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Biogeosciences Discussions

Acrylic acid and related dimethylated sulfur compounds in the Bohai and Yellow Seas during summer and winter

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Abstract. Spatio-temporal distributions of acrylic acid (AA) and related biogenic sulfur compounds including dimethylsulfide (DMS) and dissolved and total dimethylsulfoniopropionate (DMSPd and DMSPt) were investigated in the Bohai Sea (BS) and the Yellow Sea (YS) during summer and winter. AA and DMS production from DMSPd degradation and AA degradation were studied. Significant seasonal variations of AA and DMS(P) were observed. AA presented similar distributions during summer and winter, that is, relatively high values of AA emerged in the BS and the north YS and concentrations decreased from inshore to offshore areas in the south YS. Due to strong biological production from DMSP and abundant terrestrial inputs from rivers in summer, AA concentrations at surface were higher during summer (30.01 nmol L^{-1}) than during winter (14.98 nmol L^{-1}). The average concentration sequence AA>DMSPt>DMS>DMSPd at transects during summer illustrated particulate DMSP (DMSPp) as a DMS producer and terrestrial sources of AA, whereas the sequence in winter was AA>DMSPt>DMSPd>DMS. High values of AA and DMS(P) were mostly observed in the upper layers with occasional high values at bottom. High AA concentrations in porewater which could be transported into the bottom water might result from the cleavage of intracellular DMSP and reduce bacterial metabolism in sediments. In addition, the degradation/production rates of biogenic sulfur compounds were obviously higher in summer than in winter and the removal of AA was mainly attributed to the microbial consumption. Other sources of AA besides the production from DMSPd was also proved.

1 Introduction

Dimethylsulfide (DMS), biologically derived from the enzymatic cleavage of dimethylsulfoniopropionate (DMSP), is the dominant volatile sulfur compound released from the ocean to the atmosphere (Lovelock et al., 1972;Dacey and Wakeham, 1986). The annual emission of DMS from the ocean contributes 28.1 (17.6–34.4) Tg S to the atmosphere (Lana et al., 2011). Moreover, DMS also results in the formation of acid rain (Nguyen et al., 1992). DMS produced in surface waters can chemically influence the marine system, global sulfur cycle, and global climate. The CLAW hypothesis pointed that the oxidation products of DMS are the major sources of cloud condensation nuclei (CCN), which lead to an increase in aerosol albedo over the ocean and consequently to a decrease in solar radiation on Earth's surface (Charlson et al., 1987;Malin et al., 1992;Zindler et al., 2012). However, recent studies argued that other sources (for example, bubble bursting at the ocean surface), other than DMS oxidation, are the major contributions to CCN on global scales (Quinn and Bates, 2011). Therefore, more studies are needed to further our understanding of the potential links between DMS and climate changes.

DMSP, the biochemical precursor of DMS (Malin and Erst, 1997;Alcolombri et al., 2015), is produced by marine phytoplankton and marine heterotrophic bacteria (Curson et al., 2017;Keller et al., 1989). The production of DMSP is not only influenced by environmental parameters such as salinity (Stefels, 2000), temperature (Kirst et al., 1991), and

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oxidative stress (Sunda et al., 2002), but also controlled by phytoplankton species. For example, coccolithophorids, dinoflagellates, and prymnesiophytes are the high-producing algae of DMSP, whereas diatoms are only minor producers (Keller et al., 1989;Borges and Champenois, 2015). Aside from providing considerable sulfur and carbon sources for microbial food web, DMSP functions as an antioxidant, a cryoprotectant, and an osmolyte in marine phytoplankton (Kirst, 1990;Stefels et al., 2007). In addition, the degradation of DMSP is mainly through two pathways. The major one is demethylation, a complicated process generating different ultimate products through different enzymes possibly including methanethiol, hydrogen sulfide, and acrylic acid (AA) (Bentley and Chasteen, 2004;Reisch et al., 2011;Taylor and Visscher, 1996). The other pathway is enzymatic cleavage of DMSP mostly into equimolar DMS and AA by phytoplankton (Steinke et al., 2002) and bacteria (Ledyard and Dacey, 1996), a minor pathway with its contribution to DMSP degradation only 10%, on average. (Reisch et al., 2011).

As chemically the simplest unsaturated carboxylic acid, AA in coastal seawater is not only derived from DMSP cleavage, but also from anthropogenic contamination via river discharges (Sicre et al., 1994). The removal of AA is mainly through two mechanisms, that is, photochemical (Bajt et al., 1997;Wu et al., 2015) and microbial degradations (Noordkamp et al., 2000). AA plays diverse roles in the marine systems. For example, AA is an important carbon source to the microbial community (Kinsey and Kieber, 2016), while it also acts as an antibacterial agent (Sieburth, 1960;Slezak et al., 1994). Furthermore, the presence of AA always functions as grazing-activated chemical defense and thus inhibits the predation of phytoplankton by microzooplankton (Wolfe et al., 1997).

Many aspects of DMS and DMSP including spatial distributions, degradation, sea-to-air flux, and particle size fractionation have been well documented (Alcolombri et al., 2015;Espinosa et al., 2015;Yang et al., 2014). Up to date, however, the biogeochemistry of AA in the oceans has received only limited attention. Tan et al. (2017) and Wu et al. (2017) reported spatial distributions of AA in the Changjiang Estuary and the East China Sea. Liu et al. (2016) investigated the spatial and diurnal variations of AA in the Bohai Sea (BS) and the Yellow Sea (YS) during autumn and measured the apparent production rates of AA through DMSP degradation by incubations. However, much still remains unclear about sources, distributions, and transformations of AA, and thus further studies are needed to better understand the biogeochemical cycle of sulfur in the oceans. In this study, we investigated temporal and spatial variations of AA, DMS, and DMSP in seawater during summer and winter and horizontal distribution of AA in porewater of surface sediment during summer in the BS and the YS, and elucidated potential interlinks of these variations with other geophysical and biological parameters. We also examined the degradation of dissolved DMSP (DMSPd) and AA through on-deck incubations to better understand production and consumption mechanisms of AA, DMS, and DMSP. This study is expected to provide insightful information on sulfur cycling in the marginal seas.

2 Material and methods

2.1 Study area

The BS, the largest inner sea in China, is surrounded by Tianjin City, Hebei Province, Shandong and Liaodong Peninsulas. The total water area of the sea is 7.7×10^4 km^2 and the average water depth is 18 m. The hydrological conditions of the BS are substantially influenced by discharges from over 40 rivers, including the Yellow River, Haihe, Daliaohe, and Luanhe (Ning et al., 2010). Especially, the Yellow River, the world's second largest river in terms of sediment load, brings large amounts of particulates and nutrients to the BS. The YS, which is separated from the BS by the Bohai Strait, is a shallow semi-enclosed marginal sea located between the Chinese mainland and the Korean Peninsula, with a total water area of 3.8×10^5 km^2 and a mean depth of 44 m. The YS is divided into Northern Yellow Sea (NYS) and Southern Yellow Sea (SYS) by a line between Chengshan Cape on the Shandong Peninsula and Changshanchuan on the Korean

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Peninsula. The BS and YS are greatly affected by complicate water currents and two main water masses including the Bohai Sea Coastal Current (BSCC), the Yellow Sea Coastal Current (YSCC), the Korea Coastal Current (KCC), the Yellow Sea Warm Current (YSWC), the Changjiang River Diluted Water (CRDW), and the Yellow Sea cold water mass (YSCWM) (Lee et al., 2000;Su, 1998) (Fig. 1). Moreover, anthropogenic pollution in both China and Korea coasts has notable effects on the ecosystems including species diversity and community structure of phytoplankton and benthos in the BS and the YS (Liu et al., 2011).

2.2 Sampling

Two cruises were conducted aboard the R/V ‘‘Dong Fang Hong 2’’ in the BS and the YS from August 17th to September 5th 2015 (summer) and from January 14th to February 1st 2016 (winter). The summer cruise covered 52 grid stations and three transects and the winter cruise contained 39 grid stations and two transects (Fig. 1). Seawater samples were collected using 12 L Niskin bottles mounted on a Seabird 911+ Conductivity-Temperature-Depth (CTD) sensor (Sea-Bird Electronics, Inc., USA).

2.3 Analytical procedures

DMS concentrations in all samples were immediately measured onboard upon sampling with a purge-and-trap technique modified from Andreae and Barnard (1983) and Kiene and Service (1991). A 2 mL aliquot of seawater sample filtered through a Whatman glass fiber filter (GF/F) was directly injected into a glass bubbling chamber and extracted with high purity nitrogen at a flow rate of 40 mL min^{-1} for 3 min. Then, the sulfur gases were dried through Nafion gas sample dryer (Perma Pure, USA) and trapped in a loop of Teflon tubing immersed in liquid nitrogen (-196 °C). After extraction, the Teflon tubing was heated in boiling water and desorbed gases were introduced into a 14B gas chromatograph (Shimadzu, Japan) equipped with a flame photometric detector and a 3 m × 3 mm glass chromatographic column packed with 10% DEGS on Chromosorb W-AW-DMCS. The analytical precision of DMS was generally better than 10% and the detection limit was 0.4 nmol L^{-1} (Yang et al., 2015a).

A 4 mL aliquot of seawater was filtered under gravity through Whatman GF/F filter (Kiene and Slezak, 2006) for DMSPd analysis. In order for steady DMSP concentration and oxidation of endogenous DMS, 100 µL and 40 µL of 50 wt% sulfuric acid were added into samples for total DMSP (DMSPt) and DMSPd analysis, respectively (Shooter and Brimblecombe, 1989). Before analysis, the samples were injected with 300 µL of 10 mol L^{-1} KOH solutions and stored in the dark at 4 °C for at least 24 h to allow a complete conversion of DMSP into DMS. DMS concentration measured was used to estimate DMSP concentration according to 1:1 stoichiometry (Dacey and Blough, 1987).

Seawater samples for AA analyses were collected directly from the Niskin bottles and filtered under gravity through a pre-cleaned 0.2 µm AS 75 Polycap filter capsule (a nylon membrane with a glass microfiber pre-filter enclosed in a polypropylene housing; Whatman Corporation, USA) (Wu et al., 2015). The filtrate was transferred to a 40 mL glass vial with a Teflon™-lined cap and stored at 4 °C. Porewater samples for AA analyses were extracted from surface sediments via Rhizon soil moisture samplers (0.1 µm porous polymer, Rhizosphere Research, Wageningen, the Netherlands) according to Seeberg-Elverfeldt et al. (2005). All porewaters were stored at 4 °C and filtered through 0.22 µm polyethersulfone syringe filters (Membrana Corporation, Germany) before analysis. AA seawater and porewater samples were analyzed using a high performance liquid chromatograph (L-2000, Hitachi Ltd., Japan) according to Gibson et al. (1996). An Agilent SB-Aq-C18 column and the eluent of 0.35% H_3PO_4 (pH = 2.0) at a flow rate of 0.5 mL min^{-1} were used to separate AA. The column eluate was detected by a UV detector at 210 nm. Analytical precision was between 1.3% and 1.6% and the detection limit was 4 nmol L^{-1} (Liu et al., 2013).

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For Chlorophyll *a* (Chl *a*) analysis, 300 mL of seawater were filtered through Whatman GF/F filters. Then the filtrates were soaked in 10 mL of 90% acetone and kept in the dark at 4 °C. Contents of Chl *a* were measured using an F-4500 fluorescence spectrophotometer (Hitachi, Japan) according to Parsons et al. (1984) after 24 h.

2.4 Incubation experiments

The incubation experiments for DMSPd and AA degradation were conducted on deck using seawater collected at stations H19, H26, B12, B17, B53, and B63 in summer and at H19, H26, B12, and B16 in winter. To determine degradation rates of DMSPd and production rates of DMS and AA, unfiltered seawater samples were incubated in two 250 mL gas-tight glass syringes (wrapped in aluminum foil) in the dark at in situ temperature. Before the incubations, 80 μL of concentrated DMSPd solution (0.2 mmol L^{-1}) were added into the two syringes to reach an initial concentration of DMSPd higher than 50 nmol L^{-1}. One syringe was used as treatment group, the other was used as control by injecting with glycine betaine (GBT, final concentration of 50 μmol L^{-1}, 1000× the concentration of added DMSPd) to inhibit microbial degradation of DMSP within a short time (Kiene and Service, 1993;Kiene and Gerard, 1995) because it is chemically and physiologically similar to DMSP but is preferentially degraded relative to DMSP (Kiene et al., 2000;Vila-Costa et al., 2006). After 0, 3, and 6 h, 25 mL aliquots of samples were taken from the incubations for measurements of DMSPd, DMS, and AA concentrations, which were used for calculation of apparent rates of DMSPd degradation and rates of DMS and AA production according to the concentration differences between samples with and without GBT.

Two pathways of AA degradation, that is, photochemical consumption and microbial consumption, were experimentally investigated in this study. For photochemical consumption of AA, a drop of oversaturated NaN_3 solution was added into 300 mL seawater samples (the final concentration was approximately 1 mmol L^{-1}) to eliminate microbial consumption of AA. After filtration, the seawater samples were immediately injected into a 125 mL photic quartz tube and a 125 mL photophobic quartz tube (as a control) to initiate photochemical degradation. 10 mL aliquots of samples were taken for analyses of AA at 0, 3, and 6 h. The photochemical degradation rates of AA were calculated based on the concentration differences in the photic and photophobic quartz tubes (Wu et al., 2015).

For microbial consumption of AA, unfiltered seawater samples were used for incubations in 100 mL glass syringes (wrapped in aluminum foil) in the dark at in situ temperature. Prior to incubation, concentrated AA was added into one syringe to reach an initial concentration 10-50 times as high as the background concentration. Another seawater sample without exogenous AA addition was used as a control. 10 mL aliquots of samples were taken for determination of AA at 0, 3, and 6 h. Microbial degradation rates of AA were estimated based on the concentration differences between the samples with exogenous AA addition and the control (Kiene, 1996). Duplicate samples were analyzed for AA, DMS, and DMSPd in all the incubation experiments.

3 Results and discussion

3.1 Horizontal distributions of AA, DMS, and DMSP during summer

As shown in Fig. 2 and Table 1, Chl *a* contents in the BS were relatively high and an extremely high value (7.07 μg L^{-1}) occurred in the center of the sea, which can be ascribed to nutrient accumulation and consequently promotion of phytoplankton productivity due to poor water circulations in the sea (Wei et al., 2004;Wang et al., 2009). A minimum value of Chl *a* emerged in the center of the SYS, which can be ascribed to limitation of phytoplankton growth due to low nutrient contents. In contrast, a maximum value of Chl *a* appeared in the southern area of the SYS (station H37) due to high concentration of nutrients delivered via the CRDW (Wei et al., 2010).

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AA concentrations generally decreased from the north to the south (Fig. 2). The average values in the BS and the NYS were 40.76 and 38.89 nmol L^{-1}, respectively, higher than the average value of the whole study area, while the mean value in the SYS was 18.02 nmol L^{-1}, just more than half of the average value of the whole study area, which implies that terrestrial inputs may play an important role in controlling AA distribution in the BS and the NYS. It has been reported that Yalu River flows into the NYS with large amounts of organic pollutants including AA (Liu, 2001), and highly populated Chengshan Cape may also be an anthropogenic source of AA to the NYS. Furthermore, poor water circulation in the semi-enclosed NYS and inner BS favors local accumulations of AA. On the contrary, SYS is a relatively open water area and thus is much less affected by terrestrial discharges. In addition, AA was positively dependent on temperature in the NYS (Table 2), which indicates that high temperature may enhance the production of AA. AA concentrations were comparatively low in the SYS though the Chl *a* values were relatively high, which might be related to the dominance of primary phytoplankton species with low ability of AA production. Specifically, diatoms, a type of algal with low ability of DMSP and AA production, dominated in the SYS (Liu et al., 2015b). Furthermore, some freshwater algae which do not produce DMSP and AA have been found to distribute in the adjacent area of the Changjiang Estuary (Luan et al., 2006) and the north branch of the Changjiang Estuary flows into the SYS. All of those factors may have led to low AA concentrations in the SYS. DMS and DMSP data were collected from a published MS thesis (Jin, 2016, Table 1). DMS and DMSP showed diminishing tendency from inshore to offshore areas, which was coupled to the distribution pattern of Chl *a*. DMS and DMSP also presented higher values in the BS than in the YS, similar to the case of AA. AA showed positive relationships with DMSPd in the SYS, which suggests that AA in the SYS is mainly produced by DMSPd degradation rather than the terrestrial inputs. Although phytoplankton plays an important role in controlling the levels of sulfur products, some researchers still found no correlations between Chl *a* and them in this study area (Li et al., 2016;Yang et al., 2015b) .

AA concentrations in porewater of surface sediments were 13.52-136.42 μmol L^{-1}, with an average of 73.03 μmol L^{-1} (Table 3). The concentrations were extremely high and might reduce bacterial metabolism according to Slezak et al. (1994). No significant correlation of AA concentrations between porewater and bottom seawater was observed. In addition, AA concentrations in porewater were much higher than DMS and DMSP concentrations in porewater and sediments reported by Andreae (1985) and Nedwell et al. (1994). Nevertheless, DMSP catabolizing bacteria can concentrate DMSP to mmol L^{-1} intracellular levels compared to nmol L^{-1} environmental concentrations and the lower substrate affinities of DMSP lyases enable the bacteria to maintain a high intracellular concentration of DMSP (Wang et al., 2017). DddY, as the only known periplasmic DMSP lyase and widely present in β-, γ-, δ- and ε-proteobacteria which are the dominant bacteria communities in the surface sediments of the BS and the YS (Li et al., 2017;Liu et al., 2015a;Xie et al., 2017), then cleaves the large amounts of intracellular DMSP and produce more AA in sediments. In addition, we speculated that high concentrations of AA in sediments might be transported into the bottom seawater as Nedwell et al. (1994) found that DMS was emitted to water columns from the sediments. Up to date, there are only very limited studies on AA in sediment, we cannot go further to address potential factors influencing AA concentrations in porewater. For better understanding the source and fate of AA in marine sediments, a detailed investigation of multiple parameters such as dissolved organic carbon, DMS, and DMSP in sediments is needed.

3.2 Horizontal distributions of AA, DMS, and DMSP during winter

High AA concentrations appeared near the Chengshan Cape where high values of Chl *a*, DMS, and DMSP were also observed (Fig. 2). Chl *a*, AA, DMS, and DMSPd all showed declining tendency from inshore to offshore areas in the SYS (Jin, 2016). Note that the concentrations of AA, DMS, and DMSP in the BS were slightly higher than those in the NYS and the SYS, though the differences were only marginal. A positive linear correlation between AA concentrations and

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seawater temperature was observed in the BS (Table 2). However, AA showed no any correlations with Chl *a*, DMS, and DMSP in the whole area of this study, which reflects comprehensive effects of different parameters on the distributions of AA.

The Chl *a* contents were substantially lower in winter (<1 μg L^{-1} overall) than in summer due to lower temperature, light intensity, and phytoplankton activities, while the distribution pattern of Chl *a* in the two seasons is similar, which might imply that there were no marked changes in the main phytoplankton species in the two seasons. Sun et al. (2001) found that diatoms, the dominant type of phytoplankton in the study area, were mainly made up of small-celled diatoms in winter and big-celled ones in summer. AA, DMS, and DMSP concentrations in winter were about 2-4 times lower than those in summer (Table 1) but presented similar distribution patterns, which demonstrated stronger biological production in summer. They both presented relatively high values in the BS and the NYS and reduced concentrations from inshore to offshore areas in the SYS, which were also consistent with the distribution patterns in the BS and YS during autumn (Liu et al., 2016). Furthermore, the negative relationships of AA/salinity and salinity illustrated riverine delivery of AA in this study area (Fig. 3). The low slopes and intercepts in winter proved decreasing in freshwater inputs compared to those in summer. Meanwhile, the low slopes and intercepts in the SYS during both summer and winter also revealed that the SYS was less affected by the terrestrial inputs than the BS and the NYS.

3.3 Vertical distributions of AA, DMS, and DMSP during summer

In this study, three transects (H19-26, B12-17, and B57-63) were chosen to study the vertical distributions of AA, DMS, DMSP, and biogeochemical processes influencing the three compounds during summer.

Transect H19-26 was affected by the YSCWM in summer, as indicated by low temperature (<10 °C) below 40 m water depth. A tidal front divided the transect into a well-mixed shallow water area (station H19) and a stratified deep-water area occupied by the YSCWM (stations H21-H26) (Fig. 4). Concentrations of Chl *a*, AA, DMS, DMSPd, and DMSPt were shown in Table 1. Both Chl *a* and DMS did not displayed obviously stratified distributions. High values of the sulfur compounds in the surface seawater and higher concentrations in the YSCWM region than in the well mixed shallow water region were in line with the results of Yang et al. (2015b). There was a high value of DMS in the bottom layer of station H23, which might result from the release from porewater (Andreae, 1985). There were no correlations among AA, DMS, DMSPd, and DMSPt, though these compounds showed similar patterns of spatial distribution. DMSPt showed a positive correlation with temperature and a negative correlation with salinity (Table 2). Many other investigations also reported the analogous correlations (Deschaseaux et al., 2014;Shenoy and Patil, 2003;Wu et al., 2017). It has been reported that lower salinity could enhance algal DMSP lyase activity (Stefels, 2000), which might have led to the negative correlation between DMSP and salinity.

Along transect B12-17, Chl *a* and DMS concentrations presented maximum values at the 15 m depth of stations B13 and 25 m depth of station B15, respectively (Fig. 4). Concentrations of DMSPd, DMSPt, and AA declined generally with depth and high values emerged in the surface layer of station B12 and B13. Yang et al. (2015a) also found maximum values of DMS and DMSP in the upper water column along transect B12-17 during late fall, which were restricted mostly to the euphotic layer. High values of AA also occurred in the bottom water of stations B13 and B17, which might be related to release of AA from sediment porewater. DMSPd and DMSPt showed a strong positive correlation (Table 2), while AA did not have a correlation with DMSP. Meanwhile, the average value of AA was in significant excess of DMSPt, the precursor of AA, which demonstrated that terrestrial inputs were an important contribution to AA along transect B12-17.

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Along transect B57-63, All of the compounds presented high values in the upper layers. Meanwhile, Chl *a* and AA presented relatively high values at the bottom of station B61 and B57, respectively (Fig. 4). DMS and DMSPd presented positive correlations with DMSPt (Table 2), which proves DMSP as the phytoplankton-derived precursor of DMS.

In these three transects, the average concentration order was AA>DMSPt>DMS>DMSPd (Table 1), which illustrated that both DMSPd and particulate DMSP (DMSPp) produce DMS (Asher et al., 2017) and there were terrestrial sources of AA besides the contribution from in situ DMSP degradation along the three transects. Though there were only small differences in the average concentrations of sulfur compounds among the three transects, the average concentrations of AA showed differences. For instance, AA concentrations in transect B12-17 (NYS) and transect B57-63 (BS) were higher than that in transect H19-26 (SYS), which was in accordance with those distributions in surface seawater. The high concentration could be ascribed to anthropogenic addition. Average contents of both Chl *a* and DMSPt at the three transects followed the order: B57-63 > B12-17 > H19-26. This suggests that phytoplankton is the primary producer of DMSP.

3.4 Vertical distributions of AA, DMS, and DMSP during winter

Transect B57-63 was inaccessible for sampling in the winter cruise due to frozen condition, so we only reported the results of transect H19-26 in the SYS and transect B12-16 in the NYS. Along transect H19-26, the concentrations of Chl *a* and DMSPt declined from inshore to offshore areas, while DMS and DMSPd showed decreasing trends from the surface to the bottom (Fig. 5). AA concentrations did not present significant variations along transect H19-26 except the maximum value at the bottom of station H24. DMS showed strong positive correlations with temperature and salinity (Table 2), while DMSPt presented negative correlations with the two parameters (Table 2). Kirst et al. (1991) found that DMSP could function as a cryoprotectant in cold environment, thus, the low temperature would promote the production of DMSP, which may be the reason of the observed negative correlation of DMSPt vs. temperature in winter. However, the positive correlations of DMS vs. temperature might be attributed to enhanced production of DMS from DMSP with increased temperature, which is supported by the observations of Kiene and Service (1991).

Along transect B12-16, the Chl *a*, DMS, and DMSPt concentrations presented homogeneous distributions from the surface to the bottom (Fig. 5). DMSPd and AA were heterogeneously distributed with minimum values appearing at the surface and maximum values at the bottom. DMSPt had a significant positive correlation with Chl *a* (Table 2).

The average Chl *a* and DMS concentrations along transect B12-16 were about twice as high as those along transect H19-26, which suggested that Chl *a* had a direct controlling effect on DMS production. However, the average concentrations of DMSPd, DMSPt, and AA along transect H19-26 were quite similar to those along transect B12-16, which implied that the enzymatic cleavage of DMSP enhanced and river discharges did not dominate the concentrations of AA in winter. The concentration order along both transect H19-26 and transect B12-16 was AA>DMSPt>DMSPd>DMS. AA concentrations were still slightly higher than DMSPt, while the DMSPd concentrations exceeded DMS in winter.

A comparison of vertical profiles in different seasons (Figs. 3 and 4, Table 1) indicated that the Chl *a* contents in summer were about twice as high as those in winter along the same transect because of the high temperature, abundant light, and thus high activities of phytoplankton. The DMS concentrations declined dramatically (by more than 5 nmol L^{-1}) from summer to winter, while the DMSPd concentrations displayed either almost invariable concentration levels or a small increase, that is the reason for the DMSPd concentrations exceeding DMS in winter. The DMSPt concentrations were a little higher in summer than in winter, consistent with the seasonal pattern of Chl *a*, which highlighted the importance of phytoplankton in DMSP production in both the two seasons. The much higher AA concentrations in summer than in winter were a combined result of high phytoplankton biomass and terrestrial inputs. On the whole, the reduced AA, DMS, and DMSP concentrations from summer to winter in transect H19-26 were lower than those in transect B12-17(16), which

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suggested that terrestrial discharges of those compounds are an important contribution of their concentrations in the NYS, and thus have greatly influenced their spatial distribution.

3.5 Degradation of DMSPd and AA in the BS and YS

The DMSPd and AA degradation experiments were conducted using seawater at the endpoint stations of investigated transects in the BS and the YS during the two cruises. Production and/or degradation rates of DMSPd, DMS, and AA were summarized in Table 4. In summer, the rates of DMS production at all stations were lower than the rates of DMSPd degradation, while rates of AA production at stations B12 and B63 were a little higher than the rates of DMSPd degradation. This might be owing to the direct production from DMSPp at those stations besides the exogenous DMSPd during the incubation experiments. The rates of AA production at all stations were higher than those of DMS production, which implies that AA is produced by DMSP through more complicated demethylation processes besides enzymatic cleavage, which is thought to be the sole pathway of DMS production from DMSP. Enzymatic cleavage ratio of DMSP can be estimated using DMS production rate/DMSPd degradation rate. The ratios were within the range of 7.8%-64.5%, with a mean of 27.7%, which indicated that the enzymatic cleavage is not a dominant pathway of DMSP degradation (Kiene and Linn, 2000b;Ledyard and Dacey, 1996). The maximum rates of DMSPd degradation (5.76 nmol L^{-1} h^{-1}) and DMS (2.71 nmol L^{-1} h^{-1}) and AA (5.20 nmol L^{-1} h^{-1}) production appeared at stations B57 and B63 in the BS, respectively. The minimum rates of DMS (0.29 nmol L^{-1} h^{-1}) and AA (1.15 nmol L^{-1} h^{-1}) production occurred at stations H26 and H19 in the SYS, respectively. Zhao et al. (2011) found that bacteria presence was poor in the YSCWM. Therefore, the different rates of degradation/production above might result from the differences in bacteria species and abundance in the BS and the SYS (Sun et al., 2011). Assuming that DMSPd and AA degradation follow first-order kinetics, turnover times of DMSPd and rate constants of AA microbial and photochemical degradation were calculated (Table 4).Turnover times of DMSPd in the BS and the YS basically fell in the range of 0.03–2.8 d which were estimated in earlier studies using radioisotopes, inhibitors and low-level additions methods in worldwide oceanic regions (Kiene and Linn, 2000a;Simó et al., 2000;Ledyard and Dacey, 1996). Though the rates of AA microbial degradation at all stations were extremely high compared to the rates of AA production and AA photochemical degradation due to the addition of exogenous AA at the beginning of incubation, the measured rates still could reflect the capability of bacterially mediated degradation of AA. AA microbial degradation rates at inshore stations were higher than those at offshore stations, while the microbial degradation rate constants of AA were totally opposite. The higher degradation rate constants at offshore stations represented stronger AA degradation capability of bacteria, while the higher degradation rates at inshore stations might be attributed to the larger amounts of bacteria (Wang et al., 2016). The photochemical degradation rates and rate constants of AA between inshore and offshore stations presented same quantitative relations. In addition, the average AA photochemical degradation rates in the SYS were higher than those in the BS and the NYS, which could be ascribed to a promotion of photochemical degradation due to warmer temperature and stronger sunlight intensity in the SYS (Wu et al., 2015). The AA microbial degradation rate constants at most stations were higher than the AA photochemical degradation rate constants, which suggested that microbial degradation is a more important pathway of AA removal relative to photochemical degradation.

In winter, almost all degradation/production rates lowered compared to those in summer, which indicated that temperature played an important role on controlling the degradation/production rates. Furthermore, the turnover times of DMSPd in winter were much longer than those in summer but still fell in the range of earlier studies. The rates of DMS production were lower than the rates of DMSPd degradation and AA production in winter, which were in accordance with those in summer. Even though the difference of DMS production rates was not large among the stations, the maximum rates of DMSPd degradation (2.26 nmol L^{-1} h^{-1}), DMS production (0.10 nmol L^{-1} h^{-1}), and AA production (1.48 nmol L^{-1} h^{-1}) were

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all observed in the SYS, which were different from the case in summer. The difference can be ascribed to the alteration of bacteria species and abundance due to the dramatic decreasing temperature and increasing nutrients from summer to winter (Wang et al., 2018). Enzymatic cleavage ratio of DMSP (3.5%-11.1%; average: 7.0%) in winter were much lower than in summer. The microbial degradation rates of AA significantly decreased from summer to winter but the rate constants in winter did not show a dramatic decline compared to those in summer and even showed an increase at some stations, which implied that the capability of AA degradation by bacteria did not become weaker but the amounts of bacteria became lower from summer to winter (Wang et al., 2016). The AA microbial degradation rates and rate constants were higher than the photochemical rates and rate constants at most of the stations in winter, which were in accordance with those in summer.

In order to estimate the contribution of different sources and sinks of AA in surface seawater of the BS and the YS, we applied the following equation:

$$dc/dt = r_{prod} - r_{bio} - r_{photo} + r_{other}$$

We assume AA concentrations were at a steady state, so dc/dt=0. AA production rate (r_{prod}) was calculated from the AA production rate constant times the *in situ* concentration. The AA microbial degradation rate (r_{bio}) and photochemical degradation rate (r_{photo}) followed the same calculation method as r_{prod}. r_{other} represented other sources and sinks of AA except production from DMSPd. According to these equations, the mean r_{prod}, r_{bio} and r_{photo} in summer were 5.76 nmol L^{-1} h^{-1}, 8.43 nmol L^{-1} h^{-1} and 2.83 nmol L^{-1} h^{-1}, respectively, so there were certainly other sources of AA at a rate of 5.50 nmol L^{-1} h^{-1}. These sources might be production from DMSPp, riverine inputs and so on. In winter, the mean r_{prod}, r_{bio} and r_{photo} were 1.65 nmol L^{-1} h^{-1}, 2.66 nmol L^{-1} h^{-1} and 1.32 nmol L^{-1} h^{-1}, respectively, so the rate from other sources was 2.33 nmol L^{-1} h^{-1}, which was less than half of the rate in summer. This coincided with the AA concentrations in surface seawater we observed in summer and winter.

4 Conclusions

We studied the horizontal and vertical distributions of AA, DMS and DMSP in the BS and the YS during summer and winter. Significant seasonal variations were observed in the study area. AA concentrations were relatively higher in the surface seawater during summer than during winter due to strong biological production from DMSP and abundant terrestrial inputs from rivers in summer. The distribution patterns of AA during summer and winter were similar, that is, relatively high values of AA emerged in the BS and the NYS and concentrations decreased from inshore to offshore areas in the SYS. We also measured the AA concentrations in porewater of surface sediments. The extremely high values of AA concentrations in porewater can be attributed to the abundant bacteria and active bacteria DMSP lyases in sediments. In vertical profiles, high values of AA, DMS, and DMSP were mostly observed in the upper layers with occasional high values in the bottom layers along three different transects. The average concentration sequence was AA>DMSPt>DMS>DMSPd among all the three transects during summer, illustrating DMSPp as a DMS producer and terrestrial sources of AA, whereas the sequence in winter along transects was AA>DMSPt>DMSPd>DMS. DMS and AA presented a stronger decrease from summer to winter than DMSP along transects. Moreover, the DMS and AA production from DMSPd degradation and AA degradation rates were always higher during summer than during winter. The AA microbial degradation rates and rate constants were higher than the photochemical degradation rates and rate constants during both summer and winter. The AA production and degradation experiments also proved other sources of AA besides the production from DMSPd.

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Author contribution. Xi Wu participated those two cruises to collect and analyse samples. Xi Wu and Chun-Ying Liu designed the on-deck experiments and Xi Wu carried them out. Xi Wu prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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Figure Captions

Figure 1: Locations of the sampling stations in the BS and the YS during summer (a) and winter (b). (c) Schematic circulations and water masses in the BS and the YS (Su, 1998; Lee et al., 2000). BSCC: Bohai Sea Coastal Current; YSCC: Yellow Sea Coastal Current; KCC: Korea Coastal Current; YSWC: Yellow Sea Warm Current; CRDW: Changjiang River Diluted Water; YSCWM: Yellow Sea Cold Water Mass.

Figure 2: Horizontal distributions of Chl *a* (μg L^{-1}) and AA (nmol L^{-1}) in the surface water of the BS and the YS during summer and winter.

Figure 3: The relationships of AA/Salinity and salinity in the BS (a) and the SYS (b) during summer and in the NYS (c) and the SYS (d) during winter.

Figure 4: Vertical profiles of temperature (°C, transect H19-26 only), Chl *a* (μg L^{-1}), AA (nmol L^{-1}), DMS (nmol L^{-1}), DMSPd (nmol L^{-1}), and DMSPt (nmol L^{-1}) along transect H19-26, transect B12-17, and transect B57-63 during summer.

Figure 5: Vertical profiles of Chl *a* (μg L^{-1}), AA (nmol L^{-1}), DMS (nmol L^{-1}), DMSPd (nmol L^{-1}), and DMSPt (nmol L^{-1}) along transect H19-26 and transect B12-16 during winter.

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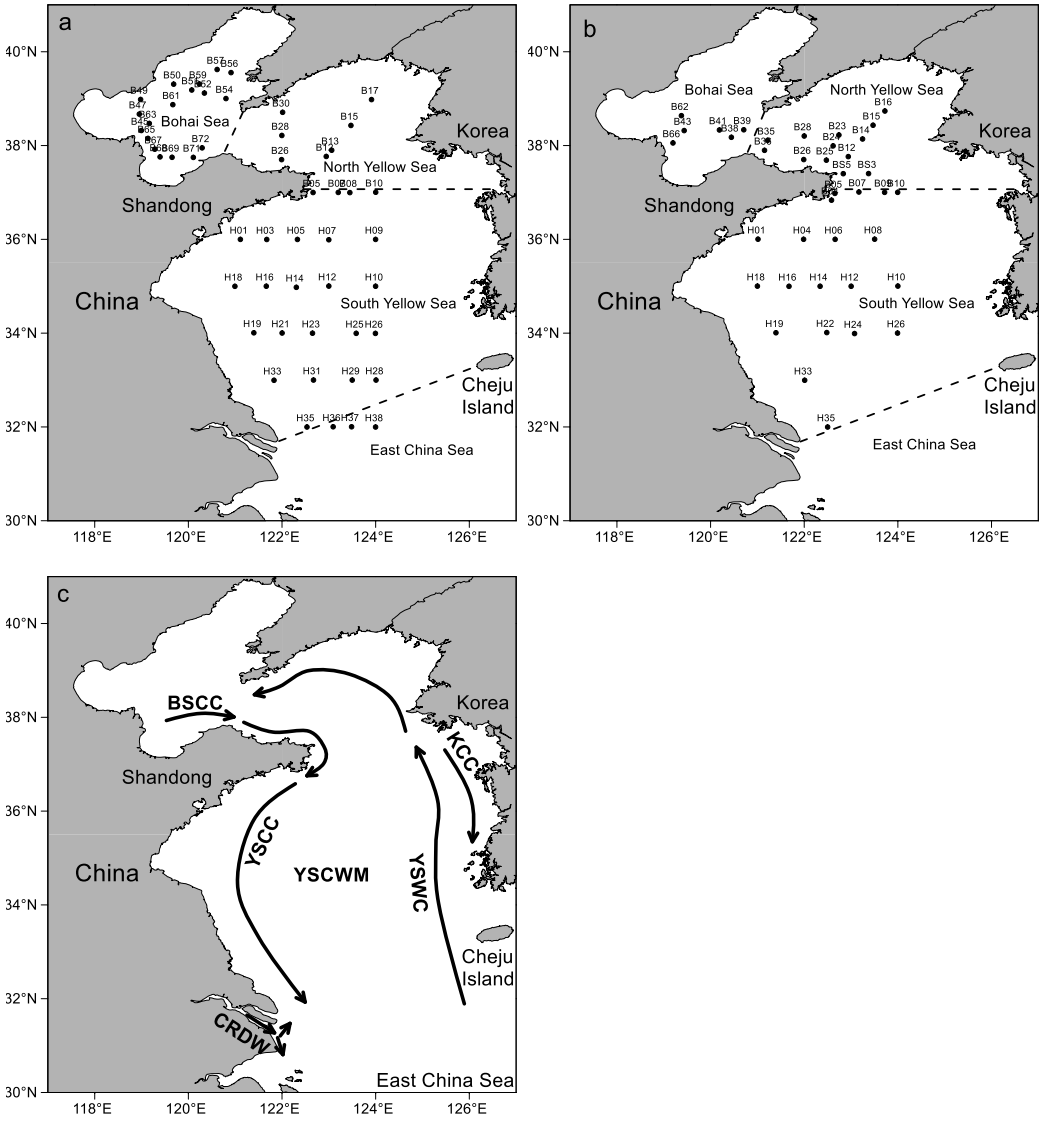

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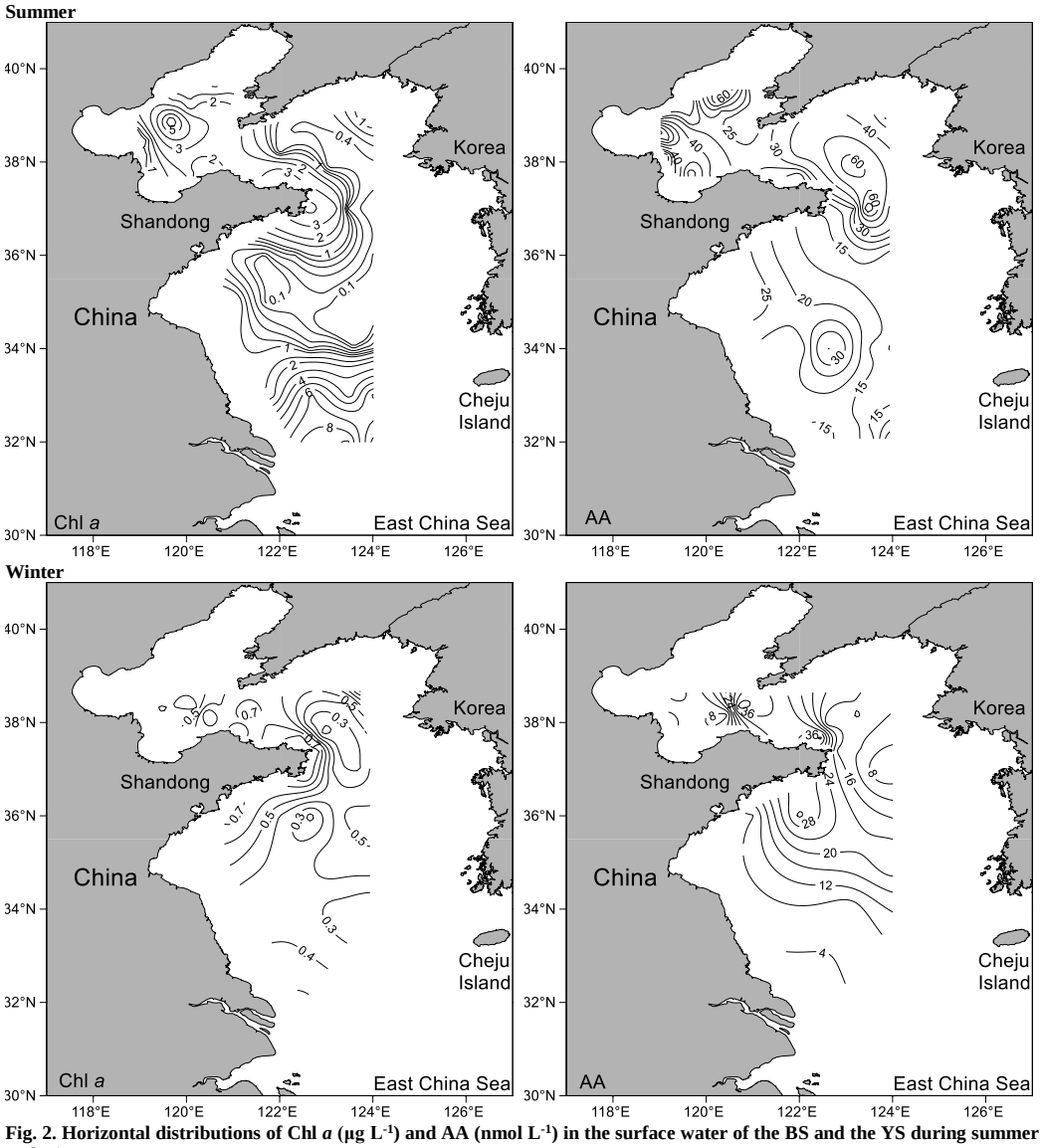

575 **Fig. 2. Horizontal distributions of Chl *a* (μg L^{-1}) and AA (nmol L^{-1}) in the surface water of the BS and the YS during summer and winter.**

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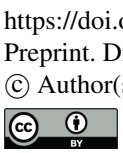

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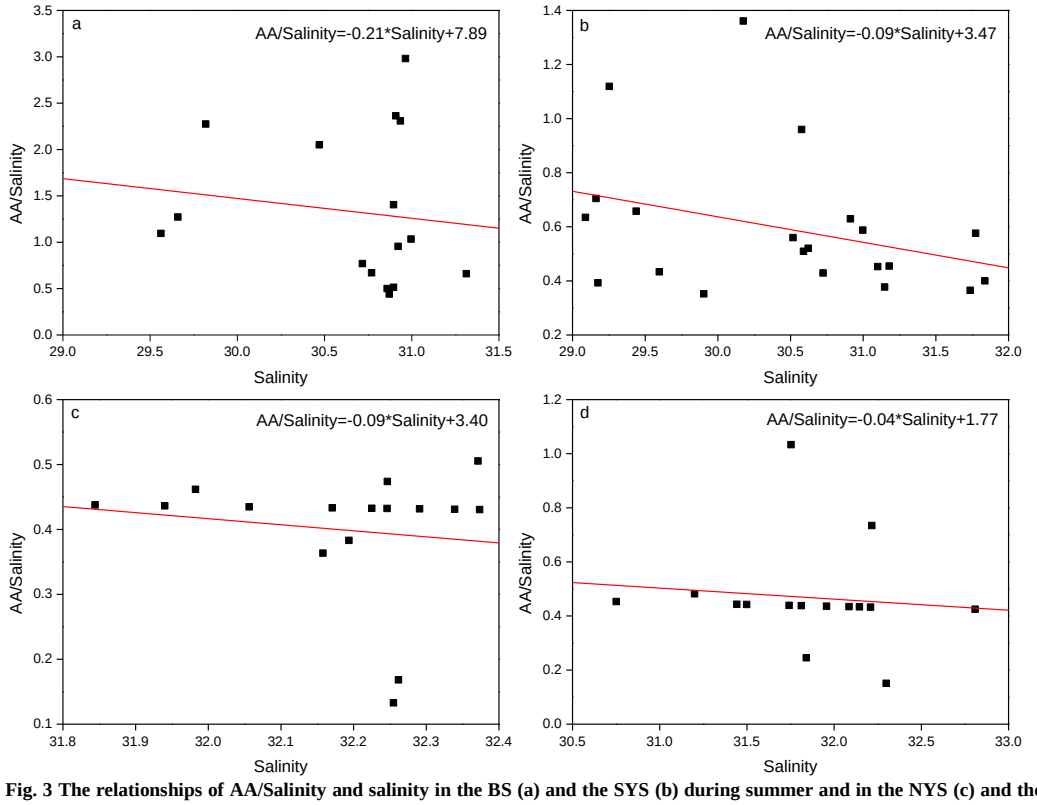

580 **Fig. 3 The relationships of AA/Salinity and salinity in the BS (a) and the SYS (b) during summer and in the NYS (c) and the SYS (d) during winter.**

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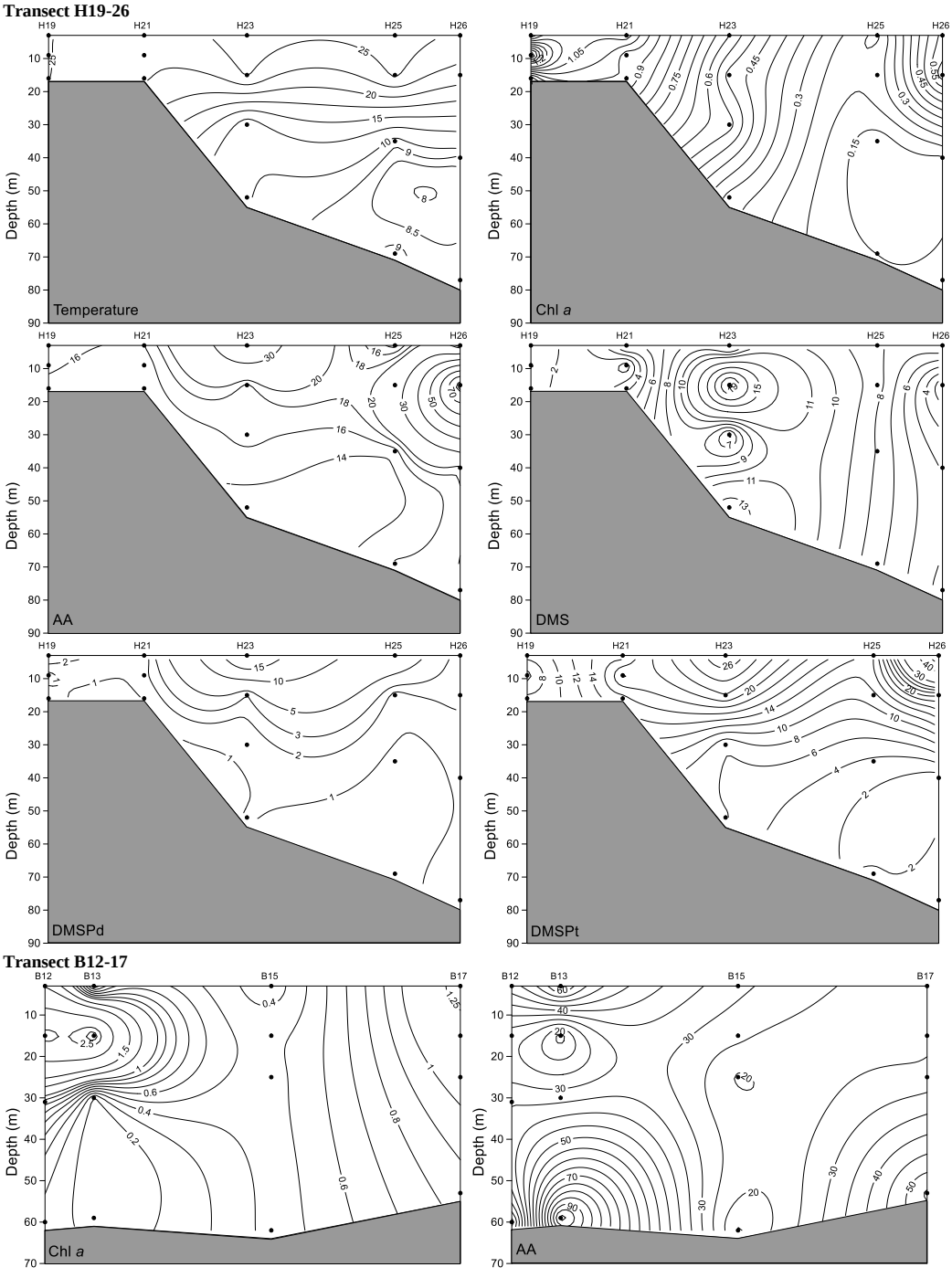

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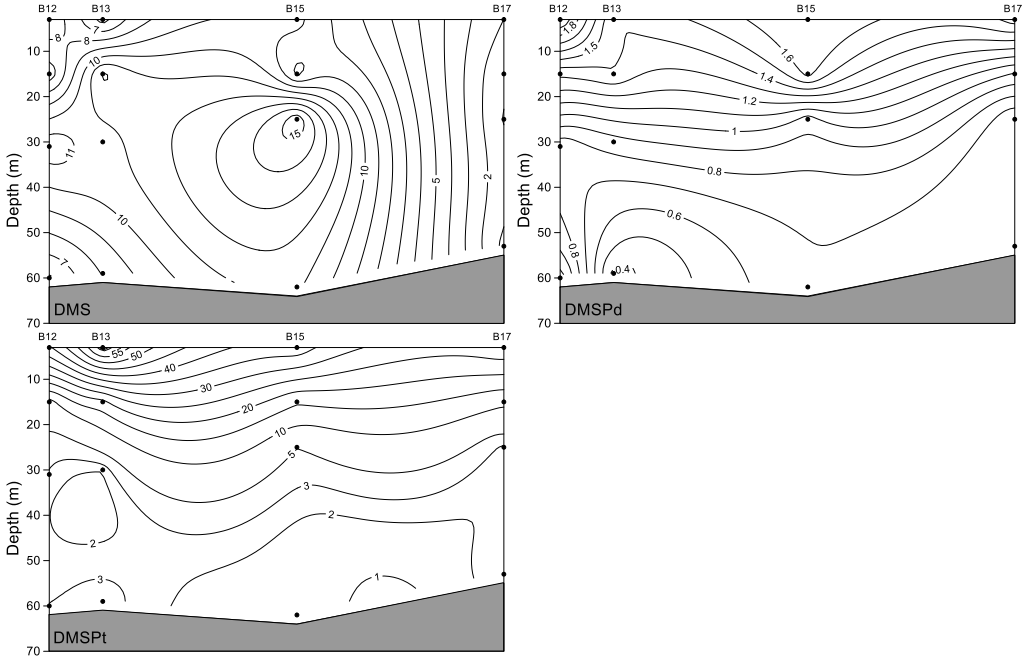

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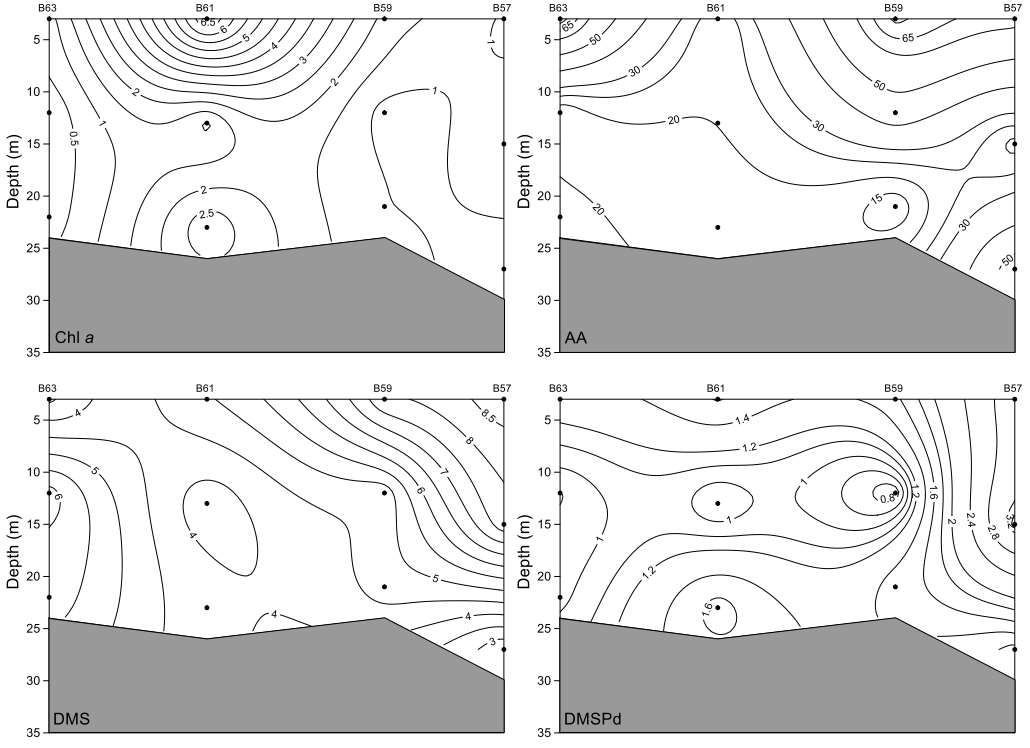
Transect B57-63



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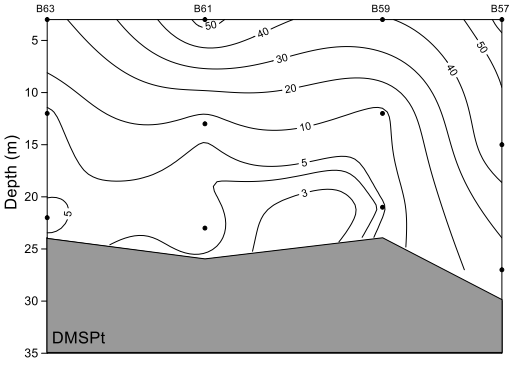

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Fig. 4. Vertical profiles of temperature (°C, transect H19-26 only), Chl *a* (µg L^{-1}), AA (nmol L^{-1}), DMS (nmol L^{-1}), DMSPd (nmol L^{-1}), and DMSPt (nmol L^{-1}) along transect H19-26, transect B12-17, and transect B57-63 during summer.

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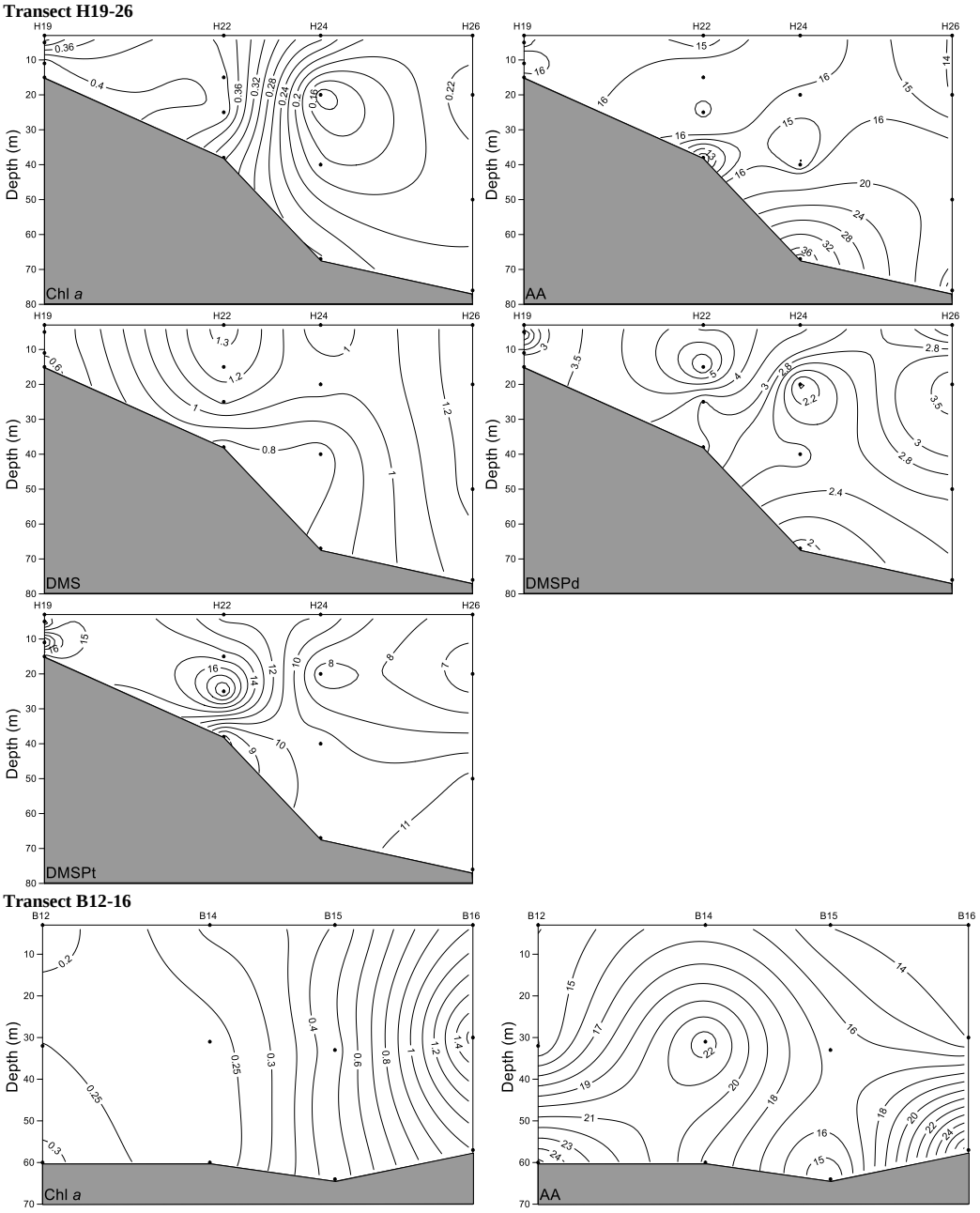

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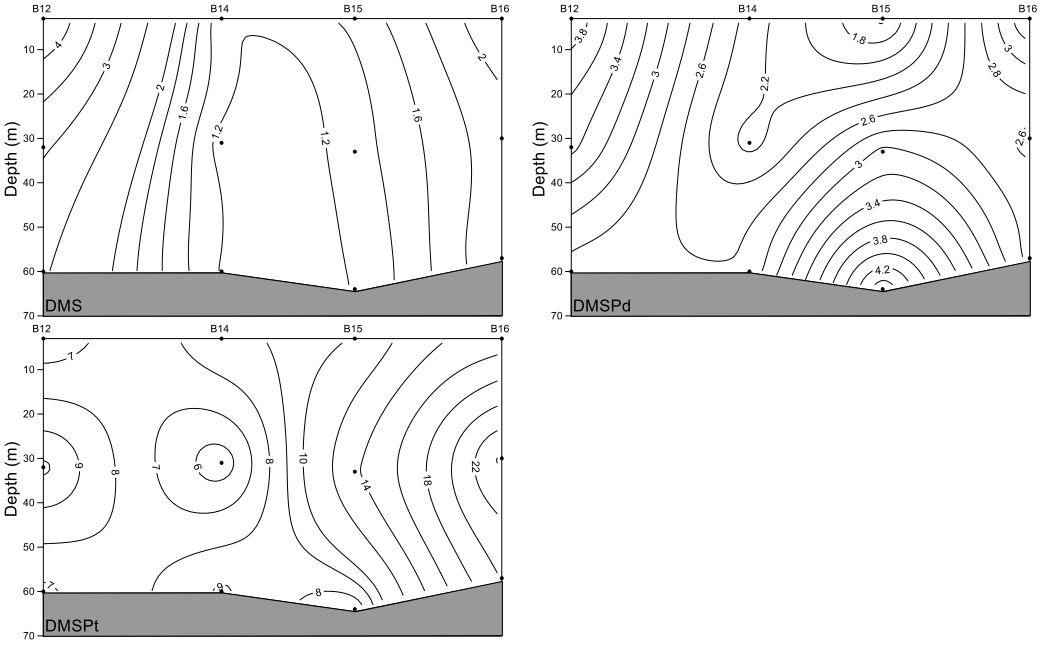

Fig. 5. Vertical profiles of Chl *a* (μg L^{-1}), AA (nmol L^{-1}), DMS (nmol L^{-1}), DMSPd (nmol L^{-1}), and DMSPt (nmol L^{-1}) along transect H19-26 and transect B12-16 during winter.

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Table Captions

Table 1 Summary of the mean values and ranges of Chl *a*, AA, DMS, DMSPd and DMSPt at surface seawater and transects during summer and winter.

Table 2 Correlations between AA, DMS, DMSP, and other biogeochemical parameters in the BS and the YS during summer and winter.

Table 3 The AA concentrations in porewater of surface sediments and in bottom seawater during summer.

Table 4 Rates and rate constants of DMSPd degradation with DMS and AA production and AA degradation in the BS and the YS during summer and winter.

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620 **Table 1 Summary of the mean values and ranges of Chl *a*, AA, DMS, DMSPd and DMSPt at surface seawater and transects during summer and winter.**

		Chl *a* (μg L^{-1})	AA (nmol L^{-1})	DMS (nmol L^{-1})	DMSPd (nmol L^{-1})	DMSPt (nmol L^{-1})
Summer	Surface	1.95 (0.01-8.91)	30.01 (10.53-92.29)	6.12 (1.10-14.32)*	6.03 (1.05-13.23)*	28.86 (8.70-63.03)*
	H19-26	0.58 (0.12-1.50)	22.24 (13.19-85.86)	6.44 (0.79-21.98)	3.05 (0.61-21.59)	13.67 (1.11-55.14)
	B12-17	0.92 (0.18-2.87)	34.60 (12.77-102.98)	7.37 (0.74-15.76)	1.12 (0.36-2.01)	15.45 (1.90-63.03)
	B57-63	1.58 (0.15-7.07)	36.36 (11.08-73.06)	5.51 (2.57-8.79)	1.56 (0.72-3.37)	22.94 (4.12-56.61)
Winter	Surface	0.47 (0.16-0.99)	14.98 (4.28-42.05)	1.38 (0.54-2.22)*	2.30 (1.16-4.29)*	10.39 (2.36-22.21)*
	H19-26	0.28 (0.13-0.42)	17.08 (11.04-39.47)	0.96 (0.52-1.35)	3.06 (1.92-6.06)	11.88 (6.12-19.92)
	B12-16	0.53 (0.17-1.56)	17.68 (13.94-27.69)	1.99 (1.12-4.56)	2.92 (1.54-4.55)	11.44 (5.33-24.50)

* collected from a published MS thesis (Jin, 2016)

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625 **Table 2 Correlations between AA, DMS, DMSP, and other biogeochemical parameters in the BS and the YS during summer and winter.**

			T	S	Chl *a*	DMS	DMSPd	DMSPt	AA
Summer	NYS surface	AA	0.676*						
	SYS surface	AA					0.626*		
	H19-26	DMSPt	0.549*	-0.555*					
	B12-17	DMSPd	0.742***	-0.626**					
		DMSPt	0.746***	-0.707**			0.725**		
	B57-63	DMSPd	0.593*	-0.843***					
		DMSPt		-0.867***		0.577*	0.745**		
Winter	BS surface	AA	0.972*						
	H19-26	DMS	0.765***	0.691**					
		DMSPt	-0.605*	-0.618*					
	B12-16	DMS	-0.859***	-0.807**					
		DMSPt			0.930***				

*Significant at $p<0.05$.
**Significant at $p<0.01$.
***Significant at $p<0.001$.

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Table 3 The AA concentrations in porewater of surface sediments and in bottom seawater during summer.

Station	H10	H12	H14	H16	H19	H23	H25	H26	B12	B13	B61	B63
Porewater AA (μmol L^{-1})	34.54	13.52	99.89	38.36	128.61	136.42	99.45	122.68	41.31	46.50	15.63	102.40
Bottom AA (nmol L^{-1})	14.34	13.41	12.32	17.54	15.59	13.25	16.23	19.01	16.74	102.98	18.95	23.68

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635 **Table 4 Rates and rate constants of DMSPd degradation with DMS and AA production and AA degradation in the BS and the YS during summer and winter.**

Summer

Stations	H19	H26	B12	B17	B57	B63
DMSPd degradation rates (nmol L^{-1} h^{-1})	3.12	3.72	1.44	1.83	5.76	4.20
DMSPd turnover times (h)	6.25	5.10	19.31	14.29	4.91	5.88
DMS production rates (nmol L^{-1} h^{-1})	0.55	0.29	0.33	0.69	0.90	2.71
AA production rates (nmol L^{-1} h^{-1})	1.15	1.90	2.53	1.15	2.63	5.20
AA microbial degradation rates (nmol L^{-1} h^{-1})	25.36	22.10	15.07	11.84	16.17	24.92
AA photochemical degradation rates (nmol L^{-1} h^{-1})	3.16	3.45	0.91	4.02	0.67	2.36
AA microbial degradation rate constants (h^{-1})	0.07	0.36	0.07	0.30	0.50	0.03
AA photochemical degradation rate constants (h^{-1})	0.01	0.02	0.03	0.14	0.04	0.12

Winter

Stations	H19	H26	B12	B16
DMSPd degradation rates (nmol L^{-1} h^{-1})	2.26	1.14	1.92	0.63
DMSPd turnover times (h)	16.53	39.68	31.55	46.73
DMS production rates (nmol L^{-1} h^{-1})	0.08	0.10	0.09	0.07
AA production rates (nmol L^{-1} h^{-1})	1.48	1.22	0.30	0.91
AA microbial degradation rates (nmol L^{-1} h^{-1})	9.41	4.73	8.54	18.66
AA photochemical degradation rates (nmol L^{-1} h^{-1})	4.30	2.31	2.72	0.97
AA microbial degradation rate constants (h^{-1})	0.06	0.36	0.18	0.17
AA photochemical degradation rate constants (h^{-1})	0.13	0.06	0.13	0.05