Vertical distributions of COS and CS$_2$ in Beijing City

MU Yu-jing[1,*], WU Hai[1], WU Peng-zhang[1], WANG Yue-si[2]

(1.Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: yujingmu @ yahoo. com; 2.Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China)

Abstract: Vertical distributions of COS and CS$_2$ were measured at a meteorological tower in Beijing City. The mixing ratios of COS and CS$_2$ are in the range of 371—1681 pptv and 246—1222 pptv, respectively. The significant high mixing ratios of the two compounds at ground level and distinct vertical distributions indicated the existence of strong anthropogenic sources of COS and CS$_2$ in Beijing City. Domestic stoves and central heaters are important sources of COS during winter season. Cesspools may play significant role on COS over whole seasons. Chemical productions may be responsible for the observed high mixing ratios of CS$_2$ in Beijing City.

Keywords: COS; CS$_2$; vertical distribution

Introduction

Carbonyl sulfide(COS) and carbon disulfide(CS$_2$) are believed to be a major source of stratospheric background sulfate aerosol during volcanically quiescent periods. The stratospheric sulfate layer plays important roles in the earth's radiation balance and possibly also the destruction of ozone in the stratosphere(Turco, 1980; Roche, 1994).

The mixing ratio of COS was approximately 510 pptv in the free troposphere(Turco, 1980; Carroll, 1985). Because increasing anthropogenic emissions of COS have the potential of causing measurable alterations in climate(Turco, 1980), considerable attentions have been given to identifying major atmospheric sources and sinks. Known sources of COS are from both natural sources such as the oceans(Mihalopoulos, 1992), volcanoes(Cadle, 1980), and marshes(Steudler, 1985) as well as from anthropogenic sources from biomass burning(Nguyen, 1994), coal-fired power plants, chemical processing, sulfur recovery(Khalil, 1984), and motor vehicles(Pos, 1993). In addition to the direct sources of COS, carbon disulfide(CS$_2$) and dimethyl sulfide(DMS) are the important sources of COS via theirs oxidation in the atmosphere(Khalil, 1984; Barnes, 1994). Sinks for COS are not so well known but are primarily thought to be vegetation and soils(Chin, 1993; Kesselmeier, 1999).

Data on the atmospheric abundance of CS$_2$ are much rare and concentrations are found to be extremely variable. The first measured ground level concentrations of CS$_2$ were reported to be between 70 and 300 pptv (Khalil, 1984). More recent measurements suggest that the typical values are between 15—20 pptv. Higher concentrations, 100—200 pptv, are also observed in polluted air(Berresheeim, 1992). The sources of CS$_2$ are mainly from ocean, soils, and industries. The major sink for CS$_2$ is thought to be the photo-oxidation of CS$_2$ in the atmosphere, which is a major source of COS(account about 30% of the sources of COS) (Chin, 1993).

Because of the importance of COS and CS$_2$ in the global environment, its sources, sinks, and particularly the effect of human activities on global sulfur cycle are of special interest. However, many parameters of COS and CS$_2$ are poorly known. Global estimates of the atmospheric COS and CS$_2$ budget show large uncertainties with respect to individual COS and CS$_2$ sources and sinks(Andreae, 1997). Clearly, there is a need to further identify and quantify new global sources and sinks of COS and CS$_2$.

Hoffmann(Hofmann, 1990) has observed a long-term trend in the stratospheric aerosol level and speculated that increased OCS levels could be responsible. Although the exact cause of this increase is open to question, it is essential that we determine the major sources and sinks for COS and ascertain whether or not its atmospheric concentration is increasing due to human activities. Recent measurements over the Atlantic Ocean (Johnson, 1993) indicated large inter-hemispheric gradient for OCS. Bingemer (Bingemer, 1990) concluded that anthropogenic sources in the northern hemisphere were likely to be responsible for the observed trend. Relatively high COS(> 1 ppb) level also has frequently been observed in urban areas(Bandy, 1992). The vertical distributions of COS and CS$_2$ were studied in Beijing City, and further evidences for anthropogenic perturbation on COS and CS$_2$ mixing ratios are presented in this study. Significant high mixing ratios of COS and CS$_2$ and distinct vertical distributions indicated the existence of strong sources of COS and CS$_2$ in or around Beijing City.

1 Experiment

Air samples were collected from the meteorological tower of Institute of Atmospheric Physics, Chinese Academy of Sciences. The tower locates in the north of Beijing City, and close to the northern three-cycle road. The height of the tower is 325 m, and divided into 15 layers. The meteorological data(wind direction and speed, air temperature, and relative humidity) in every layer has been automatically recorded in 20 seconds for many years. Air samples were collected simultaneously into 5 L Teflon bags at three levels(8 m, 160 m and 320 m) through Teflon tube by micro pump (Enomoto Micro Pump CO., Ltd. Tokyo, Japan). COS and CS$_2$ were sampled by cryogenic trapping, separated on gas chromatograph and detected by flame photometric detector(GC-6A, Shimadzu). The chromatographic separation was done on a temperature programmed glass column(3 m × 4 mm) packed with 20% SE-30 on Chromosorb P(60—80 mesh). Optimum separation

was obtained by starting the temperature program at 50℃, holding for 6 min, and then heating at 10 ℃/min up to 120℃. The injection port temperature and the detector temperature were 160℃ and 240℃, respectively. Typical gas flow rates were: nitrogen (carrier gas, 99.999%), 30 ml/min; hydrogen, 40 ml/min, air 40 ml/min. COS and CS₂ in the air samples were pre-concentrated on an adsorption tube by using liquid nitrogen (Fig.1). The adsorption tube
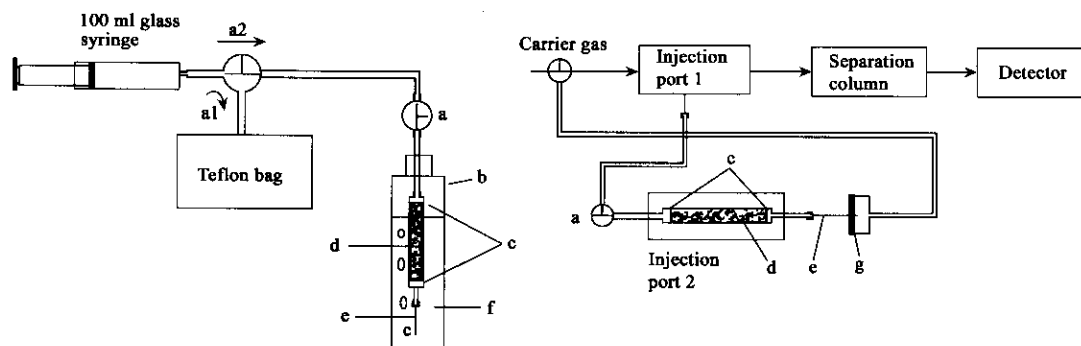
consisted of a small glass tube that is thick in the middle (6 cm × 4.3 mm I.D.) and thin at two sides. The two sides were connected with an injection needle and a three-way valve of Teflon, respectively. The thick part of the adsorption tube was filled with about 180 mg of Tenax GC. 800 ml of the air sample collected in a sampling bag was passed through the adsorption tube dipped into liquid nitrogen with a flow rate of about 50 ml/min by using a 100 ml glass syringe.

Fig.1 Pre-concentration of air sample onto Tenax-GC at 77K and GC inlet system
a.three-way valve; b.dewar; c.quartz wool; d.Tenac-GC; e.injection needle; f.liquid nitrogen; g.septum

The injection method is also shown in Fig. 1. The adsorption tube was removed from the liquid nitrogen after trapping of the sulfur volatiles and keep at room temperature for about 1 min to allow the liquid nitrogen to evaporate out of the tube. The trap tube, still cold, was then immediately inserted into the injection port 2. The adsorbed COS and CS₂ was thermally liberated in the injection port 2 for about 1 min and transferred to the GC column when the three-way valve was turned.

The column employed in this study can separate various volatile sulfur compounds (H₂S, COS, CS₂, thiols, sulfides, disulfides) (Tangerman, 1986). The standard gases of COS and CS₂ were further diluted in ppb level in 10 L Teflon bag, and pre-concentrated different quantities of the standard air sample onto the absorption tube and analyzed by GC-FPD. The calibration curves are given in Fig.2.
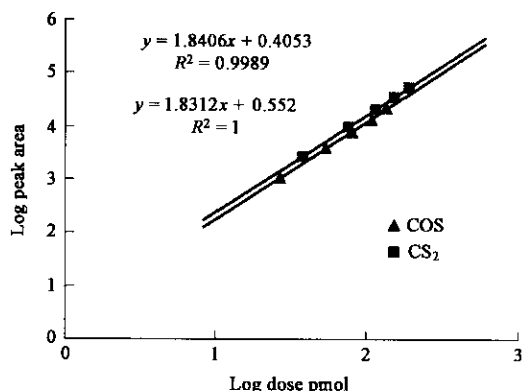
Several tests conducted in our laboratory showed that the Teflon bag did not contaminate the air samples nor absorb COS and CS₂ over half month period. Consequently, sample analyses were successfully made in the laboratory a few days after collection.

CS₂ was from Beijing Chemical factory (analytical pure), and further purified by repeat freeze-pump-thaw cycles and fractional distillation before use. The standard gas of CS₂ was prepared by mixing the vapor of CS₂ (the vapor pressure was measured by capacitance manometer, 0—10 Torr, MKS) in nitrogen in a 10 L glass-tight bulb. The standard COS air sample was from Scott Specialty Gases Inc. (2%, COS/N₂).

2 Results and discussion

2.1 Vertical distribution of COS and CS₂

The chromatograms of a standard gas mixture and the collected air sample on the tower are shown in Fig. 3. In addition to COS and CS₂, H₂S were occasionally detected under our experimental condition.
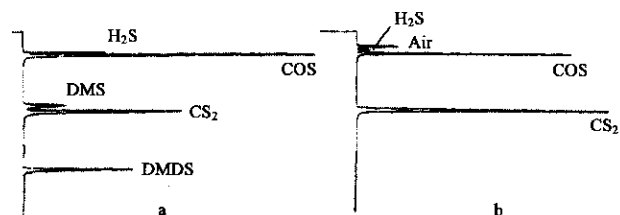

Fig.2 Standard calibration graphs

Fig.3 The chromatograms of standard gas mixture(a) and the collected air sample on the tower(b). Detector attenuation: 10 × 32

Comparing the respond values between direct injection and the injection after being concentrated, the recovery efficiencies of COS and CS₂ were about 94% and 100%, respectively. The relative precision of the measurements was less than 6%, based on reproducibility of consecutive samples over a 2 d period (number of replicates $n = 18$) with compressed air sample.

The vertical distributions of COS and CS₂ at some select time periods are shown in Fig. 4. The distinct vertical distribution of COS was obvious, with high values near the ground and low values at higher altitude. The average mixing ratio of COS at 300 m level is 512 ± 65 pptv, which was agree with the free tropospheric mixing ratio very well. The large difference among the three layers between 19:30 and 21:30 in 23 November may be caused by stable
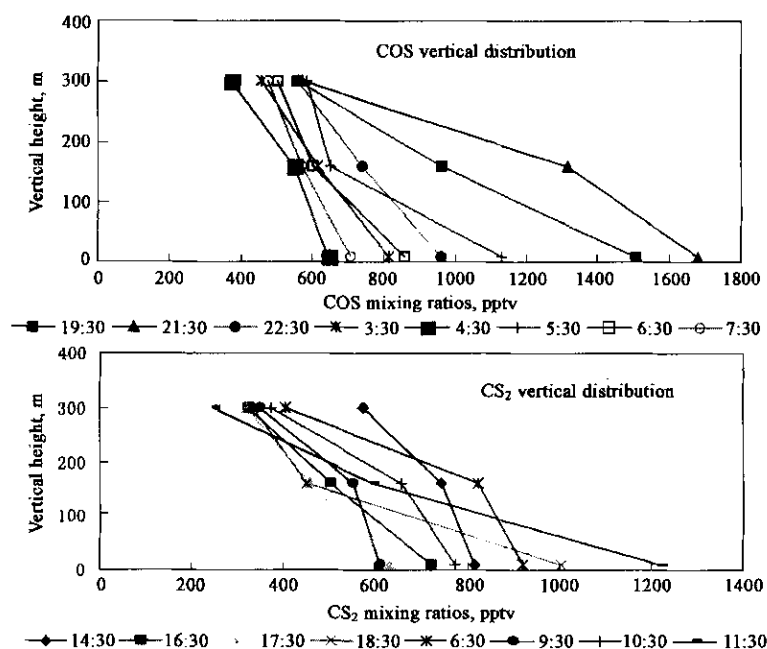
Fig.4 The vertical distribution profiles of COS and CS_2 on the meteorological tower of Institute of Atmospheric Physics, Chinese Academy of Sciences in 23—24 November 2001

meteorological conditions(such as the lower inverse temperature layer), which restricted vertical exchange.

The mixing ratios of COS at ground level were strongly affected by wind speed(Fig.5), with higher mixing ratios at slower wind speed and lower mixing ratios at fast wind speed. The rapid decreases of the COS mixing ratios when wind speed was greater than 6 m/s could be attributed to the beginning of strong convection leading to mixing of air from higher layer or remote area. When wind speed was less than 4 m/s, the mixing ratios of COS at ground level were in the range from 1279 to 1681 pptv, which is more than two times of that of free troposphere, suggesting existence of strong ground sources of COS in Beijing City.

There are some differences between the vertical distribution profiles of COS and CS_2. The mixing ratios of CS_2 at 300 m sometimes were larger than that at 8 m and 160 m, which might be caused by polluted air parcel. In general, the CS_2 profiles showed significant gradients among the three investigated layers(Fig.4), which also indicated that strong sources of CS_2 exist at ground level. The mixing ratios of CS_2 at ground level were in the range from 583 to 1361 pptv, which is about 20—40 times of that of background(30 pptv). Several diurnal courses of CS_2 at ground level were also measured in our institute. In clear day, almost all data of the mixing ratios of CS_2 were below 300 pptv at daytime, which agreed with others measured in polluted air(Khalil, 1984). Significant high mixing ratios(above 1000 pptv) of CS_2 were also measured in our institute under very stable weather condition during night. Our institute is at the northwest of the tower(about 6 km far from there), and far from the main road. Whereas, the tower close to the center of Beijing City and three cycle road. The more anthropogenic actives might be responsible for the high values of CS_2 observed on the tower.

2.2 The possible sources of COS and CS_2 in Beijing City
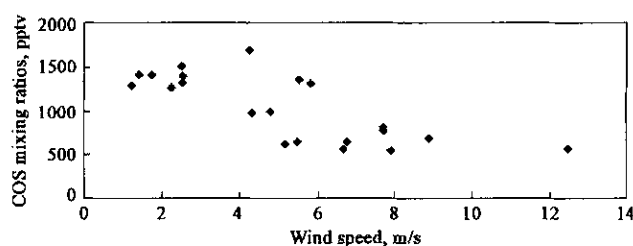
Some individual sources of COS and CS_2 were

Fig.5 The relationship between wind speeds and the mixing ratios of COS at ground level

investigated in this study and results are shown in Table 1. The mixing ratios of the two compounds were measured at the exhaust holes of a taxi and a tractor during hot idling and cold start, respectively. Previous studies (Fried, 1992) indicated that the highest COS concentration was typically measured during fuel reducing condition(such as during hot idling and cold start), and peak concentrations were around several hundred ppbv, which were about two magnitude more than the values obtained by this study. The lower values of COS may be ascribed to the low fuel-sulfur content of the investigated vehicles. If the mixing ratios of COS from the two vehicles were able to represent a broad range of motor vehicles in Beijing City, vehicles were not the dominant sources of COS because of the much higher COS values observed during this study. The mixing ratios of COS from the chimney of a coal stove and the flue of a middle heater were about 113 ppbv and 8 ppbv, respectively. These strong sources may be responsible to the observed high mixing ratios of COS during winter season. The mixing ratio of COS at the exhaust hole of a cesspool was about 13 ppbv. Cesspools may be another important anthropogenic source of COS, because there are numerous cesspools distributed in Beijing City. Natural gas burning used for cooking may have small contribution to the concentration of COS in Beijing City. The COS mixing ratios of Capital Steel Factory, Yanshan Petroleum Chemical Industry, concrete factory and coal mine

were obtained by measuring ambient air samples during spring. Most of the factories are upwind of the investigated site (in the west of Beijing City). The low COS values of these factories could not account for the observed high mixing ratios of COS in Beijing City.

Table 1   The possible sources of COS and CS$_2$ in Beijing City

Source	Mixing ratio		Source	Mixing ratio	
	COS, pptv	CS$_2$, pptv		COS, pptv	CS$_2$, pptv
Stove(coal)	112776	* *	Middle heater (coal)	8310	* *
Tractor(diesel fuel)	2106	731	Natural gas burning *	2002	202
Taxi(gasoline)	1717	1052	Capital Steel Factory *	1440	413
Cesspool	12578	1501	Yanshan Petroleum Chemical Industry *	807	209
Concrete factory *	771	391	Coal mine *	852	359

Notes: * ambient air; * * strong interference of SO$_2$

For CS$_2$, taxies and cesspools had minor contribution. The CS$_2$ mixing ratios of the stove and the heater were not detected because of the strong interference of SO$_2$. Khalil (Khalil, 1984) pointed out that combustion processes are not expected to produce CS$_2$. As to other investigated sources, the low values also indicated that the contribution of these sources were negligible. On the global scale, chemical productions (CS$_2$ is mainly from cellulosic industry and solvent application) are the dominant sources of CS$_2$ (Chin, 1993). These sources may be also ascribed to the observed high mixing ratios of CS$_2$ in Beijing City.

3 Conclusions

Vertical distributions of COS and CS$_2$ were measured at a meteorological tower in Beijing City. Significant high mixing ratios of the two compounds and distinct vertical distributions indicated the existence of strong sources of the two compounds in Beijing City.

Domestic stoves and central heaters are important sources of COS during winter season. Cesspools may play significant role on COS over whole seasons. Chemical productions may be responsible for the observed high mixing ratios of CS$_2$ in Beijing City.

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