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Seawater, atmospheric dimethylsulfide and aerosol ions in the Pearl River Estuary and the adjacent northern South China Sea

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Abstract

The spatial and temporal distribution of dimethylsulfide (DMS) was investigated in surface seawater and in the marine atmosphere in the Pearl River Estuary and northern South China Sea during three cruises in July 2000, May 2001 and November 2002. Sea-to-air fluxes of DMS were subsequently estimated based upon seawater DMS concentration, temperature of surface seawater and wind speed over sea. The seawater DMS concentration of the three cruises ranged from 0.1 to 52.7 nmol l^{-1} (n=76). DMS concentrations showed remarkable spatial and temporal distributions and highest values were observed at the mouth of the Pearl River Estuary. Throughout the study area we observed high levels of DMS in the water with great sea-to-air flux and relatively low levels of atmospheric DMS (1.70 ± 1.16 nmol m^{-3} in May 2001 and 2.25 ± 0.38 nmol m^{-3} in November 2002). Aerosol components, potentially linked with DMS oxidation, were also measured. The atmospheric concentrations of nss-sulfate and nitrate were much higher in the Pearl River Estuary than in the offshore area, with mean values of 12.11 and 4.45 μg m^{-3} for nss-sulfate, 4.88 and 2.21 μg m^{-3} for nitrate. Aerosol mass and components' concentrations decreased from the inner estuary to outer waters. High concentrations of nss-sulfate and nitrate in sea salt particles imply that oxidation of atmospheric DMS is related with anthropogenic sources and heavy ozone, NO_x and SO_2 pollution in the study area.

Keywords: Dimethylsulfide; Sea-to-air flux; Nss-sulfate; Nitrate; Pearl River Estuary; South China Sea

1. Introduction

Investigations on the possible climatic role of the biogenic sulfur cycle are numerous (Charlson et al., 1987; Andreae and Crutzen, 1997). Dimethylsulfide (DMS) is produced by marine phytoplankton species. Once released to the atmosphere, DMS is mainly oxidised by OH (by day) and NO_3 (by night) radicals to form various sulphur-containing products, such as non-sea-salt sulfate (nss-SO_4^{2-}), methanesulfonate (MSA) and dimethylsulfone (Berresheim and Eisele, 1998). In polluted areas with high NO_x concentrations

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the reaction of DMS with NO_x results in a coupling between the nitrogen and the sulfur cycles in the atmosphere (Jensen et al., 1991). HNO_3 is a main product of this reaction and can be rapidly removed by dry deposition or adsorption onto aerosols or droplets. This is an efficient night time sink for NO_x in the marine troposphere. Very high levels of nss-SO_4^{2-} and NO_3^- concentrations were measured in aerosols in the East China Sea (Gao et al., 1996). Non-sea-salt sulfate has both biogenic and anthropogenic sources, whereas MSA is thought to derive exclusively from DMS oxidation. Therefore MSA is considered to be a marker of biogenic sources (Savoie and Prospero, 1989).

Ocean margins have been identified as a significant source of DMS (Sciare et al., 2002). Estuaries and their plumes in the open sea could also be important sources of atmospheric DMS (Iverson et al., 1989; Turner et al., 1996; Simo et al., 1997). Studies on DMS in American and European estuaries (e.g. Iverson et al., 1989; Cerqueira and Pio, 1999; Sciare et al., 2002) have focused on the temperate zone. Shenoy and Patil (2003) report on temporal variations in DMSP and DMS in a tropical estuary (Zuari Estuary, India).

Some work on DMS in seawater has been done in China. Hu et al. (1995) measured the concentration of DMS in surface waters of the Bo Sea and Gulf of Jiaozhou, both belonging to the East China Sea. Both DMS concentrations and sea-air fluxes showed seasonal variations with a maximum in spring and minimum in winter. Uzuka et al. (1996) studied DMS distribution in the temperate coastal zone of the East China Sea. They observed remarkable temporal and spatial variations of seawater DMS concentrations with its fluxes. Seawater DMS concentrations were measured in the East China Sea (Yang et al., 2000) and the South China Sea (Yang, 2000). In surface water of the East China Sea, DMS ranged from1.8 to 5.7 nmol l^{-1}. Highest values were observed on the continental shelf with high biological productivity. They found that only zooplankton biomass and nitrate content were closely related to DMS concentrations. DMS concentrations in surface seawater of the South China Sea ranged from 1.9 to 4.6 nmol l^{-1}, with a mean of 2.6 nmol l^{-1}.

However, generally there is little information on DMS in the atmosphere and its oxidation products in China's coastal zones. Only Gao et al. (1996) reported on the East China Sea: atmospheric MSA concentrations ranging from 0.029 to 0.066 μg m^{-3}, nss-sulfate from10 to 12 μg m^{-3}, and nitrate from 5.6 to 7.7 μg m^{-3}. Moreover, the available information on atmospheric volatile sulfur compounds in Chinese seas is mainly based on observations during one campaign only, the Pacific Exploratory Mission (PEM-West A&B). Airborne studies from Japan, Hong Kong to the US Air Force Base in Guam show that the DMS concentrations in the free troposphere range from 10–120 pptv with a mean value of 65 pptv (Li et al., 1996). Arimoto et al. (1996) reported at Kato (Hong Kong, 16 August 1991 to 5 February 1992) that only 4.8% of total nss-sulfate was from biogenic sources and that the DMS-derived fraction of nss-SO_4^{2-} is highest in summer.

Besides the important role of DMS in the sulfur cycle, CCN formation and the global climate, there are three other reasons to investigate DMS in China at present:

Firstly, ocean margins have been identified as a significant source of DMS and several results suggest that estuaries and corresponding plumes in the open sea could represent an important source of atmospheric DMS (Iverson et al., 1989; Turner et al., 1996; Sciare et al., 2002). China has over 18 thousand km of coastline and 0.38 million km^2 of sea, but little information is available on DMS in its seas, and hardly any investigation has been done in its estuaries.

Secondly, what is the role of DMS in the acid deposition in the Pearl River Delta? As a consequence of the rapid economic development of the east coast, huge amounts of domestic, industrial and agricultural sewage are discharged into the estuaries. The Pearl River Estuary is particularly severely polluted: its water quality is beyond the fourth grade of the National Seawater Quality Standard (medium polluted, only suitable for sea ports and exploitations). The ecological environment in this region has also changed; there is a higher frequency of algal blooms and red tides as well as a decrease in biomass and biological diversity (Hu et al., 2001). These changes will inevitably affect the algae and DMS production in the seawater. The distribution of DMS in the seawater and sea-to-air flux will also be affected. Acid deposition is a major environmental problem in China: 30% of the country is suffering from acid rain