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**Spatial variations of dimethylsulfide and dimethylsulfoniopropionate in the surface
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Spatial variations of dimethylsulfide and dimethylsulfoniopropionate in the surface microlayer and in the subsurface waters of the South China Sea during springtime

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Abstract Spatial variations in dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) were surveyed in the surface microlayer and in the subsurface waters of the low productivity South China Sea in May 2005. Overall, average subsurface water concentrations of DMS and DMSP of dissolved (DMSP_d) and particulate (DMSP_p) fractions were 1.74 (1.00-2.50), 3.92 (2.21-6.54) and 6.06 (3.40-8.68) nM, respectively. No enrichment in DMS and DMSP_p was observed in the microlayer. In contrast, the microlayer showed a DMSP_d enrichment, with an average enrichment factor (EF, defined as the ratio of the microlayer concentration to subsurface water concentration) of 1.40. In the study area, none of the sulfur components were correlated with chlorophyll *a*. An important finding in this study was that DMS, DMSP and chlorophyll *a* concentrations in the surface microlayer were respectively correlated with those in the subsurface water, suggesting a close linkage between these two water bodies. The ratios of DMS:Chl-*a* and DMSP_p:Chl-*a* showed a gradually increasing trend from North to South. This might be due to changes in the proportion of DMSP producers in the phytoplankton community with the increased surface seawater temperature. A clear diurnal variation in the DMS and DMSP concentrations was observed at an anchor station with the highest concentrations appearing during the day and the lowest concentrations during the night. The higher DMS and DMSP concentrations during daytime might be attributed to the light-induced increase in both algal synthesis and exudation of DMSP and biological production of DMS. The mean flux of DMS from the investigated area to the atmosphere was estimated to be 2.06 $\mu\text{mol m}^{-2} \text{d}^{-1}$. This low DMS emission flux, together with the low DMS surface concentrations was attributed to the low productivity in this sea.

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Keywords: dimethylsulfide; dimethylsulfoniopropionate; microlayer; distribution; South China Sea

1. Introduction

Dimethylsulfide (DMS) produced by marine microbiota is by far the most abundant volatile sulphur compound found in surface water, occurring at supersaturated concentrations and, hence, giving rise to the major part of the sulfur flux from the oceans to the atmosphere. DMS is oxidized to products such as submicron-size sulphate and sulphonate particles, which contribute to atmospheric acidity and aerosols, the latter leading to cloud condensation nuclei (CCN), which have important consequences for the earth's radiation balance (Lovelock *et al.*, 1972; Wakeham *et al.*, 1984; Andreae, 1990). As a result, DMS is generally known to have a potential role in the global climate and in environmental changes.

The understanding of factors that regulate the near-surface concentrations of DMS in time and space is a significant and specific problem that hampers more accurate knowledge of the sea-to-air flux (Andreae, 1990). Seasonal studies of oceanic DMS concentrations have shown that average surface seawater DMS concentrations can vary by as much as a factor of 50 between summer and winter, ranging from approximately 0.2 nM in winter to 10 nM in summer (Leck *et al.*, 1990; Nguyen *et al.*, 1990; Berresheim *et al.*, 1991; Shenoy and Patil, 2003). This large variability necessarily introduces an uncertainty regarding the global estimates of the emission fluxes to the atmosphere. As a result, DMS data must be available from as many sites as possible for any estimate of the flux to be reliable.

DMSP, which is the main precursor of DMS, is considered to be the key link between algal cells and atmospheric DMS. DMSP acts as an osmolyte and compatible solution produced by certain groups of macro-

1 and micro-algae, having the similar structure as betaines. DMSP may constitute as much as 10% to 20% and
 2 50% to 90% of cellular organic carbon and sulfur, respectively (Bates *et al.*, 1994; Matrai and Keller, 1994;
 3 Matrai and Vernet, 1997). DMSP concentrations in seawater are usually much greater than DMS
 4 concentrations, which are generally lower than 10 nM, except in coastal waters. DMSP is found in particulate
 5 and dissolved fractions, referred to as DMSPp and DMSPd, respectively. Fractionation of the DMSP pool
 6 with particulate and dissolved phases shows that both can behave completely differently in the water column.
 7 DMSPd is believed to be more dynamic than DMSPp, with turnover times estimated to be on the order of
 8 hours in subtropical waters (Kiene *et al.*, 2000). DMSPd has been suggested as the source of most DMS, with
 9 partial conversion into DMS and partial metabolism to other products. Biosynthesis of intracellular DMSP is
 10 strongly species-dependent. It is generally thought that diatoms produce little DMSP while Dinophyceae and
 11 Prymnesiophyceae are important DMSP producers (Turner *et al.*, 1988; Keller *et al.*, 1989; Jean *et al.*, 2005).
 12 DMSP is released into seawater *via* a combination of processes involving the lysis of senescent cells, micro-
 13 and macro-zooplankton grazing, viral infections and then, converted into DMS by enzymatic cleavage
 14 (Dacey and Wakeham, 1986; Nguyen *et al.*, 1988). Because of its biogeochemical, ecological and
 15 biochemical implications, interest in DMSP is currently increasing and diversifying (Belviso *et al.*, 1990;
 16 Yang *et al.*, 2005a; Shenoy *et al.*, 2006; Jean *et al.*, 2006).

17 The sea surface microlayer has often been operationally defined as roughly the top several tens-several
 18 hundreds micrometres of the water surface, depending on the sampling method used (Liss and Duce, 1997).
 19 The microlayer has physical, chemical and biological properties that are measurably different from those of
 20 adjacent subsurface waters (Liss and Duce, 1997). Over the past two decades, although there has been a great
 21 advance in understanding the biogeochemical cycling of biogenic sulfur in the bulk seawater, there remain
 22 many unknowns in understanding the distribution of biogenic sulfur in the microlayer (Yang *et al.*, 2006).

The South China Sea is the largest marginal sea next to the western boundary of the tropical Pacific. It covers an area of $3.5 \times 10^6 \text{ km}^2$ and is characterized by high sea-surface temperatures and low productivity. Oligotrophy and low productivity of the South China Sea have caused great interest in the study of biogeochemistry of biogenic elements in this sea (Yang *et al.*, 1999). Nevertheless, in comparison with other China Seas distribution and emission of other sulfur compounds have received little attention. Considering the potential importance of DMS and thus DMSP in the global climate, an *in situ* investigation in the South China Sea was carried out to better understand the distribution of DMS and DMSP between the surface microlayer and the subsurface waters and its controlling factors. More generally this study produced a better knowledge of the DMS emission flux to atmosphere. Moreover, the enrichment factor (EF) of DMS(P) was calculated to evaluate their extent of enrichment in the microlayer relative to subsurface waters. This factor could be applied in studies carried out in other oceans and be of great importance to estimate the DMS contribution to the global climate. The present study represents the first comprehensive description of the distribution of DMS, DMSP and chlorophyll *a* in the surface microlayer of the South China Sea.

2. Methods

2.1. Sample collection

The cruise track for sampling in the South China Sea aboard the R/V “Dong Fang Hong No. 2” during May 2005 is shown in Fig. 1. This work was undertaken as part of the Chinese Surface Ocean–Lower Atmosphere Study (SOLAS). This cruise included 22 grid stations and one 24-hour anchor station. The environmental and hydrographic conditions for the sampling stations such as location, surface seawater

temperature and salinity are described in Table 1. The sampling stations, centered by S10, were set up according to $1^{\circ} \times 1^{\circ}$ resolution in the rectangular region from 115°E , 16°N – 118°E , 20°N . Additionally, seven stations (S17~S23) were scattered on a section of the continental shelf-continental slope-deep-sea basin.

Over 20 different sampling techniques have been applied to sample the sea surface microlayer (Hardy, 1982; Liss and Duce, 1997). Among these, the metal screen and the glass plate are the most commonly used samplers for microbiological and chemical investigations of the microlayer. Our field investigation showed that the screen sampler was superior to the glass plate in efficiency in collecting the microlayer DMS (Yang *et al.*, 2001). In the present study, the sea-surface microlayer samples were collected from the ship's stern using the screen sampler which was made of a 16-mesh stainless steel screen incorporated into a $40 \times 40 \text{ cm}^2$ stainless steel frame (Garret, 1965). In practice, the screen was placed through the water surface. It was then withdrawn horizontally (parallel to water) through the water surface and drained immediately into a sample bottle. Almost all (>95%) the seawater and sulfur species entrapped by the mesh spaces were retrieved from the screen sampler. This procedure was repeated until the sample bottle was filled. Approximately 20 surface contacts were required to collect a 0.6-liter sample. The sampling of the microlayer was generally achieved in 20 min. The physical thickness of the screen-collected microlayer sample was typically $200 \pm 10 \text{ }\mu\text{m}$. The subsurface water samples were simultaneously collected from a depth of 20 cm using a 1-liter brown glass bottle. The bottle was opened and closed in place to avoid surface microlayer interference. The surface seawater temperature (SST) and salinity data were obtained from the CTD apparatus (Richard Brancker, Canada).

2.2. DMS, DMSP and chlorophyll *a* analyses

1 Once collected, the DMS samples were immediately analyzed on board using a purge-and-trap
2 pre-concentration technique (Yang and Tsunogai, 2005). Briefly, the samples (typically 15 ml) were sparged
3 with high purity nitrogen at 40-50 ml/min for 15 min. The evolved gas was dried and then trapped in a
4 U-shaped tube packed with Tenax-TA at dry ice-ethanol temperature (-78°C). The trapped gases were then
5 desorbed with hot water ($\sim 90^{\circ}\text{C}$) and analyzed using a Shimadzu-14B gas chromatograph equipped with a
6 flame photometric detector. The chromatographic column used was a $2\text{ m} \times 3\text{ mm}$ glass column packed with
7 DEGS on Chromosorb W-AW-DMCS. Calibration was regularly performed by injecting known amounts of
8 DMS in an ethylene glycol solution into the bubbling chamber and treating them with the same procedure as
9 the samples. Replicate analyses were conducted for all the DMS samples. The analytical precision was
10 generally better than 5%. The detection limit for DMS was 0.1 nM.

11 DMSP was analyzed by alkaline cleavage to DMS with a 1:1 ratio (Dacey and Blough, 1987). For the
12 determination of DMSP_d, the sample was filtered through a Whatman GF/F filter (0.7 μm nominal retention).
13 The filtrate was placed into a 40 ml glass vial containing 2 ml of 10 M NaOH solution (with a final pH ~ 13.5).
14 The vial was immediately sealed, leaving no headspace. For the DMSP_p determination, the filter was quickly
15 placed into a 40 ml vial containing 2 ml of 10 M NaOH, which was immediately filled with distilled water
16 and sealed. The samples were left to react in the dark at room temperature for at least 24 h in order to
17 completely convert DMSP to DMS. The liberated DMS was measured using the method described above.
18 The precision of replicate DMSP determinations was generally better than 10%. The detection limit for
19 DMSP was 0.1 nM.

20 Chlorophyll *a* was measured fluorometrically with a Turner Design Fluorometer after filtration of 1000
21 ml of seawater on Whatman GF/F filter and extraction with 90% acetone (Parsons *et al.*, 1984).

22

3. Results and discussion

Since the South China Sea is situated in the tropical zone, its sea-surface temperature is consistently high, not dropping below 22°C throughout the year. The photic zone depth is also persistently deep and exceeds the mixed-layer depth and the top of the nutricline in most of the year (Tseng *et al.*, 2005). Thus, the primary production in the South China Sea is not limited by the availability of light, but the availability of the nutrients. A multitude of rivers bring an abundance of terrestrial material into the South China Sea and contribute to high sedimentation rates, at several cm kyear⁻¹, especially from April to September (Lee *et al.*, 1999). However, the basin-wide surface circulation gyres effectively isolate the interior of the South China Sea proper from the influence of land-runoff. As a result, the deep central South China Sea is still oligotrophic, like the interior of the major ocean basins. Besides, the South China Sea is situated between the western Pacific warm pool and the Tibetan Plateau, which is under the persistent influence of monsoonal winds: a strong northeast monsoon between November and April and a weaker southwest monsoon between June and September. Between these two monsoonal seasons, in May and October, the wind is weak and variable (Liu *et al.*, 2002). These monsoonal winds play a major role in the oceanography of the South China Sea.

3.1. DMS, DMSP and chlorophyll *a* concentrations in the subsurface water

Table 1 presents SST, salinity and water depth in the study area. Throughout the study area, surface water salinity varied little while SST strongly varied from 30.41°C to 24.83°C. In the South China Sea, owing to the pycnocline, deeper nutrient-rich water does not reach the surface (Yang *et al.*, 1999). Nutrient

1 limitation in surface water, together with high solar radiation, makes the South China Sea a low-productivity
 2 region (Han, 1998). Therefore, very low concentrations of chlorophyll *a* with a mean of 0.08 $\mu\text{g L}^{-1}$ were
 3 found in the study area. However, DMS concentrations were obviously higher than those expected based on
 4 the phytoplankton biomass in this region. The highest DMS concentration of 2.50 nM was observed at shelf
 5 station S23 where elevated inputs of continental-derived nutrients and organic matter occurred. Overall DMS
 6 concentrations in the subsurface water averaged to 1.74 nM. In oligotrophic waters, DMSP production was
 7 mostly associated with small algae that contributed little chlorophyll *a* but were better adapted to high light
 8 and nutrient deficiency (Kiene *et al.*, 2000). The field investigation has shown that the oligotrophic South
 9 China Sea contains abundant dinoflagellates which account for 43% of the total phytoplankton species, far
 10 exceeding other areas in China Seas (Han, 1998). This class of alga may be a major source of the relatively
 11 high DMS levels in this chlorophyll-poor sea.

12 Along the section of continental shelf–continental slope–deep-sea basin, namely from station S23 to
 13 station S17, DMS displayed a general decrease in concentration with distance from the land, with the low
 14 concentrations found in the open sea. This was in good agreement with the previous studies which showed
 15 that the concentrations of DMS in the oceans generally exhibited a latitudinal variation with higher values at
 16 high latitudes and lower values in equator areas (Cline and Bates, 1983; Nguyen *et al.*, 1990; Berresheim *et*
 17 *al.*, 1991).

18 In the present study, the highest DMSPd concentration was observed at station S11 and the lowest
 19 value was measured at the open sea station S16. The mean concentration of DMSPd was 3.92 nM,
 20 dominating over that of DMS. In comparison, the concentrations of DMSPp showed greater variations than
 21 those of DMSPd and DMS, with the maximum value (8.68 nM) appearing at station S22 and the minimum
 22 value (3.40 nM) occurring at station S19. Total DMSPp concentrations averaged 6.06 nM. In the study area,

DMSPd and DMSPp did not display the same distribution pattern as chlorophyll *a* or DMS. For example, continental shelf station S22 and pelagic station S17 revealed a similar chlorophyll *a* level, but DMSPd and DMSPp concentrations at station S22 were evidently higher than at station S17. Chlorophyll *a* concentrations were basically equal at two adjacent stations, S1 and S8, whereas DMSPd and DMSPp concentrations at the two sites differed largely. As a consequence, no correlation appeared between these parameters.

3.2. DMS, DMSP and chlorophyll *a* concentrations in the microlayer and their enrichment factors

The distribution of DMS in the microlayer revealed a consistent pattern with that in the subsurface water, with the maximum concentration existing at station S23 and the minimum value occurring at station S21. A statistically significant relationship ($r^2=0.4003$, $n=22$, $p=0.0016$) was found between the microlayer and subsurface water concentrations of DMS, suggesting that variation in the microlayer DMS concentration followed roughly the variation with its subsurface water concentration. In comparison with the subsurface water, the surface microlayer exhibited a greater spatial variability in the DMSPd concentrations with a range of 2.70-8.95 nM (mean: 5.18 nM). Like the case of DMS, the microlayer DMSPd concentrations were also correlated to its subsurface water concentrations ($r^2=0.4048$, $n=22$, $p=0.0015$). Similarly, the microlayer DMSPp and chlorophyll *a* concentrations were also respectively correlated with their subsurface water concentrations (for DMSPp, $r^2=0.4373$, $n=22$, $p=0.0008$; for chlorophyll *a*, $r^2=0.5147$, $n=20$, $p=0.0004$) (Fig. 2). The above observations suggested that material in the microlayer was directly dependent upon the diffusive supply from the bulk liquid below. Throughout the study period, our sampling of the surface microlayer proceeded on a calm sea surface at a relatively low wind speed, which indicated that vertical mixing of microlayer water with bulk water might play a minor part in determining the distribution of DMS

and DMSP between these two water compartments in the study area. So other transport processes such as molecular diffusion and thermodiffusion may act as the major controlling factors for the exchange of substance between the microlayer and bulk water. In addition to the above physical processes, some biological factors such as the planktonic migration might also play a role.

The microlayer is a region where physical, chemical and biological properties are most altered relative to subsurface water. Many previous studies have demonstrated that the surface microlayer is characterized by enhanced levels of various particulate and dissolved organic substances (Hardy, 1982). The enrichment factor EF is defined as the ratio of the microlayer concentration (C_M) to subsurface water concentration (C_S), which was used to indicate the extent of enrichment of material in the microlayer relative to subsurface water (Liss and Duce, 1997). As shown in Table 2, the EFs of DMS ranged between 0.53 and 1.19, with only two stations showing EF value larger than unity, indicating that no microlayer enrichment occurred for DMS. Recently, it was demonstrated that photochemical process might be important in the removal of DMS in the photic zone (Brugger et al., 1998). The microlayer is exposed to more intense solar radiation relative to the subsurface water and may enhance DMS photochemical loss. This is a probable reason why the DMS concentrations and thus derived EF values were lower in the microlayer.

In contrast, EFs for DMSPd varied in a larger range from 0.78 to 2.56 with an average of 1.40, indicating that DMSPd was accumulated to a small extent in the microlayer. This could be attributed to the Gibbs surface adsorption process (Adamson, 1976), since high surface tension of the air-water interface energetically favors adsorption of dissolved organic substances such as DMSPd. However, compared with our results obtained in the Yellow Sea of China (unpublished data), the EFs of DMSPd in the South China Sea was smaller, namely the continental shelf water samples showed a greater enrichment degree than the open sea samples. The complexity of physical factors affecting the enrichment of DMSP in the microlayer

1 had been discussed by Yang and Tsunogai (2005). Besides physical factors, biological activity may also affect
 2 the enrichment of material in the microlayer (Yang *et al.*, 2001; Yang and Tsunogai, 2005). In a previous
 3 investigation for Funga Bay, Japan, we found that high concentrations of DMSP in the microlayer generally
 4 appeared in the samples which contained high levels of chlorophyll *a*, suggesting that *in situ* production from
 5 phytoplankton may be an extremely important source for the microlayer DMSP (Yang *et al.*, 2005b). In a
 6 recent survey for the western North Atlantic, we further found that great microlayer enrichments of DMSPd
 7 were observed mostly during the phytoplankton bloom when chlorophyll *a* appeared to have accumulated in
 8 the microlayer (Yang *et al.*, 2005a). This may be attributed to the enhanced production of DMSPd in the
 9 microlayer, due to higher phytoplankton biomass here. The above observation suggested that chlorophyll *a*
 10 enrichment extent in the microlayer might be an important factor affecting the extent of enrichment of DMSP
 11 in the microlayer. Therefore, the smaller enrichment degree of DMSPd in the surface microlayer of the South
 12 China Sea may be partially attributed to very low chlorophyll *a*.

13 In comparison to DMSPd, DMSPp did not show significant enrichment in the microlayer with reference
 14 to the underlying water. The microlayer surface tension is generally an important factor for controlling the
 15 extent of enrichment of particulate species. It is known that phytoplankton can produce large amounts of
 16 surface-active materials (Frew *et al.*, 1990). These surface-active materials readily adsorb from seawater onto
 17 the surface of suspended particles, which is likely to make them adhere to the air-water interface. However,
 18 phytoplankton biomass in the study area was considerably low, as indicated by the chlorophyll *a* levels (Table
 19 2). The low phytoplankton biomass, together with inadequacy of nutrients in the surface seawater (according
 20 to investigative data obtained during the same cruise), made primary productivity here very low. This would
 21 lead to “clean seawater” and hence low surface tension in the microlayer. This force seemed not to be enough
 22 to stabilize particles at the air-sea interface. Therefore, no significant enrichment of DMSPp in the microlayer

was expected in the study area. Besides, gravitational precipitation process of particles from the microlayer to bulk water may also contribute to little difference in the DMSPp concentrations between the microlayer and subsurface water and thus low extent of enrichment of DMSPp in the microlayer.

3.3. Ratios of DMS:Chl-a and DMSPp:Chl-a in the subsurface water and surface microlayer

The ratios of DMS:Chl-a and DMSP:Chl-a can be used to compare the distribution of the biogenic sulfur in different trophic regions (Belviso *et al.*, 2000). In the subsurface water, the highest DMS:Chl-a ratio was found at station S2 where chlorophyll *a* concentration was the minimum, while the lowest ratio was observed at station S19 with relatively low DMS concentration. In comparison, the DMS:Chl-a values in the microlayer were slightly lower than those in the subsurface water, due to lower DMS concentrations here. The total average of DMS:Chl-a in the microlayer and subsurface water was 17.80 and 22.90 mmol g⁻¹, respectively. The similar distribution pattern was also observed for the DMSPp:Chl-a, with average ratios of 83.80 mmol g⁻¹ in the microlayer and 77.90 mmol g⁻¹ in the subsurface water, respectively. Both DMS:Chl-a and DMSPp:Chl-a ratios obtained in this study were typical of oligotrophic ocean waters, in good agreement with previous studies (Iverson *et al.*, 1989; Besiktepe *et al.*, 2004).

In the present study, sampling stations were divided into five transects: T1 (S17-S23), T2 (S13-S16), T3 (S9, S11, S12), T4 (S5-S8) and T5 (S1-S4). The DMS:Chl-a and DMSPp:Chl-a ratios at all stations and their averages in each transect were plotted in Fig. 3. From Fig. 3 it is apparent that the average ratio of DMS:Chl-a in each transect showed a gradually increasing trend from north to south (i.e. from T1 to T5) in the microlayer as well as in the subsurface water. The spatial changes in DMSPp:Chl-a ratios also exhibited a similar trend, indicating an increase in the proportion of DMSP producers in the total phytoplankton

1 assemblage. According to the previous study by Zhu *et al.* (2003), the phytoplankton community in the
2 summer South China Sea was dominated mainly by diatoms, dinoflagellates and cyanobacteria. Along with
3 the increase of SST from North to South, the dominant phytoplankton species changed gradually from
4 eurytopic group (e.g., diatoms) to warm water group such as dinoflagellates and cyanobacteria which are
5 generally considered to be prolific producers of DMSP. This may clearly explain why DMSPp:Chl-a ratios
6 increased gradually from T1 to T5.

8 *3.4. Diurnal variations in DMS and DMSP*

10 The diurnal changes in DMS and DMSP concentrations in the surface microlayer and subsurface
11 water were investigated at an anchor station S10, as shown in Fig. 4. It is clear from Fig. 4 that DMS
12 concentrations were the highest at 09:00 and the lowest at 00:00 in the subsurface water. DMS concentration
13 in the microlayer exhibited a similar change trend to that in the subsurface water. The increase in DMS
14 concentration in the morning might be attributed to a physiological response of algae to the increase in
15 sunlight irradiance or the photoinhibition of bacterial DMS consumption. From 09:00 to 15:00, the DMS
16 concentrations gradually decreased, probably due to enhanced photo-oxidation loss. The DMS concentration
17 remained relatively constant throughout the night but obviously lower than that in the daytime. The lower
18 DMS concentration in the night might be associated with its low biological production rate or high bacterial
19 consumption rate at the same time.

20 In comparison, DMSP showed a different variation pattern from DMS. DMSPd and DMSPp
21 concentrations in the subsurface water exhibited larger variations than DMS, with high value at noon and low
22 values in the night. The diel variation of DMSPd and DMSPp in the microlayer showed a similar pattern to

that in the subsurface water, with high values appearing in the afternoon and low values occurring during the night. Our observation may be supported by some previous researches which showed that DMSP production in unicellular algae was a diurnal process proportional to photosynthesis (Kuipers *et al.*, 2000; Simó *et al.*, 2002; Merzouk *et al.*, 2004). For instance, Simó *et al.* (2002) showed a light-induced increase in algal synthesis and exudation of DMSP which exhibited a diel pattern peaking around noon. Kuipers *et al.* (2000) found that solar UV radiation could inhibit bacterial activity and growth, causing an accumulation of DMSP during daytime.

3.5. Sea-to-air fluxes of DMS in the study area

Using the surface microlayer DMS concentrations presented here, we have made an estimate of the emission flux of DMS from the South China Sea to the atmosphere according to the equation of Liss and Merlivat (1986):

$$F = K\Delta C$$

where K is the transfer velocity of DMS in the water phase, and ΔC is the concentration difference of DMS in seawater and the atmosphere, assumed to be equal to the aqueous concentration, C_w , since atmospheric concentration of DMS was very low. The transfer velocity K was calculated as a function of the wind speed and the Schmidt number (Sc) (Liss and Merlivat, 1986). The Sc of DMS at the local temperature was derived from the equation put forward by Saltzman *et al.* (1993). The F_{DMS} values estimated according to the above approaches were presented in Table 3.

In the present study, the DMS fluxes ranged from 0.01 to 5.77 $\mu\text{mol m}^{-2} \text{d}^{-1}$ with an average of 2.06 $\mu\text{mol m}^{-2} \text{d}^{-1}$. It is lower than the DMS flux value of 7.6 $\mu\text{mol m}^{-2} \text{d}^{-1}$ obtained in the Nansha Islands area of

the South China Sea in winter (Yang *et al.*, 1999), which was primarily due to the great difference in the wind speeds during the sampling periods. Also, it is reasonably lower than the DMS flux value of $3.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ estimated by Yang *et al.* (2000) in the East China Sea which exhibited obviously higher primary productivity and DMS levels than the tropical South China Sea. However, our results were consistent with that reported by Simó *et al.* (1997) in the western Mediterranean waters, which was of $2.7 \mu\text{mol m}^{-2} \text{d}^{-1}$.

4. Conclusions

The present study provides further information for understanding the distribution of DMS, DMSPd and DMSPp in the sea-surface microlayer and subsurface water. In the study area, DMS displayed a general decrease in concentration with distance from the land, with the low concentrations found in the open sea. The data presented here demonstrated that variation in the DMS, DMSPd, DMSPp and chlorophyll *a* concentrations in the surface microlayer followed closely variation with those in the subsurface water. Thus, it is likely that the materials in the microlayer will be dependent upon the diffusive supply from the bulk liquid below. It is worth noting that increased DMS(P):Chl-*a* ratios from North to South corresponded to increased seawater temperatures resulting in changes in the phytoplankton community. Our study showed that the DMS, DMSPd and DMSPp concentrations exhibited a clear diurnal variation with the highest values observed during the daytime and the lowest valued found in the night. This pattern may indicate a light-induced increase in algal synthesis and exudation of DMSP. Consequently, temporal variations in biogenic DMS output from the surface waters may be explained by the variation in solar radiation. Of the three sulfur components investigated in the study, only DMSPd appeared to be significantly enriched in the microlayer. However, the influence of environmental factors upon the distribution and enrichment of DMSPd

in the microlayer has not been fully understood and is worthy of further study.

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Table Captions

Table 1. Description of the sampling stations.

Table 2. Distribution of DMS, DMSPd, DMSPp and chlorophyll *a* in the surface microlayer and in the subsurface waters of the South China Sea during May 2005.

Table 3. The calculated Sc and K_{DMS} values and sea-to-air fluxes of DMS in the South China Sea.

1

2

Table 1. Description of the sampling stations.

Station	Latitude	Longitude	Salinity	SST (°C)	Water Depth (m)
S1	N 16°01'80"	E 115°06'99"	34.126	28.75	4177
S2	N 16°00'20"	E 116°00'05"	34.025	29.43	4175
S3	N 16°00'28"	E 117°00'60"	34.143	30.41	4204
S4	N 16°00'16"	E 117°59'34"	34.151	29.63	4830
S5	N 17°00'55"	E 118°00'05"	34.115	29.11	4236
S6	N 16°59'59"	E 116°58'59"	34.108	29.37	3990
S7	N 17°00'83"	E 115°59'72"	34.298	29.26	4013
S8	N 17°00'10"	E 115°00'50"	34.051	29.00	2490
S9	N 18°04'01"	E 115°01'47"	34.483	28.43	3700
S10	N 17°82'97"	E 115°87'11"	34.470	28.80	3844
S11	N 18°00'44"	E 117°00'81"	34.187	29.32	3930
S12	N 18°00'14"	E 118°00'14"	34.249	29.40	4300
S13	N 18°59'85"	E 117°59'68"	34.278	28.21	3733
S14	N 19°00'10"	E 117°00'13"	34.461	27.64	3700
S15	N 18°59'76"	E 116°02'72"	34.264	28.00	3000
S16	N 19°00'51"	E 115°01'53"	34.301	27.98	2240
S17	N 19°21'92"	E 116°36'09"	34.481	27.89	2156
S18	N 19°44'07"	E 116°12'10"	34.443	27.17	1773
S19	N 20°06'08"	E 115°48'01"	34.464	26.58	979
S20	N 20°21'01"	E 115°37'17"	34.441	26.59	520
S21	N 20°33'03"	E 115°27'88"	34.413	26.38	302
S22	N 20°42'30"	E 115°75'46"	34.596	25.29	230
S23	N 20°45'49"	E 115°15'14"	34.610	24.83	195

3

Table 2. Distribution of DMS, DMSPd, DMSPp and chlorophyll *a* in the surface microlayer and subsurface water of the South China Sea during May 2005.

Station no.	DMS (nM)			DMSPd (nM)			DMSPp (nM)			Chlorophyll <i>a</i> ($\mu\text{g L}^{-1}$)		
	C_S^a	C_M^b	EF^c	C_S	C_M	EF	C_S	C_M	EF	C_S	C_M	EF
S1	1.88	1.59	0.85	6.31	7.51	1.19	8.16	8.88	1.09	0.074	0.062	0.84
S2	1.61	1.07	0.66	2.89	3.52	1.22	5.98	4.85	0.81	0.047	0.047	1.0
S3	1.00	1.02	1.02	2.59	3.05	1.18	6.41	6.92	1.08	n.d.	0.076	n.d.
S4	2.02	1.55	0.77	4.95	5.70	1.15	6.28	7.48	1.19	0.067	0.056	0.84
S5	1.70	1.22	0.72	4.88	5.40	1.11	8.45	7.06	0.84	0.076	0.060	0.79
S6	1.85	1.05	0.57	5.01	5.80	1.16	6.59	4.36	0.66	0.076	0.045	0.59
S7	2.08	1.21	0.58	2.42	5.20	2.15	5.20	4.52	0.87	0.081	0.069	0.85
S8	1.66	1.17	0.70	2.95	5.79	1.96	5.20	5.11	0.98	0.070	0.050	0.71
S9	1.41	1.32	0.94	3.20	6.60	2.06	3.89	4.50	1.16	0.065	0.100	1.5
S11	1.63	1.94	1.19	6.54	8.95	1.37	6.76	8.05	1.19	0.067	0.091	1.4
S12	1.66	1.05	0.63	2.55	5.13	2.01	5.67	7.23	1.28	n.d.	0.071	n.d.
S13	1.88	1.41	0.75	3.42	5.57	1.63	7.80	7.80	1.00	0.12	0.15	1.3
S14	1.70	1.23	0.72	2.58	3.94	1.53	5.92	7.05	1.19	0.091	0.086	0.95
S15	2.04	1.78	0.87	4.82	5.26	1.09	7.18	7.07	0.98	0.088	0.11	1.3
S16	2.05	1.65	0.80	2.21	2.97	1.34	4.52	5.85	1.29	0.072	0.072	1.0
S17	1.61	1.04	0.65	4.70	4.40	0.94	3.77	3.90	1.03	0.088	0.075	0.85
S18	1.60	1.01	0.63	3.47	2.70	0.78	5.75	6.27	1.09	0.098	0.095	0.97
S19	1.32	1.23	0.93	2.51	6.43	2.56	3.40	5.20	1.53	0.085	0.091	1.1
S20	1.46	0.81	0.55	3.23	3.31	1.02	5.50	5.59	1.02	0.086	0.095	1.1
S21	1.52	0.90	0.59	3.49	4.30	1.23	4.68	4.42	0.94	0.069	0.052	0.75
S22	2.05	1.42	0.69	5.74	5.33	0.93	8.68	7.55	0.87	0.086	0.072	0.84
S23	2.50	1.95	0.78	5.76	7.00	1.21	7.42	4.58	0.62	0.095	0.090	0.95
Average	1.74 $\pm$ 0.09 ^d	1.30 $\pm$ 0.07	0.75 $\pm$ 0.11	3.92 $\pm$ 0.34	5.18 $\pm$ 0.45	1.40 $\pm$ 0.15	6.06 $\pm$ 0.51	6.10 $\pm$ 0.57	1.03 $\pm$ 0.13	0.080	0.078	0.98

^a The subsurface water concentration;

^b The microlayer concentration;

^c The ratio of C_M to C_S ;

^d Mean $\pm$ mean standard deviation

Table 3. The calculated Sc and K_{DMS} values and sea-to-air fluxes of DMS in the South China Sea.

Station no.	Wind speed* (m s^{-1})	Sc	K_{DMS} (cm h^{-1})	F_{DMS} ($\mu\text{mol m}^{-2} \text{d}^{-1}$)
S1	6.2	621	7.84	2.99
S2	4.6	603	3.44	0.88
S3	1.2	577	0.21	0.05
S4	2.9	598	0.49	0.18
S5	0.3	611	0.05	0.01
S6	4.7	605	3.72	0.94
S7	6.4	607	8.50	2.47
S8	1.4	614	0.23	0.06
S9	9.9	630	18.0	5.70
S11	2.0	606	0.34	0.16
S12	2.5	604	0.42	0.11
S13	3.0	636	0.49	0.17
S14	6.7	652	9.01	2.66
S15	8.3	642	13.5	5.77
S16	7.1	642	10.2	4.04
S17	5.7	645	6.32	1.58
S18	5.9	665	6.76	1.64
S19	7.2	683	10.1	2.98
S20	8.2	682	12.8	2.49
S21	8.7	688	14.1	3.05
S22	7.8	722	11.4	3.89
S23	6.2	737	7.18	3.36
Average	5.3	640	6.59	2.06

*Measured at 10 m height

Figure Captions

Fig. 1. Location of the sampling stations in the South China Sea.

Fig. 2. Variations in the microlayer DMS, DMSPd, DMSPp and chlorophyll *a* concentrations with their subsurface water concentrations.

Fig. 3. Diagram of DMS and DMSPp:chlorophyll *a* ratios in all the seawater samples.

Fig. 4. Diel variations in chlorophyll *a*, DMS and DMSP at anchor station S10.

Fig. 1. Location of the sampling stations in the South China Sea.

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