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Spatial distribution of dimethylsulfide and dimethylsulfoniopropionate in the Yellow Sea and Bohai Sea during summer*

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Abstract The distributions of dimethylsulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP) in surface water of the Yellow Sea and the Bohai Sea were studied during June 2011. The mean concentrations and ranges of DMS, dissolved DMSP (DMSPd), and particulate DMSP (DMSPp) in surface waters were 6.85 (1.60–12.36), 7.25 (2.28–19.05) and 61.87 (6.28–224.01) nmol/L, respectively. There were strong correlations between DMSPp and chlorophyll *a* in the Bohai Sea and the North Yellow Sea, respectively, and concentrations of DMS and DMSP were high, with a relatively high proportion of dinoflagellates, in the region of the South Yellow Sea Cold Water Mass. Results show that phytoplankton biomass and species composition were important factors that controlled the distribution of DMS and DMSP. Complex environmental factors, including nutrients, transparency, and terrestrial runoff, might also influence the variability in DMS and DMSP. Biological production and consumption rates of DMS in the Bohai Sea were higher than those in the Yellow Sea. DMS production rates were closely correlated with DMSPd concentrations. DMS and DMSP exhibited obvious diel variations, with high concentrations occurring in the late afternoon (16:00–19:00) and low concentrations occurring during the night, implying that the intensity of solar radiation had a significant influence on these variations. Size distributions of chlorophyll *a* and DMSPp were also investigated and large nanoplankton (5–20 μm), mainly diatoms, contributed significantly to chlorophyll *a* and DMSPp at most stations. The average sea-to-air flux of DMS in the study area was estimated to be 11.07 μmol/(m^2·d) during the summer.

Keyword: dimethylsulfide (DMS); dimethylsulfoniopropionate (DMSP); sea-to-air flux; Yellow Sea; Bohai Sea

1 INTRODUCTION

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound in the ocean surface. Kettle and Andreae (2000) reported that emissions of DMS accounted for 90% of the biogenic sulfur flux from the ocean to the atmosphere. The total annual flux of biogenic DMS released to the atmosphere from ocean ranged from 28 to 45 Tg S/a, and was at least 10 fold greater than the flux from all other sources (Yoch, 2002). Over the past few decades, considerable efforts have been directed at examining the biogeochemistry of DMS in seawater as well as its effects on climate. The oxidation products of DMS in the air are a major source of non-sea-salt sulfate aerosols (nss-SO_4^{2-}) and cloud condensation nuclei (CCN), which increase the albedo of aerosols over the sea and form a further

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possible negative feedback for global warming (Charlson et al., 1987). Oxidation of atmospheric DMS may also contribute to the acidity of aerosols and rainfall (Nguyen et al., 1992; Ayers and Gillett., 2000).

The major precursor of DMS, dimethylsulfoniopropionate (DMSP), is a metabolic product that plays some important physiological roles in phytoplankton and bacteria, such as that of antioxidant, osmolyte, and cryoprotectant (Karsten et al., 1992; Kiene et al., 2000; Stefels, 2000; Steinke et al., 2002; Yost et al., 2010). Simó et al. (2008) reported that oceanic DMSP accounted for 0.3% to 7% of carbon, and 4% to 93% of sulfur, from phytoplankton, with higher contributions in summer and lower contributions in winter. DMSP is released mainly during senescence, grazing by zooplankton, and viral lysis (Dacey and Wakeham, 1986; Simó, 2004). Evans et al. (2007) indicated that concentrations of DMS and dissolved DMSP (DMSPd) significantly accumulated during viral infections, and confirmed that viral lysis of algae could lead directly to DMSP cleavage. Archer et al. (2011) reported that microzooplankton might play an important role in controlling DMSP-producing populations.

DMSP is a labile compound. Once released into seawater, it rapidly cleaves to DMS by bacterial and algal DMSP-lyases. DMS may be oxidized photochemically, metabolized by bacteria, or emitted into the atmosphere. Simó (2004) concluded that biological DMS consumption could remove 50%–80% of the DMS in seawater. Compared with photochemical oxidization and microbial consumption, sea-to-air emissions may only represent a small fraction of the DMS sink, 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 proportions of DMS removed by various pathways rely on variations in environmental parameters in different oceanic regions, such as the depth of the mixing layer, UV intensity, wind speed, and marine microbe abundance and taxa.

Since DMS and DMSP originate from marine algae, the species and biomass of phytoplankton may be the main factors controlling DMS and DMSP concentrations in surface water. Generally, chlorophyll *a* can be considered as an indicator of phytoplankton biomass. Therefore, many attempts have been made to explore the relationships between chlorophyll *a* and DMS on large spatial or temporal scales. Some previous studies have reported a significant relationship between DMS, DMSP, and chlorophyll *a* e.g., (Andreae, 1990; Uzuka et al., 1996; Yang et al., 1999; Aranami et al., 2001; Zhang et al., 2008; Yang et al., 2011), while other studies have found poor, or no, correlations e.g., (Holligan et al., 1987; Turner et al., 1988; Simó et al., 1997; Besiktepe et al., 2004; Vila-Casta et al., 2008). The wide difference in results may be attributed to the fact that the ability to produce DMSP in seawater largely depends on the phytoplankton population structure and biomass, and different sea regions have different algal species composition and abundance. Complex DMS production and consumption processes may also contribute to this difference.

The distributions of DMS and DMSP show considerable spatial and temporal variation (Kettle et al., 1999; Uher et al., 2000; Shenoy and Dileep Kumar, 2007). In general, DMSP and DMS values are high in eutrophic coastal areas and in regions of upwelling. In contrast, DMSP and DMS values are low in oligotrophic open ocean waters. A high degree of eutrophication may contribute, along with other factors, to greater phytoplankton production, which in turn increases DMS production (Andreae and Barnard, 1984). The nutrient supply and nutrient ratios have a significant influence on the species composition of phytoplankton, since different algal species have different nutrient requirements (Hodgkiss and Lu, 2004). Dong et al. (2002) reported that the dominant species of phytoplankton readily changed from diatoms to dinoflagellates when P was deficient and N was sufficient. Li (2008) found that a low N/P ratio and a high phosphate concentration were advantageous to diatom growth, while a higher N/P ratio and high levels of dissolved inorganic nitrogen (DIN) were good for dinoflagellate growth. Thus, the nutrient supply and nutrient ratios have a marked effect on the phytoplankton structure, which then influences the production of DMS and DMSP. Finally, previous studies reported that DMS and DMSP biosyntheses were diurnal processes coupled with photosynthesis. During a 24-h on-deck experiment, consistent diurnal variations in DMS and DMSP were observed in different seasons, with higher levels during the day and lower levels at night, indicating that DMS and DMSP production processes may be related to sunshine radiation (Simó et al., 2002; Yang et al., 2006).

Recently, much attention has been directed at investigating the distributions of DMS and DMSP in the Yellow Sea. Yang et al. (2006) and Zhang et al.

(2008) reported the distributions of DMS and DMSP in the microlayer and subsurface waters of the Yellow Sea in spring. More recently, Yang et al. (2011, 2012) investigated the distributions of DMS and DMSP in the South Yellow Sea and the East China Sea. To date, DMS and DMSP have not been investigated in summer in the Yellow Sea and the Bohai Sea. In this study, we focus on the spatial distributions of DMS and DMSP, and the biological and geophysical factors that govern them, throughout the Yellow Sea and the Bohai Sea in summer. Surface samples were collected during a summer cruise to determine DMS, DMSP, chlorophyll *a*, and nutrient concentrations, as well as biological production and DMS consumption rates, with the aim of understanding the biological controls on DMS and DMSP distributions in the seawater. Samples collected for chlorophyll *a* and particulate DMSP (DMSPp) analysis at 26 stations were size-fractionated by sieving them through different-sized membrane filters to investigate the planktonic origin of DMSPp. Finally, the sea-to-air fluxes of DMS in the study area were calculated to assess the contribution of the Yellow Sea and the Bohai Sea to global oceanic DMS emissions.

2 MATERIAL AND METHOD

2.1 Study area

The Yellow Sea and the Bohai Sea are continental shelf areas of the Northwest Pacific Ocean with a total surface area of 457 000 km^2, and mean depths of approximately 44 and 20 m, respectively. The Bohai Sea is made up of four parts, namely Liaodong Bay, Bohai Bay, Laizhou Bay, and the Central Bohai Sea. Over 40 rivers discharge into the Bohai Sea, of which the Huanghe (Yellow) River, Haihe, Daliao, and Luanhe Rivers are the four main sources of freshwater. Conversely, the Yellow Sea is the source of salt to the Bohai Strait. The hydrographic conditions in the Bohai Sea are substantially influenced by river discharges, wind-tide-thermohaline circulation, stratification in summer, and mixing in winter (Ning et al., 2010). The Yellow Sea sits entirely on the continental shelf and the Changjiang River is the main source of freshwater for the Yellow Sea. High fluxes of freshwater, especially during the summer monsoon season, discharge into the Yellow Sea, causing a significant drop in salinity and a significant increase in nutrients. The lower salinity and higher nutrients have a clear influence on the adjacent ecosystem. The surface circulation in the Yellow Sea consists of two main currents: the south-flowing coastal currents along both the Chinese and Korean coasts and the Yellow Sea Warm Current that separates from the Tsushima Current to the west of Jeju Island (Yuan et al., 2008). Compared with the coasts, there are no consistent strong currents in the open sea, and the Yellow Sea Cold Water Mass (YSCWM) is the most important feature of the Yellow Sea. It has a significant impact, not only on the vertical distribution of chemical elements, nutrients, and chlorophyll *a* (Diao and Shen, 1985; Zhang et al., 2002), but also on the summer growth of zooplankton in the Yellow Sea (Pu et al., 2004). The Yellow Sea and the Bohai Sea are surrounded by areas of high population and economic development in China and Korea. Over the last few decades, the impact of human activities on both seas has been increasingly apparent, resulting in accelerated eutrophication and therefore high primary production in these areas. As a result, the deterioration of the Yellow Sea and the Bohai Sea ecosystems over recent decades has been indicated by increased algal blooms.

2.2 Sampling

A summer cruise was conducted aboard the R/V *Dong Fang Hong 2* in the Yellow Sea and the Bohai Sea from 13 to 28 June 2011. Samples were collected at 77 sampling sites, shown in Fig.1. The seawater samples were collected in 12-L Niskin bottles mounted on a Seabird 911 CTD. Detailed information about the sampling stations and hydrographic parameters are described in Table 1. The seawater temperature and salinity were obtained from the CTD apparatus.

2.3 Analytical procedures

Once collected, all samples were immediately analyzed for DMS on board using the cryogenic purge-and-trap method (Zhang et al., 2008). Briefly, a 10-mL aliquot of seawater was extracted with a glass syringe and then injected directly into a glass bubbling chamber. The DMS in seawater was stripped by sparging with high purity nitrogen. A drying tube containing $CaCl_2$ was located between the chamber and the cryogenic trap to avoid ice blocking in the trap tube. The DMS was concentrated in an inert stainless steel U-shaped tube packed with Tenax-TA at the temperature of dry ice-ethanol (-78°C), and then was warmed up before being analyzed with a Shimadzu GC-14B gas chromatograph equipped with a flame photometric detector. A 3-m glass chromatographic column packed with 10% DEGS on

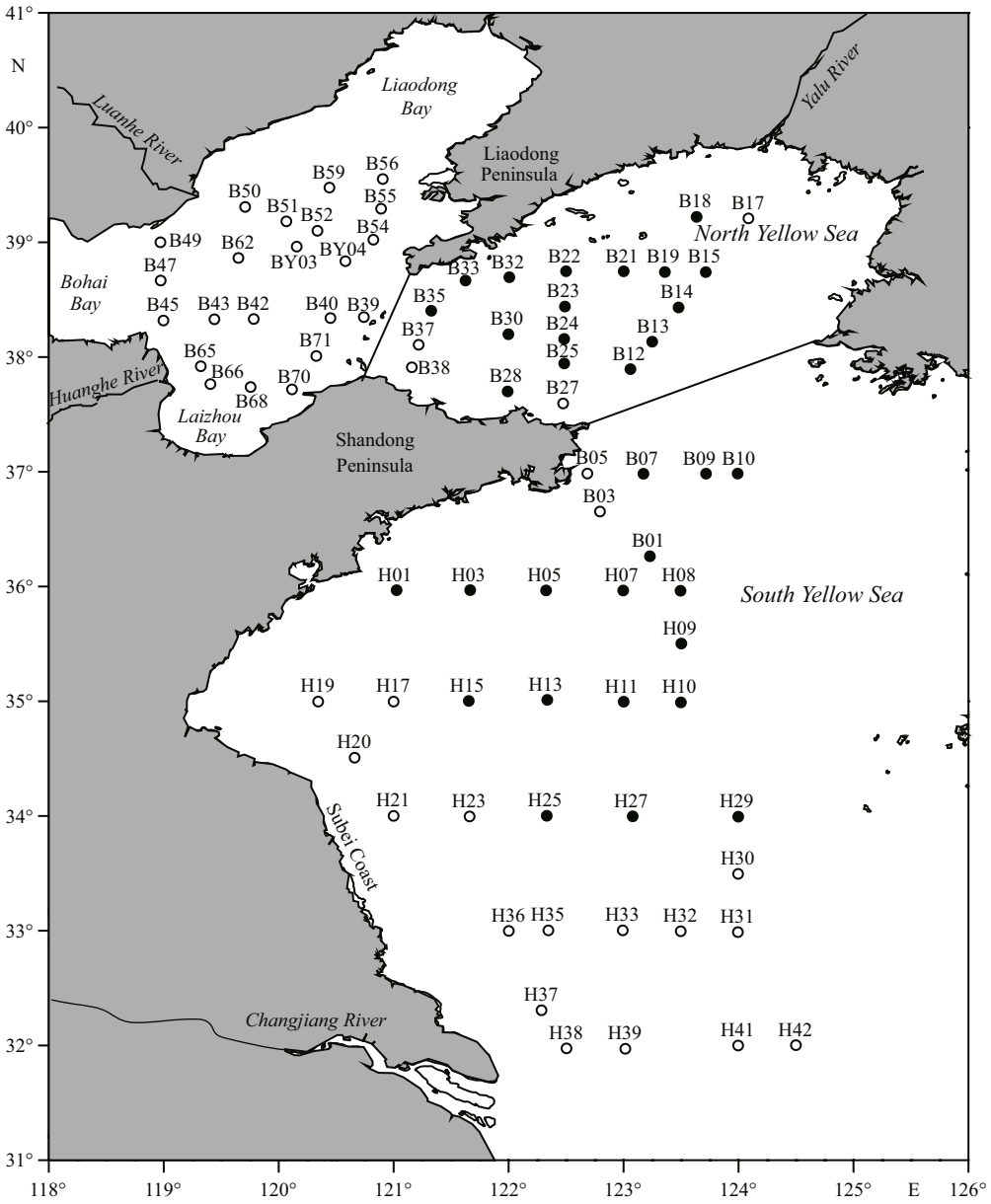

Fig.1 Location of the sampling stations in the Bohai Sea and the Yellow Sea during summer

Solid dots represent the stations located in the YSCWM region.

Chromosorb W-AW-DMGS was used to separate the sulfur gases. The calibration was done by injecting known concentrations of DMS solution, and was done by adding gravimetrically prepared standards of DMS in ethylene glycol solution to degassed seawater; calibration samples were then subjected to the same procedure as seawater samples. The analytical precision was generally better than 5% in routine sample analysis and the detection limit was approximately 0.1-pmol DMS.

DMSP samples were determined as DMS by the cold alkali treatment method (Dacey and Blough, 1987). In the analytical procedure, a gravity-filtration method was used to separate DMSPd and DMSPp (Yang et al., 2005, 2008). For DMSPp determination, a 38-mL aliquot of the seawater sample was filtered under gravity through a Whatman GF/F filter. The filter was rapidly placed in a 40-mL vial and then filled with 38 mL of distilled water and 2 mL of 10 mol/L KOH solution and sealed. To determine DMSPd+DMS, the filtrate was added to a 40-mL vial containing 2 mL of 10 mol/L KOH solution and immediately sealed with a cap inlaid with a Teflon septum, leaving no headspace. These DMSP samples were alkali-hydrolyzed in the dark at 4°C for at least 24 h. DMS generated from the breakdown of DMSP

Table 1 Summary of the locations of the sampling stations in the Yellow Sea and the Bohai Sea and their temperature and salinity in summer

Station	Longitude	Latitude	Temperature (°C)		Salinity	Station	Longitude	Latitude	Temperature (°C)		Salinity
			Surface	Bottom					Surface	Bottom	
H01	121.03°	35.97°	15.02	9.73	31.716	B17	124.09°	39.21°	11.3	10.91	31.621
H03	121.67°	35.97°	18.29	8.78	31.726	B18	123.64°	39.22°	19.75	8.68	31.388
H05	122.33°	35.97°	17.14	6.28	31.502	B19	123.36°	38.74°	19.74	7.28	31.57
H07	123.00°	35.97°	17.04	7.66	31.547	B21	123.00°	38.75°	19.71	5.24	31.292
H08	123.50°	35.96°	17.08	7.71	32.351	B22	122.50°	38.75°	17.36	3.94	30.814
H09	123.50°	35.50°	18.31	7.77	32.202	B23	122.49°	38.44°	20.13	4.94	31.661
H10	123.50°	34.99°	18.72	7.78	32.53	B24	122.48°	38.16°	19.36	4.98	31.121
H11	123.00°	35.00°	19.1	8.13	31.971	B25	122.48°	37.94°	18.43	5.22	31.173
H13	122.34°	35.01°	19.03	7.74	31.67	B27	122.47°	37.60°	18.01	14.15	31.162
H15	121.65°	35.00°	19.63	6.29	31.593	B28	121.99°	37.70°	13.34	9.37	31.466
H17	121.00°	35.00°	18.44	10.54	31.186	B30	122.00°	38.20°	18.69	3.84	31.179
H19	120.34°	35.00°	17.2	15.34	31.618	B32	122.01°	38.70°	16.15	4.6	30.608
H20	120.66°	34.51°	19.03	18.8	30.013	B33	121.63°	38.67°	18.06	5.62	30.819
H21	121.00°	34.00°	20.42	20.09	30.996	B35	121.33°	38.40°	16.98	6.27	30.808
H23	121.66°	34.00°	19.12	19.12	31.958	B37	121.22°	38.11°	17.07	11.28	31.183
H25	122.33°	34.00°	19.29	9.762	32.004	B38	121.16°	37.91°	15.15	12.09	31.185
H27	123.08°	34.00°	18.93	8.78	32.729	B39	120.74°	38.35°	13.83	12.29	31.188
H29	124.00°	33.99°	19.17	9.11	32.634	B40	120.45°	38.34°	14.36	12.14	30.971
H30	124.00°	33.50°	18.8	10.09	31.735	B42	119.78°	38.33°	19.01	12.61	30.64
H31	123.99°	32.99°	18.58	11.94	31.678	B43	119.44°	38.33°	18.82	13.94	30.931
H32	123.50°	33.00°	18.39	13.8	31.649	B45	119.00°	38.32°	19.4	17.23	31.072
H33	122.99°	33.00°	17.59	14.84	31.914	B47	118.97°	38.67°	17.4	12.98	31.182
H35	122.35°	33.00°	17.65	17.59	31.689	B49	118.97°	39.00°	17.63	16.27	31.309
H36	122.00°	33.00°	18.38	18.36	31.982	B50	119.71°	39.31°	20.7	11.76	31.253
H37	122.29°	32.31°	19.08	19.03	30.949	B51	120.07°	39.18°	19.29	14.76	31.205
H38	122.50°	31.97°	19.19	18.26	29.645	BY03	120.16°	38.96°	17.68	17.46	31.151
H39	123.02°	31.97°	18.58	18.55	31.887	B52	120.34°	39.10°	18.56	17.58	31.227
H41	124.00°	32.00°	17.17	17.09	31.414	BY04	120.58°	38.84°	16.83	15.79	31.244
H42	124.50°	32.00°	18.67	15.42	31.901	B54	120.82°	39.02°	14.7	10.75	31.186
B01	123.23°	36.26°	16.88	7.3	31.557	B55	120.89°	39.29°	16.86	13.21	31.157
B03	122.79°	36.65°	15.39	11.67	31.38	B56	120.91°	39.55°	17.53	13.99	31.29
B05	122.69°	36.98°	15.52	11.46	31.585	B59	120.44°	39.48°	17.37	12.73	31.251
B07	123.17°	36.98°	20.48	6.67	31.573	B62	119.65°	38.86°	17.86	12.67	30.99
B09	123.72°	36.98°	19.97	6.78	31.923	B65	119.32°	37.92°	20.83	-	29.574
B10	123.99°	36.98°	21.03	6.81	31.951	B66	119.41°	37.76°	21.74	21.58	29.593
B12	123.06°	37.89°	18.77	6.42	31.644	B68	119.76°	37.74°	21.47	21.14	30.845
B13	123.25°	38.13°	18.94	5.89	31.732	B70	120.12°	37.72°	20.71	19.11	31.052
B14	123.48°	38.43°	19.2	7.09	31.763	B71	120.33°	38.01°	17.8	17.22	31.179
B15	123.72°	38.74°	19.4	8.67	31.793	Average	-	-	18.16	11.56	31.374

was analyzed as described above. The concentration of DMSPd was calculated by subtracting DMS from DMS+DMSPd.

In preparation for chlorophyll *a* analysis, 300 mL of seawater was filtered through a 47-mm Whatman GF/F filter and the filters were soaked in 10-mL 90% acetone and were kept in the dark at 4°C. After 24 h, concentrations of chlorophyll *a* were measured with a HITACHI F-4500 fluorometer using the method of Parsons et al. (1984). For the bacteria enumeration, samples were stained with DAPI and counted by a fluorescence microscope, using the method described by Porter and Feig (1980). For nutrient analysis, samples were filtered through Whatman GF/F filters (0.7 μm) and were measured using a Seal Analytical AA3.

Size fractionation of DMSPp and chlorophyll *a* was conducted by gravity filtration of a 250-mL sample of seawater through a sequential filtration apparatus, with Whatman GF/F filters (pore sizes of 20, 5, 2, and 0.2 μm). The samples of DMSPp and chlorophyll *a* were analyzed as described above.

To determine the DMS biological production and consumption rates, 250 mL of seawater was placed into an acid-rinsed glass syringe. Chloroform ($CHCl_3$), an inhibitor, was added to the syringe at a final concentration of 500 μmol/L (Zhang et al., 2008). A replicate sample without the inhibitor was used for a blank sample. The glass syringes were incubated at the in situ temperature in dark conditions. Subsamples of 10 mL were withdrawn through Teflon tubing attached to a glass syringe at 0, 3, and 6 h to determine the DMS concentrations. The gross production rate of DMS was the rate of increase in the concentrations in the chloroform-treated samples over time. DMS consumption rates were estimated as the difference between the slope of the initial linear part of the DMS time-course in the inhibitor-treated sample and that of the control sample.

3 RESULT AND DISCUSSION

3.1 Horizontal distributions of DMS, DMSP, and chlorophyll *a* in the Yellow Sea

Table 1 lists the concentrations of DMS, DMSPd, and DMSPp in the surface waters. There was substantial variability in the chlorophyll *a*, DMS, and DMSP concentrations between the different sites (distribution plots are shown in Fig.2). The concentrations of chlorophyll *a* varied from 0.09 to 15.78 μg/L, with an average of 2.16 μg/L. The chlorophyll *a* concentrations gradually decreased from inshore to offshore in the Yellow Sea; chlorophyll *a* values were high in the west of the North Yellow Sea and south of 34°N, with the highest concentration (7.67 μg/L) recorded at station B27. Chlorophyll *a* values were low in the region of the YSCWM, with the lowest value observed at station H27. In comparison, chlorophyll *a* in the Bohai Sea gradually decreased from the northwest to the Bohai Strait. The maximum concentration was recorded at station BY03, which was located in the central region of the Bohai Sea. In contrast, the lowest value appeared at station B40 near the Bohai Strait.

DMS values ranged from 1.60 to 12.36 nmol/L, with an average of 6.85 nmol/L. High values appeared in the central region occupied by the YSCWM, and the value was highest (12.36 nmol/L) at station B18. DMS concentrations were low in the Subei coastal region, with the lowest value occurring at Station H27 in the highly stratified region of the Yellow Sea. In the Bohai Sea, DMS values were high in the coastal waters and low near the Bohai Strait and Huanghe River estuary.

Throughout the study area, the mean concentrations of DMSPd and DMSPp were 7.25 (2.28–19.05) and 61.87 (6.28–224.01) nmol/L, respectively. DMSPd levels were high in the coastal waters, and the maximum DMSPd value was recorded at station H01, located on the southern coast of the Shandong Peninsula. Similar to DMS, DMSPd values were low in the Subei coastal waters. DMSPp concentrations were high at the northern coast of the Shandong Peninsula and in the northwest of the Bohai Sea (Fig.2), with the highest value recorded at station B28. Similar to the DMS distribution, DMSPp levels were low in the Subei coastal waters and the Huanghe River estuary, with the lowest value recorded at station H21.

3.2 Factors affecting the DMS and DMSP horizontal distribution

It is generally known that DMS and DMSP originate from marine phytoplankton, so the biomass and species of phytoplankton control the DMS and DMSP concentrations. High chlorophyll *a* values (3.21–15.78 μg/L) indicated that there were phytoplankton blooms in the western part of the North Yellow Sea (e.g., stations B27, B28, and B30) and in the northwest of the Bohai Sea (e.g., stations B49, B52, B62, and BY03), and thereby led to high DMS and DMSP concentrations in these areas. These

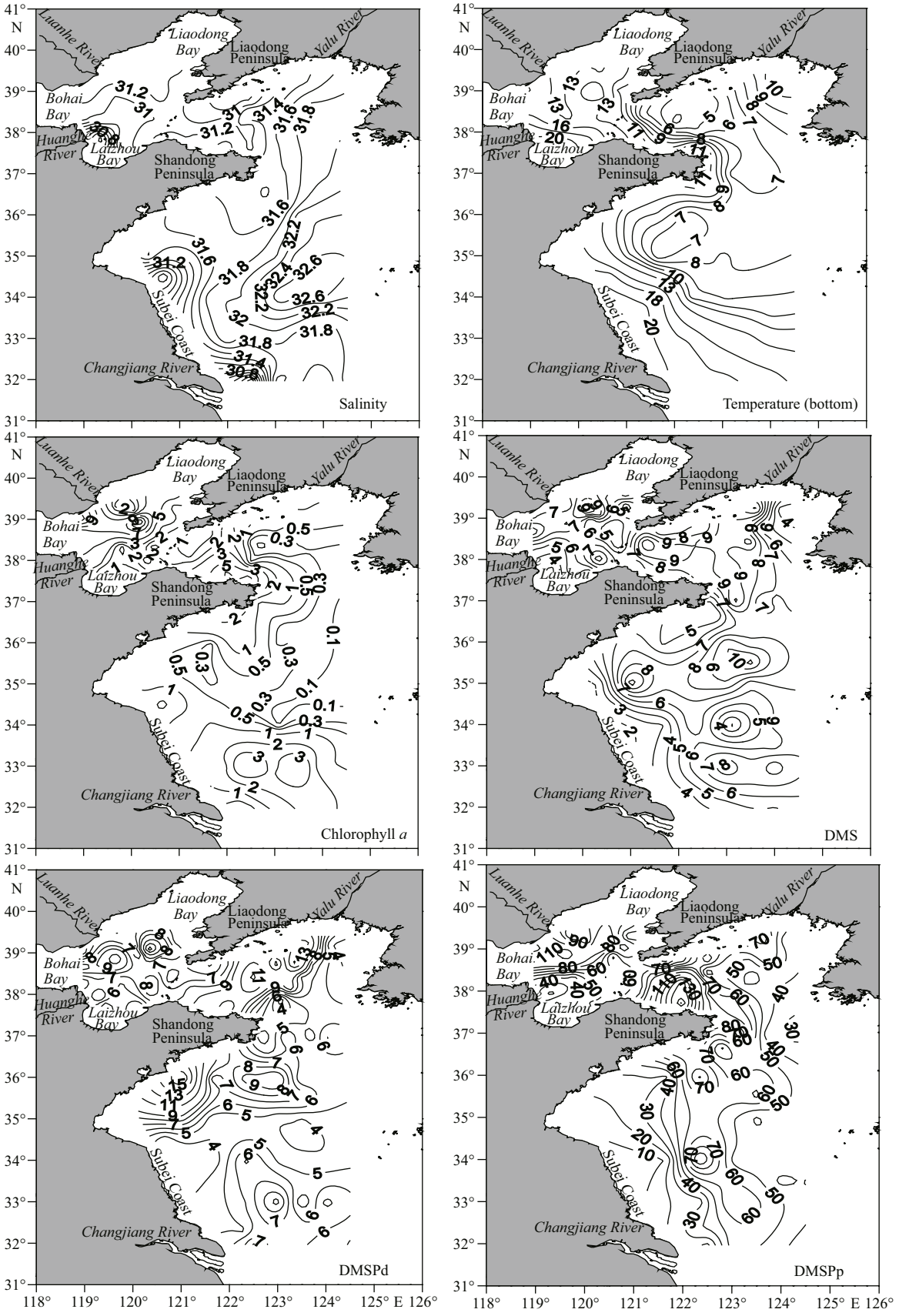

Fig.2 Horizontal distributions of salinity, bottom temperature (°C), chlorophyll *a* (μg/L), DMS, DMSPd, and DMSPp (nmol/L) in the Bohai Sea and the Yellow Sea in summer

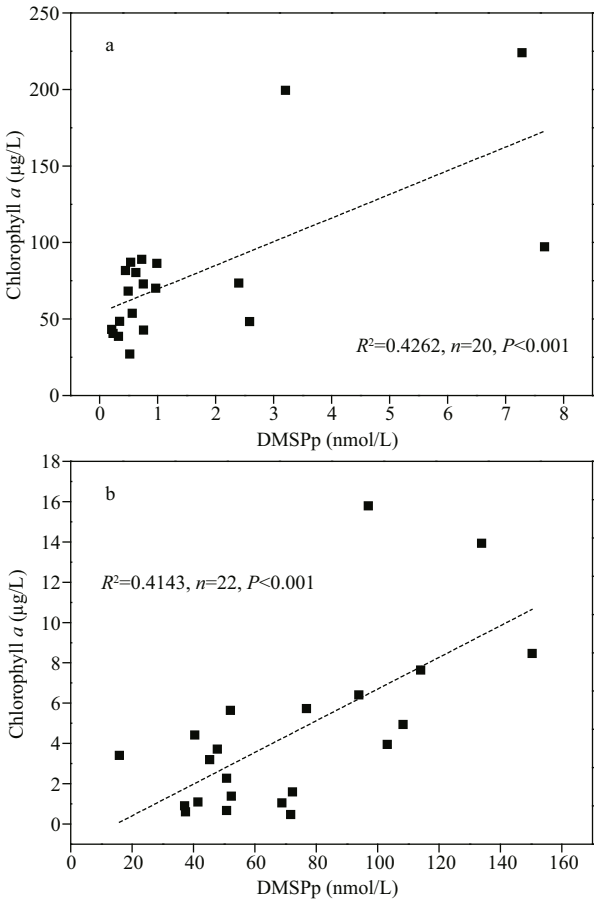

Fig.3 Linear relationships between DMSPp and chlorophyll *a* concentrations in the northern Yellow Sea (a) and the Bohai Sea (b)

results suggest that there might be a correlation between chlorophyll *a* and DMS or DMSPp in the study area. However, chlorophyll *a* and DMS were poorly correlated throughout the whole survey area (n=75, R^2=0.013 6, P=0.978 4). Although there was a weak relationship between chlorophyll *a* and DMSPp throughout the study area (n=76, R^2=0.250 6, P<0.001), there were strong correlations between DMSPp and chlorophyll *a* in the North Yellow Sea as well as in the Bohai Sea, respectively (Fig.3). Other studies have suggested that reasonable correlations are to be expected between DMS, DMSP, and chlorophyll *a* when the phytoplankton assemblages are dominated by high DMSP producers (Dacey et al., 1998; Besiktepe et al., 2004) or monospecific blooms (Groene, 1995). Data obtained in the same cruise showed that diatoms were the clear leader in species and biomass, accounting for 66% of the identified phytoplankton species and 75.27% of cell abundance in the North Yellow Sea and the Bohai Sea during the study period. The dominant species were *Paralia sulcata* (diatom), *Coscinodiscus* spp. (diatom), and *Noctiluca scintillans* (dinoflagellate) (Lu, 2012). Zhang et al. (2008) also found a significant correlation between DMSPp and chlorophyll *a* during a diatom bloom in the Yellow Sea. Our results agreed well with previous observations and indicated that DMSPp levels in the surface water were related to phytoplankton biomass when the monospecific bloom occurred.

Nutrients are fundamental for phytoplankton activity, so nutrients in seawater can affect algal growth and reproduction, change the phytoplankton population structure (Fu et al., 2012), and ultimately influence the distributions of DMS and DMSP. In the South Yellow Sea, concentrations of DMS, DMSPd, and DMSPp were higher in the region of the South Yellow Sea Cold Water Mass (SYSCWM), despite lower chlorophyll *a* levels in this area relative to the coastal area. Lower chlorophyll *a* levels and higher DMSPp concentrations indicated that the proportion of high DMSP producers in the total phytoplankton biomass was likely to increase in this area. This result might be linked to nutrient availability in surface water. After the spring bloom, the nutrients are largely consumed in the surface water in the YSCWM area and are not replenished by the nutrient-rich waters in summer because of stratification of the water and the presence of a thermocline (Wang, 2000). In the present study, the nutrient concentrations, including phosphate and silicate, were lower (Fig.4), and the ratios of N/P were considerably higher, than the Redfield ratios in this area. Previous studies have indicated that higher N/P ratios and high levels of dissolved inorganic nitrogen (DIN) are beneficial for dinoflagellate growth (Dong et al., 2002; Li, 2008). Thus, the high concentrations of DMS and DMSPp in the SYSCWM area most likely resulted from an increase in the proportion of dinoflagellates. Previous studies have shown that, compared with the spring bloom stage, dinoflagellate biomass increased significantly when the bloom was decomposing in the SYSCWM in June, especially in surface water (Tian, 2011). Thus, concentrations of DMS, DMSPd, and DMSPp were higher in the region of the SYSCWM.

An area with elevated values of chlorophyll *a* and sulfur compounds developed south of 34°N, around 123.5°E and 33°N. In summer, the Changjiang River diluted water flows to the north, due to the influence of the southwestern monsoon (Cui et al., 1984; Chen, 2007). This current transports nutrient-rich water into the southwestern part of the South Yellow Sea.

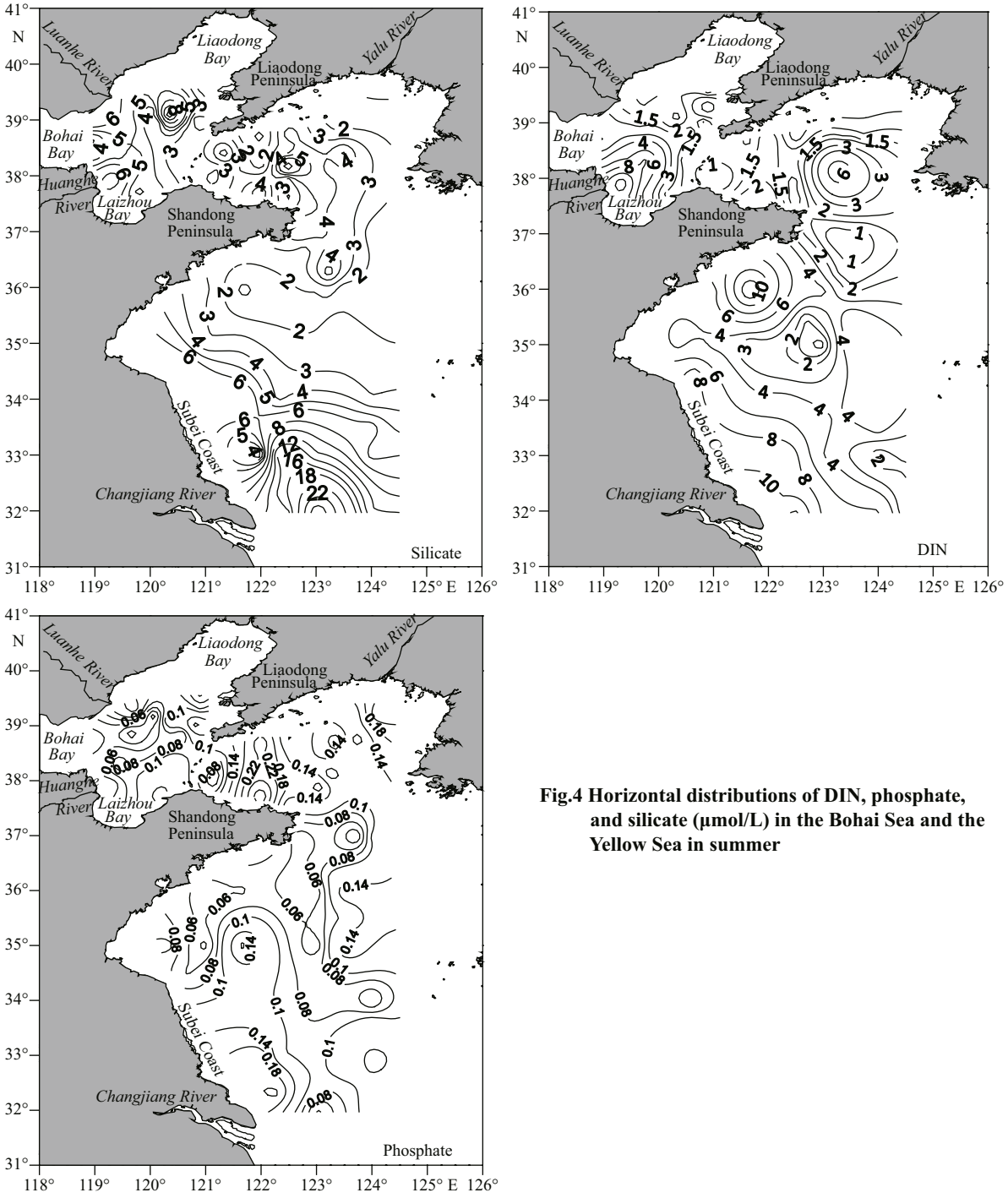

Fig.4 Horizontal distributions of DIN, phosphate, and silicate (μmol/L) in the Bohai Sea and the Yellow Sea in summer

Further, data obtained in the same cruise showed that nutrient concentrations were relatively high in the southwestern part of the South Yellow Sea, which promoted phytoplankton growth and led to higher concentrations of DMS, DMSPd, and DMSPp in this region during summer.

Some environmental factors can also stimulate primary production and thus indirectly affect the DMS and DMSP concentrations. Concentrations of DMS, DMSPd, and DMSPp were lower in the Subei coastal waters (e.g., station H21) and the adjacent area of the Changjiang River estuary (e.g., station H38) in summer. Concentrations were also relatively low in the Huanghe River estuary. This may be because large amounts of sediment are introduced into the coastal waters via terrestrial runoff, resulting in lower transparency (Shi and Wang, 2012). Hu et al. (2004) reported that lower transparency in this region

limited phytoplankton photosynthesis, which resulted in lower levels of chlorophyll *a* (e.g. 0.53 μg/L at station H21 and 0.38 μg/L at station H38) and lower concentrations of DMS and DMSP. Large quantities of freshwater were also transported into this area in summer. As shown in Fig.2, salinity was lower in the Subei coastal waters, and in the estuaries of the Changjiang River and Huanghe River, with the lowest value at station H65. Although terrestrial runoff introduced high nutrient concentrations (Fig.4), the diluting effect of freshwater might have caused the lower DMS, DMSPd, and DMSPp concentrations in this area.

3.3 Vertical profiles of DMS and DMSP

The vertical distributions of DMS, DMSPd, and DMSPp were studied along a transect (H11–H19) across the YSCWM. The presence of the YSCWM was confirmed by the low temperature and high nutrient levels below 20 m; at this level strong stratification prevented exchange between deep waters and the surface waters (Fig.5). A tidal front divided the transect into a well-mixed shallow water region (station H19) and a highly stratified deeper water region occupied by the YSCWM (stations H11, H13, and H15) (Liu et al., 2008). Station H17 was located in the tidal front region. In the YSCWM region, the concentrations of chlorophyll *a* were lower in the surface water due to a limited nutrient supply, while the values of chlorophyll *a* were higher in the lower thermocline (about 20 m), because there were sufficient nutrients and suitable light. In contrast, the concentrations of chlorophyll *a* and nutrients were distributed evenly at station H19, which was located in well-mixed coastal waters.

As shown in Fig.5, concentrations of DMS, DMSPd, and DMSPp were high in the surface water and the upper mixed layer, but decreased noticeably with increasing depth, suggesting that DMS and DMSP were predominantly produced in the upper water column. Shenoy et al. (2006) reported that DMS and DMSP were, in general, restricted to the surface layers and their concentrations decreased rapidly below 40 or 50 m so that they were almost undetectable at 120 m.

In contrast to the distribution of chlorophyll *a*, the concentrations of DMS and DMSP were clearly higher in the YSCWM region than those in the well-mixed shallow water region. Concentrations of DMS and DMSP were lower at station H19, at which the chlorophyll *a* level was higher, and the DMS(P)/chlorophyll *a* ratio was lower, in the water column. Belviso et al. (2000) indicated that the DMS(P)/chlorophyll *a* ratios could be used to calculate the DMS(P) production abilities per unit biomass and to estimate the distributions of DMS(P) producers in different regions. In the study area, the distribution of DMS(P)/chlorophyll *a* ratios was similar to that of the DMS and DMSP concentrations, with the highest value appearing in the YSCWM region (Fig.6). A previous study has shown that the abundance of dinoflagellates was higher than that of diatoms throughout the water column of the YSCWM in June (Tian and Sun, 2011). In contrast, Mei and Fang (2013) found that the cell number and species of diatoms far exceeded dinoflagellates in the Subei coastal area in summer. These results indicated that high DMSP producers were more abundant in the YSCWM region than in the coastal area, resulting in high concentrations of DMS and DMSP in this region.

Table 2 Bacterial abundance and biological production and consumption rates of DMS

Station	DMS production (nmol/(L·d))	Biological consumption (nmol/(L·d))	Bacteria (10^7 cells/L)
H09	23.69	10.06	31.25
H17	20.86	16.94	107.67
H19	7.78	2.28	132.10
H21	2.90	1.94	241.19
H30	22.44	12.48	76.99
H35	3.22	1.92	205.11
H41	17.40	7.13	97.73
B01	9.91	2.35	19.60
B19	32.45	14.52	33.33
B24	29.38	14.76	156.53
B32	17.21	6.91	46.02
B38	14.13	6.62	18.18
B42	29.86	23.21	369.60
B54	35.86	22.34	111.65
B59	30.60	21.07	181.53
B65	33.24	15.41	81.25
B66	22.27	14.16	70.74
Average	20.78	11.42	116.50

3.4 Biological production and consumption rates of DMS

As shown in Table 2, the production and consumption rates of DMS ranged from 2.90 to 35.86 nmol/d and 1.92 to 23.21 nmol/d, respectively,

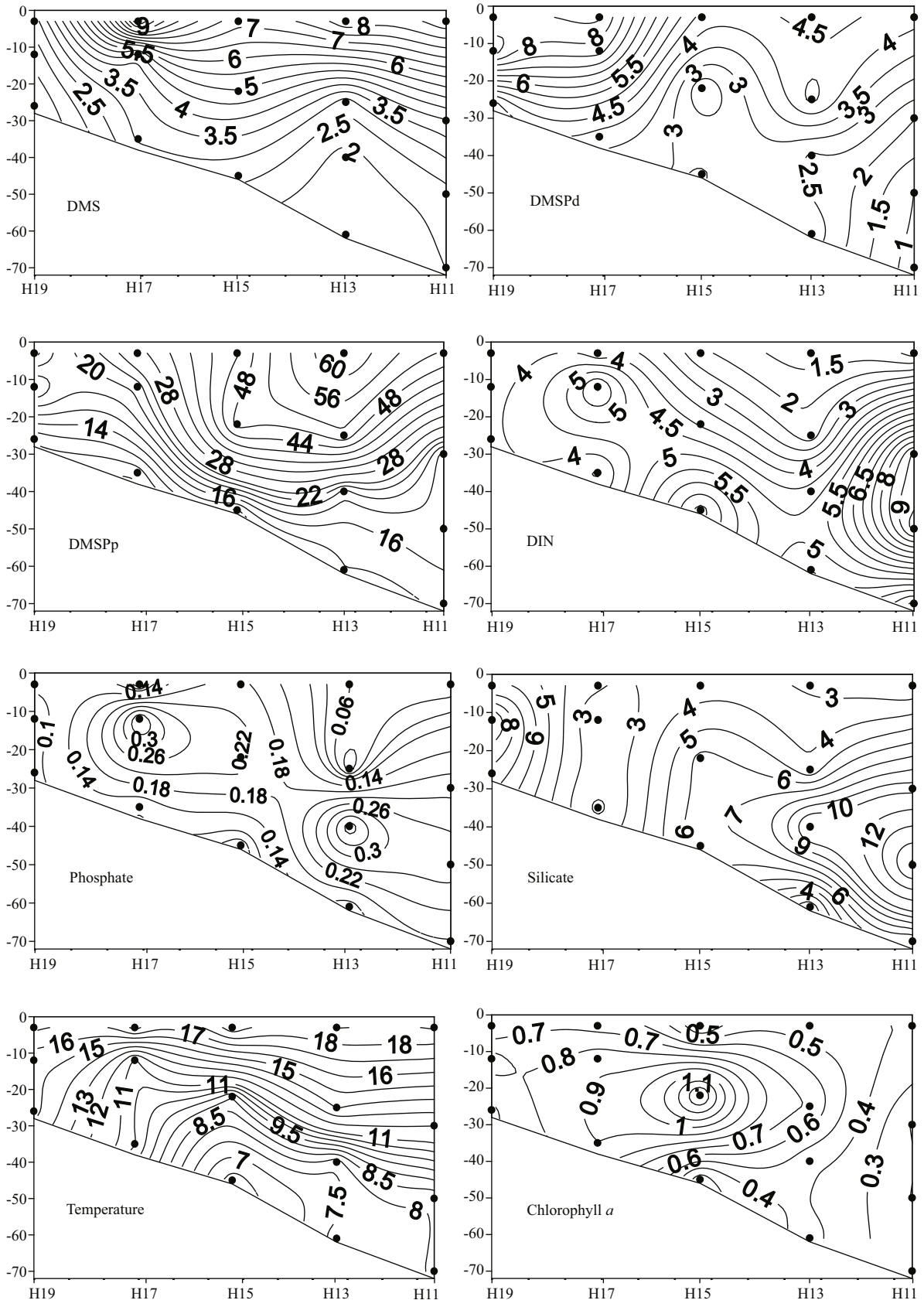

Fig.5 Vertical profiles of temperature (°C), chlorophyll *a* (μg/L), nutrients (μmol/L), DMS and DMSP (nmol/L) along transect (H11–H19)

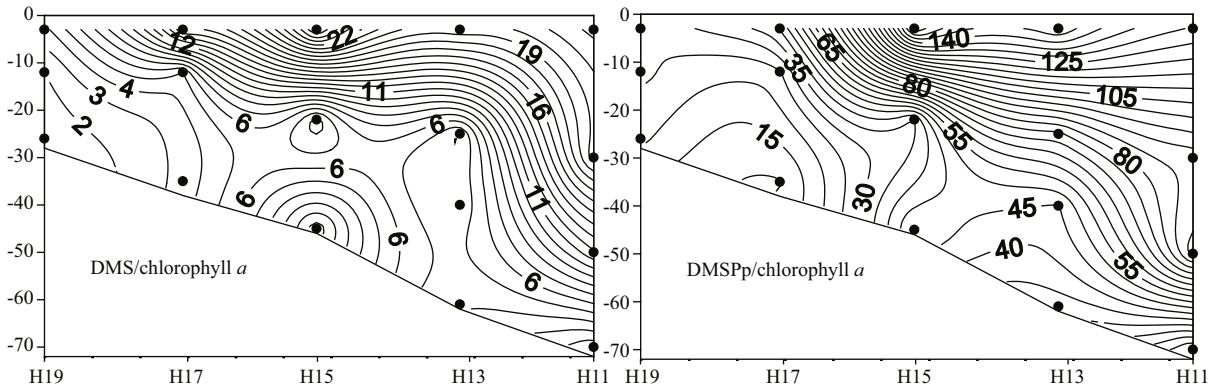

Fig.6 Vertical profiles of DMS-to-chlorophyll *a* ratios and DMSPp-to-chlorophyll *a* ratios (nmol/μg) along transect (H11–H19)

with average values of 20.78 and 11.42 nmol/d. Our results were higher than the previously reported values (7.31 and 5.56 nmol/d, respectively) in the Yellow Sea (Zhang et al., 2008). This might be due to higher microbial activity in summer than in spring. Overall, the production and consumption rates of DMS in the Bohai Sea and the North Yellow Sea were higher than those in the South Yellow Sea, and the highest rates of production and consumption all appeared in the Bohai Sea. This is because the Bohai Sea and the North Yellow Sea are surrounded by industrial zones, which result in more serious eutrophication and higher primary productivity. During our investigation period, DIN and SiO_3-Si concentrations in the Bohai Sea and the North Yellow Sea were noticeably higher than those in the South Yellow Sea. Consequently, rates of production and consumption were higher in the Bohai Sea and the North Yellow Sea. In the South Yellow Sea, high production and consumption rates of DMS mainly appeared in the YSCWM region, because of the high proportion of dinoflagellates in this region.

Within suitable temperature ranges, the activity of DMSP-lyase is elevated and leads to high DMS production rates. Kiene and Service (1991) found that rates of DMS biological production and consumption increased when temperatures were between 16 and 30°C, and that, because of low biological activity, biological production rates were low at 4 and 49°C. Scarratt et al. (2000) showed that production rates of DMS were higher when water temperatures were between 16 and 20°C. However, in this study, water temperature and DMS production or consumption rates were not correlated. DMS is mainly formed by cleavage of DMSPd, and so DMS production is intimately linked to DMSPd concentrations. Therefore, a relationship (n=17, R^2=0.271 0, P<0.05) was reasonably expected between DMSPd concentrations and DMS production rates, in agreement with previous observations (Yang et al., 2005; Zhang et al., 2008). Our results indicated that DMS production was directly controlled by the concentration of DMSPd.

Previous studies have demonstrated that high densities of bacteria might be the main factor influencing the production and consumption of DMS (Zubkov et al., 2002). In our study, the high bacteria abundances were accompanied with high consumption or production rates of DMS at some stations (e.g. stations H41, B24, B42, and B54), while the low bacteria abundances were associated with low production or consumption rates of DMS at other stations (e.g. stations B01 and B38) (Table 2). On the one hand, as the major biological production process of DMS, enzymatic cleavage of DMSP is present in diverse bacteria (Taylor, 1993) and is accelerated because of accumulated bacteria (Schultes et al., 2000). On the other hand, bacteria also play an important role in removing DMS. A previous study reported that one of the main pathways of DMS removal from the upper oceanic layers is biological consumption by bacteria (Kiene and Bates, 1990). Our study showed that the average bacterial abundance in the Bohai Sea (1.87×10^9 cells/L) was higher than that in the Yellow Sea (1.19×10^9 cells/L). This may explain why DMS production and consumption rates were higher in the Bohai Sea.

3.5 Size distribution of chlorophyll *a* and DMSPp

DMSPp and chlorophyll *a* at 26 stations in the study area were size-fractionated into >20 μm (microplankton), 2–20 μm (nanoplankton), and 0.2–2 μm (picoplankton) classes. The nanoplankton fraction was further separated into the 2–5 μm (smaller nanoplankton) and 5–20 μm (larger

Table 3 Concentrations of size-fractionated chlorophyll *a* and DMSPp in the Yellow Sea and the Bohai Sea

Station	>20 μm			5–20 μm			2–5 μm			0.2–2 μm		
	DMSPp (nmol/L)	Chl-*a* (μg/L)	DMSPp/Chl-*a* (nmol/μg)	DMSPp (nmol/L)	Chl-*a* (μg/L)	DMSPp/Chl-*a* (nmol/μg)	DMSPp (nmol/L)	Chl-*a* (μg/L)	DMSPp/Chl-*a* (nmol/μg)	DMSPp (nmol/L)	Chl-*a* (μg/L)	DMSPp/Chl-*a* (nmol/μg)
B01	1.85	-	-	43.23	0.33	132.60	5.08	0.02	220.71	1.62	0.03	52.21
B05	2.06	0.05	43.75	62.05	1.48	41.87	5.28	0.20	25.99	0.66	-	-
B09	3.22	-	-	26.80	0.14	192.80	3.15	0.02	137.10	2.27	0.02	103.00
B19	3.27	-	-	70.19	0.50	140.66	3.31	0.07	50.99	1.72	0.10	17.36
B27	4.05	1.00	4.07	82.82	6.34	13.07	4.65	0.57	8.17	2.96	0.21	14.31
B30	0.81	0.02	38.52	177.15	2.14	82.90	9.84	0.11	91.07	2.61	0.10	27.18
B39	1.07	0.06	16.97	53.01	1.73	30.71	2.69	0.11	25.64	2.28	0.07	34.00
B42	1.37	0.04	35.24	31.95	1.65	19.42	2.09	0.09	22.28	1.71	0.07	23.07
B47	1.69	0.13	12.67	78.51	5.37	14.62	7.31	0.60	12.11	2.38	0.35	6.73
B49	4.16	0.07	59.43	186.48	13.29	14.03	10.68	1.09	9.84	4.04	0.23	17.87
B50	2.97	0.02	174.61	59.55	1.66	35.98	4.25	0.20	20.95	4.63	-	-
B56	3.90	1.00	3.92	65.81	4.53	14.54	9.50	0.10	91.32	2.70	0.31	8.87
B62	0.93	0.05	20.78	123.68	3.55	34.85	8.06	0.40	20.35	3.05	0.42	7.32
B65	6.62	0.29	22.61	15.51	4.77	3.25	1.88	0.07	28.55	0.62	0.15	4.15
B68	6.75	0.23	29.21	5.52	3.84	1.44	1.08	0.06	16.83	3.40	0.02	141.66
BY04	2.85	0.19	15.08	30.84	4.35	7.09	3.12	0.65	4.83	2.14	0.35	6.14
H03	2.29	0.03	73.86	44.61	0.23	192.29	1.48	0.02	92.70	1.04	0.01	104.17
H09	1.86	-	-	49.09	0.18	277.34	3.78	0.03	140.10	2.06	-	-
H15	4.29	0.02	238.22	25.26	0.37	69.01	1.98	0.03	76.26	1.74	0.05	34.20
H21	2.66	0.18	15.22	6.13	1.04	5.87	0.66	0.01	50.47	0.64	0.03	21.24
H27	1.04	-	-	26.18	0.14	189.68	2.04	0.04	53.60	2.12	0.01	352.79
H30	1.60	-	-	73.01	1.94	37.69	5.97	0.17	35.32	1.88	0.06	30.34
H32	3.18	0.06	55.71	48.68	6.39	7.62	6.52	0.09	70.88	2.15	0.04	50.05
H36	1.84	0.29	6.41	5.12	0.94	5.44	0.73	0.02	38.17	0.63	0.03	21.72
H39	2.79	0.09	32.44	22.29	1.10	20.32	0.79	0.03	23.30	1.05	-	262.10
H41	10.45	0.58	17.89	36.19	2.23	16.22	7.74	0.06	133.40	1.78	0.08	22.49
Average	3.06	0.22	45.83	55.76	2.70	61.59	4.37	0.19	57.73	2.07	0.12	59.26

nanoplankton) fractions.

Our results showed that most of the chlorophyll *a* and DMSPp were associated with the larger nanoplankton (Table 3). Overall, the contributions of larger nanoplankton to chlorophyll *a* and DMSPp were 83.78% and 79.86%, respectively. In second place, the smaller nanoplankton contributed to 6.79% of chlorophyll *a* and 6.99% of DMSPp. The contributions of microplankton to chlorophyll *a* and DMSPp reached 5.22% and 8.72%, respectively. The picoplankton fraction accounted for only 4.21% of chlorophyll *a* and 4.23% of DMSPp. Although the larger nanoplankton fraction contained a substantial amount of DMSPp, the mean DMSPp/chlorophyll *a* ratio of larger nanoplankton fraction was 61.59 nmol/μg and was not significantly higher than that of other plankton fractions. Our study showed that the average DMSPp/chlorophyll *a* ratios of the microplankton, smaller nanoplankton and picoplankton fractions were 45.83, 57.73, and 59.26 nmol/μg, respectively. This result implies that the larger nanoplankton fraction was mainly composed of low-DMSP producers. Data obtained in the same cruise showed that diatoms were the dominant species in the Bohai Sea and the Yellow Sea during summer (Lu, 2012). Hence, diatoms may constitute a major part of the larger nanoplankton fraction.

Our results show that the microplankton fraction significantly contributed to the proportions of DMSPp and chlorophyll *a* in the estuary area. The

microplankton contribution to DMSPp was 40.31% at station B68 near the Huanghe River estuary. Microplankton contributed to 26.88% of total DMSPp at station B65 in the mouth of the Huanghe River. Sun et al. (2002) highlighted that dinoflagellates were active and abundant in the Bohai Sea during summer. Given the higher DMSPp/chlorophyll *a* ratios, the proportions of high-DMSP producers might increase at these stations. Phytoplankton identification and enumeration undertaken in the same cruise showed that the maximum abundance of *Noctiluca scintillans*, a dinoflagellate, was at station B65 near the Huanghe River estuary.

In the South Yellow Sea, microplankton contributions to DMSPp and chlorophyll *a* were found at stations H21 and H36 in the Subei coastal area, and at station H41, situated in the nutrient-rich area. Some authors have proposed that the phytoplankton community structure is affected by changes in the concentrations and proportions of nutrients (Iverson et al., 1989; Wang, 2003). Arin et al. (2005) reported that smaller-sized phytoplankton, particularly pico-phytoplankton, played a much greater role in oligotrophic waters, while microphytoplankton dominance was usually associated with nutrient-rich coastal areas. Because of the inputs of terrestrial runoff and the Changjiang River, nutrient concentrations were high in the Subei coastal waters and south of 34°N (Fig.4), which was beneficial for increasing the microplankton biomass, and therefore resulted in a high contribution of microplankton to DMSPp.

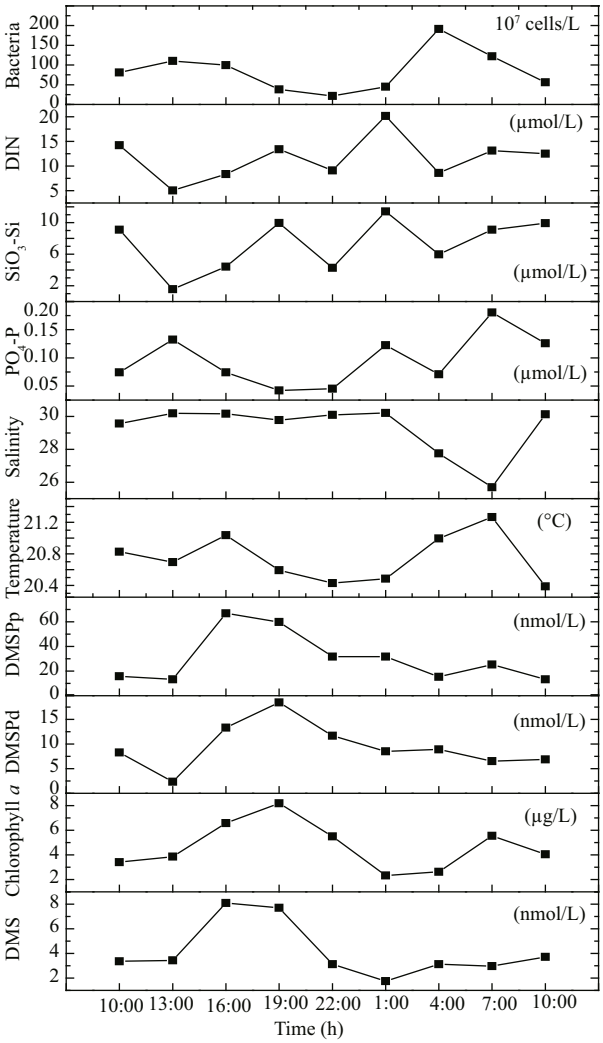

Fig.7 Diel variations of DMS, DMSP, and relevant physical, chemical and biological parameters at station B65 in the Bohai Sea

3.6 Diurnal variation of DMS and DMSP

Diurnal variations in DMS, DMSP, and chlorophyll *a* concentrations were investigated at station B65. There was a distinct daily rhythm for chlorophyll *a* and sulfur compounds, with values increasing during the daytime and decreasing during the night. As shown in Fig.7, the diel patterns of DMS, DMSPd, and DMSPp were similar to those of chlorophyll *a*. Maximum concentrations of DMS, DMSPd, DMSPp, and chlorophyll *a* appeared simultaneously between 16:00 and 19:00. The minimum DMS concentration was reported at 1:00, obviously in response to the minimum chlorophyll *a* level at the same time, while the DMSPp concentration was lowest at 4:00. These results are similar to those from other studies. For example, Yang et al. (2006) found that the maximum daily concentration of DMS occurred between 14:00 and 17:00 in the South China Sea. Kumar et al. (2009) reported that the daily maximum DMSPt (DMSPd and DMSPp) concentration was recorded at 17:00 in Dona Paula Bay.

Solar radiation is a key factor for the production of DMS and DMSP. Simó et al. (2002) found that phytoplankton production of DMSP reached a maximum at noon and concluded that DMSP biosynthesis was a diurnal process that was coupled with photosynthesis. The DMS concentration was very low at noon as DMS loss by photooxidation was greatest at that time. The concentrations of chlorophyll *a* gradually increased through the afternoon and reached a maximum at 19:00, indicating that phytoplankton growth was more active in the afternoon. Comparison of the nutrient concentrations measured at these times showed that values of phosphate and DIN were lower at 16:00–19:00 and

Table 4 Summary of the sea-to-air fluxes of DMS from the Yellow Sea in the literature

Date	DMS (nmol/L)	Wind speed (m/s)	DMS fluxes (μmol/(m²·d))	Reference
September, 1994	2.89 (0.95–7.48)	-	4.54 (0.11–18.88)	Hu et al., 2003
March, 2005	2.31 (1.20–4.54)	6.9 (0.3–10.4)	3.14 (0.01–5.68)	Yang et al., 2006
January, 2007	1.97 (0.92–3.93)	6.2 (0.7–12.2)	2.30 (0.02–12.17)	Zhang, 2009
June, 2011	7.12 (1.60–12.36)	3.87 (0.2–7.8)	4.87 (0.05–25.13)	This study

values were higher between 1:00 and 7:00, implying that more nutrients were consumed by microorganisms in the afternoon, and thus higher levels of chlorophyll *a*, DMS, and DMSP were recorded at that time. The rising levels of DMS and DMSP during the daytime might also be attributed to photo-inhibition of biological DMS and DMSP consumption. Slezak et al. (2001) showed that bacterial removal of DMSP and DMS in oceanic surface waters was severely reduced in the presence of solar radiation. In this study, bacterial abundance had a diel cycle that contrasted with DMS and DMSP concentrations, with low values during the daytime and high values during the night (Fig.7). This suggests that bacterial activity was negatively impacted by solar radiation, which resulted in the accumulation of DMS and DMSP in the daytime. Finally, the accumulation of DMS and DMSP during the daytime when oxidative stress increased might be able to be explained with reference to the antioxidative function of DMSP and its product, DMS. DMSP and DMS may serve as effective cellular scavengers of harmful hydroxyl radicals (OH) produced during photosynthesis in algal cells that are stressed by solar radiation (Sunda et al., 2002). Thus, the intensity of solar radiation could have a significant influence on the diel variations of DMS and DMSP.

3.7 Sea-to-air flux of DMS

The sea-to-air flux of DMS can be calculated using the equation of Nightingale et al. (2000):

$$F=K\Delta C_{DMS}=KC_W,$$

where K is the gas transfer coefficient, and ΔC_{DMS} is the difference in the DMS concentration between seawater and the atmosphere, which is generally equal to the concentration of dissolved DMS in the surface seawater (C_W) since the atmospheric DMS concentration is generally 2–3 orders of magnitude lower than C_W. Recent studies (Nightingale et al., 2000; Huebert et al., 2004) indicated that the most defensible gas exchange velocities fall between those of LM86 (Liss and Merlivat, 1986) and W92 (Wanninkhof, 1992). The main N2000 model (Nightingale et al., 2000) was used to calculate the gas transfer coefficients and the results were mainly between those of LM86 and W92. The *Sc* of DMS at the local temperature is obtained using the equation put forward by Saltzman et al. (1993). In this study, wind speeds were measured at about 10 m above the sea surface by ship-borne weather instruments (R.M. Young, Traverse City, MA, USA) and were automatically corrected to true wind speeds.

The sea-to-air fluxes of DMS obtained in this study extended over three orders of magnitude (0.14–92.04 μmol/(m²·d)), with an average of 11.07 μmol/(m²·d). There was large variability in the results from the equation because of the obvious differences in the DMS concentrations and wind speeds among the sampling stations. For example, the flux was highest at station B62, where the DMS concentrations and wind speeds were highest. In contrast, the flux was lowest at station H07, which had the lowest wind speed. Throughout the study area, although the average DMS concentration in the Bohai Sea was lower than that in the Yellow Sea, the mean flux in the Bohai Sea (19.07 μmol/(m²·d)) was more than twice as high as that in the Yellow Sea (7.78 μmol/(m²·d)). This result was mainly attributed to the higher wind speeds in the Bohai Sea. Other seasonal results reported previously in the Yellow Sea are listed in Table 4. To allow comparison with results from previous studies, the fluxes in the Yellow Sea were calculated by LM86 and the mean flux was higher than those previously obtained in this sea (Table 4) owing to the higher DMS concentrations observed in this study. These results suggest that the higher DMS fluxes in summer might make a greater contribution to the DMS emissions in the Yellow Sea.

Based on the average flux of DMS in this investigation, the estimated DMS emission rate in the study area was about 0.059 Tg S/a. The Yellow Sea and the Bohai Sea make up 0.12% of total ocean area. According to preliminary estimates, the annual DMS emissions from this study area accounted for 0.18%–0.39% of total annual emissions (15–33 Tg S/a) from the world's oceans (Kettle and Andreae, 2000). The

Yellow Sea and the Bohai Sea are productive coastal and shelf regions, owing to the effects of anthropogenic activities. Our results indicate that the net DMS emissions from productive coastal and shelf regions may have a significant influence on the global oceanic DMS flux, although they occupy only a small part of the world ocean.

3 CONCLUSION

The biogeochemistry of DMS, DMSP, and chlorophyll *a* in the Yellow Sea and the Bohai Sea was investigated in this study. In the North Yellow Sea and the Bohai Sea, high concentrations of DMS and DMSP were accompanied with high chlorophyll *a* concentrations and DMSPp concentrations were significantly correlated with chlorophyll *a* concentrations. In the South Yellow Sea, high concentrations of DMS and DMSP appeared in the SYSCWM area due to the relatively high proportion of dinoflagellates. These results showed that phytoplankton biomass and species composition were two important factors controlling the distribution of DMS and DMSP. In addition, we observed that terrestrial runoff, such as that from the Changjiang River and Huanghe River, could have a significant impact on the spatial variability of DMS and DMSP. Overall, the production and consumption rates of DMS in the Bohai Sea and the North Yellow Sea were higher than those in the South Yellow Sea, reflecting the impact of anthropogenic activities. There was a significant relationship between DMSPd concentrations and DMS production rates in the study area, suggesting that the DMS production was directly dependent on the in situ DMSPd concentration. Our observations showed that there was a clear diurnal pattern in DMS and DMSP concentrations, with high values during the daytime and low values at night, reflecting the fact that DMSP and DMS cycles in surface waters are influenced significantly by solar radiation. Size fractionation showed that most of the chlorophyll *a* and DMSPp were associated with the larger nanoplankton, and that the larger nanoplankton fraction mainly comprised diatoms. Preliminary estimates showed that the annual DMS emissions from the Yellow Sea and the Bohai Sea accounted for about 0.18%–0.39% of the total annual DMS emissions in the world's oceans. Relative to the small area of these two seas (only 0.12% of the world's oceans), DMS emissions from the study area make a significant contribution to the global oceanic DMS fluxes. However, it should be noted here that, owing to limited time and experimental conditions, the sampling stations were not distributed throughout the whole of the Yellow Sea and the Bohai Sea. Further research is needed to cover a wider study area.

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References

Andreae M O, Barnard W R. 1984. The marine chemistry of dimethylsulfide. *Marine Chemistry*, **14**(3): 267-279.

Andreae M O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Marine Chemistry*, **30**: 1-29.

Aranami K, Watanabe S, Tsunogai S, Hayashi M, Furuya K, Nagata T. 2001. Biogeochemical variation in dimethylsulfide, phytoplankton pigments and heterotrophic bacterial production in the subarctic North Pacific during summer. *Journal of Oceanography*, **57**(3): 315-322.

Archer S D, Safi K, Hall A, Cummings D G, Harvey M. 2011. Grazing suppression of dimethylsulphoniopropionate (DMSP) accumulation in iron-fertilised, sub-Antarctic waters. *Deep Sea Research Part II*: *Topical Studies in Oceanography*, **58**(6): 839-850.

Arin L, Estrada M, Salat J, Cruzado A. 2005. Spatio-temporal variability of size fractionated phytoplankton on the shelf adjacent to the Ebro river (NW Mediterranean). *Continental Shelf Research*, **25**(9): 1 081-1 095.

Ayers G P, Gillett R W. 2000. DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry. *Journal of Sea Research*, **43**(3-4): 275-286.

Bates T S, Kiene R P, Wolfe G V, Matrai P A, Chavez F P, Buck K R, Blomquist B W, Cuhel R L. 1994. The cycling of sulfur in surface seawater of the Northeast Pacific. *Journal of Geophysical Research*, **99**(C4): 7 835-7 843.

Belviso S, Christaki U, Vidussi F, Marty J C, Vila M, Delgado M. 2000. Diel variations of the DMSP-to-chlorophyll *a* ratio in northwestern Mediterranean surface waters. *Journal of Marine Systems*, **25**(2): 119-128.

Besiktepe S, Tang K W, Vila M, Simó R. 2004. Dimethylated sulfur compounds in seawater, seston and mesozooplankton in the seas around Turkey. *Deep Sea Research I*: *Oceanographic Research Papers*, **51**(9): 1 179-1 197.

Charlson R J, Lovelock J E, Andreae M O, Wakeham S G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, **326**(6114): 655-661.

Chen Y Z. 2007. Numerical Simulation of Seasonal Changes

of the Circulation and Changjiang Dilute Water in the Yellow Sea and East China Sea. Master Thesis, East China Normal University, Shanghai, China. (in Chinese with English abstract)

Cui M C. 1984. A study on the direction change of the Changjiang river diluted water. *Oceanologia et Limnologia Sinica*, **15**(3): 222-229. (in Chinese with English abstract)

Dacey J W H, Blough N V. 1987. Hydroxide decomposition of dimethylsulfoniopropionate to form dimethylsulfide. *Geophysical Research Letters*, **14**(12): 1 246-1 249.

Dacey J W H, Howse F A, Michaels A F, Wakeham S G. 1998. Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea. *Deep Sea Research I*: *Oceanographic Research Papers*, **45**(12): 2 085-2 104.

Dacey J W H, Wakeham S G. 1986. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. *Science*, **233**(4470): 1 314-1 316.

Diao H X, Shen Z L. 1985. The vertical distribution of the chemical factors in the Yellow Sea Cold Water. *Studia Marina Sinica*, **25**: 41-51. (in Chinese)

Dong Q, Liu H Y, Bi Y P, Jiang S, Wang W B, Li P J. 2002. Ecological study on planktonic dinoflagellates in inshore of Northern Yellow Sea. *Marine Fisheries Research*, **23**(4): 46-50. (in Chinese with English abstract)

Evans C, Kadner S V, Darroch L J, Wilson W H, Liss P S, Malin G. 2007. The relative significance of viral lysis and microzooplankton grazing as pathways of dimethylsulfoniopropionate (DMSP) cleavage: an Emiliania huxleyi culture study. *Limnology and Oceanography*, **52**(3): 1 036-1 045.

Fu M Z, Wang Z L, Pu X M, Xu Z J, Zhu M Y. 2012. Changes of nutrient concentrations and N:P:Si ratios and their possible impacts on the Huanghai Sea ecosystem. *Acta Oceanologica Sinica*, **31**(4): 101-112.

Groene T. 1995. Biogenic production and consumption of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the marine epipelagic zone: a review. *Journal of Marine Systems*, **6**(3): 191-209.

Hodgkiss I J, Lu S H. 2004. The effects of nutrients and their ratios on phytoplankton abundance in Junk Bay, Hong Kong. *Hydrobiologia*, **512**(1-3): 215-229.

Holligan P M, Turner S M, Liss P S. 1987. Measurements of dimethyl sulphide in frontal regions. *Continental Shelf Research*, **7**(2): 213-224.

Hu H G, Wan Z W, Yuan Y L. 2004. Simulation of seasonal variation of phytoplankton in the southern Huanghai (Yellow) Sea and analysis on its influential factors. *Acta Oceanologica Sinica*, **26**(6): 74-88. (in Chinese with English abstract)

Hu M, Tang X Y, Li J T, Ma Q J. 2003. Distributions of dimethylsulfide in the Bohai Sea and Yellow Sea of China. *Journal of Environmental Science*, **15**(6): 762-767.

Huebert B J, Blomquist B W, Hare J E, Fairall C W, Johnson J E, Bates T S. 2004. Measurement of the sea-air DMS flux and transfer velocity using eddy correlation. *Geophysical Research Letters*, **31**(23), http://dx.doi.org/10.1029/2004GL021567.

Iverson R L, Neaehoof F L, Andreae M O. 1989. Production of dimethylsulfonium propionate and dimethylsulfide by phytoplankton in estuarine and coastal waters. *Limnology and Oceanography*, **34**(1): 53-67.

Karsten U, Kirst G O, Wiencke C. 1992. Dimethylsulphoniopropionate (DMSP) accumulation in green macioalgae from polar to temperate regions: interactive effects of light versus salinity and light versus temperature. *Polar Biology*, **12**(6-7): 603-607.

Kettle A J, Andreae M O, Amouroux D, Andreae T W, Bates T S, Berresheim H, Bingemer H, Boniforti R, Curran M A J, Ditullio G R, Helas G, Jones G B, Keller M D, Kiene R P, Leck C, Levasseur M, Malin G, Maspero M, Matrai P, McTaggart A R, Mihalopoulos N, Nguyen B C, Novo A, Putaud J P, Rapsomanikis S, Roberts G, Schebeske G, Sharma S, Simó R, Staubes R, Turner S, Uher G. 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global Biogeochemical Cycles*, **12**(2): 399-444.

Kettle A J, Andreae M O. 2000. Flux of dimethylsulfide from the oceans: a comparison of updated data sets and flux models. *Journal of Geophysical Research*, **105**(D22): 26 793-26 808.

Kiene R P, Bates T S. 1990. Biological removal of dimethyl sulphide from sea water. *Nature*, **345**(6277): 702-705.

Kiene R P, Linn L J, Bruton J A. 2000. New and important roles for DMSP in marine microbial communities. *Journal of Sea Research*, **43**(3-4): 209-224.

Kiene R P, Service S K. 1991. Decomposition of dissolved DMSP and DMS in estuanine waters: dependence on temperature and substrate concentration. *Marine Ecology Progress Series*, **76**: 1-11.

Kumar S S, Chinchkar U, Nair S, Loka Bharathi P A, Chandramohan D. 2009. Seasonal dimethylsulfoniopropionate (DMSP) variability in Dona Paula bay. *Estuarine*, *Coastal and Shelf Science*, **81**(3): 301-310.

Li J. 2008. The Research of Nutrient Structure and its Function on the Succession of Phytoplankton Predominant Species in the High Frequent Harmful Algae Blooms Occurrence Areas in East China Sea. Master Thesis, Ocean University of China Qingdao, China. (in Chinese with English abstract)

Liss P S, Merlivat L. 1986. Air-sea gas exchange rates: introduction and synthesis. *In*: Buat-Ménard P ed. The Role of Air-Sea Exchange in Geochemical Cycling. Springer Netherlands, New York. p.113-127.

Liu Z L, Wei H, Lozovatsky I D, Fernando H J S. 2008. Late summer stratification, internal waves, and turbulence in the Yellow Sea. *Journal of Marine Systems*, **77**(4): 459-472.

Lu L. 2012. Species Diversity of Phytoplankton in Yellow Sea and Bohai Sea and Molecular Identification of Microalgal Isolates. Master Thesis, Ocean University of China

Qingdao, China. (in Chinese with English abstract)

Mei X L, Fang N J. 2013. The distribution characteristics and species diversity of phytoplankton in offshore water of Jiangsu Province in summer. *Modern Agricultural Science and Technology*, (4): 229-232. (in Chinese with English abstract)

Nguyen B C, Mihalopoulos N, Putaud J P, Gaudry A, Gallet L, Keene W C, Galloway J N. 1992. Covariations in oceanic dimethyl sulfide, its oxidation products and rain acidity at Amsterdam Island in the southern Indian Ocean. *Journal of Atmospheric Chemistry*, **15**(1): 39-53.

Nightingale P D, Malin G C, Law S, Watson A J, Liss P S, Liddicoat M I, Boutin J, Upstill-Goddard R C. 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Global Biogeochemical Cycles*, **14**(1): 373-388.

Ning X R, Lin C L, Su J L, Liu C G, Hao Q, Le F F, Tang Q S. 2010. Long-term environmental changes and the responses of the ecosystems in the Bohai Sea during 1960-1996. *Deep Sea Research II*: *Topical Studies in Oceanography*, **57**(11-12): 1 079-1 091.

Parsons T R, Maita Y, Lalli C M. 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Oxford. 173p.

Porter K G, Feig Y S. 1980. The use of DAPI for identifying and counting aquatic microflora. *Limnology and Oceanography*, **25**(5): 943-948.

Pu X M, Sun S, Yang B, Ji P, Zhang Y S, Zhang F. 2004. The combined effects of temperature and food supply on *Calanus sinicus* in the southern Yellow Sea in summer. *Journal of Plankton Research*, **26**(9): 1 049-1 057.

Saltzman E S, King D B, Holmen K, Leck C. 1993. Experimental determination of the diffusion coefficient of dimethylsulfide in water. *Journal of Geophysical Research*, **98**(C9): 16 481-16 486.

Scarratt M G, Levasseur M, Schultes S, Michaud S, Cantin G, Vézina A, Gosselin M, de Mora S J. 2000. Production and consumption of dimethylsulfide (DMS) in North Atlantic waters. *Marine Ecology Progress Series*, **204**: 13-26.

Schultes S, Levasseur M, Michaud S, Cantin G, Wolfe G, Gosselin M, de Mora S. 2000. Dynamics of dimethylsulfide production from dissolved dimethylsulfoniopropionate in the Labrador Sea. *Marine Ecology Progress Series*, **202**: 27-40.

Shenoy D M, Dileep Kumar M. 2007. Variability in abundance and fluxes of dimethyl sulphide in the Indian Ocean. *Biogeochemistry*, **83**(1-3): 277-292.

Shenoy D M, Paul J T, Gauns M, Ramaiah N, Kumar M D. 2006. Spatial variations of DMS, DMSP and phytoplankton in the Bay of Bengal during the summer monsoon 2001. *Marine Environmental Research*, **62**(2): 83-97.

Shi W, Wang M H. 2012. Satellite views of the Bohai Sea, Yellow Sea, and East China Sea. *Progress in Oceanography*, **104**: 30-45.

Simó R, Archer S D, Pedrós-Alió C, Gilpin L, Stelfox-Widdicombe C E. 2002. Coupled dynamics of dimethylsulfoniopropionate and dimethylsulfide cycling and the microbial food web in surface waters of the North Atlantic. *Limnology and Oceanography*, **47**(1): 53-61.

Simó R, Grimalt J O, Albaiglés J. 1997. Dissolved dimethylsulphide, dimethylsulphoniopropionate and dimethylsulphoxide in western Mediterranean waters. *Deep Sea Research II*: *Topical Studies in Oceanography*, **44**(3-4): 929-950.

Simó R, Vila-Costa M, Alonso-Sáez L, Cardelús C, Guadayol Ò, Vázquez-Domínguez E, Gasol J M. 2008. Annual DMSP contribution to S and C fluxes through phytoplankton and bacterioplankton in a NW Mediterranean coastal site. *Aquatic Microbial Ecology*, **57**(1): 43-55.

Simó R. 2004. From cells to globe: approaching the dynamics of DMS(P) in the ocean at multiple scales. *Canadian Journal of Fisheries and Aquatic Sciences*, **61**(5): 673-684.

Slezak D, Brugger A R, Herndl G J. 2001. Impact of solar radiation on the biological removal of dimethylsulfoniopropionate and dimethylsulfide in marine surface waters. *Aquatic Microbial Ecology*, **25**(1): 87-97.

Stefels J. 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *Journal of Sea Research*, **43**(3-4): 183-197.

Steinke M, Malin G, Gibb S W, Burkill P H. 2002. Vertical and temporal variability of DMSP lyase activity in a coccolithophorid bloom in the northern North Sea. *Deep Sea Research II*: *Topical Studies in Oceanography*, **49**(15): 3 001-3 016.

Sun J, Liu D Y, Yang S M, Guo J, Qian S B. 2002. The preliminary study on phytoplankton community structure in the central Bohai Sea and the Bohai Strait and its adjacent area. *Oceanologia et Limnologia Sinica*, **33**(5): 461-471. (in Chinese with English abstract)

Sunda W G, Kieber D J, Kiene R P, Huntsman S. 2002. An antioxidant function for DMSP and DMS in marine algae. *Nature*, **418**(6895): 317-320.

Taylor B F. 1993. Bacterial transformations of organic sulfur compounds in marine environments. *In*: OremLand R S ed. Biogeochemistry of Global Change-Radiatively Active Trace Gases. 1st edn. Springer US, New York. p.745-781.

Tian W, Sun J. 2011. Later spring phytoplankton community in Southern Yellow Sea in 2009. *Marine Sciences*, (6): 19-24. (in Chinese with English Abstract)

Tian W. 2011. Phytoplankton Community Structure and Species Succession in Bloom of Central Yellow Sea 2009. Master Thesis, Ocean University of China Qingdao, China. (in Chinese with English abstract)

Turner S M, Malin G, Liss P S, Harbour D S, Holligan P M. 1988. The seasonal variation of dimethyl sulfide and dimethylsulfoniopropionate concentrations in nearshore waters. *Limnology and Oceanography*, **33**(3): 364-375.

Uher G, Schebeske G, Barlow R G, Cummings D G, Mantoura R F C, Rapsomanikis S R, Andreae M O. 2000. Distribution and air-sea gas exchange of dimethyl

sulphide at the European western continental margin. *Marine Chemistry*, **69**(3-4): 277-300.

Uzuka N, Watanabe S, Tsunogai S. 1996. Dimethylsulfide in coastal zone of the East China Sea. *Journal of Oceanography*, **52**(3): 313-321.

Vila-Costa M, Kiene R P, Simó R. 2008. Seasonal variability of the dynamics of dimethylated sulfur compounds in a coastal northwest Mediterranean site. *Limnology and Oceanography*, **53**(1): 198-211.

Wang B D. 2000. Characteristics of variations and interrelations of biogenic elements in the Huanghai Sea Cold Water Mass. *Acta Oceanologica Sinica*, **22**(6): 47-54. (in Chinese with English abstract)

Wang B D. 2003. Nutrient distributions and their limitation on phytoplankton in the Yellow Sea and the East China Sea. *Chinese Journal of Applied Ecology*, **14**(7): 1 122-1 126. (in Chinese with English abstract)

Wanninkhof R. 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research*, **97**(C5): 7 373-7 382.

Yang G P, Jing W W, Kang Z Q, Zhang H H, Song G S. 2008. Spatial variations of dimethylsulfide and dimethylsulfoniopropionate in the surface microlayer and in the subsurface waters of the South China Sea during springtime. *Marine Environmental Research*, **65**(1): 85-97.

Yang G P, Jing W W, Li L, Kang Z Q, Song G S. 2006. Distribution of dimethylsulfide and dimethylsulfoniopropionate in the surface microlayer and subsurface water of the Yellow Sea, China during spring. *Journal of Marine Systems*, **62**(1-2): 22-34.

Yang G P, Levasseur M, Michaud S, Scarratt M. 2005. Biogeochemistry of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the surface microlayer and subsurface water of the western North Atlantic during spring. *Marine Chemistry*, **96**(3-4): 315-329.

Yang G P, Liu X T, Li L, Zhang Z B. 1999. The biogeochemistry of dimethylsulfide in the South China Sea. *Journal of Sea Research*, **57**(1): 189-211. (in Chinese with English abstract)

Yang G P, Zhang H H, Zhou L M, Yang J. 2011. Temporal and spatial variations of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the East China Sea and the Yellow Sea. *Continental Shelf Research*, **31**(13): 1 325-1 335.

Yang G P, Zhuang G C, Zhang H H, Dong Y, Yang J. 2012. Distribution of dimethylsulfide and dimethylsulfoniopropionate in the Yellow Sea and the East China Sea during spring: spatio-temporal variability and controlling factors. *Marine Chemistry*, **138-139**: 21-31.

Yoch D C. 2002. Dimethylsulfoniopropionate: its sources, role in the marine food web, and biological degradation to dimethylsulfide. *Applied and Environmental Microbiology*, **68**(12): 5 804-5 815.

Yost D M, Jones R J, Mitchelmore C L. 2010. Alterations in dimethylsulfoniopropionate (DMSP) levels in the coral Montastraea franksi in response to copper exposure. *Aquatic Toxicology*, **98**(4): 367-373.

Yuan D L, Zhu J R, Li C Y, Hu D X. 2008. Cross-shelf circulation in the Yellow and East China Seas indicated by MODIS satellite observations. *Journal of Marine Systems*, **70**(1-2): 134-149.

Zhang H H, Yang G P, Zhu T. 2008. Distribution and cycling of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in the sea-surface microlayer of the Yellow Sea, China, in spring. *Continental Shelf Research*, **28**(17): 2 417-2 427.

Zhang H H. 2009. Studies on Biogeochemistry of DMS and DMSP in the East China Sea and the Yellow Sea. Doctoral Thesis, Ocean University of China Qingdao, China. (in Chinese with English abstract)

Zhang S W, Xia C S, Yuan Y L. 2002. The physical-ecological coupling numerical models in the Yellow Sea Cold Water. *Progress in Natural Science*, **12**(3): 315-319, 323. (in Chinese)

Zubkov M V, Fuchs B M, Archer S D, Kiene R P, Amann R, Burkill P H. 2002. Rapid turnover of dissolved DMS and DMSP by defined bacterioplankton communities in the stratified euphotic zone of the North Sea. *Deep Sea Research II*: *Topical Studies in Oceanography*, **49**(15): 3 017-3 038.