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Distribution of dimethylsulfide and dimethylsulfoniopropionate and its relation with phytoneuston in the surface microlayer of the western North Atlantic during summer

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Abstract One of the key steps towards predicting dimethylsulfide (DMS) emission to the atmosphere is to understand the distribution and cycling of biogenic sulfur in the microlayer. In this study, we examined the distribution of DMS and dissolved and particulate fractions of dimethylsulfoniopropionate (DMSPd and DMSPp) in the surface microlayer and bulk water of the western North Atlantic during July 2003. DMS concentrations in the bulk water varied from 0.71 to 7.65 nM. In contrast, DMS concentrations in the surface microlayer were fairly low (0.17–1.33 nM). Average concentrations of DMSPd and DMSPp in the bulk water were 2.09 (1.87–6.25) and 44.1 (8.06–119.8) nM, respectively, and those in the surface microlayer were 15.4 (4.06–54.3) and 29.9 (7.32–97.0) nM. In general, DMS was depleted in the microlayer (mean concentration: 0.60 nM) relative to the bulk water (mean concentration: 2.38 nM) with enrichment factors (the ratio of the microlayer concentration to bulk water concentration) ranging from 0.13 to 0.54. There was no consistent enrichment of DMSPp and chlorophyll *a* in the microlayer. On the contrary, DMSPd appeared to be highly enriched in the microlayer with an average EF of 4.89. The concentration of phaeopigments was also generally greater in the microlayer than in the bulk water, presumably due to enhanced photo-oxidation of chlorophyll *a* under high surface light intensities in the microlayer. In the study area, the concentration of DMSPp was significantly correlated with the abundance of dinoflagellates in the microlayer. Moreover, a significant correlation between the distributions of DMS, DMSPp, chlorophyll *a* and phaeopigment concentrations in the microlayer and the bulk water demonstrated that the biogenic materials in the microlayer come primarily from the bulk water below.

Keywords Dimethylsulfide · Dimethylsulfoniopropionate · Distribution · Sea-surface microlayer · Western North Atlantic

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Introduction

Dimethylsulfide (DMS) is one of the major biogenic sources of sulfur to the atmosphere. The atmospheric oxidation products of DMS not only contribute to acid

precipitation, but may also influence climate due to the formation of cloud condensation nuclei (Charlson et al. 1987). The flux of DMS to the atmosphere depends strongly on the concentration of DMS in the surface layer of the ocean, which in turn is regulated by imbalances in the rates of biological, physical and chemical sources and removal processes for DMS in the water column. In the upper layers of the ocean, DMS is produced primarily from the enzymatic cleavage of the algal osmolyte dimethylsulfoniopropionate (DMSP). DMSP is found in high concentrations within Dinophyceae (dinoflagellates) and Prymnesiophyceae (including the coccolithophorids), while other taxa, such as diatoms, generally have low cellular DMSP concentrations (Keller et al. 1989). Once in seawater, DMS can be removed via various processes including microbial consumption, photochemical degradation, air-sea exchange, and vertical mixing (Kiene and Bates 1990; Kieber et al. 1996; Simó and Pedrós-Alió 1999). The relative proportions of these sink processes depend on several parameters, including mixing layer depth, UV intensity, wind speed, and the abundance and speciation of marine microbes.

Although DMSP and DMS are biogenic in origin, DMS or DMSP concentrations are not usually related to phytoplankton chlorophyll (e. g., Holligan et al. 1987; Turner et al. 1988; Leck et al. 1990; Simó et al. 1997; Dacey et al. 1998; Kettle et al. 1999), and there have also been observations indicating their correlation under certain environmental conditions (Andreae 1990, Andreae et al. 1994; Matrai et al. 1996; Sciare et al. 2002; Yang 2000). This might be not only due to the taxonomic dependence of DMSP production in algae, but also to the indirect transformation of DMSP to DMS by bacteria (Kiene and Linn 2000; Kiene et al. 2000).

The sea surface microlayer has often been operationally defined as roughly top several tens to several hundreds micrometers of a water body, depending on the collection method used. In addition, the thickness of the microlayer will vary depending on the nature of variables such as surfactants, sea state, wind speed, and so on (Liss and Duce 1997). Biological and chemical processes in the microlayer will affect the exchange of materials between the atmosphere and oceans. A wide variety of inorganic and organic substances have been reported to be enriched in the surface microlayer compared to bulk waters (Williams et al. 1986 and references therein). Moreover, many studies indicate an enrichment of microbial populations in the microlayer with, for example, higher abundances of bacteria (Hardy 1982; Hardy and Apts 1984) and phytoneuston (microalgae) densities 10–1,000 times greater than those only a few centimeters below (Hardy and Valett 1981). Although there has been a great advance in understanding the marine microlayer and its effect on near-surface ocean processes (Hardy 1982; Hardy and Apts 1984; Williams et al. 1986; Liss and Duce 1997), there remain many unknowns in estimating the effect of the microlayer on air-sea gas fluxes.

Over the last 20 years, most research has focused on the biogeochemical processes of DMS and DMSP in the upper layers of oceans, with only limited studies on DMS in the surface microlayer (Nguyen et al. 1978; Turner and Liss 1985; Yang 1999; Yang et al. 2001, 2006; Yang and Tsunogai 2005; Zemmelink et al. 2005). A prime reason to study the surface microlayer is to improve our understanding of the exchange of DMS across the sea-air interface because significant DMS enrichment or depletion in the microlayer would imply significant differences in actual emission fluxes with respect to those generally estimated from bulk concentrations.

This work describes DMS and DMSP data obtained during a comprehensive investigation by the research vessel CCGS "Martha L. Black" in the western North Atlantic during 6–24 July 2003 as part of the Canadian SOLAS (Surface Ocean Lower Atmosphere Study) programme. The main objective of this paper is to investigate the distributions of DMS and DMSP between the surface microlayer and bulk water in the western North Atlantic and evaluate the extent of enrichment of DMS, DMSPd (dissolved) and DMSPp (particulate) in the microlayer. The spatial distributions of DMS and DMSP are discussed in relation to phytoplankton biomass and taxa. Some comparisons are made between this study and an earlier investigation by Yang et al. (2005a) from the same study area to observe the seasonal variations of DMS and DMSP from spring to summer.

Methods

Sample collection

The sea surface microlayer samples and corresponding bulk water samples were collected at 8 stations

situated in the western North Atlantic (Fig. 1) during July 2003. The cruise track was designed to pass through several of the biogeochemical provinces including NW Atlantic slope water (L1, T3), Gulf Stream (T1), North Atlantic Subtropical Gyre commonly known as the Sargasso Sea (T2), North Atlantic Drift (T4, T5), Atlantic subarctic (T6), and Greenland Current (T7). The environmental and hydrographic information for the DMS sampling stations such as location, surface seawater temperature and salinity are described in Table 1.

Various sampling techniques have been applied to sample the sea-surface microlayer (Hardy 1982). One of the popular approaches is to withdraw a film of water from the sea surface by adherence to a screen or plate. The problems related to this technique have been discussed in detail in Yang et al. (2001) and the result shows that the screen sampler has significant advantages over the plate. In this study, therefore, we still used the screen sampler to collect the surface microlayer samples. The sampler was made of a 16-mesh stainless steel screen held in a 40 cm × 40 cm stainless steel frame. In use, the screen was held horizontally and immersed into the sea surface, after that it was withdrawn and the seawater and surface film material entrapped by the mesh spaces were drained into a sample bottle. Because the volume (32 ml) of water collected by single dip of the sampler was small, successive dips (20 times) were conducted until a desired volume (600–700 ml) was obtained. This technique sampled a surface layer thickness of 200 ± 10 μm. Sample of bulk water was collected from approximately 1 m water depth with Niskin bottle attached to a CTD hydrocast system.

DMS and DMSP analyzes

For the determination of DMS, samples were analyzed immediately after collection. The samples were first gravity-filtered through 2.5 cm diameter glass fiber

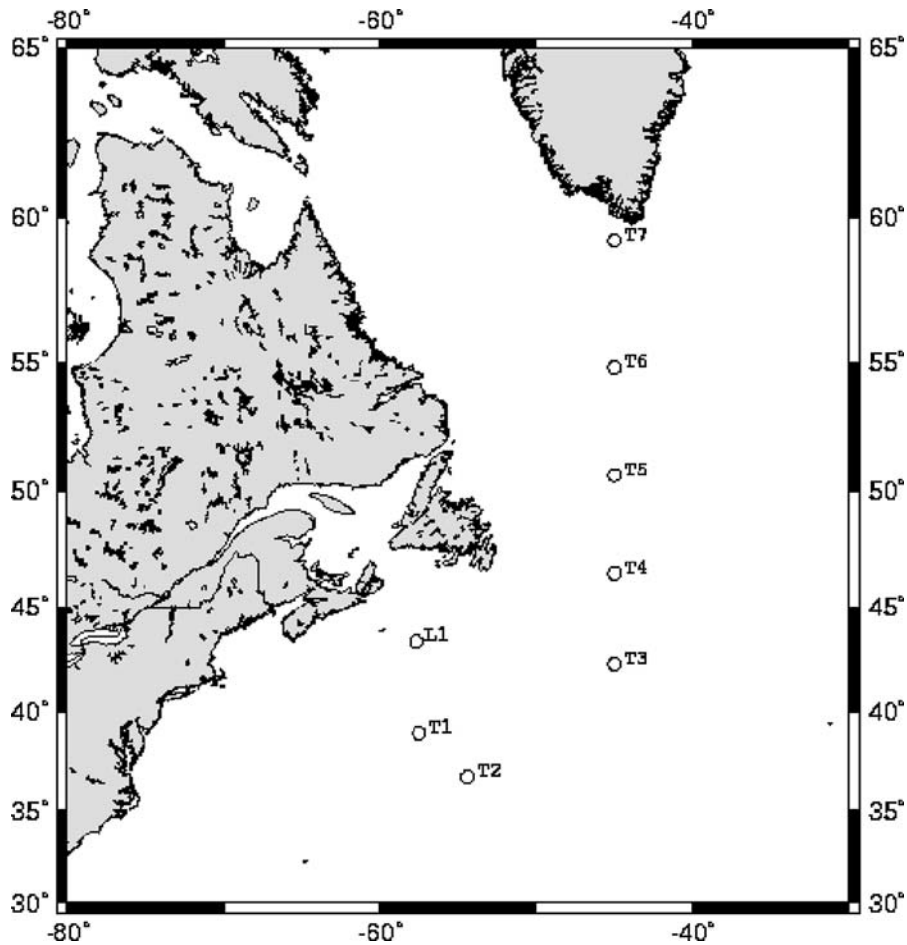

Fig. 1 Location of sampling stations in the western North Atlantic during summer 2003

Table 1 Enrichment factors (EFs) of DMS, DMSP, chlorophyll *a* and phaeopigments in the surface microlayer

Station no.	Location	Sampling date	*T*°C*	Salinity*	EF_{DMS}	EF_{DMSPd}	EF_{DMSPp}	$EF_{Chl\text{-}a}$	$EF_{Phaeopig}$	DMS:DMSPd:DMSPp ratio	
										Bulk water	Microlayer
L1	43°25.8′ N, 57°41.2′ W	8 July	19.25	34.089	0.20	16.24	0.93	ND	ND	1.0:1.2:10	1.0:97:47
T1	39°00′ N, 57°29.2′ W	10 July	26.14	36.214	0.13	2.18	0.91	1.08	2.00	1.0:1.4:6.2	1.0:24:43
T2	36°49.5′ N, 54°23.7′ W	11 July	25.70	36.223	0.13	5.17	0.65	2.38	ND	1.0:1.7:9.9	1.0:64:48
T3	42°19.9′ N, 45°0.14′ W	14 July	23.15	35.844	0.39	7.13	1.11	1.15	1.60	1.0:3.2:17	1.0:57:48
T4	46°29.8′ N, 45°0.3′ W	16 July	11.54	33.775	0.52	2.08	0.93	0.88	1.08	1.0:2.4:49	1.0:9.4:87
T5	50°39.9′ N, 44°59.3′ W	18 July	10.40	34.248	0.31	1.75	0.25	0.82	0.85	1.0:2.0:33	1.0:11:26
T6	54°50.2′ N, 45°00′ W	20 July	9.13	32.404	0.17	1.87	1.53	0.80	3.00	1.0:0.31:1.2	1.0:3.3:11
T7	59°14.7′ N, 45°0.4′ W	22 July	4.08	33.667	0.44	2.76	0.49	0.98	1.52	1.0:4.6:89	1.0:29:97
				Average	0.29	4.89	0.85	1.15	1.68	1.0:1.4:19	1.0:26:50

*Surface (0–1 m) seawater temperature and salinity collected from the CTD apparatus

filters (GF/F, Whatman). The concentrations of DMS were determined using a cryogenic purge-and-trap system with gas chromatographic separation and pulsed flame photometric detection, basically according to the method described in Scarratt et al. (2002). The samples (typically 5 ml) were degassed for 3 min using high purity helium at 40 ml min^{-1}. The gas stream passed through a Pyrex tube containing calcium chloride to remove water vapor and then was cryotrapped in a Teflon loop submerged in liquid nitrogen. The trapped gases were desorbed with hot water (ca 70°C) and analyzed on a Varian STAR 3400 CX gas chromatograph (GC). A SPB-1 sulfur capillary column (30 m, 4.0 μm thickness, 0.32 mm i.d., Supelco, Inc.) was used for chromatographic separation of the sulfur gases. Calibration of DMS was achieved using a permeation tube apparatus (Kin-Tek).

DMSPd was measured indirectly as DMS, after hydrolysis of DMSP to DMS with cold alkali (0.5 M final concentration KOH). Samples were allowed to react for at least 24 h before analysis. DMS generated from the breakdown of DMSP was analyzed on a Varian CP-3800 GC equipped with a flame photometric detector. The measured quantity of DMS in filtered samples following KOH addition represented the total amount of DMSPd and free DMS. DMSPd was obtained by subtracting DMS from DMSPd + DMS. DMSPp was determined by alkaline hydrolysis and subsequent measurement of the evolved DMS. DMSP standards were prepared from a volumetric solution of DMSP-hydrochloride (Research Plus) and dispensed into KOH-containing serum vials as for the samples above. The analytical method has a precision of ca. 10% and a minimum quantification limit for both DMS and DMSPd of ca. 0.08 nM.

Chlorophyll determination, phytoplankton and bacteria abundances

Subsamples for determination of seawater chlorophyll *a* were filtered onto Whatman GF/F glass fiber filters. Concentrations of chlorophyll *a* were analyzed fluorometrically after 24-h extraction in 90% acetone at 5°C (Parsons et al. 1984). Phytoplankton identification and enumeration were conducted on samples preserved with acidic Lugol's solution using a settling column and inverted microscope (Lund et al. 1958). For the determination of bacterial abundance, the samples were fixed with formaldehyde to a final concentration of 3% v/v. Cells were stained with DAPI (1 μg ml^{-1} final concentration) and counted by epifluorescence microscopy after

filtration using 0.2 μm black polycarbonate Nucleopore membrane (Porter and Feig 1980).

Results and discussion

Table 1 presents the sampling date, surface seawater temperature and salinity, and the enrichment factors (EFs) of DMS, DMSP, chlorophyll *a*, phaeopigments and bacteria in the surface microlayer. In this study EF values were calculated as the ratio of surface microlayer concentration (C_M) to the bulk water concentration (C_S). EF values greater than or less than one represent enrichment or depletion, respectively. Throughout the study area, surface water salinity changed from 32.4 to 36.2 while water temperature varied widely from a high of 26.1°C at Stn T1 to a low of 4.1°C at Stn T7. Water temperature has been demonstrated to be an important factor influencing the distribution of DMS in the microlayer (Yang et al. 2001) and will be discussed further below. During the sampling, low wind speeds (~2–3 m/s) were recorded at Stns T5-T7 where the sea surface was calm, while high wind speeds (~7–8 m/s) were observed at Stns T1-T4 with breaking waves at the sea surface.

DMS, DMSP and chlorophyll a distributions and their EFs in the microlayer

Figure 2 shows the distribution of DMS, DMSPd, DMSPp and chlorophyll *a* concentrations in the microlayer and bulk water. In the investigated area, DMSPp concentrations in the bulk water varied over a wide range. The highest DMSPp value (119.8 nM) was monitored at the Greenland Current station (T7). Stn T4 in the Subarctic also displayed a high DMSPp level (104.0 nM). The lowest value (8.06 nM) was observed at the Gulf Stream station (T1). The DMSPp concentrations at Stns T2, T3 and T6 varied very little (10.80 ± 1.72 nM). The distribution tendency of DMSPp in the microlayer exhibited a similar pattern to that in the bulk water, with maximum concentration occurring at Stn T4 (97.0 nM).

In comparison with DMSPp, DMSPd concentrations in the bulk water changed over a small range (1.87–6.25 nM). Very few measurements of DMSPd in the western North Atlantic have been reported for

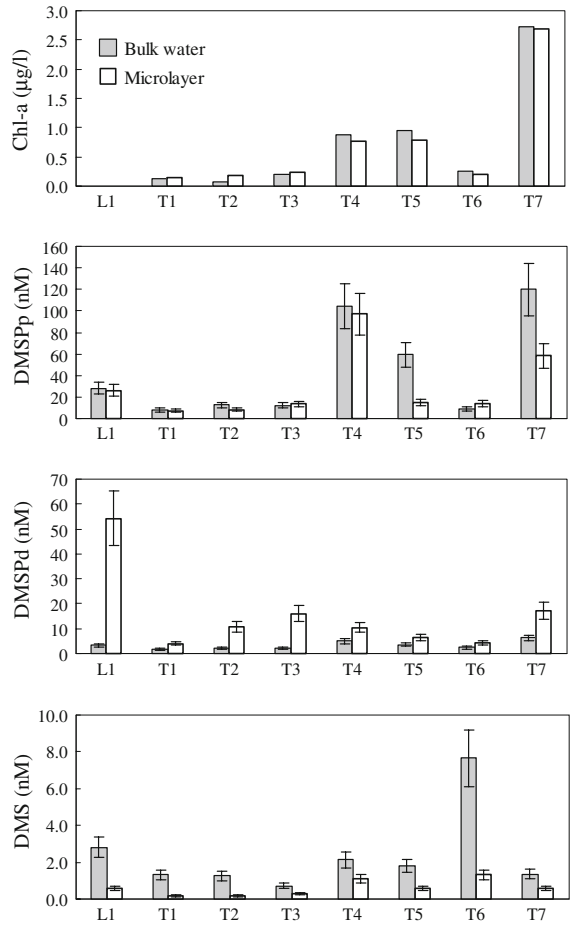

Fig. 2 Distribution of DMS, DMSPd, DMSPp and chlorophyll *a* concentrations in the microlayer and bulk water at the investigated stations

the summer season. Dacey et al. (1998) recorded surface seawater DMSPd concentrations of 5–10 nM in the Sargasso Sea in summer, apparently higher than that (2.09 nM, T2) measured in this study. The concentrations of DMSPd in the microlayer fluctuated over a larger range from 4.06 to 54.3 nM. Total microlayer concentrations of DMSPd in the study area averaged 15.4 nM and were almost equal to the spring values (Yang et al. 2005a).

DMS concentrations in the bulk water varied from 0.71 to 7.65 nM with an average value of 2.38 nM. In contrast, average concentration of DMS in the microlayer was 0.60 nM, approximately 4-fold lower than that in the bulk water. DMS in the microlayer revealed a similar spatial trend to that in the bulk water, with the highest concentration simultaneously appearing at Stn T6 (Subarctic).

Table 1 also lists the concentration ratios of DMS:DMSPd:DMSPp at 7 investigated stations. Apparently, DMSPp concentrations were in most cases higher than those of DMSPd in both the microlayer and the bulk water. The concentrations of DMSPd exceeded those of DMS by a factor of 3–97 in the microlayer samples. In contrast, the concentrations of DMSPd were only 1–4 times higher than those of DMS in the bulk water samples. The great difference in the proportions of biogenic sulfur constituents between the microlayer and bulk water was obviously due to microlayer enrichment for DMSPd, as discussed below.

In comparison with previous data (Yang et al. 2005a), an obvious spring/summer difference was observed for chlorophyll *a*, with higher levels in spring and lower levels in summer, reflecting the seasonal variation of phytoplankton biomass in the study area. Generally, a double increase in DMSPp and DMSPd concentrations in the microlayer and bulk water occurred in the investigated area from spring to summer. Similarly, the concentrations of DMS in the study area also showed a clear seasonal variation, with higher values in summer than in spring. Lower chlorophyll *a* levels and higher DMSP and DMS concentrations in summer relative to spring is likely to reflect an increase in the proportion of DMSP producers in the total phytoplankton assemblage. It is noteworthy that the extremely high DMSPp concentrations and relatively high DMSPd and DMS concentrations in the microlayer and bulk water were consistently observed at Stn T4 (North Atlantic Drift) in spring and summer. The highest sea-to-air flux of DMS was also recorded at this station (Table 2), highlighting that this area may emit potentially large amounts of DMS to the atmosphere.

To date, much effort has been devoted to studying empirical relationships between DMS(P) and other biological parameters, especially chlorophyll *a*. Data obtained in this study indicated that the concentrations of DMSPd in the bulk water changed in response to variation in the concentrations of chlorophyll *a*. For instance, the highest concentrations of DMSPd and chlorophyll *a* in the bulk water appeared simultaneously at the northernmost station (T7), while the lowest DMSPd level was observed at Stn T1 with very low chlorophyll *a* concentration. Consequently, a relationship appeared between DMSPd and chlorophyll *a* concentrations in the bulk water samples (Fig. 3, $r^2 = 0.8482, n = 7, p = 0.0032$). DMSPd has previously been shown a significant relationship with chlorophyll *a* in the surface waters of the northwest Atlantic in May 1998 (Scarratt et al. 2002). It was interesting to note that similar phenomenon to DMSPd was observed with DMSPp as well. By statistical analysis to DMSPp and chlorophyll *a*, a correlation between them was obtained for all the bulk water samples ($r^2 = 0.7604$, $n = 7$, $p = 0.0105$). Bouillon et al. (2002) also found a significant correlation between DMSPp and chlorophyll *a* in the North Water during April and May 1998. Our observations suggest that phytoplankton biomass might play an important part in determining the distributions of DMSPp and DMSPd in the study area at this time of year.

The effect of DMSPp concentration on DMSPd concentration was also examined from the field investigation data. Our data showed that the high concentrations of DMSPd in the bulk water generally appeared in the samples with high levels of DMSPp. This is particularly obvious for the sample collected at Stn T7. As a result, a linear correlation was found between the two components ($r^2 = 0.9575$, $n = 8$,

Table 2 The sea-to-air flux of DMS at the investigative stations in the western North Atlantic in summer 2003

Station no.	Wind speed u_{10} (m/s)	*Sc*	K_{DMS} (cm/h)	F_{DMS} (μmol m^{-2} d^{-1})
L1	4.6	952	2.69	1.81
T1	8.2	696	12.66	3.98
T2	8.2	709	12.53	3.79
T3	7.2	794	9.36	1.60
T4	7.7	1,414	7.86	4.04
T5	2.6	1,504	0.24	0.10
T6	2.1	1,612	0.18	0.34
T7	3.1	2,133	0.22	0.07
Average	5.5	1,227	5.72	1.97

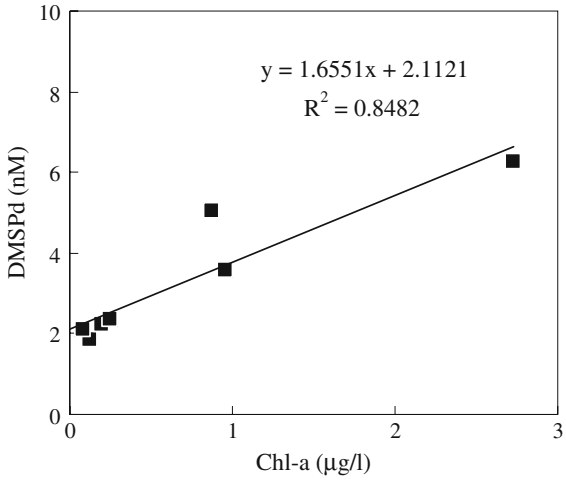

Fig. 3 Relationship between DMSPd and Chlorophyll *a* concentrations in the bulk water samples

$p = 0.0000$, [DMSPd] = 0.034[DMSPp] + 1.8475). Our investigation implies that the concentration of DMSPd in seawater is highly dependent upon the level of DMSPp.

Previous studies have compared microlayer concentrations to near subsurface values using EF values (Yang et al. 2005a, b). In the spring 2003 cruise, we obtained an average DMS EF value of 0.72 (Yang et al. 2005a). In the present study, DMS concentrations were considerably lower in the microlayer than in the bulk water, resulting in a very low mean EF of 0.29 (Table 1). The higher EF values observed in spring than in summer (this cruise) were assumed to be due to the effect of temperature, because magnitudes of enrichment of DMS in the microlayer were found to be inversely proportional to sampling temperature (Yang et al. 2001). Literature values for the EF of DMS range from 0.3 to 4 for both coastal and open sea waters (Nguyen et al. 1978; Turner and Liss 1985; Yang 1999; Yang et al. 2001, 2005b). However, it is very difficult to compare EF values of DMS obtained from different investigations, because the concentrations in the microlayer are highly dependent on biological and environmental variables including microlayer chlorophyll *a* concentration, bulk water DMS concentration, seawater temperature, wind speeds and sea state (Yang et al. 2001). Moreover, all microlayer DMS concentrations and thus derived EFs should be minimum, due to sampling constraints and artifacts for the dissolved gases. Therefore, we must exercise caution in viewing the EF values of DMS obtained.

Throughout the study, the EF values of chlorophyll *a* ranged from 0.80 to 2.38 with an average of 1.15. A similarly variable pattern for chlorophyll *a* has been reported elsewhere (Carlson 1982). The present results differ from our observations during the spring 2003 cruise (Yang et al. 2005a) in which chlorophyll *a* was consistently enriched in the microlayer. Phaeopigments (chlorophyll degradation products), on the other hand, were generally enriched in the microlayer compared to the bulk water, with EF values ranging from 0.85 to 3.0 (mean: 1.68). In this study, we found a correlation between phaeopigment and chlorophyll *a* concentrations in the microlayer ($r^2 = 0.8038$, $n = 6$, $p = 0.0155$). This means that high phaeopigment concentrations are generally observed in the microlayer samples with high chlorophyll *a* levels. High phaeopigment concentration in the microlayer may be due to enhanced photo-oxidation of chlorophyll under high surface light intensities in the microlayer.

The most striking feature of this study is the fact that DMSPd concentrations in the microlayer always far exceeded those in the bulk seawater, resulting in high EFs ranging from 1.75 to 16.24 with a mean of 4.89. The sea surface microlayer has been generally considered to be enriched, relatively to underlying water, with various organic materials (Liss and Duce 1997; Cincinelli et al. 2001). For example, Carlucci et al. (1991) reported enrichment factors of 2–6 for dissolved free and combined amino acids in the surface microlayer of the Damariscotta (Maine) estuary. Natural organic components appear to be the principal film-forming components in the surface microlayer, although lipid compounds can dominate in samples collected from polluted waters (Williams et al. 1986). The high enrichment of organic material such as DMSPd in the surface microlayer could be, in part, attributed to simple Gibbs surface adsorption, i.e., a solute is concentrated at the air–sea interface when the surface tension of the solution is reduced (Adamson 1976).

At Stations T3 and T6, the concentrations of DMSPp were higher in the microlayer relative to bulk water whereas the opposite situation was observed at Stns T2, T5 and T7. No significant difference was found in DMSPp concentrations between the microlayer and bulk water samples at Stns L1, T1 and T4.

On average, DMSPp was slightly depleted in the microlayer (mean EF = 0.85).

Abundance of phytoneuston and bacteria in the microlayer

The abundance of major algal taxa in the microlayer samples is presented in Table 3. The high abundance of phytoneuston (over 2×10^6 cells/l) was found at Stns T4, T5 and T7, which were locations of high chlorophyll *a* levels. Throughout the study area, the phytoneuston community was dominated by flagellates (16–65% of total phytoneuston cell abundances), with Prymnesiophyceae contribution ranging from 1 to 16% of the total cell abundances. Diatoms and dinoflagellates were present in low numbers at most stations.

Dinoflagellates have received much attention as major producers of DMSP (Keller et al. 1989). In the present study, maximum abundance of dinoflagellates was observed at Stn T4, coincident with the highest microlayer DMSPp concentration. As a consequence, dinoflagellates displayed a significant correlation with DMSPp (Fig. 4, $r^2 = 0.5969$, $n = 8$, $p = 0.0000$). Flagellates also co-occur with high DMSPp in many marine environments (e.g., Turner et al. 1995; Matrai et al. 2008). Flagellates have been shown to dominate Barents Sea subsurface waters (0–5 m) in late winter/early spring (Ratkova and Wassmann 2005), prior to any spring bloom, coinciding with DMSPp concentrations of up to 20 nM (Matrai et al. 2007). In nearshore waters, Turner et al. (1988) reported higher intracellular DMSP concentrations in flagellates (650 mM) than in the phytoplankton community as a whole (between 37 and 95 mM). In the present study, the distributions of DMSPp and flagellates in the microlayer basically followed the same trend, apart from the flagellate maximum that was lagged by one station (T5, rather than T4), with a corresponding increase at T7 (Fig. 4). Because the phytoneuston composition was dominated by flagellate cells, it is probable that their contribution to the DMSPp overwhelmed the contribution of dinoflagellates, which were present at low biomass levels.

We also measured bacterial abundances in the microlayer. Figure 5 shows that bacterial abundances in the investigated area ranged from 1.42×10^8 to 5.97×10^8 cells/l, with an average of 3.1×10^8 cells/l. Bacterial abundances in this study were lower than those measured in the previous studies in sea-surface microlayers in nearshore and offshore waters off the coast of southern California (Carlucci et al. 1992) and in coastal Maine (Carlucci et al. 1991). However, bacterial populations in this study were within the ranges observed in other microlayer environments including those from coastal Baja California (Carlucci et al. 1986) and Sequim Bay, Washington (Hardy and Apts 1984). Recently, a

Table 3 Abundance of phytoneuston (cells l^{-1}) in the surface microlayer

Taxon	T1	T2	T3	T4	T5	T6	T7
Diatoms	2,040	9,480	1,400	1,200	71,640	1,120	209,684
Dinoflagellates	4,840	7,944	20,744	90,040	28,480	6,024	3,800
Chrysophyceae	240	280	160	4,400	19,760	80	2,560
Dictyochophyceae	0	0	0	4,504	8,889	0	800
Cryptophyceae	8,615	2,794	1,557	43,560	173,107	8,383	261,482
Euglenophyceae	80	40	320	8,320	2,000	0	0
Prasinophyceae	0	80	440	5,944	1,440	80	640
Prymnesiophyceae	13,833	31,371	13,593	134,308	266,960	164,703	210,266
Flagellates	197,434	147,405	271,208	709,839	1,128,718	668,605	1,162,873
Cyanophyceae	285,200	29,840	96,000	1,960	0	0	0
Heterotrophic groups	880	200	2,640	18,464	30,889	6,864	2,560
Choanoflagellates	0	0	13,273	0	16,999	0	5,821
Ciliates	11,480	6,880	1,880	15,760	4,320	480	840
Other taxa	296,631	678,244	971,759	1,191,835	336,870	167,663	305,075
Total	821,273	914,558	1,394,974	2,230,134	2,092,072	1,024,002	2,166,401

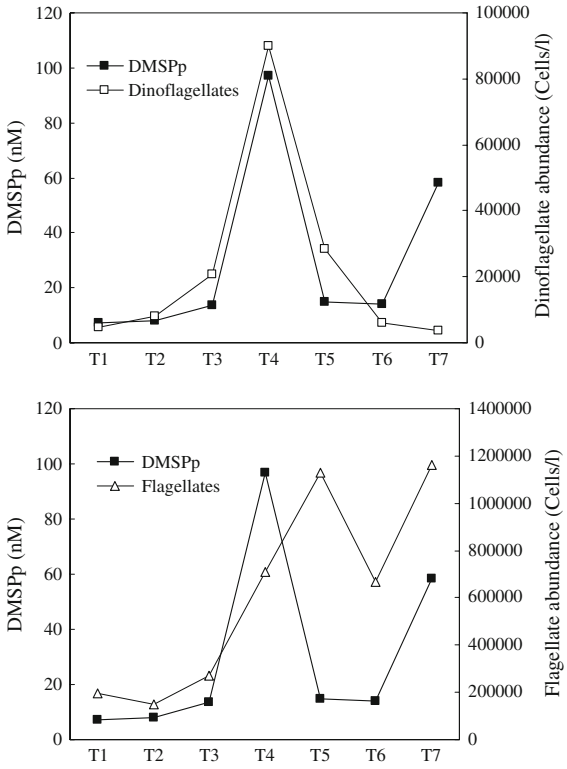

Fig. 4 Variation in DMSPp concentrations with variation in dinoflagellate (□) and flagellate (Δ) abundances in the microlayer

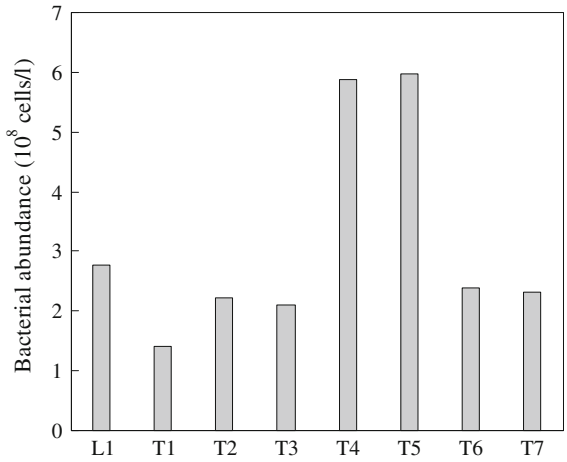

Fig. 5 Bacterial abundance in the microlayer

number of studies have reported that there is a definite link between the microbial food web and the oceanic cycling of DMS (Kiene and Bates 1990; Simó et al. 2002). However, in the present study, no significant relationship was found between bacterial abundances and DMS concentrations in the microlayer. This may be due to the complex role played by bacteria in controlling the concentration of DMS in marine surface waters, because bacteria not only mediate the production processes of DMS, but also participate in the consumption processes of DMS (Simó et al. 2002; Yoch 2002).

Relationships between the microlayer and bulk water concentrations

High concentrations of DMS and DMSPp in the microlayer were commonly observed where bulk water concentrations of those two sulfur constituents were also high (e.g., Stn T4). Similarly, low microlayer and bulk water concentrations of DMS and DMSPp appeared simultaneously at some stations (e.g., Stn T3). These data suggest that the distribution of DMS and DMSPp in the microlayer appear to be determined largely by their bulk water concentrations. As expected, the microlayer concentrations of DMS and DMSPp were correlated to their corresponding bulk water concentrations (Fig. 6, for DMS, $r^2 = 0.6176$, $n = 8$, $p = 0.0208$; for DMSPp, $r^2 = 0.7283$, $n = 8$, $p = 0.0070$). With respect to chlorophyll *a* and phaeopigments, variation in their microlayer concentrations followed roughly variation in their bulk water concentrations. It is not surprising that a linear correlation appeared between these two water body concentrations (Fig. 6, for chlorophyll *a*, $r^2 = 0.9915$, $n = 7$, $p = 0.0000$; for phaeopigments, $r^2 = 0.7850$, $n = 6$, $p = 0.0187$). In the spring 2003 cruise, we also found the significant relationships between the microlayer and subsurface water concentrations of DMS, DMSP and chlorophyll *a* (Yang et al. 2005a). These observations imply that microlayer concentrations generally co-vary with the corresponding bulk water concentrations.

DMS sea-to-air flux

The emission rates of DMS are generally estimated from the equation of Liss and Merlivat (1986), which assumes the sea-to-air flux (F) is proportional to the product of the concentration difference (ΔC) across the air-sea interface and a transfer velocity (K):

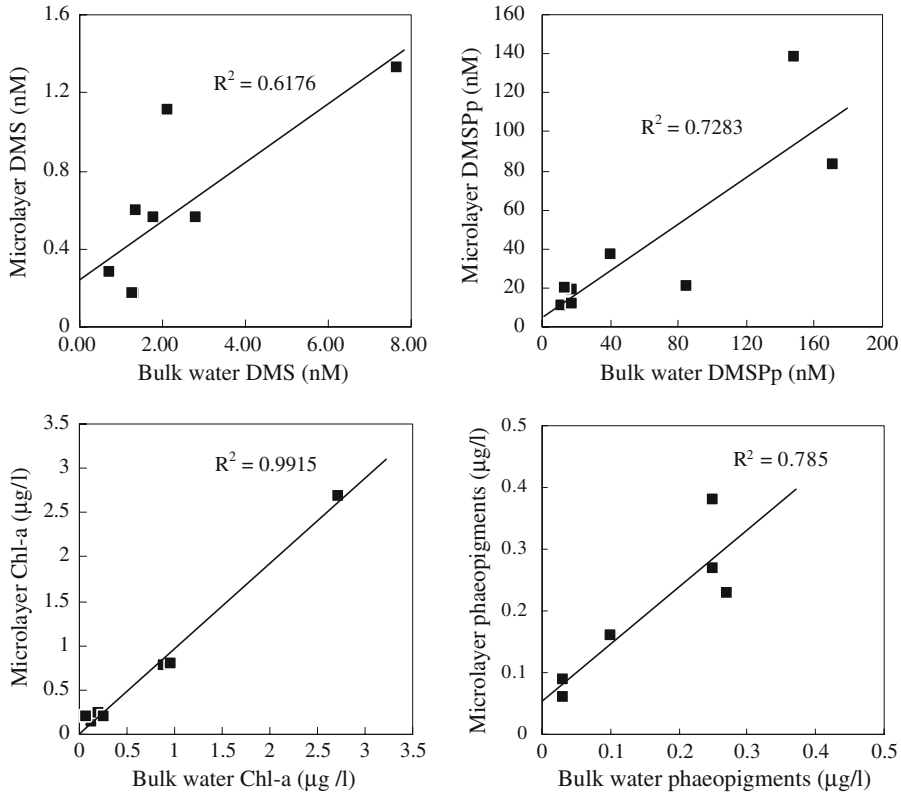

Fig. 6 Variation in the concentrations of DMS, DMSPp, chlorophyll *a* and phaeopigments in the microlayer with those in the bulk water

$$F = K\Delta C$$

ΔC is the difference between the water and air concentrations of DMS which is practically equal to the surface seawater DMS concentration, since atmospheric concentrations were insignificant with respect to the water concentrations. The transfer velocity (K) was calculated as a function of the wind speed (u_{10}) measured at the height of 10 m and the Schmidt number (Sc) (Liss and Merlivat 1986). The DMS Schmidt number at the local temperature is obtained from the equation of Saltzman et al. (1993). The F_{DMS} values estimated according the above approaches is listed in Table 2, together with the Sc and K_{DMS} values. The calculated fluxes are uncertain by at least a factor of two, due to uncertainties arising from basic model assumptions, the relative standard deviations of the individual model parameters, and K value of DMS. In addition, the intrinsic problems of microlayer sampling (Yang et al. 2001) might also contribute to uncertainties of the calculated fluxes. Nevertheless, the calculated fluxes are useful for at least a rough estimate of the summer emission flux of DMS from the study area to the atmosphere. The DMS sea-to-air flux ranged from 0.07 to 4.04 µmol m^{-2} d^{-1}, with a mean of 1.97 µmol m^{-2} d^{-1}. This flux agrees remarkably well with our gross estimate during the spring cruise, but about 50% lower in comparison with that (4.5 µmol m^{-2} d^{-1}) obtained in the western North Atlantic during May 1998 (Scarratt et al. 2002).

Concluding remarks

Results obtained from the field samples showed no consistent enrichment of DMS, DMSPp and chlorophyll *a* in the microlayer. However, all the microlayer samples were enriched with DMSPd in comparison with bulk water samples. In addition, the concentration of phaeopigments was also greater in the microlayer than in the bulk water. The enrichment of phaeopigments in the microlayer may be an evidence of enhancement of degradation processes in the microlayer. Our data indicated that both DMSPd and DMSPp concentrations in the bulk water tended to increase

with increasing phytoplankton biomass. The phytoneuston composition in the study area was dominated by flagellate cells, thus it is likely that flagellates were mainly responsible for the DMSPp levels. Moreover, we found a close correlation between the microlayer and bulk water concentrations of DMS, DMSPp and pigments, demonstrating that the microlayer materials were related to the bulk water below.

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