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Ubiquity of algal dimethylsulfoxide in the surface ocean: Geographic and temporal distribution patterns

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Abstract

We carried out analyses of dimethylsulfoxide (DMSO) in surface–sea particulate samples collected between 1995 and 2003 in the Arctic, Antarctica, Sub-polar North Atlantic, Sargasso Sea, Sub-tropical NE Atlantic, W and E Mediterranean Seas, Black Sea, the coastal North Sea and the coastal Mediterranean Sea. Particulate DMSO ($DMSO_p$) was found to co-occur with particulate dimethylsulfoniopropionate ($DMSP_p$), with concentrations in the range 1–40 nM for the former and 6–340 nM for the latter. The two compounds were significantly correlated, which suggests that they both have a common origin in phytoplankton. Conversely, no significant correlation was found between $DMSO_p$ and chlorophyll-a concentrations (which spanned more than 2 orders of magnitude: 0.04–13 mg m^{-3}), suggesting that DMSO production, like that of DMSP, is taxon-dependent. $DMSO_p$ concentrations were generally lower than concurrent $DMSP_p$ concentrations and accounted for 8–50% (on average ca. 20%) of the intracellular dimethylated sulfur pool (DMSP + DMSO). There was a trend towards higher relative proportions of DMSO in warmer waters, and lower proportions in colder waters. This pattern with temperature was particularly apparent along an annual series in the coastal NW Mediterranean, and along a transect from cold productive waters through warm oligotrophic waters in the NW Atlantic. This is the most comprehensive dataset on $DMSO_p$ reported so far, which shows that this compound is as ubiquitous as $DMSP_p$ in the surface ocean.

1. Introduction

Dimethylated sulfur occurs in the ocean mainly in the forms of the volatile dissolved compound dimethylsulfide (DMS) and the dissolved and particulate pools of the non-volatile compounds dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO). While the particulate pools are clearly dominated by DMSP on most occasions, the dissolved pools are dominated generally by DMSO (Hatton et al., 2004). Overall, dimethylated sulfur species represent major players in oceanic sulfur biogeochemistry and oceanic biosphere–atmosphere interactions (Simó, 2001). Evasion of volatile DMS from the sea surface is the main natural source of sulfur to the global troposphere (Bates et al., 1992), and its subsequent atmospheric oxidation is a major source of aerosols and cloud condensation nuclei over the oceans (Andreae and Crutzen, 1997), with potential climatic implications on a global scale (Charlson et al., 1987). In the water column, dimethy-

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lated sulfur (mostly DMSP) represents an important fraction of organic sulfur in phytoplankton (Matrai and Keller, 1994) and a major carrier for sulfur among trophic levels of the food web (Kiene et al., 2000; Simó et al., 2002; Simó, 2004). Finally, within the phytoplankton cell, DMSP and derivatives are suggested to play important physiological functions, such as osmoregulation, cryoprotection, sulfur and carbon overflow under unbalanced growth, scavenging of oxygen free radicals, and chemical signaling (see e.g. Kiene et al., 1996; Stefels, 2000; Welsh, 2000; Wolfe, 2000; Sunda et al., 2002; Hatton et al., 2004).

Although there is an increasing tendency to consider DMS, DMSP and DMSO as a group of compounds so tightly interrelated that need to be studied altogether, there is an overwhelmingly larger body of knowledge of the oceanic distribution and dynamics for DMS and DMSP than for DMSO. This is largely because the occurrence of DMS and DMSP in seawater and marine organisms was discovered earlier, but it is due also to the intrinsic difficulties in the analysis of DMSO at nanomolar levels (Simó, 1998).

While the body of data on aqueous DMSO is steadily enlarging (an excellent compilation of current knowledge can be found in the review by Hatton et al., 2004), much less is known about its particulate pool ($DMSO_p$). It was first reported by Andreae (1980), but later it was revealed that the analytical method was determining all or part of the co-occurring DMSP as DMSO. The first direct evidence (free of known interferences) for the existence of $DMSO_p$ was provided by Simó et al. (1998a). Work with algal cultures and size-fractionated marine seston led these authors to suggest that DMSO was being produced by phytoplankton. Lee et al. (1999) measured significantly higher concentrations of $DMSO_p$ than dissolved DMSO ($DMSO_d$) in the Saguenay Fjord, which they interpreted as an indication of direct biosynthesis by phytoplankton. Later, Simó et al. (2000) observed an increase in $DMSO_d$ after a whole seawater sample had been treated with chloroform. As dissolved DMSP also increased, the authors interpreted that chloroform was inducing the release of both compounds from the algal cells, and, consequently, there was a pool of intracellular DMSO associated with intracellular DMSP.

Since those pioneering papers, only a few further reports of the occurrence of $DMSO_p$ in the marine environment have been published (Lee et al., 2001; Bouillon et al., 2002; Hatton, 2002; Besiktepe et al., 2004). Even such a short body of data was enough for Sunda et al. (2002) to suggest that DMSO acts as an efficient scavenger of reactive oxygen species in phy-

toplankton. The distribution of $DMSO_p$ in the marine environment, whether it is widespread or not, and how it compares with the distribution of $DMSP_p$, remain largely unresolved. Also unresolved is its temporal variability and controlling factors. This field information is needed in parallel to lab work aimed at asking which organisms produce DMSO and what its function in the cell is.

Here we report on the concentrations of $DMSO_p$ in marine particles from a variety of oceanic regions and coastal sites (mostly in the North Atlantic and adjacent continental seas), and in different seasons. Some previously published data are included to complete the inventory. The spatial and temporal distributions of $DMSO_p$ are compared with those of chlorophyll-a and $DMSP_p$, and related to seawater temperature.

2. Methods

2.1. Sampling, filtration and storage

Samples used in this study were collected between 1995 and 2003 during oceanographic cruises to the Arctic, Antarctica, Sub-polar North Atlantic, Sargasso Sea, Sub-tropical NE Atlantic, W and E Mediterranean Seas, Black Sea, and boat trips to the coastal North Sea (Simó et al., 1998a,b) and the coastal Mediterranean

Fig. 1. Approximate locations of the samples reported in this study. 1: coastal NW Mediterranean; 2: Alboran Sea (W Med); 3: E Mediterranean; 4: Black and Marmara Seas; 5: coastal North Sea; 6: Arctic (Atlantic sector); 7: NE Atlantic; 8: Canary Basin; 9: Gulf of Maine and George's Bank; 10: Sargasso Sea; 11: North Carolina shelf; 12: Antarctic (Peninsula). The open triangle (13) corresponds to the study by Riseman and DiTullio (2004) in the Equatorial Pacific.

Table 1
Inventory of the samples collected and analyzed for $DMSP_p$ and $DMSO_p$, and compiled for this study

Region	Approx. lat. (°N)	Year	Month	Sampling platform	Chl-a (mg m^{-3})		$DMSP_p$ (nM)		$DMSO_p$ (nM)		$DMSP_p:DMSO_p$		SST (°C)		n	Reference
					Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD		
Coastal	42	1995	June	Boat	0.12		10.0		16.0		0.6		19.6		1	This work
NW Med.	42	1997	Nov	Boat	2.19		92.3		17.5		5.3		15.5		1	This work
	42	1997	Dec	Boat	3.00		123.5		33.9		3.6		15.0		1	This work
	42	1997	Sep	Boat	0.46		6.1		6.1		1.0		22.0		1	This work
North Sea	52	1996	Jun	Boat	13.26		340.0		40.0		8.5		14.3		1	Simó et al.,
	52		Jul–Aug	Boat	2.04	1.00	6.2	1.3	3.3	0.9	2.0	0.9	16.8	1.8	2	1998a,b
NE Atlantic	58	1998	Jun	R/V *Discovery*	1.09		28.2		2.8		10.1		11.0		1	This work
(S of Iceland)	60				0.67	0.09	37.0	9.8	4.9	2.1	8.9	4.0	11.3	0.5	9	
	60				1.89	0.04	173.4	1.5	33.0	0.6	5.3	0.1	11.5	0.0	2	
	60				0.95	0.43	51.4	23.7	10.4	4.7	5.1	1.7	11.1	0.1	6	
	60				1.51		117.3		24.0		4.9		12.0		1	
Antarctic	−65	1998	Feb	R/V *Hesperides*	0.30	0.06	10.2	3.2	3.2	0.8	3.1	0.4	−0.2	0.9	3	This work
(Peninsula)	−58				0.12	0.02	6.9	5.4	7.7	5.6	0.9	0.1	3.7	0.4	2	
Canary Basin	28	2000	Aug	R/V *Hesperides*	0.32	0.25	8.8	2.1	2.7	0.6	3.4	1.3	23.5	0.7	3	This work
Arctic	74	1999	Aug	R/V *Marion Dufresne*	0.38	0.17	25.1	9.5	3.0	1.6	10.8	6.0	3.4	1.2	11	This work
(Atlantic sector)	70				0.41	0.04	24.4	3.9	3.7	0.4	6.7	1.2	5.7	0.2	3	
W Med. (Alboran)	36	1999	Sep	R/V *Hesperides*	0.30	0.15	8.4	3.9	3.9	3.0	2.6	0.9	20.2	1.0	5	This work
NW Med. (open)	42	2000	Jun	R/V *Garcia del Cid*	0.28	0.09	23.8	8.9	3.7	2.5	7.7	2.8	20.1	0.4	6	This work
Black Sea	42	2000	Oct	R/V *Bilim*	0.46	0.25	10.1	4.7	4.2	2.6	3.5	2.5	21.0	0.4	6	Besiktepe et al., 2004
Marmara	40		Oct		1.31		51.3		6.2		8.3		17.8		1	
E Med.	36		Oct		0.04	0.01	8.3	1.3	1.6	1.1	7.4	5.9	19.1	1.0	2	

Region	Lat	Year	Month	Vessel											n	Reference
NW Atlantic		2002		R/V *Oceanus*												This work
Gulf of Maine	42		Apr		1.08	0.20	27.8	8.4	2.6	1.3	12.9	3.3	5.1	0.4	3	
George's Bank	40		Apr		1.15		53.6		5.5		9.7		15.1		1	
Sargasso Sea	31		Apr		0.10	0.08	7.0	4.6	2.0	1.6	3.9	1.6	20.7	0.8	5	
N Carolina shelf	32		Apr		0.20		20.0		7.4		2.7		22.5		1	
Arctic	72	2002	Aug	R/V *Johan Hjort*	1.03	0.13	36.7	18.3	3.1	1.7	12.2	0.7	10.9	2.4	2	This work
(Atlantic sector)	76		Aug		1.62	0.88	34.1	9.5	5.4	4.0	7.4	5.3	6.6	1.6	5	
Coastal	41	2003	Jan	Boat	1.4		7.5		0.9		8.3		14		1	This work
NW Med.	41		Jan		1.4		16.8		2.1		8.0		11		1	
(annual series)	41		Feb		2.1		33.3		5.6		5.9		11.5		1	
	41		Mar		1.2		45.1		7.4		6.1		13		1	
	41		Apr		0.5		16.0		3.7		4.3		14.5		1	
	41		May		0.5		28.3		7.4		3.8		17		1	
	41		Jun		0.2		22.8		11.6		2.0		25		1	
	41		Jul		0.5		22.2		11.3		2.0		25.2		1	
	41		Aug		0.3		22.9		11.3		2.0		25.2		1	
	41		Sep		0.2		12.0		1.9		6.2		22.8		1	
	41		Oct		0.44		11.9		2.0		6.0		18		1	
	41		Nov		1.08		8.0		2.1		3.8		16		1	
	41		Dec		3.93		48.3		14.0		3.4		15		1	
Eq. Pacific	−8	2000	Aug–Sep	R/V *Melville*	2.01		5.7		3.2		1.8		15.5		1	Riseman and
(off Peru)	−9		Aug–Sep		1.00	0.60	10.1	7.2	3.6	1.6	2.6	0.8	18.7	0.5	2	DiTullio, 2004
	−13		Aug–Sep			1.27	27.3	16.8	21.5	7.7	1.2	0.3	23.0	0.0	2	
	−14		Aug–Sep		0.88		9.7		3.8		2.6		23.0		1	

Some published data are included.

Within cruises, samples have been grouped according to either latitudinal changes or narrow ranges in chlorophyll-*a* concentration and/or temperature.

Sea. Fig. 1 shows the approximate locations of the sampling sites. Sample dates and coordinates, as well as ship platforms used, are given in Table 1. All ship (oceanic) samples were taken from bottles off the CTD casts. Boat (coastal) samples were collected in acid-cleaned, 2-l glass bottles directly from the sea surface. For the annual time series, seawater was sampled on two consecutive days every month, approximately 1 km offshore in the Bay of Blanes, 100 km north of Barcelona (NW Mediterranean). In all cases, samples were stored cool in the dark before filtration, which occurred typically within 1 h after collection. A volume of 25–50 ml of the sample was withdrawn with a Teflon tube attached to a glass syringe. The tube was then replaced by a filter holder containing a 25 mm Whatman GF/F glass fiber filter, and the sample was filtered in downward position with application of a very gentle pressure. It took about 2–5 min to filter each sample. For those samples that were not analyzed in the field, the filter was folded, put into a 1.8 ml cryogenic vial and immediately frozen at -80 °C or (preferably) in liquid nitrogen. Once in the lab, all filters were stored at -80 °C until analysis.

2.2. Analysis of sulfur compounds and chlorophyll-a

DMSP and DMSO were analyzed sequentially following methods of reaction, purge, cryogenic trapping and sulfur-specific gas chromatography described elsewhere (Simó et al., 1996, 1998b). For GF/F-retained DMSP ($DMSP_p$), fresh or frozen filters were placed in 40-ml gas-tight glass vials filled to the brim with Milli-Q water. Two pellets of NaOH (Fluka, Buchs, Switzerland) were added to bring the pH to >12, and the samples were left in the dark at room temperature for a minimum of 24 h. Aliquots of 20 ml were withdrawn through the vial septum with a glass syringe and injected into the purge flask, where they were sparged with high-purity He (150 ml min^{-1}) for 15 min. Two sparging systems were run in parallel for replicate analyses. Evolved DMS was cryotrapped and analyzed with a gas chromatograph equipped with a flame photometric detector. For GF/F-retained DMSO ($DMSO_p$), the sparged sample was then transferred into a glass vial and neutralized with ultrapure HCl (Baker, Phillipsburg, NJ, USA) to a pH between 4 and 6. Back in the purge flask, the sample was added a 45 mg pellet of $NaBH_4$ (98%, Aldrich Chemical Co., Milwaukee, WI, USA), sparged for 15 min, injected 1.4 ml of HCl 3.5%, and sparged again for 15 min. Evolved DMS was cryotrapped and analyzed as above. The most recent set of samples from the coastal NW Mediterranean were analyzed for DMSO with a modified, simpler and more reliable version of this method, where $NaBH_4$ is used in a cobalt-doped form (Vila-Costa et al., unpublished results). The analytical error was generally $\leq 10\%$ (coefficient of variation) for $DMSP_p$ and $<20\%$ for $DMSO_p$, and the detection limit was 3 pmol S. Calibration was performed using a DMS permeation tube (Dynacal, VICI Metronics, USA). A fluorometric method was used to measure chlorophyll-*a* in 90% acetone extracts (Parsons et al., 1984).

2.3. On-deck incubation over a day–night cycle

On July 3 1998, surface water collected with a bucket in the Sub-polar North Atlantic south of Iceland (59.77°N 20.63°E) was used to fill a 30-l polyethylene carboy. The carboy was kept on deck, immersed in seawater and under a further polyethylene screen, so that PAR intensity inside the carboy was equivalent to that at a depth of approx. 5 m. The experiment was held for 24 h under a continuous flow of surface seawater to keep the natural temperature (approx. 12 °C). Subsamples were taken every 4 h and analyzed for concentrations and production/consumption rates of dimethylated sulfur compounds. Only the concentrations of $DMSP_p$ and $DMSO_p$ are reported here. DMS concentrations and transformation rates have been reported elsewhere (Simó and Pedrós-Alió, 1999; Simó et al., 2002).

3. Results

The samples analyzed were collected in a variety of marine biomes and different seasons (Table 1). Northern latitudes between 28°N and 76°N were covered, plus two locations in the Antarctic (65°S) and the Sub-Antarctic (58°S). The inclusion of a recently published set of samples from the Equatorial Pacific (Riseman and DiTullio, 2004) allows expanding this cross-system analysis into lower latitudes (8–14°S). Seawater temperatures ranged between -0.2 and 25.2 °C, and chlorophyll-*a* (chl-*a*) concentrations spanned more than 2 orders of magnitude (0.04–13 mg m^{-3}).

Particulate DMSO ($DMSO_p$) concentrations were always detectable, ranging from 1 to 40 nM. The lowest levels were found in October 2000 in the open E Mediterranean (Besiktepe et al., 2004), in April 2002 in the Sargasso Sea, and in January and September–November 2003 in the coastal NW Mediterranean. The highest concentrations were registered in December 1997 in the coastal NW Mediterranean, in June 1996 during a *Phaeocystis* bloom in the coastal North Sea (Simó et al., 1998a), and in June 1998 in the Sub-polar
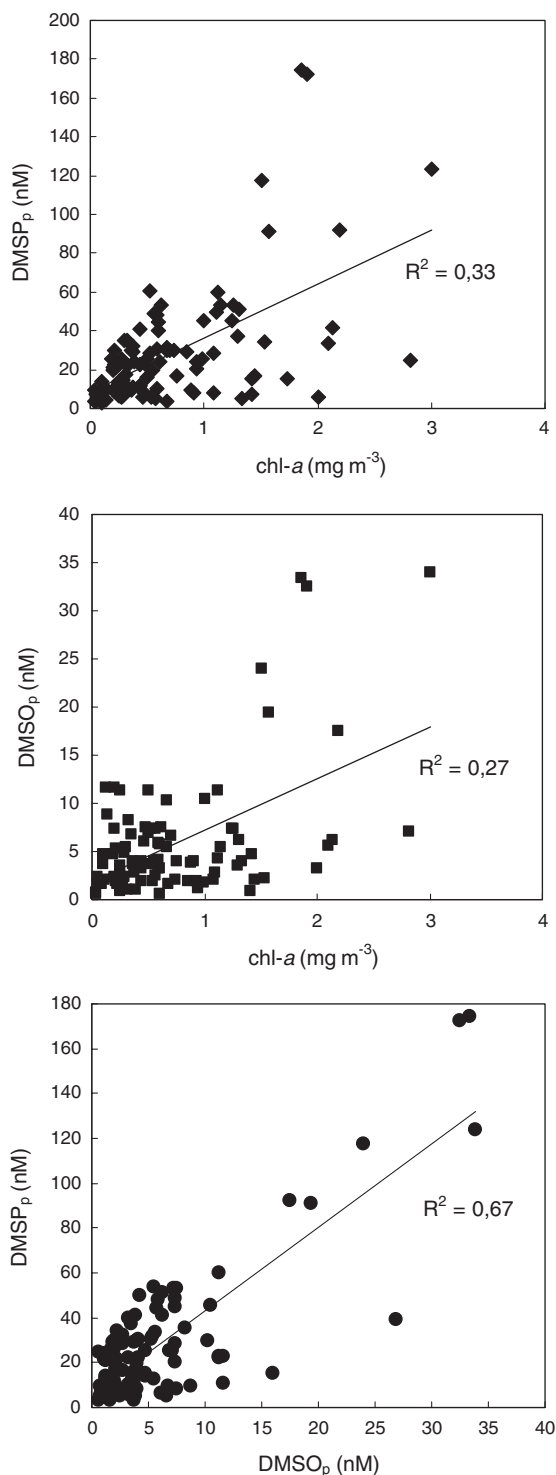
N Atlantic. Concurrent concentrations of particulate DMSP ($DMSP_p$) ranged between 6 and 340 nM, with low values (around 10 nM) coinciding with lowest $DMSO_p$ levels, and the highest values (120–340 nM) being found along with $DMSO_p$ maxima.

Putting together the data from all individual samples ($n = 101$), both $DMSP_p$ and $DMSO_p$ exhibited a weak correlation with chl-a, whereas the correlation between the two sulfur compounds was significantly stronger ($r^2 = 0.67$, Fig. 2). No significant relationship was found between either $DMSP_p$ or $DMSO_p$ and sea surface temperature, latitude or season.

Values of the ratio $DMSP_p:DMSO_p$ ranged from 1 (coastal NW Mediterranean and Equatorial Pacific) to 12–13 (Arctic and Gulf of Maine, Table 1). The average ± 1 standard deviation was 5.2 ± 3.2 ($n = 101$). Unlike for $DMSP_p$ and $DMSO_p$ taken separately, the ratio exhibited a pattern with latitude, opposite to the pattern of temperature, i.e. the $DMSP_p:DMSO_p$ ratio increased as temperature decreased with latitude (Fig. 3). Notice that this comparison is made using data obtained in different months, so that for a given latitude (e.g. $40°N$) there is a broad range of temperatures encompassing winter and summer months. The same

Fig. 2. Correlation analyses with the $DMSP_p$, $DMSO_p$ and chlorophyll-a data sets ($n = 101$).
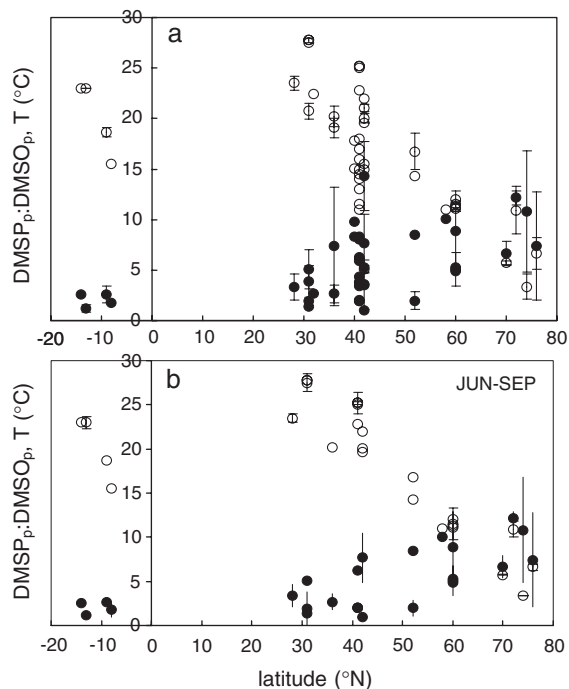
Fig. 3. Plots of seawater temperature (open circles) and the $DMSP_p:DMSO_p$ ratio (filled circles) as a function of latitude for the whole data set (a) and taking only samples collected between June and September (b). Error bars represent one standard deviation of the mean of grouped samples (as in Table 1).
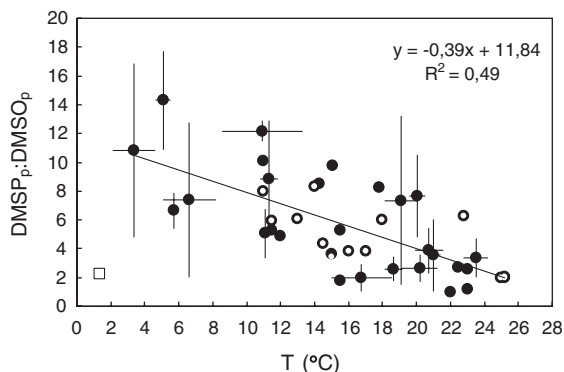
Fig. 4. The $DMSP_p:DMSO_p$ ratio versus seawater temperature for the entire data set. Error bars represent one standard deviation of the mean of grouped samples (as in Table 1). The open circles correspond to the annual time series in the coastal NW Mediterranean. The open square corresponds to the Antarctic samples.

plot was repeated using only data from boreal summer months (June to September); the opposite pattern between ratios and temperature was more apparent (Fig. 3). A correlation analysis revealed that temperature alone accounted for 50% of the variance in the $DMSP_p:DMSO_p$ ratio, with the Antarctic data falling clearly off the general trend (Fig. 4).

The annual series in the coastal NW Mediterranean (Fig. 5) showed an increase in $DMSP_p$ concentrations

from January (8 nM) to late March (45 nM), and a steady decrease further on until the end of the year (10 nM), with a sudden decline observed in April (15 nM) when samples were collected after a severe storm. Chl-*a* concentrations peaked at 2 mg m^{-3} in early March (i.e. almost one month earlier than $DMSP_p$), they were low for most of the summer (0.2–0.5 mg m^{-3}) and recovered in the late fall. Unlike $DMSP_p$ and chl-*a*, $DMSO_p$ was lowest in winter and fall (1–2 nM) and highest in the summer months (11 nM). Interestingly, although the seasonal variability was different for the three compounds, the amplitude of the variability (max./min.) was the same: a factor of 5–6. The $DMSP_p:DMSO_p$ ratio varied within a narrower range (between 8 and 2) and followed a parabola-like pattern with its minimum in summer (Fig. 5). The opposite temporal patterns between this ratio and sea surface temperature, already shown in the correlation analysis (Fig. 4), were very obvious in the annual series.

A similar approach was applied to a transect between the Gulf of Maine, the Sargasso Sea and the North Carolina shelf that was followed in April 2002. According to pigment data (D. Toole, personal communication), the northern productive waters were dominated by diatoms and *Haptophyceae*, whereas *Cyanophyceae* and small *Haptophyceae* dominated biomass in the
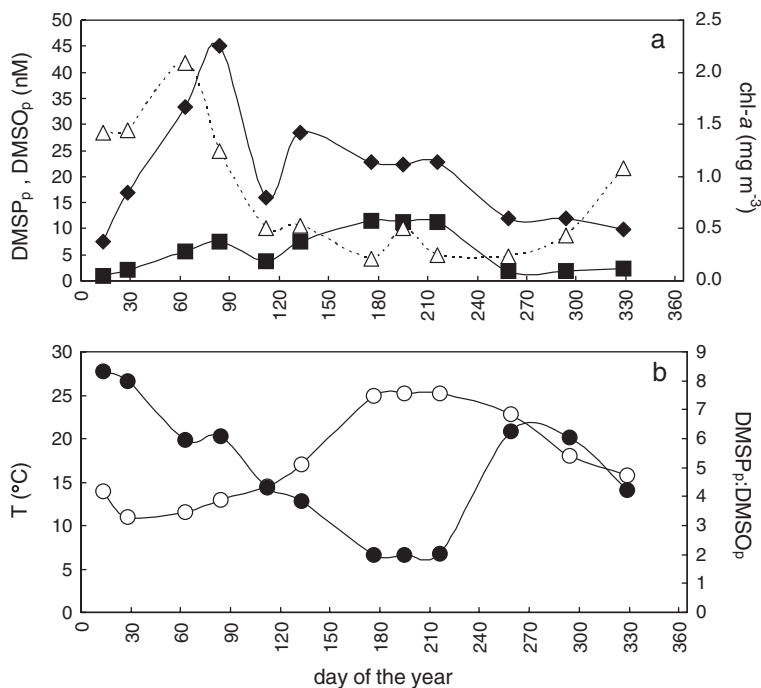

Fig. 5. The annual time series carried out in the coastal NW Mediterranean in 2003. (a) Chlorophyll-*a* (open triangles), $DMSP_p$ (diamonds) and $DMSO_p$ (squares) concentrations in surface waters. (b) The $DMSP_p:DMSO_p$ ratio (filled circles) and sea surface temperature (open circles).
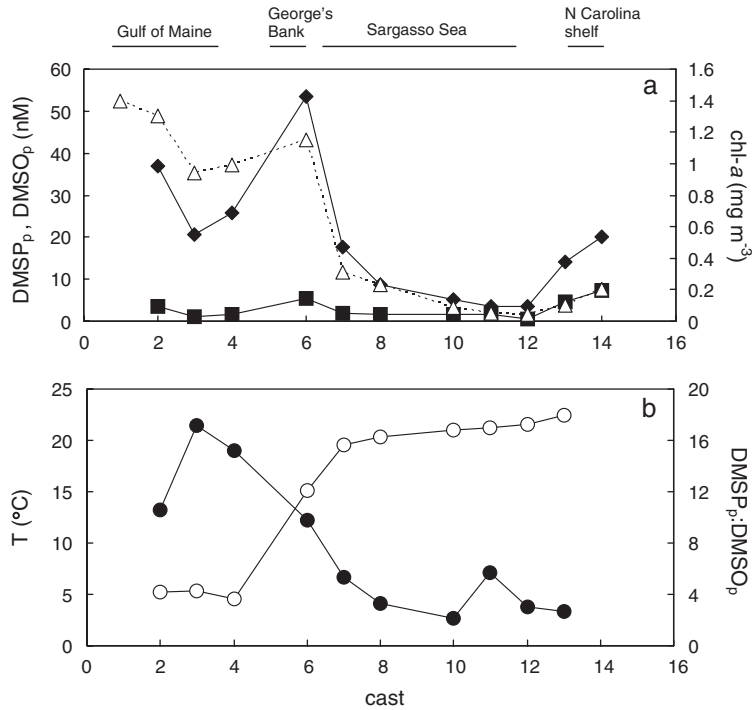
Fig. 6. The N–S–W transect followed in April 2002 in the W North Atlantic. (a) Chlorophyll-*a* (open triangles), DMSP$_p$ (diamonds) and DMSO$_p$ (squares) concentrations in surface waters. (b) The DMSP$_p$:DMSO$_p$ ratio (filled circles) and sea surface temperature (open circles).
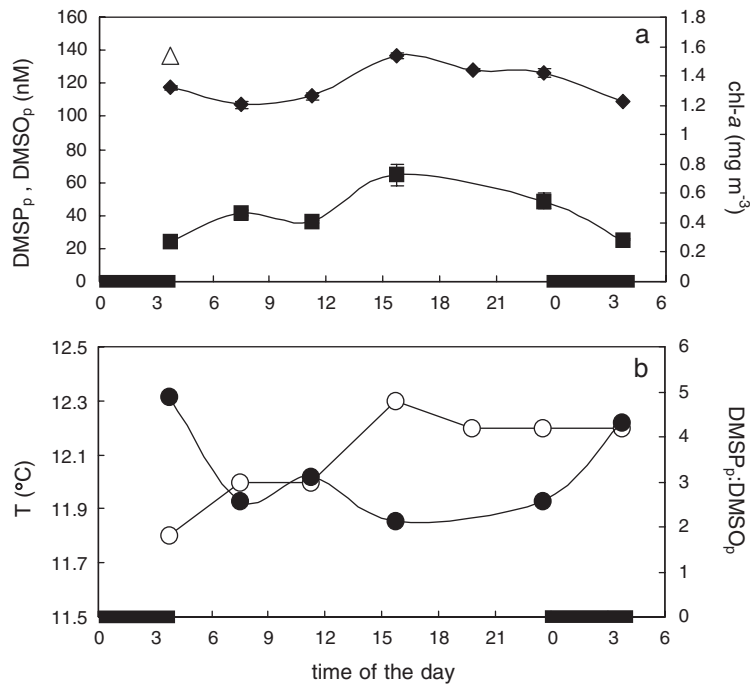

Fig. 7. A 24-h seawater incubation carried out on the deck of the RV *Discovery*, in a 30-l polyethylene carboy, with surface waters from the NE Atlantic (June 1998). (a) Chlorophyll-*a* (open triangles), DMSP$_p$ (diamonds) and DMSO$_p$ (squares) concentrations in surface waters. (b) The DMSP$_p$:DMSO$_p$ ratio (filled circles) and sea surface temperature (open circles). The dark bars indicate the dark hours.

oligotrophic Sargasso Sea. Surface concentrations are shown in Fig. 6 (top), while temperature and the $DMSP_p : DMSO_p$ ratio are shown in Fig. 6 (bottom). Chl-a and $DMSP_p$ concentrations were highly correlated, with higher levels in the Gulf of Maine and George's Bank, much lower levels in the central Sargasso Sea, and moderate levels as we approached the North Carolina shelf. The amplitude of the decrease in chl-a concentrations between the Gulf of Maine and the Sargasso Sea was by a factor of 35, while this factor was 10 for $DMSP_p$. $DMSO_p$ varied independently of $DMSP_p$ and chl-a, occurring in higher concentrations in the George's Bank and the North Carolina shelf. As a result, the $DMSP_p : DMSO_p$ ratio was high (~15) in the cold waters of the Gulf of Maine and low (~4) in the warm waters of the Sargasso and subtropical shelf. Again, an inverse relationship with temperature was observed (Fig. 6).

Fig. 7 shows the results of the diel cycle study performed in a carboy microcosm with water from the Sub-polar N Atlantic. The DMSP-rich phytoplankton assemblage (1.5 mg m^{-3}, 117 nM $DMSP_p$) was composed of a mix of picoalgae, dinoflagellates, flagellates and diatoms. Both $DMSP_p$ and $DMSO_p$ peaked with temperature in the early afternoon (15:00h). However, the increase in $DMSO_p$ was greater, so that the $DMSP_p : DMSO_p$ ratio was lower during daytime and higher at pre-dawn (03:00h).

4. Discussion

According to our measurements in various marine biomes and seasons, particulate DMSO is ubiquitous in the surface ocean, as ubiquitous as DMSP. The observed correlation between $DMSO_p$ and $DMSP_p$ indicates that both compounds are closely linked, most probably because they have a common origin in phytoplankton. Evidence for a phytoplankton source of DMSO had already been presented by Simó et al. (1998a) and Lee and de Mora (1999); here we show its geographic and temporal distribution patterns. Our results do not clarify whether the ubiquity of DMSO arises from being widespread among phytoplankton taxa or, like DMSP (Keller et al., 1989), it is produced preferentially by some algal groups that altogether exhibit a ubiquitous occurrence. The latter hypothesis is supported by the observation that neither $DMSO_p$ nor $DMSP_p$ correlated strongly with chl-a. Recent work with a few phytoplankton cultures points to DMSO being produced by the DMSP-producers and not by the non DMSP-producers (Vila-Costa and Simó, in preparation).

Other than the ones compiled in the present work, there are few $DMSO_p$ data to compare with. In the Equatorial Pacific (8–14°S), Riseman and DiTullio (2004) found concentrations of 3–22 nM (also included in Table 1), i.e. well within the range encountered in the other regions. In the Saguenay Fjord (48°N, Québec) in June, Lee et al. (1999) reported concentrations ranging 0–110 nM (average 7–10 nM). Bouillon et al. (2002) found moderate concentrations (0–11.8 nM, average 1.3 nM) in the North Water Polynya (around 78°N, Canada) in spring. In the same locations, Lee et al. (2001) reported the occurrence of DMSO in ice algae at levels of 1.4–102 nM.

Hatton (2002) measured $DMSO_p$ in the water column and sediment traps in the North Sea. The author reported standing stocks and vertical fluxes rather than concentrations. The occurrence of DMSO in the traps revealed that this compound was associated not only with suspended particles but with sedimenting particles as well. It is hard to know for sure, however, what fraction of this $DMSO_p$ was truly intracellular or bound to detrital particles. The author incubated the material collected in the traps and observed production and leaching of DMSO taking place along with DMSP degradation. She suggested that DMSO could evolve from bacterial DMS oxidation in anaerobic microenvironments within the sedimenting material. Therefore, we cannot discard that some of the $DMSO_p$ we have measured in the surface ocean (Table 1) is associated with detrital matter.

The dominance of DMSP over DMSO in surface–ocean particles seems to be a widespread feature. On average, the concentration of $DMSP_p$ is 5 times as high as that of $DMSO_p$. However, the $DMSP_p : DMSO_p$ ratio varies largely among samples, remarkably among latitudes and seasons. This is most apparent as a general inverse correlation with temperature. The exception that falls off this general pattern is the few Antarctic samples we have run, where the particles were relatively rich in $DMSO_p$ in spite of their low environmental temperature. Other authors have found high $DMSO_p$ concentrations relative to $DMSP_p$, i.e. $DMSP_p : DMSO_p$ ratios at the lower end of ours and down to <1, in cold northern waters (Lee et al., 1999; Bouillon et al., 2002).

The inverse relationship between the $DMSP_p : DMSO_p$ ratio and sea-surface temperature (within a temperature range of 3–25 °C) held for an annual series at a coastal sampling station as well as a transect through trophic regimes in the open ocean. There is no obvious reason for a direct dependence of the relative content of DMSO and DMSP on the temperature. It might result from compositional patterns of the phyto-

plankton assemblage, where nano- and picophytoplankton, generally dominant in warmer waters, would be enriched in DMSO relative to DMSP. Hitherto, there is no evidence that the ratio, or even the intracellular DMSO concentration, varies systematically among algal species, groups or size classes. Clearly, work with cultures, with natural blooms, or through successions of well-described phytoplankton assemblages is required here.

A parallel hypothesis would be that the sea-surface temperature is reflecting the degree of exposure to solar radiation, with higher temperatures being a proxy for highly irradiated, stratified waters. That is, the inverse relationship between the $DMSP_p : DMSO_p$ ratio and temperature could well reflect an inverse relationship with the solar radiation dose experienced by phytoplankton living in the surface mixed layer. It has been suggested that DMSO is so efficient a scavenger for reactive oxygen species that, together with DMSP, DMS and methanesulfinic acid, may constitute a cascade reaction system against oxidative stress in the algal cell (Sunda et al., 2002). Harmful reactive oxygen species (ROS) are produced as by-products of photosynthesis in the chloroplast, particularly so if there is an excess of UV radiation. Conversion of DMSP into DMS would supply in situ ROS scavengers by oxidation of DMS to DMSO and oxidation of the latter to methanesulfinic acid. This cascade system would operate to cope also with other ROS-producing stresses, such as lack of nutrients or exposure to toxic metals. Since an enhancement in antioxidant activity requirements would promote DMS oxidation to DMSO but at the same time it would promote DMSO oxidation to methanesulfinic acid, it is not clear, however, whether this would result in a net increase or decrease of the intracellular DMSO pool. Simó et al. (1998a) followed $DMSO_p$ and $DMSP_p$ concentrations during a 50-day culture of the dinoflagellate *Amphidinium carterae* and observed that, while the increase in $DMSP_p$ followed closely the curve of the cell growth, $DMSO_p$ took off clearly later, right on the day when the stationary phase was reached. As a result, the $DMSP_p : DMSO_p$ ratio in the late stationary phase was >5 times lower than that in the exponential growth phase. Today, this can be regarded as an indication that $DMSO_p$ was produced by intracellular DMS oxidation in response to the oxidative stress caused by nutrient exhaustion.

According to this latter hypothesis, the $DMSP_p : DMSO_p$ ratio would be a rather good indicator for oxidative stress. The influence of the solar radiation dose on the ratio would also serve to explain the midday maximum observed in the 24-h incubation

(Fig. 7), although the polyethylene of the carboy walls prevented most UV radiation from passing through.

The fact that both the few samples collected by us in the Antarctic and those collected by others in cold waters of northern latitudes (Lee et al., 1999, Bouillon et al., 2002) have anomalously high $DMSO_p$ concentrations (relative to $DMSP_p$) and fall off the general trend with temperature, is intriguing. Whether this is a response to unique environmental conditions or reflects the presence of certain algal groups remains to be solved. The possibility that $DMSO_p$ could play a cryo-protecting role in phytoplankton cells living at very low temperatures had been suggested by Lee and de Mora (1999), but later on Lee et al. (2001) calculated that the intracellular concentrations measured, even in sea-ice algal communities (tens to hundreds of millimolars), were not high enough to depress significantly the freezing point of intracellular fluids.

5. Conclusions

Albeit many aspects of the production pathways and physiological function of DMSO in marine plankton remain unresolved, the present work has shown that this compound is ubiquitous in surface water particles of coastal and open ocean environments. Its distribution seems to be linked to the distribution of $DMSP_p$, which suggests that both have a common origin in phytoplankton and that DMSP may be the biochemical precursor of DMSO. $DMSO_p$ accounts for 8–50% (an average ca. 20%) of the intracellular dimethylated sulfur pool (DMSP+DMSO), with higher proportions generally found in phytoplankton living in warmer waters, and lower proportions in colder waters. Due to its ubiquity and significant concentrations, therefore, $DMSO_p$ has to be considered, along with the commonly measured $DMSP_p$, in any budget of organic sulfur in the surface ocean.

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