Seas and in the Marmara Sea. The range of dimethylated sulfur concentrations measured in this study was within the range of those reported for adjacent waters. In our study, the range of DMS, DMSP$_d$, DMSP$_p$ and DMSO$_p$ concentrations were 0.3–9.8, 0.9–15.3, 1.5–55.9 and 0.5–7.5 nM, respectively. The mean concentration of DMS + DMSP$_d$ has been reported to range from 4.79 to 12.65 nM in the Saranikos Gulf, Aegean Sea (Vassilakos et al., 1996). In the Western Mediterranean Sea, Simó et al. (1997) found DMS and DMSP$_d$ are in the range of 0–19.3 and 0.06–18.3 nM, respectively, whereas DMSP$_p$ occurred at 24–73 nM in the Ligurian Sea, NW Mediterranean (Belviso et al., 2000).

Poor or no correlation between Chl-*a* and DMS has been reported in the literature. Even though DMSP$_p$ is generally better correlated to Chl-*a* than DMS, strong relationship is to be expected only where the phytoplankton assemblage is dominated by high DMSP producers (Holligan et al., 1987; Malin et al., 1993; Simó et al., 1997; Dacey et al., 1998; Kettle et al., 1999). We found no significant correlation between Chl-*a* and any dimethylated sulfur compound in the Black Sea, but significantly negative correlation between DMSP$_p$ and Chl-*a* in the surface waters of the Aegean and the NE Mediterranean Seas. Unfortunately, we do not have phytoplankton taxonomic composition measurements to relate directly with the distribution of DMS(P). However, this negative correlation, together with high values of DMSP$_p$:Chl-*a* ratio (see Table 4) and the fact that the vast majority of DMSP$_p$ was attributed to small phytoplankton, is clear indications that DMSP$_p$ production is taxon dependent and, in oligotrophic waters, it is mostly associated with small algae that contribute little Chl-*a* but are better adapted to high light and nitrogen deficiency (Simó, 2001). Indeed, DMSP$_p$:Chl-*a* ratios in the order of 100 nmol µg^{-1} or higher are typical of open-ocean, oligotrophic waters, whereas those in the range 3–30 are generally found in coastal, estuarine or ice-edge waters (Kiene et al., 2000).

There are few published DMSO$_p$ data for comparison. Simó et al. (1998a) reported DMSO$_p$ concentrations varying between 2.7 and 16 nM in the coastal North Sea. DMSP$_p$ occurred in the same samples at concentrations 1.3–20 times higher. DMSO$_p$:Chl-*a* (1–5 nmol µg^{-1}) and DMSP$_p$:Chl-*a* (3–26 nmol µg^{-1}) ratios were in the lower range of those found in the present work. The dominance of DMSP over DMSO in

Table 5
Abundance (ind. m^{-3}) of major taxonomic groups of two size fractionated (200–1000 and 1000–2000 μm) mesozooplankton towed from the depth of fluorescence maximum to the surface in the Black Sea, Marmara Sea, Aegean and NE Mediterranean Sea in October 2000

Major taxonomic groups	Black Sea		Marmara Sea		Aegean Sea		NE Mediterranean Sea	
	200–1000 μm	1000–2000 μm	200–1000 μm	1000–2000 μm	200–1000 μm	1000–2000 μm	200–1000 μm	1000–2000 μm
Chaetognatha	31.1±30.03	11.3±18.13	310.6	53.38	9	0.95	6.73±3.7	1.32±1.15
Appendicularia	27.3±24.9	6.4	443.69	2.1	39.15	0.092	33.38±15.38	
Copepoda	435.6±323.4	32.03±27.32	18280.2	6.24	980.7	1.1	1009.8±462.4	2.56±2.98
Cladocera	125.6±133.04	23.47	3105.85	2.1	9.1		7.87±2.3	0.065
Other crustaceans	5.19	2.4±3.23	88.74		14.4	0.25	12.16±10.1	0.32±0.25
Thaliacea (mostly salps and doliolids)						0.86	33.81±5.98	7.04±6.86
Mollusc larvae	34.13		2174.1		41.11		39.8±49.58	
Fish eggs and larvae						0.06		0.032
Polychaete larvae			177.48			0.06	7.39	
Total	658.9±511.4	75.6±48.7	24580.6	63.78	1094.2	3.36	1150.9±549.4	11.34±11.23

surface-ocean seston seems to be a widespread feature. Simó and Vila (in preparation) are preparing currently an inventory of the occurrence of $DMSO_p$ in many different latitudes of the Atlantic Ocean and the Mediterranean Sea. This inventory shows that $DMSO_p$ is ubiquitous in surface waters, at concentrations of 0.3–30 nM, and it always co-occurs with $DMSP_p$, though the levels of the latter are 1–15 (mean 5) times as high. In our study, the $DMSP_p$:$DMSO_p$ ratio at the surface ranged 1–11.5, yet there was no apparent correlation between the two variables (Table 3). Other studies carried out in cold waters have reported $DMSO_p$ concentrations higher than those of $DMSP_p$. In the Saguenay Fjord in Quebec, Lee et al. (1999) found $DMSO_p$ concentrations averaging 7–10 nM (full range 0–110 nM) co-occurring with $DMSP_p$ levels of 0.5–15 nM (full range 0.02–140 nM). In spring waters of the Arctic North Water Polynya, Bouillon et al. (2002) found $DMSO_p$ at 1.33 nM (0–11.8) together with $DMSP_p$ at 0.5 nM (0–9.5). The ratios of these two compounds to the Chl-*a* concentration (average of 1.56 and 0.84 nmol μg^{-1} for DMSO and DMSP, respectively) were much lower than those found in our study (5–34 and 25–190).

Sestonic $DMSO_p$ seems to be produced principally by phytoplankton (Simó et al., 1998a). The source and function of DMSO in the algal cell, however, are largely unknown. Simó et al. (1998a) suggested that it could be the product of the reaction of DMS with reactive oxygen radicals in the chloroplast, or serve as a carrier for exudation of excess sulfur. Lee and de Mora (1999) also speculated that DMSO could be involved in protecting the cell from photo-generated oxidants, but itself act as a radical scavenger. Building up on these hypotheses after having collected novel experimental evidence, recently Sunda et al. (2002) suggested that DMSO, together with DMSP, DMS and MSA, may constitute a cascade reaction system against oxidative stress. DMSP would cleave into DMS, which would be oxidized to DMSO while scavenging reactive oxygen species. DMSO itself would further act as an effective oxidant scavenger. This hypothesis is consistent with the ubiquity of DMSO in plankton in parallel with DMSP.

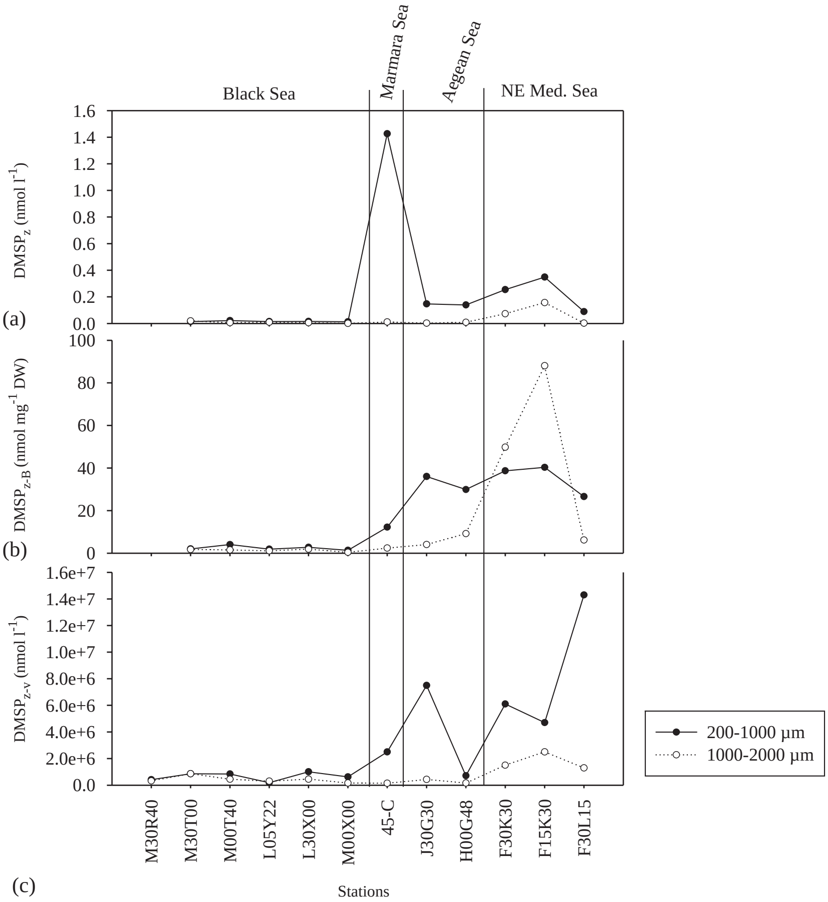

Fig. 6. Concentrations of small (solid lines) and large size (dashed lines) zooplankton DMSP: (a) spatial concentration of zooplankton DMSP (DMSP$_z$, nmol l^{-1}), (b) weight specific zooplankton DMSP (DMSP$_{z\text{–}B}$, nmol mg^{-1} dry weight) and (c) body concentration of DMSP per unit biovolume of zooplankton (DMSP$_{z\text{–}v}$, nmol l^{-1}).

Experimental evidence for whether or not DMSO is produced by the same species that produce DMSP is still weak. In the present study, both surface-water DMSP$_p$ and DMSO$_p$ were mostly concentrated in particles $<18\,\mu m$. Simó and Vila (in preparation) tested a small number of phytoplankton cultures and found that DMSO only occurred in DMSP producers. On the other hand, Lee et al. (2001) and Bouillon et al. (2002) rely on the lack of correlation between DMSO$_p$ and DMSP$_p$ concentrations (as we find in the present study) to suggest that the biosynthesis of DMSO is more widespread than the biosynthesis of DMSP.

DMSP$_p$ in particles $<18\,\mu m$ constitutes the major part of sestonic DMSP in the studied regions (Table 6). Our results emphasize the importance of nanosized particles for the DMSP$_p$ pool in the Black, Aegean and NE Mediterranean Seas as reported before by Belviso et al. (1993) for the NW Mediterranean Sea. The important contribution of small sized autotrophs ($<3\,\mu m$) to total autotroph biomass has been reported for the Aegean and Mediterranean Seas (Siokou-Frangou et al., 2002). In the eastern Black Sea diatoms and coccolithophores (*Emiliania huxleyi*) dominated the phytoplankton in October 1995 (Eker et al., 1999). However, there is no trace from the

Table 6
Percentage contributions of particles $<18\,\mu m$, particles $>18\,\mu m$ and mesozooplankton to the total particulate DMSP in the Black Sea, Marmara Sea, Aegean Sea and NE Mediterranean Sea

Regions	$DMSP_{p<18\,\mu m}$	$DMSP_{p>18\,\mu m}$	$DMSP_{z\,total}$
Black Sea	74.6	25.1	0.3
Marmara Sea	43.7	52.1	4.2
Aegean Sea	74.8	22.4	2.8
NE Mediterranean Sea	76.0	19.0	5.0

SeaWiFS imagery that coccolithophores were abundant during our sampling period (see Fig. 1). The lowest contribution of nanosized particles to total $DMSP_p$ was observed in the Sea of Marmara (~50% $DMSP_p$ from $<18\,\mu m$ size fraction). Phytoplankton assemblages in the Marmara (particularly at station 45-C) are dominated by dinoflagellates (especially *Gymnodinium*, *Prorocentrum* and *Ceratium* sp.) throughout the year (Polat-Beken et al., 2000). Since dinoflagellates are also major DMSP producers, this could explain the relatively large contribution by the large size fraction to the total $DMSP_p$ in the Marmara.

The appearance of DMSP in mesozooplankton and the roles of mesozooplankton in DMSP dynamics have been discussed (Dacey and Wakeham, 1986; Kwint et al., 1996; Tang et al., 1999, 2000a; Tang and Simó, 2003). Tang et al. (1999, 2000a) showed that ingestion and assimilation of phytoplankton-DMSP by mesozooplankton highly depend on both prey and grazer species composition. In the present study, because most of the $DMSP_p$ was associated with particles $<18\,\mu m$ (Table 6), it was more likely consumed and retained by particle feeders rather than predatory zooplankters. Consistent with this hypothesis is that $DMSP_z$ was always higher in the 200–1000 μm size fraction (Fig. 6), which was dominated by particle feeders such as copepods, cladocerans, appendicularians and mollusc larvae (Table 5). The maximum $DMSP_z$ for the 200–1000 μm fraction in Marmara Sea (Fig. 6) also coincided with elevated abundances of copepods, cladocerans and mollusc larvae at that location (Table 5). Overall, mesozooplankton were a small component of the DMSP budget, constituting $\leqslant 5\%$ of the total planktonic DMSP (Table 6). Dry-weight specific $DMSP_{z\text{–}B}$ did not correlate with $DMSP_p$, implying that the ingestion or assimilation of DMSP by zooplankton and $DMSP_p$ production were uncoupled. An interesting observation is that $DMSP_{z\text{–}B}$ for the large size fraction increased in the NE Mediterranean Sea (Fig. 6). A fair number of salps and doliolids were found in this region (Table 5) and they both are efficient filter feeders of small particles. Thus, the high $DMSP_{z\text{–}B}$ (1000–2000 μm) may reflect the accumulation of $DMSP_p$ in these filter feeders. The highest observed $DMSP_{z\text{–}B}$ was ~90 nmol DMSP mg^{-1} DW in NE Mediterranean (Fig. 6b), equivalent to 5.8 μg DMSP-C mg^{-1} DW. Assuming that carbon accounts for 60% of the zooplankton dry weight (Harris et al., 2000), the contribution of DMSP-C to the total zooplankton carbon biomass would be $<1\%$, much lower than that for DMSP-producing phytoplankton (Matrai and Keller, 1994). This analysis shows that DMSP was not an important tissue component of these zooplankton. Instead, the zooplankton likely simply retained ingested DMSP temporarily in their guts after ingestion (cf. *Temora longicornis*; Tang et al., 1999, 2000b).

Assuming a cylindrical shape for mesozooplankton, we estimated their body volume based on their linear dimensions, and calculated their body DMSP concentrations ($DMSP_{z\text{–}v}$). $DMSP_{z\text{–}v}$ was around six orders of magnitude higher than sestonic $DMSP_p$ and total dissolved DMS(P) (see Figs. 3a, 4c and 6c). These results are in agreement with the study by Tang et al. (1999, 2000a) in the Long Island Sound. As far as we know, zooplankton do not synthesize DMSP de novo, and only a few are known to accumulate DMSP in body tissues; e.g. *T. longicornis* (Tang et al., 1999, 2000b). Thus, the high $DMSP_{z\text{–}v}$ probably represents DMSP-containing food transiting zooplankton guts. Zooplankton species that do not assimilate DMSP may repackage ingested DMSP into fecal material, which may subsequently be degraded or exported to deep water (Kwint et al., 1996; Tang, 2001). Another less studied aspect is that the zooplankton gut environment may function as microbial hotspots for DMSP reactions. Zooplankton guts are often heavily colonized by bacteria, including DMSP-consuming bacteria

(DCB) (Tang et al., 2001). The reported half-saturation constant for free-living DCB in coastal to oligotrophic waters ranges from 24 to >500 nM, 5–50 folds higher than the ambient dissolved DMSP concentrations (Ledyard and Dacey, 1996); thus, free-living DCB likely consume ambient dissolved DMSP at suboptimal rates. In contrast, through feeding zooplankton can accumulate DMSP in their guts and fecal pellets to μM–mM level (Kwint et al., 1996; Tang et al., 1999; Tang, 2001), which could allow turnover of DMSP by DCB at maximum rate. Tang et al. (2001) estimated that DCB that colonize the copepod *Acartia tonsa* in Long Island Sound could consume all seston-DMSP that passes through the copepod population by grazing. Thus, while zooplankton may account for only a small fraction of the DMSP standing stock, nonetheless they may represent an active and dynamic fraction of the DMSP budget. The significance of the coupling between zooplankton and bacteria in driving DMSP reactions awaits further study.

Using the few surface DMS concentrations, wind speeds and sea surface temperature data, we have estimated the instantaneous sea–air DMS flux according to the piston velocity parameterization of Nightingale et al. (2000) applied to DMS as follows:

$$K_{\mathrm{w,DMS}} = ((5.88u_{10}^2) + (1.49u_{10}))Sc^{-1/2},$$

$$F_{\mathrm{DMS}} = [\mathrm{DMS}]_{\mathrm{surf}}\, K_{\mathrm{w,DMS}}\, 0.24,$$

where $K_{\mathrm{w,DMS}}$ is the piston velocity or air–sea exchange constant (cm h^{-1}), u_{10} is the wind speed at 10 m height (m s^{-1}), Sc is the Schmidt number of DMS calculated from the sea surface temperature according to Saltzman et al. (1993), $[\mathrm{DMS}]_{\mathrm{surf}}$ is the DMS concentration at the surface (nM) and F_{DMS} is the air–sea exchange flux of DMS (μmol m^{-2} d^{-1}).

Wind speeds were measured during the cruise at around 15 m elevation from the surface, and it varied between 1 and 20 m s^{-1} (see Table 1). Fluxes averaged 5.4, 73.5, 20.8 and 2.6 μmol m^{-2} d^{-1} for the Black, Marmara, Aegean and NE Mediterranean Seas, respectively. Highest emission fluxes mostly coincided with highest wind speeds. The average of the estimated instantaneous fluxes from NE Mediterranean was in good agreement with that observed in open areas of the Northwestern Mediterranean (average 2.5 μmol m^{-2} d^{-1}; Simó and Grimalt, 1998). The overall mean of all four regions (17.6 μmol m^{-2} d^{-1}) fell at the upper end of the range proposed for the Western European shelves and adjacent oceanic waters (Uher et al., 2000, see their Fig. 9).

This study provides the first joint measurements of DMS, DMSP and DMSO among the dissolved, particulate and zooplankton pools in the NE Mediterranean basin including the Black Sea. The results indicate that dimethylated sulfur compounds are not proportionally associated with Chl-*a* concentrations (hence phytoplankton biomass), neither spatially nor with depth. The taxonomic composition of phytoplankton and the structure of the food web are the likely critical factors that shift sulfur compounds from matching Chl-*a* distributions. Several studies have shown that mesozooplankton may be significant actors in the processing of algal DMSP, including DMS production. However, the contribution of these higher predators to the standing stock of DMSP has received much less attention. Should mesozooplankton accumulate DMSP in the body, they might contribute significantly to the removal of this substance from the surface ocean by vertical migration. The present study shows that, even though the levels of ingested DMSP per individual volume can be very high, mesozooplankton account for a very small fraction of total particulate DMSP.

Also, our estimates of the sea-to-air flux of DMS indicate that the NE Mediterranean basin can be an important source of biogenic sulfur to the atmosphere even in the low productive period of the region. To obtain a more precise picture on the importance of NE Mediterranean basin for the regional biogenic sulfur budget, a comprehensive series of measurements over different seasons should be carried out.

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