Temporal variations of dimethylsulfide and dimethylsulfoniopropionate in the southern Yellow Sea in spring and autumn

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Received 30 July 2014; accepted 26 February 2015

Abstract

Temporal distributions of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) were studied in the southern Yellow Sea (SYS) during April and September 2010. The mean concentrations (range) of DMS, dissolved and particulate DMSP (DMSPd and DMSPp) in the surface waters in spring are 1.69 (0.48–4.92), 3.18 (0.68–6.75) and 15.81 (2.82–52.33) nmol/L, respectively, and those in autumn are 2.80 (1.33–5.10), 5.45 (2.19–11.30) and 30.63 (6.24–137.87) nmol/L. On the whole, the distributions of DMS and DMSP in spring are completely different from those in autumn. In the central part of the SYS, the concentrations of DMS and DMSP in spring are obviously higher than those in autumn, but the opposite situation is found on the south of 34°N, which can be attributed to the differences in nutrients and phytoplankton biomass and composition between spring and autumn. Besides, the seasonal variations of water column stability and the Changjiang diluted water also have significant impact on the distributions of DMS and DMSP in spring and autumn on the south of 34°N. DMS and DMSPp concentrations coincide well with chlorophyll $a$ (Chl $a$) levels in the spring cruise, suggesting that phytoplankton biomass may play an important role in controlling the distributions of DMS and DMSP in the study area. Annual DMS emission rates range from 0.015 to 0.033 Tg/a (calculated by S), respectively, using the equations of Liss and Merlivat (1986) and Wanninkhof (1992). This result implies a significant relative contribution of the SYS to the global oceanic DMS fluxes.

Key words: dimethylsulfide, dimethylsulfoniopropionate, chlorophyll $a$, sea-to-air flux, the southern Yellow Sea

Citation: Yang Jian, Yang Guipeng, Zhang Honghai, Zhang Shenghui. 2016. Temporal variations of dimethylsulfide and dimethylsulfoniopropionate in the southern Yellow Sea in spring and autumn. Acta Oceanologica Sinica, 35(2): 76–87, doi: 10.1007/s13131-015-0780-y

1 Introduction

Dimethylsulfide (DMS) is an important sulfur trace gas of climatic significance. In recent years, more and more attentions have been paid to DMS and its related compounds since Lovelock et al. (1972) pointed out that DMS was enriched in the sea surface and led to a significant sea-to-air flux. DMS in sea water, which takes a large proportion in biogenic sulfur emissions from the ocean, plays an important climatic role by forming methanesulfonate (MSA) and sulfate aerosols in the atmosphere, finally leading to the formation of cloud condensation nuclei and thereby influencing cloud albedo (Charlson et al., 1987). In addition, DMS could also contribute to the acidity of rainfall (Bates et al., 1987; Nguyen et al., 1992).

DMS is produced in the ocean from the cleavage of dimethylsulfoniopropionate (DMSP) by DMSP-lyases contained in some marine bacteria and a few species of phytoplankton, where it acts as a compatible solute to counter various stresses, including osmotic, oxidative, and potential damage by UV light (Sunda et al., 2002). Dinoflagellates and prymnesiophytes are known to be important DMSP producers, while diatoms generally contain low DMSP concentration (Keller et al., 1989). However, Shenoy et al. (2006) reported that DMS was linearly related to the ratio of chlorophyll $a$/phaeopigments in some diatom-dominated waters, suggesting that diatoms also might play an important role in the biogeochemical cycling of DMS. Besides, the cleavage and release of DMSP could be accelerated by algal senescence, grazing or viral attack (Dacey and Wakeham, 1986; Levasseur et al., 1996; Li et al., 2010). Once DMS is produced in sea water, it is rapidly removed by various processes such as bacterial metabolism, photochemical oxidation and emission to the atmosphere. Gál et al. (2011) reported that bacterial consumption was the dominant sink for DMS which accounted for 9%–73% of its loss in the upper mixed layer in the arctic, while photolysis became the dominant sink at some stations which occupied 12%–65% of the total DMS loss. In contrast, the sea-to-air emission may represent only a small fraction of sink for DMS in sea water, even though the total amount of DMS emanating from the ocean to the atmosphere is significant on a global scale (Bates et al., 1994).
The concentrations of DMS in the sea surface show a considerable spatial and temporal variation (Kettle and Andreae, 2000; Uher et al., 2000). In general, higher values of DMSP and DMS are found in eutrophic coastal areas and in the regions of upwelling than in oligotrophic open ocean waters. Shenoy and Dileep Kumar (2007) reported that the highest concentrations of DMS and DMSP were found in upwelling regimes along the west coast of India in the monsoon seasons. Besides, due to differences in environmental, biological and chemical factors, the concentrations of DMS and DMSP varied significantly with season. Shenoy and Patil (2003) reported the significant variability in DMSP and DMS concentrations after 14 months of observation, with the maximal concentrations occurring in the dinoflagellate bloom season. Although the great efforts have been made to investigate the distributions of DMS and DMSP in the marginal seas of China (Yang et al., 2000, 2006, 2008, 2012), very limited data are available for the comparison of variations in DMS and DMSP among different seasons in the marginal seas of China. For instance, Yang et al. (2011) investigated the spatial-temporal variations of DMS and DMSP in the East China Sea and the SYS during summer and winter. In the present study, we investigated the spatio-temporal distributions of DMS and DMSP in the SYS during spring and autumn and probed into biogeochemical factors influencing their seasonal availability, such as nutrients and phytoplankton biomass. The sea-to-air fluxes of DMS in the study area were also calculated for assessing the contribution of the SYS to global oceanic DMS emissions.

2 Methods

2.1 Study area

The Yellow Sea is a shallow, semi-enclosed marginal sea of the northwest Pacific Ocean with an average depth of about 44 m. It is located between China and Korea and is bounded to the north by the Bohai Sea and to the south by the East China Sea. The boundary between the northern Yellow Sea and the SYS is often taken to be from the Chengshan Cape to the Changsan-got. The SYS is dominated by a strong northerly monsoon from late November to early April. By the end of May, the southerly wind begins and continues throughout the summer (Mask et al., 1998). Spring and autumn are the transitional seasons when the wind direction is variable.

The hydrographic characteristics of the SYS are greatly influenced by some circulations, including the Yellow Sea Warm Current on the eastern side and the Subei coastal current on the western side. The Yellow Sea Warm Current is a branch of the Tsushima Warm Current and flows from the southeast to the northwest, with a characteristic of high temperature and high salinity (Su, 1998). It is widely accepted that the Yellow Sea Warm Current is stronger in winter and is very weak or vanishes in summer, with a significant impact on the transport of mass and a heat flux between the East China Sea and the Yellow Sea (Zhang et al., 2008). A tidal front divides the SYS into the well-mixed shallow regions and the highly stratified deeper regions occupied by the Yellow Sea Cold Water Mass (Liu et al., 2008). The Yellow Sea Cold Water Mass forms in late spring and disappears in late autumn for about half a year, which plays an important role in controlling the phytoplankton biomass and the primary production in the Yellow Sea by recycling of chemical substances under the confluence of warm and cold waters. In the mixed shallow regions, abundant land-source materials can be emptied into the Yellow Sea along the river, especially in the Changjiang River Estuary and its adjacent areas. In spring, under the high runoff and the prevailing southerly monsoon, a part of Changjiang diluted water with a large amount of nutrients extends to the northeast into the Subei coastal area that provides conditions favorable for the biologic production in the coastal waters.

2.2 Sampling

Two cruises were conducted aboard the R/V Dongfanghong No. 2 in the SYS from 21 to 29 in April and from 8 to 15 in September of 2010, respectively. The sampling stations are shown in Fig. 1. The surface water samples were collected using 12 L Niskin bottles mounted on a Seabird 911 CTD. Detailed information about the sampling stations and hydrographic parameters are described in Table 1 (spring) and Table 2 (autumn). The surface water temperature, the salinity and the water depth were obtained from the CTD apparatus.

2.3 Analytical procedures

All DMS samples were immediately analyzed on board after...
of sea water sample was filtered under gravity through a Whatman GF/F filter. The filtrate was added into a 40 mL brown glass vial containing 2 mL of 10 mol/L KOH solution and immediately crimp-sealed with a rubber septum and aluminum lid, leaving no headspace. For DMSPa sample, the filter was rapidly placed in another vial filled with 38 mL distilled water and 2 mL of 10 mol/L KOH solution and then sealed. These DMSPa samples were alkali-hydrolyzed in the dark at 4°C for at least 24 h. DMS generated from the breakdown of DMSP was analyzed as described above. The concentration of DMSF was calculated by subtracting DMS concentration from the sum of DMS and DMSF concentrations.

For chlorophyll a analysis, 300 mL of sea water was filtered through 47 mm Whatman GF/F filter and the filters were soaked in 10 mL 90% acetone which were kept in the dark at 4°C. After 24 h, the concentrations of chlorophyll a were measured using a HITACHI F-4500 fluorometer according to Parsons et al. (1984). The filtrate was poured into a 100 mL plastic bottle and kept in -20°C for nutrients determination. The concentrations of nitrate (NO$_3^-$), nitrite (NO$_2^-$), ammonium salt (NH$_4^+$), phosphate (PO$_4^{3-}$) and silicate (SiO$_2^{4-}$) were quantified using an autoanalyzer (Seal Analytical AA3). The dissolved inorganic nitrogen (DIN) concentration is the sum of NO$_3^-$, NO$_2^-$ and NH$_4^+$ concentrations.
Mixed layer depth was defined as the depth at which the water density increased by 0.03 kg/m³ or the temperature dropped by 0.1°C (Lee et al., 2010).

The sea-to-air flux of DMS can be calculated according to the equation of Liss and Merlivat (1986),

$$F = K \Delta c_{DMS} = K c_{W},$$

where $K$ is the gas transfer coefficient, $\Delta c_{DMS}$ is the concentration difference of DMS in sea water and the atmosphere, which is actually equal to the concentration of dissolved DMS in the surface sea water ($c_{DMS}$), since atmospheric DMS concentration is generally 2–3 orders of magnitude lower than the concentration of dissolved DMS in the surface sea water. The two prevailing models of LM86 (Liss and Merlivat, 1986) and W92 (Wanninkhof, 1992) were used to calculate the gas transfer coefficients, respectively, which represent lower (LM86) and higher (W92) estimates in sea-air exchange parameterizations. The coefficient $K$ is calculated as a function of wind speed and the Schmidt number (Sc) (Liss and Merlivat, 1986). The Schmidt number of DMS at the local temperature is obtained using the equation put forward by Saltzman et al. (1993). In this study, the wind speeds were measured at about 10 m above the sea surface by ship-borne weather instrument (RM Young, USA) and had been automatically corrected to true wind speeds.

### 3 Results and discussion

#### 3.1 The distribution characteristics of DMS and DMSP in spring and autumn

The concentrations of DMS in the spring cruise ranged from 0.48 to 4.92 nmol/L, with an average of 1.69 nmol/L. The average concentrations of DMSPd and DMSPp were 3.18 (0.68–6.75) nmol/L and 15.81 (2.82–52.33) nmol/L, respectively. Our results of DMS are in good agreement with those previously reported by Yang et al. (2006) who found that DMS concentrations in the Yelllow Sea in spring varied from 1.20 to 4.54 nmol/L, with an average of 2.31 nmol/L. However, the average value of DMSPp concentration is roughly twice as much as that obtained in the same area in March 2005 (Yang et al., 2006), which might be attributed to the spring bloom in this cruise. In comparison, the concentrations of all sulfur species throughout the study area were higher.
in autumn than in spring. The concentrations of DMS, DMSPd and DMSPp in autumn fluctuated from 1.33 to 7.95, 2.19 to 11.30 and 6.24 to 137.87 nmol/L, respectively, with average values of 2.80, 5.45 and 30.63 nmol/L. Our results of DMS are consistent with previous measurements by Hu et al. (2003) who found that DMS concentrations in the Yellow Sea during September 1994 varied from 0.95 to 7.48 nmol/L with an average of 2.89 nmol/L.

The concentrations of chlorophyll \( a \) in spring and autumn varied from 0.18 to 11.52 and 0.30 to 4.96 µg/L, respectively, with average values of 1.41 and 1.26 µg/L. As shown in Fig. 2, high chlorophyll \( a \) concentrations in spring occurred in the middle region of the SYS, with the highest value (11.52 µg/L) appearing at Sta. H08. This distribution pattern showed that a spring phytoplankton bloom took place in the region of the Yellow Sea Cold Water Mass during the investigation period. In contrast to the spring distribution, the low concentrations of chlorophyll \( a \) appeared in the middle region of the SYS and the lowest concentration of chlorophyll \( a \) was observed at Sta. H09 in autumn. On the south of 34°N, the concentrations of chlorophyll \( a \) were significantly higher in autumn than in spring (Fig. 2). Besides, the lower concentrations of chlorophyll \( a \) were found in the Subei coastal waters in spring and autumn.

### 3.2 Seasonal variations of DMS and DMSP in the SYS

The seasonal variations could influence the phytoplankton parameters and the production processes of DMS and DMSP and eventually impacted on the concentrations of those sulfur compounds. Previous studies have shown that the seasonal variations of DMS and DMSP concentrations are associated with phytoplankton parameters such as species, biomass and growth.
status in various coastal and shelf waters (Lefèvre et al., 2002; Michaud et al., 2007; Shenoy and Patil, 2003). We found that the average temperature in autumn cruise was 2.7 times higher than that in spring, which was close to sea-surface temperature in summer. These result indicated that the growth of phytoplankton was still relatively exuberant during autumn cruise, due to the higher sea-surface temperature. Chlorophyll $a$ concentrations in autumn cruise were generally higher than those in spring cruise except for a few stations (H08, H09 and H11) in spring bloom region. Besides, it is well known that dinoflagellates contain more DMSP than diatoms. Song (2010) found that the contributions of diatoms and dinoflagellates to phytoplankton biomass in the SYS in spring were 92.2% and 7.19%, respectively, while their contributions were 78.59% and 17.29% in autumn. As a consequence, DMS, DMSPd and DMSPp concentrations in autumn were approximately twice as high as those in spring.

In spring, elevated levels of DMS and DMSP concentrations were found in the middle region of the SYS, which were obviously higher than those observed in the coastal areas. Huang et al. (2006) suggested that the spring bloom was initiated due to the interaction of sufficient nutrients accumulated during the winter and the increase in water temperature. Owing to the phytoplankton bloom in the middle region of the SYS, the highest concentration of DMSPp was recorded at Sta. H8 with the highest level of chlorophyll $a$. The maximum values of DMS and DMSPd appeared at Sta. H11 in the center of the SYS. In comparison, the concentrations of these sulfur compounds in autumn generally
decreased from the coast of the Shandong Peninsula to the central SYS (Fig. 2). The highest value of DMSp (137.87 nmol/L) appeared at Sta. B04 located at the inshore of the Shandong Peninsula. The low values of DMS and DMSP appeared in the central part of the SYS with the bloom decline and the lowest value of DMS was recorded at Sta. H15 in the central part of SYS. According to the investigation of Shang (2011), the Yellow Sea Cold Water Mass still exists in the bottom waters on the north of 34°N in autumn. Owing to the water stratification and the presence of the thermocline (Wang, 2000), nutrients in the upper layer were exhausted by organisms during summer and could not be replenished by the nutrient-rich waters at the bottom, which limited the algal growth and led to low DMS and DMSP values in the central part of the SYS.

In spring, the lower DMS and DMSp levels appeared in the adjacent area of the Changjiang River Estuary, which corresponded well with the lower salinities here (Fig. 2). The lowest values of DMS, DMSp-d and DMSp-p were respectively recorded at Stas H40, H40 and H42, respectively, which were located near the Changjiang River Estuary. On the contrary, the high concentrations of sulfur compounds in autumn were found in the adjacent area of the Changjiang River estuary and the highest values of DMS and DMSp concentrations were concurrently found at Sta. H40. The Changjiang River had a momentous influence on the distributions of DMS and DMSP in the south of the study area in April and September. As the material basis of life activities of phytoplankton, nutrients in sea water can affect the algal growth and reproduction, then change the phytoplankton community structure (Fu et al., 2012), and ultimately influence the distributions of DMS and DMSP. The Changjiang River diluted water is hypohaline waters (salinities of 5–31) with rich nutrients, and has an important effect on the Yellow Sea and the East China Sea by forming obvious gradient of salinity and nutrients (Wang et al., 2003). From May to September, under the combined functions of the southwestern monsoon and higher runoff, the direction of the Changjiang River diluted water gradually turns to the north and it enters the southwest area of the SYS (Cui, 1984; Chen, 2007). Compared with the spring, the nutrients in autumn, including DIN and PO4-P, all exhibited relatively high concentrations in the southwest area of the SYS (Fig. 3), which promoted the phytoplankton growth and thus led to higher concentrations of chlorophyll a, DMS and DMSP in this region.

In addition, vertical turbulent dispersion can lead to poor stability of water column and is not favorable to increase the number of phytoplankton and keep its density in the surface layer of the south of 34°N (Hu et al., 2004), thereby influencing the concentrations of DMS and DMSP. A similar conclusion was proposed by other authors in different waters. For example, Fronek et al. (2004) pointed out that the higher chlorophyll a biomass and biological production depended on the water column stability. Hashihama et al. (2008) suggested that the weak stratification potentially prevented the optimal growth of large diatoms. On the south of 34°N, the mixed layer depths in autumn were obviously lower than those in spring (Tables 1 and 2), which resulted in the stronger stability of the water layer and the higher chlorophyll a concentrations in autumn. Hu et al. (2004) reported that the concentrations of chlorophyll a significantly depended on the stability of the water layer and high concentrations of chlorophyll a appeared in the offshore waters on the south of 34°N from May to September, due to the weaker vertical turbulent dispersion. Therefore, high concentrations of DMS and DMSP in this area were also attributed to the strong stability of the water layer in autumn.

Finally, the lower concentrations of DMS and DMSP were found in the Subei coastal waters and the adjacent area of the Changjiang River Estuary in spring and autumn. The lower salinities here indicated that coastal area was influenced by the terrestrial runoff and the Changjiang River diluted water. Although high concentrations of nutrients were brought by the terrestrial runoff and the Changjiang River diluted water, lower transparency in coastal region limited the growth of phytoplankton, which resulted in the lower levels of chlorophyll a concentration (Hu et al., 2004) and thus lower concentrations of DMS and DMSP here.

In conclusion, biomass and composition of phytoplankton were the immediate causes which led to the seasonal differences in the DMS and DMSP concentrations distributions between spring and autumn. Besides, the seasonal variations of DMS and DMSP concentrations in the SYS were indirectly controlled by the differences in the temperature, nutrients and the water column stability between the two seasons.

### 3.3 Influencing factors of DMS and DMSP concentrations in the SYS

During the two cruises, the distributions of DMS and DMSP concentrations showed a high degree of spatial heterogeneity and large seasonal fluctuation. These differences were largely due to the seasonal variations in the marine biological and environmental factors.

It is well known that DMS can serve as the cryoprotectants and osmotic pressure regulator in algae cells (Vairavamurthy et al., 1985; Karsten et al., 1992). Therefore, the salinity and temperature can significantly affect the DMS and DMSP concentrations. However, our results show that no correlations are found between DMS concentration, DMSP concentration and the temperature (Table 3). As shown in Tables 1 and 2, the values of temperature in spring and autumn fluctuated from 5.74 to 11.20 °C and from 22.64 to 27.99 °C, respectively. The results indicated that the smaller temperature differences have no significant influence on DMS and DMSP concentrations. Therefore, the temperature cannot be a main limiting factor for the DMS and DMSP concentrations. Similar to the temperature, there were no correlations between DMS concentration, DMSP concentration and the salinity in spring and autumn (Table 3). Although DMSP plays a role in osmotic adjustment, the change of its concentration according to osmotic demands is very slow (Kirst, 1996). Thus, there were no obvious correlations between DMS concentration, DMSP concentration and the salinity.

Since DMS and DMSP originate from marine phytoplankton, chlorophyll a is possibly one of the primary controlling factors of DMS and DMSP. Some attempts have been made to find possible relationships between the biogenic sulfur compounds and chlorophyll a. To date, some authors have reported the significant correlations between DMS, DMSPp and chlorophyll a (Andreae et al., 1990; Yang et al., 1999, 2011; Zhang et al., 2008, 2009), whereas others have found poor or no correlations (Besiktepe et al., 2004; Holligan et al., 1987; Simó et al., 1997; Turner et al., 1988; Vila-Casta et al., 2008). The difficulties in obtaining a general correlation are usually attributed to the fact that the DMS concentration level in sea water largely depends on the phytoplankton population structure and biomass, and different sea regions have different species composition and abundance.

In spring, the significant correlations appeared between the DMS, DMSp-d, DMSp-p and chlorophyll a concentrations (Table 3), which was consistent with previous study in the Yellow Sea.
**Fig. 3.** Horizontal distributions of DIN, phosphate and silicate concentrations (µmol/L) in spring (spr.) and autumn (aut.).

**Table 3.** Relationships between DMS, DMSP concentrations and the marine biological and environmental factors in the SYS in spring and autumn

|                  | Spring          |           |           | Autumn         |           |           |
|------------------|-----------------|-----------|-----------|----------------|-----------|-----------|
|                  | n   | r²     | P         | n   | r²     | P         |
| DMS vs Chl a     | 31  | 0.453  | 3.000×10⁻⁵| 33  | 0.268  | 0.002     |
| DMS vs T         | 31  | 0      | 0.991     | 33  | 0.071  | 0.133     |
| DMS vs S         | 31  | 0.188  | 0.015     | 33  | 0.002  | 0.808     |
| DMSPd vs Chl a   | 31  | 0.458  | 2.920×10⁻⁵| 33  | 0.018  | 0.456     |
| DMSPd vs T       | 31  | 0.021  | 0.013     | 33  | 0.026  | 0.370     |
| DMSPd vs S       | 31  | 0.267  | 0.242     | 33  | 0.052  | 0.203     |
| DMSPp vs Chl a   | 31  | 0.414  | 9.540×10⁻⁵| 33  | 0.276  | 0.002     |
| DMSPp vs T       | 31  | 0.090  | 0.100     | 33  | 0.012  | 0.546     |
| DMSPp vs S       | 31  | 0.097  | 0.088     | 33  | 0.011  | 0.853     |
(Zhang et al., 2008). This result indicates that the phytoplankton biomass may play an important role in controlling the distributions of DMS and DMSP in the SYS in spring. In contrast, weak correlations were found between DMS or DMSPp and chlorophyll $a$ concentrations in the autumn cruise (Table 3). Previous studies have shown that a good relationship is to be expected only where the phytoplankton assemblage is dominated by certain type of algae (Dacey et al., 1998). Since a phytoplankton bloom took place in spring, the taxonomic composition of phytoplankton in spring might be more unitary in spring than in autumn. Xu (2007) reported that the percentage of diatoms in the total phytoplankton abundance was 99.63% in the SYS during the spring bloom, while the proportion of dinoflagellates accounted for only 0.37% in the same period. Wang (2001, 2003) pointed that a total of 72 species that belonged to 29 genera were identified in autumn, while a total of 29 species were determined belonging to 14 genera in spring in the Huanghai Sea. In summary, the composition of phytoplankton was more unitary in spring and thus the notable relationship appeared between DMS or DMSPp and chlorophyll $a$ in spring.

3.4 Seasonal variations of DMS(P)-to-chlorophyll $a$ concentrations ratios in SYS

Since the concentration of chlorophyll $a$ varies with different phytoplankton species and the ability to form DMS and DMSP is controlled by the phytoplankton species, the ratio of DMS to chlorophyll $a$ concentrations can be used for calculating the DMS production ability per unit biomass and the ratio of DMSPp to chlorophyll $a$ concentrations can be utilized as an estimate of the proportion of DMSP producers in the total phytoplankton assemblage (Turner et al., 1995). In the spring cruise, the ratios of DMSPp to chlorophyll $a$ concentrations range from 4.54 to 234.27 mmol/g, with an average of 27.66 mmol/g and the ratios of DMS to chlorophyll $a$ concentrations varied from 0.29 to 7.01 mmol/g, with a mean value of 2.31 mmol/g. In the autumn cruise, the ratios of DMS to chlorophyll $a$ concentrations and DMSPp to chlorophyll $a$ concentrations range from 0.86 to 10.92 mmol/g and from 6.65 to 116.04 mmol/g, respectively, with mean values of 3.31 and 30.62 mmol/g.

In the present study, the seasonal differences in the ratios of DMS to chlorophyll $a$ concentrations and DMSPp to chlorophyll $a$ concentrations are evident between spring and autumn (Fig. 4). In spring, the lower ratio values of DMS to chlorophyll $a$ concentrations and DMSPp to chlorophyll $a$ concentrations appeared in the central part of the SYS with the algal bloom (e.g., Stas H07, H08, H09 and H11). On the contrary, the high ratios of DMS to chlorophyll $a$ concentrations and DMSPp to chlorophyll $a$ concentrations were found in these regions in autumn. On the south of 34°N, the ratios of DMSPp to chlorophyll $a$ concentrations at most stations in autumn are higher than those in spring. Besides, the average ratio of DMS/chlorophyll $a$ in spring (2.31 mmol/g) is significantly lower than that in autumn (3.31 mmol/g) and the mean ratio of DMSPp to chlorophyll $a$ concentrations in spring (27.66 mmol/g) is also lower than that in autumn (30.62 mmol/g). This result indicates that although diatoms are the dominant species in the SYS, the proportion of diatoms in total

![Fig. 4. Horizontal distributions of the ratios of DMS to chlorophyll $a$ concentrations and DMSPp to chlorophyll $a$ concentrations in spring (spr.) and autumn (aut.).]
phytoplankton assemblage changes with seasons and dinoflagellates biomass in the SYS is higher in autumn than in spring.

Some authors have proposed that the phytoplankton community structure is affected by the change in the concentrations and proportions of nutrients (Iverson et al., 1989; Wang, 2003). Previous studies pointed that the uptake rate of phosphate by diatoms was faster than that of DIN, while the nutrient utilizations by dinoflagellates are just the opposite (Dong et al., 2002). Thus, the higher ratios of DIN to PO$_4^{3-}$ concentrations usually appeared in the region dominated by diatoms, while the lower ratios of DIN to PO$_4^{3-}$ concentrations are generally accompanied by the increase of dinoflagellates biomass. In the present study, the ratios of DIN to PO$_4^{3-}$ concentrations in the SYS are obviously higher in spring than in autumn (Fig. 5). This result indicates that although diatoms are the dominant species in the SYS, the proportion of diatoms in total phytoplankton assemblage changes with seasons and dinoflagellates biomass in the SYS is higher in autumn than in spring. Liu (2007) reported that in the SYS, the average cell abundance of dinoflagellates at each station was 2.44×10$^4$ cells/m$^3$ in the SYS during autumn, which was obviously higher than that (0.74×10$^4$ cells/m$^3$) in spring. Since the composition of phytoplankton in the SYS changes with season, with the increased abundance of dinoflagellates and the decreased diatoms proportion in autumn, the ratios of DMS or DMSP to chlorophyll $a$ are correspondingly increased in the autumn cruise.

### 3.5 Sea-to-air flux of DMS in SYS

The mean fluxes obtained by the methods of LM86 and W92 are 3.03 (0.021–13.79) and 6.92 (0.054–32.50) μmol/(m·d) in spring and 3.41 (0.020–17.86) and 7.81 (0.015–39.45) μmol/(m·d) in autumn, respectively. In the study area, the range of DMS sea-to-air fluxes exceeded three to four orders of magnitude, due to the obvious differences of DMS concentrations and the wind speeds among sample stations. In addition, although the mean wind speed in spring (6.74 m/s) is higher than that in autumn (5 m/s), the average sea-to-air flux of DMS in spring was lower than that in autumn. This might be attributed to apparently higher DMS concentrations in autumn than in spring. In order to facilitate the comparison with the previous studies, the DMS flux estimates for the HS in previous studies are summarized in Table 4. Our results in spring and autumn are in good agreement with those previously reported by Yang et al. (2006) and Hu et al. (2003). However, our results in spring are much lower than those previously reported by Zhang et al. (2008). The influence of large DMS concentration (Zhang et al., 2008) resulted in the higher flux to the atmosphere.

Combined with previously published experimental results in summer and winter (Yang et al., 2011), the mean annual fluxes of DMS in the SYS are calculated, respectively, according to the models of LM86 and W92. The annual DMS emission rates ranged from 0.015 to 0.033 Tg/a (calculated by S), taking the result by LM86 as a lower limit and the result by W92 as an upper limit. According to preliminary estimate, the annual DMS emission from the SYS accounted for 0.10%–0.22% of total annual emission (15 Tg/a) (Kettle and Andreae, 2000). Since the SYS occupies only a small part (0.08%) of the world ocean, our result indicates that the net DMS emission from the SYS may represent a non-negligible amount to the local and global oceanic DMS fluxes.

### 4 Conclusions

The temporal distributions of DMS, DMSP and chlorophyll $a$ in the SYS were investigated in the present study. The higher DMS and DMSP concentrations were observed in the central part...
of the SYS in spring. The significant correlations between DMS, DMSP and chlorophyll a concentrations were found only in spring, due to the phytoplankton bloom. On the south of 34°N, DMS and DMSP concentrations show the high values in the southwest of the SYS in autumn, which is attributed to the stronger stability of the water body and the input of nutrients in the Changjiang River diluted water. Our data showed that the concentrations and distributions of DMS and DMSP in spring and autumn are directly influenced by the seasonal variations in the phytoplankton composition and abundance. Moreover, different environmental factors (e.g., nutrients, water column stability and the Changjiang River effluent) also exhibited the significant impacts on the distributions of DMS and DMSP. The annual DMS emission rates ranged from 0.015 to 0.033 Tg/a, taking the result by LM86 as a lower limit and the result by W92 as an upper limit, which accounted for 0.10%–0.22% of total annual DMS emission in the world ocean. The SYS occupies only a small part (0.08%) of the world ocean, and thus the emission of DMS from the study area has a significant relative contribution to the global oceanic DMS fluxes.

Acknowledgements
The authors are grateful to the captain and crew of the R/V Dongfanghong No. 2 for help and cooperation during the two cruises. We also wish to thank our colleagues in our laboratory for the assistance in sample collection and pretreatment. Moreover, we thank Li Chengxuan for her help in analyzing DMS sample in the Changjiang River diluted water. We thank the assistance in sample collection and pretreatment. Moreover, we thank Li Chengxuan for her help in analyzing DMS sample during two cruises.

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