

## Biogenic emission of dimethylsulfide (DMS) from the North Yellow Sea, China and its contribution to sulfate in aerosol during summer

Gui-Peng Yang\*, Hong-Hai Zhang, Lu-Ping Su, Li-Min Zhou

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

### ARTICLE INFO

#### Article history:

Received 13 October 2008  
Received in revised form  
8 January 2009  
Accepted 10 January 2009

#### Keywords:

Dimethylsulfide  
Methanesulfonic acid  
Non-sea-salt sulfate  
Sea-to-air flux  
North Yellow Sea

### ABSTRACT

Seawater, atmospheric dimethylsulfide (DMS) and aerosol compounds, potentially linked with DMS oxidation, such as methanesulfonic acid (MSA) and non-sea-salt sulfate ( $\text{nss-SO}_4^{2-}$ ) were determined in the North Yellow Sea, China during July–August, 2006. The concentrations of seawater and atmospheric DMS ranged from 2.01 to 11.79  $\text{nmol l}^{-1}$  and from 1.68 to 8.26  $\text{nmol m}^{-3}$ , with average values of 6.20  $\text{nmol l}^{-1}$  and 5.01  $\text{nmol m}^{-3}$ , respectively. Owing to the appreciable concentration gradient, DMS accumulated in the surface water was transferred into the atmosphere, leading to a net sea-to-air flux of 6.87  $\mu\text{mol m}^{-2} \text{d}^{-1}$  during summer. In the surface seawater, high DMS values corresponded well with the concurrent increases in chlorophyll *a* levels and a significant correlation was observed between integrated DMS and chlorophyll *a* concentrations. In addition, the concentrations of MSA and  $\text{nss-SO}_4^{2-}$  measured in the aerosol samples ranged from 0.012 to 0.079  $\mu\text{g m}^{-3}$  and from 3.82 to 11.72  $\mu\text{g m}^{-3}$ , with average values of 0.039 and 7.40  $\mu\text{g m}^{-3}$ , respectively. Based on the observed MSA,  $\text{nss-SO}_4^{2-}$  and their ratio, the relative biogenic sulfur contribution was estimated to range from 1.2% to 11.5%, implying the major contribution of anthropogenic source to sulfur budget in the study area.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound emitted into the atmosphere from the ocean, where it is produced by marine microbiota (Andreae, 1990; Bates et al., 1992b). The main source of DMS in seawater is dimethylsulfoniopropionate (DMSP) that is synthesized by marine algae as an internal cell component. DMSP and DMS are given off to some extent by live phytoplankton cells, but this release is greatly accelerated by cell senescence, zooplankton grazing and viral infection (Dacey and Wakeham, 1986). DMSP is then converted via several biochemical mechanisms into DMS and other products by intra- and extra-cellular, algal or bacterial DMSP-lyase enzymes (Kiene, 1992). Relative to its level in air, DMS is supersaturated in surface waters by roughly three orders of magnitude (Andreae, 1986). Then the gas transfers into the atmosphere across the water–air interface, as a result of this appreciable concentration gradient. The global flux of DMS from the oceans is estimated to be 15–33  $\text{Tg S a}^{-1}$  (Kettle and Andreae, 2000), which accounts for more than 50% of the

global sulfur emissions from natural sources (Bates et al., 1992b; Kettle et al., 1999).

Oceanic DMS emissions, not only balance the global sulfur budget, they may also impact the Earth's climate due to its oxidation products in the atmosphere. When DMS diffuses into the atmosphere, it could be oxidized rapidly by OH (by day) and  $\text{NO}_3$  (by night) radicals to form various sulfur containing products, such as sulfur dioxide ( $\text{SO}_2$ ), methanesulfonic acid (MSA) and non-sea-salt sulfate ( $\text{nss-SO}_4^{2-}$ ). Sulfate produced by this process not only increases the natural acidity of atmospheric deposition, but also contributes to the major contributor of 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. By this mechanism it has been hypothesized that DMS may play an important role in modifying the climate (Charlson et al., 1987).

Ocean margins have been identified as a significant source of DMS, due to their high biological productivity and enhanced DMS production in turn (Sciare et al., 2002). It is thought that about 12% of global DMS emissions are from highly productive coastal and shelf regions, although they occupy only a small part of the world ocean (Andreae et al., 1995; Levasseur et al., 1997). At the same time, the atmosphere over the coastal regions is suffering from

\* Corresponding author. Tel.: +86 532 66782657/66781733; fax: +86 532 66782540.

E-mail address: [gpyang@mail.ouc.edu.cn](mailto:gpyang@mail.ouc.edu.cn) (G.-P. Yang).

land-source pollution and has enhanced oxidation capacity, which means that this kind of atmosphere can oxidize more DMS to sulfate.  $\text{nss-SO}_4^{2-}$  has both biogenic and anthropogenic sources, whereas MSA is thought to derive exclusively from biological DMS oxidation. Therefore, MSA is considered to be a marker of biogenic sources and its ratio to  $\text{nss-SO}_4^{2-}$  can be used to assess the contribution of biogenic sources to sulfate in the atmosphere (Savoie and Prospero, 1989). China has over 18,000 km of coastline and 3.8 million km<sup>2</sup> of sea area, but little information is available on DMS in the atmosphere and its oxidation products over China's coastal seas. To date, only Gao et al. (1996) and Nakamura et al. (2005) have reported the concentrations of atmospheric MSA and  $\text{nss-SO}_4^{2-}$  over the East China Sea during spring and autumn, respectively. Moreover, the available information on atmospheric volatile sulfur compounds over China sea is mainly based on observations by Ma et al. (2005), who investigated atmospheric DMS and aerosol ions over the Pearl River Estuary and the adjacent northern South China Sea. In this study, we focused on the distribution of DMS in the surface water of the North Yellow Sea, China to relate their variability to chlorophyll *a* level and to estimate the DMS emission from this region in summer. In addition, we measured the concentrations of atmospheric DMS and its main potential oxidation products MSA and  $\text{nss-SO}_4^{2-}$  and aimed to evaluate the contribution of biogenic sources to sulfate in the atmosphere over the North Yellow Sea.

## 2. Experimental

### 2.1. Study area

The Yellow Sea is a shallow, relatively flat, semi-closed epicontinental sea bordered by China and the Korean peninsula. The North Yellow Sea, the subject of this paper, 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). During summertime, the hydrography across North Yellow Sea is characterized by a pronounced cold-pool in the deeper basin overlain by 20–25 m of highly stratified warmer water. Stratification breaks down along the boundaries, reflecting in part counterclockwise circulation in the North Yellow Sea. The internal recycling of chemical substances has significant impacts upon the phytoplankton growth of the North Yellow Sea (Zhang et al., 2002). In addition, the Yellow Sea is influenced obviously by the Asian dust and land-source materials can be transported via atmosphere deposition under westerlies, characterized by a great abundance of nitrogen throughout the year (Chung et al., 1998).

### 2.2. Sampling stations

Fig. 1 shows the cruise tracks for sampling in the North Yellow Sea conducted on board R/V “Dong Fang Hong No. 2” during 20 July–7 August, 2006. Surface seawater samples were collected and measured at 30 stations while atmospheric DMS samples were simultaneously collected and measured at 21 selected stations. In addition, a total of 16 aerosol samples for analyzing water-soluble ionic species were collected concurrently over the course of the campaign. Detailed information about the sampling station locations and hydrographic conditions are described in Table 1.

### 2.3. Seawater DMS and chlorophyll *a* analyses

Seawater samples were collected using 12 l Niskin bottles mounted to a Seabird 911 CTD. The concentrations of DMS in

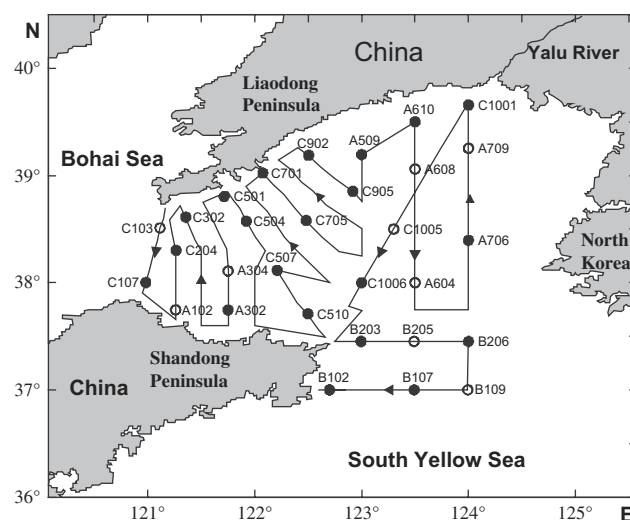


Fig. 1. Cruise track in the North Yellow Sea in summer 2006. Circles (open and solid) indicate surface sampling locations. Solid circles represent stations where atmospheric DMS was also measured. Arrows indicate the trajectory of the ship.

water samples were analyzed immediately after collection, using a cryogenic purge-and-trap system, modified from Andreae and Barnard (1983). Briefly, an aliquot of 10–20 ml of seawater sample for DMS determination was directly drawn into a glass syringe from the Niskin bottle through a silicone tube. Without containing the ambient air, the sample was gently injected into a bubbling chamber through a filter holder (Whatman GF/F, 25 mm diameter) attached to the glass syringe. This procedure avoids the production of DMS from plankton and biological debris during the analytical processes. To extract DMS from the seawater, the seawater sample in the chamber was stripped with ultra-pure nitrogen at a rate of 200 ml min<sup>-1</sup>. The extracted gas was dried through a glass tube containing anhydrous K<sub>2</sub>CO<sub>3</sub> and then trapped in an inert stainless steel U-shaped tube packed with Tenax-TA at the temperature of dry ice-ethanol (−78 °C). After extraction, the U-shaped tube was heated and the desorbed gas was introduced into a GC/FPD (Shimadzu GC-14B) for quantification. A 3-m glass chromatographic column packed with 10% DEGS on Chromosorb W-AW-DMCS was used to separate sulfur gases. Calibration was by addition of gravimetrically prepared standards of DMS in ethylene glycol to degassed seawater and subjected to the same procedure as seawater samples. The analytical precision was generally better than 5% in routine sample analysis and the detection limit was approximately 0.1 pmol DMS.

For chlorophyll *a* analysis, several hundreds of milliliter seawater samples were filtered through glass fiber filters (Whatman GF/F, 47 mm diameter). Chlorophyll *a* was extracted from the filters by soaking overnight in 10 ml 90% acetone under a cool, dark condition and then measured fluorometrically using a Turner Design Fluorometer according to Parsons et al. (1984).

### 2.4. Atmospheric DMS and aerosol sample analyses

The procedures for the collection and analysis of atmospheric DMS generally follow those employed by Ma et al. (2005). Atmospheric DMS was collected using a vacuum pump, which took air at 250 ml min<sup>-1</sup> through a U-shaped sample tube kept in liquid nitrogen for about 1.5 h. The sample tube was made of Teflon (20 cm × 4 mm) and packed with Tenax-TA (60–80 mesh). Ahead of

Download English Version:

<https://daneshyari.com/en/article/4441534>

Download Persian Version:

<https://daneshyari.com/article/4441534>

[Daneshyari.com](https://daneshyari.com)