

Seasonal and spatial variations of dimethylsulfoxide (DMSO) in the East China Sea and the Yellow Sea

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Abstract

Seasonal and spatial distributions of dissolved and particulate dimethylsulfoxide (DMSOd, DMSOp) were measured in the East China Sea and the Yellow Sea during March–April 2011 and October–November 2011. The concentrations of DMSOd and DMSOp in the surface water were 20.6 (5.13–73.8) and 8.90 (3.75–29.6) nmol/L in spring, and 13.4 (4.17–42.7) and 8.18 (3.44–22.6) nmol/L in autumn, respectively. Both DMSOd and DMSOp concentrations revealed similar seasonal changes with higher values occurring in spring, mainly because of the higher phytoplankton biomass observed in spring. Moreover, the ratios of DMSOp/chlorophyll *a* also exhibited an apparent seasonal change with higher values in autumn (35.7 mmol/g) and lower values in spring (23.4 mmol/g), thereby corresponding with the seasonal variation in the proportion of DMSO producers in the phytoplankton community between spring and autumn. In addition, DMSOd and DMSOp concentrations in the surface seawater revealed obvious diurnal variations with the maxima appearing in the afternoon.

Key words: dimethylsulfoxide (DMSO), distribution, variation, East China Sea, Yellow Sea

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1 Introduction

Considerable attention has been focused on dimethylsulphoxide (DMSO) for its involvement in the global sulfur cycle in both the atmosphere (Koga and Tanaka, 1993) and the oceans (Lee and de Mora, 1999), owing to its important role in the biogeochemical cycle of dimethylsulfide (DMS), which is the dominant volatile sulfur compound produced in marine surface waters (Lovell et al., 1972; Andreae, 1990; Bates et al., 1992; Zhang et al., 2008; Lana et al., 2011). DMS is an important source of sulfur to the atmosphere, and contributes approximately 50% of the global biological sulfur flux to the atmosphere (Bates et al., 1992). Once in the atmosphere, DMS can be oxidized to SO₂ and methylsulfonate (MSA), producing non-sea-salt sulfate aerosols, which act as an important source of cloud-condensation nuclei (CCN) potentially affecting global climate (Charlson et al., 1987). Besides, the oxidation products of DMS also contribute to the acidity of rainfall (Nguyen et al., 1992). Andreae (1990) believed that the global average temperature would change with the flux of DMS controlled mainly by its concentration in the sea surface. Therefore, it was extremely important to study the factors affecting its surface concentration (Lee et al., 1999).

In marine environments, DMSO can be produced from photochemical oxidation and biological consumption of DMS (Brimblecombe and Shooter, 1986; Zeyer et al., 1987; Toole et al., 2004). Some bacteria (Zinder and Brock, 1978; Bilou and Wein-

er, 1985; McEwan et al., 1985) and eukaryotic algae (Spiese et al., 2009) could reduce DMSO back to DMS. As a sink or source of DMS in the ocean, DMSO can indirectly influence the global climate and environment conditions through the exchange with DMS (Hatton et al., 2004). The photo-oxidation process of DMS was influenced by a variety of factors such as irradiance wavelength (Kieber et al., 1996; Toole et al., 2004), photosensitizers, nitrate concentrations (Kieber et al., 1996; Hatton, 2002; Toole et al., 2004; Brugger et al., 1998), and dissolved organic materials (Brimblecombe and Shooter, 1986; Brugger et al., 1998). Del Valle et al. (2009) found in the Ross Sea that the DMSO yield from biological DMS consumption was higher in the surface mixed water than in deep water, suggesting that light intensity and temperature might be the main factor that controlled this process. Furthermore, marine phytoplankton can also directly produce DMSO (Andreae, 1980; Simó et al., 1998a; Lee et al., 2001), which may act as intracellular electrolyte modifiers, free-radical scavengers, and cryo-osmoregulators *in vivo* (Liss et al., 1997; Lee et al., 1999); these potential functions may be the possible metabolic pathways for phytoplankton to biosynthesize DMSO (Lee and de Mora, 1999). In addition, laboratory experiments indicated that DMSO could be reduced back to DMS (Zinder and Brock, 1978), as a terminal electron acceptor, by certain bacteria and eukaryotic algae (López and Duarte, 2004; Spiese et al., 2009).

Generally, the concentrations of dissolved DMSO (DMSOd)

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are one or two orders of magnitude higher than DMS and, sometimes, are also greater than dissolved DMSP (DMSPd) (Simó et al., 1997; Hatton et al., 1999). Therefore, the dissolved pools of dimethylated sulfur are usually dominated by DMSOd (Hatton, 2002; Hatton et al., 2004). Three main sources of DMSOd exist in marine environments: (1) DMS photo-oxidation. The major products (14% to 45%) of photo-oxidation of DMS are DMSO in different sea areas. (2) Biological DMS consumption. The main product (~72%) of the biological DMS consumption (BDMSC) is DMSO (del Valle et al., 2007b). (3) Particulate DMSO (DMSOp). DMSOp is mainly produced by phytoplankton (Andreae, 1980; De Mora et al., 1996); it can be released into the water column via processes such as cell senescence and lysis, zooplankton grazing or viral attack, thereby leading to the formation of DMSOd (de Mora et al., 1996). At present, data on DMSOp in the marine environment are much less known relative to DMSOd (Hatton et al., 2004).

China has a coastline of over 18×10^3 km and a sea area of $\sim 3 \times 10^6$ km², but only very limited data are available for DMSO in China seas. Yang et al. (2011) reported the distribution of DMSOd and DMSOp in the East China Sea (ECS) in winter. The goals of our study mainly include: (1) describe the temporal and spatial distributions of DMSOd and DMSOp in the ECS and the Yellow Sea (YS) during two cruises in spring and autumn; (2) investigate the possible correlations between the DMSO and environment factors such as salinity, chlorophyll *a* (Chl *a*) and nutrient concentrations; (3) acquire preliminary characteristics of DMSO biogeochemistry in the study area. We are the first to report the seasonal variation of DMSOp and DMSOd concentrations in the ECS and the YS.

2 Methods

2.1 Study area

The ECS and the YS, which are located on the Northwest Pacific Ocean with a total surface area of $\sim 1.2 \times 10^6$ km², are typical

continental seas. The semi-enclosed YS has a maximum depth of only 140 m, with an average depth of 44 m. The more open ECS reaches the maximum depth of 2 719 m in the Okinawa, with an average depth of 370 m (Zhang and Su, 2006). The Changjiang River (Yangtze River) is one of the major rivers that discharges into this shelf region. The Changjiang River diluted water flows southward in spring and autumn (Chen, 2009; Beardsley et al., 1985). Furthermore, the China coastal water, the Taiwan Strait water, the Yellow Sea Warm Current, and the oligotrophic Kuroshio water also have significant influences on the ECS and the YS (Liu et al., 1995). Thus, the ECS and the YS is considered one of the most complicated shelf sea areas in the world (Zhao et al., 2010).

2.2 Sampling

Two cruises were conducted in the ECS and the YS on board the R/V *Dongfanghong 2* from 18 March to 8 April 2011 and from 17 October to 5 November 2011, respectively. The sampling stations are shown in Fig. 1. A total of 56 stations were set up during the spring cruise, whereas the autumn cruise contained 63 stations. In addition, both spring and autumn cruises included one 24-h anchor station (P01). The surface seawater samples (1–3 m) were collected with 12 L Niskin bottles those were attached to a CTD (conductivity-temperature-depth) rosette. For the DMSOd determination, a subsample of 50 mL seawater was gravity-filtered through a Whatman GF/F filter, and the first few millilitres of filtrate were discarded to avoid carry-over of seawater held in the filter. The filters for DMSOp samples were cryostored at -80°C until laboratory analysis. The filtrates were used to determine the DMSOd on board. The required GF/F filters were calcined for one hour at 500°C and all the sampling bottles and reaction vials were rinsed with dilute HCl solution and then dried before being used.

2.3 Analytical procedures

The concentrations of DMSO in the samples were analyzed by

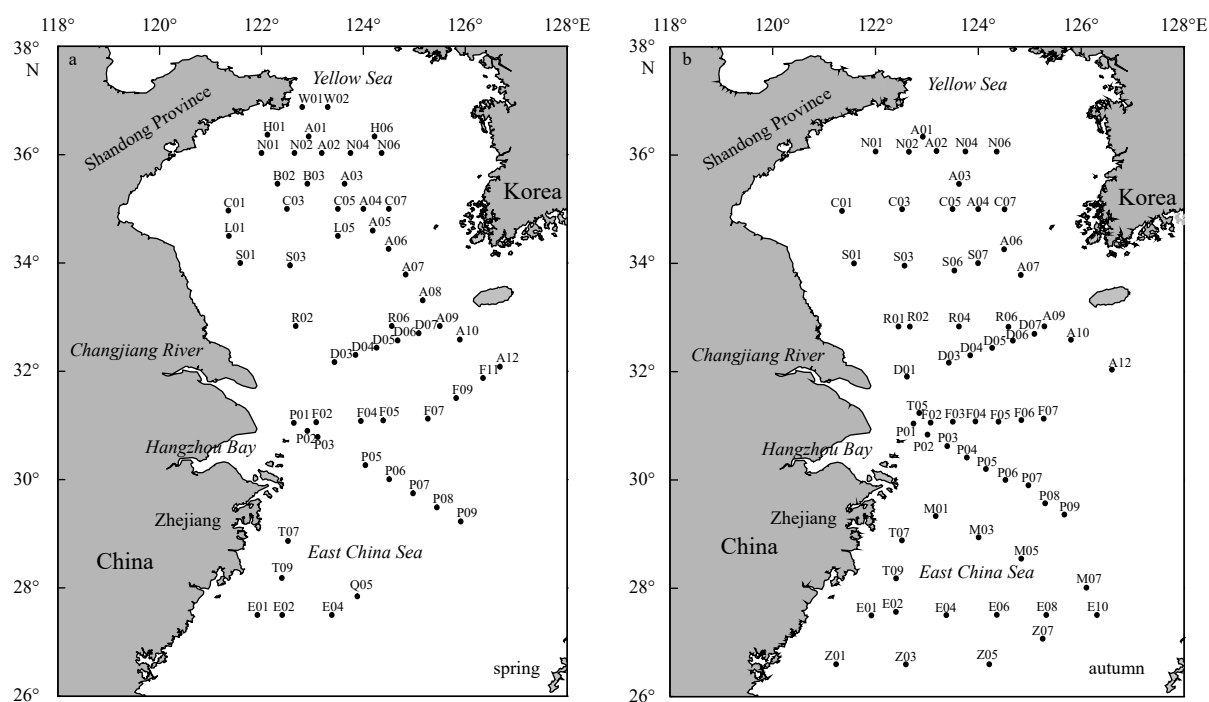


Fig. 1. Locations of sampling stations in the ECS and the YS during spring and autumn cruises.

reduction to DMS with sodium borohydride following procedures described by Simó et al. (1998b). Given that DMSO determination depends on transformation into DMS, the pre-existing DMS must be removed before the reduction. Moreover, DMSP in the seawater can also give rise to DMS at the reduction step, thereby influencing DMSO analysis. Therefore, the removal of DMS and DMSP before reduction is necessary. For the removal of DMS and DMSPd, the filtrate of 40 mL was added into a 42 mL glass vial with 2 mL of 10 mol/L KOH solution, and the vial was immediately sealed and kept in the dark at 4°C for 24 h to ensure that DMSPd had been completely converted to DMS (Dacey and Blough, 1987). After neutralizing by addition of 36% HCl to pH 4, the sample was injected into a bubbling chamber to remove the original DMS and the newly generated DMS by purging with ultra-pure nitrogen at a rate of 200 mL/min for 30 min. For the removal of particulate DMSP (DMSPp), the filter was placed in another 42 mL glass vial with 40 mL distilled water and 2 mL of 10 mol/L KOH solution and immediately sealed, similar to that of DMSPd.

The DMS and DMSPd or DMSPp free solution was added 0.12 g NaBH₄ to react for 10 min, and then was injected 1.0 mL of 5% HCl to react again for 4 min. The generated DMS was purged and then measured as described in Yang et al. (2006). Briefly, the solution in the stripping chamber was purged with ultra-pure nitrogen at a rate of 60 mL/min for 15 min. The extracted gas was dried through a glass tube that contained CaCl₂ and then trapped in a Teflon loop that was submerged in liquid nitrogen (−190°C). After extraction, the Teflon loop was quickly placed in hot water (90–100°C) and the desorbed gas was analyzed using an Agilent 7890A GC with a flame photometric detector (FPD) and a HP-5 high resolution GC column (30 m×0.32 mm, 0.25 μm). Distilled water treated with the same reagents used in these procedures were used as blanks. A small signal with the same retention time as DMS (equivalent to concentrations lower than 0.2 nmol/L DMSO) sporadically appeared after addition of NaBH₄ and HCl to blanks. Calibration was conducted by injecting a certain volume of DMSO standard (HPLC grade, Sigma-Aldrich) into the stripper which was filled with blank seawater without DMSO and subjecting them to the same manipulations as the sample. The resulting calibration curves were linear over the concentration range of interest. The detection limit for DMSO was 0.75 nmol/L for a 40 mL sample and mean relative standard deviation for routine sample replicates was generally better than 5%.

The concentrations of phosphate, silicate, and nitrate were determined onboard within 2 h of sample collection, using a Technicon Autoanalyser AAI (SEAL Analytical, UK) based on the procedure described by Strickland and Parsons (1972). In addition, the samples of Chl *a* were obtained by filtering 300 mL seawater through 47 mm Whatman GF/F glass fiber filters. Chl *a* retained on the filter was extracted with 10 mL 90% acetone for 24 h under a cool, dark condition and was then determined fluorometrically with an F-4500 Fluorometer (Hitachi, Japan) based on Parsons et al. (1984).

3 Results and discussion

3.1 Horizontal distributions of DMSOp and DMSOd in spring

The horizontal distributions of Chl *a*, salinity, DMSOp, DMSOd and nutrients in the surface water in spring are shown in Fig. 2. In general, Chl *a* can be used as an indicator of phytoplankton biomass. In the study area, the concentrations of Chl *a* fluctuated from 0.08 to 2.16 μg/L, with an average of 0.65 μg/L. The highest concentration of Chl *a* appeared at Sta. W01 near Shan-

dong Peninsula, whereas the lowest value occurred at offshore Stas A03 and P05. Chl *a* showed a general decrease in concentration from inshore to offshore sites (Fig. 2), with the higher values at Stas W01, W02, H01 and T07 in the coastal region. Similar to Chl *a* distribution, high nutrient levels occurred at Stas F02 and T07 in the Changjiang River Estuary and coastal waters, thereby reflecting the influence of terrestrial inputs.

The concentrations of DMSOp in the surface seawater ranged from 3.75 to 29.6 nmol/L, with an average of 8.90 nmol/L. The maximum concentration of DMSOp was found at Sta. H06 in the north of the investigated area. The second highest DMSOp concentration was observed at Sta. T07, where the highest Chl *a* level and the highest nutrient levels occurred. As shown in Fig. 2, DMSOp and Chl *a* displayed the similar distribution pattern, with higher concentrations in the coastal waters and lower values in the open sea. Given that DMSOp is produced by phytoplankton, the higher DMSOp concentrations in the coastal waters might be attributed to the high primary production here because of high nutrients and Chl *a* levels. Yang and Yang (2011) found that mean (range) DMSOp concentrations in the surface water were 21.3 (2.4–80.0) nmol/L in winter and the minimum value (2.4 nmol/L) appeared in the south-west ECS and the maximum value (80.0 nmol/L) occurred at the offshore station. Compared with Yang and Yang (2011), there was significant difference in DMSOp concentrations, with average value from Yang and Yang (2011) being by a factor of 2.4 higher than average value from the present study. Yang and Yang (2011) reported Chl *a* levels ranging from 0.20 to 1.06 μg/L, with an average of 0.51 μg/L. A Chl *a* levels variation from 0.08 to 2.16 μg/L with an average of 0.65 μg/L was observed in our study. The difference in the concentrations of DMSOp might be due to temporal variation of Chl *a* concentrations and different oceanic regions.

Throughout the study area, the concentrations of DMSOd were in most cases higher than those of DMSOp and ranged from 5.13 to 73.8 nmol/L with a mean of 20.6 nmol/L. Similar to DMSOp, DMSOd concentrations were higher in the coastal area than those in the open sea (Fig. 2). The highest concentration of DMSOd occurred at inshore Sta. T07 near the Zhejiang Province with the higher nutrients, Chl *a* and DMSOp concentrations, which was likely due to a coastal upwelling and anthropogenic input. The nutrient-rich water in the mixing layer is brought to the surface by the coastal upwelling of Zhejiang (Cao, 1986; Xu, 1986), which generates a burst of primary production (Wen, 2010; Yang et al., 2012), thereby leading to the higher DMSOd and DMSOp concentrations at this station. In addition, DMSO is widely used as a lubricant, solvent, stabilizer, and preservative in a large number of agricultural, industrial, and pharmaceutical applications (Simó, 1998). We therefore speculated that anthropogenic input might also contribute to the high DMSOd concentration in the coastal area. The high concentrations of Chl *a* and DMSOd were also observed in the coastal of Shandong Peninsula with relatively low concentrations of DMSOp, suggested that the DMSOp consumption rates seemed to be high enough to supply the high DMSOd concentrations. Simó (1998) found that the decrease of DMSOp corresponded to the increase of DMSOd, which indicated that DMSOp in seawater existed in plankton cells and could penetrate through the membrane to form DMSOd. The relatively high DMSOd concentrations were in the east of the Changjiang River Mouth where Chl *a* concentrations were very low. Therefore, we speculated that anthropogenic input might also contribute to the high DMSOd levels.

3.2 Horizontal distributions of DMSOp and DMSOd in autumn

The horizontal distributions of Chl *a*, salinity, DMSOd, DMSOp and nutrients in the surface water in autumn are shown in Fig. 3. Overall, the concentrations of DMSOd, DMSOp, Chl *a* and nutrients were lower compared with those in the spring cruise. During the autumn, the Changjiang River diluted water flows southward along the coast (Chen, 2009). As a result of terrestrial runoff, high nutrient levels occurred at Stas P01, P02, T05 and F02 located near the Changjiang River Estuary. The concentrations of Chl *a* in the surface water varied from 0.06 to 1.75 $\mu\text{g/L}$ with a mean of 0.34 $\mu\text{g/L}$. High Chl *a* levels appeared in the coastal area and in the northwest of the ECS. This was likely due to massive

nutrient input from anthropogenic input to stimulate the growth of phytoplankton, resulting in an increase in primary productivity.

Throughout the study area, the concentrations of DMSOp ranged from 3.44 to 22.6 nmol/L, with average values of 8.18. The highest DMSOp concentration appeared at the offshore station P08 where a moderate Chl *a* level of 0.35 $\mu\text{g/L}$ and low silicate level of 0.357 $\mu\text{mol/L}$ occurred. As shown in Fig. 3, DMSOp did not display a distribution pattern similar to Chl *a*, indicating that DMSOp concentrations were not only affected by phytoplankton biomass, but also depended on phytoplankton species composition. It is generally known that prymnesiophytes and dinoflagellates are the main DMSO producers, while diatoms are relatively

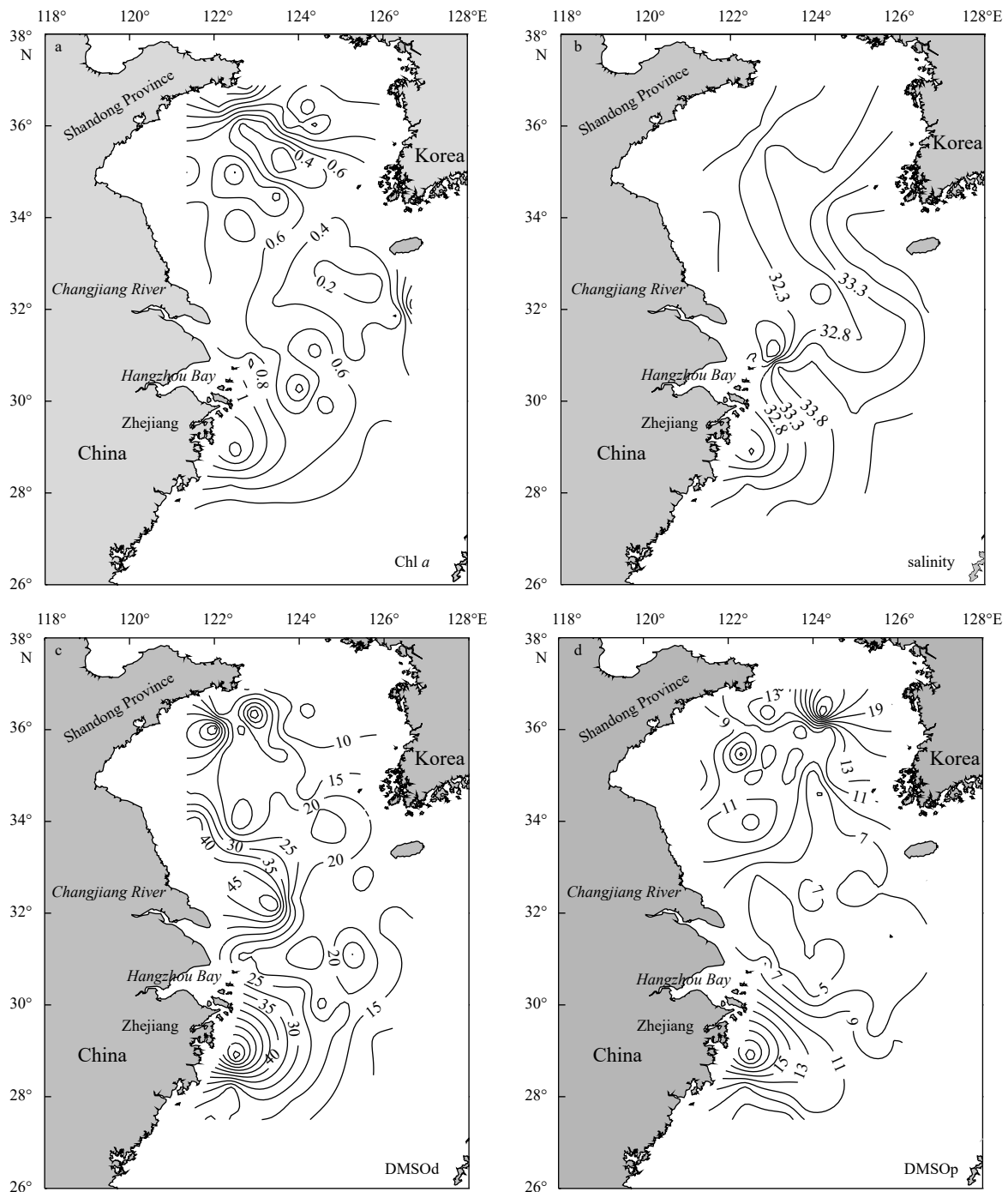


Fig. 2.

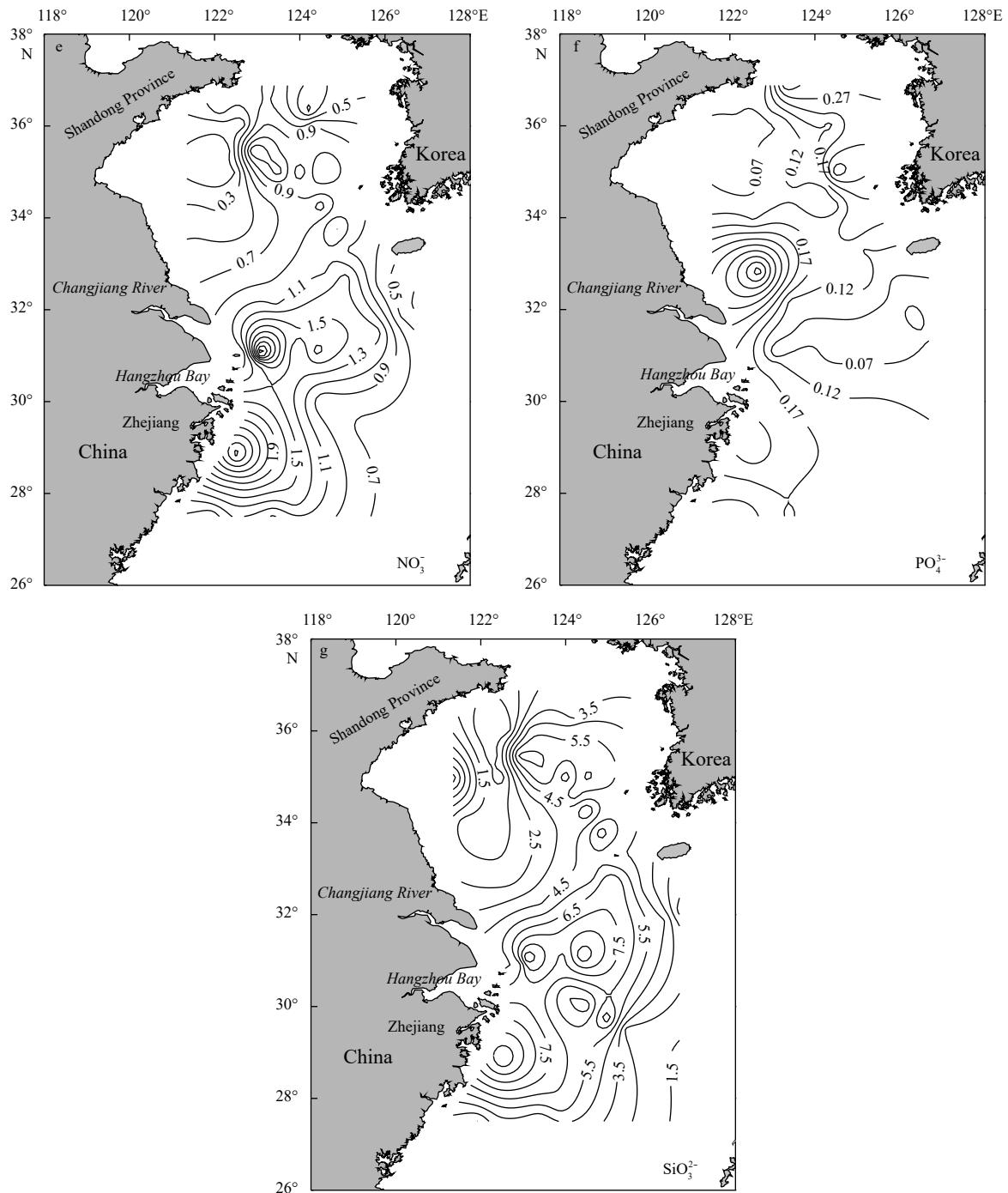


Fig. 2. Horizontal distribution of Chl *a* ($\mu\text{g/L}$), salinity, DMSOd (nmol/L), DMSOp (nmol/L) and nutrients ($\mu\text{mol/L}$) in spring.

poor DMSO producers (Hatton and Wilson, 2007). The highest concentration of DMSOp (p08) might be due to the low silicate concentration which restricted the growth of diatoms, thus leading to a significant increase in the proportion of dinoflagellates. The lower DMSOp concentrations were observed on the eastern continental shelf of the ECS, which might be attributed to the influence of Kuroshio water from the North Pacific. Additionally, other currents are present in autumn in the study area, such as the Yellow Sea Warm Current and Taiwan Strait water (Chen, 2009), which may affect the distributions of DMSOp (Zhang et al., 2008; Yang et al., 2011, 2012).

In autumn, the concentrations of DMSOd varied from 4.71 to

42.7 nmol/L with a mean of 13.4 nmol/L. These DMSOd concentrations were consistent with those measured in coastal and marine waters (Bouillon et al., 2002; Yang et al., 2011). The highest DMSOd concentration of 42.7 nmol/L was observed at the in-shore Sta. M01 near the Hangzhou Bay, which was similar to the distribution pattern in spring. Anthropogenic input and a coastal upwelling might contribute to the high DMSOd levels in this region. The minimum DMSOd concentration of 4.71 nmol/L appeared at Sta. P01 where the low Chl *a* level of 0.12 $\mu\text{g/L}$ occurred. In contrast, the DMSOd concentrations in the ECS were remarkably higher than in the YS.

3.3 Seasonal variation of DMSOp and DMSOd concentrations in the ECS and the YS

The horizontal distributions of DMSOd, DMSOp, Chl *a*, temperature, salinity and nutrients in the surface water during the two cruises are shown in Figs 2 and 3, respectively. In the study area, DMSOd average concentration in spring was 1.5-fold higher than the average value in autumn, while the average concentration of DMSOp in spring was only 1.1 times higher than the average concentration in autumn. Although DMSOp concentrations revealed little seasonal variations, the concentrations in spring were generally higher than those in autumn. In this study, the mean concentration of Chl *a* in spring was 0.65 $\mu\text{g/L}$, which

was two times higher than the average autumn concentration (0.34 $\mu\text{g/L}$). Simó and Vila-Costa (2006) also reported the seasonal variability of DMSOp concentration, which showed a maximum in summer (11 nmol/L) and a minimum in winter and autumn (1–2 nmol/L). Moreover, the nutrient concentrations in spring were also greater than the values in autumn. Harmful algal blooms frequently occurred in spring in the ECS and the YS because of the high nutrient levels (Yang et al., 2012), thereby leading to the relatively high concentrations of DMSOp in spring in this study.

In contrast with DMSOp, surface DMSOd concentrations showed a pronounced seasonal variation. The average concen-

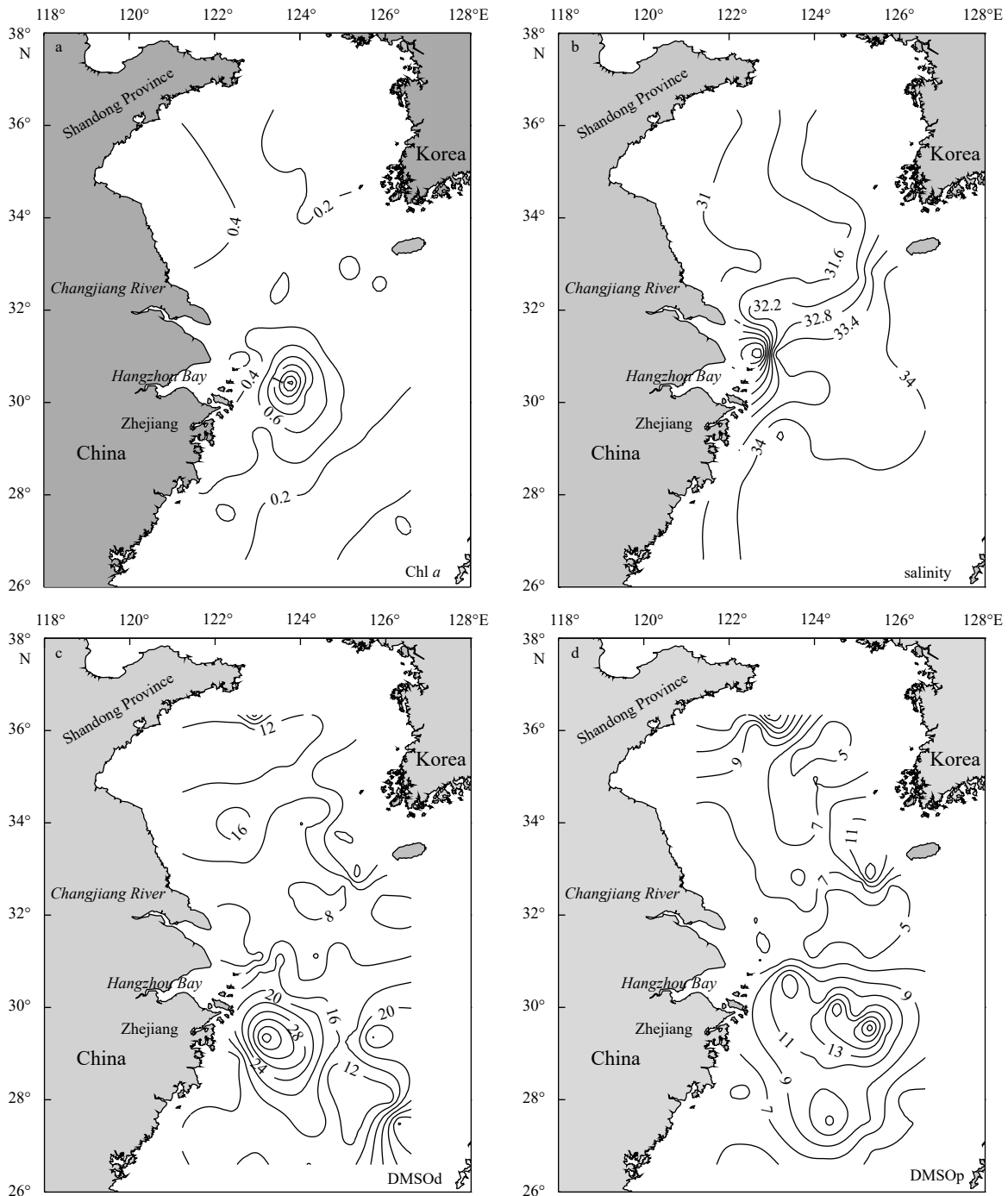


Fig. 3.

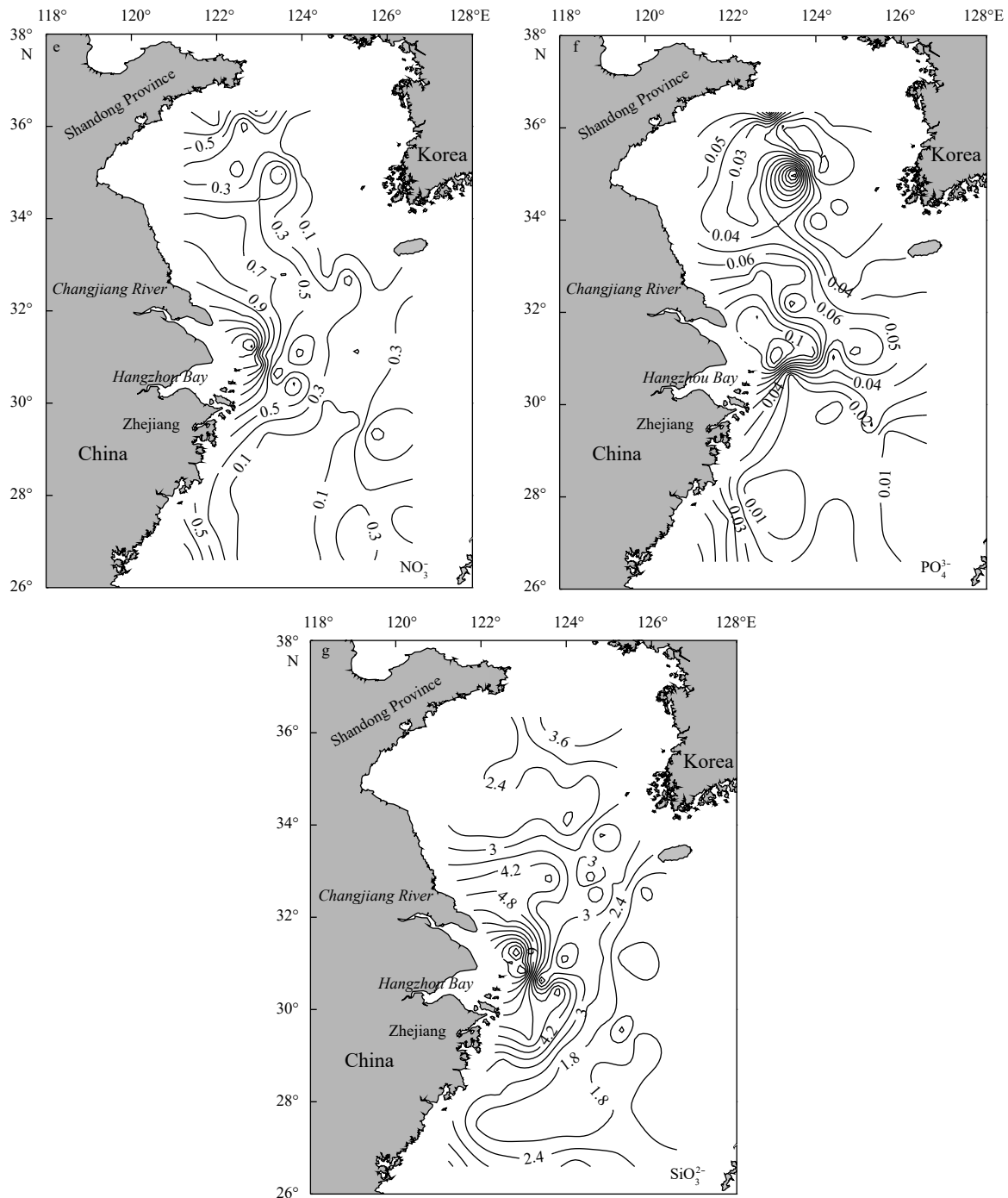


Fig. 3. Horizontal distribution of Chl *a* ($\mu\text{g/L}$), salinity, DMSOd (nmol/L), DMSOp (nmol/L) and nutrients ($\mu\text{mol/L}$) in autumn.

tration of DMSOd in spring (20.6 nmol/L) was higher than the mean value in autumn (13.4 nmol/L), which might be attributed to different sources of DMSOd in different seasons. In a recent study carried out in the Ross Sea, [Del Valle et al. \(2009\)](#) indicated that DMSOd concentrations in surface water exhibited an obvious seasonal variation. DMSOd concentrations in pre-bloom waters were extremely low (<1 nmol/L), but rapidly increased to 41 nmol/L during the spring *Phaeocystis antarctica* bloom. Furthermore, the concentrations of DMSOd were higher during summer than spring bloom due to the stronger ultraviolet radiation ([Del Valle et al., 2009](#)). DMSOd originates from photochemical oxidation and biological oxidation of DMS ([Brimblecombe](#)

[and Shooter, 1986](#)), and also from intracellular release of DMSOp ([del Valle et al., 2007a](#)). Therefore, seasonal variation of DMSOd concentrations is not only related to light and temperature, but also to seasonal changes of phytoplankton in different oceanic regions ([Simó et al., 1997](#)).

3.4 DMSOp-to-Chl *a* ratios

DMSOp/Chl *a* ratios have been used to compare distribution patterns of DMSOp in different hydrographic or trophic regimes, as well as to better understand the ability of different phytoplankton species to produce DMSO ([Simó et al., 1997](#)). The ratio of DMSOp/Chl *a* usually depends on the dominant algal species in

the study area, and it eliminates the effects of phytoplankton biomass. In the present study, a large DMSOp/Chl *a* ratio variation from 4.08 to 156 mmol/g with an average of 23.4 mmol/g was observed in spring. In comparison, the ratios of DMSOp/Chl *a* in autumn showed a small variation from 6.80 to 139 mmol/g, with a mean of 35.7 mmol/g. Yang et al. (2014) reported DMSOp/Chl *a* ratios ranging from 1.39 to 192.5 mmol/g in spring and from 8.07 to 106.98 mmol/g in autumn, with an average of 41.36 mmol/g and 31.05 mmol/g in the Bohai Sea and the Yellow Sea, which correspond well with the results from this study. The results indicated that DMSOp/Chl *a* ratios showed a seasonal difference between the spring and autumn, with autumn average value being a factor of 1.5 higher than spring one. The variation in the phytoplankton species composition and abundance between spring and autumn might play an important role in the difference. A previous study by Vila-Costa et al. (2008) indicated that the ratios of DMSOp/Chl *a* exhibited a clear seasonality with the maximum in summer because of the higher DMSO-producers. In general, the dominant species in the ECS and the YS are diatoms and dinoflagellates (Yang et al., 2011). The phytoplankton data obtained during the spring cruise indicated that diatoms and dinoflagellates accounted for 90.0% and 3.76% of the total phytoplankton species (unpublished data). In autumn, the percentage of dinoflagellates in the total phytoplankton assemblage increased significantly because of the higher nutrient than that in spring, and accounted for 5.65% of the total phytoplankton species. In addition, the algal cell abundance of dinoflagellates in autumn was 1.35 times higher than that in spring (unpublished data). Laboratory studies have shown that dinoflagellates and prymnesiophytes are the main producers of DMSO in seawater, while diatoms are relatively poor producers (Hatton and Wilson, 2007). Furthermore, Simó et al. (2000) found that high DMSOp/Chl *a* ratio of 133.3 mmol/g occurred in the Mediterranean water, which was dominated by the dinoflagellates and flagellates. Therefore, diatoms may supply the majority of total Chl *a* and contribute to the low DMSOp/Chl *a* ratios in the study area in spring. DMSOp/Chl *a* ratios variation is mainly attributed to the variation in the phytoplankton communities in different hydrographic regimes.

3.5 Diurnal variation of DMSOp and DMSOd

The diurnal variations of DMS, DMSOd, DMSOp and Chl *a* concentrations in the surface water were observed at an anchor Sta. P01 during the two cruises. As shown in Fig. 4, both DMSOd and DMSOp concentrations in the surface water exhibited a clear diurnal variation.

In spring, an interesting observation was that DMSOd and DMS concentrations revealed the same variation pattern. The concentrations of DMSOd and DMS reached the maximum simultaneously at 18:00 and were followed by a fairly rapid decrease within a few hours. Three main sources of DMSOd are found in the daytime named photochemical oxidation and biological consumption of DMS as well as exudation of intracellular DMSO. In the daytime, the rate of the production was far greater than the loss rate of DMSOd by microbial consumption, so that DMSOd concentration reached the highest value. The lowest DMSOd concentration occurred at 15:00 when the higher DMS and DMSOp concentration appeared, thereby suggesting that loss process of DMSOd might exist (Yang and Yang, 2011). DMSO can be oxidized by radical $\cdot\text{OH}$ to methane sulphonic acid (MSNA) and methyl sulfonic acid (MSA) under the condition of strong UV irradiation (Sunda et al., 2002), probably resulting in the minimum DMSOd concentration at 15:00. Another interesting observa-

tion in spring was that the diurnal change in the DMSOp concentrations appeared to follow roughly the change in the levels of Chl *a*. Positive correlation between DMSOp and Chl *a* concentrations had also been observed by Bouillon et al. (2002) in the North Water. Yang et al. (2014) found that a positive correlation was observed between DMSOp and Chl *a* concentrations in the surface water in the Bohai Sea and the Yellow Sea. These suggested that phytoplankton biomass might play an important role in controlling the distribution of DMSOp. The highest concentration of DMSOp occurred at 15:00, whereas the lowest concentration appeared at 9:00, which was attributed to the potential biological functions of DMSO. Similar to DMSP, biosynthesized DMSO may act as a free-radical scavenger, cryoprotectant, and cryosmoregulator in the algal cells. Intracellular DMSP can be cleaved into DMS and acrylic acid under the condition of excessive UV irradiation, and the generated DMS can be oxidized to DMSO by reactive oxygen species to resist oxidative stress (Sunda et al., 2002).

However, the concentrations of DMSOd, DMSOp and Chl *a* in autumn revealed different diurnal variation patterns from those in spring. The higher DMS values were not associated with higher DMSOd levels. For example, the highest DMS concentration occurred in the morning (9:00), whereas the highest DMSOd concentration appeared at noon (12:00). The low DMSOd level was found in the afternoon (15:00), but the DMS concentration at this time was relatively high. Additionally, DMSOp concentrations in autumn did not exhibit a clear diurnal variation. There was no consistent diurnal variation in spring and autumn. The reasons were not obvious, but they may involve differences in the biological factors and environmental conditions between these two seasons. The lower temperature and higher salinity observed at Sta. P01 in spring than in autumn may have a significant effect on the diurnal cycles of DMSOd and DMSOp by controlling algal DMSO synthesis.

Little data has been reported on the diurnal variations of DMSO to date. Yang and Yang (2011) indicated that the highest concentrations of DMSOd and DMSOp appeared at 21:00 and 12:00, respectively, whereas Lee and de Mora (1999) found that the concentrations of DMSOd did not show significant diurnal variation. Furthermore, Simó and Vila-Costa (2006) reported that DMSOp concentrations exhibited a clear diurnal variation, with a maximum value appearing at 15:00. The observed differences may be caused by the complex environmental factors in different study areas. The diversity of phytoplankton and the complex biogeochemical processes that control the source and transfer of DMSO in seawater might contribute to the different patterns of diurnal variation. It should be noted that illumination might be an important decisive factor, which may simultaneously influence the photo-oxidation and bacterial oxidation of DMS into DMSO and the direct biosynthesis of DMSO in seawater. In addition, overirradiation could inhibit the photosynthesis of phytoplankton and the microbial activity. In brief, in order to assess the processes controlling the diurnal changes, the photochemical and biological production and consumption rates of DMSO as well as more environmental parameters should be investigated in the future study, including phytoplankton, bacteria, and sunlight radiation.

4 Conclusions

The seasonal and spatial distributions of DMSOd and DMSOp in the ECS and the YS were investigated in this study for the first time. The concentrations of DMSOd and DMSOp in the surface water of the ECS and the YS exhibited considerable spatio-

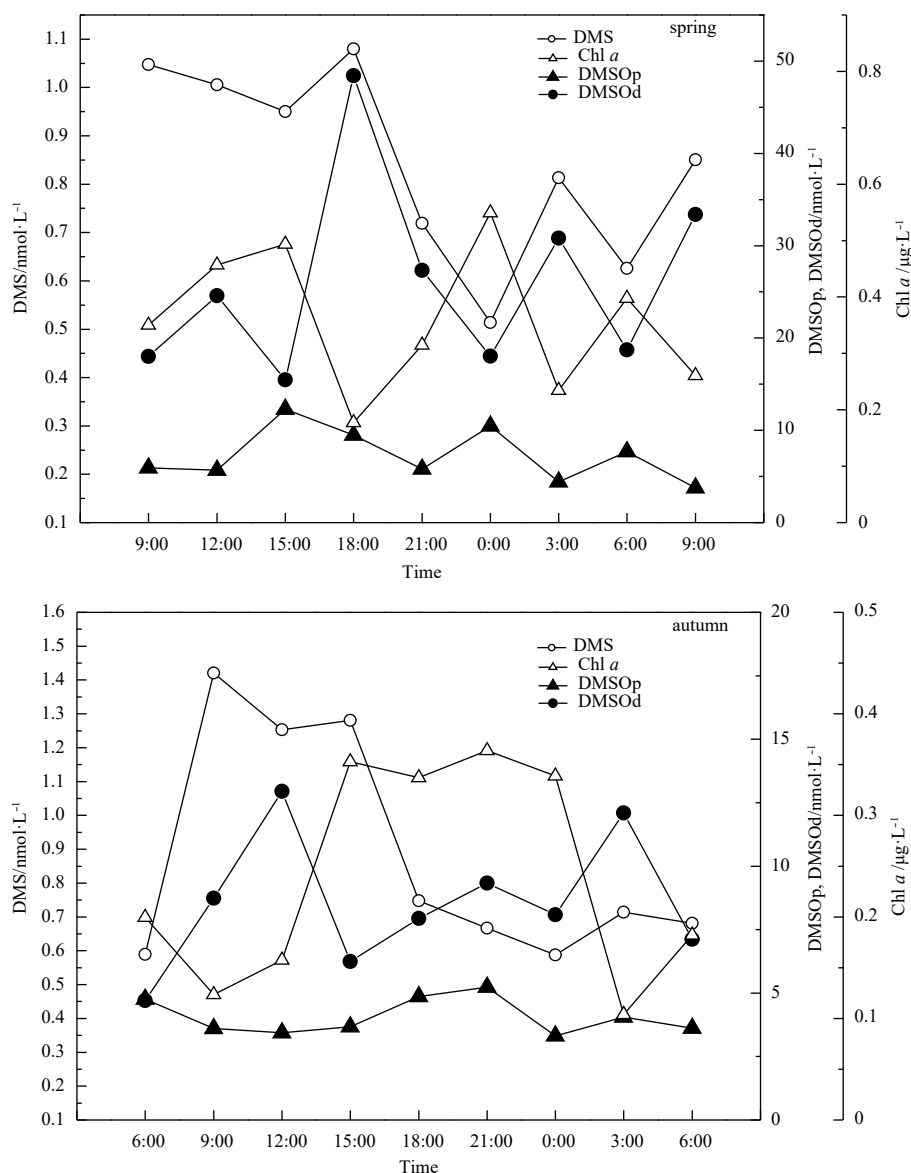


Fig. 4. Diurnal variation of DMS, DMSOd, DMSOp and Chl *a* concentrations in the surface water at Sta. P01 in spring and autumn.

temporal variation. The higher DMSOd concentrations were observed in the coastal waters because of the influence of anthropogenic activities and terrestrial runoff. The distribution pattern of DMSOp was consistent with those of Chl *a* and nutrients, thereby indicating that phytoplankton biomass might play an important role in controlling the distribution of DMSOp.

Both DMSOd and DMSOp concentrations exhibited similar seasonal variation in the surface water with higher concentrations in spring than those in autumn, which could be ascribed to higher phytoplankton biomass observed in spring. By contrast, the ratios of DMSOp/Chl *a* displayed different seasonal change with higher value in autumn, likely because of changes in phytoplankton biomass and community structure in the ECS and the YS.

DMSOd and DMSOp revealed obvious diurnal variations during the spring cruise; the maximum concentrations appeared in the afternoon. The concentrations of DMSOd and DMS in spring presented the same variation pattern, thereby suggesting that the photochemical oxidation and biological consumption of DMS

might be an important source of DMSOd in the study area. However, the diurnal changes of DMSOd and DMSOp during the autumn cruise were different from those in spring. The differences may be caused by the complex environmental factors in the study area.

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