

Distribution of biogenic sulfur in the Bohai Sea and northern Yellow Sea and its contribution to atmospheric sulfate aerosol in the late fall



Gui-Peng Yang*, Sheng-Hui Zhang, Hong-Hai Zhang, Jian Yang, Chun-Ying Liu

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao 266100, China
College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

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ABSTRACT

Spatial distributions of biogenic sulfur compounds including dimethylsulfide (DMS), dissolved and particulate dimethylsulfoniopropionate (DMSPd and DMSPp) were investigated in the Bohai Sea (BS) and northern Yellow Sea (NYS) in November 2011. DMS and DMSP concentrations were significantly correlated with chlorophyll *a* (Chl-*a*) in the surface water and larger nanoplankton (5–20 μm) was the most important producer of DMSPp in the study area. Silicate had statistically significant influence on the growth of phytoplankton and DMSP concentration. The vertical profiles of DMS and DMSP were characterized by a maximum at the upper layer and the bottom concentrations were sometimes relatively higher compared with the overlying layer. The sea-to-air fluxes of DMS in the study area were estimated to be from 0.05 to 27.4 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with a mean of 4.21 $\mu\text{mol m}^{-2} \text{d}^{-1}$. The contribution of biogenic non-sea-salt SO_4^{2-} (nss- SO_4^{2-}) to total nss- SO_4^{2-} in the atmospheric aerosol over the study area varied from 0.46% to 5.49% with an average of 1.40%. Therefore, the contribution of biogenic sulfur to nss- SO_4^{2-} was not significant and anthropogenic source was dominant for atmospheric sulfate.

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1. Introduction

Dimethylsulfide (DMS) is a climatically active biogenic gas emitted from the ocean surface to atmosphere (Lovelock et al., 1972; Andreae, 1990; Malin and Kirst, 1997). Emissions of DMS from the ocean are a significant source of sulfate aerosol in the marine boundary layer. There are approximately 28.1 (17.6–34.4) Tg sulfur transferred from the oceans into the atmosphere annually in the form of DMS (Lana et al., 2011). DMS emissions not only balance the global sulfur budget, but also impact climate of the Earth due to its oxidation products in the atmosphere. When DMS diffuses into the atmosphere, it can be oxidized rapidly by OH (by day) and NO_3 (by night) radicals to form various sulfur containing products, such as sulfur dioxide (SO_2), methanesulfonic acid (MSA) and non-sea-salt sulfate (nss- SO_4^{2-}). Sulfate produced by this process not only increases the natural acidity of atmospheric deposition, but also contributes to the condensation nuclei (CN) and eventually cloud condensation nuclei (CCN) in remote marine environments. Changes in CCN concentration affect the cloud droplet number concentration, which influences the cloud albedo and subsequently the climate (Charlson et al., 1987).

The production of DMS occurs via enzymatic cleavage of dimethylsulfoniopropionate (DMSP), a molecule that occurs worldwide

in prodigious amounts (10^9 tons or more) in marine algae, where it acts as a compatible solute to counter various stresses, including osmotic, oxidative, and potential damage by UV light (Sunda et al., 2002). When released from marine algae, following grazing or viral attack, DMSP becomes available for subsequent microbial catabolic conversions, some of which release DMS. In addition, DMSP from algae shows large seasonal and geographic variations, linked to seasonal variations in phytoplankton abundance and speciation. Diatoms generally contain less DMSP than Dinophyceae and Prymnesiophyceae (Keller et al., 1989). DMSP and DMS are given off to some extent by live phytoplankton cell, but this release is accelerated during senescence, grazing or viral attack (Dacey and Wakeham, 1986; Lavoie et al., 1996; Hill et al., 1998). DMSP is then cleaved into DMS and other products by intra- and extra-cellular, algal or bacterial DMSP-lyase enzymes (Stefels, 2000). However, the major portion is demethylated by bacterial activity, and does not lead to the formation of DMS (Kiene and Linn, 2000; Yoch, 2002). Only a minor fraction of DMSP, varying between 9% and 21%, is enzymatically cleaved to DMS and acrylate by some species of bacteria and phytoplankton (Kiene and Linn, 2000). DMSP also acts as a carbon or sulfur store and its synthesis may prevent the depletion of important nitrogen precursors during periods of N-limitation (Stefels et al., 2007). However, the enzymatic conversion of DMSP to DMS has been suggested to be part of an anti-grazing defence mechanism in phytoplankton and macroalgae (Wolfe et al., 1997; Van Alstyne and Houser, 2003). There is also the possibility that DMS production during grazing can stabilize marine food webs and functions

* Corresponding author at: College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China.
E-mail address: gpyang@mail.ouc.edu.cn (G.-P. Yang).

in multitrophic interactions (Pohnert et al., 2007; Lewis et al., 2012). In addition, sediment also acted as a source of DMS at the bottom. Previous research showed that the bottom sediments contained much higher concentration of DMS in the porewater than in the overlying water column, presumably derived from detritus settled onto the bottom (Andreae, 1985). In the upper ocean, a subtle interplay of biological, chemical and physical factors determines the seawater concentration of DMS. DMS can be removed through bacterial consumption, photolysis, ocean mixing and ventilation. Galí et al. (2011) reported that bacterial consumption was the dominant sink for DMS which accounted for 9–73% of its loss in the upper mixed layer in the Arctic, while photolysis accounting for 12–65% of the total DMS loss became the dominant sink at some stations.

The distribution of DMS in the surface water of northern Yellow Sea (NYS) and its contribution to atmospheric sulfate aerosol were investigated in 2006 (Yang et al., 2009; Zhang and Yang, 2009). However, the contribution of DMS to sulfate aerosol over the Bohai Sea (BS) has not previously been examined. The rapid development of economy has caused serious haze in northern China especially in Beijing in recent years (Liu et al., 2013). The polluted air may also cause significant change in the atmospheric environment of the BS and NYS, so the aerosol ions and the contribution of biogenic sources to sulfate over the BS and NYS should be further assessed. In the present study, we investigated the distributions of DMS, DMSP, chlorophyll *a* (Chl-*a*) and bacteria in the BS and NYS to further understand the biogeochemical cycling of biogenic sulfur in China marginal seas and the contribution of biogenic sulfur to sulfate in aerosol. Meanwhile, different particle sizes of Chl-*a* and particulate DMSP (DMSPp) samples were collected to study their contributions to DMSP. In addition, the sea-to-air fluxes of DMS were estimated, and MSA and nss-SO_4^{2-} concentrations were measured to evaluate the contribution of biogenic source to sulfate in the aerosol over the BS and NYS.

2. Experimental

2.1. Study area

The BS and NYS are semi-enclosed marginal seas of the northwestern Pacific Ocean. The line connecting the southernmost end of the Liaodong Peninsula and the northernmost end of the Shandong Peninsula is geographically defined as the boundary between the BS and NYS. The mean depth of the BS is <20 m, with the deepest region of about 70 m near the northern part of the Bohai Strait. The NYS is separated from the south by the Shandong Peninsula. Most of the central portion of the sea is deeper than 50 m and characterized by a relatively flat bottom, although large symmetrical bed forms occur in the northeast adjacent to the Yalu River (Liu et al., 2004). The BS and NYS are influenced obviously by the Asian dust and land-source materials which are transported via atmospheric deposition under westerlies, characterized by a great abundance of nitrogen throughout the year (Chung et al., 1998). Moreover, high socio-economic development in both China and Korea coastal regions has significant effects on the ecosystems of the BS and NYS. Anthropogenic pollution has caused notable effects on the species diversity of the phytoplankton and benthos communities in the BS and NYS (Liu et al., 2011; Xu, 2011).

2.2. Sampling

Samples were collected in the BS and NYS aboard the R/V 'Dong Fang Hong 2' in the late fall from 21 November to 1 December 2011. The locations of sampling stations are shown as black dots in Fig. 1. Seawater samples were sampled at 40 stations in which the spatial distributions of DMS, DMSP, Chl-*a* and bacteria in surface water were measured. The maximum depth of 77 m appeared at station B10. The surface seawater temperature at these stations ranged from 10.49 to 15.77 °C, with an average of 12.79 °C. The temperature was lower than that

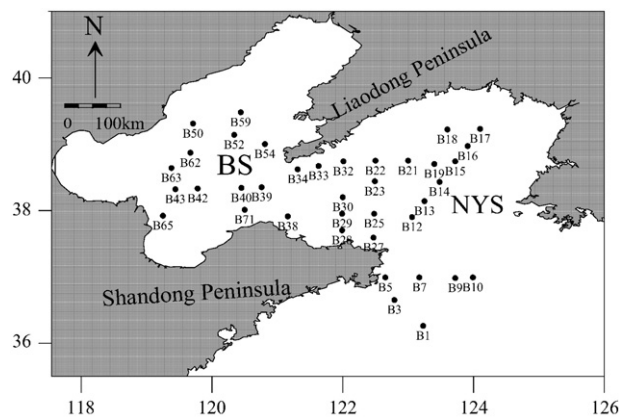


Fig. 1. Locations of the sampling stations in the BS and NYS in the late fall from 21 November to 1 December 2011.

measured in summer with an average of 22.03 °C (Yang et al., 2009). Vertical distributions of DMS, DMSP and Chl-*a* were investigated at transects B12–B17. Seawater salinity and temperature were determined using a Conductivity–Temperature–Depth (CTD) probe (Sea-Bird SBE 9/11 plus) mounted on a rosette sampler. In addition, 8 aerosol samples were collected concurrently during the cruise for analyzing water-soluble ionic species. The detailed information about sampling stations is described in Table 1.

2.3. Analytical procedures

All DMS samples were measured immediately onboard using a modified purge and trap method following Zhang et al. (2008). Briefly, A 2 ml sample was taken up into a glass bubbling chamber through a GF/F filter. Sulfur gases were sparged from the seawater with a stream of nitrogen and trapped in a loop of Teflon tubing immersed in liquid nitrogen. Then the trapped gases were desorbed with hot water (90 °C) and analyzed on a Shimadzu GC-2014 gas chromatograph (GC) equipped with a flame photometric detector. A 3 m × 3 mm glass column packed with 10% DEGS on Chromosorb W-AW-DMCS was used to separate sulfur gases at 70 °C. The analytical precision for DMS was better than 10% and the detection limit of this method was about 0.4 nM DMS.

Gravity filtering of samples for dissolved DMSP (DMSPd) followed a protocol that was modified by Kiene and Slezak (2006). Total DMSP (DMSPt) and DMSPd samples were both fixed with 50% sulfuric acid and stored on board. For DMSPd samples, the first few milliliter of filtrate were rejected, and a 4 ml sample was transferred to a glass vial containing 40 µl of concentrated sulfuric acid and sealed. For DMSPt samples, 100 µl of 50% sulfuric acid was directly added to 10 ml unfiltered seawater samples and sealed. Both of the DMSPt and DMSPd samples were incubated in the dark at room temperature (23 °C) for at least 2 days. When analyzed, 300 µl of 10 mol l⁻¹ KOH were injected to 2 ml of preservative DMSP samples and incubated in the dark at 4 °C for at least 24 h, fully converting DMSP to DMS. Then the liberated DMS was measured using the method described above.

A seawater sample of 50 ml for DMSPp size-fractionation was filtered by gravity through a sequential series of 47 mm filters, i.e., 20, 5, 2 and 0.2 µm glass-fiber filters (Whatman). The filters with DMSPp were directly added to 50 ml brown glass vials filled with 48 ml of Milli-Q water and 2 ml of 10 mol l⁻¹ KOH and sealed. For Chl-*a* size-fractionation, a seawater sample of 250 ml was filtered through different pore size filters (as above) and size-fractionation filters were sealed with aluminum foil and stored in the dark at -20 °C.

Subsamples for dissolved oxygen (DO) analyses were collected, fixed, and titrated onboard, following the classic Winkler procedure. A small quantity of NaN₃ was added during subsample fixation in order

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