Characterization of PM_{10} atmospheric aerosol at urban and urban background sites in Fuzhou city, China

Lingling Xu · Xiaoqiu Chen · Jinsheng Chen ·
Fuwang Zhang · Chi He · Ke Du · Yang Wang

Abstract

Background PM_{10} aerosol samples were simultaneously collected at two urban and one urban background sites in Fuzhou city during two sampling campaigns in summer and winter. PM_{10} mass concentrations and chemical compositions were determined.

Methods Water-soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}), carbonaceous species (elemental carbon and organic carbon), and elements (Al, Si, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, and Pb) were detected using ion chromatography, thermal/optical reflectance, and proton-induced X-ray emission methods, respectively.

Results PM_{10} mass concentrations, as well as most of the chemical components, were significantly increased from urban background to urban sites, which were due to enhanced anthropogenic activities in urban areas. Elements, carbonaceous species, and most of the ions were more uniformly distributed at different types of sites in winter, whereas secondary ion SO_4^{2-}, NO_3^-, and NH_4^+ showed more evident urban-background contrast in this season. The chemical mass closure indicated that mineral dust, organic matters, and sulfate were the most abundant components in PM_{10}. The sum of individually measured components accounted for 86.9–97.7% of the total measured PM_{10} concentration, and the discrepancy was larger in urban area than in urban background area.

Conclusion According to the principal component analysis–multivariate linear regression model, mineral dust, secondary inorganic ions, sea salt, and motor vehicle were mainly responsible for the PM_{10} particles in Fuzhou atmosphere, and contributed 19.9%, 53.3%, 21.3%, and 5.5% of PM_{10}, respectively.

Keywords PM_{10} · Water-soluble ions · Elements · Carbonaceous species · Mass balance closure · PCA–MLR

L. Xu · J. Chen (✉) · F. Zhang · C. He · K. Du · Y. Wang
Key Lab of Urban Environment and Health,
Institute of Urban Environment, Chinese Academy of Sciences,
Xiamen 361021, China
e-mail: jschen@iue.ac.cn

K. Du
e-mail: kdu@iue.ac.cn

X. Chen
Environmental Monitoring Center of Fujian,
Fuzhou 350003, China

L. Xu · F. Zhang
Graduate School of Chinese Academy of Sciences,
Beijing 100049, China

1 Introduction

Scientific research has focused on human exposure to different pollutants in particulate matter (PM) in recent decades due to their significant impact on human health and climate change (Polissar et al. 2001; Duarte et al. 2008; Pisoni and Volta 2009). Epidemiological studies have demonstrated that PM exposure was associated with the occurrence of acute respiratory infections, lung cancer, and chronic respiratory and cardiovascular diseases (Chiaverini 2002; Samet et al. 2000; Sorensen et al. 2003). Although fine particle (e.g., $PM_{2.5}$) exhibited stronger relation with health risk than PM_{10} aerosol, measurement of PM_{10} was also necessary because it contributed to health effects, such as exacerbation of asthma attacks (Kappos et al. 2004). PM_{10} particle is a complex mixture of ammonium, sulfate, nitrate, elemental and organic carbons, mineral dust, and trace elements. The chemical

composition of atmospheric PM has been investigated in previous studies. The results indicated that the PM mass concentration and the fraction of composition varied on the different types of sites (e.g., the urban, rural, roadside, and background areas) (Hueglin et al. 2005; Vercauteren et al. 2011). Both natural sources and anthropogenic sources, such as road dust, vehicular emissions, secondary aerosol, sea salt, and oil burning, could influence the aerosol characteristics (Mishra et al. 2004; Almeida et al. 2005; Tsai and Chen 2006; Minguillon et al. 2008; Moreno et al. 2009; Guo et al. 2009).

Fuzhou, with an area of 11,968 km^2 and a population of ~7 million, is the political and economic center of Fujian province and located in western coast of Taiwan Strait. Fuzhou has a typical subtropic climate and abundant precipitation of 1,342.5 mm per year. The number of motor vehicles in Fuzhou city has increased up to about one million at the beginning of year 2011. Like other mega cities in China such as Beijing, Hangzhou, and Guangzhou (Zhang et al. 2010; Cao et al. 2009; Tan et al. 2009), the fast industrialization and urbanization process in Fuzhou city also introduced more air pollution problems. The Fuzhou atmosphere is relatively stable, with frequent calm wind and temperature inversion in winter and spring. Prevailing wind direction is southerly in summer and northeasterly in winter. Although more and more air pollution occurred in Fuzhou city during the past decade, characterizations and source apportionment of PM$_{10}$ aerosol in different locations are scant. Therefore, this study aimed to characterize the

chemical compositions of PM$_{10}$ atmospheric aerosol at two urban and one urban background sites in summer and winter seasons and to identify the possible sources for PM$_{10}$ in Fuzhou city using principal components analysis–multivariate linear regression (PCA–MLR) method.

2 Methodology

2.1 Sampling sites and sample collection

Two sampling campaigns were conducted during the summer time and the winter time in Fuzhou city. The samples with abnormal (extremely high or low) PM$_{10}$ concentrations were excluded, and for comparison purposes, the samples collected simultaneously at two urban sites (Ziyang and Wusibei) and one urban background site (Gushan; see Fig. 1), i.e., samples in September 20 and 24–28, 2007 and January 15–17 and 21–24, 2008, were analyzed. Although the number of samples was limited, the standard deviation of parallel samples (in ion detection) or the two measurements (in elements and carbonaceous species detection) of each compound was less than 10%. To make the PCA model more stable, appropriate number of variables was applied due to the limited samples in PCA, and the MLR was run using a stepwise method for PCA-derived variables selection. For these reasons, we believe that the data reported here are representative for the long-term averages in the areas studied. Ziyang (26°4′45.1″ N; 119º19′8.2″

Fig. 1 Two urban (Ziyang and Wusibei) and one urban background (Gushan) sampling sites in Fuzhou city, China
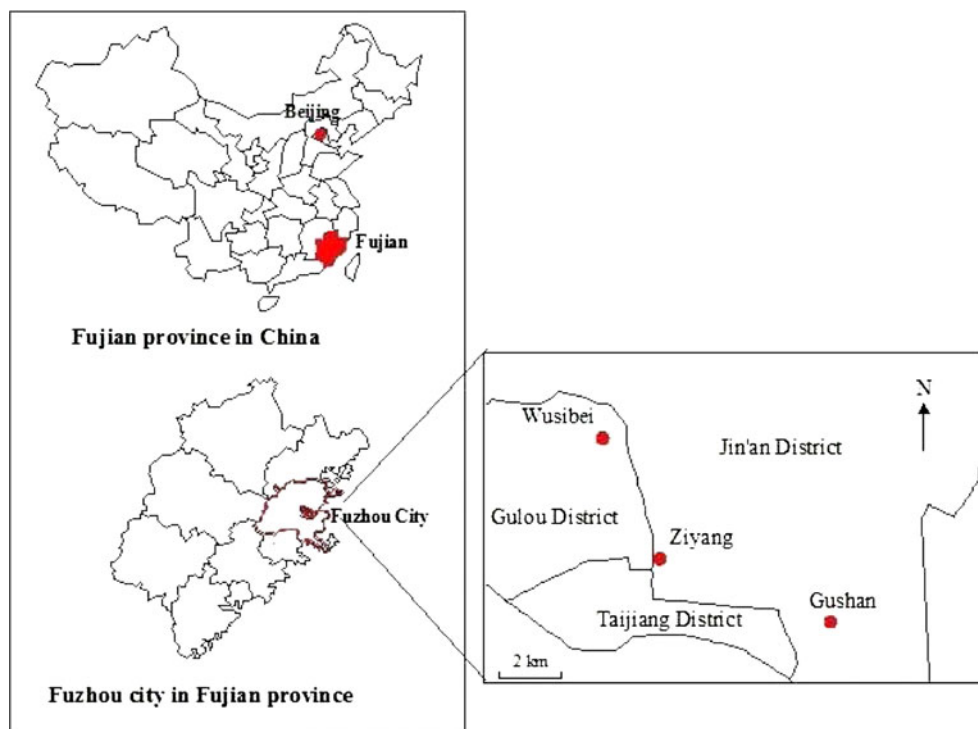
E) was located about 30 m south of Fuma Road with dense traffic, representing a traffic and residential area. Wusibei (26°6′33.3″ N; 119°17′56.2″ E) was situated on the west side 200 m away from busy Wusi Road, which acted as a commercial and residential area. An urban background site was chosen in Gushan mountain scenic spot (26°3′15.5″ N; 119°23′22.6″ E), where no polluted sources surround but the ring road up to the mountain. However, Gushan site was about 8 km away from urban areas and therefore to a certain extent was affected by pollutants transported from urban areas.

The PM_{10} aerosol samples were collected by medium-volume samplers (Tianhong Th-150C Ш, China) with a flow rate of 100 $L min^{-1}$ for 23 h (from 8:00 a.m. to 7:00 a.m. the next day), and retained on quartz fiber filters (QFFs, Ø90 mm, Whatman) and polypropylene filters (PPFs, Ø90 mm, Whatman), respectively. The samplers were mounted on the flat roofs of buildings at heights of about 23 m at Ziyang, 22 m at Wusibei, and 15 m at Gushan site above the ground, respectively. QFFs, prepared for the analysis of water-soluble inorganic ions and carbonaceous species, were pre-annealed at 450°C for 5 h to eliminate organic species, while PPFs were preheated at 60°C for 2 h for element analysis. Filters were stabilized under constant temperature (25±1°C) and relative humidity (50±1%) before weighed and then kept in baked aluminum foil within sealed polyethylene plastic bags before and after sampling. Loaded filters were preserved at −20°C until extraction.

2.2 Chemical analysis

PM_{10} mass loading was obtained gravimetrically with an analytical balance (Sartorius 0.01 mg, Germany) and determined by the difference between the weights of QFFs before and after sampling. The measurement precision was less than ±5% of the total aerosol mass of field samples.

Elements were determined in a polypropylene filter by proton-induced X-ray emission method at the 2.5-MeV proton bombardments in the Institute of Low Energy Nuclear Physics of Beijing Normal University. The measured 17 elements included Al, Si, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, and Pb.

Three anions (Cl^-, NO_3^-, and SO_4^{2-}) and five cations (NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}) were analyzed in one half of quartz filter by ion chromatography (ICS-3000, Dionex, USA). The details of analytical procedure were given elsewhere (Zhao et al. 2011). Standard reference materials, purchased from the National Research Center of Certified Reference Materials, China, were used for the quality assurance. The result was corrected by blank value, and the recovery rates were in the range of 80–120%.

One fourth of quartz filter samples was analyzed for organic carbon (OC) and elemental carbon (EC) by IMPROVE thermal/optical reflectance method with DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, USA). A typical punch size of 0.5 cm^2 from the filter was heated stepwise at 140°C (OC1), 280°C (OC2), 480°C (OC3), and 580°C (OC4) in a He atmosphere, and 580°C (EC1), 740°C (EC2), and 840°C (EC3) in an O_2/He (2%/98%, v/v) atmosphere. After analysis, concentrations of four OC fractions, OP (a pyrolyzed carbon fraction determined when reflected or transmitted laser light attained its original intensity after O_2 was added to the analyzer's atmosphere) and three EC fractions, were obtained. According to the IMPROVE protocol, OC was defined as OC1+OC2+OC3+OC4+OP and EC as EC1+EC2+EC3−OP. The detection limit for the carbon analyzer was 0.05 μg carbon cm^{-2} for a typical punch size of 0.5 cm^2.

2.3 The mass balance closure of PM_{10}

The mass balance of PM_{10} aerosol was performed based on several assumptions. Firstly, the trace elements were assumed to exist as elemental forms. Secondly, based on the crustal elements of Al, Mg, K, Ca, Fe, and Si (preferred to exist in oxidation forms), mineral dust was estimated as mineral dust=1.89×Al+1.66×Mg+1.21×K+1.40×Ca+1.43×Fe+2.14×Si (Hueglin et al. 2005). And lastly, organic matter (OM) concentration was calculated by multiplying OC concentration by a constant factor of 1.4 to account for unmeasured hydrogen and oxygen mass (Christoforou et al. 2000; He et al. 2001).

3 Results and discussion

3.1 PM_{10} mass concentrations

The average and standard deviation (SD) for component concentrations of PM_{10} at Ziyang, Wusibei, and Gushan sites are summarized in Table 1. It could easily be seen that a large portion of investigated components showed increasing mass concentration shifting from urban background to urban sites. Another feature of higher mass concentrations in winter than in summer also could be drawn from chemical compositions data set. Seasonally, the mean concentrations and SD of PM_{10} were 38.13±5.56, 32.69±4.15, and 23.92±6.13 μg/m³ in summer, a factor of 1.8, 1.7, and 1.8 lower than the values of 69.62±30.10, 54.80±22.75, and 41.93±6.93 μg/m³ in winter at Ziyang, Wusibei, and Gushan sites, respectively. The seasonality was likely associated to the strength of local and regional sources. Frequent calm wind and inversion events in winter and more precipitation in summer might be also partly responsible for this seasonality. In urban areas, PM_{10} mass concentrations at Ziyang site were slightly higher than those at Wusibei site during

Table 1 Average concentrations and standard deviations of chemical components in PM$_{10}$ aerosol during the sampling periods (elements in nanograms per cubic meter and others in micrograms per cubic meter)

	Urban–Ziyang		Urban–Wusibei		Background–Gushan	
	Summer	Winter	Summer	Winter	Summer	Winter
PM$_{10}$	38.13±5.56	69.62±30.10	32.69±4.15	54.80±22.75	23.92±6.13	41.93±6.93
OC	7.49±2.17	10.97±3.89	5.70±1.43	10.14±4.07	3.22±1.52	6.70±0.86
EC	2.94±0.28	3.10±0.83	2.29±0.17	2.40±0.91	0.94±0.36	1.78±0.35
Cl$^-$	2.48±1.43	4.35±1.21	2.51±1.18	1.52±0.76	1.53±0.64	2.66±0.93
NO$_3^-$	4.30±1.53	10.48±7.68	2.76±0.94	7.27±3.93	2.39±1.48	4.94±1.75
SO$_4^{2-}$	7.97±2.21	16,14±9.61	7.68±2.16	15.23±9.35	7.74±2.25	9.06±1.68
NH$_4^+$	1.04±0.81	7.20±4.84	1.16±1.04	5.39±3.27	1.18±0.77	4.51±1.66
K$^+$	0.16±0.05	0.29±0.17	0.17±0.06	0.33±0.18	0.12±0.08	0.37±0.06
Na$^+$	0.32±0.01	2.51±0.31	0.35±0.01	1.04±0.48	0.34±0.01	2.29±0.28
Ca^{2+}	1.01±0.19	1.56±0..39	0.90±0.16	1.54±0.53	0.25±0.12	0.82±0.10
Mg^{2+}	0.17±0.08	0.18±0.06	0.23±0.10	0.18±0.07	0.21±0.09	0.10±0.02
Al	569±89	589±118	508±132	436±146	237±92	326±215
Si	2,435±269	2,680±440	2,234±451	1,958±604	1,034±428	1,508±801
Mg	71.6±22.7	41.7±3.6	65.4±66.5	36.6±5.5	98.6±50.2	40.5±10.3
K	477±67.1	631±190	480±88	482±145	274±143	519±368
Ca	1,837±274	1,747±344	1,213±183	1,068±377	648±219	648±274
Ti	62.4±14.0	70.2±17.4	45.7±9.9	46.2±16.6	20.5±11.8	38.4±34.8
V	2.3±0.8	3.0±0.9	2.9±1.6	2.1±1.0	1.4±1.1	3.0±1.3
Cr	7.3±2.4	18.5±8.3	7.5±3.7	13.8±5.2	5.0±2.1	9.8±6.3
Mn	35.8±4.9	69.1±25.0	28.5±7.8	48.5±18.9	13.1±7.0	38.6±29.9
Fe	798±97	1,039±212	694±132	729±219	282±123	571±360
Ni	4.3±1.3	6.0±4.0	4.3±1.8	3.5±1.9	2.6±1.1	3.2±2.2
Cu	109±13	370±83	130±32	236±76	21.4±4.6	168±159
Zn	161±66	281±90	245±102	293±89	87±58	210±121
As	10.1±3.2	45.9±22.6	13.7±8.7	29.8±10.5	6.2±3.3	22.6±14.7
Se	5.8±6.4	19.8±8.3	7.3±5.9	9.3±6.8	5.7±4.1	7.1±5.2
Br	11.5±5.5	15.4±6.5	7.8±4.7	11.3±7.2	10.6±6.7	15.6±6.0
Pb	15.8±5.3	27.6±23.4	33.0±26.1	33.0±21.8	18.5±3.3	40.2±36.7

individual season, which could be due to the closer location to major traffic road at Ziyang site than Wusibei site. On average, PM$_{10}$ mass concentrations at urban sites were about 1.5 times of those at urban background site, Gushan, during the entire sampling period. The major chemical components of PM$_{10}$ were grouped as: carbonaceous species, elements (including crustal elements and trace elements), water-soluble inorganic ions, and other materials, which would be further discussed in the following sections.

3.2 Chemical compositions of PM$_{10}$ aerosol

3.2.1 Water-soluble inorganic ions

Water-soluble inorganic ions, including three anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) and five cations (NH$_4^+$, K$^+$, Na$^+$, Ca^{2+}, and Mg^{2+}), were investigated in this study. The sum of these ions contributed up to around half of PM$_{10}$ mass independent from sites and seasons. The concentrations of ions

almost showed comparable or higher levels at urban sites, Ziyang and Wusibei, compared with those at urban background site, Gushan. The highest rates of average concentration at urban to urban background were both for Ca^{2+} in summer (3.8) and winter (1.9), while the lowest rates were 0.9 for Mg^{2+} in summer and 0.8 for K$^+$ in winter. Ion balance was considered a clue of acidity of particles. Anion equivalents (AE) and cation equivalents (CE) were calculated as the following equations:

$$AE = \frac{[SO_4^{2-}]}{48} + \frac{[NO_3^-]}{62} + \frac{[Cl^-]}{35.5} \tag{1}$$

$$CE = \frac{[Na^+]}{23} + \frac{[NH_4^+]}{18} + \frac{[K^+]}{39} + \frac{[Mg^{2+}]}{12} + \frac{[Ca^{2+}]}{20} \tag{2}$$

The AE/CE ratios obtained from this study were 2.1, 1.8, and 2.1 in summer and 1.0, 1.0, and 0.8 in winter at Ziyang, Wusibei, and Gushan sites, respectively. The AE/CE ratio of

1 indicated that all major ions were quantified, while ratios higher than 1 might be ascribed to H^+ that was not counted in calculation, and/or NH_4^+ that partly vaporized into the gas phase. It could be seen that high acidity of atmospheric aerosol presented evidently in summer and that acidic aerosol distributed uniformly among different types of locations in Fuzhou city.

In the sampling campaigns, SO_4^{2-} was the major component, accounting for 21.6–32.4% of PM_{10} mass, followed by NO_3^- (10.0–14.3%) and NH_4^+ (3.1–10.8%). The homogenous distribution of NH_4^+ among different sampling sites might be explained by the fact that ammonium was converted from the precursor gas ammonia originated from agriculture as well as vehicles with catalysts and industrial sources, which have little difference between urban and urban background sites (Sutton et al. 2000). For the same reason, seasonal variations of NH_4^+ concentrations might be resulted from higher precursor concentrations in winter than in summer. Slight spatial variation was observed for SO_4^{2-} in summer, whereas its concentration in winter largely declined from urban to urban background site, which might be attributed to the increased sulfate precursor at urban areas and the enhanced stagnation favored for second conversion in winter time. The NO_3^- concentration also decreased from urban to urban background site, and this contrast was pronounced in winter, which might be due to dense traffic-derived NO_2 at urban locations and low temperature in winter suitable for formation of NH_4NO_3 (Zhao et al. 2011). The mass ratio of NO_3^-/SO_4^{2-} is used as an indicator of relative importance of mobile vs. stationary source of

sulfur and nitrogen in the atmosphere (Wang et al. 2005; Cao et al. 2009). In our study, NO_3^-/SO_4^{2-} ratios in Fuzhou ranged from 0.1 to 0.9, with an average and SD of 0.5±0.2, which were much lower than those of Log Angeles and Rubidoux (2–5) (Kim et al. 2000) in Southern California, where there is little coal combustion. However, the ratios of NO_3^-/SO_4^{2-} in Fuzhou city were relatively high compared to other cities in China (Fig. 2; the ratio at urban site was the average of the two urban sites). The results revealed that stationary sources (e.g., coal combustion) were still predominant in China, but the influence of mobile sources was also important, such as in Fuzhou city. In urban areas, NO_3^-/SO_4^{2-} ratio was close to that in urban background area in winter, which well agreed with similar spatial difference of NO_3^- and SO_4^{2-} as mentioned before. However, in summer, elevated NO_3^-/SO_4^{2-} ratios were found at urban sites. Little difference in SO_4^{2-} concentrations was observed between urban and urban background sites. Therefore, the increased NO_3^- that was converted from traffic-derived NO_2 might be regarded as the major reason for the high NO_3^-/SO_4^{2-} ratio at urban areas in this warmer season.

3.2.2 Elements

Mass concentration ratios of elements and carbonaceous components between urban (the average of the two urban sites) and urban background areas are illustrated in Fig. 3. Most of the elements had higher mass concentrations at urban sites than urban background site (ratios >1), except Mg and Br in both seasons, and V and Pb in winter, which

Fig. 2 The comparison of NO_3^-/SO_4^{2-} ratios between Fuzhou city and other cities in China (*a* Xiao and Liu 2004, *b* Fang et al. 2002, *c* Pathak et al. 2003, *d* Hu et al. 2002, *e* Cao et al. 2009, *f* Wang et al. 2006, *g* Wang et al. 2005, *h* Tan et al. 2009)
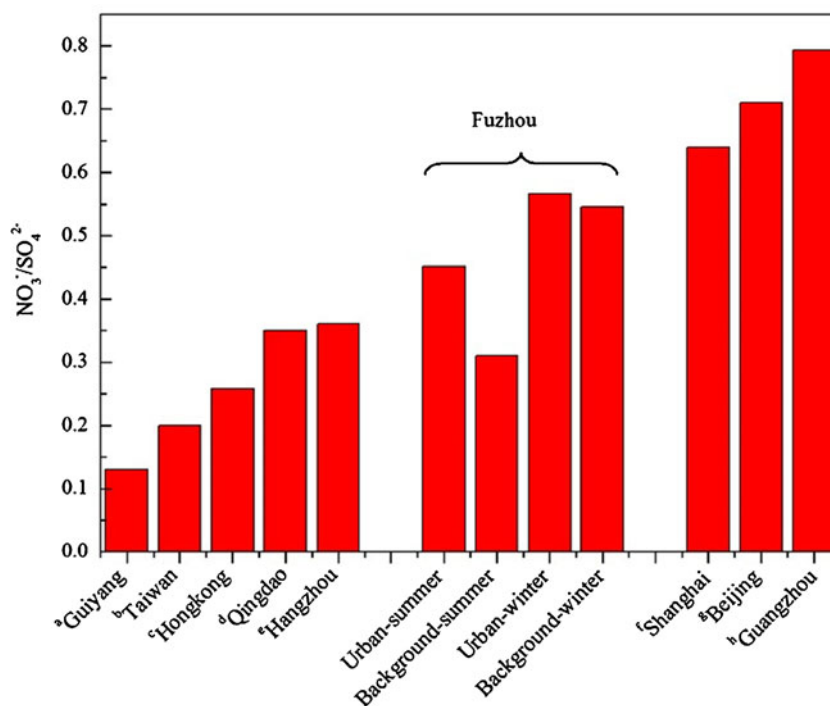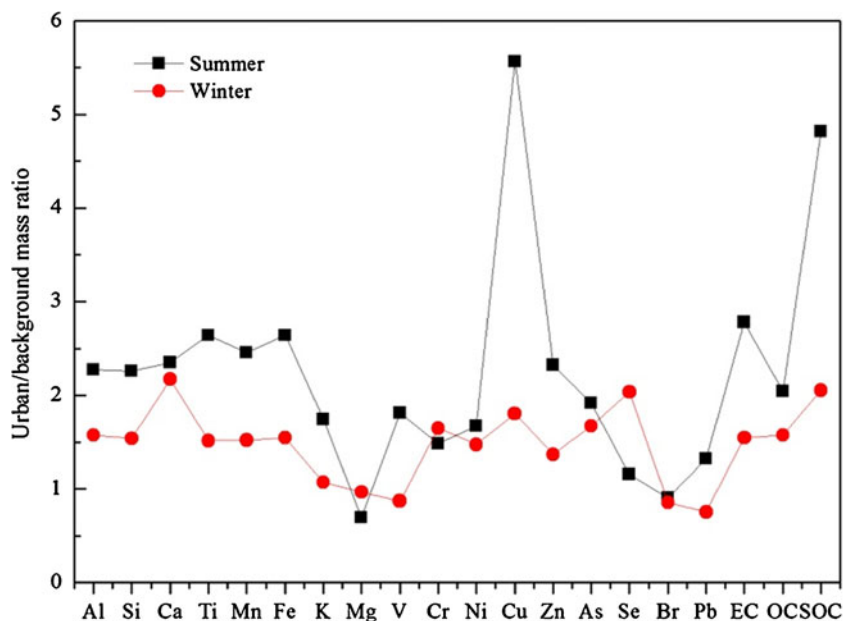
Fig. 3 Mass concentration ratios of elements and carbonaceous components between urban and urban background sites in Fuzhou city

contrarily presented comparable or slightly lower concentrations at urban locations. It is evidently seen, on the whole, that spatial distributions of element mass concentrations were more uniform in winter than in summer, which was surprising due to the known fact that meteorological conditions in summer (such as less inversion) were favorable for pollutant dispersion (e.g., Röösli et al. 2001). Therefore, it could be inferred that the influence of meteorological conditions on pollutant distribution was weak and the local emissions were more uniform among the three sampling sites in the cold season.

Seventeen elements measured in this study could be grouped to crustal elements and trace elements. As anticipated, crustal elements Al, K, Ca, Fe, Si, Ti, and Mn (Formenti et al. 2001) showed constantly increasing mass concentrations from urban background to urban sites, ranging from 1.7 to 2.6 times in summer and a factor of 1.1–2.2 in winter, which could be attributed to increased road traffic emissions due to resuspension of road dust at urban areas. The sudden decline of urban/background ratios of K mass concentration might be due to enhanced biomass burning at urban background site, especially in winter. However, the biomass burning also brought an increase in emission of carbonaceous components, but their urban/background ratios did not decline visibly. This might be explained by other contributors of carbonaceous components that were also enhanced at urban site, such as coal combustion and motor vehicle exhaust (Streets et al. 2001). Ca/Al mass ratio was used to evaluate the contribution of mineral and construction dust (Wang et al. 2005). Distinct urban-background contrast was found for Ca in winter, compared with other crustal elements. Low level of Ca at urban background site in the cold season might be the major reason, which was supported by low Ca/Al ratio in

this sampling campaign due to less construction activities. Trace elements, such as V, Ni, Pb, Cr, Br, Zn, As, Cu, and Se, also existed in PM_{10} aerosol, but only contributed about 1.0% of PM_{10} mass during sampling campaigns. The much variable trend from urban to urban background locations which occurred for these non-crustal elements might be resulted from their random dispersion and mixed sources. Cu, remarkably abundant at urban than urban background site, was mainly derived from wearing of brake pads of vehicles (Amato et al. 2009; Apeagyei et al. 2011). As and Se also yielded higher concentrations (by a factor of 1.9 and 1.2 in summer and 1.7 and 2.0 in winter, respectively) at urban sites, which implicated the increased coal combustion at urban areas. V/Ni levels in this study were anomalously low (0.58 at urban and 0.74 at urban background site) compared with that of Algeciras Bay area (1.20–5.60), indicating the presence of a Ni-rich pollution source. The obvious candidate for such a source is the metallurgical plant (Moreno et al. 2010), which produced more Ni-rich aerosol and dropped the V/Ni value. The weak correlation was obtained between V and Ni ($R^2 < 0.25$, figure was omitted) throughout sampling campaigns, reflecting the mixed sources contaminating this area. Therefore, petrochemical complex, power plant, and shipping might also be considered. Leaded gasoline was legally banned from May 1999 in China; however, lead still presented in gasoline at a low level mainly derived from raw oil; therefore, Pb and Br were considered as tracers of vehicle exhaust in this study. Higher concentrations of Pb and Br were both observed in winter, indicating that enhanced accumulation often occurred under the inversion conditions during this period.

3.2.3 Carbonaceous species analysis

For carbonaceous species, as shown in Fig. 3, elevated OC, EC, and secondary organic carbon (SOC) concentrations appeared at urban locations, and much more pronounced variations were found in summer. As for fractions of OC and EC to PM_{10} mass, comparable proportions in winter distributed from urban to urban background site, while in summer, larger contribution of OC and EC was found in urban areas. Fractions of OC and EC, mass concentrations of SOC, and their ratios are listed in Table 2. The observed OC/EC ratios during the sampling campaigns exceeded 2, which indicated the presence of SOC (Chow et al. 1996). A method to estimate SOC concentrations roughly was given by Turpin and Huntzicker (1995):

$$OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min}$$

where OC_{sec} represented the concentration of secondary OC (SOC), OC_{tot} was the concentration of total OC, and $(OC/EC)_{min}$ was the minimum ratio of OC concentrations to EC observed. There were declined trends of SOC level and SOC fractions to total OC varying from urban to urban background site in each sampling period (2.04 to 0.42 μg/m^3 and 30.9% to 13.1% in summer and 2.36 to 1.15 μg/m^3 and 22.4% to 17.1% in winter). The spatial variations might be accounted for the enhanced emission of organic precursor at urban areas.

3.3 The mass balance closure

The major chemical components which were considered for mass closure were mineral dust, trace elements, OM, EC, sulfate, nitrate, ammonium, and other materials. Figure 4 displays the fractions of grouped components at urban and background sites during sampling periods. At urban sites, chemical compositions in summer obeyed the order of mineral dust>OM>SO_4^{2-}>NO_3^->EC>NH_4^+>trace elements, while in winter, the sequence was SO_4^{2-}>OM>mineral

Table 2 Fractions of OC and EC to PM_{10} mass, concentrations of SOC, and ratios of carbonaceous species

	Urban[a]		Urban background	
	Summer	Winter	Summer	Winter
SOC (μg/m^3)	2.04	2.36	0.42	1.15
OC/PM_{10} (%)	18.6	17.0	13.5	16.0
EC/PM_{10} (%)	7.4	4.4	3.9	4.2
SOC/OC (%)	30.9	22.4	13.1	17.1
OC/EC	2.5	3.8	3.4	3.8

[a] Averaged at two urban sites

dust>NO_3^->NH_4^+>EC>trace elements. Mineral dust and OM had much more partition in PM_{10} mass at urban than urban background site in summer, with the proportions of 28.0% and 26.1% compared to that of 18.7% and 18.9%, whereas SO_4^{2-} made maximum contribution (32.4%) at urban background site, while it only took 22.1% of PM_{10} mass at urban sites. The higher SO_4^{2-} partition in PM_{10} at urban background site could be resulted from the coal-fired power plants with huge capacity (2,600 MW) located about 12 km east of Gushan. In winter, almost all components showed slightly lower portions at urban background than those of urban sites, except nitrate, but more unaccounted and/or not analyzed mass presented at urban background area.
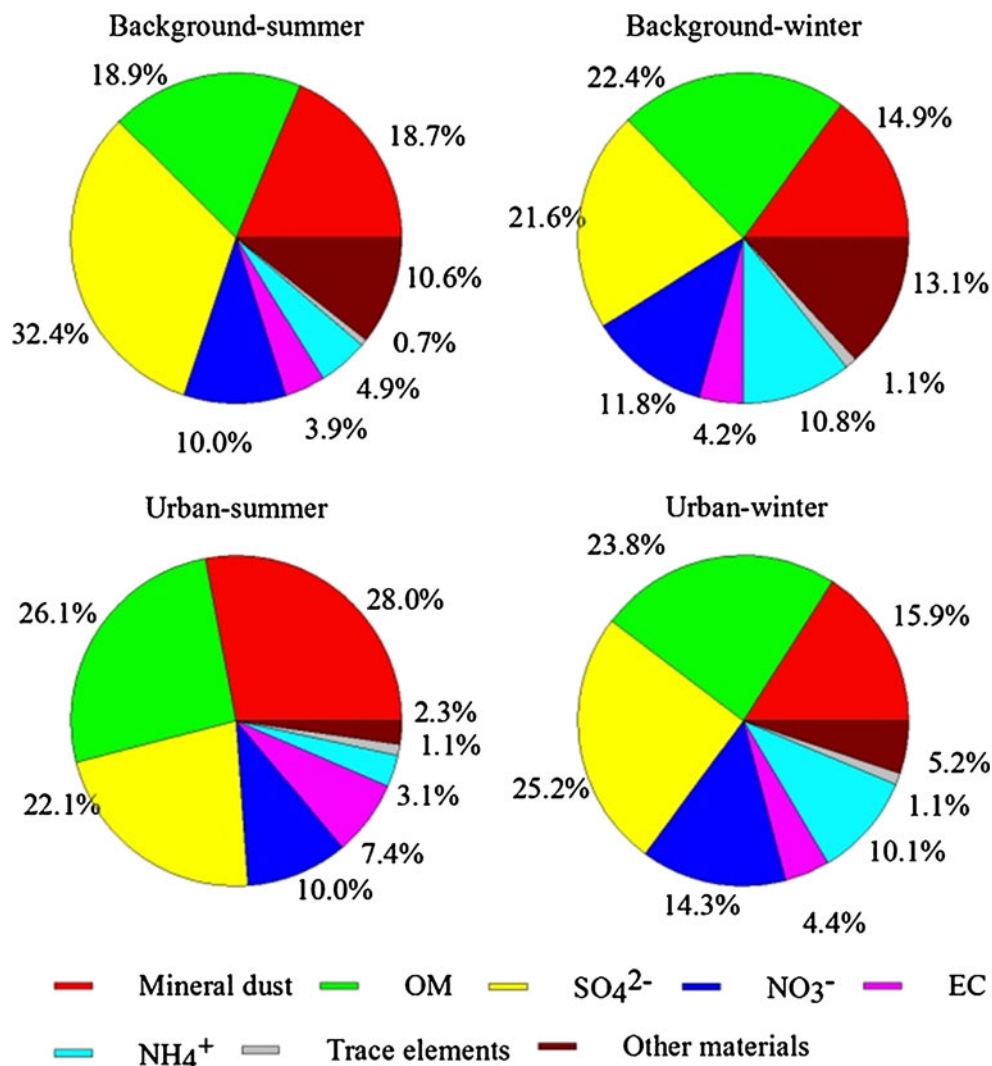
As previous studies reported (Chow et al. 1994; Heintzenberg et al. 1998; Röösli et al. 2001; Putaud et al. 2004; Hueglin et al. 2005), it was hard to achieve total mass closure of measured PM mass concentrations and the sum concentrations of detected components. At urban locations, the undetected materials constituted 2.3% in summer and 5.2% in winter to the total PM_{10}, while at urban background site constituted 10.6% and 13.1%, respectively. That is, larger portion of unmeasured material occurred in winter and at urban background site. There were several reasons responsible for the discrepancy between PM mass and the sum of measured components. For mineral dust, different selected crustal elements in calculation might lead to discrepancy. Cao et al. (2009) estimated the soil dust from the oxides of indicator elements Al, Si, Ca, Fe, and Ti, with conversion factors of 2.2, 2.49, 1.63, 2.42, and 1.94, respectively. According to this method, much higher fractions of mineral dust were obtained in our study, with discrepancy of 1.7% throughout the sampling period in urban background area and 2.5% in winter and 4.2% in summer in urban areas. The varied discrepancies of mineral dust were inconsistent with the seasonal and spatial variations of unaccounted mass in PM_{10}. Uncertainties in estimating other chemical components were also expected to be responsible for varied patterns. Part of trace elements might exist as oxides and were multiplied with corresponding factors to account for the oxygen masses, but in this study, they were assumed to be in elemental form. The OM mass concentrations in this study were obtained by multiplying OC concentration by a factor of 1.4, which was currently used to estimate the average organic molecular weight per carbon weight (Chow et al. 1994; Christoforou et al. 2000; He et al. 2001). However, according to the reports of Turpin and Lim (2001), OM concentration was underestimated by the ratio of 1.4, and the conversion factors of 1.6±0.2 for urban aerosols and 2.1±0.2 for non-urban aerosols were recommended. In addition to the differences on estimating chemical species, the presence of moisture associated with particles and the loss of volatile material (e.g., ammonium, nitrate, and

Fig. 4 Mass balance of PM$_{10}$ in Fuzhou city during the sampling campaigns

organic matter) also partly resulted in the discrepancy in closure study (Hueglin et al. 2005; Almeida et al. 2006).

3.4 The quantitative source apportionment by PCA–MLR

In this work, the principal components analysis–multiple linear regression (PCA–MLR) model approach developed by Thurston and Spengler (1985) was performed to identify and quantify the major PM$_{10}$ source components in Fuzhou city. Considering the background site, Gushan, was not far away from urban areas, PCA–MLR (SPSS statistics 17.0) was carried out on the basis of three-site data set. PCA was used to reduce the set of original variables and to extract a small number of latent factors (principal components) to analyze the relationships among the observed variables. The species to be quantified in PCA should be over the detection limit and/or higher than field blanks (Almeida et al. 2005). The minimum required number of samples N should be $>50+V$ (where V is the number of variables)

(Thurston and Spengler 1985), or a less restrictive condition: $N>30+(V+3)/2$ (Callén et al. 2009). In this study, the variables that were not associated with any known pollution sources or with higher similarity were excluded in the principal component analysis, according to Godoy et al. (2009). Take EC for example; EC was not selected in PCA because it had dominant common source with OC due to their strong correlation ($R^2 \geq 0.50$, figure was omitted). Therefore, 22 variables and 39 samples have been chosen in the PCA model. MLR was conducted to carry out the quantitative sources apportionment, which used the PCA factor scores as the new variables. MLR was run using a stepwise method, and the standardized coefficients were used to represent the relative contributions from various sources (Larsen and Baker 2003; Zuo et al. 2007).

The factor loading matrix after Varimax rotation and the contribution of each component are summarized in Table 3 (only loads larger than 0.30 were listed). The system extracted the principal component with eigenvalue larger

Table 3 Varimax rotated factor loading and the estimated contribution of each component by PCA–MLR analysis

	PC1	PC2	PC3	PC4	Communality
Al	**0.94**[a]				0.94
Si	**0.95**				0.98
Ca	**0.93**				0.93
Ti	**0.88**			0.32	0.95
V					0.59
Cr	0.46	0.34	0.52	0.31	0.73
Mn	0.55	0.52	0.36	0.47	0.91
Fe	**0.85**		0.31		0.98
Ni					0.60
Cu		0.36	0.69		0.74
Zn	0.46			0.53	0.70
As	0.37	0.57	0.52		0.81
Se		0.35	0.69		0.71
Br				**0.74**	0.63
Pb				**0.82**	0.74
NO_3^-		**0.83**	0.37		0.92
SO_4^{2-}		**0.94**			0.94
NH_4^+		**0.89**	0.36		0.95
K^+		**0.82**		0.35	0.84
Na^+		0.45	**0.73**		0.83
Cl^-			**0.74**		0.66
OC	0.43	**0.76**			0.88
Variance (%)	25.69	22.95	15.39	11.27	
Apportion (%)	19.9	53.3	21.3	5.5	

[a] Bold loadings > 0.70

than 1. Although the first five components in this study have the eigenvalues of 10.7, 3.2, 1.7, 1.2, and 1.1, respectively, the difference of the last two component eigenvalues was small. Therefore, the first four principal components were reasonable to be retained, which covered a large part (75.3%) of the cumulative variance. The R^2 value for MLR is 0.984, and the P values for the regression coefficients are less than 0.05. The principal component 1 (PC1) was associated with Al, Si, Ca, Ti, and Fe, and it explained 25.7% of the variances. This component represented crustal dust (Castanho and Artaxo 2001; Godoy et al. 2009; Guo et al. 2009), which was likely derived from local resuspended road dust due to traffic and regional dust resuspension by wind and convective process. Ca was also originated from construction activities. Ti might be additively emitted from copper metallurgy (Querol et al. 2007), and Fe emitted from steel industry (Yatkin and Bayram 2007). Therefore, PC1 might be a mixed source. The estimated contribution of PC1 was 19.9%. The second component (PC2), explaining 23.0% of the total variances, had relevant loads for SO_4^{2-}, NO_3^-, and NH_4^+, and to a smaller extent K^+ and OC. This

component could be interpreted as secondary inorganic aerosol (Guo et al. 2009; Viana et al. 2008), and the sources of their precursors might also be the contributors of K^+ and OC (e.g., biomass burning and coal combustion). The secondary inorganic aerosol was the largest contributor, accounting for 53.3% of the PM_{10} concentration. The third component (PC3) was characterized by Na^+ and Cl^-, which represented marine aerosol contribution (Contini et al. 2010), accounting for 15.4% of total variance. The contribution of marine aerosol was comparable with crustal dust, which constituted 21.3% of the PM_{10} concentration. The fourth component (PC4) correlated well with Pb and Br, which had been identified as traffic emission (Yatkin and Bayram 2007; Cao et al. 2009). The deduction was further supported by a moderate loading for Zn, a good marker for tire wear emission (Salvador et al. 2007). The contribution of traffic emission was accounted for 5.5% of PM_{10} concentration. Mass concentration of each source contributing to PM_{10} aerosol was computed from the factor scores and the regression coefficients. Quantitatively, crustal dust, secondary ions, marine aerosol, and traffic emission contributed 7.4, 19.4, 7.7, and 2.0 μg/m³ to the PM_{10} aerosol in Fuzhou city.

4 Conclusions

PM_{10} aerosol samples were collected at two different types of sampling sites (two urban and one urban background) in Fuzhou city during summer and winter campaigns. The averaged PM_{10} mass concentration of two urban sites, Ziyang and Wusibei, showed around 1.5 times higher than those at background site, Gushan, during the sampling periods. Most of the water-soluble ions, elements, as well as the carbonaceous species showed high abundance at urban than urban background area. Seasonally, the spatial distributions of elements, carbonaceous species, and most of the ions (except secondary ions) were more homogeneous in winter compared to those in summer, suggesting that the local emissions among the three sampling sites were uniform. The total mass balance closure was achieved in this study by 86.9–97.7%. Uncertainties in estimating OM, mineral dust, etc. and unanalyzed components (e.g., water content) might be responsible for the negative discrepancies (2.3% in summer and 5.2% in winter at urban sites, and 10.6% and 13.1% at background site) between measured PM_{10} concentration and the sum of detected chemical compositions. According to the results obtained with PCA–MLR model, mineral dust, secondary ions, sea salt, and traffic emission might be the major contributors to PM_{10}, which accounted for 19.9%, 53.3%, 21.3%, and 5.5% of the total mass of PM_{10} aerosol.

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