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Biological production and spatial variation of dimethylated sulfur compounds and their relation with plankton in the North Yellow Sea

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ABSTRACT

The concentrations of dimethylated sulfur compounds and chlorophyll *a*, as well as biological production and consumption rates of dimethylsulfide (DMS), were measured in the surface water of the North Yellow Sea (NYS, 37–40°N to 121–124°E) in winter 2007. Surface DMS, dissolved and particulate dimethylsulfoniopropionate (DMSPd and DMSPp) concentrations in the study area increased significantly from offshore to inshore sites, with the average values of 2.00, 4.52 and 7.21 nM, respectively. The biological production and consumption rates of DMS were estimated, with the average values of 5.41 and 3.84 $\mathrm{nM\,d^{-1}}$, respectively. The spatial variation of chlorophyll *a* was consistent with that of DMS and DMSP, as well as with that of DMS biological production, suggesting that phytoplankton biomass might play an important role in controlling the distribution of DMS and DMSP in the study area. According to the collective data of dimethylated sulfur compounds and DMS biological conversion in China Seas, the dimethylated sulfur compounds concentrations in the NYS during winter were a factor of 2 and 1.3 higher than those in the East China Sea and South China Sea, respectively. Less DMS (DMSP) in NYS was released in winter than that in spring and summer, which could be attributed to the shift in phytoplankton community composition dominated by diatoms to non-diatoms from winter to summer. Quantitative comparison analysis pointed to DMSPp rather than DMSPd as an important precursor of DMS in the surface water. The estimated sea-to-air fluxes of DMS using Liss and Merlivat (LM86), Wanninkhof (W92) and Nightingale (N2000) formulae were 2.72, 5.12 and 4.28 $\mu\mathrm{mol\,m^{-2}\,d^{-1}}$, respectively. In the surface water, the biological turnover time of DMS varied from 0.21 to 1.73 d with an average of 0.83 d, which was about 5.43-fold faster than the mean DMS sea–air turnover time (3.12 d), implying that microbial consumption was a main sink of DMS in the surface water.

1. Introduction

In the surface layer of the ocean, dimethylsulfide (DMS) produced by plankton is the most dominant reduced active sulfur gas that exchanges from the sea to the air (Lovelock et al., 1972). In the atmosphere, DMS can be oxidized to non-sea-salt sulfate and methane sulfonic acid which is responsible for a proportion of cloud condensation nuclei formation. These processes thereby affect the Earth's radiative balance both directly, through the backscatter of solar radiation, and indirectly, through formation of cloud condensation nuclei (Charlson et al., 1987). Thus, planktonic production of DMS and its ultimate emission to the atmosphere could counteract the global warming trend; in turn, this climatic change may exert an impact on the biogenesis of DMS in the ocean (Charlson et al., 1987; Malin et al., 1992).

In the ocean, DMS originates from a compatible solute, dimethylsulfoniopropionate ($(CH_3)_2S^+CH_2CH_2COO^-$; DMSP). This tertiary sulfonium compound is an osmolyte, antioxidant and cryo-protectant synthesized chiefly by a wide variety of marine phytoplankton, macroalgae and submerged aquatic plants (Keller et al., 1989; Sunda et al., 2002). DMSP is widely distributed in the ocean euphotic region at a higher level of 10–100 nM (Curran et al., 1998; Shenoy et al., 2006) throughout the oceans. Moreover, DMSP production is associated with algal speciation, with Dinophyceae and Prymnesiophyceae being major sources (Keller et al., 1989); therefore, the distribution of DMSP is heterogeneous and, in most cases, not strictly tied to total algal biomass (e.g., Kettle et al., 1999). There have also been observations indicating the correlation between DMSP concentrations and phytoplankton chlorophyll under certain environmental conditions (Yang et al., 2009a). Additionally, DMSP is a crucial substrate in the microbial food web (Sunda et al., 2002) in which it supplies enough sulfur

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and carbon to satisfy the requirements for marine bacterial growth (Kiene et al., 2000) by the biological-mediation of DMSP, further affecting directly the DMS yield from the DMSP.

Thus, DMS and its precursor DMSP form the major pool of organic sulfur in the marine environment and the production and transformation of these compounds comprise an important part of the oceanic sulfur cycle. The release and degradation of DMSP, as well as the turnover of DMS, are closely linked with food web activities (Malin et al., 1992). DMS concentrations are determined by the balance between its production and loss mechanisms (Gabric et al., 1999), which are the parts of a complex web of ecological and biogeochemical processes. Factors which control the release of DMS into the water are not clearly understood, but possible mechanisms are metabolic excretion accompanying phytoplankton growth (Belviso et al., 1990), phytoplankton grazing by zooplankton (Dacey and Wakeham, 1986), the senescence of microalgae (Nguyen et al., 1988), the interaction of bacterioplankton (Kiene and Bates, 1990) and viral pathogens (Hill et al., 1998). Once produced, DMS is lost from seawater by three major pathways: sea–air exchange, biological consumption and photochemical transformation (Kieber et al., 1996; Kiene and Bates, 1990), with the latter two processes leading to formation of dimethylsulfoxide (DMSO). Certainly, the intimate interplay between DMS formation and degradation make a considerable contribution to in situ DMS concentration as well as its spatio-temporal variability.

To date relatively few studies of DMS distribution and turnover have been conducted in the North Yellow Sea (NYS). Therefore, we carried out a basic study of DMS biogeochemistry, for the first time, in the NYS during winter. Here we determined the spatial distribution of DMS and DMSP concentrations and estimated the biological production and consumption rates of DMS in the surface water. Furthermore, we assessed the role of plankton communities in DMS and DMSP cycling in this temperate zone. What is more important, we evaluated the dominant removal processes of DMS in this region by calculating its ventilation and biological consumption rates with the aim of obtaining a better understanding of biogeochemical sulfur cycle in the surface water of the NYS.

2. Materials and methods

2.1. Study area

The study area is located between 37–40°N and 121–125°E in the Yellow Sea (YS), namely the NYS. The division between the North and South Yellow Sea (SYS) is usually marked by the Qinling–Dabie–Sulu collisional belt (Wu, 2002). The NYS lies on a shallow, semi-enclosed, low-gradient shelf between the Chinese mainland and the Korean Peninsula, connecting with the Bohai Bay to the northwest (Fig. 1). Korea Bay (or West Korea Bay) and the Liaodong Gulf are its major inlets. The East Asian monsoon dominates the YS throughout the year. During winter, a strong northerly monsoon prevails over the area from late November to early April with an average wind speed of 10 m s^{-1} in January. In addition, the Yellow Sea Warm Current (YSWC) is likely to play an important role in the transport of mass and heat flux from the East China Sea (ECS) to the YS. The main river, the Yalu River, empties into the NYS along the continental landmasses of China and Korea. It carries huge quantities of fresh water, containing dissolved and suspended matters into this area. The NYS, as a part of the northwest Pacific region, is rich in natural resources and plays an important role in human life and economic exploitation of the Chinese eastern littoral. Thus the environment of this region, especially along the coast, should be of importance to the climate change in the whole China Seas and the surrounding mainland.

2.2. Sampling methods

Seawater samples were collected in the NYS during 4–16 January 2007 on board the R/V "*Dong Fang Hong 2*". The background information on the sampling locations and hydrographic conditions are depicted in Table 1. Surface seawater samples (<5 m) were collected with Niskin bottles attached to a CTD rosette. Subsequently, samples from 12-l Niskin bottles were transferred to acid-cleaned polycarbonate containers (for in situ sulfur compound measurements and biological turnover of DMS), which was rinsed thoroughly with seawater prior to sampling, using silicone

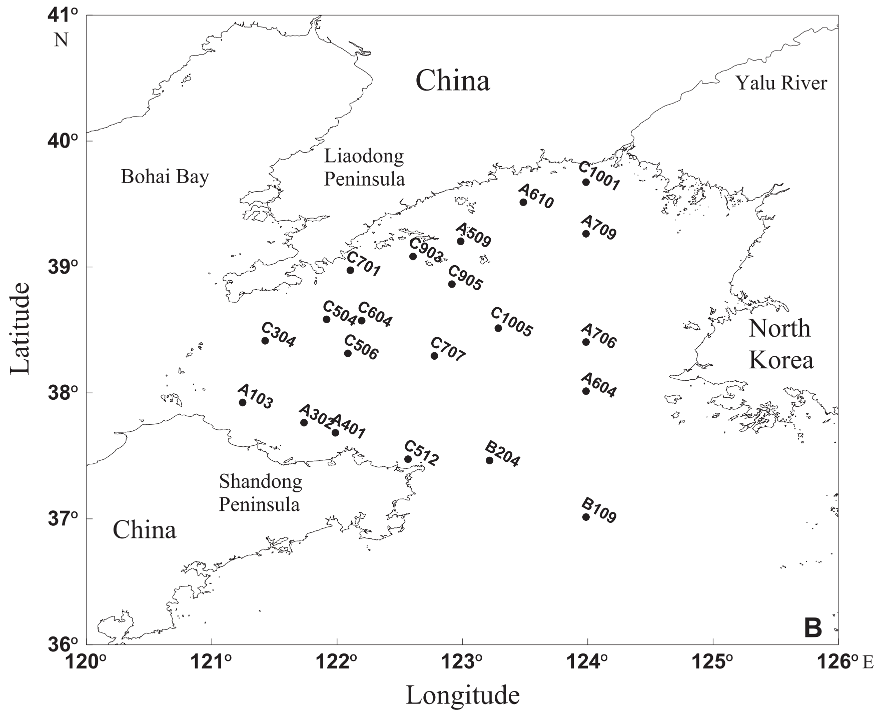

Fig. 1. Map of study area and locations of the sampling stations in the North Yellow Sea.