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Characteristics and anthropogenic sources of carbonyl sulfide in Beijing

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ARTICLE INFO

Article history:

Received 18 March 2014

Revised 30 May 2014

Accepted 30 May 2014

Available online 18 December 2014

Keywords:

Carbonyl sulfide

Anthropogenic sources

Vehicle tire wear

Coal combustion

Carbon monoxide

ABSTRACT

Atmospheric mixing ratios of carbonyl sulfide (COS) in Beijing were intensively measured from March 2011 to June 2013. COS mixing ratios exhibited distinct seasonal variation, with a maximum average value of 849 ± 477 pptv in winter and a minimal value of 372 ± 115 pptv in summer. The seasonal variation of COS was mainly ascribed to the combined effects of vegetation uptake and anthropogenic emissions. Two types of significant linear correlations ($R^2 > 0.66$) were found between COS and CO during the periods from May to June and from October to March, with slopes ($\Delta\text{COS}/\Delta\text{CO}$) of 0.72 and 0.14 pptv/ppbv, respectively. Based on the emission ratios of COS/CO from various sources, the dominant anthropogenic sources of COS in Beijing were found to be vehicle tire wear in summer and coal burning in winter. The total anthropogenic emission of COS in Beijing was roughly estimated as 0.53 ± 0.02 Gg/year based on the local CO emission inventory and the $\Delta\text{COS}/\Delta\text{CO}$ ratios.

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Introduction

Carbonyl sulfide (COS) is thought to be the longest lived reduced sulfur gas in the atmosphere, with a residual lifetime of approximately 2–6 years and a tropospheric background mixing ratio of about 500 pptv (Griffith et al., 1998). Most of the COS in the troposphere will be subsequently transported into the stratosphere and converted into sulfate by photo-oxidation, which has long been regarded as the dominant source of nonvolcanic sulfate aerosol in the stratosphere (Crutzen, 1976). The sulfate aerosol can backscatter sunlight, thereby reducing solar irradiation onto the earth's surface and causing measurable alterations in climate (Turco et al., 1980; Charlson et al., 1991; Roche et al., 1994). Furthermore, the sulfate aerosol provides surfaces for heterogeneous reactions that contribute to stratospheric ozone destruction (Rodriguez et al., 1991; Fahey et al., 1993; Solomon et al., 1993; Andreae and Crutzen, 1997). Finally, the sulfate aerosol can be scavenged by dry and wet deposition as an important part of sulfur transport and cycling on the global scale (Andreae and Crutzen, 1997).

Many industrial and residential human activities have resulted in the augmentation of atmospheric COS burdens (Seinfeld and Pandis, 2012). Considering the significant effects of atmospheric COS on the climate and environment, considerable attention has been given to the identification of anthropogenic sources. Besides the known natural sources such as the oceans (Ferek and Andreae, 1984; Johnson and Harrison, 1986; Mihalopoulos et al., 1992), volcanoes (Khalil and Rasmussen, 1984; Chin and Davis, 1993), anaerobic soil (Adams et al., 1981; Castro and Galloway, 1991; Chin and Davis, 1993; Kanda et al., 1995), marshes (Stuedler and Peterson, 1984, 1985) and precipitation (Mu et al., 2004; Mu and Xu, 2009), approximately 25% of current COS in the atmosphere has been attributed to multifarious human activities (Aydin et al., 2002), including biomass burning (Crutzen et al., 1985; Nguyen et al., 1994), coal-fired power plants (Khalil and Rasmussen, 1984), chemical processing (Khalil and Rasmussen, 1984), aluminum production (Harnisch et al., 1995), sulfur recovery (Khalil and Rasmussen, 1984), and motor vehicles (Fried et al., 1992; Pos and Berresheim, 1993). On the other hand, vegetation uptake of COS is responsible for 50%–70% of

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atmospheric COS sinks (Chin and Davis, 1993; Watts, 2000; Kettle et al., 2002; Montzka et al., 2007), and can strongly reduce the COS mixing ratios at ground levels (Campbell et al., 2008).

However, the estimation of global anthropogenic COS sources' strength varies from 0.04 ± 0.02 (Chin and Davis, 1993) to 0.124 ± 0.06 Tg/year (Watts, 2000) due to the small number of investigations of source inventories. Recently, an indirect method has been used for estimation of regional anthropogenic COS emissions based on the linear correlation of COS with CO mixing ratios and the regional CO emission estimates (Blake et al., 2004; Guo et al., 2010). Nevertheless, these studies only made use of short-term data without considering the possible seasonal variation of the sources for both COS and CO. Until now, few long-term and intensive measurements have been performed to study the diurnal and seasonal variations of atmospheric COS.

In this study, we carried out year-round intensive measurements of COS mixing ratios in Beijing to study the diurnal/seasonal variations and to estimate the anthropogenic COS emissions. The correlations of COS with CO as well other tracer gases were analyzed to distinguish the possible dominant COS sources in different seasons. Based on the linear correlations of COS with CO in different seasons, anthropogenic emissions of COS around Beijing were estimated.

1. Materials and methods

From March 2011 to June 2013, a total of 765 air samples distributed in 73 days and 16 months were collected for analyzing atmospheric COS, at a height of about 20 m above ground level in the Research Center for Eco-Environmental Sciences (RCEES) located in the north of Beijing (116.34E, 40.01N). The sampling frequency of this study was about 5 days per month, and about 10 air samples were collected each sampling day.

Atmospheric COS was sampled by cryogenic trapping and analyzed by a gas chromatograph equipped with a flame photometric detector (GC-FPD, Shimadzu, Japan). Similar to our previous studies (Mu et al., 2002, 2004), an air sample of 500 mL was directly introduced into an enrichment tube packed with Tenax-GC (60–80 mesh, Alltech Associates, Inc. America) and cooled to about -90°C by a copper pillar with the bottom end immersed into liquid nitrogen. The air sample enriched in the enrichment tube was transferred into a separation column (2 m \times 4 mm) packed with 20% SE-30 on Chromosorb P, Chrompack, America (60–80 mesh) just after the enrichment tube was moved into a thermal oven kept at 160°C , and detected by the FPD. The optimum separation conditions were: GC oven temperature of 40°C , detector temperature of 260°C , carrier gas (nitrogen, 99.999%) flow rate of 40 mL/min, hydrogen flow rate of 75 mL/min, and air flow rate of 35 mL/min. The relative standard deviation of COS measurements was 1.11%, based on the reproducibility of consecutive injections of a standard COS gas (COS, 600 pptv) prepared by dilution of a standard COS gas mixture in N_2 (104 ppmv, National Sharing Platform for Reference Materials) over a 3-day period (number of replicates $n = 21$). Comparing the response values between direct injection (number of replicates $n = 10$) and injection after being concentrated, the recovery rate was around $111.5\% \pm 5\%$.

To reveal the possible anthropogenic sources of atmospheric COS, various species including CO, CH_4 , N_2O , SO_2 , CS_2 and $\text{PM}_{2.5}$ were simultaneously measured during a 17-day campaign in June 2013. Several meteorological parameters

were simultaneously monitored at the same location, including wind speed and direction, temperature, relative humidity and visibility.

2. Results and discussion

2.1. Characteristics of atmospheric COS in Beijing

2.1.1. Frequency distribution and annual average

The frequency distribution of COS mixing ratios measured from October 2011 to February 2013 is illustrated in Fig. 1. The mixing ratios of COS mainly ranged from 450 to 650 pptv, which is much lower than the range of 600–900 pptv observed in our previous study in 2001 (Mu et al., 2002). The COS mixing ratios lower than 600 pptv accounted for more than 47% of the total, while they accounted for only 8% in 2001. The frequency (<1%) of COS mixing ratios higher than 2000 pptv, which were occasionally measured under stagnant air conditions (haze days), was much lower than the 13% frequency observed in 2001. The significant difference of COS mixing ratios between the two measurements revealed that COS sources around Beijing had been greatly reduced since 2001, for example most boilers fueled by coal have been replaced by boilers fueled by relatively clean oil and natural gas in recent years, and the numbers of domestic coal stoves in the urban fringe of Beijing have been greatly reduced with the fast development of urbanization.

Compared to other studies, the annual average mixing ratio of 639 ± 332 pptv ($n = 555$) in this study is much higher than the background value of 512 ± 119 pptv in the free troposphere of the Northern Hemisphere (Torres et al., 1980; Bandy et al., 1992) and comparable to the value of 646 ± 48 pptv observed in Hong Kong (Guo et al., 2010), but much lower than that of 1021 ± 221 pptv measured in the inner Pearl River Delta (PRD) (Guo et al., 2010).

2.1.2. Seasonal variation

As shown in Fig. 2 and Table 1, COS mixing ratios in Beijing exhibited distinct seasonal variation, with average mixing ratios of 608 ± 262 , 372 ± 115 , 651 ± 275 and 849 ± 477 pptv in spring, summer, autumn and winter, respectively. The average mixing ratio observed in spring was close to 574 ± 40 pptv observed in Hong Kong (Guo et al., 2010) and 580 pptv measured over the Western Pacific (Blake et al., 2004), but was greater than 440 ± 10 pptv measured in Wakasa Bay, Japan (Inomata et al., 2006). The similarity in COS mixing ratios in

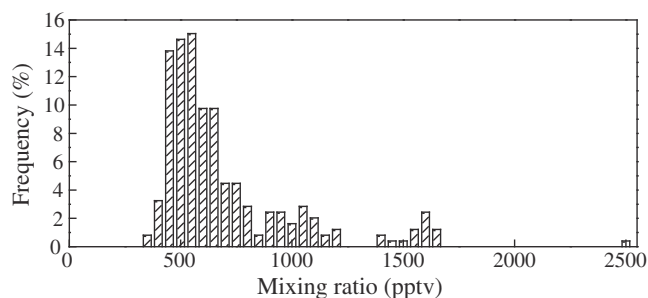


Fig. 1 – Annual frequency distribution of carbonyl sulfide (COS) mixing ratios.

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