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Carbonyl sulfide, dimethyl sulfide and carbon disulfide in the Pearl River Delta of southern China: Impact of anthropogenic and biogenic sources

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ABSTRACT

Reduced sulfur compounds (RSCs) such as carbonyl sulfide (OCS), dimethyl sulfide (DMS) and carbon disulfide (CS_2) impact radiative forcing, ozone depletion, and acid rain. Although Asia is a large source of these compounds, until now a long-term study of their emission patterns has not been carried out. Here we analyze 16 months of RSC data measured at a polluted rural/coastal site in the greater Pearl River Delta (PRD) of southern China. A total of 188 canister air samples were collected from August 2001 to December 2002. The OCS and CS_2 mixing ratios within these samples were higher in autumn/winter and lower in summer due to the influence of Asian monsoon circulations. Comparatively low DMS values observed in this coastal region suggest a relatively low biological productivity during summer months. The springtime OCS levels in the study region (574 ± 40 pptv) were 25% higher than those on other East Asia coasts such Japan, whereas the springtime CS_2 and DMS mixing ratios in the PRD (47 ± 38 pptv and 22 ± 5 pptv, respectively) were 3–30 times lower than elevated values that have been measured elsewhere in East Asia (Japan and Korea) at this time of year. Poor correlations were found among the three RSCs in the whole group of 188 samples, suggesting their complex and variable sources in the region. By means of backward Lagrangian particle release simulations, air samples originating from the inner PRD, urban Hong Kong and South China Sea were identified. The mean mixing ratio of OCS in the inner PRD was significantly higher than that in Hong Kong urban air and South China Sea marine air ($p < 0.001$), whereas no statistical differences were found for DMS and CS_2 among the three regions ($p > 0.05$). Using a linear regression method based on correlations with the urban tracer CO, the estimated OCS emission in inner PRD (49.6 ± 4.7 Gg yr^{-1}) was much higher than that in Hong Kong (0.32 ± 0.05 Gg yr^{-1}), whereas the estimated CS_2 and DMS emissions in the study region accounted for a very few percentage of the total CS_2 and DMS emission in China. These findings lay the foundation for better understanding sulfur chemistry in the greater PRD region of southern China.

1. Introduction

The chemistry of reduced sulfur compounds (RSC) in the atmosphere has significant implications for global climate change, ozone layer depletion and the acidity of precipitation (Turco et al., 1980; Rodriguez et al., 1991; Solomon et al., 1996; Andreae and Crutzen, 1997). Carbonyl sulfide (OCS), dimethyl sulfide (DMS) and carbon disulfide (CS_2) are the main RSCs found in the marine and continental atmosphere (Chin and Davis, 1993; Kettle et al., 2002; Montzka et al., 2007). These RSCs are ultimately oxidized via sulfur dioxide to sulfuric acid in the troposphere and/or stratosphere (Johnson and Bates, 1993; Andreae and Crutzen, 1997). The formed sulfate particles alter the radiative properties of the Earth's atmosphere, potentially leading to the climate change, particularly due to augmented RSC emissions from anthropogenic sources (Seinfeld and Pandis, 2006). Further, these particles can affect the environment and ecosystem by acidification of precipitation (Andreae and Crutzen, 1997); and provide surfaces for heterogeneous reactions related to ozone destruction processes by chlorine and nitrogen radical chemistry (Rodriguez et al., 1991; Andreae and Crutzen, 1997). The atmospheric sources of RSCs include natural and biogenic emissions such as oceans (Leck and

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Persson, 1996; Kettle et al., 2002; Aranami and Tsunogai, 2004; Lee et al., 2010), volcanoes (Vasilakos et al., 2005), soil and marshes (Steinbacher et al., 2004; Liu et al., 2010), and vegetation (Geng and Mu, 2006; White et al., 2010); and anthropogenic emissions i.e. biomass burning (Meinardi et al., 2003), coal combustion (Chin and Davis, 1993), automobiles (Fried et al., 1992), aluminum production (Harnisch et al., 1995), and sulfur recovery (Chin and Davis, 1993).

OCS is the most abundant and stable RSC present in the troposphere and lower stratosphere due to its long lifetime (∼16 years). Therefore OCS is the most likely source of stratospheric background sulfate aerosols due to the photochemical dissociation of OCS in the stratosphere to SO_2. Globally, about 14–32% of the atmospheric OCS is attributed to human activities (Chin and Davis, 1993; Kettle et al., 2002). It is reported that 20–39% of OCS is removed from the stratosphere and troposphere through the reaction with hydroxyl radicals (OH) whereas 52–71% is due to vegetation uptake (Chin and Davis, 1993; Watts, 2000; Kettle et al., 2002). In addition, the possible use of OCS to track gross plant CO_2 exchange increases the importance of understanding OCS sources and sinks (Stimler et al., 2010).

The major source of CS_2 (lifetime: ˜2–3 days) is chemical industrial emissions (52–58%), followed by the ocean contribution (27–34%). The rest is from soil and marsh, volcano and sulfur recovery (8–21%) (Chin and Davis, 1993; Watts, 2000). The atmospheric reaction of CS_2 with OH radicals is the dominant sink for CS_2 in the atmosphere as well as a source of OCS (Seinfeld and Pandis, 2006). Atmospheric CS_2 is therefore important in determining the stratospheric sulfur balance during non-volcanic periods.

DMS (lifetime: ∼1 day) is mainly released from the oceans (∼85–98% of total emissions) with about 2–15% from other sources i.e. vegetation, tropical forests, soil and wetlands (Watts, 2000; Gondwe et al., 2003). DMS is also emitted from bush fires (Meinardi et al., 2003) but the contribution of anthropogenic sources to ambient DMS levels is negligible (∼0.5%) (Schäfer et al., 2010). The major fate of DMS is reaction with OH radicals during daytime and NO_3 radicals during night-time (Turnipseed and Ravishankara, 1993; Boucher et al., 2003).

In the past decades, the Asian continent has been recognized as a major source region of chemically active and radiatively important trace gases and aerosols, due to rapid urbanization and industrialization (Akimoto and Narita, 1994; Thornton et al., 1996; Streets et al., 2003; Blake et al., 2004). Both aircraft-borne and ground level measurements i.e. PEM-West A, TRACE-P and the Jeju Island study, have sought to understand the relative significance of biogenic and anthropogenic emissions for the local or regional sulfur cycles (Thornton et al., 1996; Kim et al., 2004; Blake et al., 2004; Inomata et al., 2006). These studies have provided valuable information about the sulfur chemistry in the Asian continent. However, each of these studies only covered limited time periods, usually 1–2 months during spring. In particular, the impact of biogenic and anthropogenic emissions on the sulfur budgets in China's premiere industrial region – the Pearl River Delta (PRD) area of southern China – remains unclear.

A 16-month sampling campaign was carried out at a strategically located rural/coastal site in the PRD from August 2001 to December 2002, in order to understand the physical and chemical properties of air masses in this region. Using this dataset, the causes of a multi-day ozone episode were analyzed (Wang and Kwok, 2003), the temporal variability and emission patterns of pollution plumes during October–December 2001 were characterized (Wang et al., 2003), and the seasonal profiles and atmospheric processes of trace gases (including NMHCs) were overviewed (Wang et al., 2005). C_1–C_5 alkyl-nitrates and their relation to their parent NMHCs and to ozone were also examined (Simpson et al., 2006), and the regional and local source contributions to NMHCs were quantified using a PCA/APCS receptor model (Guo et al., 2006) and by chemical ratios (Zhang et al., 2008). In addition, the source origins, profiles and apportionments of halocarbons in this region were studied (Guo et al., 2009a). In this study, our focus is the RSC data. The spatiotemporal variations of RSCs will be presented, and the source emissions of these RSCs will be estimated.

2. Experimental method

2.1. Sampling site

The sampling site, Tai O, was located in a rural/coastal area on the western coast of Lantau Island in southwest Hong Kong (22.25°N, 113.85°E), bounded to the south by the South China Sea and to the north by the rapidly developing greater PRD region (Fig. 1). The greater PRD is a home to around 40 million inhabitants and is also the most important industrial base in southern China. Meteorological conditions over this region and a large part of Asia are strongly influenced by Asian monsoon circulations. During the winter, prevailing winds are northerly and northeasterly. By contrast, southerly and southwesterly winds are predominant in the summer. Such meteorological conditions make the coastal region of southern China an ideal place to measure the chemical composition of polluted continental outflow in the winter and clean South China Sea air during summer. A detailed description of the site is provided in Wang et al. (2003). In brief, Tai O site is about 32 km to the west of the Hong Kong urban center and 32 km to the east of Macau. The three largest population centers in the PRD lie to the north of Tai O: Guangzhou (10 million), Hong Kong (6.9 million) and Shenzhen (4 million). Power plants, airports and seaports are mainly located along the two sides of the Pearl Estuary.

The study site was located on a hill 80 m above sea level, overlooking the Pearl Estuary to the west and north, the South China Sea to the south, and the Hong Kong urban center to the east. Local anthropogenic emissions are very small due to a sparse population and light traffic at Tai O. Many deciduous trees, sources of biogenic trace gases, immediately surround the site.

2.2. Sampling and chemical analysis

Whole air samples were collected into evacuated 2-L electropolished stainless steel canisters and pressurized to about 20 psi using a metal bellows pump. The canisters were cleaned and evacuated at the University of California, Irvine (UCI) before being shipped to Tai O. Details of the preparation and pre-conditioning of the canisters are described in Blake et al. (1994). Whenever a canister sample was taken, the canister valve was slightly opened, allowing about 1 min for the collection of the integrated whole air samples. The canisters were then shipped to UCI for chemical analysis. The samples were analyzed within two weeks. A 6-column multiple GC–MS system was used to identify and quantify volatile organic compounds. The combination that was used to quantify the sulfur gases was a DB-5ms (J & W Scientific) column (60 m; i.d., 0.25 mm; film, 0.5 μm) coupled to an HP-5973 quadrupole Mass Spectrometric Detector (MSD). The MSD was placed in the single ion monitoring (SIM) mode, choosing the most abundant ion of each compound without interference. The stability of these sulfur gases in the stainless steel canisters was tested for more than one week and no statistical difference was found between the first and last samples. The measurement precision was 5% and the measurement accuracy was 1–10% for these RSCs. The detection limits were 0.5 pptv for CS_2, 1 pptv for DMS, and 20 pptv for OCS. Detailed descriptions of the chemical analysis and relevant quality assurance/quality control for each species are given by Colman et al. (2001) and Blake et al. (2004).