Research papers

Dimethylsulfide and dimethylsulfoniopropionate production along coastal waters of the northern South China Sea

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A B S T R A C T

The gross biological dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) production in surface and bottom waters along the coasts of the northern South China Sea (SCS) were investigated during summer of July–August 2000. In surface water, the averaged concentrations of particulate DMSP (DMSPp) and DMS were 42.60 ± 31.94 nM and 2.12 ± 1.38 nM, respectively. In bottom water, the mean DMSPp and DMS contents were 26.37 ± 20.83 nM and 2.09 ± 1.55, respectively. Both DMSPp and DMS contents significantly varied spatially ($P < 0.05$, $n=40$), but not vertically ($P > 0.05$, $n=40$). The highest DMSPp concentration (100.62 nM) was recorded on the surface of Shenzhen waters, whereas the lowest (4.33 nM) was on the surface of Zhanjiang waters. DMS fluctuated correspondingly; the highest (6.79 nM) and lowest (0.83 nM) values occurred on the surface of Shenzhen water and bottom water of Nan'ao Island (Shantou), respectively. Correlation analysis further revealed that DMS/DMSPp production was not closely related with salinity and chlorophyll a content ($P > 0.05$, $n=40$). However, the bottom DMS increased with increasing temperature when it is lower than 28.2 °C ($r^2=0.52$, $P < 0.01$, $n=13$), whereas it decreased as the temperature further increased ($r^2=0.86$, $P < 0.01$, $n=8$). Moreover, in surface waters, light intensity showed a significant positive effect on DMSPp production ($r^2=0.37$, $P < 0.01$, $n=20$), with elevated DMSP concentration under high irradiance. Overall, the sea-to-air fluxes of DMS across the coastal area of the northern SCS in summer were within the range of 0.24–15.07 μ mol m^{-2} d^{-1}, with a mean flux of 2.12 ± 3.20 μmol m^{-2} d^{-1}.

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1. Introduction

Dimethylsulfide (CH$_3$–S–CH$_3$, DMS) is an important sulfur compound in marine environments; its annual flux from the oceans is within the range of 13–37 Tg S year^{-1}, thereby contributing about 50% of the global biogenic sulfur flux to the atmosphere (Moller, 1984; Yoch, 2002). DMS can chemically influence not only the marine system and global sulfur cycle, but also the global climate. Once in the atmosphere, its oxidized compounds (non-sea-salt sulfate aerosol particles) can directly affect the climate by backscattering the solar radiation and indirectly as cloud condensation nuclei (Charlson et al., 1987). The earth's climate may be partly modulated by variations in DMS production, which resulted from the changes of sea surface temperature and solar radiation (Nguyen et al., 1983; Charlson et al., 1987).

DMS is mainly produced from a precursor compound dimethylsulfoniopropionate (DMSP) in many marine organisms, such as microalgae, macroalgae, and invertebrates (Malin et al., 1992; Michaud et al., 2007; Verity et al., 2007; Yost and Mitchelmore, 2010). The ability to produce DMSP varies considerably among different taxa, and Prymnesiophyceae and Dinophyceae are known to generate higher DMSP/DMS than other groups, such as diatom (Liss et al., 1993). For example, spring blooms dominated by Phaeocystis (belonging to Prymnesiophyceae) have been associated with considerable production of DMS in sea water around the world (Turner et al., 1996; Kwint and Kramer, 1996). Moreover, although the exact function of DMSP in algal physiology is still unclear, DMSP and its cleavage products may act as a compatible solute, cryoprotectant, antioxidant, and in the biochemical cycle of methionine in DMSP-producing organisms; therefore, production of DMSP and DMS may be related with physiological stresses, which affect the growth and metabolism of organisms (Stefels, 2000; Sunda et al., 2002; Wang et al., 2003). In addition to composition and abundance, DMSP/DMS concentration in seawater is subject to many environmental factors, such as temperature, salinity, light, nutrients, currents, and velocity. Consequently, the

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DMS concentration in global marine waters shows a significant spatial distribution worldwide, which makes it difficult to estimate the global flux precisely.

It has been suggested that the warmest, most saline, and most intensely illuminated regions of the oceans have the highest rate of DMS emission into the atmosphere (Charlson et al., 1987). In this regard, the tropical and subtropical areas are supposed to be more abundant than the temperate regions in DMS production. As the largest marginal sea, the South China Sea (SCS) covers an area of 3.5×10^6 km^2 and is characterized by high temperature, salinity, and irradiation, but with relatively low productivity. The DMS distribution in the SCS had been studied; well correlation was found between DMS concentration and chlorophyll a (Chl-a) content in the southern SCS (Yang et al., 2000), but no correlation was observed in the central SCS (Yang et al., 2008). Moreover, investigation along the transect from the Pearl River estuary (PRE) to the northern SCS showed significant spatial and temporal DMS variations, and the highest values occur in the mouth of the estuary (Ma et al., 2005), which coincides with the view that ocean margins (estuaries and corresponding plumes) are significant source of DMS (Sciare et al., 2002). As the nearest coastal province to the SCS, Guangdong, particularly the Pearl River Delta, is suffering from sulfur deposition with a mean pH of acid rain of only 4.64 (DEP of Guangdong, 2002). Non-sea-salt sulfate aerosol from DMS oxidation in marine troposphere is a major contributor to the acidity of natural precipitation in coastal areas (Charlson and Rodhe, 1982). Therefore, understanding the contribution of natural DMS products to the local sulfur deposition is necessary.

However, less is known about their sources, distributions, and impacts in the coasts of SCS, specifically eutrophic coastal areas and upwelling regions that are supposed to be richer in DMSP/DMS than the oligotrophic open oceans. Based on above hypothesis and given the specific characteristics of the tropical and subtropical regions of the SCS, we made specific attempts to quantify the DMSP and DMS contents in the eutrophic coastal waters of the northern SCS. The effects of salinity, temperature, and light intensity on the production of biological DMS in coastal waters and DMSP in microalgae were also tested in field condition. Correlation between DMS/DMSP and Chl-a contents was further analyzed, and sea-to-air fluxes of DMS were subsequently estimated based on Stagnant film model (Liss and Slater, 1974) to interpret the horizontal DMS distributions in the coasts of the SCS, as basis for estimating regional DMS flux from the sea to the atmosphere.

2. Materials and methods

2.1. Field sampling and treatment

A total of 20 sampling sites were selected to cover different areas along the coasts of the northern SCS, including offshore, aquaculture area, and harbor stations, to investigate the distribution of DMS and particulate DMSP (DMSPp) during summer season (from 31 July to 29 August 2000; Fig. 1). At each station, vertical profiles of temperature and salinity were measured using a YSI instrument (Yellow Springs Instrument Co., USA). Light intensity (illumination) was measured with a portable illumination meter LX-2 (Japan). Both surface (0–0.2 m) and bottom (0.5–1.0 m above the seabed at sampling stations) seawaters were collected using a 2.5 L Niskin sampler during daytime from 10:00 to 15:00. A measured volume of water samples for DMS and DMSPp determination was filtered immediately on board through GF/C filter; both water samples were stored in polyethylene bottles (100 mL) without headspace, and filters were preserved in dark at 4 °C until further analysis (within 1 month after collection). Subsamples for Chl-a (500 mL each sample) were immediately filtrated onto

0.45 μm cellulose filters and analyzed fluorometrically with a Turner Design Fluorometer after extraction with 90% acetone in the laboratory according to the method of Parsons et al. (1984).

2.2. Plankton sampling and analysis

Mesozooplankton was collected through vertical tow from 1.0 m above the sediment to the water surface with a 169 μm mesh-size plankton net (0.5 and 1.45 m in mouth diameter and length, respectively). Samples were fixed and preserved with formalin in 5% final concentration, and the abundance was counted under an inverted microscope. Microphytoplankton was collected using a 55 μm mesh-size plankton net (0.37 and 1.3 m in mouth diameter and length, respectively) and preserved with 1% Lugol's iodine solution. Phytoplankton species were further identified and enumerated under a microscope (Leica DM2000). No flow meter was fitted in the net mouth to measure the quantity of seawater, thus the total abundance of phytoplankton and zooplankton was unavailable, and only a draft relative abundance of dominant species (described as high, medium, and low abundance in a given volume, such as 5 and 1 mL of concentrated sample for zooplankton and phytoplankton, respectively) was used in later analysis.

2.3. Determination of DMS and DMSPp content

Both DMS and DMSPp were analyzed according to the method described in Turner et al. (1990). DMS in seawater (20 mL) was directly purged using nitrogen gas for 11 min, concentrated in Tekmar3000 system, and analyzed using a Hewlett Packard Gas Chromatograph (QP-5000)-Mass Spectrum (HP5973) fitted with a Selected Ion Monitor (SIM). The chromatographic column was a fused silica capillary DB-17 column (0.25 mm × 30 m). For the filtered DMSPp samples, 2.0 mL of 5 M NaOH was added followed by 2.0 mL n-hexane to recover the solution. After 12-h hydrolyzing (DMSPp to DMS) at room temperature in darkness, approximately 1.0 μL of n-hexane-DMS extraction (supernatant) was collected and DMS concentration was measured using the GC–MS(HP6890-HP5973) fitted with SIM as the method described above. Calibration was based on the addition of known amounts of standard DMS in an ethylene glycol solution to degassed seawater, that was subsequently subjected to the same procedure as seawater samples. The analytical precision was generally better than 5% in routine sample analysis, and the detection limit for DMS was 0.1 nM.

2.4. Sea-to-air DMS flux calculations

DMS fluxes were calculated using the simplified equation given in Ma et al. (2005), which is based on the air–sea gas exchange equation of Liss and Slater (1974):

$$F = K\left(\frac{C_g}{H} - C_l\right) \tag{1}$$

where F is the sea-to-air fluxes of DMS (μmol m^{-2} d^{-1}), K is the DMS transfer velocity, H is the Henry's law constant, and C_g and C_l are DMS concentrations (nmol L^{-1}) in the atmosphere and seawater phase, respectively. The atmospheric DMS concentration is negligible, hence the flux can be approximated using the following equation:

$$F = -KC_l \tag{2}$$

where K can be estimated based on wind speed and sea temperature according to the formula of Liss and Merlivat (1986).