

## Chemical Characteristics of Submicron Particles in Winter in Xi'an

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### Abstract

Daily submicron aerosol samples (PM<sub>1</sub>, particles less than 1 μm in diameter) were collected continuously from Dec. 1 to Dec. 31, 2006 and the concentrations of 11 water-soluble ions (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and elemental carbon (EC) and organic carbon (OC) were determined in the filter samples to characterize the chemical composition of PM<sub>1</sub> over Xi'an during winter. The mean PM<sub>1</sub> mass concentration was 149.7 μg/m<sup>3</sup>. Water-soluble ions were dominant chemical species and occupied to 46% of PM<sub>1</sub> mass. Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were the major species of ionic compounds, which accounted for 95.3% of total ions concentration. The average OC and EC concentrations were 23.7 ± 10.27 μg/m<sup>3</sup> and 4.6 ± 1.8 μg/m<sup>3</sup>, respectively. Carbonaceous aerosol is another major component of PM<sub>1</sub>, and total carbonaceous aerosol occupied to 27.5% of PM<sub>1</sub> mass. High OC and OC/EC ratio were found in Xi'an in comparison with the past studies in Hong Kong and Taipei. Factor analysis on the eight carbon fractions shows that coal combustion and gasoline automobile exhaust, diesel automobile exhaust, and biomass burning were found to be statistically significant and explained 93% of the carbonaceous aerosols contributions.

**Keywords:** PM<sub>1</sub>; Water-soluble ions; Carbonaceous aerosol.

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### INTRODUCTION

The chemical composition of ambient aerosol were demonstrated an important factor in component deposition, human health and

visibility in urban regions (Horvath, 1996; Lundgren *et al.*, 1996; Yadav *et al.*, 2003; Schichtel *et al.*, 2001; Tsai and Cheng, 1999; Tsai *et al.*, 2003; Zhang *et al.*, 2003; Zhang *et al.*, 2008a, b). The major components of urban ambient TSP (Total suspended particulate), PM<sub>10</sub> (particles less than 10 μm in diameter), and PM<sub>2.5</sub> (particles less than 2.5 μm in

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diameter) were extensively measured and reported as sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), organic carbon (OC) and elemental carbon (EC). However, much less is known, and even less has been done about  $\text{PM}_{10}$  (particles with a diameter  $1.0 \mu\text{m}$ , submicron particle). Although some literatures (Vallius *et al.*, 2000; Cabada *et al.*, 2004) reported that the major components of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  originated from the same sources by using MOUDI sampler, and they concluded the investigation of  $\text{PM}_{10}$  did not yield significant new information in comparison with that obtained from the  $\text{PM}_{2.5}$ , it is clear that  $\text{PM}_{10}$  was a better indicator for anthropogenic sources than  $\text{PM}_{2.5}$ , because, compared with  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , it minimized interference from natural sources (Lundgren *et al.*, 1996; Lee *et al.*, 2006). Epidemiological studies (Dockery *et al.*, 1993; Schwartz *et al.*, 1996; Wilson and Suh, 1997; Pope, 2000) have suggested a statistical association between health effects and ambient fine particle concentrations, especially the submicron fraction that can penetrate into the alveolar region of the lungs.

Xi'an, the capital of Shaanxi province, (area of  $1066 \text{ km}^2$ , population 5.1 million), is one of the largest cities in Northwest China. Air quality in Xi'an has become a serious concern due to the persistently high mass levels of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  (Cao *et al.*, 2005a, b; Zhang *et al.*, 2002). Although clean fuels such as natural gas have progressively replaced coal for residential heating and cooking inside Xi'an's Second Ring Road since 1998, the number of motor vehicles in Xi'an has grown rapidly, increasing from  $\sim 180,000$  in 1997 to  $\sim 500,000$

in 2006. Therefore, PM pollution in Xi'an continues to be a serious problem. Prior studies mainly focused on the chemical characteristics of TSP,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  in Xi'an (Cao *et al.*, 2005a, b; Shen *et al.*, 2008; Zhang *et al.*, 2002). Up to now, much less data about  $\text{PM}_{10}$  in Xi'an have been available. In this paper,  $\text{PM}_{10}$  mass, 11 kinds of water-soluble ions, organic carbon (OC) and elemental carbon (EC) were measured in winter (heaviest pollution season) in Xi'an. The objectives of this study were to: (1) determine the mass levels of  $\text{PM}_{10}$ , ionic species, and carbonaceous aerosol and (2) to evaluate the  $\text{PM}_{10}$  pollution levels in Xi'an.

## METHODOLOGY

### *Aerosol Samples Collection*

The  $\text{PM}_{10}$  samples were collected on 47 mm Whatman quartz microfibre filters (Whatman Ltd, Maidstone, UK) from the roof surface of a 15-m high building. The sampling site is located in the southeastern part of downtown of Xi'an, only about 100 m from the South Second Ring Road. North and east of the sampling site are residential areas and the campus of Xi'an Jiaotong University, while to the south and west are the South Second Ring and Xingqin Roads, where the traffic is always heavy. Daily 24-h  $\text{PM}_{10}$  (10:00 am to 10:00 am, local time) samples were obtained from 1st Dec 2006 to 31 Dec 2006 using a mini-volume sampler (BGI, USA) operating at a flow rate of 5 L/min. A total of 31 of aerosol samples were collected. During the sampling period, field blank filters were also collected by exposing filters in the sampler without drawing air

through them; these were used to account for any artefacts introduced during the sampling procedure. The quartz filters were pre-heated to 800°C for 3 h before use to remove the carbonaceous contamination.

Aerosol mass loadings were determined gravimetrically using a Sartorius MC5 electronic microbalance ( $\pm 1 \mu\text{g}$  sensitivity, Sartorius, Göttingen, Germany). The filters were equilibrated for 24 hours at a constant temperature between 20°C and 23°C and relative humidity between 35% and 45% before weighing. Each filter was weighed at least three times before and after sampling following the 24 h equilibration period. The mean net mass for each filter was obtained by subtracting the pre-deployment weight from the average of the post-sampling readings.

#### ***Water-soluble Ions Analysis***

One-fourth of each filter sample was used to determine the ion mass concentrations. Six anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$  and  $\text{NO}_2^-$ ) and five cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in aqueous extracts of the sample filters were determined by an ion chromatography (IC, Dionex 500, Dionex Corp, Sunnyvale, CA). To extract the water-soluble species from the quartz filters, each filter was put into a separate 20 mL vial containing 10 mL distilled-deionized water (a resistivity of 18 M $\Omega$ ), and then shaken first by an ultrasonic instrument for 60 min and then by mechanical shaker for 1 hr for complete extraction the water-soluble compounds. The extracts were stored at 4°C in a clean tube before analysis. Cation concentrations were determined with the use of

a CS12A column (Dionex Corp.) with 20 mM MSA eluent. Anions were separated by an AS11-HC column (Dionex Corp.), using 20 mM KOH as the eluent. The limits of detection were less than 0.05 mg/L for anions and cations. Standard Reference Materials produced by the National Research Center for Certified Reference Materials, China were analyzed for quality assurance purposes. Blank values were subtracted from sample concentrations. Replicate analyses were performed at the rate of one per group of 10 samples for quality control.

#### ***Carbonaceous Aerosol Measurement***

The quartz PM<sub>1</sub> sample filters were analyzed for elemental carbon (EC) and organic carbon (OC) with the using of a DRI Model 2001 Thermal and Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). A 0.5 cm<sup>2</sup> punch from the quartz filter was analyzed for eight carbon fractions following the Interagency Monitoring to Protect Visual Environments total organic carbon protocol (IMPROVE TOC, Chow *et al.*, 1993; 2001; Fung *et al.*, 2002). 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 (OPC, 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 analyzer was calibrated with known quantities of CH<sub>4</sub> daily. Replicate analyses were performed at the rate of one per group of ten samples. Blank sample was also analyzed and the sample results were corrected by the blank sample concentration. Additional quality assurance and quality control procedures have been described in detail in

Cao et al. (2003) and Chow et al. (2007).

## RESULTS AND DISCUSSION

### Mass Concentration of PM<sub>1</sub>

Fig. 1 showed the temporal variation of PM<sub>1</sub> mass in winter in Xi'an. The mass concentrations of PM<sub>1</sub> in winter were in the range of 51.1 μg/m<sup>3</sup>-251.4 μg/m<sup>3</sup> with a mean

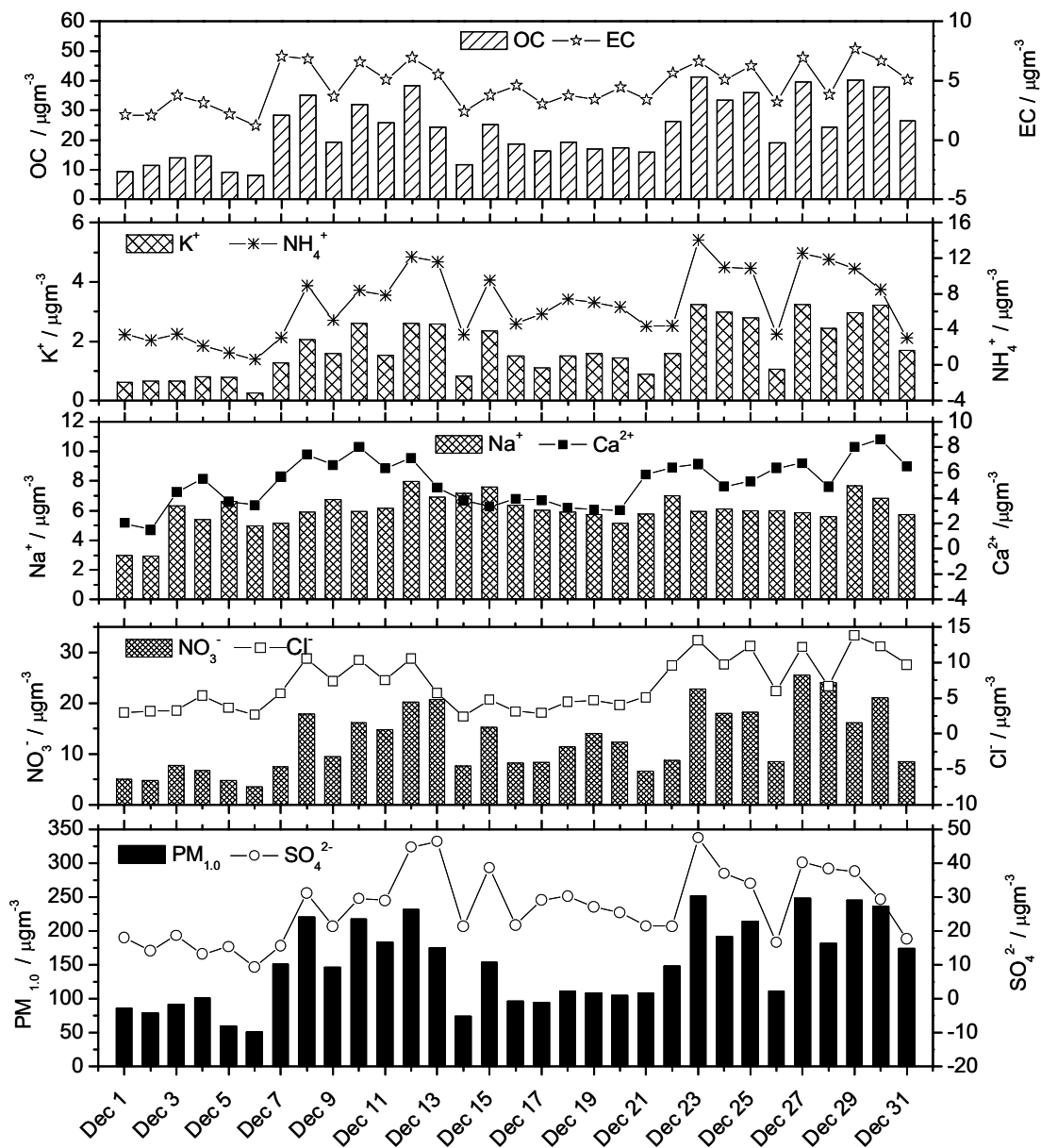


Fig. 1. Temporal variation of mass concentration for PM<sub>1</sub> and its chemical species in winter.

value of  $149.7 \mu\text{g}/\text{m}^3$ . The  $\text{PM}_{10}$  mass exceeded the 24-hour America  $\text{PM}_{2.5}$  standard of  $35 \mu\text{g}/\text{m}^3$  and annual mean value of  $15 \mu\text{g}/\text{m}^3$  concentrations for 31 days observation all (EPA, 2006). Our result can also compare with past studies in other cities. Lee *et al.* (2006) conducted the sampling with a Partisol-Plus Model 2025 Sequential Air Sampler operated at  $16.7 \text{ L}/\text{min}$  at a road site. The literature reported that the  $\text{PM}_{10}$  level in Hong Kong during winter was  $40.9 \mu\text{g}/\text{m}^3$ . Another study by Li and Lin (2002) demonstrated the  $\text{PM}_{10}$  loading in an ambient general site (Chung-Shan) and a traffic monitoring station (Da-Tung) in Taipei were  $14.0 \mu\text{g}/\text{m}^3$  and  $37.6 \mu\text{g}/\text{m}^3$  respectively. As a result, remarkable high  $\text{PM}_{10}$  levels were observed in winter in Xi'an and controlling measurement should be taken by the local government to alleviate the submicron particles pollution. High  $\text{PM}_{10}$  levels should be linked to increasing emission from coal combustion and biomass burning for heating as we discussed in following sections.

#### **Composition of Ionic Species in $\text{PM}_{10}$**

The total ions concentration was  $68.0 \pm 25.4 \mu\text{g}/\text{m}^3$  on average, which occupied about 46% of  $\text{PM}_{10}$  mass. The result indicated water-soluble ions were the major components of submicron particles in Xi'an in winter. Prior literatures reported that water-soluble ions occupied one third or more in  $\text{PM}_{2.5}$  mass in Chinese urban regions (He *et al.*, 2001; Hu *et al.*, 2002; Wang *et al.*, 2002; 2006). The mean concentrations for five cations of  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  were  $6.8 \pm 3.8 \mu\text{g}/\text{m}^3$ ,  $6.0 \pm 1.1 \mu\text{g}/\text{m}^3$ ,  $5.2 \pm 1.8 \mu\text{g}/\text{m}^3$ ,  $1.8 \pm 0.9 \mu\text{g}/\text{m}^3$

and  $0.5 \pm 0.2 \mu\text{g}/\text{m}^3$ , respectively, which account for 9.8%, 9.2%, 8.1%, 2.4% and 0.8% in total ions concentration. For the ambient concentrations of  $\text{NO}_2^-$  and  $\text{Br}^-$  were below the IC detection limitation, other four anions were discussed here in detail. The mean mass concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$  were  $27.2 \pm 10.5 \mu\text{g}/\text{m}^3$ ,  $12.7 \pm 6.4 \mu\text{g}/\text{m}^3$ ,  $7.0 \pm 3.6 \mu\text{g}/\text{m}^3$  and  $0.9 \pm 0.2 \mu\text{g}/\text{m}^3$ , which occupied to 40.0%, 17.9%, 10.1% and 1.4% in total ions mass concentrations, respectively. Our observation demonstrated that  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were major ions in  $\text{PM}_{10}$ , which account for 95.3% in total water-soluble ions mass concentration.

The relationships between 11 chemical species were calculated as shown in Table 1.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have a good relationship and with a high correlation coefficient value of 0.9, indicating that they originated from the same source. The molar ratio of  $\text{Mg}^{2+}/\text{Ca}^{2+}$  was a useful indicator to identify their source. As Xi'an is located at south margin of Chinese Loess Plateau, it was often suffered eolian dust from the arid and semi-arid regions in northwest China. Calculation of the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  molar ratio in  $\text{PM}_{10}$  in Xi'an was 0.18 in average (ranges from 0.14 to 0.25), which is a little higher than the value observed in soil dust of 0.15 (Osada *et al.*, 2002). A little abundance of  $\text{Mg}^{2+}$  in  $\text{PM}_{10}$  indicated not only soil dust, but other sources, such as combustion during heating season, also have an important contribution to  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (Zhang *et al.*, 2002). It was demonstrated that water-soluble K has been commonly used as a marker for biomass burning (Andrea *et al.*,

1983; Watson *et al.*, 2001). Recently study by Cao *et al.* (2008) reported that  $K^+$  was in a relative low level in fugitive dust of  $PM_{10}$  fraction in Xi'an. In fact, wheat straw and maize stalks are burned for heat during winter in suburban region of Xi'an. As Xi'an is an inland city, marine influences on the urban aerosol particles can be disregarded. In addition, the Cl/Na ratio in the  $PM_{10}$  samples was 4.35 in average, which were much higher than 1.8 of Cl to Na ratio of sea salt (Pytkowicz *et al.*, 1975). The relative abundance of Cl compared with Na can be explained by emissions from suburban biomass burning because strong relationship between  $Cl^-$  and  $K^+$  was observed (Table 1).

As ammonium, sulfate and nitrate were the major components of  $PM_{10}$ , the source and formation of these species are our primary concern. The high  $NH_4^+$  concentrations in aerosols from Xi'an may be related to the use of fertilizers on the Guanzhong Plain as well as contributions from local sanitary wastes (Zhang *et al.*, 2002).  $SO_4^{2-}$  commonly represents the stationary pollution sources such as coal combustion, while nitrate represents the mobile sources like vehicle exhaust (Arimoto *et al.*, 1996; Hu *et al.*, 2002; Yao *et al.*, 2002). High concentration of sulfate should be connected to the coal consumption for heat in winter. While high  $NO_3^-$  concentration should attribute to mobile emission source. It can be seen that  $NH_4^+$  was strongly correlated with  $SO_4^{2-}$  and  $NO_3^-$  in  $PM_{10}$ , suggesting that these three major ions were in the form of ammonium sulfate/bisulfate and ammonium nitrate. To evaluate the chemical form among

ammonium sulfate/bisulfate and ammonium nitrate and ammonium, comparisons between calculated and observed ammonium concentrations were conducted (Zhang *et al.*, 2002). If one assumes that the dominant compounds are  $NH_4HSO_4$  and  $NH_4NO_3$ , one can calculate ammonium ion using Eq. (1); whereas if ammonium is in the form of  $(NH_4)_2SO_4$  Eq. (2) applies:

$$\text{Ammonium } (\mu\text{g}/\text{m}^3) = 0.29 (\text{NO}_3^-) + 0.19 (\text{SO}_4^{2-}) \quad (1)$$

$$\text{Ammonium } (\mu\text{g}/\text{m}^3) = 0.29 (\text{NO}_3^-) + 0.38 (\text{SO}_4^{2-}) \quad (2)$$

where  $(\text{NO}_3^-)$  and  $(\text{SO}_4^{2-})$  represent the mass concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

The correlation of calculated versus observed concentrations is higher when Eq. (1) is used; and this suggests that these three secondary ions exist mostly in the form of  $NH_4HSO_4$  and  $NH_4NO_3$ .

Ion balance calculations are useful for evaluating the acid-base balance of aerosol particles. The microequivalents of cation and anion in  $PM_{10}$  samples were calculated using following equations:

$$C \text{ (cation microequivalents)} = \text{Na}^+/23 + \text{H}_4^+/18 + \text{K}^+/39 + \text{Mg}^{2+}/12 + \text{Ca}^{2+}/20 \quad (3)$$

$$A \text{ (anion microequivalents)} = \text{F}^-/19 + \text{Cl}^-/35.5 + \text{NO}_3^-/62 + \text{SO}_4^{2-}/48 \quad (4)$$

Fig. 2 showed the relationship between cation and anion equivalents for all samples. A

**Table 1.** Correlation coefficients between chemical species.

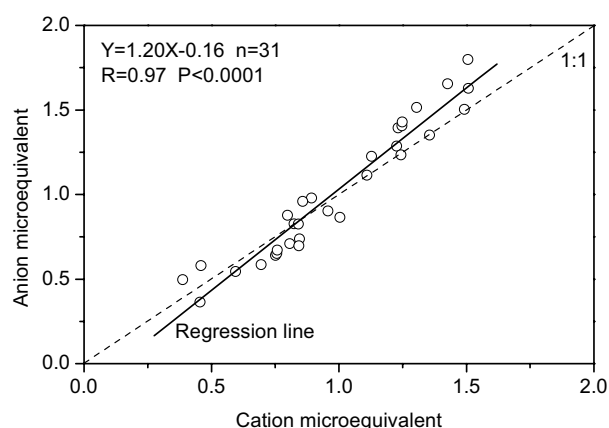
R	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	OC	EC
Na <sup>+</sup>	1	0.40	0.44	0.62	0.49	0.39	0.37	0.31	0.46	0.42	0.41
NH <sub>4</sub> <sup>+</sup>		1	0.92	0.45	0.49	0.67	0.71	0.93	0.98	0.79	0.66
K <sup>+</sup>			1	0.62	0.63	0.74	0.85	0.88	0.88	0.89	0.78
Mg <sup>2+</sup>				1	0.90	0.75	0.77	0.50	0.43	0.73	0.74
Ca <sup>2+</sup>					1	0.77	0.83	0.58	0.42	0.77	0.77
F <sup>-</sup>						1	0.85	0.63	0.64	0.78	0.69
Cl <sup>-</sup>							1	0.70	0.63	0.93	0.85
NO <sub>3</sub> <sup>-</sup>								1	0.87	0.72	0.62
SO <sub>4</sub> <sup>2-</sup>									1	0.67	0.62
OC										1	0.94
EC											1

strong correlation ( $R = 0.97$ ) between cation and anion equivalents was observed, which indicates that these nine ionic species in Eq. 3 and 4 were the major ions existed in submicron particles in Xi'an. We note the slope of the orthogonal regression line is higher than the unity, which implies PM<sub>1</sub> samples tend to be acidic. In addition, other anions, such as CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> were not investigated in this study. Prior study demonstrated their concentrations are typically low in aerosol samples from China (Wang *et al.*, 2005). The huge consumption of coal during heating season should carry the responsibility for the acidity of PM<sub>1</sub> samples.

### Concentration and Sources of Carbonaceous Aerosol

The temporal variation of mass concentration for PM<sub>1</sub> OC and EC was given as shown in Fig. 1. The mean levels of PM<sub>1</sub> OC and EC were demonstrated to be 23.7  $\mu\text{g}/\text{m}^3$  and 4.6  $\mu\text{g}/\text{m}^3$ , respectively. OC levels

were in the range of 8.2  $\mu\text{g}/\text{m}^3$ -41.3  $\mu\text{g}/\text{m}^3$ , and EC was in the range of 1.2  $\mu\text{g}/\text{m}^3$ -7.7  $\mu\text{g}/\text{m}^3$ . In addition, OC and EC attributed to 15.8% and 3.1% of PM<sub>1</sub> mass. Lee *et al.* (2006) investigated the carbon concentration via the same analysis technique in Hong Kong during Jan and Feb.



**Fig. 2.** Total anion microequivalents versus total cations microequivalents.

The mean OC and EC concentrations at a heavy traffic sampling site were 8.3  $\mu\text{g}/\text{m}^3$  and 9.0  $\mu\text{g}/\text{m}^3$  respectively. In generally, OC

concentration in Hong Kong at roadside is lower than the value in Xi'an of this research, but EC levels in Hong Kong is a little higher than that measured in Xi'an. Another literature by Li and Lin (2002) reported the PM<sub>1</sub> carbon measurement at an ambient general site (Chung-Shan) and a traffic monitoring station (Da-Tung) in Taipei area by using a combustion technique. At Chung-Shan, PM<sub>1</sub> OC and EC concentrations on average were 3.4 µg/m<sup>3</sup> and 1.3 µg/m<sup>3</sup> in winter. While OC and EC levels in Da-Tung were 11.5 µg/m<sup>3</sup> and 11.3 µg/m<sup>3</sup> in August and 19.0 µg/m<sup>3</sup> and 13.4 µg/m<sup>3</sup> in June. In generally, carbon concentrations at Chung-Shan were much lower than those observed at Xi'an and Hong Kong. In addition, PM<sub>1</sub> OC level at the traffic monitoring station in Taipei was higher than that found in Hong Kong, but lower than the value in Xi'an. But the PM<sub>1</sub> EC concentration in Da-Tung was much higher than those found both in Hong Kong and Xi'an.

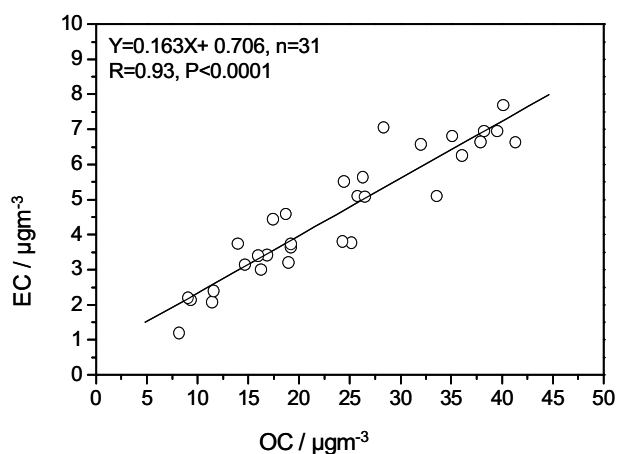
The correlation between OC and EC was used as an indicator of the source of carbonaceous aerosol. As shown in Fig. 3, a strong correlation between OC and EC was observed in PM<sub>1</sub> with a correlation coefficient of 0.93, indicating that OC and EC were from the same sources. The OC/EC ratios in PM<sub>1</sub> were in the range of 3.7-6.8 with a mean value of 5.2. The OC/EC ratios in current study are much higher than those observed at Hong Kong and Taipei (Lee *et al.*, 2006; Li and Lin, 2002), indicating PM<sub>1</sub> carbon in Xi'an is more abundant in organic carbon and shortage of elemental carbon. Some literatures studied the source profiles of OC/EC ratios applicable to

speciated the emission inventories and receptor model of source apportionment (Cao *et al.*, 2003, 2005; Chow *et al.*, 2004; Dan *et al.*, 2004; Duan *et al.*, 2004). Watson *et al.* (2001) reported that the OC/EC ratios for coal combustion, vehicle emission, and biomass burning were 2.7, 1.1 and 9.0, respectively. Meanwhile, the author indicates that the source profiles are influenced heavily by many factors, such as the chemical composition of fuel, pollution control devices, sampling methods, sampling periods, and analytical techniques. Cao *et al.* (2005a) gave the OC/EC ratio source profile in PM<sub>2.5</sub> in Xi'an. That is the OC/EC ratios were 12.0 for coal combustion, 4.1 for vehicle exhaust, and 60.3 for biomass burning. From these two studies, we inferred that the source profile of carbonaceous aerosol were more complicated and influenced by many factors. Moreover, EC originates from the incomplete combustion of carbon containing materials directly, and does not form in atmosphere due to its nearly inert property. While ambient OC includes primary OC (originate from the combustion process directly) and secondary OC (produced by gas to particle conversion or chemical reaction in atmosphere). Only the ratio of primary OC to EC was proper to conducting the source identification. Therefore, one should care when using OC/EC ratio to trace the carbonaceous aerosol source. The strong correlation between K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> with OC and EC showed in Table 1, implying biomass burning, coal combustion, and vehicle exhaust were the major contributor to PM<sub>1</sub> carbon in Xi'an.

The concentration of organic matter (OM) in



atmosphere can be estimated by multiplying OC by 1.6 (Turpin and Lim, 2001). Total carbonaceous aerosol (TCA) was calculated by the sum of OM and EC. In winter, the mean TCA concentration is  $42.5 \mu\text{g}/\text{m}^3$ , which attributed to 28.4% of  $\text{PM}_{10}$  mass. It showed that carbonaceous aerosol is one of the major components of  $\text{PM}_{10}$ .



**Fig. 3.** Relationship between OC and EC.

By using the TOR method, the concentrations of OC1, OC2, OC3, OC4, EC1,

EC2, EC3 and OP were measured separately in a run by the Thermal/Optical Carbon Analyzer. Carbon abundances in each of these fractions vary with different carbon sources (Watson *et al.*, 1994; Cao *et al.*, 2006). To determine the characteristic source and the contributing factors of carbonaceous aerosol observed in Xi'an, factor analysis (SPSS 8.0 software) was performed on the eight carbon fractions. The analysis was done with principal components extraction and varimax normalized rotation. The factor was not considered if its eigenvalue was  $< 1$ . Table 2 showed the results of factor analysis. Three factors were extracted to explain the sources and their contribution to carbonaceous aerosol. For all samples, these three factors were found to be statistically significant and explained 93% of the total variance. Factor 1 was highly loaded with OC1, OC2, OC3, OC4 and EC1. This factor was demonstrated to represent the coal combustion and gasoline vehicle exhaust (Chow *et al.*, 2004). Factor 2 was more abundant of high

**Table 2.** Factor analysis result of eight carbon fraction.

	Factor 1	Factor2	Factor3
OC1	0.761	0.233	0.344
OC2	0.813	0.197	0.438
OC3	0.901	0.186	0.367
OC4	0.911	0.158	0.302
EC1	0.63	0.147	0.76
EC2	0.317	0.906	0.106
EC3	6.61E-02	0.967	8.60E-02
OP	0.487	0.103	0.864
Variance	45.3%	24.2%	23.5%
	Coal Combustion and Gasoline Exhaust	Diesel Exhaust	Biomass Burning

temperature EC2 and EC3 and should represent diesel vehicle exhaust (Watson *et al.*, 1994). The highly loading of OP and EC1 in Factor 3 reflects contribution of biomass burning. Furthermore, the source attribution can be resolved for carbonaceous aerosol in PM<sub>1</sub>. 45.3% of carbonaceous aerosol can explain by coal combustion and gasoline vehicle exhaust, 24.2% by diesel vehicle exhaust and 23.5% by biomass burning.

#### Material Balance of PM<sub>1</sub>

The relative contributions of chemical species to PM<sub>1</sub> mass in winter is shown in Fig. 4. Carbonaceous aerosol, sulfate and nitrate were major chemical species and they attributed to 27.5%, 18.1% and 9.1% of PM<sub>1</sub> mass, respectively. As elemental composition were not identified in this study, soil dust and other uncertain fractions occupied to 34.2%. Therefore further work is recommended to identify those substances that make up the missing mass and to investigate the seasonal variation of PM<sub>1</sub>.

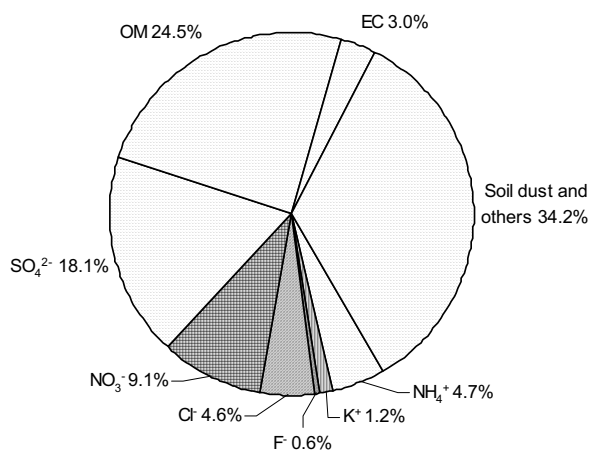


Fig. 4. Material balance of PM<sub>1</sub> in winter.

## CONCLUSIONS

PM<sub>1</sub> level in winter in Xi'an was 149.7 µg/m<sup>3</sup>, which was higher than those observed in Hong Kong and Taipei. Ionic species and carbonaceous aerosol were dominant of PM<sub>1</sub>, which attributed 46.0% and 27.5% to the total particle mass. SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> were major ions, which occupied to 18.1%, 9.1%, 4.6% and 4.7% of PM<sub>1</sub> mass. The three secondary ionic species were in the form of NH<sub>4</sub>HSO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. OC concentration in Xi'an in winter is higher than those at Hong Kong and Taipei. High OC/EC ratios were observed in Xi'an, which maybe due to more complicated sources of PM<sub>1</sub> carbon. Factor analysis for the eight carbon fractions demonstrated that coal combustion and gasoline exhaust, diesel exhaust, and biomass burning were three significant factors and explained 93% contributions of carbonaceous aerosol. The information obtained here is especially important for helping to enhance the current understanding of fine particles pollution problems confronting Xi'an.

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