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Spatial–temporal distribution of dimethylsulfide in the subtropical Pearl River Estuary and adjacent waters

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Abstract

Three cruises were carried out in the Pearl River Estuary (PRE) and adjacent northern South China Sea (SCS) in July 2000, May 2001 and November 2002 to collect seawater samples. Concentrations of dimethylsulfide (DMS), chlorophyll *a* (chl *a*), nutrients (N, P, Si), salinity and temperature in seawater were measured. The spatial and temporal distribution of DMS concentrations showed larger fluctuations compared with other estuaries reported in the literature. The mean DMS concentrations in three cruises ranged from 0.05 nM (nM $= 10^{-9}$ mol l^{-1}) to 52.7 nM ($n = 76$). The higher concentrations of DMS were observed at the mouth of the estuary. In wet season, high variations of environmental salinity might stimulate algae to release more DMSP to adjust osmotic pressure. Most of these DMS 'hotspots' were coincident with the area of high chl *a* concentrations, although no significant correlation between DMS and chl *a* was found. The values of DMS/chl *a* showed a clear trend along the north to the south transect, increasing sharply from estuary to shelf and open sea. There was no significant correlation between DMS and salinity in the wet season (July and May), but a significant positive correlation in the dry season. High primary production and more iron deposition implied that the NE monsoon might influence DMS production in the dry season.

Keywords: Dimethylsulfide; Spatial–temporal distribution; Phytoplankton; Nutrients; Pearl River Estuary; South China Sea

1. Introduction

Dimethylsulfide (DMS) is the most abundant volatile sulfide emitted from the ocean. Once DMS is oxidized in the atmosphere, the by-products can contribute to the acidity of rain, and also the formation of sulfate aerosols, which are a major source of cloud condensation nuclei over remote oceans (Andreae and Crutzen, 1997). DMS is formed from its precursor dimethylsulfoniopropionate (DMSP), which is produced by marine

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phytoplankton. DMSP is involved in osmoregulation in algae and bacteria, and cryoprotection in algae (Liss et al., 1997; Simó, 2001). The production of DMSP has been found to vary with phytoplankton species. Prymnesiophytes and dinoflagellates are phytoplankton groups with high intracellular DMSP concentrations (Liss et al., 1997). Generally, DMS concentration is high when high DMSP-producing groups dominate the phytoplankton population. Diatoms have low intracellular DMSP concentrations and it is generally believed that diatoms are less important than Prymnesiophytes and dinoflagellates in DMS production. However, in some diatom-dominated waters with high biomass, DMS concentrations were as high as in those dominated by those major DMSP-producing groups (Iverson et al., 1989). In addition, several investigators are now showing that microzooplankton grazing of particulate DMSP to dissolved DMSP, and bacterial conversion of this to DMS is also important. Jones et al. (1998) found that in polar waters increased microzooplankton grazing in diatom-dominated waters, may lead to above-average concentrations of DMS. This does not appear to be the case when the biomass was dominated by dinoflagellates in subantarctic waters.

Due to the growing human population and urbanization processes, coastal waters are heavily disturbed. The amount of natural and anthropogenic materials, which are carried from land to coast, has increased by a factor of 1.5–2 over the past 50 years (Christophe and Fred, 2001). Discharges of industrial and municipal waste have contributed to the eutrophication of the coastal areas of oceans on a global scale. Red tide outbreaks are hence most frequent in near-shore waters. For example, 53 red tides were recorded from 1981 to 1992 in the Pearl River Estuary (PRE) (Qian and Liang, 1999; Yan et al., 2001).

The eutrophication process changes the chemical and physical characteristics of seawater. These changes may affect the phytoplankton biomass, species composition and physiological processes. In the northwestern Black Sea, eutrophication induced a shift in plankton speciation from diatoms to flagellate-dominated populations (Mee, 1992; Lancelot et al., 1987). VandenBerg et al. (1996) suggested that the trend in eutrophication could be explained by a shift of plankton population to *Phaeocystis* species in the coastal zones of the North Sea, leading to an increase in DMS emissions. A model about the effects of eutrophication on DMS production in the southern part of the North Sea suggested that the anthropogenic eutrophication of the southern North Sea had caused an increase of a factor 2.5 in the mean annual emission of DMS to the atmosphere in the period of the 1900–1980 (VandenBerg et al., 1996). Andreae (1990) observed high DMS concentration in oligotrophic areas of the Sargasso Sea. The culture experiments conducted by Turner et al. (1988) suggested that the cocclithophore *Emiliania huxleyi* produces less internal DMSP in higher nitrate medium. Furthermore, if nitrate is added to a culture medium with low nutrients, the intracellular DMSP concentration will decrease within 24 h. Gage et al. (1997) outlined a pathway of DMSP biosythesis in marine algae, and explained why nitrogen deficiency enhances DMSP production.

Estuaries are transition zones between rivers and marine ecosystems. Pritchard (1967) defined an estuary as a semi-enclosed coastal body of water which has free connection with the open sea, and within which seawater is measurably diluted with fresh water derived from land drainage. High concentrations of DMS have been reported from several estuary plumes (Turner et al., 1996; Simó et al., 1997; Amouroux et al., 2002). A few studies about DMS in American and European estuaries have been reported (Iverson et al., 1989; Cerqueira and Pio, 1999; Sciare et al., 2002), and all the researches were focused on the temperate zone. Estuaries in the subtropical zone are quite different from the temperate ones due to abundant precipitation and higher temperature. Studying spatio-temporal distribution of DMS in subtropical estuaries will help us to understand the biogeochemical characteristics of DMS in estuarine waters. The PRE has long suffered from heavy eutrophication pressures (Huang et al., 2003). Studying DMS spatial and temporal distribution in this area may also give us some insight in how human activities can modify the natural cycle of DMS.