Characteristics of Traffic-related Emissions: A Case Study in Roadside Ambient Air over Xi'an, China

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ABSTRACT

Traffic-related emissions were measured at a heavy-traffic roadside in Xi'an at the end of April, 2008 to survey the exposure levels of freshly emitted carbon monoxide (CO), mass and chemical composition (OC, EC, inorganic ions, and PAHs) of PM_{10}, and ozone (O_3). In general, high levels of mass concentration and chemical species in PM_{10} were observed during daily heavy traffic periods (morning, noon, and evening traffic rush hours), especially in the morning traffic rush hour. OC and EC accounted for 9.3% and 3.0% of PM_{10} mass, respectively, and the ratios of OC/EC were constant during the heavy traffic periods (with a mean value of 3.2). Water-soluble ions constituted 14.0% of PM_{10} and the dominant ionic species were Ca^{2+}, SO_4^{2-}, and NO_3^- in the roadside samples. Re-suspended road dust constituted a large fraction of PM_{10}, causing the PM_{10} samples to become more alkaline. The concentrations of 12 prior-controlled PAHs revealed the potential high health risk of this roadside area in Xi'an. The diurnal variation in CO and O_3 exhibited a different trend, which indicated that CO level was largely influenced by the instantaneous emission of vehicles while O_3 was closely associated with the overall traffic conditions and meteorological status.

Keywords: Roadside; PM_{10}; Chemical composition; CO; O_3.

INTRODUCTION

In the last decade, the number of motor vehicles used has increased, and their emissions have become the dominant contributors to air pollution. Traffic-related emissions, such as particulate matter (PM), organic carbon (OC), elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), and carbon monoxide (CO) are the primary air pollutants in most urban areas, and many corresponding exposure studies and epidemiologic investigations have been carried out to evaluate their adverse effects (Kok *et al*., 2005; Kok *et al*., 2006; Samet, 2007; Garshick *et al*., 2008; Umbuzeiro *et al*., 2008).

Ambient particles generated by vehicular traffic have received intensive scrutiny, partly because particulates generated from combustion processes pose more serious adverse health effects than those from non-combustion processes and account for more than 50% of the total emissions of PM in the urban areas of highly industrialized countries (Han and Naeher, 2006). In China, respirable suspended particulate (PM_{10}) is considered one of the routine environmental monitoring indices carried out by the Ministry of Environmental Protection of China and is currently a major concern to air quality in Chinese cities (www.zhb.gov.cn). In addition, traffic-related gases have also received a great deal of interest due to their inherent toxicities and possible heterogeneous reactions with other components in the atmosphere (Saunders *et al*., 1997; Bogo *et al*., 1999; Kley *et al*., 1999; Ramon *et al*., 2006). On account of the design and technology of motor vehicles, fuel structures, meteorological conditions, and because socioeconomic development levels vary in different areas, the chemical compositions and characteristics of traffic-related emissions can change significantly.

With a permanent population density of 1791 person/km^2 in urban districts (2007), Xi'an is the largest city in northwest China. According to Xi'an Municipal Bureau of Statistics, there were 759029 civil vehicles, including 473216 motorcars and 284594 motorcycles at the end of 2007. Vehicles in Xi'an are typically natural gas-fueled in buses without air conditioning and in taxis, gasoline-fueled in private cars and diesel-fueled in heavy duty trucks, traveling buses, and air conditioned buses. With the rapidly growing number of vehicles, more accurate studies on exposure estimates using ground level measurement data of traffic-generated air pollutants needs to be conducted in Xi'an. However, although some

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physical and chemical properties of PM and other air pollutants in different locations of Xi'an City have been reported (Cao *et al.*, 2005; Han *et al.*, 2008; Shen *et al.*, 2008; Cao *et al.*, 2009; Shen *et al.*, 2009), to our knowledge, detailed studies concerning traffic-related emissions are scarce. Therefore, the objectives of this study were 1) to investigate the exposure level of roadside CO, O_3, and PM_{10} together with their chemical compositions (OC, EC, water-soluble inorganic ions, and PAHs) in Xi'an, and 2) to evaluate the air quality at a roadside microenvironment.

METHODOLOGY

Sampling and Measurement

The sampling site was located at a heavy traffic roadside near the south secondary ring road in southeast downtown Xi'an, China (Fig. 1). All the instruments were installed about 1 m above ground level. The intensive sampling campaign was conducted during traffic rush hours on sunny weekdays from 23rd to 25th April and from 29th April to 1st May, 2008. Detailed sampling information is described in Table 1.

PM_{10} samples were collected on Φ 90 mm quartz micro-fiber filters (Whatman QMA, England) using a medium volume sampler (KC-120H, Qingdao Laoshan Electric CO., Ltd., China) operated at a flow rate of 100 L/min. Before sampling, the filters were preheated in a 900°C muffle furnace for at least 3 h to avoid inherent carbonaceous contaminants. The PM_{10} mass loadings were determined gravimetrically using a 1 μg sensitivity electronic microbalance (Model MC5, Sartorius AG, Goettingen, Germany). The filters were equilibrated for 24 h at a constant temperature between 20 and 23°C and relative humidity ranging from 35% to 45% (USEPA, 1997) before weighing. After sampling, each filter was sealed in aluminum foil and stored at −18°C until analysis.

CO and O_3 concentrations were simultaneously measured every 10 min using a real-time Model 7565 Q-TRAK monitor (TSI Inc., St. Paul, MN, USA) and a Model 9810B ozone analyzer (Ecotech Pty Ltd., Blackburn, VIC, Australia). The detection limits were 0.1 mg/m^3 and 0.001 mg/m^3 for CO and O_3, respectively. Before the experiments, Model 7565 Q-TRAK monitor and Model 9810B ozone analyzer were calibrated using the standard gas by the TSI Beijing branch and the Beijing Magee Scientific incorporation. Vehicle numbers were recorded by students rare eyes and a digital camera over 5 min (finally averaged to per min) in each hour from 06:00 am to 10:00 pm.

Chemical Analysis

OC and EC in PM_{10} samples were analyzed using a Thermal and Optical Carbon Analyzer (Model 2001, AtmAA Inc, USA) with IMPROVE (Interagency Monitoring of Protected Visual Environment) thermal/optical reflectance (TOR) protocol. The method produced data for four OC fractions (OC1, OC2, OC3, and OC4 in a helium atmosphere at 140°C, 280°C, 480°C, and 580°C, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a 2% oxygen/98% helium atmosphere at 580°C, 740°C, and 840°C, respectively). The IMPROVE protocol defined OC as OC1 + OC2 + OC3 + OC4 + OPC and EC as EC1 + EC2 + EC3 – OPC. The detailed determination procedures of OC and EC together with quality assurance and controls were described in the study of Cao *et al.* (2003).

Four anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in PM_{10} samples were determined by ion chromatography (Dionex 600, Dionex Corp, Sunnyvale, USA). The detailed procedures for ion analysis were previously described by Shen *et al.* (2008). The detection limits were less than 0.05 μg/mL for all ions. Standard reference materials produced by the National Research Centre for Certified Reference Materials of China were analyzed for quality assurance purposes. Blank values were subtracted from the total sample concentrations.
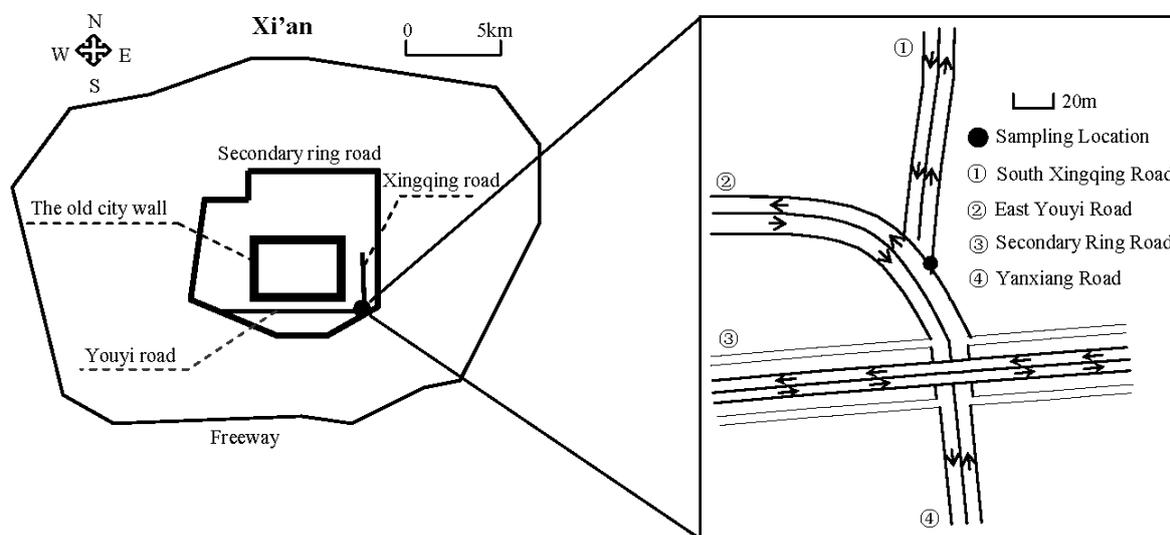
Fig. 1. Sampling location.

Table 1. Details of sampling time.

Samples	Date	Time	Samples	Date	Time
M1	23-Apr	07:00–09:30	M2	30-Apr	07:00–09:30
	24-Apr	07:00–09:30		1-May	07:00–09:30
N1	23-Apr	11:00–14:00	N2	30-Apr	11:00–14:00
	24-Apr	11:00–14:00		1-May	11:00–14:00
E1	23-Apr	17:00–20:00	E2	30-Apr	17:00–20:00
	24-Apr	17:00–20:00		1-May	17:00–20:00
T1	25-Apr	07:00–20:00	T2	29-Apr	07:00–20:00

Twelve prior-controlled PAHs (including phenanthrene (Phe), anthracene (Ant), fluoranthene (FLA), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(l,2,3-cd)pyrene (IP), dibenz(a,h)anthracene (dBahA), and benzo(g,h,i)perylene (BghiP)) in accordance with United States Environmental Protection Agency (US EPA) for M1, N1, and E1 samples were detected by gas chromatography/mass spectrometry (Agilent Technologies, Inc., CA, USA, GC 6890/MS 5975). One quarter of each filter was Soxhlet extracted with 200 mL dichloromethane for 24 h and the extracts were concentrated to 1 mL using a rotary evaporator. The total extracted organics were then fractionated by 15 mL hexane/dichloromethane (1:1) on a silica gel cleanup column, which was washed with 20 mL hexane prior to use. The eluate was collected and evaporated to 0.5 mL under a stream of purified nitrogen gas. Treated PAHs samples were subsequently analyzed by GC/MS, using a fused silica capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) installed in a gas chromatograph interfaced with a Hewlett-Packard 5975 mass selective detector (SIM mode). 1 μL sample was injected into the splitless inlet at a high temperature of 270°C. The separation process was performed using the GC oven with the temperature increased from 2-min hold at 70°C to 120°C (10 °C/min) to the final temperature of 300°C (6 °C/min) with a 5-min hold. The ion trap and transfer line were maintained at 230°C and 280°C, respectively. Data for qualitative analysis were acquired in electron impact (EI) mode at an electron ionization energy of 70 eV. The recoveries of the multistep procedure for PAH species were all above 89%, with the exception of naphthalene (36%), acenaphthene (58%), and acenaphthylene (63%). Therefore, the data of these three species were not reported and discussed in the following. Before Soxhlet extraction, neat deuterated internal standards of phenanthrene-D10 and perylene-D12 were added to the samples to evaluate the reliability of the pretreatment process. The percent recoveries of these two standard materials were 66.4%–108.6% and 76.4%–122.4%, respectively.

RESULTS AND DISCUSSION

Level of PM_{10} Mass

The PM_{10} concentration at the roadside microenvironment in Xi'an ranged from 337.9 to 718.0 μg/m³, with an average value of 569.2 μg/m³ (Table 2). Previous study reported that the PM_{10} concentration at a general ambient monitoring site were 400 μg/m³ in spring (Zhang *et al.*, 2002). Recently, Xie *et al.* (2009) reported the spring PM_{10} concentration at Baoji city, which also locates in the Guanzhong Plain and is 200 km away from Xi'an, was about 410 μg/m³ in average. PM_{10} levels varied significantly with different traffic conditions. For example, PM_{10} concentration in the morning exceeded the value at noon by a factor of 1.5. The highest PM_{10} level occurred during the morning rush period and may have been largely due to stable atmospheric conditions, whereas the lower concentration at noon primarily depended on an increasing trend in mixing layer height which reached a maximum at about 14:00 local time. Again, PM_{10} concentration would have been enhanced due to the slow decrease in mixing layer height towards sunset (Ulke and Mazzeo, 1998; Mok and Rudowicz, 2004). In addition, the meteorological conditions, such as wind speed and direction, as well as relative humidity, also heavily influenced roadside PM_{10} level. The slight change in daily PM_{10} concentration during the same rush period indicated that the traffic flow rate was almost constant. Nevertheless, the difference between E1 and E2 might have been due to increased public activities on 1st May, i.e. International Labor Day, in which people like to go out visiting the suburb sites and leading a high concentration in the E2 sample. Daily variations in PM_{10} during each rush period were not evident except in the evening. For example, the difference in PM_{10} concentration during the morning and noon rush episodes was less than 10%. However, the difference in PM_{10} mass between evening, morning and noon was larger than 50%. Moreover, the PM_{10} levels for the two daytime samples (T1 and T2) were lower than those in the morning and evening rush periods, but slightly higher than the value at noon.

PM_{10} concentrations during rush periods at this roadside microenvironment in Xi'an were higher than those observed at normal downtown areas with no major industrial activities, where the average PM_{10} levels were 261.9 μg/m³ in fall and 450.6 μg/m³ in winter (Cao *et al.*, 2005). These values showed a heavy PM_{10} pollution in comparison with other traffic hotspots. For example, the mean PM_{10} was 47 μg/m³ at Bastarreche and 46–50 μg/m³ in Spain (Negral *et al.*, 2008; Querol *et al.*, 2008). Wang and Xie (2009) reported that the traffic-related PM_{10} concentrations before and during the 2008 Olympic Games traffic control period were 142.6 μg/m³ and 118.7μg/m³, respectively.

Table 2. Concentrations of PM_{10} and chemical species.

	PM_{10}	OC	EC	TCA	OC/EC	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	SO_4^{2-}	NO_3^-	Total ions	CO	O_3
	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$		$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	mg/m^3	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	mg/m^3	$\mu g/m^3$
M1	670.1	66.7	21.3	128.1	3.1	3.8	5.6	2.9	1.7	27.8	1.0	8.6	24.5	16.4	92.3	3.2	24.0
N1	476.9	35.2	10.7	67.1	3.3	3.5	2.0	0.9	1.2	17.8	0	2	19.4	8.3	55.1	1.5	166.3
E1	337.9	35.2	11.2	67.5	3.2	1.9	1.1	1.0	1.0	11.2	0	3	13.7	5.1	38.0	2.0	142.4
M2	687.1	73.6	26.3	144.0	2.8	2.7	6.3	3.7	1.9	20.8	1.2	9.7	43.8	26.4	116.5	2.9	57.8
N2	430.1	44.7	15.3	86.9	2.9	1.6	8.6	2.4	1.3	15.4	0	1.4	37.3	12.1	80.1	1.3	172.1
E2	718.0	55.9	17.4	106.9	3.2	1.9	7.0	2.2	1.5	22.5	0	2.2	36.3	11.8	85.4	1.9	115.8
T1	649.7	59.6	14.4	109.7	4.2	2.3	3.6	2.1	1.0	13.9	1.1	3.2	26.4	18.5	72.1	2.2	119.9
T2	584.1	52.7	19.7	104.1	2.7	3.5	6.1	3.6	1.6	20.9	0.8	3.8	37.6	18.7	96.6	2.6	131.1
Ave.	569.2	53.0	17.0	101.8	3.2	2.7	5.1	2.4	1.4	18.8	0.5	4.3	29.9	14.7	79.8	2.1	114.5

Carbonaceous Aerosol

The concentrations of OC, EC, and eight carbonaceous fractions are summarized in Table 2. The average OC and EC levels were 53.0 and 17.0 $\mu g/m^3$, respectively, which were remarkably higher than those measured at a roadside in Birmingham (Yin and Harrison *et al.*, 2008), where OC and EC were 4.6 and 3.8 $\mu g/m^3$, respectively. OC and EC had similar trends in variation to that of PM_{10}. OC concentrations changed significantly in different rush periods in the same day, whereas there was little change in EC except when it was high in the morning. The organic matter (OM) content was calculated by multiplying OC by a factor of 1.6 (Turpin and Lim, 2001) and the total carbonaceous aerosol (TCA) was calculated by adding OM and EC. TCA constituted 17.9% of the PM_{10} mass.

The ratios of OC/EC during the three rush periods were in the range of 2.8–3.3, with a mean value of 3.2. As a whole, the OC/EC ratio during the three rush periods, to some extent, may reflect the source profile of vehicle exhaust over Xi'an. The OC/EC ratio in this study was higher than the value of 1.0 observed at a roadside site in Hong Kong (Cao *et al.*, 2006; Lee *et al.*, 2006). OC includes PAHs and other organic matter which can be directly emitted from primary sources or produced from secondary atmospheric reactions involving gaseous organic precursors. EC is graphitic carbon mainly formed from incomplete fuel combustion at high temperatures. Watson *et al.* (2001) reported the carbon source profile of vehicle exhaust with an OC/EC ratio of 1.0 in the USA, and some researchers have applied this as an indicator to trace the origin of the carbonaceous aerosol (Cao *et al.*, 2003; Duan *et al.*, 2004; Cao *et al.*, 2005). Cao *et al.* (2005) reported that the OC/EC ratio for 24-h $PM_{2.5}$ roadside samples was 4.1, which is higher than the value in this study. In addition to the diversity of particle size properties and meteorological conditions, re-suspended dust (Ho *et al.*, 2003), the energy fuel structure and quality, and the engine working conditions may be the dominant factors influencing the OC/EC ratio. Therefore, the large number of gasoline-fueled motorcars would contribute to the high levels of OC and the high OC/EC ratio in Xi'an. An investigation into the carbonaceous aerosols in fourteen Chinese cities also showed high OC/EC ratios (Cao *et al.*, 2007). In conclusion, the carbon source profile for traffic related emissions in Xi'an was reflected in the OC/EC ratio

of approximately 3.2. In contrast, the OC/EC ratio for T1 was a little higher than those observed during rush periods, while the OC/EC ratio for the T2 sample was close to these values.

The Carbon Analyzer operated with the IMPROVE thermal/optical reflectance (TOR) protocol can determine the concentrations of eight carbonaceous fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OPC) in different temperature gradients. The eight fractions have been used to differentiate the source profiles of carbonaceous aerosol particles (Cao *et al.*, 2006; Shen *et al.*, 2009). Fig. 2 plots the mass concentrations of the eight carbon fractions during the rush periods. The average concentrations of OC2, OC3, OC4, and EC1 were relatively abundant in this study, while OC1, OP, EC2, and EC3 were at a lower level. Previous studies showed that OC1 and OP were related to biomass burning, EC2 and EC3 had a strong correlation with diesel vehicles, and OC2, OC3, OC4, and EC1 were more enriched following gasoline and coal combustion (Watson *et al.*, 1994; Cao *et al.*, 2006), Therefore, the distribution of the eight carbon fractions demonstrated the predominant contribution of gasoline vehicles to the carbonaceous aerosol at this roadside site.
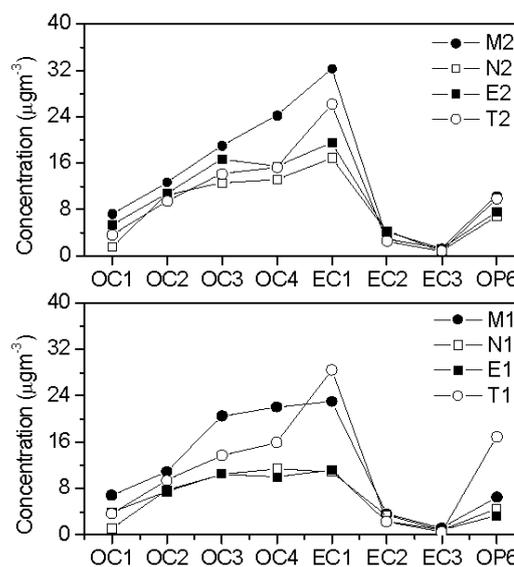
Fig. 2. Mass concentrations of eight carbon fractions.

PAHs Levels

PAHs, which are one of the important persistent organic compounds (POPs), are largely formed by the incomplete combustion of fossil fuel (Khalili *et al.*, 1995; Wingfors *et al.*, 2001; Ciganek *et al.*, 2004; Kok *et al.*, 2005). In this study, 12 types of US EPA prior-controlled PAHs were determined in three rush period PM_{10} samples. As shown in Table 3, total PAHs concentrations were 318.6, 281.8, and 235.5 ng/m³ during the morning, noon, and evening periods, respectively, which accounted for 4.8‰, 8.0‰, and 6.7‰ of PM_{10} OC, respectively. In contrast, a recent study by Xie *et al.* (2009) reported that the PM_{10} total PAHs levels at a roadside station in Baoji city, which is about 200 km to the west of Xi'an and in Shaanxi Province, were 142 ng/m³ in spring and 573 ng/m³ in winter. A previous study by Wingfors *et al.* (2001) investigated the total particle PAHs concentrations inside the 2.1 km long Lundby tunnel (Gothenburg, Sweden) at two sites, approximately 200 m from the entrance and exit. These values were found to be 47.8 ng/m³ at the entrance and 257.5 ng/m³ at the exit. The highest individual PAH in traffic-related emission samples in this study was observed to be the 6-ring of BghiP. BaP is usually considered an indicator for PAHs when carrying out health exposure risk evaluation. The concentration of BaP during the rush periods exceeded the value of the Chinese Ambient Air Quality Standard for BaP (10 ng/m³), which indicated that a high health risk existed close to the roadside environment. Moreover, BaP concentration at the roadside exceeded the World Health Organization (WHO-AQG) prescribed emission standard for PAHs (1.0 ng/m³ for BaP) by a factor of 15–22. In recent years, benzo(a)pyrene-equivalent carcinogenic power (BaPE) has been introduced to estimate the potential carcinogenicity of whole PAH fractions instead of BaP, because BaP is easily decomposed in reactive air parcels by light or oxidants and the carcinogenicity of total PAHs could be underestimated (Kavouras *et al.*, 2001; Yassa *et al.*, 2001; Mastral *et al.*, 2003; Bi *et al.*, 2005). BaPE can be calculated using the following equation:

$$BaPE = 0.06 \times BaA + 0.07 \times BFA + BaP + 0.6 \times dBahA + 0.08 \times IP \tag{1}$$

Table 3. Composition of traffic-related PAHs (ng/m³).

	mol.wt	M1	N1	E1
Phe	178	18.9	30.2	12.8
Ant	178	17.0	24.8	14.3
FLA	202	5.4	3.8	4.5
Pyr	202	10.4	23.4	7.5
BaA	228	14.3	9.1	9.7
Chr	228	30.8	22.9	22.7
BbF	252	47.9	32.8	33.0
BkF	252	34.0	26.3	25.8
BaP	252	22.7	17.1	15.9
IP	276	23.5	11.2	13.0
dBahA	278	25.0	22.1	20.9
BghiP	276	68.7	58.1	55.4
total		318.6	281.8	235.5
PAHs/OC		20.9%	12.5%	14.9%

In this study, the BaPE concentration was 46.1, 36.0, and 34.2 ng/m³ during the morning, noon, and evening periods, with a mean value of 38.8 ng/m³. This was a much higher value for PM_{10} BaPE when compared with other regions of China, such as the urban and rural areas of Guangzhou (6.2–20.1 ng/m³) and an industrial area of Shanghai (5.95 ng/m³) (Bi *et al.*, 2005; Cheng *et al.*, 2007). The potential health risk of traffic-related PAHs at the roadside area of Xi'an should be considered significant.

The IP/(IP + BgP) ratio has been used to identify the characteristics of gasoline (0.18) and diesel engine (0.35–0.7) emissions (Kavouras *et al.*, 2001). Mastral *et al.* (2003) demonstrated that the IP/(IP + BgP) ratio was about 0.29 for gasoline engines and approaches 0.5 for diesel engines. In this study, the ratio of IP/(IP + BgP) in the morning, noon, and evening periods was 0.25, 0.16, and 0.19, respectively. These ratios are in agreement with the diagnostic ratio for gasoline-fueled emission reported in previous studies. The source profiles of vehicle exhausts are heavily influenced by many factors, such as fuel quality and engine power status. This study demonstrated that the source profile of PAHs from gasoline vehicles in Xi'an was similar with that observed in other countries, and these fingerprints can be reliably used in China.

Inorganic Water-soluble Ions

Table 2 shows the concentration of water-soluble inorganic ions in the roadside PM_{10} samples. On average, the detected ionic species showed a total concentration of 79.8 µg/m³ which accounted for 14.0% of the PM_{10} mass. Ca^{2+}, SO_4^{2-} and NO_3^- were the dominant water-soluble ions which constituted 80% of the total detected ionic species mass. This was consistent with the TSP observation at the roadside site in Xi'an (Shen *et al.*, 2008). Variations in SO_4^{2-} and NO_3^- during the three rush periods were similar to that of PM_{10}, however, Ca^{2+} showed some difference, as shown in Table 2. Ca^{2+} was mainly derived from re-suspended road dust due to vehicle tires. Urban ambient nitrate and sulfate were typical secondary aerosols through the gas-particle conversion which evolved from photochemical reactions. Ammonium and chloride were another two important species following these three major ions. Ion composition in the two daytime samples were similar with those in the rush periods. Because of the their hygroscopic nature, water-soluble components of atmospheric aerosols can change size, composition, number and the lifetime of particles, and increase the solubility of toxic organic compounds (Bogo *et al.*, 2003; Tsitouridou *et al.*, 2003; Castillo *et al.*, 2005; Fang *et al.*, 2006).

The ratio of cation microequivalents to anion microequivalents was calculated to evaluate the ionic balance and particle acidity. The cation and anion microequivalents were calculated using the following equations:

$$\text{cation microequivalents} = Na^+/23 + NH_4^+/18 + K^+/39 + Mg^{2+}/12 + Ca^{2+}/20 \tag{2}$$

$$\text{anion microequivalents} = F^-/19 + Cl^-/35.5 + NO_3^-/62 + SO_4^{2-}/48 \tag{3}$$

In this study, the cation/anion microequivalents ratio ranged from 1.1 to 2.2 with a mean value of 1.6, which suggested that PM_{10} aerosol particles were alkaline. As the sum of the carbonaceous aerosol and water-soluble ions only constituted about 32% of the PM_{10} mass, the remaining large fraction was mainly re-suspended road dust, which caused the PM_{10} to become more alkaline. A previous study on PM acidity over Xi'an also showed that coarse particles were alkaline, while fine particles tended to be acidic (Shen *et al.*, 2008).

Carbon Monoxide (CO) and O_3

CO and O_3 levels in the various traffic periods are presented in Table 2. The average CO levels in the rush periods were 3.1, 1.4, and 1.9 in the morning, noon, and evening, respectively, which were lower than the hourly mean value of the China Air Quality Standard of CO (10 mg/m^3), and also lower than the hourly mean value of the US EPA National Ambient Air Quality Standard (NAAQS) of CO (40 mg/m^3). The diurnal variation in CO levels at the roadside station associated with vehicle numbers are shown in Figs. 3(b) and (c). Relatively higher concentrations of CO occurred during the rush periods. The daytime values of CO were 2.2 and 2.6 mg/m^3 on April 25 and 29 respectively, which were also lower than the 4 mg/m^3 daily mean value of the China Air Quality Standard, and lower than the 10 mg/m^3 of the 8-hour mean value of the NAAQS. Wang and Xie (2009) reported that the traffic-related CO concentrations in Beijing before and during the 2008 Olympic Games were 3.02 and 2.43 mg/m^3, respectively, which were close to the values obtained in this study. Therefore, CO concentration at the roadside site in Xi'an

demonstrated a relatively low level.

O_3 is a highly reactive oxidant gas and is substantially associated with acute and chronic respiratory diseases, mortality and morbidity (Kley *et al.*, 1999; Ramon *et al.*, 2006). In this study, the mean O_3 concentrations during the rush periods were 31.6, 179.9, and 131.9 μg/m^3 in the morning, noon, and evening. The morning and evening O_3 concentrations were lower, while the noon value was higher than the Class II Value of China Air Quality Standard (160 μg/m^3). The diurnal variation in ozone levels is presented in Fig. 3(a). O_3 levels showed a significant peak value around the time of 14:00 and the mean value was 134.1 mg/m^3 during the daytime.

Dissimilarly, CO has comparatively stable chemical properties in the atmosphere and is mainly generated from the incomplete combustion of natural gas, gasoline and diesel oil in vehicular traffic engines. As shown in Fig. 3, the variation trend between CO and vehicle numbers is consistent; therefore, CO can be considered a proxy of primary emission. However, unlike CO, roadside O_3 levels were less affected by instantaneous emission due to vehicles (as shown in Fig. 3). Previous studies have demonstrated that urban ozone formation is a complex phenomenon since O_3 is not emitted into the atmosphere directly but results from the mixing of clean air masses, meteorological effects, and interaction of exhaust gases (Saunders *et al.*, 1997; Bogo *et al.*, 1999). Herein, the good correlation between O_3 and ambient temperature was plotted and is shown in Fig. 4. Such a result implies that O_3 can be used as an indicator of the secondary formation of aerosols to some extent.
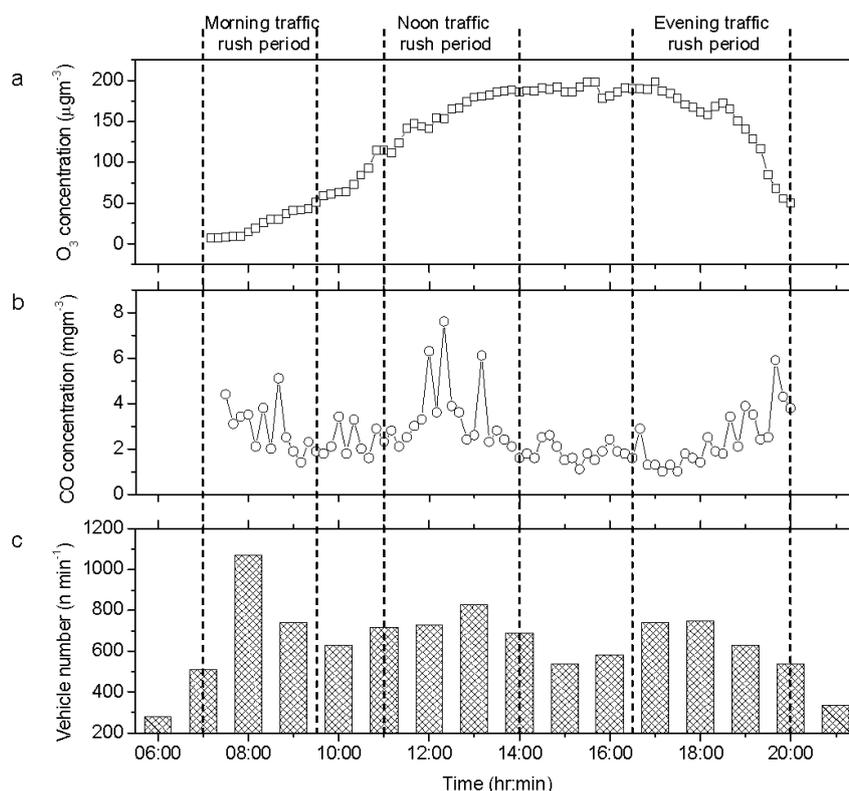
Fig. 3. Diurnal variation of O_3 (a) and CO (b) concentration with vehicle number (per minute in average, c) on 29 April.
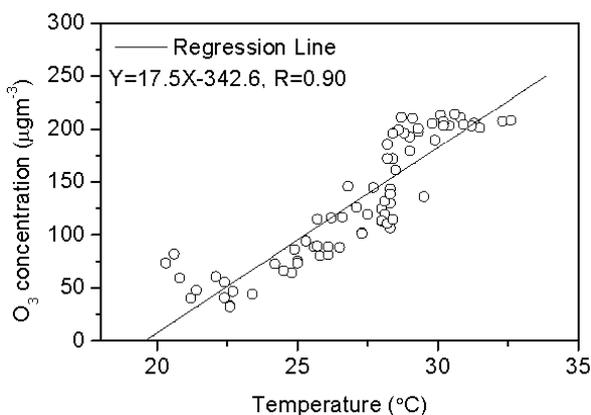
Fig. 4. Correlation between ozone levels and ambient temperature.

CONCLUSIONS

High levels of PM_{10} mass were observed at a roadside environment in Xi'an. The PM_{10} concentration in three daily heavy traffic periods exceeded the Class II value of the Chinese Air Quality Standard by a factor of 2–4. Roadside PM_{10} OC and EC concentrations were 53.0 and 17.0 $\mu g/m^3$, respectively, and TCA accounted for 17.9% of the PM_{10} mass. The ratios of OC/EC during the three heavy traffic periods were approximately equal and averaged 3.2. The level of eight carbonaceous fractions showed a predominant contribution from gasoline exhaust and carbonaceous aerosol. Water-soluble inorganic ions constituted 14.0% of the PM_{10} mass, and the dominant ions were Ca^{2+}, SO_4^{2-}, and NO_3^-. The total ion concentration was 79.8 $\mu g/m^3$, which constituted 14.0% of the PM_{10} mass. Ion balance revealed that the PM_{10} samples were alkaline, which was mainly due to large fractions of re-suspended dust in the PM_{10} mass. High concentrations of BaP and BaPE demonstrated the potential health risk of traffic-related PAHs at the roadside area in Xi'an. The ratio of IP/(IP + BgP) and IP/BgP indicated that the primary source of PAHs was gasoline vehicles at this roadside area. CO concentration was generally lower than the value of China air quality standard, and was largely influenced by the instantaneous emission of vehicles. O_3 showed a different diurnal variation compared with CO, which indicated that they have a totally different formation mechanism in roadside ambient air.

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