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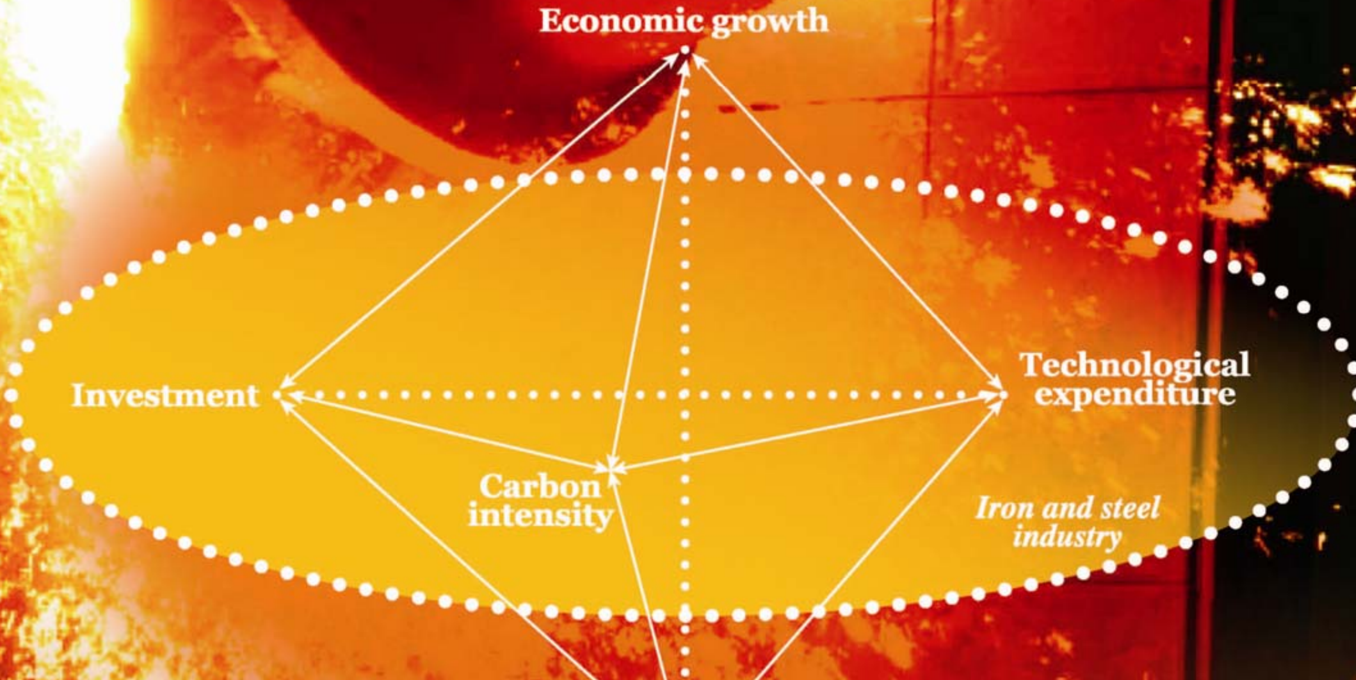

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Characteristics and anthropogenic sources of carbonyl sulfide in Beijing

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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 (ΔCOS/ΔCO) 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 ΔCOS/ΔCO ratios.

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 (Steudler 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 × 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% ± 5%.

To reveal the possible anthropogenic sources of atmospheric COS, various species including CO, CH_4, N_2O, SO_2, CS_2 and $PM_{2.5}$ 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

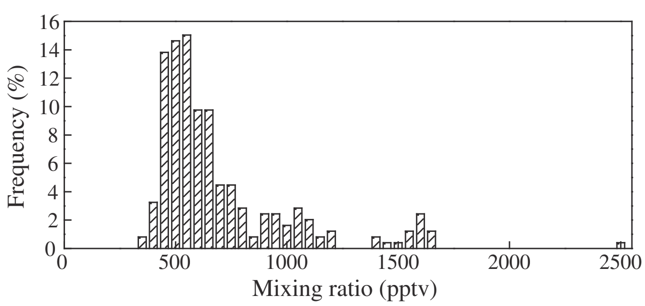

Fig. 1 – Annual frequency distribution of carbonyl sulfide (COS) mixing ratios.

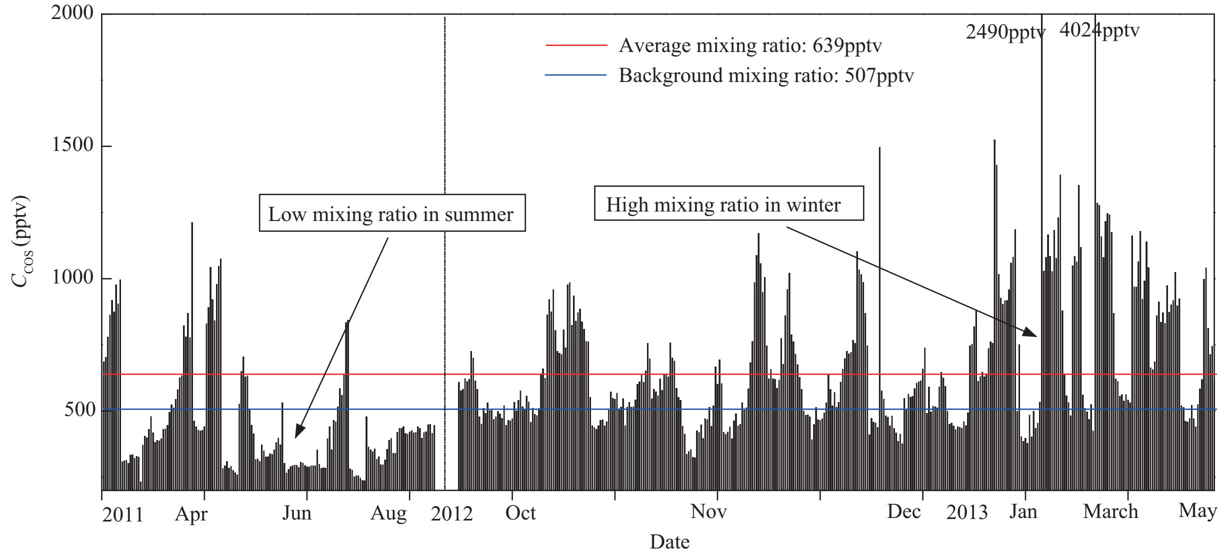

Fig. 2 – Seasonal variation of the carbonyl sulfide (COS) mixing ratios. This includes 555 data samples across March 2011 to May 2013 without data from September 2011 to September 2012.

most areas indicated that the prevailing monsoon in spring favors even distribution of the species with relatively long residual lifetime. The average COS mixing ratio in summer observed in this study was much lower than the background level (about 500 pptv), indicating strong COS uptake by vegetation (Chin and Davis, 1993; Xu, 2001; Watts, 2000; Campbell et al., 2008), whereas the extremely high levels of COS observed in winter indicated that additional COS emissions made remarkable contributions to atmospheric COS in Beijing.

To illustrate the influence of the strong vegetation uptake in summer and extra ground emissions in winter on atmospheric COS, the diurnal variations of COS in two typical clear days in summer and winter are shown in Fig. 3. As shown in Fig. 3a, COS mixing ratios during the summer day with wind speed less than 1 m/sec gradually decreased during morning hours, and slightly increased during noontime (12:00–14:00), and then decreased again in the afternoon followed by an increase after sunset. The typical diurnal variation of COS in the summer day was consistent with strong COS uptake by vegetation, because COS uptake by vegetation is mainly controlled by stomatal aperture (Xu et al., 2002) and the stomatal aperture is usually closed at noontime under strong sunlight irradiation and extremely high temperature. In addition, the relatively fast exchange between the lower layer and the upper layer of the atmosphere at noontime also can result in elevation of the ground COS level because of the relatively high COS mixing ratio in the upper layer. In contrast with the summer day, COS mixing ratios during the winter day (Fig. 3b) with small wind speed (less than 1 m/sec) exhibited extremely high values in both late morning and early evening when heating activity was the most extensive.

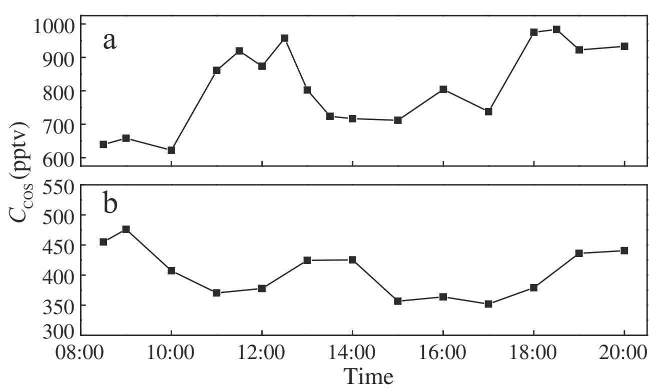

Fig. 3 – Different diurnal variation trends of mixing ratios for carbonyl sulfide (COS) under stationary weathers in different seasons. (a) Observed in 26th May 2012. (b) Observed in 12th November 2012.

Strong wind can accelerate the blending of the air at ground level with that from the free troposphere and background areas, and hence the levels of trace gases with long atmospheric lifetime, such as COS, in polluted areas under strong wind conditions are usually close to their background levels. For example, the average COS mixing ratio of 507 ± 96 pptv for 61 samples measured in Beijing under strongly windy conditions (wind speed > 6 m/sec) was consistent with the COS background level of 512 ± 119 pptv in the Northern Hemisphere (Torres et al., 1980; Bandy et al., 1992). Based on this fact, more convincing evidence for the strong vegetation uptake in summer and extra ground emissions in winter could be found in the diurnal variations of COS under typical windy days. As shown in Fig. 4a for the windy winter day, the concentrations of COS, SO_2 and CO sharply decreased when strong wind (ca. 8 m/sec) occurred around noontime (12:00), and approached their background levels after the wind lasted about 2 hr, indicating that strong sources existed in Beijing. In the windy summer day (Fig. 4b), the continuous decreases of SO_2 and CO under windy conditions (~7 m/sec) were similar to those in the windy winter day, whereas COS gradually increased until becoming nearly stable at about the background level after wind lasted for ~4 hr, revealing strong COS uptake by vegetation.

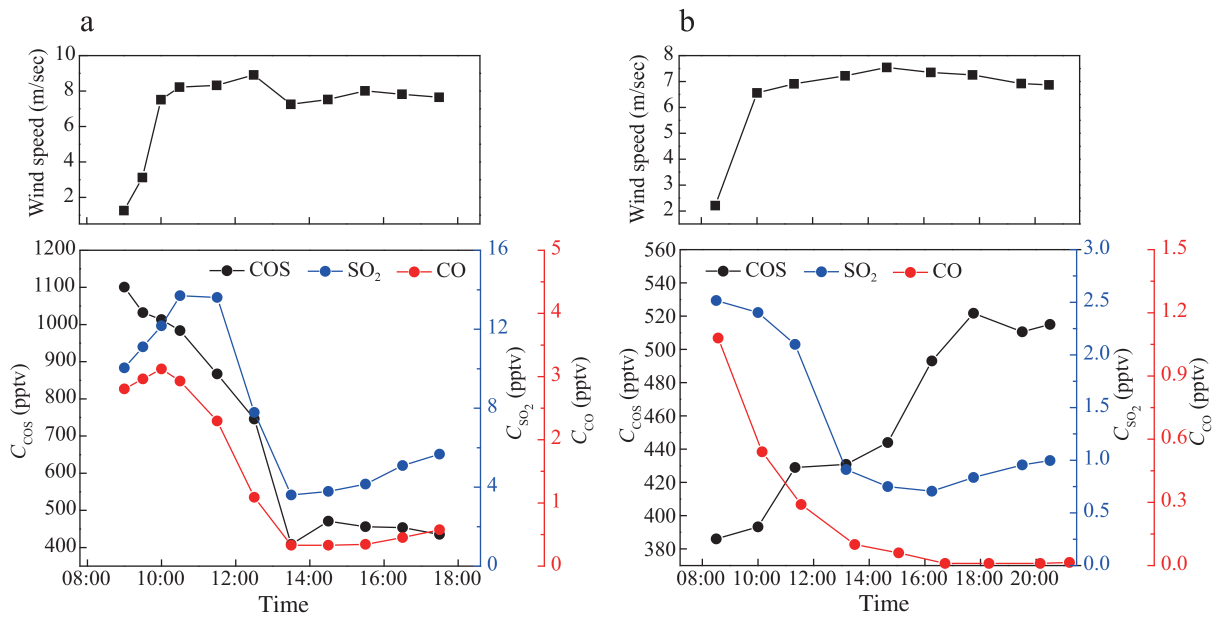

Fig. 4 – Different diurnal variation trends of mixing ratios for carbonyl sulfide (COS), sulfur dioxide (SO_2) and carbon monoxide (CO) under strong winds in different seasons. (a) Observed in 16th November 2012, (b) observed in 4th July 2012.

2.2. Anthropogenic sources

2.2.1. Combustion emissions

Combustion can emit both CO and COS, and CO has been considered as a typical combustion tracer for COS emission (Blake et al., 2004; Guo et al., 2010). As shown in Fig. 5, significant correlations between COS and CO mixing ratios in Beijing were found. In the early summer (2013.5–2013.6), the linear correlation ($R^2 = 0.68$, $p < 0.01$) had a slope (ΔCOS/ΔCO) of 0.72 ± 0.03 pptv/ppbv, which is similar to the slope of 0.79 pptv/ppbv observed in the urban subset plumes, and the average ratio for COS *versus* CO of 0.73 ± 0.03 pptv/ppbv from the plume of North China observed in the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) project, which took place in the early spring of 2001 (Blake et al., 2004). Another comparable ΔCOS/ΔCO value of 0.96 ± 0.09 pptv/ppbv for inner PRD has also been reported (Guo et al., 2010). A significant correlation ($R^2 = 0.66$, $p < 0.01$) between COS and CO was also found during the period from late autumn to early spring (2012.10–2013.3). However, the slope of 0.14 ± 0.006 pptv/ppbv was much smaller than that measured in summer and those reported in the literature.

Remarkable correlation ($R^2 > 0.5$) between COS and CO was also found for individual diurnal data in different seasons (Table 2). For the days in June, the ΔCOS/ΔCO ratios were within the range from 0.52 to 1.22 pptv/ppbv, and the values greater than 1 occurred on the days with extremely high air temperature. In contrast, the ΔCOS/ΔCO ratios from October to February exhibited much lower values, from 0.083 to 0.410 pptv/ppbv, with the average value of 0.20 ± 0.09 pptv/ppbv.

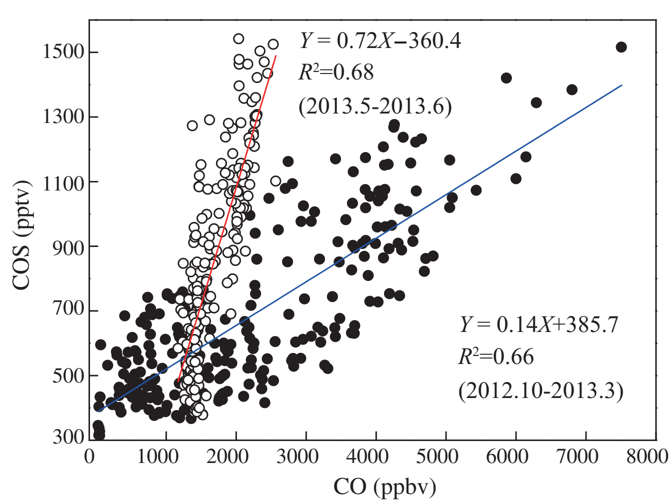

Fig. 5 – Scatter plots and linear regression of carbonyl sulfide (COS) and carbon monoxide (CO).

Table 1 – Comparison of seasonal carbonyl sulfide (COS) mixing ratios in different studies (unit: pptv).

	This study		Other studies	Location
Spring	608 ± 262			Beijing
			574 ± 40 (Guo et al., 2010)	Hong Kong
			580 (Blake et al., 2004)	Western Pacific
			440 ± 10 (Inomata et al., 2006)	Wakasa Bay, Japan
Summer	372 ± 115			Beijing
			397 (Campbell et al., 2008)	North U.S. continent
Autumn	651 ± 275	690 ± 312 [a]	841 ± 293 [a] (Mu et al., 2002)	Beijing
Winter	849 ± 477			

[a] The average value of data in both autumn and winter (October to February).

As listed in Table 3, different types of sources have characteristic emission ratios for COS *versus* CO. The variation of ΔCOS/ΔCO ratios among various seasons and dates in this study might be attributed to the change of the strength of each type of source.

Atmospheric CO in urban areas is usually dominated by vehicle emissions. However, the COS/CO ratio in the exhaust from the dominant gasoline vehicles is only 5.8×10^{-3} pptv/ppbv (Fried et al., 1992) which cannot account for the relatively high ΔCOS/ΔCO ratios observed in this study. Although the emission COS/CO ratio from diesel vehicles (0.2 pptv/ppbv) is very close to the ΔCOS/ΔCO ratios measured in Beijing from late autumn to early spring (October 2012–March 2013), the small proportion of diesel vehicles to gasoline vehicles in Beijing make it difficult to explain the ΔCOS/ΔCO ratios observed. Therefore, additional combustion sources with relatively high emission COS/CO ratios were suspected to exist around Beijing.

Table 2 – Enhancement ratios for carbonyl sulfide (COS)/ carbon monoxide (CO) in different months and individual days.

Date	ΔCOS/ΔCO (pptv/ppbv)	R^2 (n)
Annual datasets		
Oct [a]–Mar [b]	0.72	0.68 (259)
May–Jun [b]	0.14	0.66 (212)
Diurnal datasets		
29th Oct [a]	0.41	0.89 (13)
1st Nov [a]	0.30	0.83 (16)
6th Nov [a]	0.19	0.58 (13)
16th Nov [a]	0.22	0.95 (11)
4th Dec [a]	0.08	0.86 (11)
18th Dec [a]	0.13	0.65 (10)
25th Dec [a]	0.20	0.86 (13)
26th Dec [a]	0.15	0.50 (10)
27th Dec [a]	0.17	0.87 (11)
27th Feb [b]	0.19	0.78 (9)
28th Feb [b]	0.20	0.97 (8)
10th Jun [b]	1.08 [c]	0.84 (13)
12th Jun [b]	1.07 [c]	0.66 (12)
17th Jun [b]	1.12 [c]	0.58 (12)
19th Jun [b]	1.22 [c]	0.90 (14)
21st Jun [b]	0.61	0.56 (13)
25th Jun [b]	0.52	0.59 (12)

[a] Observed in 2012.
[b] Observed in 2013.
[c] The maximum temperature in these days were more than 35°C.

The additional combustion sources may include biomass, coal and natural gas. Biomass burning, including agricultural waste, defoliation waste and so on, is a prevailing phenomenon around Beijing through late autumn to early spring. An approximate COS/CO emission ratio of 0.1 pptv/ppbv (Blake et al., 2004) was derived from the plume of biomass burning during the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) project, which took place in the early spring of 2001. Because evidence of the influence of biomass burning on the air quality in Beijing has been found by Li et al. (2010) and CO emission from biomass burning accounted for a large proportion of the total CO emission around Beijing (as discussed in Section 2.2.3), the contribution of biomass burning to atmospheric COS in Beijing may be considerable.

Natural gas is a kind of clean energy. Although the addition of odorous sulfur compounds for safety reasons may produce COS during combustion, the emission COS/CO ratio measured from a domestic stove using natural gas for cooking was only 0.01 pptv/ppbv, and CO emission was found to be very small. Although a large proportion of boilers use natural gas for heating during the winter season in Beijing, the contribution of natural gas combustion to atmospheric COS in Beijing was suspected to be unimportant.

Coal combustion has long been regarded as an important contributor both for atmospheric CO and COS (Chin and Davis, 1993; Blake et al., 2004; Streets et al., 2006). Even though most boilers have replaced coal by natural gas or oil for heating during winter in Beijing, coal is still commonly used for heating or cooking by farmers who are living around the Beijing urban area. Regrettably, no data are available for the emission ratio of COS/CO from coal combustion. The emission

Table 3 – The carbonyl sulfide (COS)/carbon monoxide (CO) emission ratios from different types of COS combustion sources (pptv/ppbv).

	COS/CO	Reference
Biomass/biofuel burning	0.1	Blake et al. (2004)
Coal burning	0.30	Khalil and Rasmussen (1984)
		Streets et al. (2006)
Natural gas	0.01	This study
Vehicle		
Gasoline exhaust	5.8×10^{-3}	Fried et al. (1992)
Diesel exhaust	0.2	Fried et al. (1992)
Tires wear	1.21 [a]	Pos and Berresheim (1993)

[a] The ratio of COS emitted from tire wear to CO in engine exhaust.

ratio of COS/CO from coal combustion could only be indirectly and roughly estimated by the existing data of the COS/CO_2 ratio and the emission factors for CO and CO_2. There is only one available data point for the COS/CO_2 mass ratio of 2.3×10^{-6} at the Cherokee Power Plant in Denver, Colorado (Khalil and Rasmussen, 1984). The emission factors of CO and CO_2 from coal combustion were adopted as 8 and 2250 g/kg (Streets et al., 2006), respectively. The emission COS/CO ratio from coal combustion was then estimated as 0.30 pptv/ppbv, which is within the range of the ΔCOS/ΔCO (0.13–0.41 pptv/ppbv) measured in this study during winter. In comparison with the seasons other than winter, the remarkable increase of atmospheric CO in winter indicated that coal combustion for heating still accounts for a large proportion of CO in Beijing. Therefore, the relatively high COS/CO ratios measured in winter implied that coal combustion for heating is an important source of atmospheric COS in the winter of Beijing.

However, the extremely high ΔCOS/ΔCO measured in summer could not be explained by the direct emissions from various combustion sources. Because CO is relatively inert in the atmosphere, with an atmospheric lifetime of about 48 days, the extremely high ΔCOS/ΔCO measured in summer cannot be ascribed to the chemical removal of atmospheric CO by OH radicals. Considering the strong COS uptake by vegetation in summer, much stronger additional COS sources were suspected to account for the high value of ΔCOS/ΔCO measured. The remarkable linear correlation between COS and CO observed in summer also indicated that the additional COS sources should be related to combustion processes. Pos and Berresheim (1993) found that tire wear of automobiles is an important source for atmospheric COS, with a maximum fraction of S released as COS of 43% ± 7%. Because tire wear of automobiles is synchronous with the engine combustion processes, and COS emission from tire wear positively correlates with temperature (Pos and Berresheim, 1993), tire wear is suspected to make a great contribution to atmospheric COS in Beijing during the hot summer. The average S content is 1.5% in tread rubber (Hofmann, 1967; Mroczkowski, 1992) and the average tread loss rate is 0.12 g/km per tire under urban conditions (Pierson and Brachaczek, 1974; Councell et al., 2004), thus the maximum emission factor of COS from tires wear was calculated as 14.6×10^{-4} g/km per tire. The CO emission factor of 2.27 g/km per car was adopted, which was the upper threshold value of the fourth level of the National light-duty Vehicle Exhaust Standard applied in 2011 in Beijing (Ministry of Environmental Protection, 2005). Combining the engine processes and tire wear, the comprehensive maximum emission ratio of COS *versus* CO from the automobile processes was calculated as 1.21 pptv/ppbv, which is very close to the ΔCOS/ΔCO upper values measured in summer under high air temperatures. Due to relatively low temperatures from October to April, the contribution of tire wear to atmospheric COS in Beijing may be modest, and relatively small values of ΔCOS/ΔCO were measured.

2.2.2. Non-combustion emissions

Besides the combustion sources, non-combustion sources may also make a contribution to atmospheric COS, including cesspools (Mu et al., 2002), waste landfills, rice paddies, animal feedlots (Blake et al., 2004), and industrial processes such as aluminum production, carbon black production, pigment production, and sulfur recovery (Blake et al., 2004). Although aluminum production, carbon black production, pigment production and sulfur recovery factories have been found to have considerable emission factors of COS and high COS/CO emission ratios (Johnson and Harrison, 1986; Chin and Davis, 1993; Blake et al., 2004), these polluting factories have been moved far away from Beijing. The almost total lack of correlation ($R^2 = 0.02$, $n = 205$, $p = 0.02$) between COS and CH_4 indicated that the contributions of cesspools, rice paddies, animal feedlots and waste landfill, which are typical CH_4 sources, made negligible contribution to atmospheric COS in Beijing.

2.2.3. Emission estimates

Compared with COS, the regional CO emission inventory has been known in more detail, and thus the significant correlation between atmospheric CO and COS has been used for estimates of regional COS emissions (Blake et al., 2004; Guo et al., 2010). However, the two previous estimates based on short period measurements must have large uncertainty because they did not consider the strong seasonal variation of the sources for COS and CO. COS emission from Beijing was more accurately estimated in this study based on two typical ΔCOS/ΔCO ratios during the two time periods: the ratio of 0.14 pptv/ppbv for the "Winter Half-year" from October to March (designated as WH), and of 0.72 pptv/ppbv for the "Summer Half-year" from April to September (designated as SH). The value adopted for the SH may be less representative, because the ΔCOS/ΔCO ratio was derived based only on the data from May to June, due to missing CO data in other months.

The CO emissions from the Beijing areas that were used for this calculation are based on the energy consumption and industrial output data from the 2011 National Statistical Yearbook (National Bureau of Statistics (NBS), 2012) and the TRACE-P emission factors updated inventory for the year 2001 (Streets et al., 2006). Particularly, the CO emission from light-duty vehicles was adopted from the China Ministry of Environmental Protection (2005). For all the CO emissions we considered, automobile exhaust (0.170 Tg/year), residential cooking (0.052 Tg/year), industries (0.185 Tg/year) and power plants (0.014 Tg/year) are regarded as Non-Seasonally Dependent emission (CO_{NSD}) which is homogeneously distributed in both WH and SH. Residential heating (0.158 Tg/year) and centralized heating (0.047 Tg/year) by coal combustion, biofuel/biomass burning (0.205 Tg/year) and natural gas combustion (0.001 Tg/year) are regarded as Seasonally Dependent emission (CO_{SD}) which is assumed only to occur in WH.

The COS emission in SH (COS_{SH}) can be calculated as:

$$COS_{SH} = \frac{1}{2}CO_{NSD} \times \frac{M_{COS}}{M_{CO}} \times 0.72 = 0.32 \ \text{Gg/year}. \quad (1)$$

And the COS emission in WH (COS_{WH}) can be calculated as:

$$COS_{WH} = \left(\frac{1}{2}CO_{NSD} + CO_{SD}\right) \times \frac{M_{COS}}{M_{CO}} \times 0.14 = 0.21 \ \text{Gg/year}. \quad (2)$$

The total direct anthropogenic COS emission in Beijing was roughly estimated as 0.53 ± 0.02 Gg/year and the emission density for Beijing was 0.033 Gg/year km^2, which was a factor of 3 times greater than the value of 0.011 Gg/year km^2 estimated by Blake et al. (2004) for all of China, reflecting high emission from intensive human activities in Beijing. However, the emission density for Beijing was much lower than the estimation of Guo et al. (2010) of 0.89 Gg/(year·km^2) for inner PRD.

It should be mentioned that large uncertainty still exists in the estimate of COS direct emission around Beijing, which was mainly ascribed to the uncertainties in the CO emission inventory for various combustion sources and the correlation between COS and CO measured. In addition, the estimate of COS_{SH} might be underestimated because residential coal combustion was not considered.

3. Conclusions

The distinct diurnal and seasonal variations of atmospheric COS in Beijing plainly revealed strong COS sources' strength in winter and evident vegetation COS uptake in summer. The remarkable reduction of atmospheric COS in comparison with 10 years ago was ascribed to the effective control measures adopted by the Beijing government.

The significant correlation between atmospheric COS and CO indicated that COS in Beijing was mainly from sources related to various combustion processes. The two different types of correlations at different seasons evidently implied seasonal variation of the proportion of various combustion sources for COS, that is, COS emission was dominated by coal combustion in winter and vehicle tire wear in summer.

The direct COS emission from various combustion sources in Beijing was estimated by using the correlations between COS and CO derived from the measurements combined with the CO inventory, and the COS source strength estimated was still remarkable.

Acknowledgments

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